A Side Reaction of Acid Hydrazides in Qualitative Organic Analysis

By Louis Sattler and F. W. Zerban

In the course of the identification of small amounts of carbonyl derivatives obtained from heated fructose solutions which had been subsequently fermented with baker's yeast, *p*-nitrobenzhydrazide[1] and diphenylacethydrazide[2] were used.

With the *p*-nitrobenzhydrazide in 50% acetic acid, we obtained a small amount of a by-product of *s*-bis-(*p*-nitrobenzoyl)-hydrazine which crystallized in the form of yellow needles, and which on recrystallization from nitrobenzene melted at 288°.[3a] Previously reported melting points are 291°[3b] and 283°[3c].

Anal. Calcd. for $C_{14}H_{10}O_6N_4$: C, 50.91; H, 3.05. Found: C, 50.52; H, 3.21.

Similarly, diphenylacethydrazide in 60% ethanol plus 2 drops of glacial acetic acid[2b] yielded a white crystalline by-product of *s*-bis-(diphenylacetyl)-hydrazine. It was purified by recrystallization from a mixture of equal volumes of dioxane and 99% isopropyl alcohol. The pure crystals melted at 307°.

Anal. Calcd. for $C_{28}H_{24}O_2N_2$: C, 79.97; H, 5.75; N, 6.67. Found: C, 79.65; H, 5.60; N, 6.70.

Strain[4] has pointed out that while aqueous solutions of *m*-nitrobenzhydrazide are stable over long periods of time, strong acid solutions and elevated temperatures cause the formation of the symmetrical *bis*-hydrazine. It is evident that in addition to the normal reaction of acid hydrazides, a side reaction can also take place even in the absence of prolonged heating or strong acids. The ease with which these by-products are formed and isolated complicates the identification of expected derivatives. Consequently, due caution should be exercised in using hydrazides as derivatives of carbonyl compounds.

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(1) Eastman Kodak Co., #3341.

(2a) Aspelund, *Ber.*, **63B**, 1197 (1930), has described this compound but we found it more convenient to prepare it from ethyl diphenylacetate according to the general procedure (b) Sah and Ma, *J. Chinese Chem. Soc.*, **2**, 40 (1934).

(3a) The melting points are uncorrected.

(3b) Dann and Davies, *J. Chem. Soc.*, 1050 (1929).

(3c) Heller and Ebeling, *J. prakt. Chem.*, **142**, 274 (1935).

(4) Strain, This Journal, **57**, 758 (1935).

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4-Phenyl-*m*-dioxane

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4-Phenyl-*m*-dioxane is produced in small amounts when styrene and formaldehyde react in acetic acid solution in the presence of a mineral acid catalyst such as sulfuric acid. The major product is 1-phenyl-1,3-diacetoxypropane, formed by the participation of the acetic acid in the reaction.

Prins,[1] in his original study of this reaction, erroneously formulated the products as derivatives of 2-phenyl-1,3-propanediol. Later, Fourneau, Benoit and Firmenich[2] proved their correct structure as derivatives of 1-phenyl-1,3-propanediol. Recently the structure of these compounds has been discussed by Emerson[3] on the basis of the results of the earlier workers.

It became necessary in the course of some research in this Laboratory to prepare moderate amounts of 4-phenyl-*m*-dioxane. To this end it was decided to study the reaction of Prins with a view to increasing the yield of the desired compound and the convenience of obtaining it.

An obvious change in the Prins procedure was to employ an inert mutual solvent in place of the acetic acid; such a change, of course, would eliminate entirely the formation of the undesired 1-phenyl-1,3-diacetoxypropane. It might be expected that the corresponding glycol would be formed under these changed conditions; this, however, proved not to be the case. When styrene and formaldehyde (in the form of trioxane) in a molar ratio of 1:2 were allowed to stand at room temperature in dioxane solution in the presence of sulfuric acid, a 78% yield of 4-phenyl-*m*-dioxane was obtained. There was no evidence of glycol formation and the remainder of the yield was accounted for by the production of polymers of styrene and of formaldehyde.

In a further step toward simplification the mutual solvent was eliminated completely and the reaction was run as a heterogeneous system, containing styrene, 37% aqueous formaldehyde and sulfuric acid. It was found necessary in this instance to work at reflux temperature. Carried out under these conditions the reaction yielded a maximum of 88% of 4-phenyl-*m*-dioxane. The sole identifiable by-products were polymers of styrene and of formaldehyde.

Since the completion of these studies, a patent[4] has issued claiming the preparation of a phenyl-*m*-dioxane in undisclosed yield by the reaction of styrene and 37% aqueous formaldehyde in the presence of hydrochloric acid and an inert hydrocarbon diluent. It is stated that only resinous products are obtained in the absence of the diluent. It appears, however, that under the conditions specified in the present paper the use of such a diluent is unnecessary.

Experimental

Reaction in Dioxane Solution.—A mixture of 220 g. of dioxane, 32 g. of 96% sulfuric acid, 30 g. of trioxane (du Pont) and 52 g. of styrene (Dow N-99) was allowed to stand at room temperature over a week-end. At the end of this time the reaction mixture was poured into 600 ml. of water and the organic layer was separated. The aqueous layer was extracted with three 50-ml. portions of benzene and the combined organic layer and extracts were washed with three portions of water and distilled. After removal of the benzene 64 g. (78%) of 4-phenyl-*m*-dioxane was obtained, b. p. 94–104° at 3 mm.

Reaction as a Heterogeneous System.—A mixture of 104 g. of styrene, 300 ml. of 37% aqueous formaldehyde and 16 g. of 96% sulfuric acid was refluxed and stirred overnight. The organic layer was washed successively

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(1) Prins, *Proc. Acad. Sci. Amsterdam*, **22**, 51 (1919).

(2) Fourneau, Benoit and Firmenich, *Bull. soc. chim.*, **47**, 894 (1930).

(3) Emerson, *J. Org. Chem.*, **10**, 464 (1945).

(4) Engel, U. S. Patent 2,417,548 (March 18, 1947).