A Rearrangement in the Reaction of αα-Dichloroacetophenone with Sodium Methoxide

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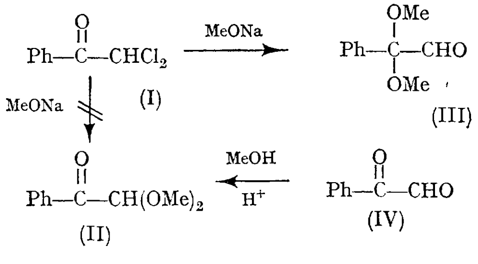
ALTHOUGH the reaction of α-halogeno- and ααα-trihalogeno-ketones with nucleophilic reagents has been studied extensively, almost no information is available on the corresponding reactions of αα-dihalogeno-ketones. The high reactivity of phenacyl halides with weakly basic nucleophiles has been ascribed to the activating influence of the carbonyl group,[1] but with strongly basic nucleophiles the *carbonyl carbon* is attacked and epoxides have been isolated.[2] With ααα-trihalogeno-ketones, the haloform reaction is observed.

It has been reported that the reaction of αα-dichloroacetophenone (I) with sodium methoxide afforded phenylglyoxal dimethyl acetal (II).[3] However, the product of the reaction is clearly shown by chemical and spectral evidence to be the isomeric aldehyde: phenylglyoxal dimethyl ketal (III). Authentic acetal (II) was prepared from phenylglyoxal (IV) and methyl alcohol.

Treatment of (I)[4] with sodium methoxide in methyl alcohol afforded in 80% yield a product, b.p. 123—130°/25 mm.,† resembling the compound previously described (lit.,[3] b.p. 110—114°/13 mm.). Structure (III) is assigned on the basis of the following data: n.m.r. spectrum (internal standard Me_4Si) δ (CCl_4) 3·22 (6 H, CH_3), 7·28 (5 H, broad multiplet, phenyl protons) and 9·24 p.p.m. (1 H, s, aldehyde proton); ν_{max} (film) 1745 $cm.^{-1}$. Chemical evidence for (III) was provided by a positive Fehling test. In addition, by using a procedure for the conversion of aldehydes into nitriles,[5] compound (III) was converted into phenylglyoxal dimethyl ketal *NNN*-trimethylhydrazonium iodide, which underwent an elimination reaction with sodium isopropoxide in propan-2-ol to give phenylglyoxylonitrile dimethyl ketal, characterized by molecular weight (mass spectrum), n.m.r., i.r. and u.v. spectroscopy.

Heating a solution of (IV) (freshly distilled from its hydrate) under reflux in methyl alcohol–benzene with a catalytic amount of sulphuric acid



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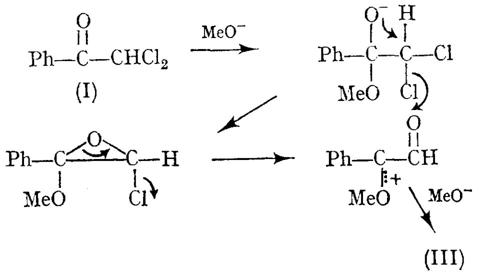
† Satisfactory elemental analyses have been obtained on all new compounds.

afforded the acetal (II), b.p. 85—86°/0·25 mm. Structure (II) is assigned on the basis of the following data: δ (CCl_4) 3·46 (6 H, s, CH_3), 4·88 (1 H, s) and 7·38 and 8·02 p.p.m. (5 H, broad multiplets, phenyl protons); ν_{max} (film) 1700 cm.$^{-1}$.



Compound (II) gave a negative Fehling test. The i.r. spectra show the conjugated carbonyl group in (II) and the absence of conjugation in (III). The n.m.r. spectrum of (III) has the characteristic low-field aldehyde proton.

The mechanism for the formation of ketal (III) proposes the intermediate formation of an epoxide and resembles that of the reaction of α-halogenoketones with sodium methoxide.[2,6] Attack by the methoxide on the epoxide occurs at the more hindered carbon indicating that the reaction has considerable S_N1 character or proceeds by a carbonium–oxonium ion.[6]

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