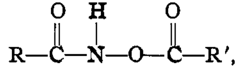
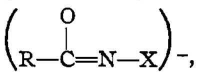
ammonia was allowed to remain in a thermostat at 30° for three days. Twenty-five cc. aliquots of this solution were refluxed for seven hours with 15 cc. of concentrated hydrochloric acid, after which the solution was cooled in an ice-bath and made alkaline by the addition of solid sodium hydroxide. The alkaline solution was extracted with two 50-cc. and one 25-cc. portion of ether. The ether extracts were washed with 30 cc. of water and extracted with one 60-cc. and two 20-cc. portions of a solution of 15 cc. of concentrated hydrochloric acid in 85 cc. of water. The acid solution was boiled to expel ether. To the cooled acid solution was added 12 cc. of 10% potassium bromide solution, after which it was titrated with approximately 0.15 *N* standard potassium bromate solution. The end-point was determined by spotting on starch–potassium iodide paper. One cubic centimeter of 0.1 *N* potassium bromate is equivalent to 1.551 mg. of aniline. This method gave results reproducible to within 0.8%.

The yield of amine from benzoyl *p*-methoxybenzhydroxamate, benzoyl *p*-methylbenzhydroxamate, *m*-nitrobenzoyl *p*-methylbenzhydroxamate, *m*-nitrobenzoyl *p*-methoxybenzhydroxamate, benzoyl *m*-methylbenzhydroxamate, benzoyl *m*-methoxybenzhydroxamate and *m*-fluorobenzoyl benzhydroxamate was determined by dissolving 1 to 2 g. of the potassium salt of the dihydroxamic acid in the amount of 0.1 *N* ammonia calculated to make a 0.025 molar solution and allowing the salt to decompose in the thermostat at 30°. The solution was then made acid with 20 cc. of concentrated hydrochloric acid and refluxed for seven hours. The solution was concentrated to about 50 cc. by distillation, cooled in an ice-bath and made alkaline by addition of solid potassium hydroxide. The alkaline solution was extracted with two 50-cc. and one 25-cc. portion of ether and the combined ether extracts washed with 30 cc. of water. The ether solution was extracted with two 25-cc. portions of 3 *N* hydrochloric acid. The acid solutions were combined in a weighed beaker, evaporated to dryness on a water-bath and finally dried in a desiccator over Drierite until their weight did not change after a day in the desiccator. The yield of amine was calculated from the weight of amine hydrochloride obtained in this way. This method gave results that were reproducible to within 2%.

Summary

1. The rates of decomposition of the potassium salts of a series of meta and para substituted dibenzhydroxamic acids,  $R-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}-O-\overset{\overset{O}{\|}}{C}-R'$, have been determined at 30°. A qualitative inverse relationship has been found between the ionization constants of benzoic acids corresponding to R and the rates of decomposition of dihydroxamic acid salts in which the effect of substituents in R alone was considered. A quantitative direct relationship has been found between the ionization constants of benzoic acids corresponding to R′ and the rates of decomposition of dihydroxamic acid salts in which the effect of substituents in R′ alone was being considered.

2. These results support the hypothesis that the rate determining step in a Hofmann or Lossen reaction is the release of X as a negative ion from the anion,  $\left(R-\overset{\overset{O}{|}}{C}=N-X\right)^-$, of the salt of a halogen amide or dihydroxamic acid.

3. A general method for the preparation of a number of hydroxamic and dihydroxamic acids has been described.

DURHAM, N. C. RECEIVED SEPTEMBER 5, 1937

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

3-Acetoxy-4-chloro-2,5-diphenylfuran

BY ROBERT E. LUTZ, A. H. STUART, F. N. WILDER AND W. C. CONNOR

The two compounds supposed in earlier papers to be acetoxychlorodiphenylfuran, VII, and diacetoxydiphenylfuran[1] have been shown by Kohler and Woodward[1f] to be, respectively, chlorodiphenylfuranone, III, and acetoxydiphenylfuranone, IV. These two compounds were prepared by the action of acetyl chloride and acetic anhydride (with sulfuric acid) on diphenylbutanetrione enol and the open-chain and cyclic ethers. The erroneous furan formulations[1d] were based on these preparations and upon the reactions with phosphorus pentachloride to give dichlorodiphenylfuran, II. The latter reactions are outlined correctly in the diagram.

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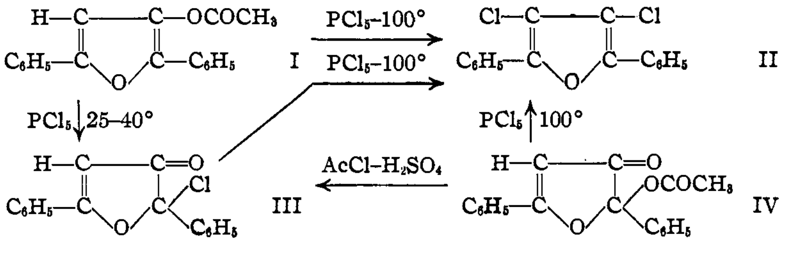
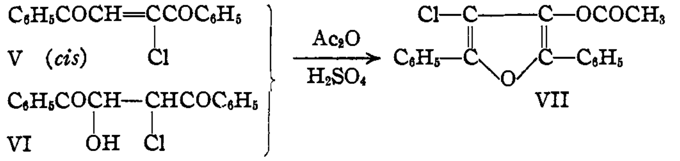
[1] (a) Lutz, Wilder and Parrish, THIS JOURNAL, **56**, 1980 (1934); Lutz and Wilder, *ibid.*, **56**; (b) 1987; (c) 2065; (d) 2145 (1934); (e) Lutz and Stuart, *ibid.*, **58**, 1885 (1936); (f) Kohler and Woodward, *ibid.*, **58**, 1933 (1936).

The discussion of results in previous papers dealing with diphenylbutanetrione enol (refs. a–d) are confused by the erroneous formulation of diphenylmethoxy and chlorofuranones (III) as open-chain compounds. The corrections are outlined in a later paper (ref. e) together with discussion of the ring-chain tautomerism involved; simultaneously a similar discussion and rigorous proof of the cyclic formulations of this type was published by Kohler and Woodward (ref. f).



The reaction between phosphorus pentachloride and acetoxydiphenylfuran I proceeds at a relatively low temperature, involves in effect chlorination, and gives the chlorofuranone, III, rather than the chloro- or dichlorofuran, II. Further reaction with phosphorus pentachloride under slightly more drastic conditions, however, produces the dichlorofuran II through rearrangement and replacement of the elements of hydroxyl by chlorine.

Diacetoxydiphenylfuran is unknown. The true acetoxychlorodiphenylfuran VII, however, has actually been in hand from the first[1b (footnote 2)] but it was not formulated because it was not converted by phosphorus pentachloride into the dichlorofuran, II. It may be prepared by the action of acetic anhydride and sulfuric acid on *cis*-dibenzoylchloroethylene, V, and on dibenzoylethylene chlorohydrin, VI, and its acetate. In view of these reactions there can be no doubt about its structure.



In connection with these experiments it is noteworthy that under given conditions the *cis*-dibenzoylchloroethylene reacts readily with acetic anhydride and sulfuric acid to give the furan, VII, a reaction for which there are many analogies among the unsaturated 1,4-diketones and quinones, whereas the *trans* isomer is stable. Similarly the *cis* isomer is converted into the dichlorofuran, II, by acetyl chloride and sulfuric acid whereas the *trans* isomer is stable under these conditions.[2] Thus the *cis* isomer is consistently the more reactive of the two, as would be expected.

Experimental Part

3-Acetoxy-4-chloro-2,5-diphenylfuran, VII.—A solution of 0.1 g. of *cis*-dibenzoylchloroethylene (V) in 1 cc. of acetic anhydride was treated with two drops of concd. sulfuric acid and the mixture heated for five minutes in a boiling water-bath. On hydrolysis in an excess of water a quantitative yield of nearly pure product precipitated. In a similar experiment a sample of the *trans* isomer (melting at 72–73°) was recovered practically quantitatively with its melting point lowered only slightly to 66–67°.

In an alternative preparation 0.5 g. of dibenzoylethylene chlorohydrin (VI) in 5 cc. of acetic anhydride was treated with 3 drops of concd. sulfuric acid. A reaction occurred with the formation of a greenish-brown solution and subsequent deposition of needle crystals. On hydrolysis a yield of 0.4 g. of nearly pure material was obtained.

In a similar experiment the chlorohydrin acetate gave the furan in good yield.

It was purified by repeated crystallization from ethanol; m. p. 119°.

Anal. Calcd. for $C_{18}H_{13}O_3Cl$: C, 69.05; H, 4.3; Cl, 11.6; CH_3CO, 13.8. Found: C, 69.1; H, 4.2; Cl, 11.4, 11.6; CH_3CO, 14.3.

The conversion of cis-dibenzoylchloroethylene into dichlorodiphenylfuran was effected by dissolving 0.05 g. in 0.6 cc. of acetyl chloride and a drop of concd. sulfuric acid, warming gently and immediately pouring into water. The product was not pure but after crystallization 0.02 g. of nearly pure dichlorodiphenylfuran (II) was obtained and identified.

Summary

The preparation of the true acetoxychlorodiphenylfuran is described and its relation to preceding work on diphenylbutanetrione discussed.

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[2] Lutz, THIS JOURNAL, **48**, 2916 (1926).