and water, the white precipitate was collected, weight 4.40 g., analysis: C, 28.31; H, 2.65.

Summary

There has been isolated from the nitration of melamine a product of the empirical formula, $C_3H_{3-4}N_7O_5$. A convenient procedure for the preparation of triacetylmelamine has been developed, and by nitration of this compound there has been obtained a compound whose formula is $C_9H_9N_{15}O_{12}$. By heating this compound in water, there has been obtained another compound, $C_9H_9N_9O_9$. Salts of these three new compounds have been obtained, and some of their properties have been determined, but their structures have not been elucidated. A possible structure for the compound, $C_9H_9N_9O_9$, has been suggested.

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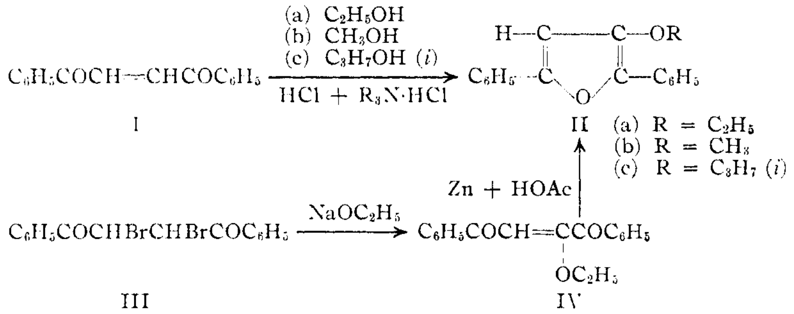
The Reaction of Alcohols with Dibenzoylethylene

BY PHILIP S. BAILEY AND ROBERT E. LUTZ

Ethanol, methanol and *i*-propanol have been found to react with dibenzoylethylene (I) under slightly acidic conditions in the presence of secondary or tertiary amine salts. The product in each case was the corresponding 2,5-diphenyl-3-alkoxyfuran (II). Although the yields were low (around 13%), it is of interest that such a reaction occurs under the conditions employed.



The ethoxy and *i*-propoxyfurans (IIa and IIc) are new compounds. The structure of the former was proved by synthesis along another path; namely, reaction of dibenzoyldibromoethane (III) with sodium ethoxide to yield IV, followed by reductive cyclization to IIa. The methoxyfuran (IIb) had previously been prepared in the same way.[1] Attempts to prepare the *i*-propoxyfuran (IIc) by this method failed in the first step, namely, treatment of dibenzoyldibromoethane (III) with sodium *i*-propoxide, which led to resin formation. There can be little doubt as to the structure of the compound, however, since it was obtained in a reaction identical with those which yielded the corresponding methoxy and ethoxy furans. The new reaction constitutes the only way by which the *i*-propoxy compound (IIc) (and perhaps other higher ethers) can be prepared at the present time.

The conditions under which the alcohol addition reactions occurred were quite specific and involved the presence of an amine hydrochloride and enough hydrogen chloride to show a *p*H of 2–3 when indicator paper was dipped into the reaction mixture. When either the amine hydrochloride or the hydrogen chloride was omitted, the reaction could not be detected. An increase in hydrogen chloride concentration tended to eliminate the formation of the alkoxyfurans and increase the formation of by-products. Replacement of the amine hydrochloride with alcohol-soluble inorganic salts (lithium chloride or magnesium chloride, all other conditions remaining the same) gave negative results. Negative results were also obtained when ammonium chloride was used, but this might have been due to its low solubility in alcohols. The high specificity of these conditions is perhaps not surprising in view of the low yield at best and of the many competing reactions which are possible.

In these reactions there was obtained along with the furans a mixture from which two colorless, high-melting substances were isolated. These were obtained also in several experiments which produced no furan. These new compounds of composition close to that of dibenzoylethylene are under investigation.

The addition of alcohols to α,β-unsaturated esters[2] and ketones (dibenzoylacetylene)[1] has been carried out in the presence of a sodium alkoxide catalyst. In the present work, however, such a process led to resinification. Under somewhat different conditions, fulvenes have been obtained by the treatment of dibenzoylethylene with sodium ethoxide.[3]

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(1) Conant and Lutz, THIS JOURNAL, **47**, 881 (1925).

(2) Purdie and Marshall, *J. Chem. Soc.*, **59**, 468 (1891); Rehberg, Dixon and Fisher, THIS JOURNAL, **68**, 544 (1946).

(3) Gardner and Rydon, *J. Chem. Soc.*, 48 (1938); Fuson, Fleming, Warfield and Wolf, *J. Org. Chem.*, **10**, 121 (1945).

Experimental[4]

The Reaction of Ethanol with Dibenzoylethylene.—To a solution of 5 g. of dibenzoylethylene, 5 g. of triethylamine hydrochloride and 80 ml. of absolute ethanol was added ethanolic hydrogen chloride until a *p*H of 2–3 was indicated when the mixture was tested with *pHydrion* indicator paper. The reaction mixture was refluxed for twenty-four hours. It was then allowed to crystallize fractionally and the several fractions were fractionally recrystallized from ethanol. Thus was obtained 0.7 g. of material which melted at 88–92° and which was shown to be 2,5-diphenyl-3-ethoxyfuran (IIa) by a mixture melting point with a sample prepared from α-ethoxydibenzoylethylene (IV); yield, 13%. There was also obtained 0.4 g. of white material which melted at 140–150°, 0.4 g. (white) which melted at 184–188° and 0.2 g. (white) which melted at 219–225°. The remaining material (after extraction of the triethylamine hydrochloride) was an oil which would not crystallize, even after slow distillation at 100° and 1 mm. pressure. The batch, melting at 140–150°, was found to be a mixture, one constituent of which was the 184°-melting compound.

The 184°-melting material, after several recrystallizations from ethanol, methanol and *i*-propanol, melted at 189–191°. It gave negative tests for halogen and nitrogen.

Anal. Found: C, 80.73, 80.82; H, 5.33, 5.25; mol. wt., 236, 283.

The 219°-melting material also gave negative tests for halogen and nitrogen. After several recrystallizations from ethanol–dioxane it melted at 225–227°.

Anal. Found: C, 80.81; H, 5.28; mol. wt., 262, 288.

In a similar reaction in which diethylamine hydrochloride was used as the amine salt, 0.8 g. of the ethoxyfuran (IIa) was obtained from 10 g. of dibenzoylethylene (I). In another experiment, identical with the original, except that 5 mole per cent. of benzoyl peroxide was added, only starting material (15%) and an oil which resisted crystallization were obtained.

Attempts to prepare the ethoxyfuran (IIa) failed when either the amine hydrochloride or the hydrogen chloride was omitted. Mixtures were obtained from which were isolated starting material (50%), a trace of the 225°-melting compound (in the first case) and an oil.

In another experiment the reaction mixture was made more acidic (1 *N*) with hydrogen chloride; it turned dark after refluxing for one hour. The product consisted of an oil and a crystalline mixture (2.6 g., m. p. 130–170°) from which was isolated a small amount of the 189°-melting substance.

When α-chlorodibenzoylethane was substituted for dibenzoylethylene in a reaction identical with the original, none of the ethoxyfuran (IIa) was obtained; the product was a mixture of white crystals (2 g., m. p. 130–150°) and an oil. α-Chlorodibenzoylethane is thus eliminated as an intermediate in the reaction although the enol form of it (from 1,4-addition of hydrogen chloride to dibenzoylethylene) is not necessarily eliminated.

2,5-Diphenyl-3-ethoxyfuran (IIa) from α-Ethoxydibenzoylethylene.—To a suspension of 1 g. of α-ethoxydibenzoylethylene[1] (IV) in 20 ml. of glacial acetic acid was added two porcelain spatulafuls of zinc dust. The mixture was warmed at 60° for two minutes and filtered. The filtrate was diluted with water and the product filtered; 0.6 g., m. p. 93–94°. Several recrystallizations from ethanol raised the melting point to 94–95°. The compound produced no depression in a mixture melting point with the 90°-melting compound obtained in the preceding experiment.

Anal. Calcd. for $C_{15}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 81.92; H, 6.21.

The reaction of methanol with dibenzoylethylene was carried out and the products worked up in a manner practically identical with the successful experiment with ethanol, using in one case triethylamine hydrochloride and in the other morpholine hydrochloride. The yields of pure 2,5-diphenyl-3-methoxyfuran (IIb) were in each case 7%; m. p. 113–115° (no depression in a mixture melting point with an authentic sample[1]). The crude yield in the first case was 23%; m. p. 107–120° (the methoxyfuran was extremely difficult to separate from impurities). There were also obtained mixtures of materials which were not separated.

In several experiments (identical in other respects) various salts were substituted for the amine hydrochloride; among these were potassium, magnesium, lithium and ammonium chlorides. From none of these reactions was any of the methoxyfuran obtained. In each case 10–20% of starting material was recovered, some of the 185°-melting substance was isolated, and the remainder of the product was an oil.

Experiments were also run in which either the amine hydrochloride or the hydrogen chloride was omitted, the other conditions remaining the same. The results were similar to those of the like experiments carried out with ethanol.

When the reaction was attempted using sodium methoxide (about 3 mole per cent.) in place of the amine hydrochloride and hydrogen chloride, the reaction turned dark at room temperature and the product was a tar. Attempted cyclization of the tarry product to a furan also yielded a tar.

The Reaction of *i*-Propanol with Dibenzoylethylene.—When a reaction mixture similar to that of the successful experiment using ethanol, but using *i*-propanol instead, was refluxed for forty hours, and was worked up in the same way, 0.7 g. (10%) of pure 2,5-diphenyl-3-*i*-propoxyfuran (IIc) was obtained from 5 g. of dibenzoylethylene; white crystals, recrystallized from methanol and ethanol, m. p. 87–88°. There was also obtained 0.6 g. of impure *i*-propoxyfuran (m. p. 70–80°), starting material (10%), a mixture of white crystals from which was isolated a small amount of the 220°-melting substance, and an oil. The total yield of the *i*-propoxyfuran was 19%.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 81.98; H, 6.52. Found: C, 82.01; H, 6.55.

Attempts to prepare 2,5-diphenyl-3-isopropoxyfuran (IIc) from dibenzoyldibromoethane (III) by treatment with sodium *i*-propoxide solution followed by reductive cyclization to a furan gave only resinous products in the first step.

Summary

Alcohols have been added to dibenzoylethylene under slightly acidic conditions and in the presence of an amine hydrochloride to yield 3-alkoxy-2,5-diphenylfurans. The structures of these substances have been proved by synthesis.

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[4] The melting points reported here are corrected. Most of the micro-analyses were performed by Mr. C. W. Beazley of Skokie, Illinois.