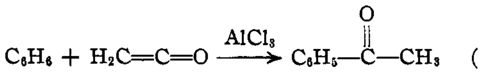
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF ILLINOIS AND INDIANA UNIVERSITY]

Carbon Suboxide in the Friedel–Crafts Reaction. I

BY JOHN H. BILLMAN,[1] GEORGE E. TRIPP AND R. VINCENT CASH

It was first shown by Hurd[2] that ketene would react with aromatic hydrocarbons or aromatic ethers in the presence of aluminum chloride to form primarily simple ketones according to the equation



$$C_6H_6 + H_2C{=}C{=}O \xrightarrow{AlCl_3} C_6H_5{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3 \quad (1)$$

Since Hurd's discovery, several investigators[3] have studied ketene more extensively in an endeavor to increase the yield of the expected ketone or to identify the other products formed in some of the reactions. Recently Boese[4] has found that diketene also would react in a manner similar to ketene, for with benzene and aluminum chloride he was able to prepare benzoylacetone.

As the above ketenes are the only two ketenes that have been tried in a Friedel–Crafts reaction, we felt that it would be of value to extend this type of reaction using carbon suboxide as the ketene, for in carbon suboxide there is a duoketene structure which should offer double the possibility for reaction and thereby lead to the formation of an entirely different series of products than could be obtained from any other simple ketene.

If carbon suboxide should react with benzene in the presence of aluminum chloride exactly as does ketene, then one would expect to obtain dibenzoylmethane. However, if only one of the two ketene functional groups participated in the Friedel–Crafts reaction, then benzoylacetic acid, or acetophenone by decarboxylation of the latter, would be anticipated.

$$C_6H_6 + O{=}C{=}C{=}C{=}O \xrightarrow{AlCl_3} C_6H_5COCH_2COOH \quad (2)$$

$$C_6H_5COCH_2COOH \longrightarrow C_6H_5COCH_3 + CO_2 \quad (3)$$

Except for a large amount of polymerized carbon suboxide, the only product identified in the reaction after hydrolysis by dilute acids was acetophenone. This ketone must have come by way of benzoylacetic acid, which is known[5] to undergo decarboxylation in the presence of dilute acids, whereas dibenzoylmethane is stable in this medium.

Despite the fact that all of the runs were carried out at nearly ice temperature, polymerization of carbon suboxide could not be prevented. As it has been shown that in certain instances anhydrous stannic chloride causes less polymerization than aluminum chloride,[6] the former condensing agent also was used. However, no difference in the results could be observed.

Whereas previous workers have reported the liberation of hydrogen chloride during the condensation of ketenes with aromatic hydrocarbons, in the presence of aluminum chloride, we were unable to detect any of the gas. Only upon refluxing the mixtures was hydrogen chloride evolved.

Further work is being done in this Laboratory on carbon suboxide in the Friedel–Crafts reaction.

Experimental

Preparation of Carbon Suboxide.—The carbon suboxide used in our experiments was prepared by a method similar to that used by Hurd[7] in which diacetyltartaric anhydride was pyrolyzed by heating in an electric furnace to 625°. The gas, as it formed, was collected in a trap cooled to $-78°$ by solid carbon dioxide and acetone. Before using the liquid carbon suboxide it was first distilled to free it from the dark colored impurities that also collected in the trap. The carbon suboxide, as it distilled over, was run directly into a calibrated receiver containing dry benzene cooled to approximately 4°. At the completion of the distillation, a measured volume of the benzene solution was removed and treated with an excess of aniline. From the amount of malonanilide formed, the amount of carbon suboxide in solution was determined.

Procedure.—Seven and five-tenths grams (0.12 mole) of carbon suboxide dissolved in 400 cc. of benzene, as prepared above, was added to 200 cc. of benzene and cooled to approximately 4°. Forty grams (0.27 mole) of aluminum chloride was then added slowly with vigorous stirring. A deep reddish-brown precipitate formed immediately. After all of the aluminum chloride had been added it was found that there was no noticeable odor of carbon suboxide in the reaction flask. The mixture was then refluxed, at which time large amounts of hydrogen chloride were evolved. Hydrolysis was accomplished by the addition of ice and water and the mixture allowed to stand over-

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[2] Hurd, THIS JOURNAL, **47**, 2777 (1925).

[3] (a) Ploeg, *Rec. trav. chim.*, **45**, 342–344 (1926); (b) Packendorff, Zelinsky and Leder-Packendorff, *Ber.*, **66**, 1069 (1933); (c) Spring and Vickerstaff, *J. Chem. Soc.*, 1873 (1935); (d) Williams and Osborn, THIS JOURNAL, **61**, 3438 (1939).

[4] Boese, *Ind. Eng. Chem.*, **32**, 16 (1940).

[5] Beckmann and Paul, *Ann.*, **266**, 17 (1891).

[6] *Org. Syntheses*, **28**, 2 (1938).

[7] Hurd and Pilgrim, THIS JOURNAL, **55**, 757–759 (1933).

night. When hydrolysis was complete the mixture was worked up in the usual manner. A small amount of an oil with the odor of acetophenone was found after evaporation of the benzene layer. A similar product was obtained by steam distillation of the water layer. This oil solidified at approximately 19° and formed a semicarbazone melting at 195–196°, which corresponds to that of acetophenone. An authentic sample of the semicarbazone of acetophenone also melted at 195–196°; a mixed melting point evidenced no lowering of this value.

Summary

1. It has been shown that carbon suboxide will undergo a Friedel–Crafts reaction with benzene.

2. We conclude that benzoylacetic acid was formed as an intermediate in the reaction.

3. Acetophenone was isolated from the reaction mixture.

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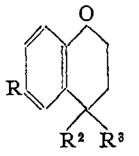
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

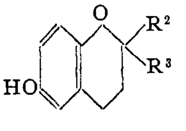
Polymethylbenzenes. XXV. The Reaction between Dimethylacrylic Acid and the Trimethylbenzenes[1]

BY LEE IRVIN SMITH AND WILLIAM W. PRICHARD[2]

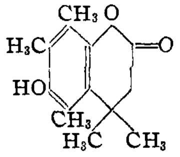
The work described in this paper was begun as an attempt to synthesize some 4,4-disubstituted chromans (I) or hydrocoumarins (III) in which the 6-position was occupied by a hydrogen atom or hydroxyl group.



I, R = H or OH
R^2 and R^3 = alkyl



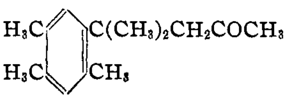
II



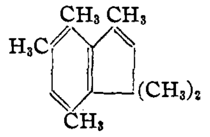
III

Such compounds were of interest because of their relationship to the tocopherols (vitamin E) which are analogous 2,2-dialkyl chromans, II. Very few examples of 4,4-disubstituted chromans are known,[3] and there is only a single example (III) of the synthesis of a 4,4-disubstituted hydrocoumarin.[4]

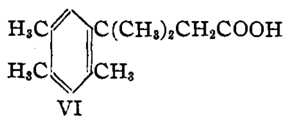
The difficulty in the synthesis of these substances appeared to be the introduction of the quaternary carbon atom,[5,6] hence attention was turned to methods for closing the chroman and hydrocoumarin rings after introduction of the quaternary carbon atom. The necessary intermediates, however, proved impossible to prepare. Appropriate alkylation of malonic ester failed because dimethyl-*o*-hydroxyphenylcarbinol[7,8] could not be converted to the chloride. Likewise unsuccessful were all attempts to obtain any crystalline products when mesityl oxide in the presence of aluminum chloride was condensed with any of a number of substituted phenols and hydroquinones or their ethers,[3a,9] and it appeared that the unsaturated ketone could be condensed successfully only with hydrocarbons.[7] It was known that β-[2,4,5-trimethylphenyl]-propionic acid could be converted into a quinone and then to a 6-hydroxyhydrocoumarin[10] and the analogous propionic acid, completely substituted in the β-position, should be accessible through the ketone IV resulting from the condensation of pseudocumene and mesityl oxide. The result of this condensation, however, was an indene V, although in view of the rearrangements described below the orientation of the methyl groups in the benzene ring of this compound is not certain.



IV



V



VI

The possibility remained that the condensation of pseudocumene with β,β-dimethylacrylic acid might lead to the acid VI, in which case the series of reactions could be carried out as planned. The product of this condensation was a mixture of

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[1] Polymethylbenzenes, XXIV, THIS JOURNAL, 61, 989 (1939).

[2] Abstracted from a thesis by W. W. Prichard, presented to the Graduate Faculty of the University of Minnesota, in partial fulfillment of the requirements for the Ph.D. degree, October, 1939.

[3] (a) Niederl, THIS JOURNAL, 51, 2426 (1929); (b) Dianin, *J. Russ. Phys.-Chem. Soc.*, 46, 1310 (1914).

[4] John, Günther and Schmeil, *Ber.*, 71, 2617 (1938).

[5] Kostanecki, *et al.*, *Ber.*, 35, 861, 2889 (1902); 37, 774 (1904).

[6] Hill, *Chem. Rev.*, 19, 25 (1936).

[7] Hoffman, THIS JOURNAL, 51, 2542 (1929).

[8] Béhal and Tiffeneau, *Bull. soc. chim.*, [4] 3, 315 (1908).

[9] Liebermann and Hartmann, *Ber.*, 24, 2586 (1891).

[10] Smith and Denyes, THIS JOURNAL, 58, 304 (1936).