procedure yielded phenylglyoxime which, after two recrystallizations from chloroform, melted at 168° alone or mixed with authentic phenylglyoxime prepared from ω,ω-dibromoacetophenone. This shows the oil to be ω,ω-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.

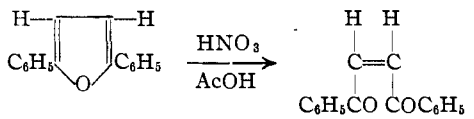
WASHINGTON, D. C. RECEIVED JANUARY 12, 1934

[CONTRIBUTION NO. 124 FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

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

BY ROBERT E. LUTZ AND FRANK N. WILDER

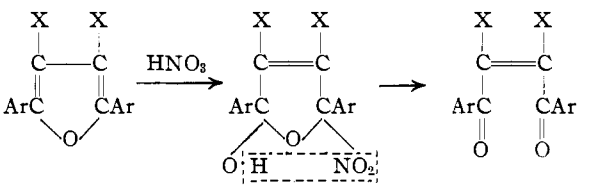
The nitric–acetic acid oxidation of α,α′-diphenylfurans to unsaturated 1,4-diketones is a reaction which proceeds easily with good yields and which promises to be of value in synthesis and also in the determination of structure of certain furans and the configurations of unsaturated 1,4-diketones. The method was first used by Zinin in the preparation of *cis* dibenzoylstilbene from tetraphenylfuran.[1] 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* dibenzoylethylene (II) and *cis* dibenzoyl dichloro and dibromo ethylenes, the configurations of which are known.[2]



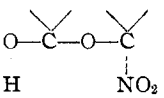
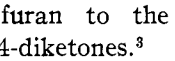
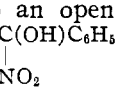
I II

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.[3]

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 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.[4] 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



III IV V

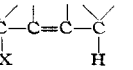
In this mechanism the system  of IV may be regarded as losing the elements of nitrous acid 1,4, generating two new double bonds,[5]  , and forming the highly conjugated unsaturated 1,4-diketone V. The latter factor probably in any case constitutes some measure of the driving force of the reaction. It is also possible that the intermediate IV, if formed, undergoes rearrangement into an open chain compound, $C_6H_5CO(X)=C(X)C(OH)C_6H_5$ (NO₂ group), 

(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.

(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)].

with subsequent loss of nitrous acid, generating the unsaturated diketone.

Since the splitting of the furan ring with nitric acid takes place in a consistent stereochemical manner, it would appear to be safe to utilize the reaction as a means of determining configurations of new unsaturated 1,4-diketones, providing of course that both *cis* and *trans* isomers are known and both are stable under the conditions involved in this synthesis.

Experimental Part

Since all the compounds dealt with in this paper are known, a brief outline of the oxidation method only will be given: 1 g. of the furan to be oxidized was suspended or dissolved in 5 cc. of glacial acetic acid and a solution of 1 cc. of concd. nitric acid (sp. gr. 1.42) in 3 cc. of glacial acetic acid was added slowly, and the mixture allowed to stand for one hour. The temperature was maintained constant at 100° for the 2,5-diphenyl-dichloro and dibromofurans, and at 25° for 2,5-diphenylfuran itself. The solutions were then diluted with ice water and the precipitated organic material washed with water and recrystallized from ethanol. The products were obtained in about 80% yields and were identified by mixed melting points with authentic samples.

Summary

Various 2,5-diphenylfurans are oxidized consistently to *cis* unsaturated 1,4-diketones, probably through a 1,4 addition mechanism.

UNIVERSITY, VIRGINIA RECEIVED JANUARY 12, 1934

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

A Further Study of the Toxicity of Derivatives of Rotenone with the Goldfish as the Test Animal

BY W. A. GERSDORFF

The preparation[1] of various derivatives of rotenone in the Insecticide Division of the Bureau of Chemistry and Soils afforded an opportunity to investigate the effect of slight changes in chemical structure on toxicity. Previous toxicological studies on rotenone,[2] dihydrorotenone,[2] acetylrotenone,[3] and rotenolone[3] have shown that the dihydro derivative has higher toxicity whereas the acetyl and hydroxy derivatives have lower toxicity than rotenone. This paper presents the results of similar investigations made with acetyldihydrorotenone, acetylrotenolone, dihydrorotenolone and acetyldihydrorotenolone. The method used by the author, in which the goldfish is used as the test animal, has been described in a previous paper.[4] The size of the fish, however, was greater, averaging for one of the two lots used 2.4 g. and for the other, 2.9 g.

Acetyldihydrorotenone (m. p. 209–211°), an acetate of the enol type, was prepared[5,6] by treating dihydrorotenone with acetic anhydride and sodium acetate.

Acetylrotenolone (m. p. 184°) was obtained[7,8] as the main product of the reaction of iodine and an alkali acetate with an alcoholic solution of rotenone. It is the acetate of a hydroxyrotenone in which the hydroxyl group is attached to one of the adjacent asymmetric carbon atoms of the dihydro-γ-pyrone system.

Acetyldihydrorotenolone (m. p. 189°) was prepared[7,8] in a similar reaction with dihydrorotenone. It differs from acetylrotenolone only in that the double bond in the isopropylene group is saturated with hydrogen.

Dihydrorotenolone was prepared[7,8] by the saponification of the preceding compound. This substance failed to crystallize with the methods tried, but its purity was established by a methoxyl determination. Its formula is that of the hydroxy derivative corresponding to the preceding compound.

Although two lots of goldfish were used in the tests, they were apparently similar in their resistance to these toxic substances, comparative results falling well within the limit of error.

The survival time curves and the velocity of fatality curves, which were plotted from the toxicity data, are given in Figs. 1 and 2.

Comparative data obtained from the velocity of fatality curves are given in Table I. In each case the straight line which is an approximation of that portion of the curve corresponding to the

(1) LaForge, Haller and Smith, *Chem. Rev.*, **12**, 181–213 (1933).
(2) Gersdorff, THIS JOURNAL, **52**, 5051–5056 (1930).
(3) Gersdorff, *ibid.*, **55**, 1147–1152 (1933).
(4) Gersdorff, *ibid.*, **52**, 3440–3445 (1930).
(5) LaForge, Haller and Smith, *loc. cit.*, p. 191.
(6) Smith and LaForge, THIS JOURNAL, **54**, 2996–3000 (1932).
(7) LaForge, Haller and Smith, *loc. cit.*, p. 202.
(8) LaForge and Smith, THIS JOURNAL, **52**, 1091–1098 (1930).