THE SYNTHESIS OF CERTAIN
VINYL KETONES

by

DONALD EARL PAULSEN

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APPROVED:

_____

Professor of Chemistry

In Charge of Major

_____

Head of Department of Chemistry

_____

Chairman of School Graduate Committee

_____

Dean, Graduate School

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THE SYNTHESIS OF CERTAIN VINYL KETONES

In 1936 Wulzen and Bahrs (12)[*] discovered that guinea pigs fed on a skim milk diet developed stiff wrists and finally became extremely sick and died. Autopsies showed that there were deposits of calcium phosphate just under the skin and in the vital organs as well as in the joints. The symptoms were similar to those of guinea pigs deprived of vitamin A, but further studies showed a marked difference. Those suffering in the early stages from the lack of this dietary factor, showed prompt recovery when returned to a normal diet. Others, on the other hand, kept on the same diet but given generous doses of vitamin A, were little better off than those animals continued on the deficient diet.

In 1941 Gouley (4) found that methyl vinyl ketone, which is quite toxic, possessed definite anti-stiffness properties. Since this time, other complex mixtures have been discovered which have been reported to be active.
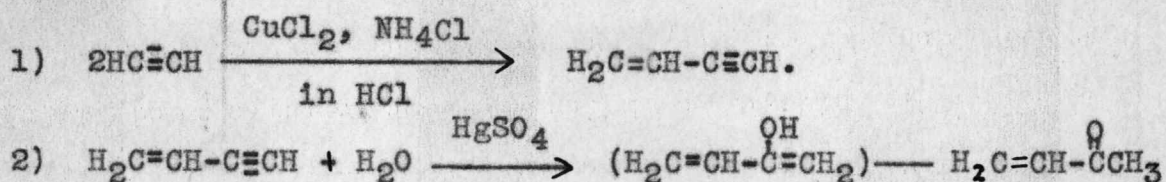
Blaise and Maire (1) found that methyl vinyl ketone is a compound with a strong odor characteristic of unsaturated compounds having a negative group adjacent to one of the carbon atoms having the double bond. It polymerizes spontaneously in about five days upon standing.

[*]Numerals in parentheses indicate references. The bibliography is alphabetized at the end.

Since methyl vinyl ketone has definite anti-stiffness properties, an attempt was made to synthesize other vinyl ketones in the search for a non-toxic drug.

The properties of vinyl ketones eliminate several of the general methods of ketone synthesis. Ordinary oxidation procedures would attack the double bond. The temperature of dry distillation of calcium salts and that of dehydrogenation of alcohols over copper are both considerably above the decomposition temperature of vinyl ketones. Vinyl Grignard reagents cannot be prepared because of the non-reactivity of vinyl halides. An alkyl Grignard reagent would not likely react with acrylonitrile to give a vinyl ketone in good yield because of the tendency for the Grignard reagent to add to the double bond.
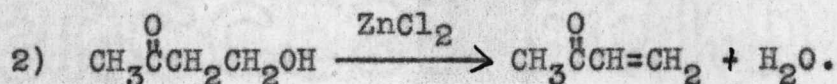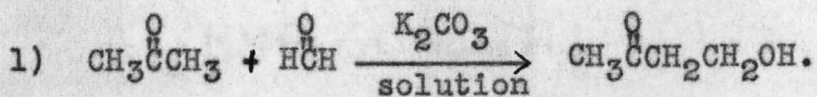
Vinyl ketones can be made by addition of water to vinyl acetylene or its homologs with mercury sulfate as a catalyst. The reactions for this method are as follows:

1) $2HC\equiv CH \xrightarrow[\text{in HCl}]{CuCl_2,\ NH_4Cl} H_2C=CH-C\equiv CH.$

2) $H_2C=CH-C\equiv CH + H_2O \xrightarrow{HgSO_4} (H_2C=CH-\overset{OH}{\underset{}{C}}=CH_2) \text{---} H_2C=CH-\overset{O}{\overset{\|}{C}}CH_3$

Numerous procedures for making methyl vinyl ketone by this reaction are patented. The difficulty of obtaining homologs of vinyl acetylene make this approach impractical.

Another method particularly adapted to the preparation

of methyl vinyl ketone is that of Wohl and Prill (11). It
is undoubtedly the most practical method for use on a
laboratory scale even though the yield is low. The
equations are as follows:

1) $CH_3\overset{O}{\overset{\|}{C}}CH_3 + H\overset{O}{\overset{\|}{C}}H \xrightarrow[\text{solution}]{K_2CO_3} CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2OH.$

2) $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2OH \xrightarrow{ZnCl_2} CH_3\overset{O}{\overset{\|}{C}}CH=CH_2 + H_2O.$
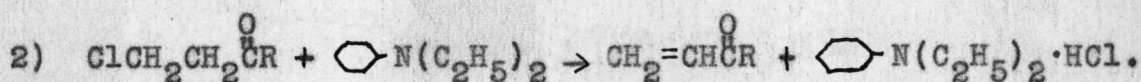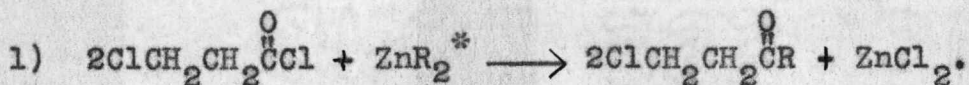
The use of higher homologs of acetone usually results in
a mixture, the principle product being a methyl ketone;
for this reason the method is not adaptable to preparation
of other vinyl ketones.

A method which is reported by Krapivin (7) for the
preparation of vinyl ketones in general is that illustrated
in the following reaction:

1) $HC\!\equiv\!CH + CH_3\overset{O}{\overset{\|}{C}}Cl \xrightarrow{AlCl_3} CH_3\overset{O}{\overset{\|}{C}}CH=CH_2 + HCl.$
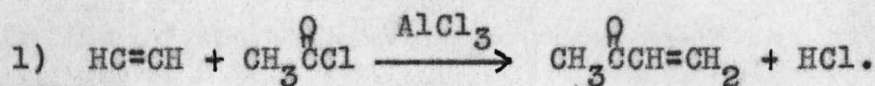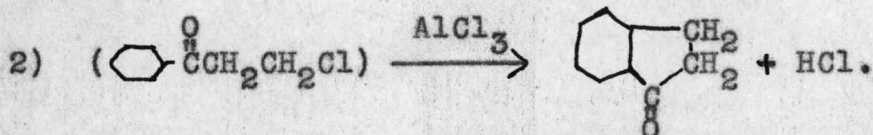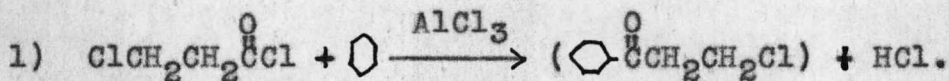
This method does not appear to have been much used nor
developed as a general method for vinyl ketones. In an
attempt to prepare methyl vinyl ketone by this method,
Gouley (4) reported the hydrolysis as proceeding uncon-
trolably and with the formation of a dark brown tarry mass
from which he was unable to obtain any pure methyl vinyl
ketone.

The only general method found for preparing alkyl vinyl ketones is one developed by Blaise and Maire (1). The following reactions illustrate the method:

1) $2ClCH_2CH_2\overset{O}{\overset{\|}{C}}Cl + ZnR_2^* \longrightarrow 2ClCH_2CH_2\overset{O}{\overset{\|}{C}}R + ZnCl_2.$

2) $ClCH_2CH_2\overset{O}{\overset{\|}{C}}R + \langle \rangle N(C_2H_5)_2 \rightarrow CH_2{=}CH\overset{O}{\overset{\|}{C}}R + \langle \rangle N(C_2H_5)_2 \cdot HCl.$

There is a tendency for the β-chloroethyl ketones formed in the first reaction to lose hydrogen chloride. It is therefore necessary to pass in excess hydrogen chloride to prevent this because any vinyl ketone formed at first would otherwise be lost by distilling over with the toluene which is used as the solvent for the reaction.
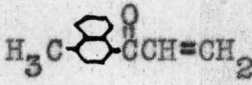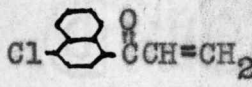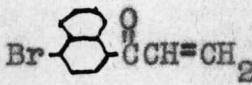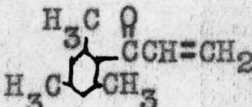
The Friedel-Crafts reaction has been employed by Mayer and Muller (8) using ordinary aromatic hydrocarbons and β-chloropropionyl chloride yields as the principle product the indanone:

1) $ClCH_2CH_2\overset{O}{\overset{\|}{C}}Cl + \langle \rangle \xrightarrow{AlCl_3} (\langle \rangle \overset{O}{\overset{\|}{C}}CH_2CH_2Cl) + HCl.$

2) $(\langle \rangle \overset{O}{\overset{\|}{C}}CH_2CH_2Cl) \xrightarrow{AlCl_3} \text{(indanone)} + HCl.$

When benzenes and naphthalenes with ortho-para-directing groups were used, several of the intermediate β-chloropropionyl compounds were isolated in good yields. By

*R stands for any alkyl radical of low molecular weight.

vacuum distilling some of these, they were able to obtain

the following:

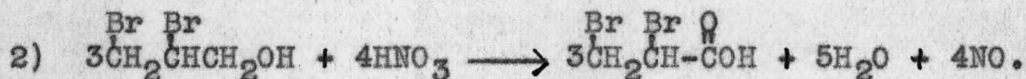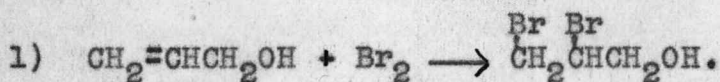| compound	formula	distillation pressure and temperature	yield	melting point of dibromo-derivative
*1-methyl 4-acrylo-naphthone	H_3C—[ring]—$CCH=CH_2$ (O)	b_{14}, 180-190°	18%	89°
*1-chloro 4-acrylo-naphthone	Cl—[ring]—$CCH=CH_2$ (O)	b_{12}, 180-192°	14%	89°
*1-bromo 4-acrylo-naphthone	Br—[ring]—$CCH=CH_2$ (O)	b_{15}, 210-215°	34%	106°
‡acrylo-mesitylene	H_3C—[ring](CH_3)($CCH=CH_2$)(O)—CH_3	$b_{3.5}$, 99-101°	63%	79°

Upon steam distillation, the compound is cleaved to phenyl

vinyl ketone, which passes over to the distillate, and to

dimethylamine hydrochloride, which remains in the distill-

ing flask. The yield in this case is almost quantitative.

Kohler (6) obtained phenyl vinyl ketone by the follow-

ing series of reactions:

1) $CH_2\text{=}CHCH_2OH + Br_2 \longrightarrow \overset{Br}{C}H_2\overset{Br}{C}HCH_2OH.$

2) $3\overset{Br}{C}H_2\overset{Br}{C}HCH_2OH + 4HNO_3 \longrightarrow 3\overset{Br}{C}H_2\overset{Br}{C}H\text{-}\overset{O}{C}OH + 5H_2O + 4NO.$

*These compounds were not further purified, but their
dibromo-derivatives were obtained pure.

‡Prepared similarly by Fuson and McKeever (3).

3) $\overset{Br}{\underset{}{C}}H_2\overset{Br}{\underset{}{C}}H\text{-}\overset{O}{\underset{}{C}}OH + SOCl_2 \longrightarrow \overset{Br}{\underset{}{C}}H_2\overset{Br}{\underset{}{C}}H\text{-}\overset{O}{\underset{}{C}}Cl + SO_2 + HCl.$

4) $\overset{Br}{\underset{}{C}}H_2\overset{Br}{\underset{}{C}}H\text{-}\overset{O}{\underset{}{C}}Cl + \bigcirc \xrightarrow{AlCl_3} \overset{Br}{\underset{}{C}}H_2\overset{Br}{\underset{}{C}}H\text{-}\overset{O}{\underset{}{C}}\bigcirc + HCl.$
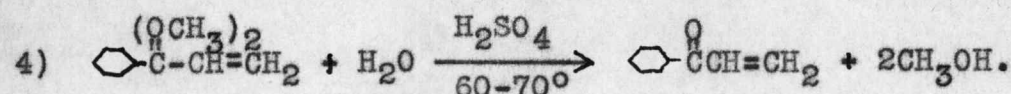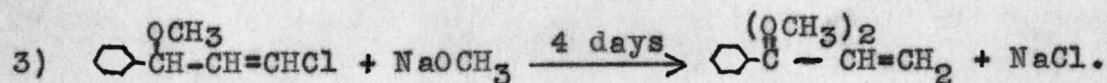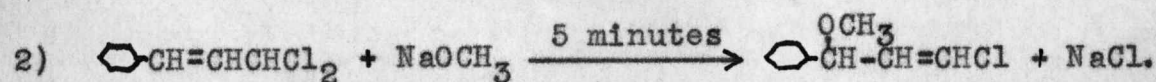
5) $\overset{Br}{\underset{}{C}}H_2\overset{Br}{\underset{}{C}}H\text{-}C\bigcirc + 2KI \text{ (in ethanol)} \longrightarrow CH_2{=}CH\overset{O}{\underset{}{C}}\bigcirc + 2KBr.$
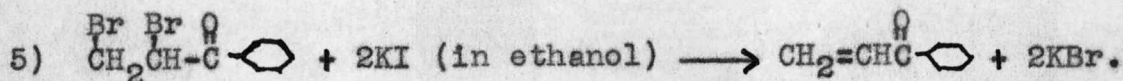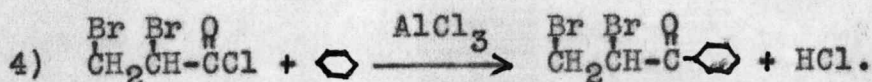
The yields are fairly good; the last reaction yields only 25-60% of the product indicated. This must be fractionated under vacuum to separate it from a biproduct, β-ethoxyethyl phenyl ketone, $C_2H_5OCH_2CH_2\overset{O}{\underset{}{C}}\bigcirc$.

Straus and Berkow (9) worked out a method for synthesizing phenyl vinyl ketone from cinnamaldehyde. It involves a shift of the double bond and migration of a hydrogen atom. The reactions are as shown by the following equations:

1) $\bigcirc CH{=}CH\overset{O}{\underset{}{C}}H + PCl_5 \longrightarrow \bigcirc CH{=}CHCHCl_2 + POCl_3.$

2) $\bigcirc CH{=}CHCHCl_2 + NaOCH_3 \xrightarrow{5 \text{ minutes}} \bigcirc \overset{OCH_3}{\underset{}{C}}H\text{-}CH{=}CHCl + NaCl.$

3) $\bigcirc \overset{OCH_3}{\underset{}{C}}H\text{-}CH{=}CHCl + NaOCH_3 \xrightarrow{4 \text{ days}} \bigcirc \overset{(OCH_3)_2}{\underset{}{C}}\text{-}CH{=}CH_2 + NaCl.$

4) $\bigcirc \overset{(OCH_3)_2}{\underset{}{C}}\text{-}CH{=}CH_2 + H_2O \xrightarrow[60\text{-}70^\circ]{H_2SO_4} \bigcirc \overset{O}{\underset{}{C}}CH{=}CH_2 + 2CH_3OH.$

The fact that the third reaction takes so long was evidence that led the investigators to the proof of the structure of the product of the second reaction, viz 1-chloro-3-methoxypropene-1. The chlorine atom, being attached to the

vinyl group, is very non-reactive. The yields for the reactions are, on the whole, good.

The general method for alkyl vinyl ketones of Blaise and Maire (1) involves the use of zinc alkyls. This method was not used because the zinc alkyls, which are volatile and spontaneously inflammable in air, are too dangerous.

The method of Mayer and Müller (8) using β-chloro-propionyl chloride and aluminum chloride gave low yields of products of only moderate purity. From a large number of homologous intermediates reported, only three vinyl ketones were reported; consequently as a method of synthe-sis, this was not believed to be very promising.

In this laboratory the method of Kohler (6) was used to make α,β-dibromopropiophenone. Rather than immediately make the phenyl ketone from this, the method was used with equimolar quantities of hydrocarbons other than benzene, viz toluene, m-xylene, naphthalene, and phenanthrene. Isolation of homologs of α,β-dibromopropiophenone was not possible as it was for the α,β-dibromopropiophenone, itself.

Using the method of Straus and Berkow (9), phenyl vinyl ketone was prepared from cinnamaldehyde. When similar conditions as for phenyl vinyl ketone were used with furfuryl acrolein in place of cinnamaldehyde, there was an uncontrollable reaction, and no pure product could be

obtained.   In a similar treatment of m-nitrocinnamaldehyde,
a new compound, m-nitrocinnamal chloride, was isolated.
This in turn was treated with 5% sodium methoxide.
Attempts to isolate anything from the reaction mixture
were not successful.

EXPERIMENTAL

2,3-DIBROMOPROPANOL-1. According to the procedure of
Kohler (6), in a two-liter, round-bottom flask, 125 g. of
allyl alcohol were dissolved in 500 ml. of carbon disulfide,
and the solution cooled in an ice-salt mixture. To this
solution was added a solution of 340 g. (109 ml.) of
bromine in an equal volume of carbon disulfide until a
distinct yellow color persists after ten minutes of shak-
ing. The solvent was distilled off, and the 2,3-dibromo-
propanol was distilled at 115-120° at 18 mm.; yield: 35 g.
(84%).

α,β-DIBROMOPROPIONIC ACID. By the method of Kohler
(6), in a 200 ml. round-bottom flask, 30 g. of fuming
nitric acid were mixed with 70 g. of concentrated nitric
acid. This was cooled in an ice water bath and with stir-
ring, 50 g. of cooled 2,3-dibromopropanol-1 was added. The
cooling was continued for four to five hours. The oxi-
dation was then allowed to proceed at room temperature over
night. The stirring was continued during the entire period.
The water and excess nitric acid were removed under vacuum
on a boiling water bath. The product was distilled at
150-160° at 20 mm. The yield was 23 g. of α,β-dibromo-
propionic acid (43%). The procedure was repeated using
308 g. of 2,3-dibromopropanol-1 and a proportionate amount
of the same nitric acid mixture yielding 180 g. (55%).

α,β-DIBROMOPROPIONYL CHLORIDE. In a 125 ml. Erlenmeyer flask ten grams of α,β-dibromopropionic acid were refluxed with 35 ml of thionyl chloride for one hour. After distilling off the thionyl chloride at atmospheric pressure, the product was distilled at 85-93° at 20 mm. The yield of α,β-dibromopropionyl chloride was 3.5 g. (33%). This procedure was repeated with 50 g. of the acid, but using only 150 ml. of thionyl chloride. The yield was 33 g. (61%). In another repetition of this method using 140 g. of the acid and 375 ml. of thionyl chloride the yield of the acid chloride was 101 g. (78%).

α,β-DIBROMOPROPIOPHENONE. Following the method of Kohler (6), 3.5 g. of α,β-dibromopropionyl chloride were dissolved in 1.4 g. of benzene and 7 ml. of carbon disulfide in a 50 ml. Erlenmeyer flask. The solution was immersed in an ice-salt bath and when cooled, about 2.2 g. of aluminum chloride were added in three portions until further addition no longer produced rapid evolution of hydrogen chloride. The mixture was poured into a mixture of cold, concentrated hydrochloric acid and ice. In a separatory funnel the carbon disulfide layer was removed to an evaporation dish, and the solvent allowed to evaporate. The crude, brown, oily solid was dried under suction. This was treated with activated charcoal and recrystallized from alcohol. Repetition of this procedure

yielded 0.5 g. (12%) of pure α,β-dibromopropiophenone melting at 58°. This procedure was repeated using 20 g. of the acid chloride, 8 g. of benzene, 40 g. of carbon tetrachloride and about 12.5 g. of aluminum chloride added in about two-gram portions. The yield of the pure ketone was 11.7 g. (50%).

In a 50 ml. erlenmeyer flask, 20 g. of α,β-dibromo-propionyl chloride and 18.3 g. of phenanthrene were dissolved in 40 ml. of carbon tetrachloride. The solution was treated while cooled by an ice-salt bath with about 12.5 g. of aluminum chloride. There was evolution of considerable hydrogen chloride. After hydrolysis as in the synthesis above and evaporation of the solvent, it was possible to crystallize out considerable phenanthrene from an alcohol solution of the solid residue from the reaction mixture. From the mother liquor nothing but a tarry material resulted, even though other solvents, viz, mixtures of benzene and petroleum ether and of ether and petroleum ether, and activated charcoal were used in the attempt. The recovered phenanthrene was recrystallized and the mother liquor failed to yield any other pure material when treated as the original mother liquor was.

This procedure was carried out using the same quantities of reagents on 13.1 g. of naphthalene, 9.2 g. of toluene, twice attempted, 10.5 g. of m-xylene; 13 g. of

the acid chloride, about 8.3 g. of aluminum chloride and 26 ml. of carbon disulfide were used again with 6.8 g. of m-xylene. From these, nothing could be obtained pure.

CINNAMAL CHLORIDE. Following the method of Straus and Berkow (9), 25 g. of dry cinnamaldehyde was added dropwise or in small portions to 43 g. of phosphorus pentachloride in a 200 ml. round-bottom flask. The flask was immersed in an ice water bath during the addition. After completion of the addition, the mixture was heated in a boiling water bath for two hours with frequent shaking. The phosphorus oxychloride and excess phosphorus pentachloride were distilled off under vacuum. The cinnamal chloride was distilled at 145-148° at 35 mm.; the yield was 12 g. (51%). This product was recrystallized from petroleum ether to give 10 g. of quite pure cinnamal chloride. It was found in this case that hexane was less satisfactory than petroleum ether (of b.p. 35-65°).

In a repetition of this procedure 100 g. of cinnamaldehyde and 170 g. of phosphorus pentachloride were mixed and then heated. This time the product was distilled at such a rapid rate that about 5% of the distillate consisted of the impure product carried over as a result of bumping. In this rapid, preliminary distillation decomposition was minimized. The product was distilled a second time at 147° at 35 mm. Even at a similar rapid

rate of distillation, bumping was not a problem. The yield was 90 g. (64%).

1-CHLORO-3-PHENYL-3-METHYOXYPROPENE-1. By the method of Straus and Berkow (9), 100 g. (0.535 mole) of cinnamal chloride were dissolved in an equal volume (73 ml.) of dry ether in a 500 ml. round-bottom flask. To this was added 282 ml. (0.535 mole.) of 5% sodium methoxide. The solution was refluxed for five minutes during which time sodium chloride caked onto the bottom. This mixture was concentrated by distilling off from one-half to two-thirds of the solvent. By adding about 200 ml. of dry ether to the resulting cooled mixture the methyl ether was isolated from the remaining sodium methoxide which, along with the sodium chloride was removed by filtration. The ether and any remaining methanol was distilled, over a hot water bath. The brown, crude 1-chloro-3-phenyl-3-methoxypropene was distilled at 112-114° at 20 mm.; yield: 74 g. (76%).

PHENYL VINYL KETONE, DIMETHYL ACETAL. By the method of Straus and Berkow (9), 74 g. of the ether (0.41 mole.) was refluxed with 764 ml. (1.46 moles.) of 5% sodium methoxide in a two-liter, round-bottom flask. Half of the methanol was distilled and about 200 ml. of ether was added. The ether solution was filtered and extracted with a little water to remove the methanol. After the ether was

distilled off, the acetal was distilled at 95-97° at 20 mm.; yield: 23 g. (32%).

PHENYL VINYL KETONE. By the procedure of Straus and Berkow, the dimethyl acetal was converted into phenyl vinyl ketone by hydrolysis. This was accomplished under rigid conditions because of the ease of polymerization and because of the tendency for the formation of addition products. In a 600 ml. beaker, 400 ml. of 5% sulfuric acid were heated to 75°. The beaker was then slipped into a black jacket which had been prepared for it and placed into fairly dark cupboard so that the rod of a mechanical stirrer extended into the acid solution. By this time the temperature had dropped to about 66°, which is between the optimum limits (60-70°). The acetal was added, and while stirring, the mixture was allowed to cool slowly. It was poured into a separatory funnel which had been covered with a jacket. Ether, the first portion of which was used to rinse out the beaker, was used to extract the phenyl vinyl ketone from the dilute acid. After the ether was distilled, the phenyl vinyl ketone was distilled at 99-103° at 6 mm.; yield: 10.5 g. (59%).

1,3-Diphenylpyrazoline was prepared in the customary manner for preparing phenylhydrazones. Two grams of pure phenylhydrazine hydrochloride, 3 g. of sodium acetate, 20 ml. of water and 2 g. of phenyl vinyl ketone were

refluxed for about thirty minutes. On cooling, 0.5 g. of the product crystallized out. After two recrystallizations from alcohol a trace of the 1,3-diphenylpyrazoline was obtained of melting point 152° as reported by Straus and Berkow (9).

FURFURYL ACROLEIN. By the procedure of Burdick and Adkins (2), 40 g. of (0.91 mole) freshly distilled acetaldehyde were added dropwise with vigorous stirring to 88 g. of (0.91 mole) freshly distilled furfural, 8 g. of sodium hydroxide and 800 g. of crushed ice and ice water. After standing for one hour without agitation, the yellow crystals were filtered, washed with water and steam distilled. After drying in the desiccator, the furfuryl acrolein melted at 51-51.6°. The yield was 40 g. (35%). This was used in place of cinnamaldehyde with phosphorus pentachloride. Even when added in small amounts and placed in a bath cooled by dry ice, considerable evolution of a grey smoky material resulted. All that remained in the reaction flask was a hard, black, vitreous, solid material. This was insoluble in acetone and other organic solvents and nothing could be isolated from it.

m-NITROBENZALDEHYDE (10). A mixture of 1250 ml. of concentrated sulfuric acid, 150 ml. of concentrated nitric acid and 100 g. of finely powdered sodium nitrate in a four-liter erlenmeyer flask was loosely stoppered and cooled

in the refrigerator. It was further cooled in an ice-salt mixture. During the addition of 200 g. of benzaldehyde, dropwise, the temperature was not allowed to rise above 5°. The flask was shaken frequently. When all of the aldehyde had been added, the mixture was heated slowly to 40° and was then cooled again to 5°. It was then poured slowly and with vigorous stirring into a crock containing 4 kg. of crushed ice and 1 l. of ice-water. The impure precipitate, m-nitrobenzaldehyde, was filtered by suction, washed well with water, and pressed to remove all acid and oil. The crude material was dried in a vacuum desiccator and recrystallized from a mixture of benzene and petroleum ether. The yield was 109 g. (37%); m.p. 57-57.6°.

m-NITROCINNAMALDEHYDE. According to the method of Kinkelin (5), 109 g. of m-nitrocinnamaldehyde were condensed with 38 g. (47.5 ml.) of acetaldehyde in 76 g. of 10% sodium hydroxide, 4360 ml. of water and 2180 ml. of alcohol. The mixture was let stand over night and was then filtered. The crude, sticky material was dried by a fan at 50°. Dilute alcohol, as called for, was not found very satisfactory for the recrystallization of the crude product. After recrystallization from a benzene-petroleum ether mixture, a fairly pure product was obtained; m.p.: 111-112°; yield: 74 g. (58%). By using the same solvent twice more, a melting point of 113.6-114.1° was obtained.

By using dilute alcohol as solvent in two more recrystal-
lizations, the melting point rose to 114.0-114.4°; this
was the highest point that could be reached. The samples
were placed in the Abderhalden dryer to insure complete
dryness before taking the last few melting points. A
sample melting at 116° was reported by Kinkelin (5).

The moderately pure portion of m-nitrocinnaldehyde of
m.p., 111-112° was treated with phosphorus pentachloride
as in the method of Straus and Berkow (9). The phosphorus
oxychloride and excess phosphorus pentachloride was removed
under vacuum by almost completely submerging the reaction
flask in boiling water to prevent condensation of solid
phosphorus pentachloride on a cooler portion of the flask.
The mixture was cooled and crystallized from a mixture of
ether and petroleum ether. A portion was twice recrystal-
lized from a mixture of benzene and petroleum ether. The
last recrystallization caused a rise in melting point of
only about 0.3°. The highest melting point obtainable was
86.5-87.0°. The results of analysis are not offered as
conclusive proof of the compound but rather, evidence that
the compound is probably a new one, m-nitrocinnamal
chloride. Analysis calculated for $C_9H_7NO_2Cl_2$: Cl, 30.6
Found: Cl, 29.2, 28.4, 27.5. This is an analog of
cinnamal chloride, a known compound formed by an analogous
reaction. The latter is visibly very hygroscopic and is

readily decomposed by water. The material which is probably m-nitrocinnamal chloride is not only slightly hygroscopic as observed while weighing, but is decomposed somewhat by the absorbed moisture. This statement is offered as explanation for the greatly decreasing findings for the percent chlorine even though the sample was dried in the Abderhalden dryer each time before weighing.

The remaining portion of the cinnamal chloride only crystallized once was treated with sodium methoxide. Nothing could be crystallized from the reaction mixture. Half of the residual, viscous, brown oil after evaporation of solvents, was steam distilled. The only result was that the oil became as viscous as tar. Using ether, nothing was found to be extracted from the distillate. The other portion of oil was vacuum distilled. Nothing distilled over until decomposition was quite complete.

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