

AN ABSTRACT OF THE THESIS OF

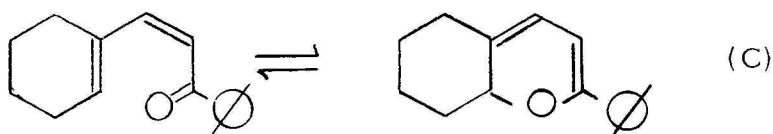
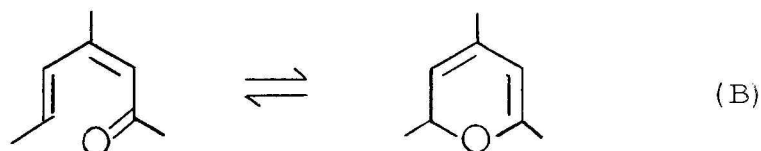
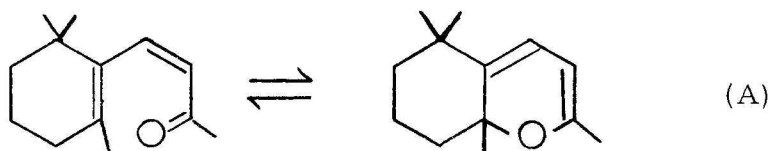
THOMAS ANTHONY GOSINK for the Ph. D. in Chemistry
(Name) (Degree) (Major)

Date thesis is presented August 13, 1965

Title SOME FEATURES INFLUENCING THE VALENCE
ISOMERISM OF CIS-DIENONES TO α -PYRANS

Abstract approved Redacted for privacy
(Major professor)

A study of the valence isomerization of cis-dienones and α -pyrans has been carried out involving three examples (A, B and C). Example A was investigated with temperature variable n. m. r.



At room temperature the pyran form is the more stable isomer and at equilibrium the mixture consists of 96% pyran and 4% dienone.

At 73° the equilibrium mixture contains 79% pyran and 21% dienone, and at 112° the mixture consists of 55% pyran and 45% dienone. On

the basis of these data the enthalpy difference is 700 cal./mole with the pyran the more stable form. The rate of interconversion is rapid. At 73° when the system has reached thermal equilibrium, chemical equilibrium has already been attained. The rate at room temperature is slow enough so that the disappearance of dienone shows a half-life of a few minutes.

The dienone of example B was obtained by reduction of 2, 4, 6-trimethylpyrylium perchlorate with sodium borohydride. Evidence for the presence of a transient intermediate in this reaction was obtained. This intermediate was not isolable and was not unequivocally identified. However its spectral properties were in accord with those expected of a pyran. The intermediate was converted to the dienone with $k \sim 7 \times 10^{-3} \text{ sec.}^{-1}$ at 21°. The dienone is in this case the dominant isomer at room temperature. The presence of the pyran in the equilibrium mixture could not be conclusively proven.

Addition of one mole of hydrogen to 1-phenyl-3-cyclohexenyl-2-propyn-1-one gave a mixture of products. A rather unstable compound having $\lambda_{\text{max}}^{338 \text{ m}\mu}$ was isolated in a somewhat impure state from this mixture. The physical properties of this substance were in reasonable agreement with those to be expected of the α -pyran form (equation C). Further addition of hydrogen gave a mixture of the tetrahydro-pyran, 1-phenyl-3-cyclohexylpropan-1-one and an

unidentified ketone. On the basis of these data the substance with λ_{max} 338 was tentatively assigned the α -pyran structure in equation C. Its instability with respect to polymerization prevented the accumulation of further data with respect to the valence isomerization process.

It is concluded that while cis-pentadienal is more stable than α -pyran itself, the valence equilibrium is rather finely balanced, and may be typed in favor of either valence isomer by rather minor changes in structure. By comparison with the valence isomerization of cis-hexatrienes to cyclohexadienes the dienone and α -pyran isomerization is at least one million times faster.

SOME FEATURES INFLUENCING THE VALENCE
ISOMERISM OF CIS-DIENONES TO α -PYRANS

by

THOMAS ANTHONY GOSINK

A THESIS

submitted to

OREGON STATE UNIVERSITY

in partial fulfillment of
the requirements for the
degree of

DOCTOR OF PHILOSOPHY

June 1966

APPROVED:

Professor of Chemistry
In Charge of Major

Head of Department of Chemistry

Dean of Graduate School

Date thesis is presented August 13, 1965

Typed by Opal Grossnicklaus

ACKNOWLEDGMENTS

The author wishes to express his sincere thanks to Professor Elliot N. Marvell for his understanding encouragement and leadership.

Financial aid from the Chemistry Department in the form of teaching assistantships, and through the Stauffer Chemical Company's Graduate Research Fellowship (1964-1965) is gratefully acknowledged. This work was also supported in part by the National Science Foundation Grant G-23072.

I wish also express my thanks to my wife, Joan, for her help over the years, and in helping to prepare this manuscript.

TABLE OF CONTENTS

INTRODUCTION	1
HISTORICAL	4
DISCUSSION	14
Spectral Properties of Dienones and α -Pyrans	14
The Ultraviolet Regions	15
The Infrared Region	27
Proton Magnetic Resonance Spectra	29
RESULTS	
Valence Isomerism of <u>cis</u> - β -Ionone and 2-Oxa-1, 3, 7, 7-tetramethylbicyclo[4, 4, 0] deca-e, 5-diene	35
Valence Isomerization of 2, 4, 6-Trimethyl-2H-pyran and 4-Methyl-3, 5-heptadien-2-one	38
Some Studies of the Partial Reduction of 1-Phenyl-3-cyclohexenyl-2-propynone	43
CONCLUSIONS	51
EXPERIMENTAL	57
1-Phenyl-3-cyclohexenyl-2-propyn-1-one	57
Semihydrogenation of 1-Phenyl-3-cyclohexenyl-2- Propyn-1-one	58
Compound A (3-phenyl-2-oxabicyclo[4, 4, 0] deca-3, 5-diene?)	60
1-Phenyl-3-cyclohexyl-1-propanone	61
3-Phenyl-2-oxabicyclo[4, 4, 0] decane	62
A. From Compound A	62
B. From 2-(3-phenyl-3-hydroxypropyl)cyclohexanol	62
Cis-2-(γ -phenylpropyl)cyclohexanol	63
2-(3-phenyl-3-hydroxypropyl)cyclohexanol	63
2-(γ -Phenylpropyl) cyclohexanone	64
<u>Trans</u> -1-Phenyl-3-cyclohexenyl-2-propen-1-ol	65
<u>Trans</u> -1-Phenyl-3-cyclohexenyl-2-propen-1-one	65
1, 3, 7, 7-tetramethyl-2-oxobicyclo(4, 4, 0)-deca-3, 5-diene	66
4-Methylhepta-cis-3-trans-5-dien-2-one	66

TABLE OF CONTENTS (Continued)

The Transient Intermediate (XIII)[2, 4, 6-trimethyl-2H-pyran?]	67
A. Ultraviolet Studies	67
B. N. M. R. Studies	67
Spectral Measurements	68
BIBLIOGRAPHY	69
APPENDIX	78

LIST OF FIGURES

I	N.M. R. data for α -pyran VI	36
II	N.M. R. data for <u>cis</u> - β -ionone	36

LIST OF CHARTS

I	Chemical shifts (in δ referred to TMS=0) for some types of protons	31
II	Predicted chemical shifts and coupling constants for the <u>cis</u> -dienone and the α -pyran	47

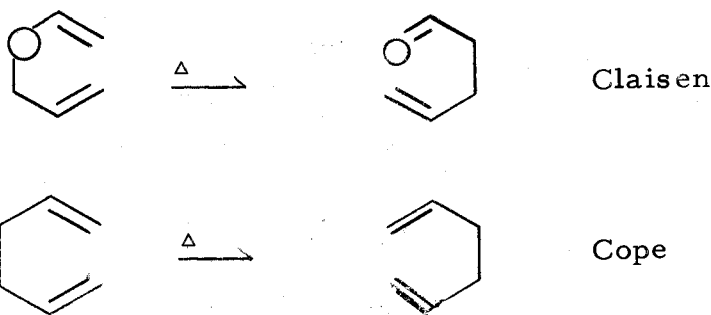
LIST OF TABLES

I	N. M. R. data reported by Hinnen and Dreux for compounds VIII and IX	10
II	Woodward's rules for prediction of λ_{max} (EtOH)	15
III	Ultraviolet spectra of <u>trans</u> -dienones	16
IV	Ultraviolet spectra of some <u>cis</u> - and <u>trans</u> -dienones	17
V	Ultraviolet spectra of homoannular dienes	19
VI	Ultraviolet spectra of some conjugated enol ethers	21
VII	Molar extinction coefficients of <u>cis</u> - and <u>trans</u> -dienones	24
VIII	Molar extinction coefficients of dienes	25
IX	Infrared spectra of some dienones	28
X	Infrared absorption of enols, dienols and α -pyrans	30
XI	Extraneous peaks in the α -pyran spectrum	37
XII	Valence isomers reported for α -pyran- <u>cis</u> -dienone equilibria	54
XIII	Variations in conditions for the reduction of 1-phenyl-3-cyclohexenyl-propynone with 5% Pd/CaCO ₃ .	59

SOME FEATURES INFLUENCING THE VALENCE ISOMERISM OF CIS-DIENONES TO α -PYRANS

INTRODUCTION

Ingold in 1922 coined the term valence tautomerism in connection with some attempts to prepare isomers of benzene (34). Ten years prior to this, Claisen had shown that ethyl O-allylacetoacetate rearranged when heated to give ethyl C-allylacetoacetate (20). Several decades later Cope found that ethyl 2-allyl-2-cyano-3-butenolate rearranged similarly to give ethyl 2-cyano-2,6-heptadienolate (21). Today we recognize both of these reactions as typical examples of



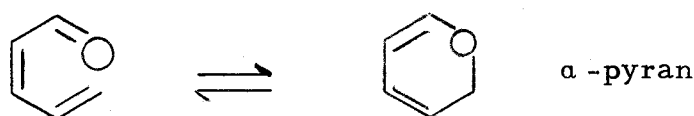
valence isomerization. This process may be simply defined as the uncatalyzed intramolecular interconversion of isomers.

Recent work in these laboratories has involved a study of the mechanism of the triene-cyclodiene thermal isomerizations (67, 87).

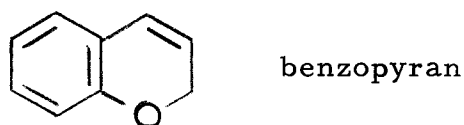


This is a logical extension of earlier studies of the Claisen

rearrangement. As a part of this work, the valence isomerization of cis-dienones and α -pyrans, recently termed electrocyclic reactions (94), is of great interest since α -pyran is one of very few



simple molecules still unknown today. In fact the number of α -pyrans in which neither of the two double bonds is stabilized as a part of an aromatic ring (the well known benzopyrans), is exceedingly small,



and the chemistry of these simple α -pyrans is virtually unknown (17, p. 809). One reason that may be advanced for this apparent gap in our chemical knowledge is that for the all carbon system, the cyclohexadiene form is predicted from heats of formation data to be of lower enthalpy than the cis-triene by 12-16 kcal./mole (77). On the other hand, the enthalpy difference favors the cis-dienone form when an oxygen is present by approximately 10-15 kcal./mole (30, 31, 77). The isolability of the α -pyran form will thus depend in many cases on the rate of the valence isomerization.

Prompted by these facts, we initiated an investigation of the valence isomerization of cis-dienones and α -pyrans. In particular, the features influencing the interconversion rate and the equilibrium

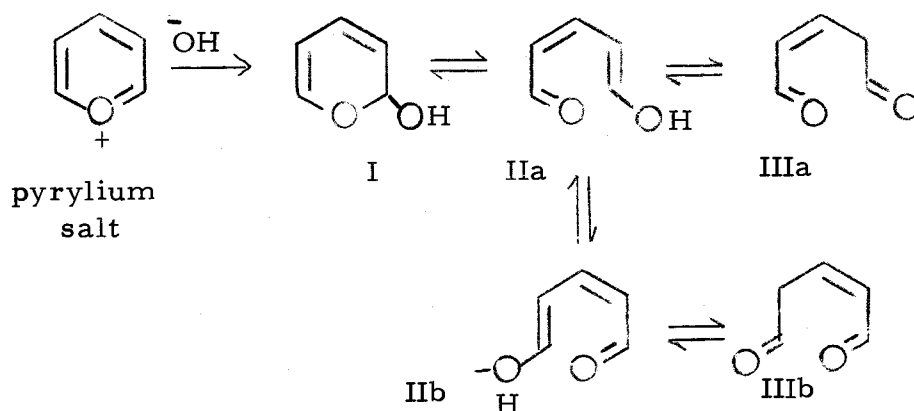
constant for the isomerization were the first targets for our studies.

This thesis will describe some of the results of a first survey of these factors.

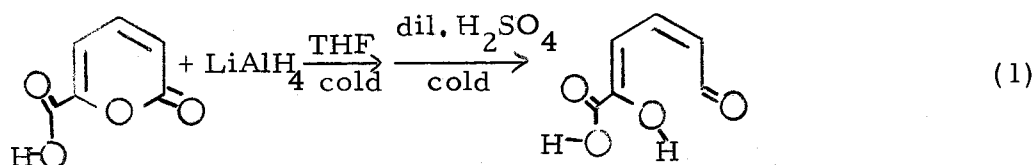
HISTORICAL

One distinguishing characteristic of the literature of α -pyrans is the scarcity of material. Until Windaus (93) reported in 1917 that mannitol could be converted to α -methyl- α -pyran, no mention of the simple heterocycle appears in the literature. Even this early report of a simple α -pyran has not passed the test of time, for Auwers (2) showed in 1921 that the structure assigned the product was incorrect, and that it was really 2-vinyl-2,5-dihydrofuran. Three decades then passed by before a further communication with respect to a simple α -pyran appeared in the literature. This also was to prove to be a negative result.

Though α -pyrans are not common substances, their aromatic equivalents, pyrylium salts, are very well known. These substances react readily with hydroxide ion to give a new substance, called a pseudo base. These pseudo bases can be formulated as hydroxy- α -pyrans (I), unsaturated ketones (III) or as monoenols (II) thereof. In 1952, Berson (8) presented good spectral evidence that for the 2,4,6-triphenyl derivative, the unsaturated diketo form (III) is the only identifiable material present, though he admitted that the method could not disprove the presence of traces of the other desmotropes.

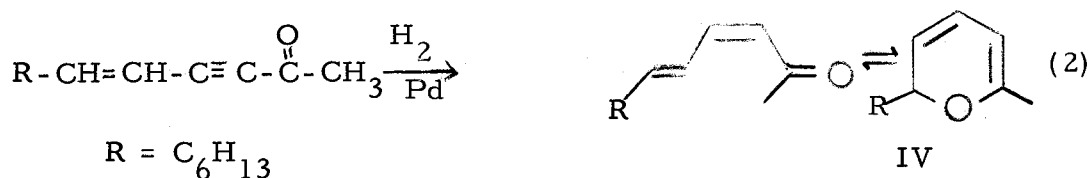


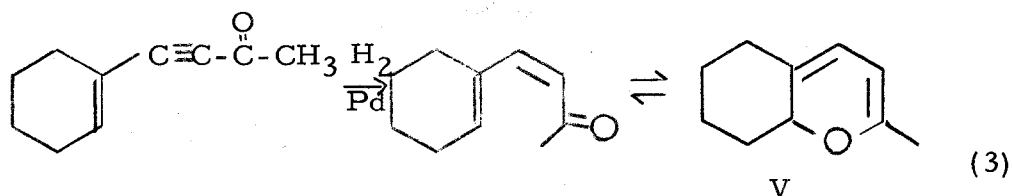
In this connection it should be mentioned that L. R. Morgan, Jr. (71) has assigned the open-chain enol aldehyde structure to the pseudo bases obtained from lithium aluminum hydride reduction of an α -pyrone, equation 1.



The assignment was based on spectral evidence, *viz* λ_{max} 230m μ (9333), 280m μ (27, 120) and 315m μ (7000) and $\tilde{\nu} = 1650 \text{ cm}^{-1}$. No further studies of such pseudo bases have been reported.

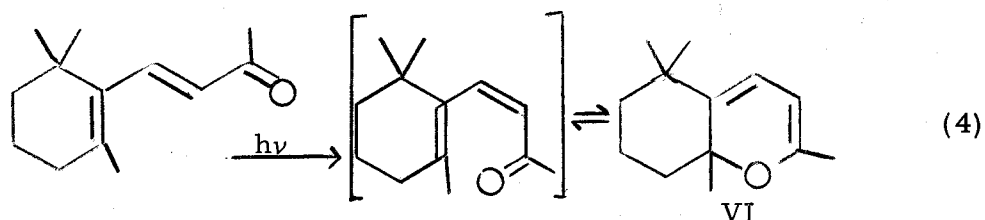
In 1956 Schinz, who was studying the chemistry of ketones conjugated with cis double bonds, reported (86) that the spectral properties of the products obtained by the addition of one mole of hydrogen to some enynones (equations 2 and 3)



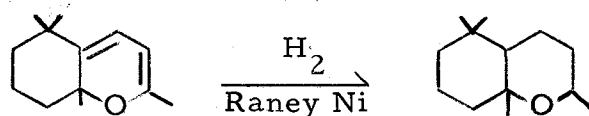


were not in agreement with those expected for the dienones. Thus he was led to assign his products the α -pyran structures IV and V. In general he found that the hydrogenation step led to mixtures from which he was unable to separate analytically pure substances. An attempt to prepare a phenylsemicarbazone of V provided only the trans-dienone derivative.

In an attempt to prepare the unknown cis- β -ionone, Büchi and Yang (15) irradiated trans- β -ionone. The main monomeric product obtained from the irradiation mixture was not the desired cis- β -ionone. Büchi and Yang provided convincing evidence that it possessed the α -pyran structure (VI). The product has $\lambda_{\max}^{286\text{m}\mu}(7240)$,



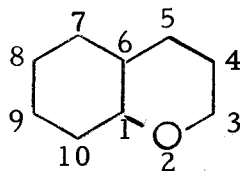
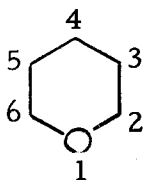
$\tilde{\nu} = 1650, 1595, 1215, 1120, 1085, 1020, 780$ and 690 cm^{-1} , all of medium to strong intensity. Catalytic hydrogenation over Raney nickel; with the uptake of two moles of hydrogen, gave the known



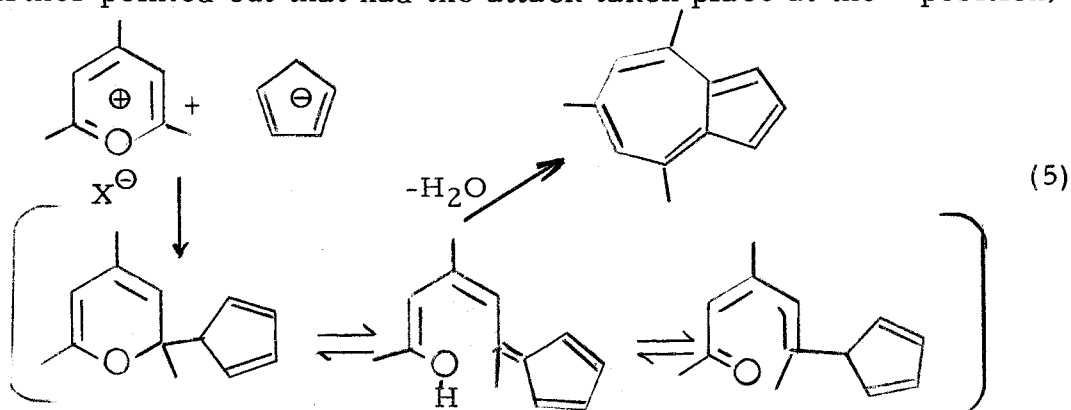
1, 3, 7, 7-tetramethyl-2-oxabicyclo [4. 9. 0] decane.* The pyran was reported to form an unstable semicarbazone, different from that of trans- β -ionone, and assumed to be that of the unknown cis- β -ionone. Upon hydrolysis, the semicarbazone gave again the α -pyran. The authors suggested that cis- β -ionone and the α -pyran (VI) are in mobile equilibrium with the α -pyran form being the predominant component at room temperature. They were unable to find any spectral evidence for the cis-ketone form.

The formation of pseudo bases by treatment of pyrylium salts with hydroxide ion has been found to be an example of a general reaction of pyrylium salts with nucleophiles. The nucleophile may attack at either the α - or γ -position. Between 1955 and 1962, three research groups reported the formation of α -pyrans or α -pyran intermediates as the result of treating pyrylium salts with organometallic reagents. Hafner and Kaiser (45) reported that if a pyrylium salt is treated with cyclopentadienyl anion, substituted azulenes are formed in good yield via an α -pyran intermediate, equation 5. They

* Numbering order for the α -pyran and for the 2-oxabicyclo-4, 4, 0-decane systems. (Confer Chemical Abstracts.)

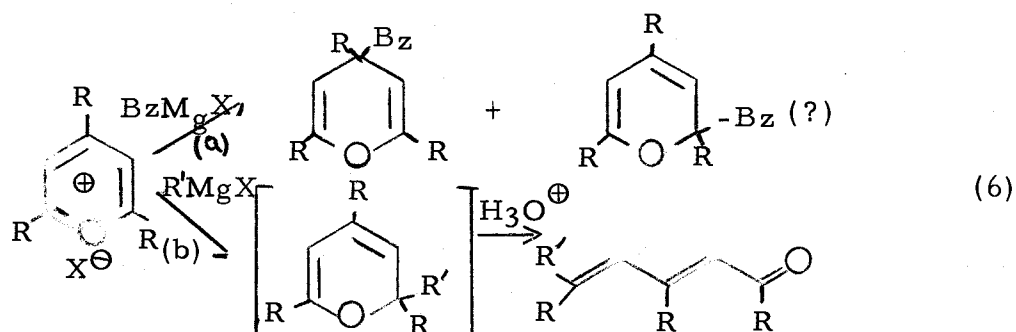


further pointed out that had the attack taken place at the 4 position,



the resulting γ -pyran, which was not detected, could not have led to the formation of an azulene.

Dimroth and Wolf (28) reported that the reaction of pyrylium salts with benzyl magnesium bromide led to the formation of γ -pyrans (equation 6a). Their report suggested that some α -pyran was formed as well, though the latter product was not conclusively identified. A later report (see p. 13) provided further information about the source of the α -pyran product. Kobrich and Wunder (59, 60) reported a similar reaction between pyrylium salts and Grignard reagents. During the work-up of the reaction mixture they used dilute solutions of mineral acids, and reported the isolation of dienones only. Presumably the α -pyran was an intermediate in the reaction. Their structural assignments were made from spectral information, and confirmed by reduction or oxidation of the products to known compounds.



Reaction of vinyl Grignard reagents with the monoenol ethers of β -diketones was reported by Crisan and Normant (24) to give dienones (equation 7). Hinnen and Dreux reinvestigated the products of this reaction using n. m. r. spectroscopy, and reported on the basis of the data listed in Table I that VIII and IX were obtained (50). Furthermore, they reported that the same products were obtained when 4,6-dimethyl- α -pyrone was treated with methyl Grignard. In the original paper describing this reaction, Gompper and Christman (42) had reported the isolation of VIII but not IX. Unfortunately the properties ascribed to VIII by Gompper and Christman do not agree with those found by Hinnen and Dreux. Thus the former report

$\lambda_{\max} 272, 278\text{m}\mu(1660)$ and $\tilde{\nu} = 1600, 1720$ while the latter gave $\lambda_{\max} 282\text{m}\mu(3800)$

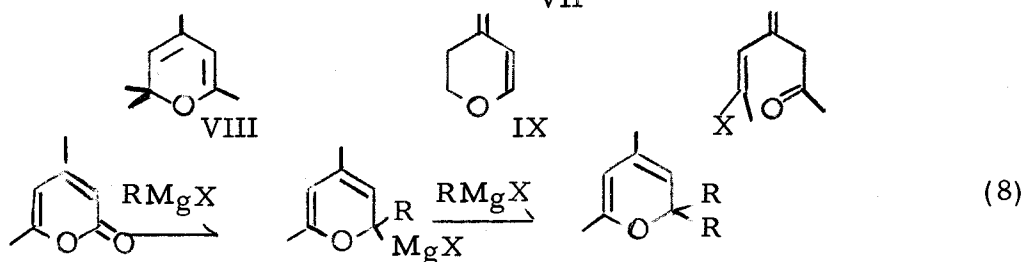
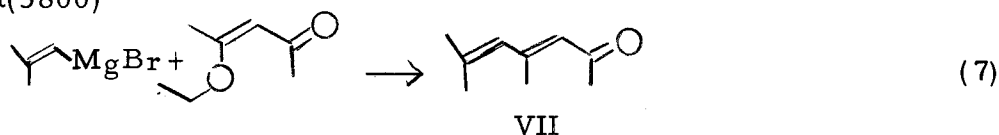


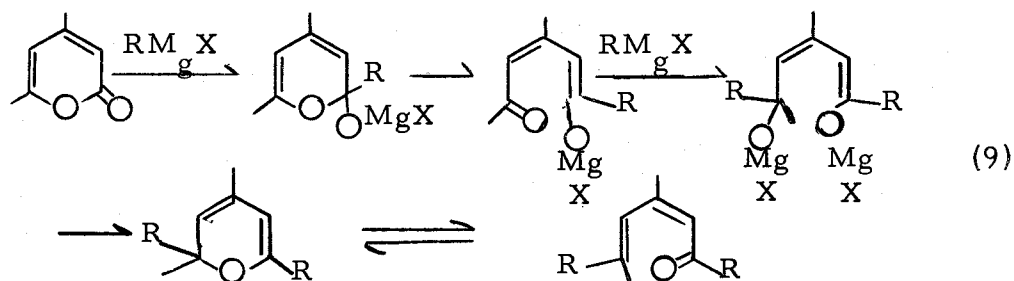
Table I. N.M.R. data* reported by Hinnen and Dreux for compounds VIII and IX

δ value	No. H's	Assignment and Coupling Constants
at 25 mc for VIII		
1.23	6	Geminal methyls
1.61	6	Methyls at C-4 and C-6
4.70	2	Vinyl hydrogens
at 60 mc		
1.61 (d)	3	Methyl at C-6 $J = 1.5$ cps
1.72 (q)	3	Methyl at C-4
at 25 mc for IX		
1.21	6	Geminal methyls
1.72	3	Methyl at C-6
2.16	2	Methylene hydrogens
4.35 and 4.55	2	Terminal vinyl hydrogens
5.20	1	Hydrogen at C-5
at 60 mc		
2.16 (t)	2	Methylene hydrogens $J = 1.5$ cps

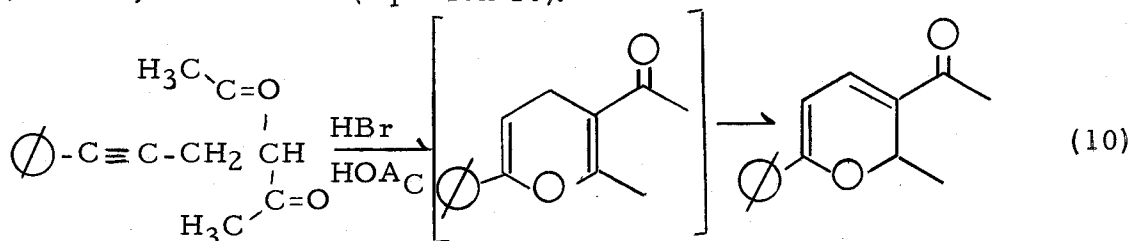
* CCl_4 solvent TMS standard

Köbrich (60) has also raised some questions about the structural assignments of Gompper and Christman. The latter had reported that 4, 6-dimethyl- α -pyrone reacted with phenyl Grignard reagent to give 2, 2-diphenyl-4, 6-dimethyl-2H-pyran, $\lambda_{\text{max}} 204 \text{ m}\mu$ (22,400), 227 (11,200) and 323 (10,000). Noting that the ultraviolet spectral data were not in accord with the structure assigned, Köbrich suggested an alternate reaction pathway (equation 9) leading

to products whose ultraviolet spectra are in better agreement with the findings reported.

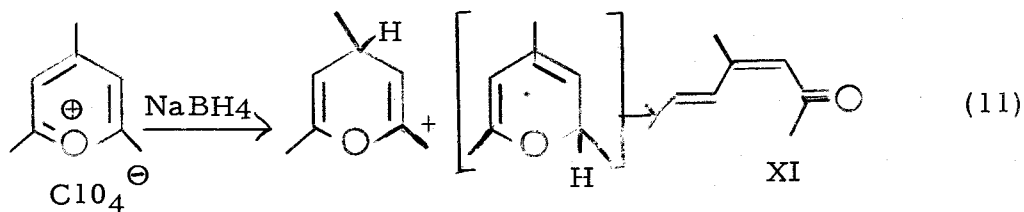


While engaged in the synthesis of a series of γ -pyrans, Schulte and his coworkers (81) noted that the product obtained from the reaction of 3-(γ -phenylpropargyl) acetylacetone with hydrogen bromide in glacial acetic acid possessed properties suggestive of an α -pyran form (equation 10). It appeared to these authors that the γ -pyran originally formed underwent an acid-catalyzed hydrogen shift to give the fully conjugated α -pyran, $\lambda_{\max}^{290m\mu}(9000)$, $360(7500)$, $\bar{\nu} = 1610, 1225 \text{ cm}^{-1}$ (equation 10).

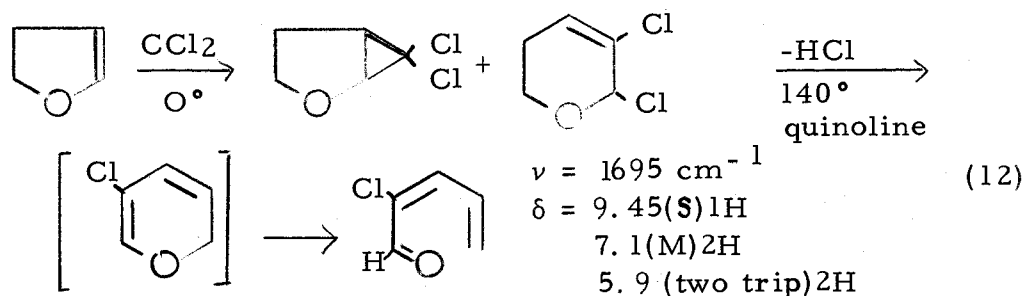


Another example of a nucleophilic attack on a pyryllium salt was recorded by Balaban and Nenitzescu (4). Sodium borohydride was found to react with an aqueous solution of 2, 4, 6-trimethylpyryllium perchlorate overlaid with ether to give two compounds, 2, 4, 6-trimethyl-4H-pyran and 4-methyl-3, 5-heptadien-2-one (equation 11). They proposed that the dienone was formed from

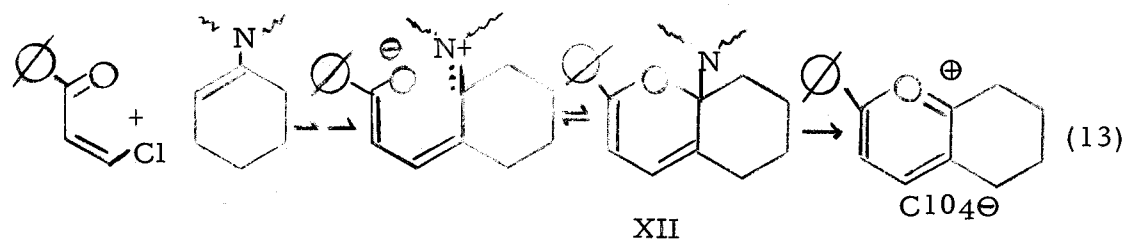
an α -pyran intermediate, but this was not detected.



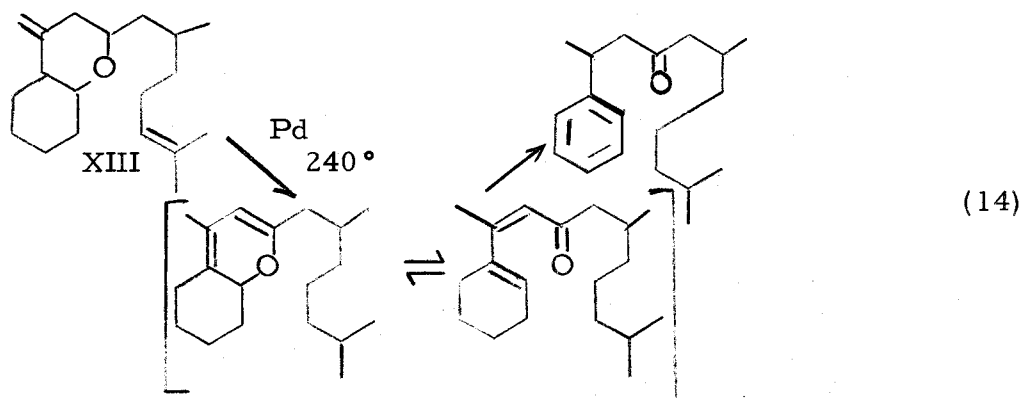
The synthesis of 5-chloro-2H-pyran was attempted recently via the route of equation 12 by two groups working independently (1, 79). Both groups reported that the only isolable substance was 2-chloropentadienal. Neither could find any evidence for the existence of the α -pyran.



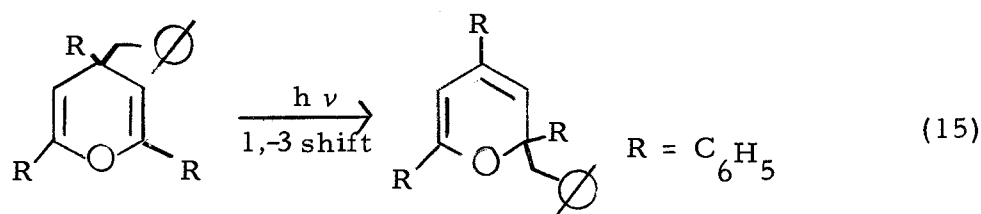
Fischer and Schroth (36) reported recently that enamines react with chlorovinyl ketones to give an intermediate readily convertible to a pyrylium salt on treatment with strong acid (equation 13). While no particulars were supplied, the authors indicated the intermediate as a tautomeric pair of structures (XII).



An α -pyran was proposed by Dolby and Debono as an intermediate in the thermal dehydrogenation of XIII (equation 14). No evidence that the intermediate might be isolable was given (32).



The early report of Dimroth and Wolf (see p. 8) on the possible formation of an α -pyran by treating a pyrylium salt with benzyl magnesium bromide has been elaborated on by those authors (29). They now report the initial formation of a γ -pyran only. However irradiation of the γ -pyran produced an unusual 1,3-shift of the benzyl group forming an α -pyran (equation 15). The various structural assignments were supported by spectral evidence.



DISCUSSION

Studies of the relations between cis-dienones and α -pyrans have been rendered extremely difficult since no adequate syntheses for either of the isomers have been worked out, no completely satisfactory methods of purification have been developed, and no generally applicable techniques of structure identification are available. Kinetic complications may exist, and indeed for the cases under investigation will be shown to be the source of considerable difficulty. This difficulty stems from the fact that when the valence isomerization becomes rapid at normal working temperatures, only processes which proceed far faster than the interconversion rate will provide useful information. Furthermore, the isolation of individual isomers is precluded under such conditions, and all studies must be made on mixtures. The major investigative weapons of value in such cases are the various spectral measurements. Thus we shall consider first the predictable utility and limitations of each of the spectra for the cis-dienone- α -pyran system.

Spectral Properties of Dienones and α -Pyran

Structural identity of isolated compounds is often established today by conjunctive use of ultraviolet, infrared and n. m. r. spectroscopy. Similarly, the identity of one or more components of a

mixture may be established purely by spectral means, and in some instances a quantitative measure of the amount present may be obtained.

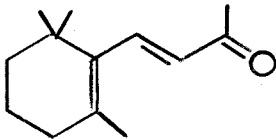
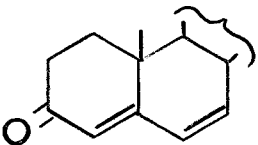
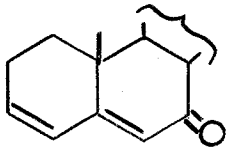
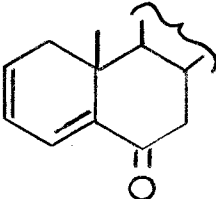
The Ultraviolet Regions

Ultraviolet spectral theory has not reached a level which will permit the calculation of the complete spectrum of a given complex substance. Thus we are dependent upon model compounds and empirical rules for establishing the frequency of the maximum absorbance expected of a new substance. The common set of empirical rules used to predict λ_{\max} for conjugated ketones and olefins is known as Woodward's rules. These are given in modified form in Table II. The values given under the enone heading permit the calculation of λ_{\max} for trans-dienones.

Table II. Woodward's rules for prediction of λ_{\max} (EtOH). (35, p. 17, 19).

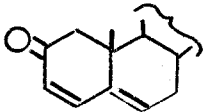
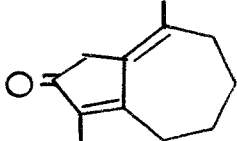
	enones	dienes
Parent Chromophore	215	214
Homoannular	39	253
Double bond added	30	30
Alkyl group or ring		5
α position	10	
β position	12	
γ and other	18	
OR	same as alkyl	0
exo double bond	5	5
solvent correction		0
hexane	+11	
ether	+ 7	

Table III. Ultraviolet spectra of trans-dienones.

Compound	λ_{\max}		ref.
	calc.	found	
$\text{CH}_2 = \text{CH}-\text{CH} = \text{CH}-\text{CHO}$	245	259	(11)
$\text{CH}_2 = \text{CH}-\overset{\text{Me}}{\underset{ }{\text{C}}} = \text{CH}-\text{CHO}$	257	268	(11)
$\text{CH}_2 = \text{CH}-\text{CH} = \text{CH}-\text{COMe}$	245	260	(47)
$\text{MeCH} = \text{CH}-\text{CH} = \text{CH}-\text{COMe}$	263	272	(47)
hex $\text{CH} = \text{CH}-\text{CH} = \text{CH}-\text{COMe}$	263	278	(86)
$\text{MeO}-\text{CH} = \text{CH}-\text{CH} = \text{CH}-\text{CO Me}$	263	297	(47)
	299	296	(15)
	280	289	(35, p. 20)
	280	279	(35, p. 20)
	317	315	(35, p. 20)

In Table III a comparison of the calculated vs. observed results in a series of examples is given to illustrate the kind of accuracy to be expected. In the present case, however, one difficulty arises in that we are dealing with the cis-dienone, not the trans. Generally, such a change in configuration has only a small influence on the position of λ_{\max} . Table IV shows the λ_{\max} for a series of comparable cis- and trans-dienones. Since a similar situation pertains with cis and trans enones as well, it seems safe to conclude, that the values calculated from Woodward's rules will be applicable to either cis or trans-dienones with about equal accuracy.

Table IV. Ultraviolet spectra of some cis- and trans-dienones.

Compound	λ_{\max}		ref.
	<u>trans</u>	<u>cis</u>	
$\text{CH}_2 = \text{CH}-\text{CH} = \text{CH}-\text{CHO}$	250	259	(11)
$\text{CH}_2 = \text{CH}-\overset{\text{Me}}{\text{C}} = \text{CH}-\text{CHO}$	268	265	(11)
$\text{CH}_3\text{CH} = \text{CH}-\text{CH} = \text{CH}-\text{COCH}_3$	272 (Δ^5 <u>cis</u>)	279	(15)
	286(calc.)	292	(35, p. 20)
	331(calc.)	305	(26, p. 15)

It is not clear whether the lower accuracy, clearly obtained with acyclic dienones, is a function of the mobility of these systems, or the lower degree of substitution. Thus, for the moment at least,

some degree skepticism must apply to the predictions made to acyclic dienones.

The wavelength of maximum absorption of dienes can also be predicted by Woodward's rules. The diene system of an α -pyran is a homoannular diene. Table V shows the general accuracy to be expected for dienes of this type. One major modification in the α -pyran is the presence of the enolic ether function. Though the oxygen possesses unshared electrons, capable of playing a role in the diene chromophore, the rules report that such an oxygen has no influence on the λ_{max} . However, the point is of sufficient importance to warrant a more careful inspection. The available data pertinent to the question are listed in Table VI. It seems reasonable to conclude that the enol ether or enol ester function may in many non-steroidal cases cause a bathochromic shift of 15-20 m μ . In the original derivation of the modified Woodward's rules, the Fiesers deduced, apparently on the basis of a number of steroid enol ethers and esters, that such a shift was unlikely. The overall data do not support that view, even though the source of the anomaly is not at present indicated.

The molar extinction coefficient is often useful in differentiating between cis- and trans-dienones, and between homoannular and heteroannular or acyclic dienes. Normally the extinction coefficient is smaller for the cis- than for the trans-dienone, and

Table V. Ultraviolet spectra of homoannular dienes.


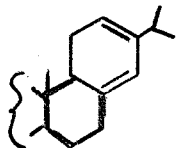
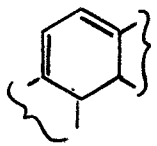
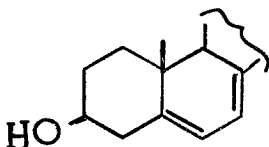
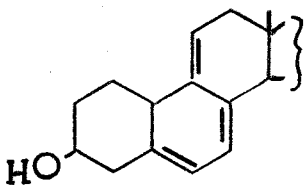
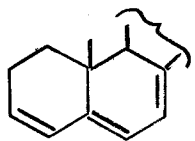
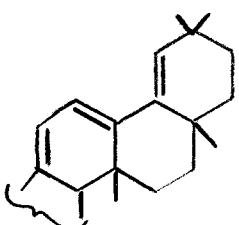
Compound	calc.	λ_{max} found	ref.
	273	263	(26, p. 12)
	278	272	(26, p. 13)
	278	281	(26, p. 13)
	283	282	(35, p. 16)
	323	329	(35, p. 17)
	313	315	(35, p. 17)
	323	310	(26, p. 13)

Table V (Continued)


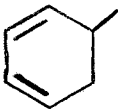
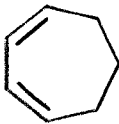
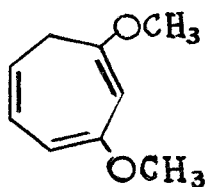
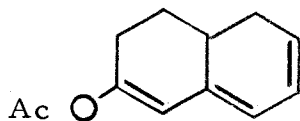
Compound	λ_{max}		ref.
	calc.	found	
	263	235	(88, p. 33)
	263	259	(88, p. 111)
	263+11 (isooctane) 248		(58, p. 157)

Table VI. Ultraviolet spectra of some conjugated enol ethers.

Compound	λ_{\max}		ref.
	calc.	found	
$\text{CH}_3\text{CH}=\text{C}(\text{OEt})-\text{CH}=\text{CH}_2$	219	230	(58, p. 165)
$\text{A}_c\text{OCH}_2\text{CH}_2\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{OMe}$	219	246	(12)
$\text{EtOCH}=\text{CH}-\text{CH}=\text{CH}_2$	214	237	(81)
$\text{AcOCH}=\text{CH}-\text{CH}=\text{CH}_2$	214	231	(81)
$\text{HOCH}_2-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}=\text{CHOMe}$	--	237	(12)
$\text{HOCH}_2-\text{CH}=\text{CH}-\text{C}\equiv\text{CH}$	--	223	(58, p. 53)
$\text{HOCH}_2-\text{C}\equiv\text{C}-\text{CH}=\text{CH}_2$	--	232	(58, p. 53)

(cycloheptatrien
actual)

262	279	(75, p. 239)
		(88, p. 186)



313	315	(25)
-----	-----	------

Table VI. (Continued)

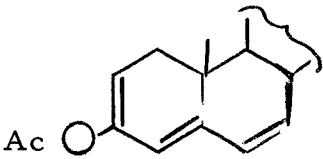
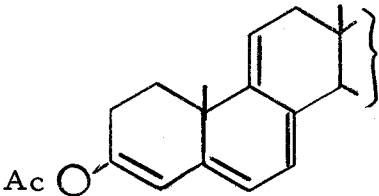
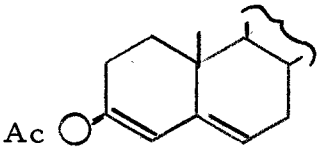
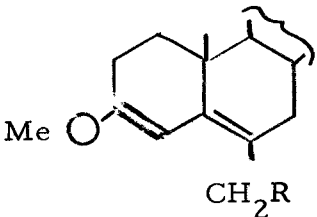
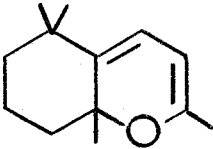
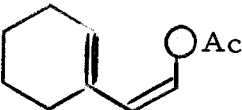
Compound	λ_{max}		ref.
	calc.	found	
	303	306	(35, p. 17)
	353	355	(35, p. 18)
	234	238	(91)
	239	246-261	(16)
	273	286	(15)
	224	242	(75, p. 302)

Table VI. (Continued)

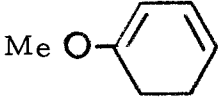

Compound	λ_{max}		ref.
	calc.	found	
	263	272	(58, p. 160)
	263	275	(88, p. 152)

Table VII. Molar extinction coefficients of cis- and trans-dienones.

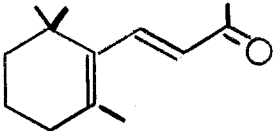
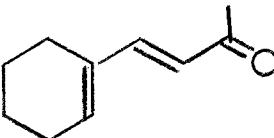
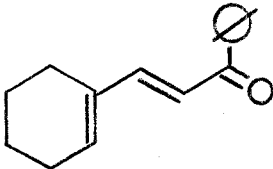
Compound	ϵ		ref.
	cis	trans	
$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CHO}$	19,100	--	(11)
in hexane	25,300	34,000	(11)
$\text{CH}_2=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}-\text{CHO}$	14,300	15,000	(11)
in hexane	19,100	24,000	
$\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{COCH}_3$	9,780 (Δ^5_{cis})	20,000	(15)
$\text{C}_6\text{H}_{13}\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{COCH}_3$	(7,780)	26,300	(86)
$\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CHO}$	--	26,900	(9)
$\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)=\text{CH}-\text{COCH}_3$	14,100	--	
	--	10,700	(15)
	--	24,000	(49)
	--	23,800	

Table VIII. Molar extinction coefficients of dienes.

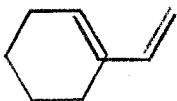

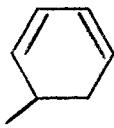
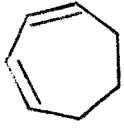
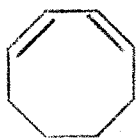
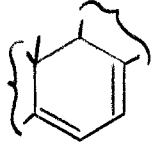
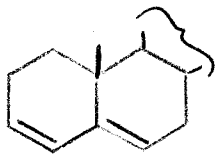
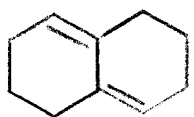
Compound	ϵ	ref.
$\text{CH}_2 = \text{CH}-\text{CH} = \text{CH}_2$	20,900	(58, p. 27)
$\text{CH}_3\text{CH} = \text{CH}-\text{CH} = \text{CH}-\text{CH}_3$	22,400	(58, p. 107)
	8,520	(58, p. 129)
	2,240	(88, p. 31)
	4,900	(88, p. 111)
	7,410	(58, p. 157)
	5,620	(58, p. 219)

Table VIII. (Continued)

Compound	ϵ	ref.
	11,900	(35, p. 16)
	20,000	(35, p. 16)
	13,670	(53)
$\text{CH}_2=\text{CH}-\text{C}\equiv\text{CH}_3$	8,900	(58, p. 48)

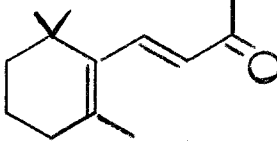
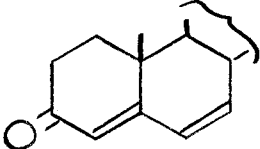
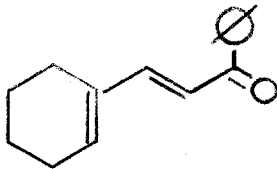
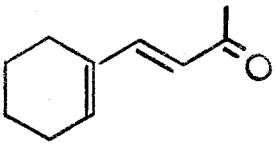
smaller for the homoannular than other dienes. Table VII shows representative values for several cases of dienones, and Table VIII for dienes.

The Infrared Region

The most important band which can be used to identify a dienone is that due to the carbonyl stretching frequency. This is expected to appear near $1660\text{-}1670\text{ cm}^{-1}$ (7, p. 136), and should be the most intense band in the spectrum. Though generally the carbon-carbon stretching vibrations give rise to very low intensity bands, conjugation with a carbonyl group both intensifies these bands and shifts them toward lower frequencies. Representative values are shown in Table IX for both $\text{C}=\text{O}$ and $\text{C}=\text{C}$ bands of dienones. The characteristic feature of the $1550\text{-}1750$ region of the spectrum of a dienone is the presence of three bands between $1670\text{-}1580\text{ cm}^{-1}$ decreasing in intensity as the frequency decreases.

With only a single α -pyran clearly and completely identified, information about the infrared spectra of these compounds is minimal. However, certain predictions can be made with reasonable certainty by extension from the spectra of related compounds. Essentially α -pyrans are enol ethers having a second double bond conjugated to the first, and should show modified enol ether spectra. It is known that the enol oxygen notably enhances the intensity of the

Table IX. Infrared spectra of some dienones.

Compound	band			ref.
	C=O	C=C	C=C	
$\text{CH}_3\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CHO}$	1677	1642	1608	(10)
n-hex $\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{COMe}$	ca 1675	1640	1600	(86)
	1780	1660	1600	
	1669-1666	1616-1619	1587	(57)
	ca 1670	1630	1605	
$\text{CH}_3\text{CH}=\text{CH}-\text{C}(\text{CH}_3)=\text{CH}-\text{COCH}_3$	1667	1640	1620	
	ca 1675	1629	1603	(86)

carbon-carbon stretching absorption of a double band but does not appreciably alter the frequency (70). While strong, these bands are normally sharper and less intense than those associated with the carbonyl stretching mode. When two double bonds are present, two absorption bands are to be expected in this region (7, p. 41).

Table X shows the pattern of bands expected.

Enol ethers generally have strong ether bands in the region between $1180-1250\text{ cm}^{-1}$. These lie however close to a band present in the spectra of dienones, and are therefore not generally too helpful for structure analysis in the case at hand. Thus the major region which can be used a priori to distinguish between the dienone and the isomeric α -pyran is the $1550-1700\text{ cm}^{-1}$ area. The α -pyran is expected to give rise to two relatively strong bands in this region rather than the three of a dienone. The α -pyran bands may be expected to be less intense and often at lower frequencies than the two higher frequency dienone bands.

Proton Magnetic Resonance Spectra

Chemical shifts for some of the types of protons found in the valence isomeric dienones or α -pyrans are listed in Chart I. Where appropriate values have not been determined, some model compounds are shown to provide reference data. The data clearly show that for the valence isomers, the following changes in chemical shift for

Table X. Infrared absorption of enols, dienols and α -pyrans.

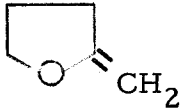
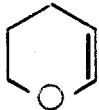

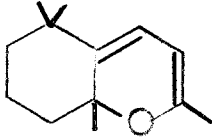
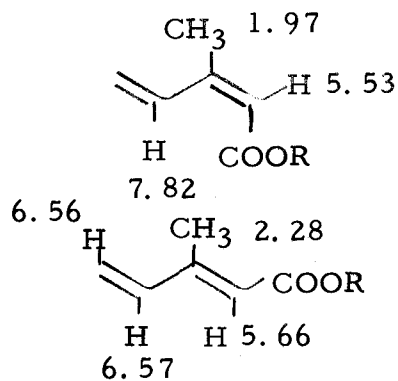
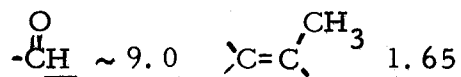
Compound	Absorption	ref.
$R-O-CH=CH_2$	1615 ± 5	70
$C_4H_9-\overset{\overset{OEt}{ }}{C}=CH_2$	1655	69
$C_4H_9O-CH=CH_2$	1650	69
	1669	69
	1644	69
	1630	69
$Me-\overset{\overset{OCH_3}{ }}{C}=CH-C\equiv C-Me$	1630	69
	1650 1595	15

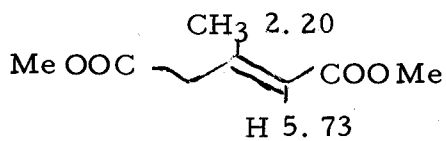
CHART I

Chemical shifts (in δ referred to TMS=0) for some types of protons.

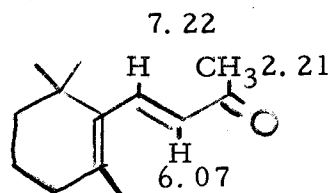
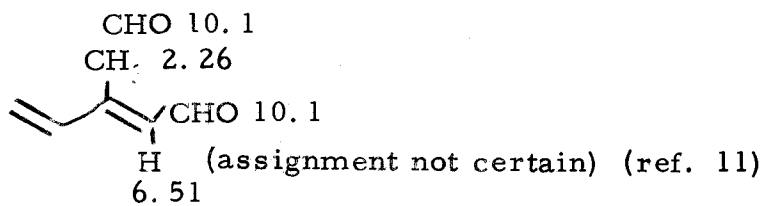
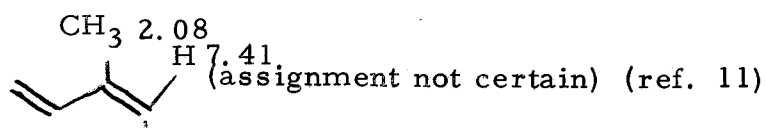


(ref. 61)

(ref. 61)

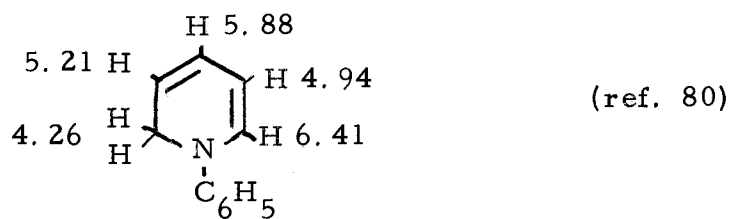
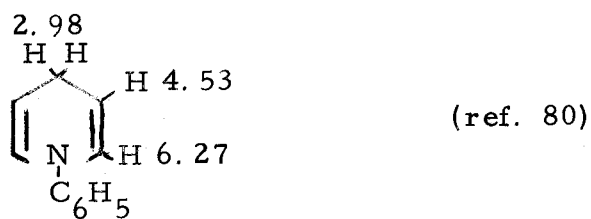
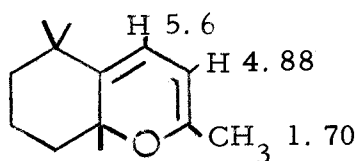
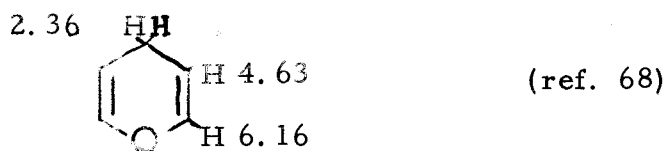
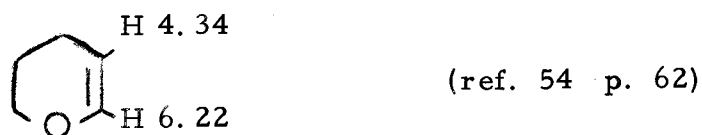
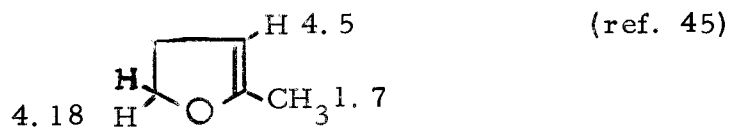


(ref. 56)



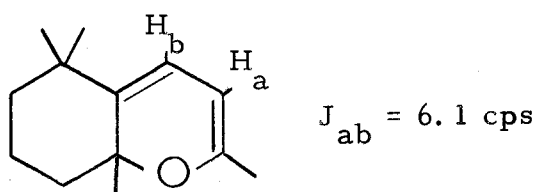
(see also ref. 6)

CHART I (Continued)

Chemical shifts (in δ referred to TMS-0) for some types of protons.

equivalent protons are to be expected. All are based on clear cut models except the values for the β -protons of the *cis*-dienal. These were derived from the values obtained from the trans-dienone combined with the shifts noted in the cis and trans-ester examples. Since however the γ -proton in the ester is situated nearer to the carbonyl group, the deshielding effect should be larger in that case than for the β -proton of the dienone. Accordingly a shift approximately three-fourths that noted for the ester was used. The chemical shift assignments for the various protons of the valence isomers are without doubt accurate enough to show that a clean differentiation of the two will be possible on this basis alone.

In certain instances coupling constants may help to confirm a decision reached on the basis of chemical shift data. For example, the known α -pyran has a coupling constant for the protons



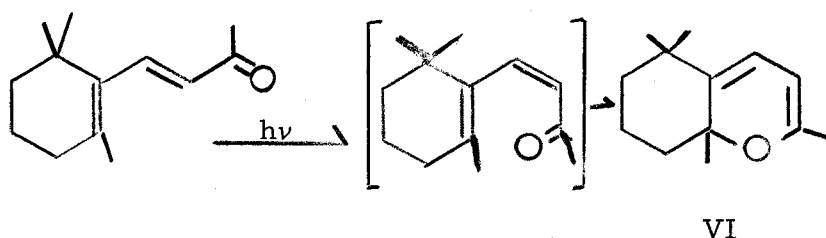
on the β - and γ -carbons of 6.1 cps. For a cis double bond the coupling constant is normally in the 8-12 cps. range, and in conjugated systems commonly tends toward the upper limit. The

ratios among protons of the various types present in the molecule, easily assessed by integration when sufficient separation is present, may provide further assistance.

RESULTS

Valence Isomerism of cis- β -Ionone and
2-Oxa-1,3,7,7-tetramethylbicyclo[4,4,0]
deca-3,5-diene

Büchi and Yang (15) reported the formation of the α -pyran (VI) by the irradiation of trans- β -ionone. They provided a firm experimental foundation for their α -pyran assignment. Though they were unable to find any direct evidence to indicate a valence isomerization



between the α -pyran and cis- β -ionone, treatment of the pyran with semicarbazide gave a semicarbazone different from that of trans- β -ionone, and presumed to be the derivative of the elusive cis- β -ionone. Mild hydrolysis of the semicarbazone regenerated the α -pyran. The results suggest a mobile equilibrium between the two valence isomers.

Having experienced a number of experimental problems with the investigation of a similar valence isomerization in a related system (19, 66) we were prompted to study this apparently stable α -pyran as a model. The generation of the α -pyran (VI) proceeded

exactly as described by Büchi and Yang, with the physical properties of our product coinciding exactly with those reported by them. Our investigation of the product via n. m. r. spectroscopy once again provides complete confirmation of the α -pyran structural assignment. The relevant chemical shifts and coupling constants are shown for the various protons in figure I. However, certain extraneous peaks

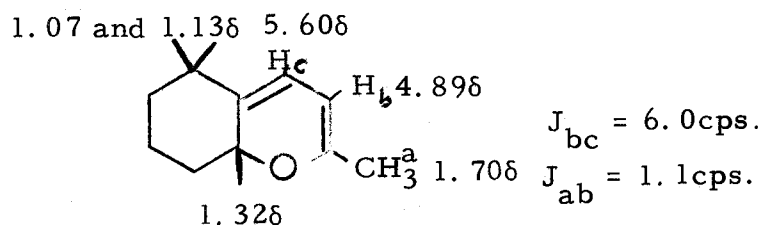


Figure I. N. M. R. data for α -pyran VI.

in the spectrum, which could not be attributed to the α -pyran moved us to make a more careful inspection. Ultimately a set of six bands was uncovered which is listed in Table XI. It is of great interest to note that the entire set of peaks are exactly those which might be expected of the cis- β -ionone. The assignments on such a basis are shown in figure II. The J_{ab} found is in very reasonable accord with a cis-coupling constant in a conjugated system, and is smaller than the 17 cps value we have observed for the trans-coupling

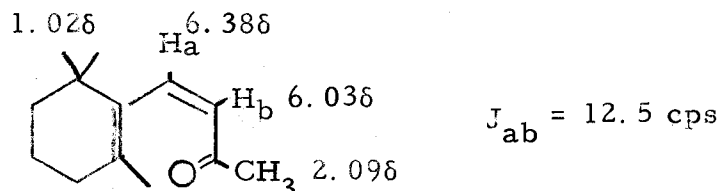


Figure II. N. M. R. data for cis- β -ionone.

constant for trans- β -ionone. The shift of the H_a protons from

7.23 δ (trans- β -ionone) to 6.38 δ is in the direction expected when a carbonyl group is moved from the position cis to one trans to that proton (56). A careful integration of the peak areas for the two AB protons of the α -pyran and of the assumed cis-dienone showed a 9:1 ratio of the α -pyran to dienone. Unfortunately the temperature of the sample in the n. m. r. probe was not determined. It was well above room temperature, and we may estimate that it was between 35 and 40°.

Table XI. Extraneous peaks in the α -pyran spectrum.

Singlet	1.02 δ
Singlet	2.09 δ
Modified AB doublets (low field pair split into two unresolved multiplets)	6.03 and 6.38 δ $J_{AB} = 12.5$ cps

When a variable temperature probe for the n. m. r. spectrometer was obtained, the α -pyran was examined further. If the above interpretation is correct, the amount of the dienone (less stable isomer) at equilibrium should increase with increasing temperature, and the process should be reversible. Both predictions are borne out by experimental results. At 73°, the bands attributed to the cis-dienone have increased in intensity relative to those of the α -pyran. In fact it is possible from this spectrum to find yet another peak assignable to the cis-dienone. A band at 1.52 δ , which can be

assigned to the allylic methyl group on the cyclohexenyl ring clearly shows a weak coupling to the Ha olefinic proton. At this temperature the ratio of the α -pyran to cis-dienone is 79:21, an equilibrium constant of 3.8 for the dienone to pyran interconversion. At 112° the ratio reached the equilibrium level of 55:45, or a K of 1.2.

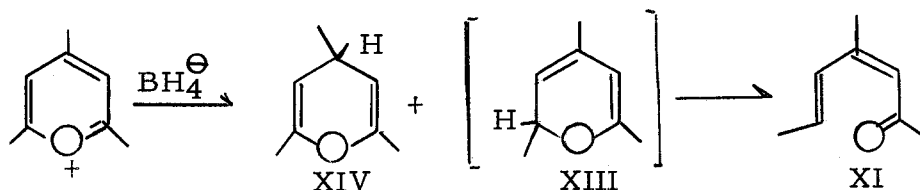
From this data it can be calculated that $\Delta F_{35}^{\circ} = -0.92$ kcal/mole, $\Delta H^{\circ} = -0.71$ kcal/mole and $\Delta S = 0.66$ e. u. Based on these data, 4% of the dienone is to be expected at 20°.

The rate of interconversion of these two valence isomers is rapid enough at 73° so that chemical equilibrium is established at least as fast as thermal equilibrium in the sample tube. On cooling to 40°, the approach to chemical equilibrium was slow enough to see after the sample had reached thermal equilibrium. Though we did not measure the rate or the order of the reaction, complete equilibrium was attained in a few minutes at 40°. Compared with the rate of valence isomerization of cis-hexatriene to cyclohexadiene, this rate is roughly six powers of ten faster (67).

Valence Isomerization of 2, 4, 6-Trimethyl-2H-pyran
and 4-Methyl-3, 5-heptadien-2-one

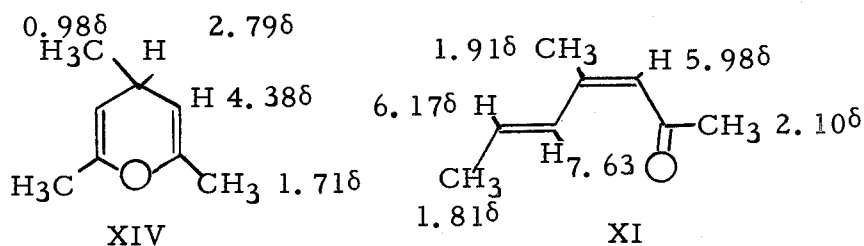
Balaban and Nenitzescu (4) found that the action of sodium borohydride on 2, 4, 6-trimethyl-pyrylium perchlorate gave two products which were separable by distillation. They assigned the

lower boiling product the γ -pyran structure (XIV) and the higher boiling one the dienone structure (XI). The spectral data published were rather sketchy for both substances. The authors suggested that the dienone was formed via a valence isomerization of the



α -pyran, but no evidence for the presence of such an intermediate was given. Fascinated by the idea that such apparently minor alterations in the α -pyrans VI and XIII could produce such a drastic change in the apparent equilibrium, we decided to reinvestigate this system.

Repetition of the directions of Balaban and Nenitzescu gave rise to two products, separable by fractional distillation, exactly as they had described. The n. m. r. spectrum of the lower boiling material (contaminated with the higher boiling material) showed a doublet ($J=6.8$ cps) at 0.98 ppm, a doublet ($J=0.8$ cps) at 1.71 ppm, an unresolved multiplet centered at 2.79 ppm, and a third doublet ($J=3.2$ cps) at 4.38 ppm. These data clearly demonstrate that the γ -pyran from XIV is correct.



Similarly, the n. m. r. spectrum of the higher boiling product, discussed in detail below, unequivocally identified it as the dienone. The dienone spectrum consisted of a quartet ($J=6.7$, $J'=1.0$ cps) at 1.81 ppm, a doublet ($J=1.0$ cps) at 1.91, a sharp singlet at 2.10 ppm, a singlet at 5.98 ppm (a spectrum at -22° begins to resolve this peak to a quartet, $J=1.0$ cps) and the AB portion of a modified ABX_3 pattern ($J_{AB}=15.0$, $J_{AX}\approx 1.0$, $J_{BX}=6.7$ cps) with $\nu_A=7.63$ and $\nu_B=6.17$ ppm. Comparing these chemical shifts with those given by Jackman and Wiley (56) shown in Chart I, p. 31, it is quite clear that the 3,4-double bond has a cis-configuration since the C_5 -proton is shifted to low field (7.63 δ) due to their cis and trans relationships to the deshielding carboxyl group. The 4,5-double bond must be of trans-configuration because the J_{AB} of 15 cps is too large for a cis related hydrogen pair in this situation.

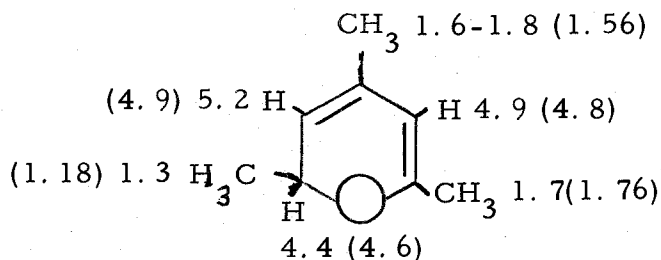
If the dienone were formed via the α -pyran XIII as seems eminently reasonable, it would be expected to have exactly the geometry which it has been shown to possess by our n. m. r. studies. Two separate attempts were made to gather more evidence pertaining to the question of the valence isomerization between XIII and XI. First there appear peaks of low intensity in the spectrum of the dienone in three areas which cannot be attributed to the dienone or the γ -pyran XIV which is present as a trace impurity. These peaks are a doublet or pair of peaks at 4.77 and 4.85 ppm, and two

further multiplets at 5.20 and 5.36 ppm. When the dienone is heated to 100°, the series from 4.77 to 5.36 show a slow increase in intensity over a 35 minute period. Allowed to cool to 35°, the sample shows some diminution of the absorption at 4.77, 4.85 and 5.36, but the 5.20 band remains unaltered. While it is indeed possible to assign the doublet at 1.18, and two of the four peaks between 4.77 and 5.36 to the α -pyran, this explanation is in itself not sufficient to account for all of the observations.

If the α -pyran XIII were indeed formed by attack on the borohydride on the pyrylium salt, and then the α -pyran underwent an uncatalyzed ring opening, it seemed possible that the pyran might be identified as a transient intermediate. In order to render the rate of disappearance of such a possible intermediate as low as possible, the reaction was carried out at low temperature. When the borohydride reaction was carried out at 0° for a short time under an overlayer of either pentane or carbon tetrachloride, an unstable substance was shown to be present in the organic layer by spectral studies.

The carbon tetrachloride solution was dried at -78°, thawed and placed in the n. m. r. probe at -22° C. Aside from peaks due to the dienone and the γ -pyran there appeared in the spectrum the doublet ($J=6.5$) at 1.18, a singlet at 1.56 ppm, another singlet at 1.76 ppm superimposed on a band due to the dienone, a poorly resolved multiplet near 4.6 ppm and two singlets near 4.8 and 4.9

ppm. All of these peaks diminish rapidly from the spectrum when the solution is warmed to 35° C. The final spectrum corresponds to that of a mixture of XI and XIV with a trace of XIII.



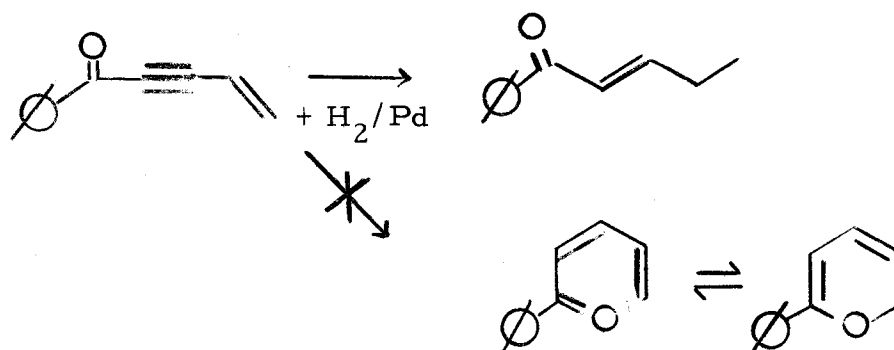
In the figure above the values for the chemical shifts of the various protons in XI are predicted, and the values given above in the spectrum of the transient material are listed in parentheses. The correspondence is not unreasonable.

Similarly, the pentane solution was diluted suitably with pentane and examined in the ultraviolet region. An absorption peak at 277m μ was observed which disappeared in 10 min at room temperature leaving only a single stronger peak at 273m μ . The dienone shows λ_{max} 283 in the ethanol which when corrected for the solvent change would be 272 m μ in pentane. From the λ_{max} of 286 for Büchi's pyran a value of 280 would be predicted for XIII. Again the correspondence is reasonable. Measured via the absorbance changes at 253.5 m μ , a rate of $7 \times 10^{-3} \text{ sec.}^{-1}$ at 21° was obtained for the rate of disappearance of the transient intermediate.

At present we consider that these data are more suggestive than demanding of the valence isomerization process.

Some Studies of the Partial Reduction of
1-Phenyl-3-cyclohexenyl-2-propynone

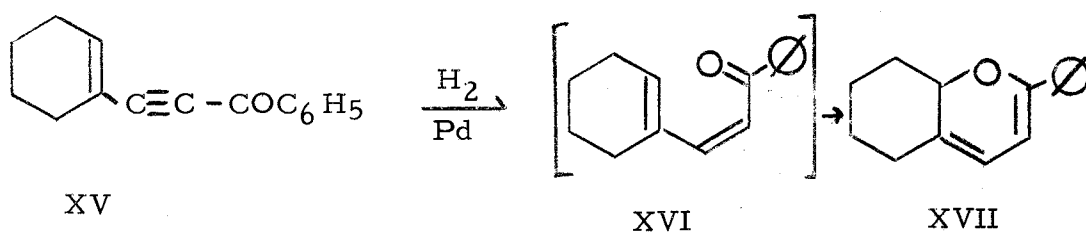
The initial attempt made in these laboratories to investigate valence isomerizations of dienones and α -pyrans made use of the 1-phenyl-2,4-pentadienone/6-phenyl-2H-pyran system (19, 66).



The rationale underlying this choice of reactants was the larger bathochromic shift expected when a phenyl group is linearly conjugated to a chromophore than when it is cross-conjugated. Hence the pyran form should have a λ_{\max} near 315 m μ and the dienone near 275 m μ . Differentiation between the two purely on the basis of ultraviolet spectra should be possible, and indeed an analysis of mixtures of the two should also be feasible. Attempted synthesis of the cis-dienone by partial reduction of 1-phenyl-2-pentyn-4-en-1-one failed because the terminal vinyl group added hydrogen too

rapidly, and only 1-phenyl-2-penten-1-one was isolated.

To alleviate this competition a more heavily substituted double bond was indicated and thus 1-phenyl-3-cyclohexenyl-2-propyn-1-one was chosen. This compound was easily prepared, was reasonably stable and was cleanly characterized. Addition of about one mole of hydrogen to this acetylenic ketone over palladium-on-calcium carbonate or Lindlar catalyst gave a mixture of products. The mixture proved most intractable to attempts to separate pure compounds from it by distillation or chromatography. However two features characterized the mixture in all cases. In no mixture was the triple bond ever absent, even when 1.3 moles of hydrogen had been added. Also the ultraviolet spectrum of the mixture always showed a new absorption band at 338 m μ . The acetylenic ketone has $\lambda_{\text{max}} = 304$, and a synthetic sample of trans-1-phenyl-3-cyclohexenyl-2-propen-1-one was found to have $\lambda_{\text{max}} = 307.5$ m μ . Since trans-chalcone has $\lambda_{\text{max}} = 307.5$ and its cis isomer, $\lambda_{\text{max}} = 295$, the most likely candidate for the substance with the 338 m μ absorption seemed to be the α -pyran (XVII). Unfortunately the substance responsible for this



absorption (referred to hereafter as compound A) resisted all our

attempts to isolate it in pure form. Despite this we have been able to provide a considerable body of evidence which suggests that compound A is most reasonably assigned the structure I.

The major problem relating to compound A and its isolation became apparent very quickly. Compound A was not stable in the reaction mixture, since the 338 m μ band diminished in intensity quite rapidly. Absorption at 338 m μ would vanish after the reaction mixture had been stored in the refrigerator under nitrogen for a few days. Partial separation of compound A from other components of the mixture was achieved by rapid chromatography over silica gel. Compound A eluted with hexane shortly before the acetylenic ketone. Though the rate of disappearance of A was lower in the purified state, it seemed to be inherently unstable even in solution, and rapidly decomposed to form a tacky polymer when isolated neat.

Compound A was isolated in semi-pure form as a light yellow oil, λ_{max} 338 m μ in cyclohexane. An extinction coefficient of about 10,000 was determined via direct examination of an eluate, followed by evaporation of an aliquot. This extinction is based on an assumed molecular formula of C₁₅H₁₆O for compound A. Analysis of several different samples gave carbon-hydrogen values in fair accord with this formula, but the carbon value was always too low. The ultra-violet spectrum of A showed no absorption between 338 and 260 m μ where solvent absorption prevented further measurement.

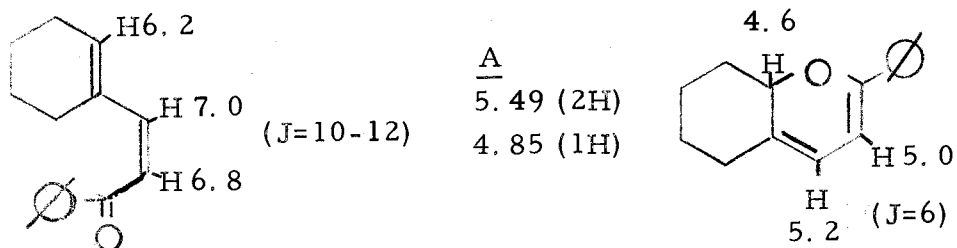
The infrared spectrum of compound A was obtained on a neat sample obtained by evaporation of the solvent and immediate examination of the resultant liquid. Certain conclusions are immediately obvious. The monosubstituted phenyl ring is present as indicated by bands at 686 and 755, as well as a strong band at 1500 and one of lower intensity at 1600 cm^{-1} . There is no carbonyl group present, but there are bands of moderate intensity at 1575 and 1660 cm^{-1} . Though the band at 1660 might be attributed to a carbonyl impurity, it is at a lower frequency than that of trans-1-phenyl-3-cyclohexenyl-2-propen-1-one prepared for comparison purposes. Furthermore the trans dienone shows the expected series of bands at 1665, 1610, 1590 and 1585 of decreasing intensity, whereas the spectrum of compound A has only bands at 1660 and 1575, and these are of reversed intensity relationship. This pattern is more nearly the one expected of a conjugated enol ether. Finally the trans-dienone has a strong band at 1115 cm^{-1} , the original acetylenic ketone showed a strong doublet at 1280 and 1290 cm^{-1} , while compound A had only a single strong band at 1083 cm^{-1} . The data do not provide unequivocal evidence for a structural assignment, but are in better accord with a pyran than a dienone form.

Considerable difficulty was experienced in obtaining a reasonable sample for examination in the n. m. r. spectrometer. The best spectrum obtained showed a complex series of peaks lying between

427 and 456 cps (phenyl group), a single sharp peak at 5.49 ppm, a poorly resolved doublet (?) at 484 ppm, and a group of unresolved bands between 75-130 cps. The ratios of the areas under the peaks are 5.0:1.7:0.75:8.5. These ratios do not correspond to those expected for a dienone. The spectrum differs in several other characteristics from the spectrum expected of a dienone. Thus the aromatic protons show a smaller range of chemical shift values (29 cps) than for the trans-dienone (48 cps). There is no nearly equal absorption due to allylic and non-allylic protons as is expected of the dienone. Predicted values of the various chemical shifts and couplings for the cis-dienone and the α -pyran are shown along with the values obtained for compound A in the chart below. Once again the predicted chemical shifts for the three protons given

CHART II

Predicted Chemical Shifts and Coupling Constants
for the cis-dienone and the α -Pyran

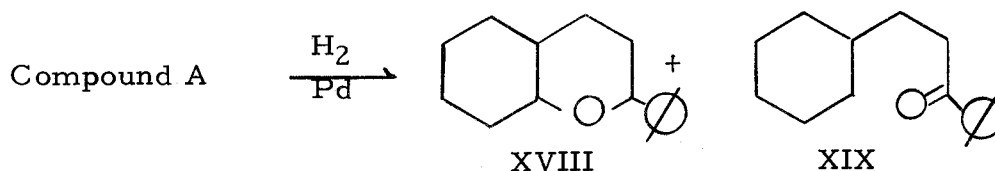


confirm the idea that A is not the cis-dienone. And once again the data are in better agreement with the pyran structure than any other.

One peculiar feature of the spectrum of A is disturbing if the α -pyran form is assigned. The protons of C_4 and C_5 of the pyran are expected to show up as an AB pair with $J \sim 6$ cps. A gives one singlet at 5.49 δ . These are indeed the two hydrogens introduced in the reduction, since use of deuterium gave a deuterium-bearing A which showed no 5.49 singlet but was otherwise identical with the normal spectrum of A. One possible explanation for this is that the phenyl group is so situated with respect to the proton at C_4 that it gives rise to enough deshielding to move it downfield, and coincidentally to exactly the same position as the C_5 proton.

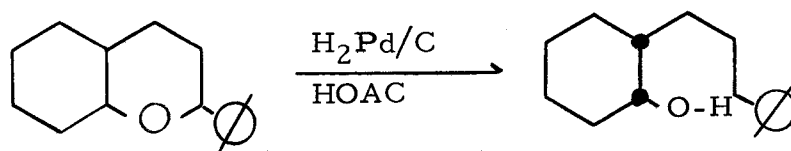
It is quite certain from these data that compound A is not the cis-dienone. Providing that no skeletal rearrangement has occurred, the α -pyran XVII provides the best fit for the properties of compound A. Certainly the mild conditions used for the hydrogenation and purification process should reduce the probability of such a rearrangement to a minimum. However further evidence supporting the unrearranged skeleton for compound A was obtained. A sample of compound A was reduced under more vigorous conditions over a Pd catalyst. Careful chromatography of the reduction product on alumina gave three fractions, one identified as the tetrahydropyran (XVIII), a second as 1-phenyl-3-cyclohexyl-1-propanone (XIX), and the third an unidentified ketone having $\tilde{\nu} = 1710 \text{ cm.}^{-1}$. This latter ketone was not 2-(γ -phenylpropyl) cyclohexanone, since its

infrared spectrum was not identical with that of an authentic sample



of the substituted cyclohexanone. The ratio of the three products was approximately 20% XVIII, 30% XIX and 50% of the unknown ketone.

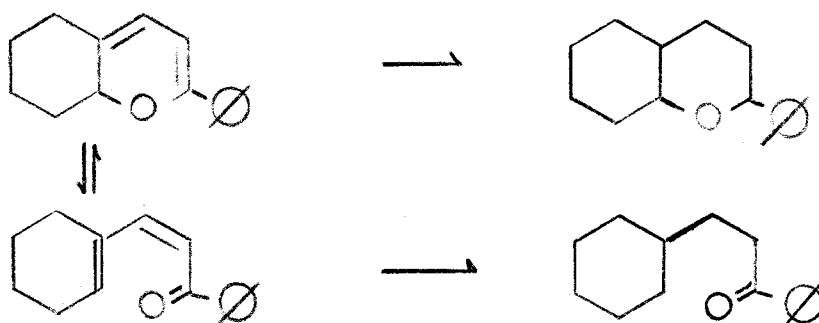
The structure of XVIII was confirmed by its hydrogenolysis over Pd to form the known 2-(γ -phenylpropyl) cyclohexanol (23).



This alcohol was isolated in the cis form. Direct reduction of the acetylenic ketone over platinum gave XIX in high yield.

On the basis of these data we have tentatively assigned compound A the structure of the α -pyran XVII. If this is a correct assignment the pyran is not in equilibrium with any large amount of the cis-dienone. Treatment of compound A with 2,4-dinitrophenylhydrazine gave a 2,4-dinitrophenylhydrazone different from that obtained from the trans-dienone. While the derivative was not conclusively identified as derived from the cis-dienone, the formation of a ketonic derivative from a non-ketone reluctant is certainly explicable if A is the α -pyran. The results of the hydrogenation of compound A are also nicely explained if A

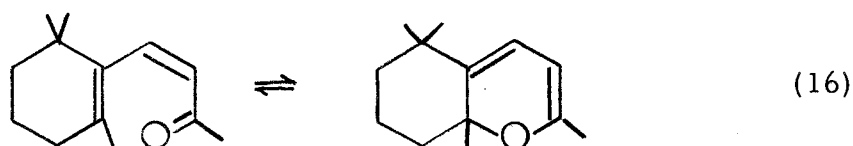
is the pyran and it is in mobile equilibrium with traces of the



cis-dienone. Unfortunately the instability of A with respect to polymerization has prevented further investigation of its properties.

CONCLUSIONS

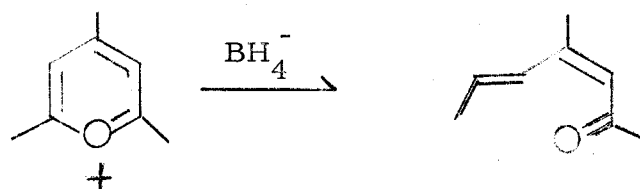
This work has produced the first direct evidence of a valence isomerization between an α -pyran and a cis-dienone. For the molecules shown in equation (16), temperature variable n. m. r. studies



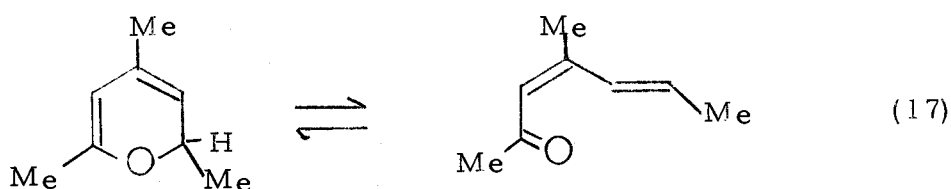
allowed us to identify the spectrum due to the hitherto unknown cis-dienone. The equilibrium constant for the reaction was measured at three temperatures. It was shown thereby that the enthalpy difference between the two valence isomers was 700 cal. with the pyran being more stable. Rough thermochemical calculations indicate the dienone to be more stable by 10-15 kcal/mole. It appears that this calculation gives a gross overestimate of the enthalpy difference, since it is unlikely that the dienone above is some 13 kcal less stable than pentadienal, or alternatively that the pyran is more stable by a similar amount than α -pyran itself.

The structure, configuration and conformation of the 4-methyl-3,5-heptadien-2-one obtained from the reaction of 2,4,6-trimethylpyrylium ion with borohydride ion was established. Though it proved impossible to obtain unequivocal evidence to show that the dienone was formed by ring opening of an α -pyran, reasonable evidence in

support of this hypothesis was obtained. Assuming this mechanism

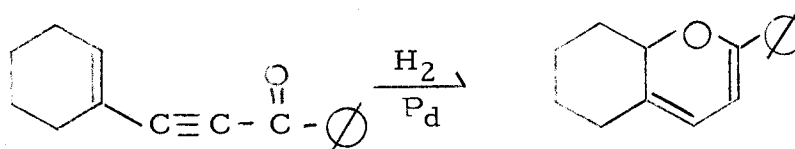


to be correct, we deduce that the valence isomerization in this case favors the cis-dienone at equilibrium with $K \sim 100$. The drastic



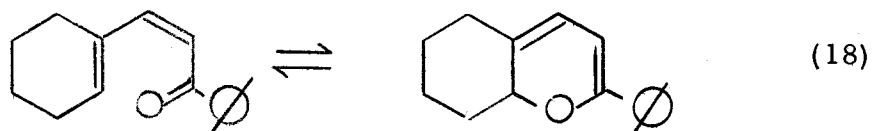
change in equilibrium constants between cases (16) and (17) by comparison with the slight alteration of substitution pattern again supports the conclusion that the basic energy difference between the dienone and α -pyran is less than the rough thermochemical estimate.

Finally, we have obtained evidence which permits the tentative assignment of the pyran structure to one product of the semi-hydrogenation of 1-phenyl-3-cyclohexenyl-2-propyn-1-one. The



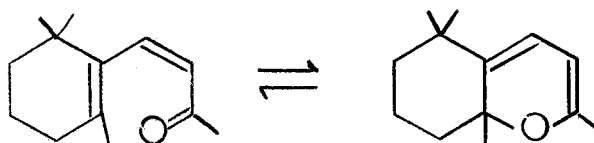
spectral properties of this substance, which was not obtained in

pure form, show that no identifiable amount of cis-dienone is present in equilibrium with it. Once again if the structural





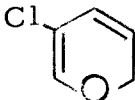
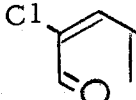
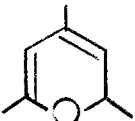
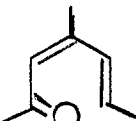
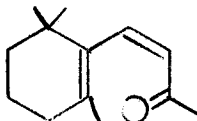
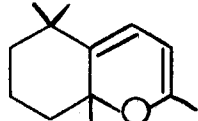
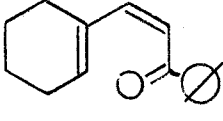
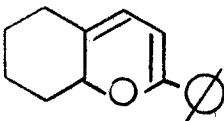
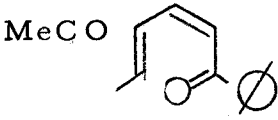
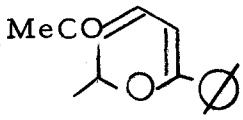
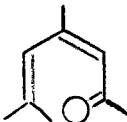
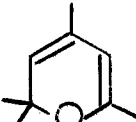
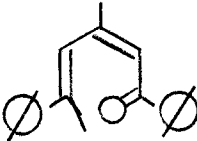
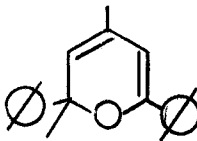
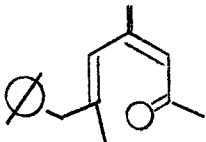
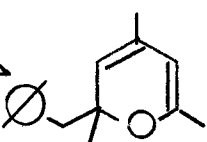
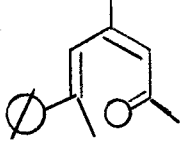
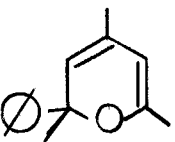
assignment of the pyran is correct $K > 100$ as shown. Again a minor structural alteration has produced a profound change in the equilibrium.

In Table XII the various α -pyrans or related cis-dienones which have been reported either in this thesis or the literature are listed with the more stable valence isomer as assigned listed at the right.



Only in the case of our first example shown above is evidence provided for the presence of both isomers at equilibrium. It must be noted that the considerable difficulties we experienced in attempting to provide reliable structural evidence for the pyran of equation 18 suggests that some of the structural assignments reported in the literature should be viewed with reservation. Taken at their face value however, the data of Table XII provide no simple rules for predicting the more stable valence isomer in a given case. We can suggest that a phenyl group tends to stabilize the pyran form. Also

Table XII. Valence isomers reported for α -pyran-cis-dienone equilibria.

		<u>reference</u>
	\longrightarrow	 11
	\longrightarrow	 1, 79
	\longrightarrow	 4 and this work
<hr/>		
	\rightleftharpoons	 15 and this work
	\longrightarrow	 this work
	\longrightarrow	 82
	\longrightarrow	 42, 50
	\longrightarrow	 42
	\longrightarrow	 29
	\longrightarrow	 42

in the absence of other stabilizing features an α -pyran having a hydrogen on the α -carbon will be less stable than the isomeric cis-dienone. A structural basis for these suggestions is not immediately apparent. All the results reported support our earlier observation that pentadienal is more stable than α -pyran itself, but that the enthalpy difference is considerably smaller than is estimated from thermochemical data.

In the discussion given above it has been tacitly assumed that the data reported were observed with equilibrated mixtures. Since in most cases no attempt to equilibrate the material was made, the assumption need not necessarily be accurate. If however the valence isomerization process is rapid at room temperature the equilibration will be achieved automatically. Explicit evidence is provided in this thesis that the valence isomerization of equation 16 is indeed rapid at room temperature. At 70-100° the conversion of α -pyran to dienone form is rapid enough so that when the sample has achieved thermal equilibrium it has already reached chemical equilibrium. At 35° the dienone reconverts to α -pyran so rapidly that the half-life of the dienone is only a minute or two with respect to the valence isomerization of equation 17, we have shown that a transient intermediate is formed during synthesis of the dienone. This intermediate which has spectral properties compatible with those expected of the α -pyran converts to the cis-dienone with $k \sim 7 \times 10^{-3} \text{ sec.}^{-1}$ at 21°. Review of the literature shows that in all cases where the synthesis produced

one valence isomer directly and the other form was more stable, no evidence has been reported for the appearance of the direct product. We conclude therefore that valence isomerizations between cis-dienones and α -pyrans are generally rapid at room temperature.

EXPERIMENTAL

1-Phenyl-3-cyclohexenyl-2-propyn-1-one. -XV

A solution containing 0.61 mole of the bromomagnesium salt of 1-ethynylcyclohexene in 250 ml of ether was prepared according to the procedure of Churchley (19). To this cold solution was added 65 g. (0.6 mole) of freshly distilled benzaldehyde in 100 ml of ether. The reaction mixture was allowed to stand overnight and was then hydrolyzed with saturated ammonium chloride. The ether layer was dried over anhydrous magnesium sulfate, and the ether was removed in vacuo. The crude 1-phenyl-3-cyclohexenyl-2-propyn-1-ol was used directly in the next step.

A mixture of 22 g (0.22 mole) of chromium trioxide, 50 ml of water and 18 ml of concentrated sulfuric acid was added slowly to a cold solution of 41 g (0.19 mole) of the above alcohol in 46 ml of acetone. Addition required 1 hr., after which the mixture was stirred for 2 hrs. more. The reaction mixture was extracted with ether, the ether extracts dried over magnesium sulfate, and the ether removed in vacuo. The product was chromatographed over activity III alumina using petroleum ether (b.p. 35-60°) as eluant. A light yellow oil, n_D^{25} 1.6040, λ_{\max} 304 (10,800), $\tilde{\nu}$: 1630, 1608, 1580, 1320, 1280-90, 800, 702 cm^{-1} was isolated in 84% yield. This substance gave an n.m.r.

spectrum consisting of a pair of singlets at 7.8 and 7.4, (5H), a multiplet at 7.45 (1H), another at 2.25 (4H) and a third at 1.685 (4H). Churchley (19) has reported n_D^{23} 1.5960 and λ_{\max} 304 (9500), 286 (10,900) and 260 (12,800) for this substance.

Semihydrogenation of 1-Phenyl-3-cyclohexenyl-2-Propyn-1-one

All hydrogenations were carried out using a catalyst containing 5% palladium on freshly precipitated calcium carbonate. A variety of conditions was employed including the catalyst poisoned according to Lindlar (63), added synthetic quinoline and several different solvents. Some conditions are listed in table XIII. In all cases the crude reduction product was essentially the same judged by the infrared spectra obtained. Directions for the procedure finally adopted as a normal operating method are given below.

A suspension of 200 mg of 5% palladium on freshly precipitated calcium carbonate in ca. 15 ml of cyclohexane was saturated with hydrogen at one atmosphere pressure. A solution containing 400 mg. of freshly chromatographed 1-phenyl-3-cyclohexenyl-2-propyn-1-one was added to the reaction flask via a serum cap. The reaction mixture was stirred vigorously at room temperature with a magnetic stirrer. Hydrogenation was carried out under one atm. of hydrogen and was arbitrarily interrupted after one mole of hydrogen had been taken up. The entire process was carried out in a flask wrapped in

in black paper to exclude light. The rate of hydrogen absorption depended upon the purity of the substrate in a marked degree. Samples stored 24 hrs. in the refrigerator after chromatography virtually completely inhibited the reduction. It was imperative that the substrate be chromatographed immediately prior to hydrogenation. After the predetermined amount of hydrogen had been absorbed, the catalyst was removed by filtration, and the solvent by evaporation, in vacuo.

Table XIII. Variations in conditions for the reduction of 1-phenyl-3-cyclohexenyl-propynone with 5% Pd/CaCO₃.

Weight (g.) of Substrate	Catalyst % by Weight of Substrate	Solvent	remarks
0.25	5	4 ml EtOAc	
0.25	10	10 ml EtOAc	
0.25	27	10 ml EtOAc	
0.25	50	10 ml EtOAc	
0.25	20	1 ml EtOAc	
0.25	20	25 ml EtOAc	
0.25	20	10 ml EtOAc	heat lamp used
0.25	260	10 ml EtOAc	
0.19	10	10 ml cyclohexane	
0.19	20	20 ml cyclohexane + 9 drops of quinoline	
0.25	20	10 ml EtOAc	Lindlar catalyst

Compound A (3-phenyl-2-oxabicyclo 4.4.0 deca-3,5-diene?). XVII

The crude hydrogenation product from above was chromatographed on ca 25 times its weight of silica gel (Mallinckrodt silicic acid 100 mesh, chromatography grade) using a low boiling saturated aliphatic hydrocarbon (pentane, hexane or petroleum ether b.p. 30-60 were all used successfully) as eluant. Pressure was used to speed the flow of eluant. A small amount of the over reduced ketone XIX eluted first and was followed quickly by an unstable yellow oil, $\lambda_{\text{max}}^{338}$ (ca. 10,000)(cyclohexane solvent), $\bar{\nu} = 1660\text{m}, 1600\text{m}, 1575\text{m}, 1500\text{s}, 1373\text{m}, 1340\text{m}, 1265\text{m}, 1240\text{w}, 1225\text{w}, 1083\text{vs}, 1050\text{w}, 1025\text{m}, 755\text{s}, 686\text{s cm}^{-1}$. The substance polymerized to a tacky semi-solid on brief storage. The acetylenic ketone XV followed this fraction.

Anal. Calc'd for $\text{C}_{15}\text{H}_{16}\text{O}$: C, 84.95; H, 7.59. Found: C, 84.10; H, 7.62; C, 83.84; H, 7.61; C, 83.00; H, 7.57.

When the yellow oil was treated with the 2,4-dinitrophenylhydrazine reagent according to Shriner and Fuson (85, p. 111) a 2,4-dinitrophenylhydrazone, m.p. $151-2^{\circ}$, was obtained in low yield.

Anal. Calc'd for $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_4$: C, 64.28; H, 5.14. Found: C, 63.99; H, 5.61.

1-Phenyl-3-cyclohexyl-1-propanone XIX

A suspension of 2.66 g. of platinum oxide in 39.0 g. (0.184 mole) of 1-phenyl-3-cyclohexenyl-2-propyn-1-one was shaken under 20 psi. of hydrogen in a Parr Shaker. Approximately 3.3 moles of hydrogen was absorbed. Chromatography of the crude reduction product over activity III alumina gave ca. 80% of a white solid, m. p. 43° , $\nu = 1676$ vs, 1593 w, 750 m, 736 M, 690 S cm.^{-1} , $\delta = 7.4$ and 7.5 mult. (5H), 2.85 triplet (2H) and broad absorption between 1.9 and 1.0 (14H).

Anal. Calc'd for $\text{C}_{15}\text{H}_{20}\text{O}$: C, 83.28; H, 9.27. Found: C, 83.54; H, 9.15.

A 2,4-dinitrophenylhydrazone, m. p. 181-2, was prepared according to the directions of Shriner and Fuson (85, p. 111).

Anal. Calc'd for $\text{C}_{21}\text{H}_{24}\text{N}_4\text{O}_4$: C, 63.62; H, 6.10. Found: C, 63.40; H, 6.01.

A solution of 12.0 g. (0.057 mole) of 1-phenyl-3-cyclohexenyl-2-propyn-1-one in cyclohexane was hydrogenated over 1.0 g. of 5% palladium or calcium carbonate until 0.9 mole of hydrogen has been absorbed. Silicic acid chromatography, as described under the preparation of compound A, gave 6.95 g. of material, $\lambda_{\text{max}}^{338}$ (10,400). This 6.95 g. of compound A was again hydrogenated over 2.2 g. of 5% palladium on calcium carbonate in cyclohexane.

Absorption ceased after 1.58 moles of hydrogen had been used. Chromatographic separation of this product over 30 times its weight of activity II-III alumina using gradient elution with pentane containing increasing amounts of benzene gave 30-40% of 1-phenyl-3-cyclohexyl-1-propanone, m. p. 42-43°, in the later fractions.

3-Phenyl-2-oxabicyclo[4.4.0] decane XVIII

A. From Compound A

The two step hydrogenation of 1-phenyl-3-cyclohexenyl-2-propyn-1-one described above gave a product which was chromatographed over activity II-III alumina. The early fractions containing 750 mg. (ca 20%) of an oil which was rechromatographed on activity II alumina to give 600 mg. of a colorless oil, b. p. ~ 100° (0.5mm.), $n_D^{20} = 1.455$, $n_D^{25} = 1.383$, $n_D^{30} = 1.215$, $n_D^{35} = 1.155$, $n_D^{40} = 1.095$, $n_D^{45} = 1.060$, $n_D^{50} = 0.988$, $n_D^{55} = 0.950$, $n_D^{60} = 0.750$, $n_D^{65} = 0.696$ cm.⁻¹, $\delta = 7.2$ m, (5H), 4.3, m(1H), 3.65m(1H), 1.9-1.2m(13+H).

Anal. Calc'd for C₁₅H₂₀O: C, 83.28; H, 9.32. Found: C, 83.00; H, 9.12.

B. From 2-(3-phenyl-3-hydroxypropyl)cyclohexanol

One gram (6.0043 mole) of 2-(3-phenyl-3-hydroxypropyl)cyclohexanol was heated under reflux with 25% sulfuric acid for 3 hrs. The reaction mixture was cooled and the organic products extracted with ether. The ether extracts were washed with dilute

sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Removal of the ether gave a colorless oil which the n. m. r. and infrared spectra showed to be a mixture of the various stereoisomeric forms of the desired ether, b. p. 100-110° (0.5mm), n_D^{20} 1.538.

Anal. Calc'd for $C_{15}H_{20}O$: C, 83.28; H, 9.32. Found: C, 82.97; H, 9.32.

Cis-2-(γ -phenylpropyl)cyclohexanol

A sample (100 mg.) of 3-phenyl-2-oxabicyclo[4.4.0] decane obtained by further hydrogenation of compound A was treated with hydrogen at 1 atm pressure over 25 mg. of 5% palladium on charcoal in 5 ml of glacial acetic acid. The product was a clear oil which gave a 3, 5-dinitrobenzoate, m. p. 101-102°. The dinitrobenzoate of cis-2-(γ -phenylpropyl)cyclohexanol has been reported (23) to melt at 101-102°.

2-(3-phenyl-3-hydroxypropyl)cyclohexanol

A sample of 2-(β -benzoylethyl) cyclohexanone, $\tilde{\nu}$ = 1710, 1680, was prepared from cyclohexanone and phenyl vinyl ketone according to the procedure of Cope (22). To 2.3 g. (0.01 mole) of this dione in ether solution was added 0.38 g (0.01 mole) of lithium aluminum hydride. Excess hydride was destroyed with moist ether and the

reaction mixture was treated with saturated ammonium chloride solution. The product was taken up in ether, the ether solution was dried over magnesium sulfate and the ether removed in vacuo. The diol was recrystallized from pentane, m. p. 110-111°, $\tilde{\nu} = 3332s$, 1587w, 1486m, 1442s, 1058s, 760m, 6955 cm.^{-1} and was obtained in 80% yield.

Anal. Calc'd for $\text{C}_{15}\text{H}_{22}\text{O}_2$; C, 76.88; H, 9.46. Found: C, 77.05; H, 9.65.

2-(γ -Phenylpropyl) cyclohexanone

Cinnamyl bromide, 29 g. (0.15 mole), was added slowly to a solution of 21 g. (0.14 mole) of cyclohexanone pyrrolidine enamine in 150 ml of acetonitrile. The mixture was heated under reflux for 18 hrs. in a nitrogen atmosphere. Most of the acetonitrile was removed by distillation and 75 ml. of water was added to the residue. This was boiled for 15 min., cooled and the organic product was taken up in ether. The ether solution was dried over magnesium sulfate and the ether removed in vacuo. An oil, b. p. 109-121 (0.15 mm.), n_D^{21} 1.5570, 14.9 g. (50%) was obtained. This compound has been reported to have b. p. 193° (13 mm), n_D^{24} 1.5620 (23).

One gram of the cinnamyl ketone was hydrogenated in 10 ml of glacial acetic acid over 100 mg of platinum oxide at one atm. of hydrogen pressure. The product, isolated in the usual manner,

$\bar{\nu} = 1710 \text{ cm.}^{-1}$, has been prepared previously by Cornubert (23).

Trans-1-Phenyl-3-cyclohexenyl-2-propen-1-ol

A solution containing 5.0 g. (0.029 mole) of 1-phenyl-3-cyclohexenyl-2-propyn-1-one in 100 ml of ether was added slowly to a cold suspension of 0.82 g. (0.024 mole) of lithium aluminum hydride in ether. The mixture was stirred 5 hrs. at room temperature and then was heated for 15 min. under reflux. After having been cooled, the mixture was carefully treated with a saturated ammonium chloride solution. The ether layer was washed with water, dried over anhydrous magnesium sulfate and finally concentrated to ca. 100 ml. total volume. An equal volume of petroleum ether (b. p. 30-60°) was added and a white solid, m. p. 64-65°; $\bar{\nu}$: 3160, 1630, 1185, 1088, 1015, 960, 915, 838, 755, 700 cm.^{-1} , 3.0 g., precipitated.

Anal. Calc'd for $\text{C}_{15}\text{H}_{18}\text{O}$: C, 84.61; H, 8.46. Found: C, 84.30; H, 8.46; C, 84.50; H, 8.83.

Trans-1-Phenyl-3-cyclohexenyl-2-propen-1-one

The alcohol above was oxidized with Jones' reagent as described in the preparation of 1-phenyl-3-cyclohexenyl-2-propyn-1-one. Chromatography of the oxidation product on activity II alumina using 5% benzene in petroleum ether (b. p. 30-60°) gave a yellow oil which crystallized from petroleum ether (b. p. 30-60) as an off-white

solid, m.p. 68.5-69.5°, $\lambda_{\text{max}}^{307.5}$ (23, 850), $\tilde{\nu} = 1665\text{s}, 1610\text{m}, 1590\text{w}, 1585\text{m}, 1280\text{s}, 1205\text{m}, 1170\text{m}, 1115\text{s}, 1012\text{m}, 975\text{m}, 760\text{m}, 685\text{m}, \text{cm.}^{-1}$, $\delta = 7.8$ and 7.4 , m(5H), 7.0 , q(2H) $J = 15.5$ cps, 6.2 , m(1H), 2.2 , m(4H), 1.7 , m(4H).

Anal. Calc'd for $\text{C}_{15}\text{H}_{16}\text{O}$: C, 84.95; H, 7.59. Found: C, 85.05; H, 7.77.

A 2,4-dinitrophenylhydrazone, m.p. 225°d., was prepared according to the procedure of Shriner and Fuson (85, p. 111).

Anal. Calc'd for $\text{C}_{21}\text{H}_{20}\text{N}_4\text{O}_4$: C, 64.28; H, 5.14. Found: C, 64.10; H, 5.80.

1, 3, 7, 7-tetramethyl-2-oxobicyclo-(4,4,0)-deca-3,5-diene VI

This compound was prepared by the method described by Büchi and Yang (15) except that a Hanovia ultraviolet lamp #679A (450 watt) was used for a 3 hour irradiation period. Product ratios were similar to those reported by Büchi and Yang.

4-Methylhepta-cis-3-trans-5-dien-2-one XI

This compound was prepared according to the directions of Balaban, Mikai and Nenitzescu (4) from 2, 4, 6-trimethylpyrylium perchlorate (27).

The Transient Intermediate (XIII) [2, 4, 6-trimethyl-2H-pyran?]

Spectral studies on the transient intermediate in the formation of a 4-methyl-hepta-3, 5-dien-2-one were carried out as follows.

A. Ultraviolet Studies

A suspension of 0.5 g. (2.1 M moles) of 2, 4, 6-trimethylpyrylium perchlorate in 100 ml. of pentane and 10 ml. of water was cooled to 0° in an ice-bath and 0.2 g. (53 M moles) of sodium borohydride was added. The mixture was stirred vigorously for 10-15 secs. and about 25 ml of the pentane layer was poured into a test tube stored in a Dry-Ice acetone bath. A few drops of this solution was added to 3 ml. of pentane and the behavior of this solution was examined in the region between 250-280 m μ with a Cary model 15 spectrophotometer.

The rate of disappearance of this intermediate was measured by determining the absorbance of a pentane solution at various time intervals at 253.5 m μ . A plot of $2.3 \log \left(\frac{A_{\infty} - A_t}{A_{\infty}} \right)$ vs time gave a straight line with slope $7 \times 10^{-3} \text{ sec.}^{-1}$.

B. N. M. R. Studies

Preparation of the intermediate was carried out exactly as described above except that spectral grade carbon tetrachloride (10ml.)

was used in place of pentane. After the reaction had proceeded for 15 secs. a portion of the carbon tetrachloride layer was pipetted into a test tube containing ca 2 g. of anhydrous magnesium sulfate. The test tube was placed in a Dry-Ice bath for several minutes. The frozen material was quickly thawed, the drying agent was removed by filtration, and the filtrate was transferred to an n. m. r. sample tube. The n. m. r. spectrum was determined at -22°C .

Spectral Measurements

Nuclear magnetic resonance spectra were determined on the Varian A-60 High Resolution NMR Spectrophotometer equipped with a variable temperature probe. All runs were made on neat samples or with solutions in carbon tetrachloride. Tetramethylsilane (TMS) was used as an internal standard.

Infrared Spectra were run on the Beckman IR8 Infrared Spectrophotometer equipped with a sodium chloride prism.

Ultraviolet spectra were determined on the Beckman model DB Spectrophotometer equipped with a Beckman recorder. The kinetic study using ultraviolet data was carried out with the Carey model 15 Spectrophotometer.

Melting points (corrected) were determined in a Buchi melting point apparatus.

BIBLIOGRAPHY

1. Anderson, J. C., D. G. Lindsay and C. B. Reese. The reaction between 2,3-dihydrofuran and dichlorocarbene. An attempted 2-H-pyran synthesis. *Tetrahedron* 20:2091-2096. 1964.
2. Auwers, K. V. Effects of ring closure on spectrochemical properties II. Unsaturated heterocyclic compounds. *Justus Liebig's Annalen der Chemie* 422:133-195. 1921.
3. Baker, John William. *Tautomerism*. London. G. Routledge and Sons Ltd., 1934. 250 p.
4. Balaban, A. T., G. Mikai and C. D. Nenitzescu. Reduction of pyrylium salts with sodium borohydride. *Tetrahedron* 18: 257-295. 1962.
5. Balaban, A. T., V. E. Sahini and E. Keplinger, Electronic absorption spectra of alkyl- and phenyl-substituted pyrylium salts. *Tetrahedron* 9:163-174. 1963.
6. Barber, M. S., et al. Studies in nuclear magnetic resonance. Part I. Methyl groups of carotenoids and related compounds. *Journal of the Chemical Society*, 1960, p. 2870-2881.
7. Bellamy, L. J. *The infrared spectra of complex molecules*. 2nd Ed. New York, Wiley and Sons, 1958. 422 p.
8. Berson, Jerome A. Ring chain tautomerism of pyrylium pseudobases. *Journal of the American Chemical Society* 74:358-360. 1952.
9. Blout, Elkan R. and Melvin Fields. Absorption spectra. V. The ultraviolet and visible spectra of certain polyene aldehydes and polyene azines. *Journal of the American Chemical Society* 70:189-193. 1948.
10. Blout, Elkan R., Melvin Fields and Robert Karplus. Absorption spectra. VI. The infrared spectra of certain conjugated double bonds. *Journal of the American Chemical Society* 70: 194-198. 1948.

11. Boehm, E. E. and M. C. Whiting. The stereoisometric penta-2,4-dienals and 3-methylpenta-2,4-dienals. *Journal of the Chemical Society*, 1963, p. 2591-3.
12. Bohlmann, Ferdinand and Heinz Gunter Viehe. Syntheses starting with 1-methoxy-1-butene-3-yne. *Abhandlung der Braunschweigerischen Wissenschaftlichen Gesellschaft* 6:41-6. 1954 (Abstracted in *Chemical Abstracts* 50:185h. 1956.)
13. Bowden, Kenneth, Ernest A. Braude and E. R. H. Jones. Studies in light absorption. Part III. Auxochromic properties and the periodic system. *Journal of the Chemical Society*, 1946, p. 948-52.
14. Braude, E. A. and F. C. Nachod. Determination of organic structure by physical methods. New York, Academic Press, 1955. 600 p.
15. Büchi G. and N. C. Yang. Light-catalyzed organic reactions. VI. The isomerization of some dienones. *Journal of the American Chemical Society* 79:2318-2323. 1957.
16. Burns, D., et al. Modified steroid hormones XXXVI. Steroidal 6-aminomethyl-3-alkoxy-3,5-dienones and their reactions. *Tetrahedron* 21:(3)569-82. 1965.
17. Campbell, Neil. Compounds containing a six membered ring with one heteroatom, oxygen or sulfur. In: *Chemistry of Carbon Compounds*, ed. by E. H. Rodd. vol. 4B. Amsterdam, Elsevier, 1959. p. 809-1004.
18. Cheronis, Nicholas D. and John B. Entrikin. Identification of organic compounds. A students text using semimicro techniques. New York, Interscience, 1963. 477 p.
19. Churchley, Phillip Leslie. Preparation and semihydrogenation of some α , β -acetylenic ketones. Master's Thesis. Corvallis, Oregon State University, 1963. 38 numb. leaves.
20. Claisen, L. Rearrangement of phenyl allyl ethers into C-allylphenols. *Berichte der Deutschen Chemischen Gesellschaft* 45: 3157-66. 1912.

21. Cope, Arthur C., Kathryn E. Hoyle and Dorothea Heyl. Rearrangement of allyl groups in three-carbon systems II. Journal of the American Chemical Society 63:1843-52. 1941.
22. Cope, Arthur C. and Edward C. Hermann. Cyclic polyolefins. X. Synthesis of phenylcycloocta-1,3-diene. Journal of the American Chemical Society 72:3405-3410. 1950.
23. Cornubert, Raymond, et al. Contribution a l etude de la stereochemie cyclanique. Bulletin de la Société Chimique de France, 1955, p. 400-407.
24. Crisan, C. and H. Normant. Recherches sur les magnesiens vinyliques (XVI). Preparation de cetones biethyleniques conjugies. Bulletin de la Société Chimique de France, 1957, p. 1451-54.
25. Dauben, W. G. et al. The preparation of $\Delta^{5,7}$ -steroidal dienes. Journal of the American Chemical Society 75:3255-58. 1963.
26. De Mayo, Paul. Mono- and sesquiterpenoids. The chemistry of natural products. Vol. 1. New York, Interscience. 1959. 320 p.
27. Dimroth, K. Neuere Methoden Der Präparativen Organischen Chemie III. 3. Aromatische Verbindung aus Piryliumsalzen. Angewandte Chemie 72:331-342. 1960.
28. Dimroth, Karl and D. H. Wolf. The preparation of 4H-(or 2H)-pyrans from pyrylium salts. Angewandte Chemie 72:777. 1960.
29. Dimroth, Karl, Karlheinz Wolf and Hermann Kroke. 2H- and 4H-thiopyran derivatives. Justus Liebig's Annalen der Chemie 678:183-201. 1964.
30. Dolliver, M. A., et al. Heats of organic reactions. V. Heat of hydrogenation of various hydrocarbons. Journal of the American Chemical Society 59:831-841. 1937.
31. Dolliver, M. A., et al. Heats of organic reactions. VI. Heats of hydrogenation of some oxygen containing compounds. Journal of the American Chemical Society 60:40-50. 1938.

32. Dolby, Lloyd J. and Manuel Diebono. Studies of terpene chemistry. I. The acid catalyzed dimerization of citronellal. *Journal of Organic Chemistry* 29:2306-10. 1964.
33. Eugester, C. H., C. Garbers und P. Karrer. Carotinoid-Synthesen IX. Sterioismere 1, 18-Diphenyl-3, 7, 12, 16-tetramethyloctadeca-nonaene. *Helvetica Chimica Acta*; 35:1179-1189. 1952.
34. Farmer, Ernest Harold, Christopher Kelk Ingold and Jocelyn Field Thorpe. XIX. The chemistry of polycyclic structures in relation to their homocyclic unsaturated isomerides. Part II. Intra-annular tautomerism. *Journal of the Chemical Society (Transactions)*, 1922, p. 128-159.
35. Fieser, L. F., and M. Fieser. *Steroids*. Baltimore, Md., Reinhold, 1959. 945 p.
36. Fischer, G. and W. Schroth. Reactions of enamines with β -chlorovinyl ketones. *Angewandte Chemie, International Edition* 2:394. 1963.
37. Forbes, W. F. and R. Shilton. Electronic spectra and molecular dimensions III. Steric effects of methylsubstituted α, β -unsaturated aldehydes. *Journal of the American Chemical Society* 81:786-90. 1959.
38. Frost, Arthur A. and Ralph G. Pearson. *Kinetics and mechanism*. 2nd Ed. New York, Wiley and Sons, 1961. 405 p.
39. Fujimoto, George I. Labeling of steroids in the 4-position. *Journal of the American Chemical Society* 73:1856. 1951.
40. Gagnaire, Didier and Elisea Payo-Subiza. Couplages des protons d'un methyle a travers cinq liaisons en resonance magnetique nucleaire: Ethers vinyliques heterocycliques. *Bulletin de la Societe Chimique de France* (3) 2623-27. 1963.
41. Gillam, A. E. and E. S. Stern. *An introduction of electronic absorption spectra in organic compounds*. London, Edward Arnold Pub. Ltd. 1958. 326 p.
42. Gompper, Rudolf und Otto Christmann. Pyrans. I. α und γ Pyrans. *Berichte der Deutschen Chemischen Gesellschaft* 94: 1784-1794. 1961.

43. Gompper, Rudolf und Otto Christmann. Synthese von α und γ -Pyranen. *Angewandte Chemie* 71:32-3. 1961.
44. Gould, Edwin S. Mechanism and structure in organic chemistry. New York, Henry Holt and Co., 1959. 790 p.
45. Hafner, Klaus und Hans Kaiser. Zur Kenntnis der Azulene, III. Eine Einfache Synthese Substituierter Azulene. *Justus Liebig's Annalen der Chemie* 618:140-152. 1958.
46. Hamlet, J. C., G. B. Henbest and E. R. H. Jones. Researches on acetylenic compounds. Part XXXII. Dehydration of acetylphenyl- and vinylacetylenyl- alcohols derived from cyclohexanone, and the hydration of the resultant hydrocarbons. *Journal of the Chemical Society*, 1951. p. 2652-2659.
47. Heck, R. F. The preparation of 1-Acyl-1,3-butadiene-derivatives from acylmethyl- π -allylcobalt tricarbonyl. *Journal of the American Chemical Society* 85:3383-3390. 1963.
48. Heilbron, Sir Ian. E. R. H. Jones and R. W. Richardson. Studies in the polyene series. Part XXV. Molecular structure and vitamin A activity. The synthesis of a biologically active C_{17} acid. *Journal of the Chemical Society*, 1949. p. 287-293.
49. Heilbron, Sir Ian, et al. Studies in the polyene series. Part XXVI. The synthesis of analogues to β -ionone. *Journal of the Chemical Society*, 1949, p. 737-741.
50. Hinnen, Alain, Jacques Dreux et M. Marcel Delépine. Identification et syntheses du tetramethyl-2,2,4,6-pyranne. *Comptes Rendus hebdomadaires des Seances de l'Academie des Sciences* 255:1747-49. 1962.
51. Hockstein, F. A. and Weldon G. Brown. Addition of lithium aluminum hydride to double bonds. *Journal of the American Chemical Society* 70:3484-3486. 1948.
52. Houben, J. Über die Einwirkung magnesium organischer Verbindungen auf Lactone. I. *Berichte der Deutschen Chemischen Gesellschaft*, 37:489-502. 1904.
53. Hückel, Walter and Udo Wörfler. Reduktionen in flüssigem ammoniac VII: Hexahydro-naphthalin. *Berichte der Deutschen Chemischen Gesellschaft* 89:2098-2104. 1956.

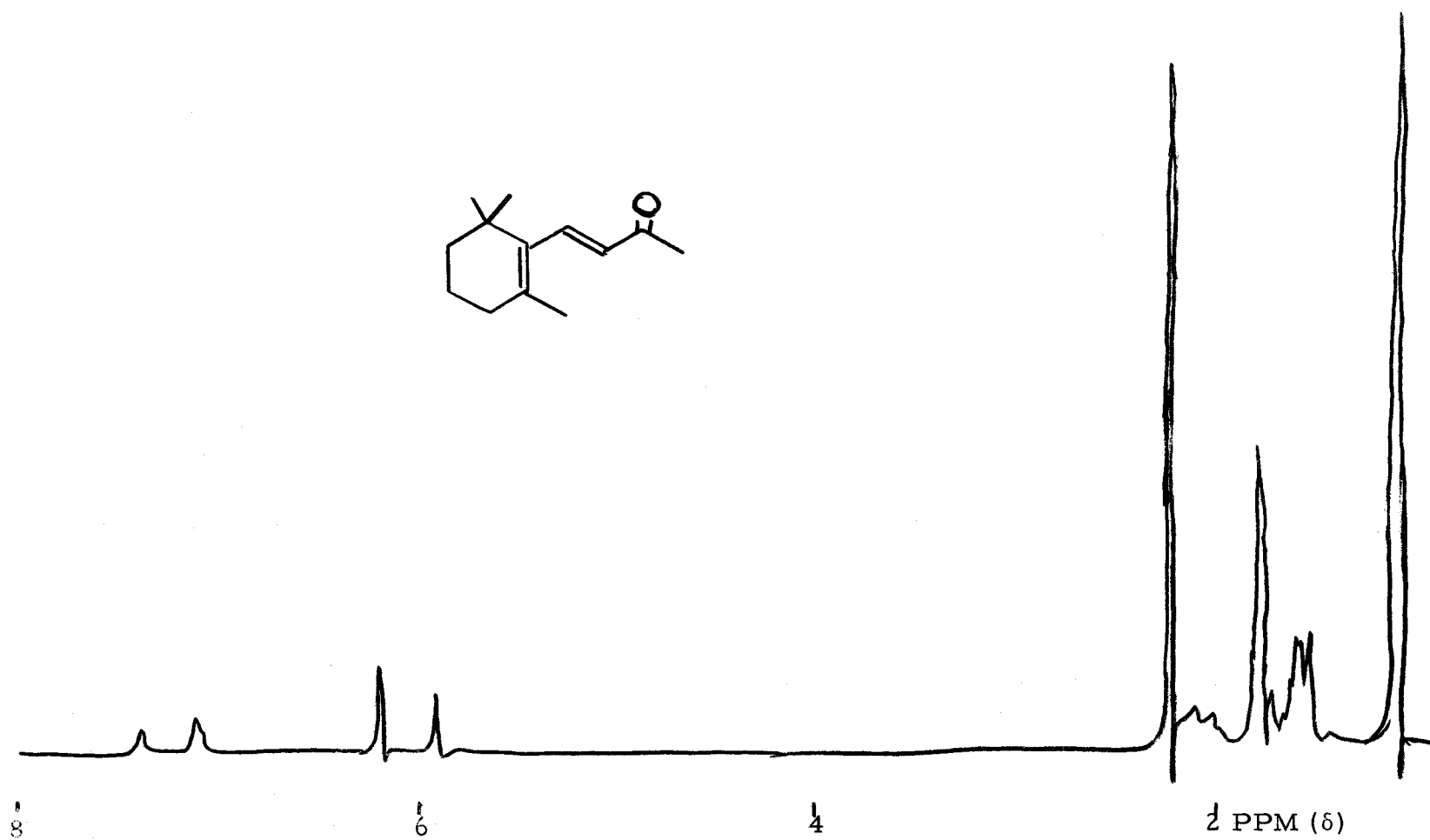
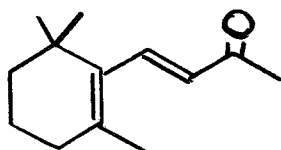
54. Jackman, L. M. Application of nuclear magnetic resonance in organic chemistry. N. Y. Pergamon Press, MacMillan Co., 1959. 134 p.
55. Jackman, L. M. and R. H. Wiley. Studies in nuclear magnetic resonance. Part II. Application to geometric isomerism about the ethylenic double bond. Journal of the Chemical Society, 1960. p. 2881-2885.
56. Jackman, L. M. and R. H. Wiley. Studies in nuclear magnetic resonance. Part II. Assignment of α - β unsaturated esters and isolation of pure trans- β -methylglutaconic acid. Journal of the Chemical Society, 1960. p. 2886-2890.
57. Jones, R. Norman and F. Herling. Characteristic group frequencies in the infrared spectra of steroids. Journal of Organic Chemistry 19:1252-680. 1954.
58. Kamlet, Mortimer J., ed. Organic electronic spectral data. Volume I. 1946-1952. New York, Interscience, 1960. 1208 p.
59. Köbrich, Gert von. Ungesättigte Ketone aus Pirylium-Verbindungen. Angewandte Chemie 72:348. 1960.
60. Köbrich, Gert von und Dietrich Wunder. Ringspaltung von Piryliumsalzen mit Metalorganischen Verbindungen. Justus Liebig's Annalen der Chemie 654:131-145. 1962.
61. Lauer, Walter M. et al. The abnormal Claisen rearrangement of crotyl-p-carbethoxyphenyl ether. Journal of Organic Chemistry 26:4285-90. 1961.
62. Levisalles, Jacques et Pierre Baranger. Sur les 3-hexene-2, 5-diones. Bulletin de la Société Chimique de France 240:444-446. 1955.
63. Lindlar, H. A new catalyst for selective hydrogenations. Helvetica Chimica Acta 35:446-450. 1952.
64. Löwenbein, Adabert. Über 2,4-Diarylchromene. Berichte der Deutschen Chemischen Giesellschaft 57B:1517-1526. 1924.
65. Mariella, Raymond P. and Richard R. Raube. Ultraviolet absorption spectra of alicyclic compounds. III. Phenyl cycloalkyl and styryl cycloalkyl ketones. Journal of the American Chemical Society 74:521-524. 1952.

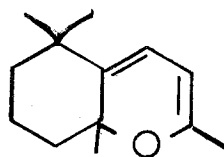
66. Marvell, Elliot N. and Philip Churchley. Valence isomerism of α -pyrans. In: American Chemical Society 144th Meeting, Los Angeles, California, March-April 1963. Abstracts of Papers, p. 47M.
67. Marvell, E. N., J. Caple and B. Schatz. Thermal valence isomerism: stereochemistry of the 2,4,6-7 octatriene to 5,6-dimethyl-1,3-cyclohexadiene ring closure. *Tetrahedron Letters* 1965(7), p. 385-389.
68. Masamune, S. and N. T. Castellucci. γ -Pyran. *Journal of the American Chemical Society*, 84:2452. 1962.
69. Meakins, G. D. The infrared absorption of vinyl ethers. *Journal of the Chemical Society*, 1953, p. 4170-4177.
70. Mikawa, Yukio. Characteristic absorption bands of vinyl ethers. *Bulletin of the Chemical Society of Japan* 29:110-115. 1956.
71. Morgan, L. R. Jr. The formation of α -hydroxy-trans, cis-muconic acid semialdehyde in the reduction of 2-pyrone-6-carboxylic acid. *Journal of Organic Chemistry* 27:343-344. 1962.
72. Nenitzescu, C. D., I. G. Gavat and D. Cocora. Über die wanderung von Halogenatomen in Kohlenstoff Ketten und Ringen. V. *Berichte der Deutschen Chemischen Gesellschaft* 73:233-237. 1940.
73. Noyce, Donald S., Harvey S. Averböck and Wilmer L. Reed. Isotope effects in the acid-catalyzed isomerization of cinnamic acids. *Journal of the American Chemical Society* 84:1647-1650. 1962.
74. Noyce, Donald S. and Margaret Jeffraim Jorgenson. The isomerization of substituted cis-chalcones in sulfuric acid. Consequences of the two mechanisms. *Journal of the American Chemical Society* 85:2420-2426. 1963.
75. Phillips, J. D. and F. C. Nacod, eds. Organic electronic spectral data. Volume IV. 1958-1959. New York, Interscience, 1963. 1179 p.

76. Pippen, E. L. and M. Novaka. Method for synthesizing normal aliphatic 2,4-dienals. *Journal of Organic Chemistry* 23:1580-2. 1958.
77. Pitzer, Kenneth S. Repulsive forces in relation to bond energies, distances and other properties. *Journal of the American Chemical Society* 70:2140-2145. 1948.
78. Roberts, John D. Notes on molecular orbital calculations, New York, W. A. Benjamin. 1962. 156 p.
79. Sarel, S. and J. Rivlin. Ring-chain Tautomerism in the 5-chloro-2H-pyran system. *Israel Journal of Chemistry* 1:221-2. 1963.
80. Saunders, M. and E. H. Gold. Preparation of N-phenyl-1,2-dihydropyridine. *Journal of Organic Chemistry* 27:1439-40. 1962.
81. Schubert, W. M. and Wayne A. Lanke. Use of metals to prepare 1,3-butadiene and derivatives. *Journal of the American Chemical Society* 76:1956-7. 1954.
82. Schulte, K. E., J. Reisch und A. Mock. Die Darstellung von Furan-und Pyran Derivaten aus α -alkinyl- β -dicarbonyl Verbindungen. *Archiv der Pharmazie und Berichte der Deutschen Pharmazeutischen Gesellschaft* 295:627. 1962.
83. Shine, H. J. A new technique in preparing 2,4-dinitrophenylhydrazones. Use of diglyme as solvent. *Journal of Organic Chemistry* 252. 1959.
84. Shriner, R. L. and A. G. Sharp. The action of alkylmagnesium halides on coumarin and related compounds. Synthesis of 2,2-dialkyl-1,2-benzopyrans. *Journal of Organic Chemistry* 4:575-587. 1939.
85. Shriner, Ralph L., Reynold C. Fuson and David Y. Curtin. The systematic identification of organic compounds. 4th ed. New York, Wiley, 1956. 426 p.
86. Surber, W., V. Theus, L. Colombi und H. Schinz. Über die cis, trans-Stereoisomerie bei dodecadien-(3,5)-on-(2) und 4- Δ^1 -cyclohexenylbuten-(3)-on-(2). *Helvetica Chimica Acta* 39:1299-1311. 1956.

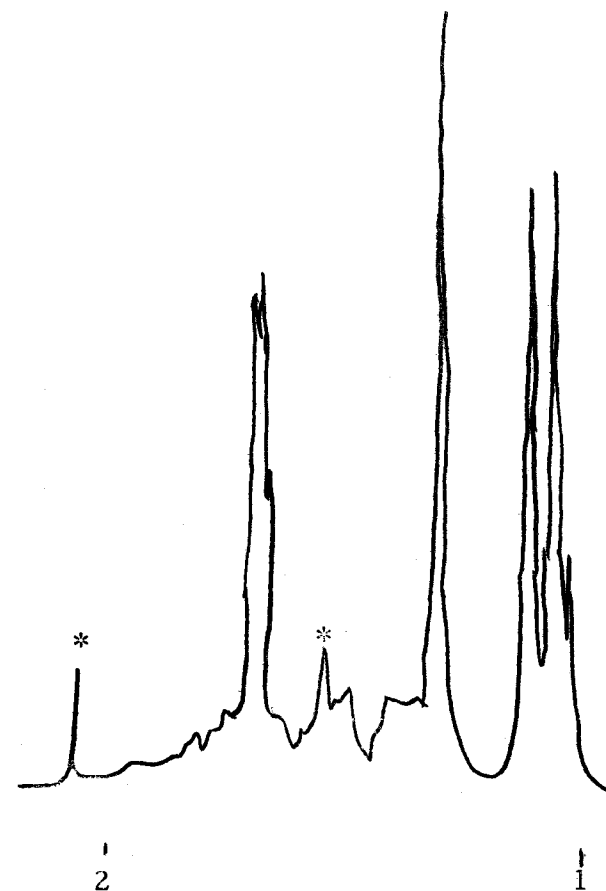
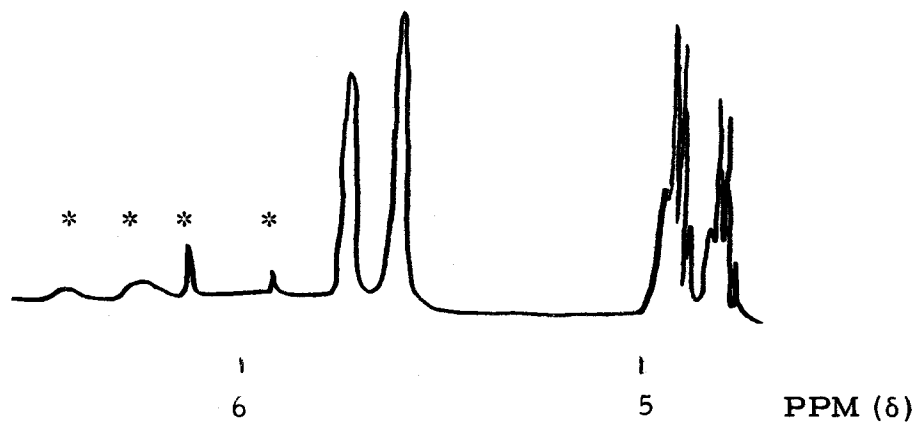
87. Tashiro, John Toshiyuki. Semihydrogenation in conjugated systems and its application in the synthesis of trienes. Ph.D. Thesis. Corvallis, Oregon State University, 1965. 73 numb. leaves.
88. Ungnade, Herbert E. ed. Organic electronic spectral data. Volume II, 1933-1955. Interscience, New York, 1960. 919 p.
89. Untch, K.G. and Robert J. Kurland. The conformational equilibration of cis, cis, cis-1,4,7-cyclononatriene; a determination of activation energy and entropy by n. m. r. II. Journal of the American Chemical Society 85:346-7. 1963.
90. Vogel, E. Valence isomerization in compounds with strained rings. Angewandte Chemie, International Edition 2:1-16. 1962.
91. Wesphal, Ulrich. Über enol derivate des progesterones und anderer α , β -ungesättigter steroid ketone. Berichte der Deutschen Chemischen Gesellschaft 80:2128-36. 1937.
92. Wilds, A. L., et al. The ultraviolet absorption spectra of α , β -unsaturated ketones conjugated with an aromatic nucleus. Journal of the American Chemical Society 69:1985-94, 1947.
93. Windaus, A. und A. Zomich. Conversion of mannitol into methyl- α -pyran. Nachrichten von der Koniglichen Gesellschaft der Wissenschafter zu Gottingen 11:462-68, 1917.
94. Woodward, R. B. and Roald Hoffmann. Stereochemistry of electrocyclic reactions. Journal of the American Chemical Society 87:3956. 1963.

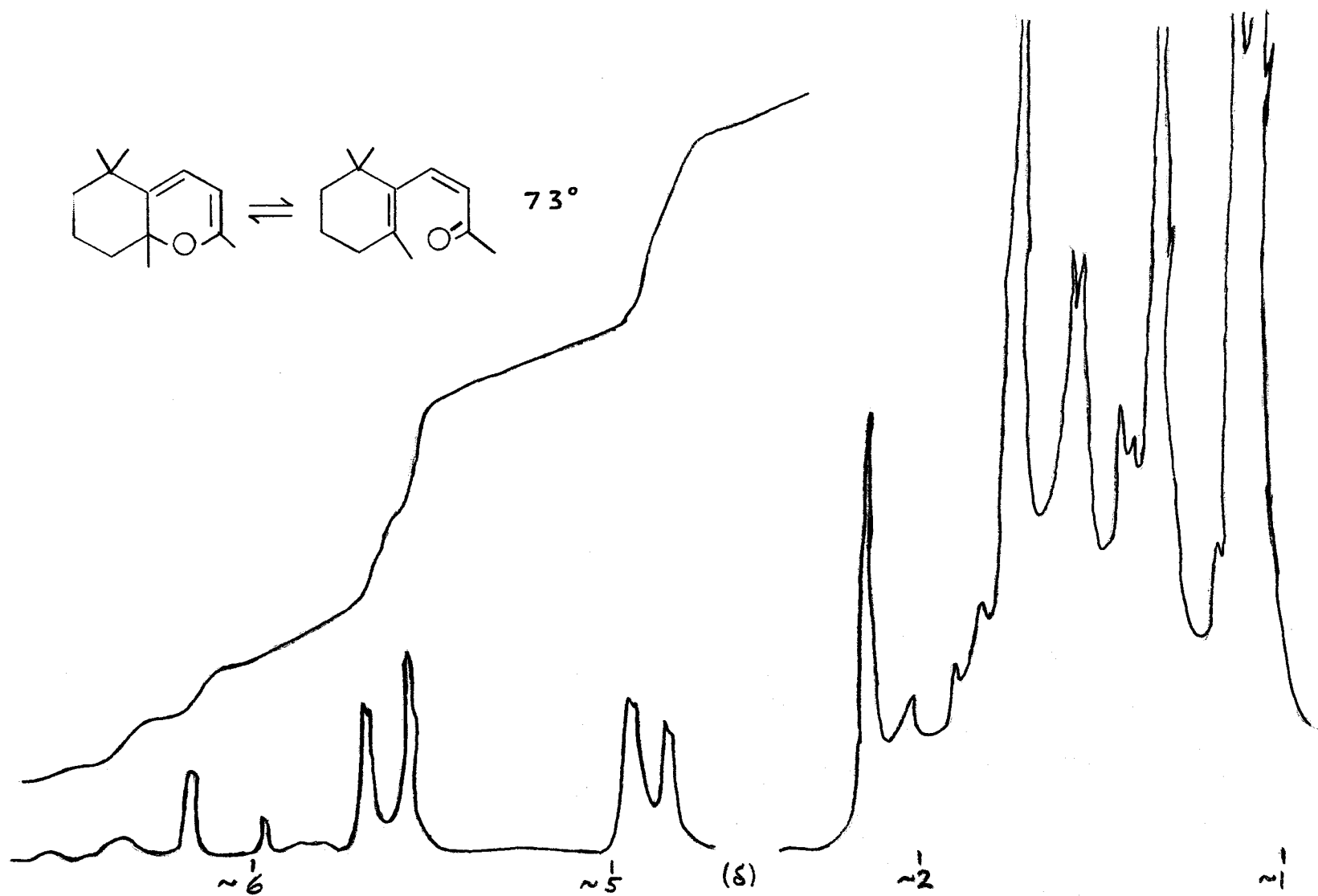
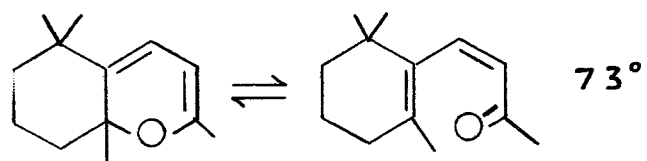
APPENDIX

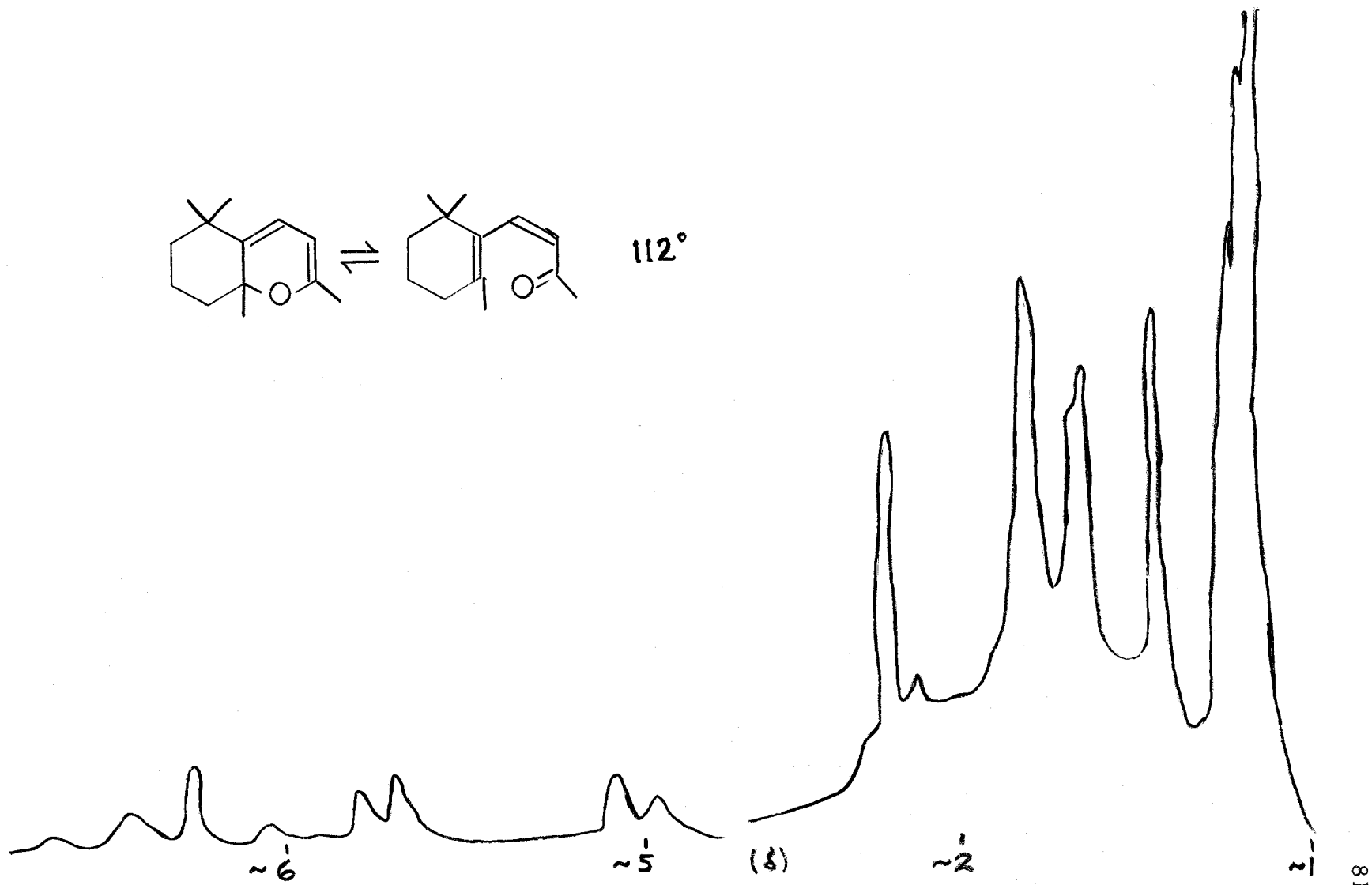
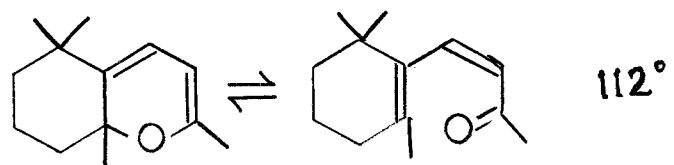


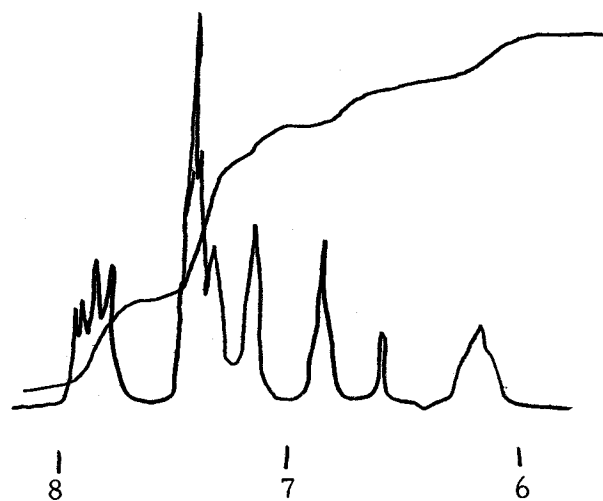
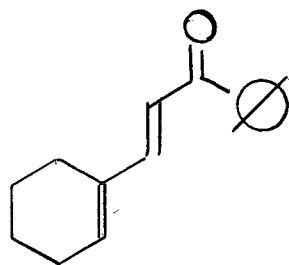


* = peaks due to cis-dienone.
 The amplitude of lower field spectra is three times that at higher field.

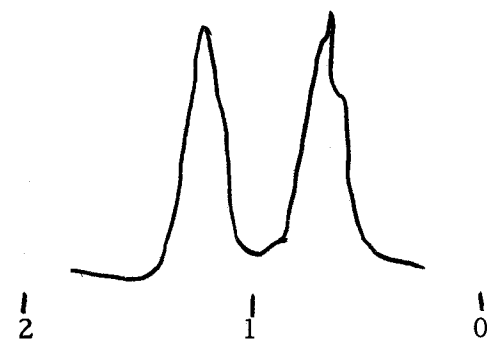




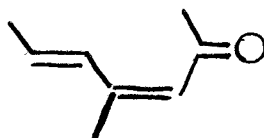




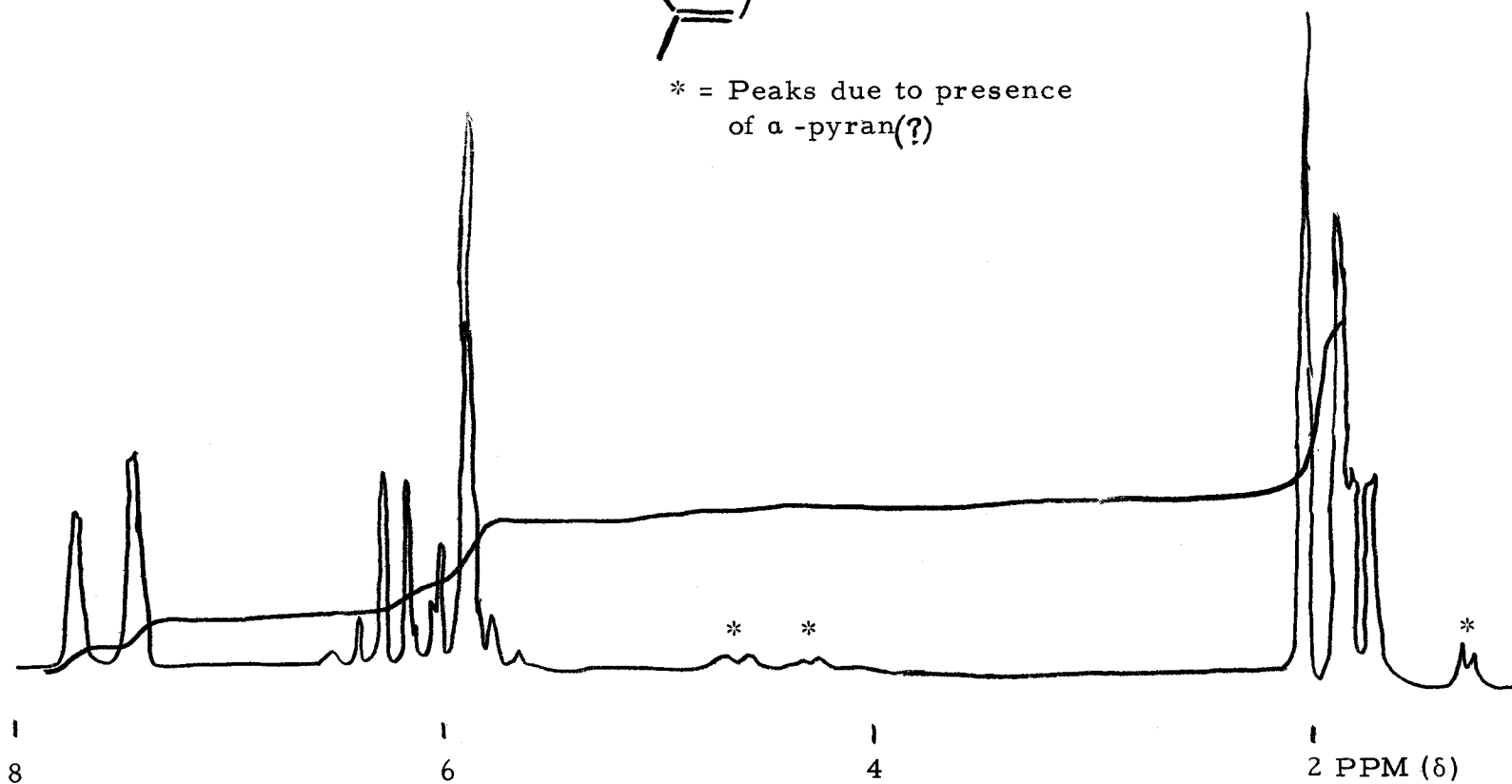
PPM (δ)

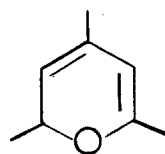






* = Peaks due to presence
of α -pyran(?)





Freshly generated material.
Spectra run at -22° .

