

3. It has been suggested that the absorption spectra of benzaurin in neutral alcohol are due to the presence of a quinoid hydrate form of benzaurin, in acid solutions to a benzaurin salt of the acid, in the alkaline (potassium hydroxide) solution to the quinoid potassium salt of benzaurin, and in the strongly alkaline (33% potassium hydroxide) solution to the dipotassium salt of the carbinol.

4. A table showing the positions of maximum absorption, expressed in frequency numbers, for all the bands in each of the solutions studied has been prepared.

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KETENES IN THE FRIEDEL AND CRAFTS REACTION

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In recent years, two modifications of the Friedel and Crafts reaction have received prominence because of their successful application. In one of them¹ it has been demonstrated that ethylene, with high-speed stirring, may be used instead of ethyl halides for the attachment of ethyl groups to an aromatic nucleus. In the other it has been found that acid anhydrides² may be used quite generally instead of acid chlorides for the production of aromatic ketones. The use of acetic anhydride in particular was emphasized.

From a theoretical standpoint, it is but a short step from acetic anhydride to ketene. Both compounds generate acetic acid on the addition of water, and thus both compounds may be considered as anhydrides of acetic acid. The similarity of the two compounds made it natural to wonder whether or not ketene would also be a successful reagent in the Friedel and Crafts reaction. It was considered probable that the greater reactivity of ketene might offset the disadvantage of immiscibility, due to the fact that ketene is a gas. There was a likelihood, also, that one molecular proportion of aluminum chloride might suffice. With acetic anhydride, two molecular proportions are necessary.

From the results of this investigation, it will be seen that ketene does react with various types of aromatic nuclei with the resultant production of ketones. Benzene and anisole were the first compounds studied. Reaction occurred readily even when the reaction vessel was surrounded by an ice-bath. The progress of the reaction was not a simple one, however, inasmuch as a complex mixture of substances invariably resulted. Acetophenone and methoxyacetophenone were undoubtedly formed, as

¹ Milligan and Reid, *THIS JOURNAL*, **44**, 206 (1922); *Ind. Eng. Chem.*, **15**, 1048 (1923).

² Noller with Adams, *THIS JOURNAL*, **46**, 1889 (1924).

shown by characteristic, physical and chemical properties. With the amounts of material used, however, it was impossible to isolate them in a state of purity.

Ketene, prepared by the pyrogenic decomposition of acetone,³ was found to be inert towards carbon disulfide. Somewhat more than an equivalent of ketene was passed into a mixture which contained equivalent amounts of aluminum chloride and anisole dissolved in carbon disulfide. The reaction mixture was worked up in the usual way. About 45% of a mixture of ketones was obtained, b. p. 90–155° (8 mm.), which probably contained chiefly *o*- and *p*-methoxyacetophenone. Nearly an equal amount of higher-boiling material was also formed. By fractionation, the *ortho*-*para* mixture appeared to be about two-thirds *para*, but there seemed to be no constant boiling point. The fraction which contained most of the *para* formed a phenylhydrazone, m. p. 120–133°, with preliminary softening at 110°. This was proof of the presence of ketones, and also proof of the complexity of the mixture.

Similarly, with benzene, about a 20% yield of an oil, b. p. 190–215°, was produced which was shown to contain much acetophenone. When this oil was oxidized for six hours with a 6% chromic acid solution at 150–165°, benzoic acid was produced. As with anisole, much higher-boiling material was also isolated.

It was thought possible that the complexity of the reaction was caused by the attachment of more than one acetyl group to the aromatic nucleus. Support for this idea was lacking when it was observed that ketene, in the presence of one or two equivalents of aluminum chloride, scarcely reacted with acetophenone, a compound in which one acetyl group is already present. Although this is evidence, it must not be interpreted as proof against the point in question. For example, Wieland⁴ has shown that benzene reacts with nitrogen dioxide to produce nitrobenzene, trinitrobenzene, picric acid and other compounds, whereas nitrobenzene itself fails to react with nitrogen dioxide.

Because of the complexity encountered in these cases, attention was turned to naphthalene, a compound known⁵ to react sluggishly in the Friedel and Crafts reaction. With naphthalene and ketene, there was reaction even at ice temperature, and from the reaction mixture, it was found possible to isolate individual ketones or their derivatives in a high state of purity. Both the α - and the β -naphthylmethyl ketones were produced. The equation is: $C_{10}H_8 + CH_2=CO \longrightarrow C_{10}H_7COCH_3$. The yield varied between 21 and 37%, the higher yields appearing when

³ Hurd and Tallyn, *THIS JOURNAL*, **47**, 1427 (1925). "Organic Syntheses. IV," John Wiley and Sons, New York, 1925, p. 39.

⁴ Wieland, *Ber.*, **54B**, 1776 (1921).

⁵ Holleman, *Rec. trav. chim.*, **10**, 221 (1891). Rousset, *Bull. soc. chim.*, [3] **15**, 58 (1896).

the reaction flask was surrounded by an ice-bath. From an experiment with naphthalene carried out at the temperature of boiling carbon disulfide (solvent), dinaphthyl was isolated, formed⁶ by the action of aluminum chloride on the hydrocarbon.

The procedure with naphthalene, except for the treatment of the reaction mixture, was the same as with benzene or anisole. After removal of the aluminum chloride, the carbon disulfide and the excess of naphthalene were eliminated by distillation. The residue was vacuum-distilled to 300°. Usually the liquid distillate and the dark, resinous solid (m. p., 110–160°) left in the flask were of about equal weight.

Two methods were used to separate the substances in the distillate. One plan used fractional distillation in a vacuum. A better scheme was to extract the mixture first with hot alcohol, then with hot *n*-butyl alcohol, and fractionate the residue for low-boiling material. From the alcoholic solutions there precipitated, on cooling, a mixture which was largely β,β -dinaphthyl with some of the α,α -isomer; m. p., 167.5–168°. The pure β,β -dinaphthyl, m. p. 181°, was easily isolated through the picrate.⁶

Anal. Calcd. for $C_{20}H_{14}$: C, 94.5; H, 5.55. Found (by combustion): C, 94.2; H, 5.79.

A mixture of about equal amounts of α - and β -naphthylmethyl ketones was produced by distillation of the alcoholic solutions; b. p., 180–187° (20 mm.). The α -ketone was separated from the β -ketone by Rousset's method, which made use of the fact that the picrate of the former is quite insoluble in alcohol. This picrate melted at 114–115.5°; Rousset gave 116°.

It seems reasonable to infer that the mixture of products which was formed in these reactions was due to ketene itself, rather than to methane, ethylene, or to carbon monoxide which were also present. This is borne out by the fact that in the ethylation of benzene with ethylene,¹ much more of the mono-ethyl compound was formed than the diethyl; only small amounts of triethylbenzene were reported. No material was observed, however, in the present study with benzene, which boiled at temperatures as low as that required for mono-ethyl- or for diethylbenzene. Therefore, very little, if any, triethylbenzene could have been present in the acetophenone fraction which boiled at 190–215°.

An interesting development of the present work was the observation that ketene formed an addition product with aluminum chloride when the latter was suspended in carbon disulfide. Little or no hydrogen chloride was evolved. When made at 10° or lower, the addition product was a white powder. It reacted readily with benzene and with anisole when warmed gently, with the rapid evolution of hydrogen chloride. The products obtained by hydrolysis seemed to be identical with those obtained

⁶ Compare Homer, *J. Chem. Soc.*, 91, 1110 (1907).

when ketene was passed directly into the solution of the aromatic compound, in the presence of aluminum chloride.

If the reaction was performed at 40–45°, the aluminum chloride layer gradually became fluid. In appearance it resembled the aluminum chloride layer formed in Combes' reaction,⁷ which was performed in a simultaneous experiment. Combes discovered acetylacetone by hydrolyzing the product formed when a solution of acetyl chloride in chloroform was dropped upon aluminum chloride. In this reaction, hydrogen chloride was evolved vigorously. This is interesting, since the empirical formulas of ketene and of acetyl chloride differ only in the elements of hydrogen chloride. However, despite the similarity of the two products, that from ketene produced only acetic acid on hydrolysis, whereas that from acetyl chloride gave a small amount of acetylacetone, as well as acetic acid.

Summary

Ketene, in the presence of aluminum chloride, has been found to react with benzene, with anisole and with naphthalene to form rather complex mixtures from which ketones may be isolated. Scarcely any reaction occurred between ketene and acetophenone.

A reaction product of ketene and aluminum chloride has been observed which is capable of reacting with aromatic compounds, with the evolution of hydrogen chloride. Ketones are observed in the reaction mixture.

It is pointed out that ketenes might be expected to take part in the Friedel and Crafts' reaction because, in reality, ketenes are acid anhydrides. Acid anhydrides are known to enter into this reaction with success.

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CONDENSATION PRODUCTS OF ETHYL ACETO-ACETATE. I. A NEW COMPOUND OF GLYOXAL AND ETHYL ACETO-ACETATE, FORMYLMETHYLENE-BIS-ACETO-ACETIC ESTER

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Shaffer¹ and Shaffer and Friedemann² have demonstrated that acetoacetic acid is oxidized by hydrogen peroxide in alkaline solution if any one of several compounds be present, namely, glucose, fructose, glyceric aldehyde, glycol aldehyde, etc. The reactions by which these sugars accomplish the oxidation of acetoacetic acid *in vitro* are considered by Shaffer to be probably similar to the reactions by which carbohydrate

⁷ Combes, *Ann. chim. phys.*, [6] 12, 207 (1887).

¹ Shaffer, *J. Biol. Chem.*, 47, 433 (1921).

² Shaffer and Friedemann, *ibid.*, 61, 585 (1924).