

tate of 4,4'-diaminoarsenobenzene through a plug of cotton into a second bulb, the benzene solution washed with dilute hydrochloric acid, with water and the solvent then removed; 5.2 g. of tetraphenyldiarsyl was obtained; m. p. 123-126° in a sealed tube under nitrogen; when treated with iodine diphenyliodoarsine was formed; m. p. 42-44°.

Summary

4,4'-Dihydroxytetraphenyldiarsyl has been obtained by the action of hypophosphorous acid on 4-hydroxydiphenylarsinic acid.

3,3',3'',3'''-Tetra-(hydroxyphenyl)-diarsyl was

prepared from 3,3'-dihydroxydiphenylarsinic acid and hypophosphorous acid and also by interaction of 3,3',3'',3''' - tetra - (hydroxyphenyl) - arsyl oxide and diphenylarsine.

4-Hydroxyphenylarsine and tetraphenylarsyl oxide yield 4,4' - dihydroxyarsenobenzene and tetraphenyldiarsyl; from 4-aminophenylarsine and tetraphenylarsyl oxide there was obtained 4,4' - diaminoarsenobenzene and tetraphenyldiarsyl.

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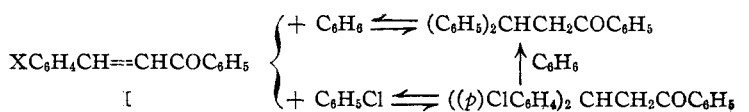
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Reversible Addition of Aromatic Compounds to Benzalacetophenones

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The addition of benzene and chlorobenzene to benzalquinaldines and to nuclear halocinnamic acids in the presence of aluminum chloride and hydrogen chloride appears to take place reversibly.¹ It was to be expected that this type of behavior would be general for α,β -unsaturated carbonyl compounds;² and in the hope of simplifying the experimental work the investigation has been extended to the benzalacetophenones.

The results obtained with this system have furnished some new types of evidence in support of the theory of reversibility previously outlined. Substituted benzalacetophenones of the class represented by I react with benzene in the presence of aluminum chloride and hydrogen chloride to give β,β -diphenylpropiofenone (II). This reaction has been effected with benzalacetophenones in which X = Cl (*o*, *m* and *p*), Br (*m* and *p*) and CH₃ (*p*).



The replacement of the tolyl group by the phenyl radical is noteworthy as an indication that such replacements are not due primarily to differences in the radicals involved, since in this instance these differences are slight.

(1) Hoffman, Farlow and Fuson, THIS JOURNAL, **55**, 2000 (1933); Fuson, Kozacik and Eaton, *ibid.*, **55**, 3799 (1933).

(2) It should be mentioned that it has frequently been demonstrated that the addition of aromatic hydrocarbons to olefins is reversible. (For a good example, see Boedtker and Halse, *Bull. soc. chim.*, [4] **19**, 444 (1916).) To what extent the behavior of the conjugated systems under consideration resembles that of simple olefins is not yet clear.

The condensation of chlorobenzene with benzalacetophenones of the type under investigation (I) gives β,β -di-(*p*-chlorophenyl) - propiofenone (III).³ When X is a halogen atom this product is obtained regardless of the position or nature of the halogen atom involved. This type of reaction has been observed in cases in which X = Cl (*o* and *p*) and Br (*m*). The last-named is the first example of a replacement of one halophenyl group by another and, like the replacement already referred to of the tolyl group by the phenyl radical, suggests that any aromatic radical (if the orientation of substituents is disregarded) may under suitable conditions replace any other aromatic radical. This is a necessary consequence of the assumption that the reaction is reversible.

The most striking result obtained in this series is the conversion of one β,β -diarylpropiofenone into another. When the dichloro ketone (III) is treated with benzene under the usual conditions it is transformed into the corresponding chlorine-free ketone (II). This substitution of one aryl radical for another in a β,β -diarylpropiofenone is a realization of one of the steps previously postulated to explain the replacement which occurs when I is converted into II or into III.

Experimental

m-Chlorobenzalacetophenone.—This compound was

(3) The structure of the dichloro compound was established by oxidation which gave *p,p'*-dichlorobenzophenone.

prepared by the method used by Walther and Rätze⁴ in the synthesis of the corresponding para derivative. The compound, after recrystallization from alcohol, melted at 75–76°.

Anal. Calcd. for C₁₈H₁₁OCl: C, 74.2; H, 4.5; Cl, 14.6. Found: C, 74.6; H, 4.4; Cl, 14.4.

The Action of Benzene, Aluminum Chloride and Hydrogen Chloride on the Benzalacetophenones

(a) *p*-Chlorobenzalacetophenone.⁴—A solution of 20 g. of the unsaturated ketone in 200 cc. of dry benzene was saturated with dry hydrogen chloride and 25 g. of anhydrous aluminum chloride was added. A vigorous evolution of hydrogen chloride took place and a yellow paste precipitated. The mixture was then stirred for fifteen hours at room temperature. The end of the reaction was indicated by the complete disappearance of the yellow color. The greenish-brown mixture was poured into a mixture of 200 g. of cracked ice and 100 cc. of concentrated hydrochloric acid. The resulting mixture was subjected to steam distillation until all volatile materials were removed and the non-volatile brown residue was allowed to cool. The product solidified and was recrystallized from 95% alcohol. The yield of crude product was practically quantitative but losses in recrystallization were high. After repeated recrystallizations the β,β -diphenylpropiofenone obtained melted at 92–93° and was halogen-free. The ketone was converted into the oxime according to the method of Kohler.⁵ The product after five recrystallizations from alcohol melted at 130–131°. Hydrolysis of the oxime regenerated the ketone which then melted at 93–94°.

(b) *m*-Chlorobenzalacetophenone.—The procedure was similar to that for the *p*-chloro isomer. Again the product was halogen-free and melted at 92–93°. A mixed melting point with the product from (a) showed no lowering.

(c) *o*-Chlorobenzalacetophenone.⁴—The procedure used was that of (a). The β,β -diphenylpropiofenone obtained melted at 92–93° and was identical with that of (a).

p-Bromo,⁶ *m*-Bromo,⁷ and *p*-Methylbenzalacetophenone.⁸—The procedure used in these cases was similar to that in (a) and in each case the product was identical with that from (a).

The Action of Chlorobenzene, Aluminum Chloride and Hydrogen Chloride on the Benzalacetophenones

(d) *p*-Chlorobenzalacetophenone.—The procedure was similar to that for (a) above. The reaction proceeded smoothly but somewhat more slowly. The color appearing at the start of the reaction was bright red and slowly

gave way to a dark brown. The β,β -di-(*p*-chlorophenyl)-propiofenone was purified by boiling with 5% alkaline permanganate for three hours. The melting point was 120–121°.

Anal. Calcd. for C₂₁H₁₆OCl₂: C, 71.0; H, 4.5; Cl, 20.0. Found: C, 71.0; H, 4.4; Cl, 20.2.

(e) *o*-Chloro- and *m*-Bromobenzalacetophenone.—A procedure identical with that of (d) was used. The product in each case melted at 120–121°.

4,4'-Dichlorobenzophenone.—One-half gram of β,β -di-(*p*-chlorophenyl)-propiofenone was added to a solution containing 10 cc. of pyridine, 90 cc. of water, 5 g. of sodium hydroxide and 2 g. of potassium permanganate. The mixture was boiled for one hour and decomposed with sulfuric acid and sodium bisulfite. The product melted at 142–143°. A mixed melting point with known 4,4'-dichlorobenzophenone showed no lowering.

The Action of Benzene and Aluminum Chloride on β,β -Di-(*p*-chlorophenyl)-propiofenone.—One gram of the ketone and 100 cc. of benzene, which had been distilled from phenylmagnesium bromide, were treated with 5 g. of anhydrous aluminum chloride in a flask stoppered with a calcium chloride tube. The mixture immediately assumed a faint yellow color. After standing for fifteen hours, with intermittent shaking, there had been no evidence of any reaction whatever either in color change or precipitate formation. The flask was stoppered and dry hydrogen chloride was passed in for one minute. The mixture was again allowed to stand. There was a noticeable deepening in the color in the flask in fifteen minutes, and on standing overnight the mixture developed a deep greenish-brown color. The β,β -diphenylpropiofenone, isolated as in the case of (a) above, was obtained in a 30% yield and melted at 92–93°. There was never any perceptible evolution of gas or precipitate formation.

Summary

A number of substituted benzalacetophenones of the type XC₆H₄CH=CHCO-C₆H₅ have been found to react with benzene in the presence of aluminum chloride and hydrogen chloride to give β,β -diphenylpropiofenone, (C₆H₅)₂CHCH₂CO-C₆H₅.

With chlorobenzene under similar conditions these benzalacetophenones give β,β -di-(*p*-chlorophenyl)-propiofenone, (*p*-ClC₆H₄)₂CHCH₂CO-C₆H₅.

The dichloro compound reacts with benzene to give β,β -diphenylpropiofenone.

These results are in accord with the theory that the addition of aromatic compounds to α,β -unsaturated carbonyl compounds (and similarly constituted compounds) is reversible.

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(4) Walther and Rätze, *J. prakt. Chem.*, [2] **65**, 280 (1902); see also Weitz and Scheffer, *Ber.*, **54**, 2339 (1921); and Diltney, Neuhaus, Reis and Schommer, *J. prakt. Chem.*, **124**, 81 (1930).

(5) Kohler, *Am. Chem. J.*, **42**, 375 (1909).

(6) The method of preparation used was a modification of that of Weygand, *Ann.*, **459**, 118 (1927).

(7) See Stevens, *J. Chem. Soc.*, **137**, 2107 (1930), for the method of preparation.

(8) This compound was prepared according to the method of Hanzlík and Bianchi, *Ber.*, **32**, 2283 (1899).