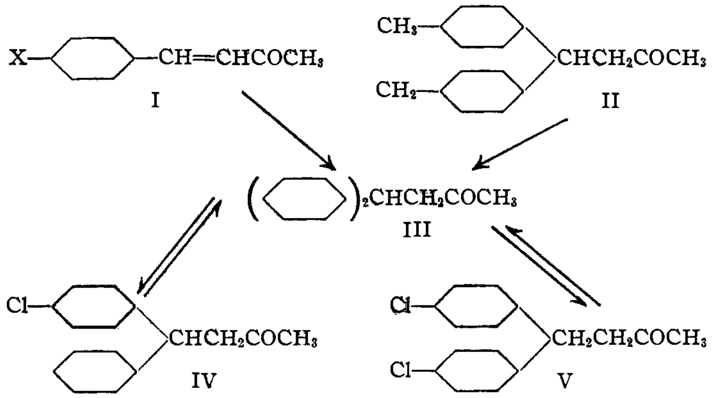
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reversibility of the Friedel–Crafts Condensation. The Benzal- and Dibenzalacetones

BY C. F. WOODWARD, GERALD T. BORCHERDT AND REYNOLD C. FUSON

Benzalacetone is the simplest member of the series of α,β-unsaturated ketones which are known to undergo reversible addition with aromatic compounds. In keeping with this fact, it has been found that the conversion of benzalacetones (I) into benzohydrylacetones and the interconversion of the latter take place more readily and afford better yields than did the analogous transformations of systems previously examined.[1] The improved yields are due to some extent to the fact that, on account of their low boiling points, the products can be separated by fractional distillation.

When treated with benzene in the presence of anhydrous aluminum chloride and hydrogen chloride, benzalacetone (I, X = H), *p*-methylbenzalacetone (I, X = CH_3) and *p*-chlorobenzalacetone (I, X = Cl) are transformed into benzohydrylacetone (III). The intermediate product (IV), required by theory in the latter case, has been arrived at in two ways. It is formed by the addition of chlorobenzene to benzalacetone and by the action of chlorobenzene on benzohydrylacetone. In both of these conversions IV as well as V—the ultimate product—can be isolated by interrupting the reaction at the proper point. This is convincing evidence that in the interconversion of III and V the monochlorobenzohydryl compound (IV) is actually formed as an intermediate.



In the **dibenzalacetone** series a very similar result has been obtained in the transformation of di-(*o*-chlorobenzal)-acetone (VI) into *sym*-dibenzohydrylacetone (VIII). The intermediate, VII, can be isolated if the process is interrupted at the proper point. It has, in turn, been converted to VIII by renewing the action of benzene under the usual conditions. It is remarkable that both of the chlorine atoms in VII have remained in the *ortho* positions—a fact which was established by the synthesis of VII from VI by the action of phenylmagnesium bromide.

The generality of the reversible addition phenomenon in this series is evident from the fact that IX and X give, with benzene, the same product (VIII) which is obtained from XI and XII under similar conditions. The stepwise conversion of XI to VIII through XII by the action of phenylmagnesium bromide attests the validity of these structures.[2]

Experimental

***p*-Chlorobenzalacetone** (I, X = Cl).—This compound was prepared by the method of Walther and Rätze,[3] who reported a melting point of 51°. After distillation and subsequent recrystallization from petroleum ether, the product melted at 58–59.5°.

Anal. Calcd. for $C_{10}H_9OCl$: Cl, 19.65. Found: Cl, 19.55.

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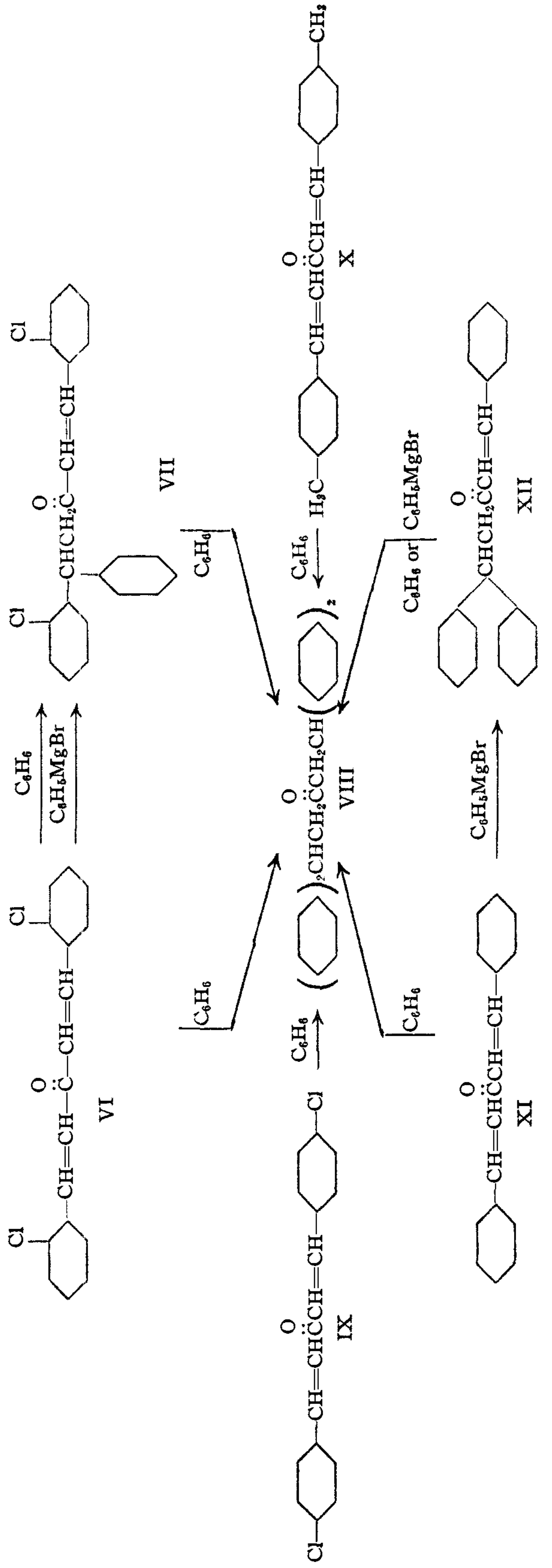
[1] Previous articles in this series are (a) Hoffman, Farlow and Fuson, THIS JOURNAL, **55**, 2000 (1933); (b) Fuson, Kozacik and Eaton, *ibid.*, **55**, 3799 (1933); (c) Eaton, Black and Fuson, *ibid.*, **56**, 687 (1934); (d) Weinstock and Fuson, *ibid.*, **56**, 1241 (1934).

[2] It is interesting from the standpoint of the theory of 1,4 addition assumed in such condensations that this transformation of XI into VIII by the action of the Grignard reagent cannot be carried out in a single process as would be the case if the reagent added in the 3,4 manner.

[3] Walther and Rätze, *J. prakt. Chem.*, [2] **65**, 279 (1902).



p,p'-Dimethylbenzohydrylacetone (II).—To a mixture of 100 g. of anhydrous aluminum chloride and 200 cc. of toluene was added, over a period of two hours, a cold solution of 75 g. of p-methylbenzalacetone in 400 cc. of toluene. The mixture was cooled for three hours after the addition was complete, and then allowed to stand for twenty hours at room temperature. An additional 20 g. of the aluminum halide was then added and the reaction was allowed to proceed for fifteen hours longer. Mechanical stirring was used throughout the entire process. The toluene solution remaining after the decomposition of the reaction mixture with ice and hydrochloric acid was dried and fractionally distilled. There was obtained 50% of the theoretical yield of II; b. p. 175–180° (4 mm.). The compound melted at 73.5–74.5° after two recrystallizations from petroleum ether followed by four recrystallizations from alcohol.

Anal. Calcd. for $C_{18}H_{20}O$: C, 85.71; H, 7.93. Found: C, 85.74; H, 7.93.

The semicarbazone melted at 140–141.5°.

Anal. Calcd. for $C_{19}H_{23}ON_3$: N, 13.59. Found: N, 13.63.

p,p'-Dichlorobenzohydrylacetone (V).—This ketone was prepared by a procedure similar to that used for II. In this case the reaction time was twenty-four hours and the excess chlorobenzene was removed by steam distillation. From 27 g. of p-chlorobenzalacetone and 350 cc. of chlorobenzene there was obtained 37 g. of V; b. p. 202–207° (4 mm.). The melting point, after one recrystallization from petroleum ether and three recrystallizations from alcohol, was 91–92.5°.

Anal. Calcd. for $C_{16}H_{14}OCl_2$: Cl, 24.2. Found: Cl, 24.4.

The semicarbazone (from alcohol) melted at 180–181°.

Anal. Calcd. for $C_{17}H_{17}ON_3Cl_2$: N, 12.03. Found: N, 12.19.

Oxidation with sodium dichromate in glacial acetic acid converted V into p,p'-dichlorobenzophenone.

p-Chlorobenzohydrylacetone (IV).—When the reaction between benzalacetone and chlorobenzene was interrupted at the end of five hours IV was obtained. From 75 g. of benzalacetone and 500 cc. of chlorobenzene there resulted 84.7 g. of IV, boiling at 176–186° (4 mm.). The pure ketone boiled at 180–182° (4 mm.); n^{20}_{D} 1.5816; d^{20}_{D} 1.1684; mol. ref. calcd., 73.77; found, 73.81.

Anal. Calcd. for $C_{16}H_{15}OCl$: Cl, 13.72. Found: Cl, 13.80.

The semicarbazone (from alcohol) melted at 155.5–157°.

Anal. Calcd. for $C_{17}H_{18}ON_3Cl$: N, 13.31. Found: N, 13.46.

Benzohydrylacetone (III)

(a) From Benzalacetones (I).—Benzalacetone, p-chlorobenzalacetone and p-methylbenzalacetone were each converted into III, by the usual treatment with aluminum chloride and hydrogen chloride in an excess of benzene, in yields of 59, 92 and 68%, respectively, of the theoretical amounts.

(b) From Substituted Benzohydrylacetones.—The procedure in (a) applied to II, IV and V gave III in yields of 34, 85 and 33%, respectively, of the theoretical amounts.

The conversion of V into III was reversed by using chlorobenzene in place of benzene. However, in this case the chief product was IV.

Di-(*o*-chlorobenzal)-acetone (VI).—This ketone was made from acetone and *o*-chlorobenzaldehyde by a modification of the method used in the synthesis of dibenzalacetone.[4] The principal difference was that in this case the reaction was much more rapid. The compound (from ethyl acetate) melted at 124–125°; yield, 90% of the theoretical amount.

Anal. Calcd. for $C_{17}H_{12}OCl_2$: C, 67.4; H, 4.0; Cl, 23.4. Found: C, 67.1; H, 4.2; Cl, 23.8.

o-Chlorobenzohydrylmethyl *o*-Chlorostyryl Ketone (VII)

(A) **By the Friedel–Crafts Method.**—To obtain VII the reaction between VI and benzene in the presence of aluminum chloride was interrupted when the mixture had become entirely liquid and the original bright red color had faded to a brown. The compound (from alcohol) melted at 144°.

Anal. Calcd. for $C_{23}H_{18}OCl_2$: C, 72.43; H, 4.76; Cl, 18.61. Found: C, 72.70; H, 4.73; Cl, 18.79.

(B) **By the Grignard Method.**—Phenylmagnesium bromide added to VI to give VII, which was identified with the product from (A) by the method of mixed melting points.

Sym-Dibenzohydrylacetone (VIII).—When the reaction described under (A) was continued for twelve hours VII was not isolated; under these conditions VIII was obtained. By similar methods VII, IX, X, XI and XII were in each case found to yield VIII.

The saturated ketone (VIII) was also prepared by the addition of phenylmagnesium bromide to XII; the latter compound was made in turn from XI by a similar procedure.

Summary

Benzalacetones (I), substituted benzohydrylacetones (II, IV, V), dibenzalacetones (VI, IX, X, XI) and benzohydrylmethyl styryl ketones (VII, XII) are transformed by the action of benzene in the presence of aluminum chloride into the corresponding unsubstituted benzohydryl compounds (III, VIII).

In the conversion of di-(*o*-chlorobenzal)-acetone (VI) into *sym*-dibenzohydrylacetone (VIII) the intermediate, VII, has been isolated. Similarly, in the conversion of benzalacetone and benzohydrylacetone into *p*,*p*′-dichlorobenzohydrylacetone, the intermediate, chlorobenzohydrylacetone (IV), has been obtained by interrupting the process.

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[4] "Organic Syntheses," John Wiley and Sons, New York, 1932, Vol. XII, p 22.

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The Thermal Decomposition of Organic Compounds from the Standpoint of Free Radicals. IX. The Combination of Methyl Groups with Metallic Mercury

BY F. O. RICE AND B. L. EVERING

Fragments produced in the thermal decomposition of propane and butane[1] can be combined with metallic mercury to form mercury alkyls, which in turn react with alcoholic mercuric bromide to give crystalline alkyl mercuric bromides. Sublimation of these from the excess of mercuric bromide permitted the positive identification of the bulk of the material as methyl mercuric bromide. The remaining 5% was not identified although it seemed probable that it consisted mainly of the ethyl derivative.

In the past months we have attempted to make a complete analysis of the products formed in the above experiments. The work proved to be unexpectedly difficult, partly owing to the formation of a small quantity of an extremely unstable alkyl mercurous compound which decomposes in a few hours even at −80° (this may possibly be the compound $CH_3HgHgCH_3$), and partly because the presence of mercuric bromide catalyzes some change (which is not mentioned in the literature) in the alkyl mercuric bromides. However, we have proved that ethyl or higher derivatives are absent and that the material produced by the action of the fragments from propane or butane on metallic mercury is upward of 95% dimethyl mercury.

A method for the separation and estimation of methyl and ethyl groups has been developed by Willstätter and Utzinger;[2] this depends on the insolubility of tetramethylammonium iodide in such solvents as water, acetone, chloroform and absolute alcohol, in all of which trimethylethyl ammonium iodide dissolves easily. Accordingly

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(1) Rice, Johnston and Evering, THIS JOURNAL, **54**, 3529 (1932).

(2) Willstätter and Utzinger, *Ann.*, **382**, 148 (1911).