[CONTRIBUTION FROM THE THOMPSON LABORATORY OF THE PHILLIPS EXETER ACADEMY]

β-Alkoxy Derivatives of 2-Chlorochalcone

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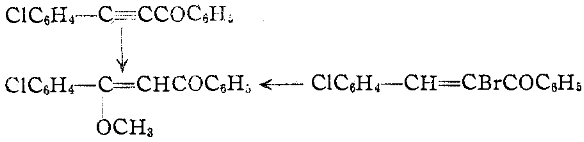
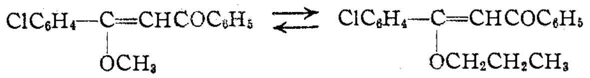
Earlier reports from this Laboratory described the preparation of β-methoxy-2-chlorochalcone either by the addition of methanol to *o*-chlorophenylbenzoylacetylene[1] or by the action of methanol and potassium hydroxide on α-bromo-2-chlorochalcone.[2] β-Ethoxy-2-chlorochalcone and β-propoxy-2-chlorochalcone have now been prepared by the addition of the appropriate alcohol to *o*-chlorophenylbenzoylacetylene.



$$\begin{array}{l} ClC_6H_4{-}C{\equiv}CCOC_6H_5 \\ \qquad\downarrow \\ ClC_6H_4{-}\underset{OCH_3}{C}{=}CHCOC_6H_5 \longleftarrow ClC_6H_4{-}CH{=}CBrCOC_6H_5 \end{array}$$

In the presence of potassium hydroxide, these alkoxy derivatives can be converted one into the other by the use of the proper alcohol as solvent and reagent. For example, β-methoxy-2-chlorochalcone is converted into β-propoxy-2-chlorochalcone when treated with propanol-1 and potassium hydroxide, and the reverse reaction is realized by using methanol and the base.



$$ClC_6H_4{-}\underset{OCH_3}{C}{=}CHCOC_6H_5 \rightleftarrows ClC_6H_4{-}\underset{OCH_2CH_2CH_3}{C}{=}CHCOC_6H_5$$

These interconversions bear a resemblance to the interchange of esters but a closer examination indicates that the resemblance is only superficial. Ester interchange is catalyzed by a trace of a base while the interconversions herein described may proceed in the presence of a quantity of base exceeding one equivalent of the β-alkoxy compound. The reaction corresponding to the saponification of an ester, the liberation of the enol form of the β-diketone, apparently does not occur since the compound thus liberated would be cleaved by the base. Moreover, ester interchange is catalyzed by acids but β-alkoxychalcones are converted cleanly into β-diketones by the action of acids.

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Experimental

Preparation of β-Alkoxy Derivatives from *o*-Chlorophenylbenzoylacetylene.—The preparation of β-methoxy-2-chlorochalcone from *o*-chlorophenylbenzoylacetylene appeared in an earlier paper.[1] Application of the same general procedure gave the ethoxy and propoxy derivatives.

β-Ethoxy-2-chlorochalcone is extremely soluble in ether, appreciably soluble in low-boiling petroleum ether, crystallizes as stout colorless prisms and melts at 39°.

Anal. Calcd. for $C_{17}H_{15}O_2Cl$: C, 71.2; H, 5.28. Found: C, 70.5, 71.0; H, 5.33, 5.22.

β-Propoxy-2-chlorochalcone is very soluble in ether, sparingly soluble in low-boiling petroleum ether, crystallizes as long fibrous white needles resembling glass wool and melts at 55°.

Anal. Calcd. for $C_{18}H_{17}O_2Cl$: C, 71.8; H, 5.71. Found: C, 71.5; H, 5.77.

Each of the above new compounds was converted quantitatively into *o*-chlorodibenzoylmethane by concentrated hydrochloric acid.[2]

Interconversion of β-Alkoxy Compounds.—The same general procedure was employed in all cases and can be illustrated by the following conversion of β-methoxy-2-chlorochalcone into β-propoxy-2-chlorochalcone.

A solution of 20 g. of the methoxy compound in 50 ml. of propanol-1, containing 1.5 g. of potassium hydroxide pellets, was heated on a steam-bath for five hours. The resulting solution was cooled, water added to a pronounced turbidity, the turbid mixture seeded with the propoxy compound and placed in the refrigerator until crystallization was complete. During the crystallization, water was added from time to time in sufficient quantity to produce turbidity but not enough to precipitate the product as an oil. The solid was filtered, washed with a cold mixture of propanol and water, and then washed thoroughly with water. The dry product weighed 19 g. and melted at 53–55°, recrystallization from ether and petroleum ether giving 18.5 g. of pure white needles melting at 55°.

The yields in the conversions varied from 60 to 90%. The highest yields were realized in the preparation of the methoxy compound, undoubtedly due to its higher melting point and lower solubility; the lowest yield was obtained in the preparation of the ethoxy compound which is very low melting and has a marked tendency to separate as an oil. However, in each case the residual oily product was converted into *o*-chlorodibenzoylmethane by the action of concentrated hydrochloric acid, indicating the absence of side reactions.

Action of Potassium Hydroxide and Methanol on the Methoxy Compound.—In order to test the action of an excess of potassium hydroxide on an alcoholic solution of the alkoxy derivatives, a solution containing 5.00 g. of β-methoxy-2-chlorochalcone, 1.5 g. of potassium hydroxide pellets and 50 ml. of methanol was refluxed for ten hours. A recovery of 4.95 g. of the starting material was realized.

Action of Potassium Hydroxide and Methanol on *o*-Chlorodibenzoylmethane.—A solution containing 5 g. of *o*-chlorodibenzoylmethane, 1.5 g. of potassium hydroxide and 50 ml. of methanol was refluxed for ten hours. The extent of cleavage was about 50%, both benzoic acid and *o*-chlorobenzoic acid appearing in the cleavage products.[2]

Summary

The interconversion of certain β-alkoxy derivatives of 2-chlorochalcone is reported.

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[1] Bickel, THIS JOURNAL, **69**, 74 (1947).

[2] Bickel, *ibid.*, **68**, 866 (1946).