

## The Addition of Methyl Hypochlorite to Phenylacetylene

BY ERNEST L. JACKSON

The reaction of ethyl hypochlorite with phenylacetylene in carbon tetrachloride solution was shown by Goldschmidt, Endres and Dirsch<sup>1</sup> to yield only  $\omega,\omega$ -dichloroacetophenone which apparently resulted from the addition of hypochlorous acid to the triple bond of the unsaturated compound. The intermediate formation of the diethyl ketal by the addition of ethyl hypochlorite, however, was considered possible, but the easy hydrolysis of the ketals by hydrochloric acid was thought to preclude its isolation under their experimental conditions. The addition of ethyl hypochlorite to phenylacetylene might possibly be accomplished by its reaction with chlorine and absolute ethyl alcohol in the manner described in a previous paper<sup>2</sup> for the addition of ethyl hypochlorite to cinnamic acid, but as shown this method is complicated by a number of side reactions and the yield would probably be very low. The addition of methyl hypochlorite to phenylacetylene through its reaction with chlorine and absolute methyl alcohol, however, seemed feasible in view of our successful application<sup>3</sup> of this reaction to certain ethylene derivatives. I have accordingly investigated this method and have found that phenylacetylene reacts quite readily with chlorine and absolute methyl alcohol to give about a 70% yield of the beautifully crystalline methyl hypochlorite addition product. The reaction was carried out by introducing dry chlorine into an efficiently stirred solution of phenylacetylene in anhydrous methyl alcohol at room temperature, no precautions being taken to neutralize the hydrochloric acid which was formed along with methyl hypochlorite by the interaction of chlorine and methyl alcohol. The pure product melted at 66° and proved to be phenyldimethoxydichloroethane, showing that two molecules of methyl hypochlorite combined with a molecule of phenylacetylene. Since the dimethoxy compound is hydrolyzed by hot 0.4 *N* hydrochloric acid to yield  $\omega,\omega$ -dichloroacetophenone it must be 1-phenyl-1,1-dimethoxy-2,2-dichloroethane.

### Experimental Part

**Reaction of Phenylacetylene with Chlorine and Absolute Methyl Alcohol.**—A moderately rapid stream of chlorine,

- (1) Goldschmidt, Endres and Dirsch, *Ber.*, **58**, 572 (1925).
- (2) Jackson and Pasiut, *THIS JOURNAL*, **49**, 2071 (1927).
- (3) Jackson, *ibid.*, **48**, 2166 (1926).

dried by passing through concentrated sulfuric acid, was introduced into a thoroughly stirred solution of 11 g. of phenylacetylene (b. p. 142–144°) in 100 cc. of anhydrous methyl alcohol at room temperature. The reaction solution was protected from atmospheric moisture by a calcium chloride drying tube. The absorption of chlorine was rapid and the reaction was accompanied by a moderate rise in temperature. After the solution had ceased to absorb chlorine, which was shown by a test with starch-potassium iodide paper, it was neutralized with silver carbonate, the silver chloride was filtered off and washed with methyl alcohol. Concentration of the filtrate under reduced pressure to about 50 cc. yielded 15.8 g. of colorless crystals melting at 63–64°. The mother liquor was concentrated under reduced pressure to a small volume and finally allowed to evaporate spontaneously to dryness. The resulting crystals were separated from some oil by suction filtration and washed with a little cold methyl alcohol. The second crop weighed 2.2 g. and melted at 62–63°, the total yield being 71% of the theoretical. One recrystallization from absolute methyl alcohol gave the pure compound which, after drying in an evacuated desiccator over calcium chloride, melted at 66–66.5° (uncorr.). Methoxyl and chlorine determinations showed the substance to be phenyldimethoxydichloroethane.

*Anal.*<sup>4</sup> Calcd. for  $C_8H_8Cl_2(OCH_3)_2$ : OCH<sub>3</sub>, 26.4; Cl, 30.2. Found: OCH<sub>3</sub>, 26.1; Cl, 29.9.

The compound is easily soluble in benzene, chloroform and ether, soluble in cold absolute methyl alcohol and insoluble in cold water. It crystallizes readily from absolute methyl alcohol as colorless flat prisms. The pure crystals possess a faint odor resembling that of camphor and the camphor-like odor is considerably more marked when the substance, apparently undecomposed, is in the molten state.

**Structure of the Dimethoxy Compound.**—A suspension of 5 g. of pure compound in 100 cc. of *N* aqueous hydrochloric acid solution, to which was added 150 cc. of absolute methyl alcohol, was heated on the steam-bath under a reflux condenser and shaken until the substance was in solution. After refluxing for ten hours it was neutralized to phenolphthalein with sodium hydroxide solution and extracted thoroughly with benzene. The benzene solution was dried over anhydrous sodium sulfate and the solvent was distilled off under reduced pressure, yielding a somewhat lachrymatory oil, most of which distilled at 131–132° (11 mm.).

*Anal.* Calcd. for  $C_8H_8OCl_2$ : Cl, 37.5. Found: Cl, 37.0.

Oxidation of some of the oil with hot alkaline potassium permanganate solution gave benzoic acid; m. p. 121°. The reaction of the oil, prepared from 1 g. of dimethoxy compound, with 0.7 g. of hydroxylamine hydrochloride in alkaline aqueous alcohol solution by Schramm's<sup>5</sup>

(4) I am indebted to Mr. H. W. Williams of Cleveland, Ohio, for the analyses.

(5) Schramm, *Ber.*, **16**, 2186 (1883); Russauow, *ibid.*, **24**, 3497 (1891).

procedure yielded phenylglyoxime which, after two recrystallizations from chloroform, melted at 168° alone or mixed with authentic phenylglyoxime prepared from  $\omega,\omega$ -dibromoacetophenone. This shows the oil to be  $\omega,\omega$ -dichloroacetophenone and the dimethoxy compound to be 1-phenyl-1,1-dimethoxy-2,2-dichloroethane. In accord with this structure the dimethoxy compound is stable toward potassium hydroxide in methyl alcohol solution. By refluxing a solution of 1 g. of pure compound and 3 g. of potassium hydroxide in 15 cc. of absolute methyl alcohol for four hours, evaporating the solvent and extracting the potassium hydroxide from the residue with cold

distilled water, 85% of the pure dimethoxy compound was recovered.

### Summary

Phenylacetylene reacts rapidly with chlorine and absolute methyl alcohol to produce about a 70% yield of 1-phenyl-1,1-dimethoxy-2,2-dichloroethane of m. p. 66°, which is evidently formed by the addition of two molecules of methyl hypochlorite to the triple bond of the unsaturated compound.

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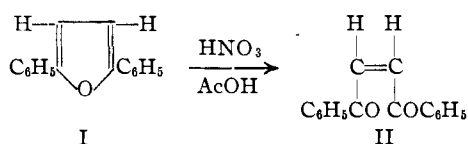
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## The Nitric Acid Oxidation of 2,5-Diphenylfurans to *Cis* Unsaturated 1,4-Diketones

BY ROBERT E. LUTZ AND FRANK N. WILDER

The nitric-acetic acid oxidation of  $\alpha,\alpha'$ -diphenylfurans to unsaturated 1,4-diketones is a reaction which proceeds easily with good yields and which promises to be of value in synthesis and also in the determination of structure of certain furans and the configurations of unsaturated 1,4-diketones. The method was first used by Zinin in the preparation of *cis* dibenzoylstilbene from tetraphenylfuran.<sup>1</sup> We have applied the method with very satisfactory results to 2,5-diphenylfuran (I) and to the 3,4-dichloro and dibromo derivatives, and have obtained in each case in good yields, respectively, *cis* dibenzoyl ethylene (II) and *cis* dibenzoyl dichloro and dibromo ethylenes, the configurations of which are known.<sup>2</sup>



Mention should be made here also of the oxidation by this method of di-(bromophenyl)-dichloro and dibromofurans and of triphenylfuran to the corresponding *cis* unsaturated 1,4-diketones.<sup>3</sup>

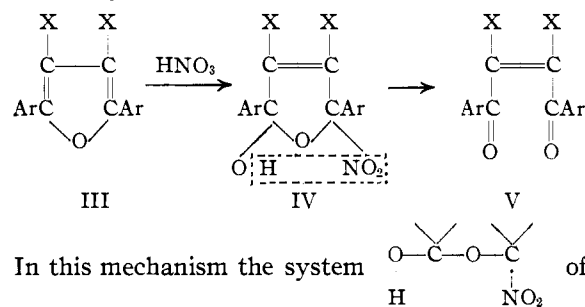
In all of these seven instances the reaction between nitric acid and the furan has proceeded without exception exclusively in a consistent stereochemical sense to give the unsaturated 1,4-diketone of *cis* configuration. This indicates that the double bond is established by readjustment of the furan double linkages before the ring

(1) Zinin, *J. prakt. Chem.*, [I] **101**, 164 (1867); cf. also Japp and Klingemann, *J. Chem. Soc.*, **57**, 675 (1890).

(2) Cf. Lutz, *THIS JOURNAL*, **52**, 3405, 3423 (1930).

(3) See more extensive studies involving these compounds, to be published shortly.

opens, since otherwise a mixture of *cis* and *trans*, or more likely the stable *trans* isomer alone, would be expected. There is evidence that furans add nitric acid or its equivalent 1,4 to give intermediates which lose water or its equivalent to give nitrofurans.<sup>4</sup> It seems very likely that here also 1,4 addition occurs, but that loss of water or its equivalent from the resulting intermediate IV being impossible, nitrous acid is eliminated instead, giving the *cis* unsaturated 1,4 diketone in some such way as



In this mechanism the system of IV may be regarded as losing the elements of nitrous acid 1,4, generating two new double bonds,<sup>5</sup> and forming the highly conjugated unsaturated 1,4-diketone V. The latter factor probably in any case constitutes some measure of the driving force of the reaction. It is also possible that the intermediate IV, if formed, undergoes rearrangement into an open chain compound,  $C_6H_5CO(X)=C(X)C(OH)C_6H_5$

(4) Freure and Johnson, *THIS JOURNAL*, **53**, 1142 (1931); Shepard and Johnson, *ibid.*, **54**, 4385 (1932).

(5) Cf. Loss of hydrogen chloride from the system [Thiele, *Ann.*, **306**, 109 (1899)].