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Philip Leslie Churchley for the M.S. in Organic Chemistry
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Title PREPARATION AND SEMIHYDROGENATION OF SOME
a,β-ACETYLENIC KETONES

Abstract approved (Major professor)

Pure samples of the previously unknown ketones, $C_6H_5COC=CH=CH_2$ and $C_6H_5COC=CH-C=CH_2$, were synthesized and derivatives prepared. In an attempt to prepare cis-dienones for a valence isomerization study, these compounds were semihydrogenated with a variety of catalysts and under a variety of conditions. A mixture of products invariably resulted. The spectral properties of the semireduced products suggest that the first ketone gives only a small amount of $C_6H_5COCH=CH=CH_2$ while the second ketone yields in part the ring closed pyran isomer, $O\begin{array}{c}C_6H_5\end{array}$.
PREPARATION AND SEMIHYDROGENATION OF SOME $\alpha$, $\beta$-ACETYLENIC KETONES

by

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PREPARATION AND SEMIHYDROGENATION OF SOME 
α, β-ACETYLENIC KETONES

INTRODUCTION

It is interesting that the two parent compounds of the pyran ring system, α-pyran (I) and γ-pyran (II), are both unknown despite the apparent simplicity of these molecules. Of the two, perhaps α-pyran is the more interesting since theoretically it can exist as either of two valence isomers as illustrated below. Valence isomers may be defined as substances which differ in the positions of the electrons, but whose interconversion requires an activation energy. Though the interconversion of a few such isomers has been studied, as for example the 1,3,5-cyclooctatriene bicyclo [4,2,0]octa-2,4-diene system (11, p. 4867-4871), little is known about the factors influencing such processes. As a part of a general program aimed at the study of the valence isomerization phenomenon, a study of the dienone α-pyran reaction was initiated. This thesis describes some attempts to approach the valence isomers through synthesis of some substituted cis-dienones.
HISTORICAL

This survey of the literature relating to the simple pyrans will be divided into two sections. However, the benzopyrans will not be included. The first section will include the general knowledge of the pyrans as reported up to early 1962, and the second section will survey what is known about the valence isomerizations of the α-pyrans.

A. The Pyrans

Simple monocyclic pyrans have not been widely studied due primarily to synthetic problems and the general instability of many members of the family. Since the γ-pyrans are more readily accessible, we shall consider the older literature of these first. One of the earliest authentic accounts of the synthesis of a pyran was that of Blaise and Gault of the formation of γ-pyran-2,6-dicarboxylic acid by the dehydration of diketopimelic acid (5, p. 129-146). All attempts to decarboxylate this acid have led to decomposition.
Corvalho (12, p. 1430-1432) prepared 2, 4, 4, 6-tetraphenyl-γ-pyran by a similar method and recently Conrow and Radlich (10, p. 2260-2263) showed that this substance absorbs at 1675 cm\(^{-1}\) in the infrared.

An alternate approach to the synthesis of a γ-pyran, but one of lesser generality, was developed by McElvain and McKay (23, p. 5601-5610). These authors eliminated methanol from a cyclic orthoester to give an unstable light yellow liquid whose structural assignment

\[
\begin{array}{c}
\text{MeO} \\
\text{MeO} \\
\end{array}
+ \text{Al(O-t-Bu)}_3 \xrightarrow{140^\circ} \begin{array}{c}
\text{MeO} \\
\text{O} \\
\end{array}
\]

rests mainly on its infrared spectrum (ν=1642 cm\(^{-1}\) CH=C-O-C, 1695 cm\(^{-1}\) (C-O-)\(_2\)C=C) and the formation of γ-formylbutyric acid on hydrolysis.

The α-pyrans have proven more resistant to isolation. An early report (32, p. 462-468) of the preparation of 2-methyl-α-pyran has since been shown (1, p. 133-159) to be erroneous, and the substance actually formed was 2-vinyl-2, 5-dihydrofuran. Recently Schinz and his students (30, p. 239-255), who were studying the preparation of cis-α, β-unsaturated aldehydes and ketones, assigned the structure of a substituted α-pyran to the semireduction product of some 2-oxo-3-alkyn-5-enes. The assignment was made principally on the basis of the infrared spectrum which differed rather
unexpectedly from those of the known trans-dienones. A similar result was obtained by Büchi and Yang (7, p. 2318-2323) by irradiation of β-ionone. The pyran formula was supported by infrared data,

\[
\text{R-CH=CH-C≡C-C-Me + H}_2\overset{\text{Pd}}{\longrightarrow} \text{RCH=CH=CH-C-Me} \quad (\text{cis})
\]

\[\text{Me} \quad \begin{array}{c}
\text{O} \\
\text{R} \\
\text{Me} \\
\text{H}
\end{array}
\]

\[v = 1668, 1610, \text{ and } 1215 \text{ cm}^{-1}, \text{ by ultraviolet spectrum}
\]

\[\lambda_{\text{max}} = 286 \text{ m} \mu (\log \epsilon = 3.68), \text{ and by reduction to the tetrahydropyran which was prepared by an alternate route. This completes the literature relating to simple pyrans prior to 1960.}
\]

Since 1960 there has been a flurry of activity in this field almost completely centered around the reactions of pyrones and pyrylium salts which can lead to substituted pyrans. Pyrylium salts have long been known to react with ammonia to form pyridinium salts and thus Dimroth and Wolf (13, p. 777) were led to suggest that other nucleophiles such as carbanions or Grignard reagents might react with these salts also. They found this to be the case and assigned γ-pyran structures to the products. A similar reaction of
2,4,6-trisubstituted pyrylium salts gave also γ-pyrans though some data pointed to the presence of small amounts of α-pyrans in the reaction product. The structural assignments are based on the formation of 1,5-diketones on acid hydrolysis.

Köbrich (19, p. 131-145) has also investigated the reaction of organometallic compounds with 2,4,6-trisubstituted pyrylium salts. Whereas Dimroth assigned a γ-pyran structure to the product of the reaction of benzyl Grignard with 2,4,6-trimethylpyrylium perchlorate, Köbrich finds an entirely different result in the case of phenyl Grignard. The latter author states that his ketone has $\nu_{C=O} = 1685 \text{ cm}^{-1}$

and $\lambda_{\text{max}} = 302.5 \text{ m}\mu$ (11,700). The product absorbs two moles of hydrogen and forms the known saturated ketone. The extinction coefficient for the 302.5 band in the ultraviolet is extraordinarily low.

In view of the high reactivity of pyrylium salts with nucleophilic
reagents, it is not surprising to find that these substances react readily with sodium borohydride (3, p. 257-259). These authors report that a mixture of products was obtained, which were separable by distillation. The major product was reported to be a ketone, \( \nu_{C=O} = 1680 \text{ cm}^{-1} \) which forms a 2,4-dinitrophenylhydrazone. The lower boiling minor product had an infrared band at 1720 cm\(^{-1}\) and gave a dinitrophenylhydrazone in acid medium. However, it was differentiated from the 1,5-diketone by differences in the infrared spectra and a lower boiling point.

A \( \gamma \)-pyran dimer was obtained unexpectedly by Conrow and Radlisch (10, p. 2260-2263) when they treated 2,4,6-trimethylpyrylium fluoborate with the potassium salt of cyclooctatetraene. A very careful study of the dipyran via ultraviolet, infrared and NMR spectroscopy showed \( \nu = 1705 \text{ cm}^{-1} \), \( \lambda_{\text{max}} < 200 \text{ m}\) and no carbons bearing hydrogen directly attached. Chemically the substance showed the
presence of four double bonds, a minimum of five C-Me groups and did not form carbonyl derivatives. There appears to be little reason to question the assignment of structure in this case.

From a synthetic standpoint α- and γ-pyrones appear to be reasonably well-suited as starting materials for the preparation of pyrans. Gomppers and Christman (16, p. 1784-1794) have studied the reaction of Grignard reagents with a number of α- and γ-pyrones. The products were assigned α- and γ-pyran structures as is shown.

\[
\begin{align*}
\text{Me} & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \qua
All are said to have an infrared band between 1600-1720 cm\(^{-1}\) and to react with permanganate readily. The ultraviolet spectral properties are not in accord with the structures assigned. One \(\alpha\)-pyran was reduced to a substance said to be a tetrahydroxyxpyran.

\[
\begin{align*}
\text{Me} & \quad \text{Bu} \\
\text{O} & \quad \text{O} \\
\text{Me} & \quad \text{Bu}
\end{align*}
\] + \(2\text{H}_2\) \quad \text{Raney Ni} \quad \text{Me} \\
\text{Me} & \quad \text{Bu} \\
\text{O} & \quad \text{O} \\
\text{Me} & \quad \text{Bu}
\]

Recently Morgan (25, p. 343-344) has reduced a series of \(\alpha\)-pyrones with \(\text{LiAlH}_4\). The products were assigned open-chain enol aldehyde structures. The ultraviolet spectrum for the product,

\[
\begin{align*}
\text{HOOC} & \quad \text{O} \\
\text{O} & \quad \text{O} \\
\text{HOOC} & \quad \text{OH} \\
\end{align*}
\]

\[
\begin{align*}
\text{LiAlH}_4 & \quad \text{THF} \quad \text{cold} \\
\text{cold} & \quad \text{dil} \\
\text{H}_2\text{SO}_4 & \quad \text{HOOC} \\
\end{align*}
\]

\(\lambda_{\text{max}}\) 230 m\(\mu\) (9333), 280 m\(\mu\) (27,120), 315 m\(\mu\) (7000) and \(\nu = 1650\) cm\(^{-1}\) in the infrared agree with the proposed structure but do not unequivocally eliminate the hydroxypyrann form. Perhaps the most convincing point is the infrared spectrum of the acetylated methyl ester, which shows an enol acetate band at 1783 cm\(^{-1}\) which would not appear in the pyran form.
However, in view of the work of Schinz (29, p. 1290-1298), the double bond α, β to the aldehyde should undoubtedly be assigned a trans geometry because exposure to the sulfuric acid would cause rapid cis-trans isomerization.

\[
\text{HOOC} \quad \text{C} = \quad \text{C} \quad \text{H} \\
\text{HO} \quad \text{C} = \quad \text{C} \quad \text{H} \\
\text{H} \quad \text{C} = \quad \text{C} \quad \text{CHO}
\]

B. Valence Isomerization

It is quite apparent from the preceding material that unlike the γ-pyrans which have generally been quite adequately characterized, the α-pyrans have occasioned considerable confusion in their characterization. This difficulty is occasioned by the fact that α-pyrans and cis-dienones are valence isomers, and that the infrared and ultraviolet spectra of the isomers are in many cases expected to be very similar. Thus in many instances conflicting structural assignments have been made. The lack of adequate absolute criteria of structure,
particularly of a physical nature, have prevented the development of any body of data relating the position of equilibrium to structural parameters and no investigation has been made of the rate of interconversion of these valence isomers. An attempt will be made here to provide a brief survey of the recent knowledge of this subject, and none of the early work of Dilthey (15, p. 677) and others will be treated because useful surveys of that work already exist (9, p. 810).

The problem of ascertaining whether in any given case the a-pyran or the dienone form predominates or whether reasonable amounts of both are present in an equilibrium mixture is a difficult one. Physical measurements such as spectral properties can be useful but since no exact model compounds are known the most useful methods will be those for which values can be accurately predicted by theory and where a considerable difference in absolute value can be confidently predicted for the two isomers. Chemical data, on the other hand, may be quite misleading since, if even a small amount of one isomer is present at equilibrium, reaction may proceed via that isomer. In the absence of a complete kinetic analysis of the reacting system, it is generally unwise to place serious dependence upon chemical activity for the analysis in these cases.

For the simple unsubstituted system, \( \alpha \)-pyran \( \rightleftharpoons \) pentadienal, the ultraviolet spectra can be predicted with a reasonable degree of accuracy from the modified Woodward's rules (14, p. 15-24). Thus
for the α-pyran form the rules predict a $\lambda_{\text{max}}$ near 264 μ, and for the pentadienal a $\lambda_{\text{max}}$ near 245 μ. Some predicted values for a few substituted cases are indicated below. While these values apply

strictly to the trans-dienones, only small shifts in position are to be expected with cis-isomers unless considerable steric compression is present in the planar molecule. Thus it is clear that the ultraviolet spectra cannot always serve as a useful criteria of structure in these systems.

The infrared spectra for complex molecules of these types are not predictable except for certain bands which are to be expected. Aliphatic enol ethers of the type ROCH = CH₂ generally have strong bands at 1630 - 1655 cm⁻¹ and at 1190 - 1225 cm⁻¹ (24, p. 110-115). In 3,4-dihydro-2H-pyran these bands appear at 1650 cm⁻¹ and 1225 cm⁻¹ respectively. In general the added double bond may be expected to lower the frequency of each band in some degree, but this is
not predictable with great certainty. As models for the cis-dienones we can once again look at trans-dienones. In the absence of powerful steric factors, the change in geometry can be expected to give rise to little change in position of the bands described here. Thus dodeca-3,5-dien-2-one has strong bands at 1670, 1640, 1600 and 1290 cm\(^{-1}\) (28, p. 1299-1311) and compound I below has bands at 1668, 1629, 1603 and 1185 cm\(^{-1}\). (same). Thus like the ultraviolet spectra, the infrared spectra show differences but these are generally insufficient to provide really reliable differentiation in structure.

Consideration of the point of equilibrium for these valence isomeric systems can be conveniently grouped into two cases. The first of these will consider systems with only alkyl or aryl substituents while in the second the problem of hydroxyl substitution or the so-called pseudobases will be treated. In the first category five authors provide conflicting interpretations. These are the work of Schinz (28, p. 1299-1311), Büchi (7, p. 2318-2323), Köbrich (19, p. 131-145), Balaban (2, p. 3566-3772; 3, p. 257-259) and Gomppers (16, p. 1784-1794) and will be discussed in that order. Due to the general lack of applicability of the infrared data, these will not be considered and only the ultraviolet data will be examined.
Schinz (28, p. 1299-1311) reports that for the case noted below the $\lambda_{\text{max}}$ appears at 272 m$\mu$ and he concludes that the only substance present in identifiable amount is the $\alpha$-pyran. However, trans-

\[ \text{hex} \ O \ Me \quad \leftrightarrow \quad \text{hex} \ O \ Me \]

dodeca-3, 5-dien-2-one shows $\lambda_{\text{max}}$ 278 m$\mu$ and trans-hepta-3, 5-dien-2-one at 270 m$\mu$ (18, p. 287-293) and the calculated value for the $\alpha$-pyran is 263 m$\mu$. While Professor Schinz may indeed be correct, the ultraviolet spectral data do not provide effective confirmatory data.

Büchi and Yang (7, p. 2318-2323) irradiated trans-$\beta$-ionone and obtained a pure material from the reaction product. This substance, $\lambda_{\text{max}}$ 286 m$\mu$, was afforded the pyran structure. Since

\[ \text{trans-}\beta\text{-ionone} \quad \leftrightarrow \quad \text{trans-}\beta\text{-ionone} \]

trans-$\beta$-ionone shows $\lambda_{\text{max}}$ 296 m$\mu$ and the calculated value for the pyran is 273 m$\mu$, the data point toward the pyran form. However, since the treatment with iodine in the light regenerates the starting material, and since an unstable semicarbazone is obtained from the irradiation product, the pyran is clearly in mobile equilibrium with the
cis-\(\beta\)-ionone. The work of Büchi and Yang probably provides the most carefully documented case of this tautomerism investigated to date and in view of all their data, the conclusions appear valid.

Recently Köbrich reported that the product of treating trimethylpyrylium perchlorate with phenyl Grignard or phenyl lithium was an unsaturated ketone, \(\lambda_{\text{max}} \approx 302.5\) m\(\mu\). If Büchi is correct then the corresponding pyran in Köbrich's case would have \(\lambda_{\text{max}} \approx 280\) m\(\mu\). However, since \(\text{C}_6\text{H}_5\text{CH}=(\text{CH}=\text{CH}-\text{CH}-(\text{COMe})\) has \(\lambda_{\text{max}} \approx 319\) m\(\mu\). (31, p. 1985-1994) and the added methyl group should shift this value near to 330 m\(\mu\), Köbrich's data fails to fit either expectation very well.

Steric factors could cause such a hypsochromic shift in the unsaturated ketone but changes of such magnitude are not often observed. This case is complicated because the geometric isomer of the ketone was not identified, and since the product was exposed to acid conditions, isomerization could have produced one not capable of entering into equilibrium with the pyran. The presence of the phenyl group does enhance the stability of the ketone, thus tending the equilibrium in the direction suggested by Köbrich, but steric factors should favor the pyran.
The failure of Balaban to report ultraviolet data except for the 2,4-dinitrophenylhydrazones makes analysis of his results impossible. It may be noted that they are however in direct conflict with the findings of Schinz and Büchi. The ultraviolet spectral data for α-pyran reported by Gomppers and Christman are listed in Table 1. Clearly there are some interesting disparities in the data, but for brevity here only two cases will be discussed. The tetramethylpyran shows several peaks near 270 μ and the problems of interpretation are the same as those of Schinz. However, in this case, the choice of the λ<sub>max</sub> to consider is arbitrary. Perhaps the complexity indicates that the product is actually a mixture with reasonable amounts of several isomeric ketones and the α-pyran all present in detectable amount. However, the band at 323 μ of the substance assigned the 2,2-diphenyl-4,6-dimethyl-α-pyran structure is completely inexplicable on the basis of that structure. It is not an unreasonable value for the isomeric dienone though the extinction coefficient is once again awkwardly low. Köbrich (19, p. 131-145) has suggested that the product is actually 2,6-diphenyl-2,4-dimethyl-α-pyran and has presented some evidence to support his conclusions. Thus for the
Table I. Ultraviolet Spectral Data for α-pyrans from Gomppers and Christman (16, p. 1784 - 1794).

<table>
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<th>Pyran</th>
<th>$\lambda_{\text{max}}$</th>
<th>log $\epsilon$</th>
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<tbody>
<tr>
<td>2, 2, 4, 6-tetramethyl</td>
<td>221</td>
<td>3.89</td>
</tr>
<tr>
<td></td>
<td>265</td>
<td>3.18</td>
</tr>
<tr>
<td></td>
<td>272</td>
<td>3.22</td>
</tr>
<tr>
<td></td>
<td>278</td>
<td>3.22</td>
</tr>
<tr>
<td>2, 2-diethyl-4, 6-dimethyl</td>
<td>208</td>
<td>3.64</td>
</tr>
<tr>
<td></td>
<td>257</td>
<td>3.39</td>
</tr>
<tr>
<td>2, 2-dipropyl-4, 6-dimethyl</td>
<td>201</td>
<td>3.58</td>
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<tr>
<td></td>
<td>253</td>
<td>3.75</td>
</tr>
<tr>
<td>2, 2-dioctyl-4, 6-dimethyl</td>
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<td></td>
<td>290</td>
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<td>2, 2-dimethyl-4, 6-diphenyl</td>
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</tr>
<tr>
<td></td>
<td>337</td>
<td>3.94</td>
</tr>
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moment the work of Gomppers and Christman does not provide useful information with respect to the question of valence isomerism.

The pyran pseudobases are those compounds derived from pyrylium salts by treatment with a base. They can be formulated as hydroxy-α-pyrans, unsaturated ketones or the monoenols thereof. Berson (4, p. 358-360) has presented rather convincing evidence
that for the 2, 4, 6-triphenyl derivative the unsaturated diketo form is the only identifiable substance present. A related conclusion in a somewhat different case (25, p. 343-344) is really not relevant to the problem at hand. Since the reaction product was treated with acid,

\[
\begin{align*}
\text{HOOC CHO} & \quad + \text{LiAlH}_4 \quad \xrightarrow{\text{H}^+} \quad \text{HOOC} \quad \text{OH} \quad \text{CHO} \\
\text{HOOC} & \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{O}
\end{align*}
\]

the geometric form must be trans at the double bond next to the aldehyde, because Schinz and his students (29, p. 1290-1298) have shown that cis double bonds conjugated to a carbonyl group are rapidly converted to the trans-isomers. The mechanism of such processes has been studied by Noyce (26, p. 1647-1650).

At the present then the status of the valence isomerization problem in \(\alpha\)-pyran systems is very much undecided. At least in one case the evidence in favor of the \(\alpha\)-pyran is quite convincing, and in the case of pseudobases the diketone form is apparently favored as might well have been predicted. The influence of other substituents on the equilibrium is an open question.
DISCUSSION

The work to be described here was initiated to study the valence isomerization of simple pyrans in an attempt to bring some order into this area. At the time this work was done (1959-60) the majority of the work described in the historical section had not been published. Therefore, the use of infrared and ultraviolet spectra for investigative tools was considered appropriate in view of the experience of Buechi and Yang. In order to magnify the differences to be expected in the ultraviolet spectra, a phenyl group, cross-conjugated in the ketone and linearly conjugated in the pyran as indicated below, was used. Since a phenyl group in a cross-conjugated position produces

\[
\begin{align*}
\text{C}_6\text{H}_5\text{O} & \quad \leftrightarrow \\
\text{C}_6\text{H}_5 & \text{O}
\end{align*}
\]

a small (ca. 10 m\(\mu\)) bathochromic shift while a linearly conjugated phenyl introduces a large (45-60 m\(\mu\)) bathochromic shift, the values expected for the groups above are 260-270 m\(\mu\) for the ketone and 315-330 m\(\mu\) for the pyran.

When this study was initiated two generally applicable methods
for the preparation of cis-\(\alpha,\beta\)-unsaturated carbonyl compounds were known. Schinz and his students (28, p. 1299-1311; 29, p. 1290-1298) had studied the semihydrogenation of enynones and Büchi (7, p. 2318-2323) had used ultraviolet initiated trans to cis isomerization. Unfortunately this latter process had obstinately refused to work in some instances, and the former method appeared more generally useful. Therefore a sample of 5-phenylpent-1-en-3-yn-5-one was prepared by the following process. The unsaturated alcohol has been prepared

\[
\text{C}_6\text{H}_5\text{CHO} + \text{CH}_2=\text{CH-CH}≡\text{CMgBr} \rightarrow \text{C}_6\text{H}_5\text{CH-CH}≡\text{CH=CH}_2
\]

\[
\text{C}_6\text{H}_5\overset{\text{OH}}{-\text{C}-\text{CH=CH=CH}_2} \overset{\text{CrO}_3}{\rightarrow} \text{C}_6\text{H}_5\text{COC}=\text{C-CH=CH}_2
\]

\[
\text{C}_6\text{H}_5\overset{\text{OH}}{-\text{C}-\text{CH=CH=CH}_2} \overset{\text{H}_2}{\text{Pd}} \text{C}_6\text{H}_5\text{COC}=\text{C-CH=CH}_2
\]

previously (33, p. 643-649), and it was conveniently oxidized by the use of Jones’s reagent (6, p. 39). The acetylenic ketone was purified and its infrared and ultraviolet spectra were in good accord with those expected for such a compound.

Semihydrogenation of this ketone proved to be thoroughly disappointing as a means of synthesis of the cis-ketone. Palladium on calcium carbonate with or without added quinoline, Lindlar catalyst (20, p. 446-450) and palladium on charcoal were all about equally disappointing. The addition of zinc acetate slows the reduction and appears to enhance the specificity for reduction of the triple bond since the same amount of hydrogen uptake reduces the intensity of
the acetylenic peak to a greater extent than occurred in the other runs. A careful examination of the spectral data from the products of the various runs shows a consistent pattern of change, and the tentative interpretation given below provides a complete rationale for these data.

In the infrared spectrum the starting material is characterized by strong absorption at 1640, 1260, 967 and 937 cm\(^{-1}\). The first two are due to the conjugated carbonyl group and the latter pair are characteristic of the C=CH=CH\(_2\) grouping. The addition of one mole of hydrogen diminishes the intensity of all of these peaks but none disappear entirely. Consequently, a certain amount of starting material is still present in the product. The product exhibits new absorption bands at 2960, 2930, 1665, 1612, 1225 and 734 cm\(^{-1}\). In the ultraviolet region the 270 m\(\mu\) peak due to the starting material is of diminished intensity but still present in the product. Estimation of the amount of starting material still present and subtraction of its absorption shows that a new chromophore \(\lambda_{max} 256-259\) m\(\mu\) (\(\epsilon \sim 12,000\)) is present in the product.

Clearly then, since a considerable amount of starting material remains unreduced, the remainder must have absorbed more than a single mole of hydrogen per mole of acetylenic ketone. The pattern of hydrogenation reactions possible is shown below. The extra hydrogen used in this process can only be employed in reactions C and/or
D, because neither $\text{C}_6\text{H}_5\text{COBu}$ nor $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_2\text{CH}=\text{CH}_2$ can be formed as indicated by the absence of a band near 1690 cm$^{-1}$ in the infrared. Since we can estimate the amount of starting material in the product as 40 ± 5%, an equal amount of cis-1-phenyl-2-penten-1-one must be present. This is in accord with the spectral properties of the product since the α,β-unsaturated ketone is expected to absorb near 1670 and 1620 cm$^{-1}$ (28, p. 1299-1311) and in the ultraviolet at 256 mμ [ $\text{C}_6\text{H}_5\text{COCH}=\text{CH}-\text{Me}$ absorbs at 256 mμ (21, p. 521-524)].

Thus the properties observed are in good accord with a mixture containing mainly starting material and cis-1-phenyl-2-penten-1-one along with smaller amounts of 1-phenyl-2-pentyn-1-one and the cis-dienone or its related pyran form. However, the amount of the dienone present is not sufficient to permit any conclusions to be reached regarding the question of valence isomerization.

In order to enhance the specificity of the reduction, a substance of similar nature but no longer possessing a terminal double bond
was prepared as indicated. Again a pure acetylenic ketone was prepared and exhibited the expected properties. Again semihydrogenation failed to provide an adequate specificity for the triple bond.

\[ \text{OH} \quad \text{C} = \text{CH} \quad \xrightarrow{\text{EtMgBr}} \quad \text{C} = \text{CH} \]
\[ \downarrow \text{1. EtMgBr} \]
\[ \downarrow \text{2. C}_6\text{H}_5\text{CHO} \]

\[ \text{C} = \text{C} - \text{C} - \text{C}_6\text{H}_5 \quad \xrightarrow{\text{CrO}_3} \quad \text{C} = \text{C} - \text{CH} - \text{C}_6\text{H}_5 \]

Once again a certain pattern of changes appeared in the infrared spectrum which suggests certain conclusion. The carbonyl band originally near 1645 cm\(^{-1}\) is replaced in part by two new bands at 1690 and 1675 cm\(^{-1}\) respectively. The triple bond peak is diminished in intensity but is still present. and a small but distinct OH band at 3450 cm\(^{-1}\) appears. Two rather weak bands appear at 1230 and 1210 cm\(^{-1}\) and a reasonably strong peak appears near 1100 cm\(^{-1}\). These data suggest that several reactions are occurring in the solution.
These are illustrated below.

The evidence which points to the various reactions is as follows: The cyclohexenyl double bond being trisubstituted is not reduced in competition with the triple bond (22), so the initial step is probably the semireduction of the triple bond. Whether the cis-dienone is desorbed from the catalyst surface is impossible to say, but the reaction product obtained by reduction in the cold was not
altered by heating several hours at 80°C. Hence it is reasonable to suppose that the reaction is complete even in the cold. For simplicity therefore, it is suggested that two further reactions occur on the catalyst before desorption. The cis double bond is reduced completely giving a ketone conjugated solely to the benzene ring \( (\nu_{C=O} = 1690 \text{ cm}^{-1}) \), and ring closure occurs during desorption of the dienone as indicated by the equations below. The formation of the pyran is indicated by the peaks at 1675 and 1210 cm\(^{-1}\) in the infrared and by the appearance of a peak at 335 m\(\mu\) in the ultraviolet. Though this
seems surprisingly far toward the visible region for the pyran it is not impossible and it should be noted that Büchi's pyran had a larger bathochromic shift than would be predicted by Woodward's rules. The mechanism suggested for the ring closure is completely hypothetical but is in complete accord with mechanisms suggested previously for catalytic reactions on active metal surfaces (8, p. 895-934). The presence of the pyran can also explain the appearance of a hydroxyl band in the infrared. The carbonyl group would not be expected to undergo hydrogenation under the conditions employed, and the lack of this hydroxyl band in the earlier case supports this argument. However, the pyran is an allylic ether and, after reduction of one of the double bonds as shown, is also a benzyl ether. Thus hydrogenolysis could occur with formation of an alcohol. Since further hydrogen uptake increases the intensity of this hydroxyl absorption, this explanation seems reasonable.

While the picture obtained from the spectral data is cohesive and reasonably satisfying, the evidence is somewhat insubstantial. Further work using NMR and chemical methods will be needed in an attempt to confirm the conclusions reached in this study.
SUMMARY

Pure samples of the previously unknown ketones, \( \text{C}_6\text{H}_5\text{COC}=\text{C}-\text{CH}=\text{CH}_2 \) and \( \text{C}_6\text{H}_5\text{COC}=\text{C} \), have been synthesized and derivatives prepared. Both compounds have been submitted to semihydrogenation over a variety of catalysts and under a variety of conditions. In all cases mixtures of products result because the selectivity of the catalysts toward the triple bond is not great in these systems. An interpretation of the results on the basis of spectral data alone suggest that the first ketone gives in part the cis-dienone, \( \text{C}_6\text{H}_5\text{COCH}=\text{CH}-\text{CH}=\text{CH}_2 \), which does not provide useful data about (cis) valence isomerization while the second gives in part the ring closed pyran isomer.
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EXPERIMENTAL

1-Phenylpent-4-en-2-yn-1-ol

A solution of monovinylacetylene (61 g. or 1.18 moles) prepared by the method of Zal'kind and Kulikov (33, p. 643-649), in 100 ml. of cold anhydrous ether at -10.0° was added slowly under nitrogen to 0.8 mole of ethyl magnesium bromide in 250 ml. of ether. During the addition the solution was cooled in an ice bath, and after addition was complete the solution was heated under reflux for three hours. The ice bath was replaced and 85 g. (0.8 mole) of freshly-distilled benzaldehyde in 100 ml. of ether was added slowly. The reaction mixture was stirred for six hours. After standing overnight, the complex was decomposed with saturated ammonium chloride solution. The yellow ether layer was dried over anhydrous magnesium sulfate, the solvent removed in vacuo and the residue distilled to give 40.0 g. (32.5%) of 1-phenylpent-4-en-2-yn-1-ol, a light yellow oil, b.p. 125° (5 mm.), n\textsuperscript{18}D 1.5730 (lit. reported n\textsuperscript{17}D 1.57467 b.p. 125° (5 mm.) (33, p. 643-649).

1-Phenyl-3-(cyclohexen-1-yl)-2-propynol

A solution of 1-ethynylcyclohexene (65.0 g. or 0.61 mole) prepared by the method of Hamlet, Henbest and Jones (17, p. 2652) was
converted to 1-phenyl-3-(cyclohexen-1-yl)-2-propynol by the process described above. The alcohol, m. p. 42\(^\circ\)C, was recrystallized from pentane, and was used directly in the next step.

**1-Phenylpent-4-en-2-yn-1-one**

A mixture of 2.18 g. (0.022 mole) of chromium trioxide, 6.0 ml. of water, and 1.8 ml. of concentrated sulfuric acid was slowly added under nitrogen to 5 g. (0.32 mole) of 1-phenylpent-4-en-2-yn-1-ol in 10 ml. of acetone. During addition the solution was cooled in an ice bath. After one hour the addition was complete, and the solution was extracted with ether. The ether extracts were dried over magnesium sulfate. Portions of the ethereal solution were evaporated in vacuo and chromatographed. In a typical case, one gram of the crude ketone was chromatographed on 25 g. of activity III (Brockman) alumina using petroleum ether as eluant. A yield of 0.65 g. of light yellow oil was obtained, \( \lambda_{\text{max}} \) 270\( \mu \) (5,480), \( \nu = 3085 \) (m), 2219 (s), 1640 (vs), 1598 (s), 1580 (s), 1452 (s), 1415 (m), 1315 (m), 1260 (vs), 1177 (m), 1136 (w), 1025 (m), 967 (sh), 937 (m), 890 (s), 795 (m) and 695 (vs) cm\(^{-1}\).

**Anal.** Calc'd for C\(_{11}\)H\(_8\)O: C, 84.63; H, 5.13.

**Found:** C, 84.43; H, 5.30.

A 2,4-dinitrophenylhydrazone, m. p. 192-192.5, was prepared according to the instructions of Shriner and Fuson (27, p. 219).
Anal. Calc'd for $^{15}C_{15}H_{14}O$: C, 85.71; H, 6.66.

Found: C, 85.64; H, 6.69.

A 2,4-dinitrophenylhydrazone, m.p. 213-214, was prepared according to the instructions of Shriner and Fuson (27, p. 219).

Anal. Calc'd for $^{21}C_{17}H_{18}N_{4}O_4$: C, 64.62; H, 4.61; N, 14.36.

Found: C, 64.47; H, 4.83; N, 14.19.
Hydrogenations

All hydrogenations were performed using 5% Pd/CaCO₃ at atmospheric pressure. The catalyst was prepared from palladium chloride and freshly precipitated calcium carbonate, and in some cases the lead poisoned catalyst according to Lindlar(20, p. 146-450) was employed.

In a typical example, 0.2088 g. of unsaturated ketone was hydrogenated over 402 mg. of prehydrogenated catalyst in 10 ml. of solvent until one mole of hydrogen was absorbed. Light was excluded from the reaction mixture. The catalyst was removed by filtration, and the solvent by evaporation in vacuo. Care was taken to keep the reduced material under nitrogen and to exclude light at all times.

The following tables summarize the runs performed.

Reduction products of 1-phenylpent-4-en-2-yn-1-one

After tests showed that separation of the reaction mixture into individual components by chromatography or distillation was not feasible, the spectroscopic data were obtained directly on the crude product after removal of the solvent. Runs 1-7 below show the following pattern of changes in the infrared spectrum: bands at 2210, 1640, 1260, 967 and 937 cm⁻¹ diminish in intensity but are still present, and new bands at 2960, 2930, 1665, 1612, 1225, 1005, 925 and
<table>
<thead>
<tr>
<th>Run number</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Percent weight(^a) of catalyst</th>
<th>Moles of substrate x 10(^{-3})</th>
<th>Mole equivalent of hydrogen absorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethyl acetate</td>
<td>Pd/CaCO(_3)</td>
<td>32</td>
<td>1.52</td>
<td>1.24</td>
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<tr>
<td>2</td>
<td>Heptane</td>
<td>Pd/CaCO(_3)</td>
<td>20</td>
<td>1.33</td>
<td>1.13</td>
</tr>
<tr>
<td>3</td>
<td>Methanol</td>
<td>Pd/CaCO(_3)</td>
<td>20</td>
<td>1.42</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 mg. Zn(OAc)(_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Methanol</td>
<td>Pd/CaCO(_3)</td>
<td>20</td>
<td>1.42</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4 mg. Zn(OAc)(_2)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Methanol</td>
<td>Pd/CaCO(_3)</td>
<td>20</td>
<td>2.00</td>
<td>0.92</td>
</tr>
<tr>
<td>6</td>
<td>Methanol</td>
<td>Pd/CaCO(_3)</td>
<td>20</td>
<td>2.00</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 ml. quinoline</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Methanol</td>
<td>Pd/CaCO(_3)</td>
<td>23</td>
<td>1.35</td>
<td>0.90</td>
</tr>
<tr>
<td>8</td>
<td>Ethyl acetate</td>
<td>Pd/CaCO(_3)</td>
<td>56</td>
<td>1.25</td>
<td>2.30</td>
</tr>
<tr>
<td>9</td>
<td>Ethyl acetate</td>
<td>PtO(_2)(^b)</td>
<td>32</td>
<td>0.60</td>
<td>3.0</td>
</tr>
</tbody>
</table>

\(^a\) Percent weight of catalyst was calculated from the weight of the substrate.

\(^b\) Catalyst was not completely prehydrogenated.
<table>
<thead>
<tr>
<th>Run number</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>Percent weight of catalyst</th>
<th>Moles of substrates $\times 10^{-3}$</th>
<th>Mole equivalent of hydrogen absorbed</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Hexane</td>
<td>Pd/CaCO$_3$</td>
<td>25</td>
<td>7.7</td>
<td>1.01</td>
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<tr>
<td>2</td>
<td>Ligroin</td>
<td>Lindlar</td>
<td>20</td>
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<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>Methylcyclohexane</td>
<td>Pd/CaCO$_3$</td>
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<td>12.5</td>
<td>0.800</td>
</tr>
<tr>
<td>4</td>
<td>Ethyl acetate</td>
<td>10% Pd/charcoal</td>
<td>15</td>
<td>3.92</td>
<td>2.08</td>
</tr>
</tbody>
</table>
734 cm⁻¹ appear. In the ultraviolet region the \( \lambda_{\text{max}} \) 270 mµ (4,000) peak diminishes and a new peak at \( \lambda_{\text{max}} \) 255-259 mµ (11,150) appears.

In run 8 the infrared spectrum of the product showed peaks at 3085, 2960, 2930, 1680, 1598, 1580, 1452, 1415, 1315, 1260, 1177, 1136, 1025, 965, 750 and 695 cm⁻¹. The product showed \( \lambda_{\text{max}} \) 259 mµ (4,200).

**Reduction products of 1-phenyl-3-(cyclohexen-1-yl)-propynone**

Infrared spectra of the products from runs 2 and 3 showed the following pattern of changes. Peaks at 2220, 1645, 1015, and 958 cm⁻¹ diminish in intensity and new peaks at 3450 (w), 1690, 1675, 1230, 1210, 1095 and 765 cm⁻¹ appear. In the ultraviolet region a new peak at \( \lambda_{\text{max}} \) 335 mµ (3600) appears superimposed on the diminished spectrum of the starting material. In run 4 the infrared spectrum shows absorption at 3450 (w), 3070, 3030, 2930, 1705 (w), 1500, 1460, 1220, 1105, 1080, 1040, 770, 745 and 702 cm⁻¹.
Figure 1. The ultraviolet spectrum of 1-phenyl-3-(cyclohexen-1-yl)-2-propynone and its semihydrogenated product (run 3).
BIBLIOGRAPHY


