

## 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<sup>1</sup> and diphenylacetylhydrazide<sup>2</sup> 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°. Previously reported melting points are 291°<sup>3b</sup> and 283°<sup>3c</sup>.

*Anal.* Calcd. for C<sub>14</sub>H<sub>10</sub>O<sub>6</sub>N<sub>4</sub>: C, 50.91; H, 3.05. Found: C, 50.52; H, 3.21.

Similarly, diphenylacetylhydrazide in 60% ethanol plus 2 drops of glacial acetic acid<sup>2b</sup> 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<sub>22</sub>H<sub>24</sub>O<sub>2</sub>N<sub>2</sub>: C, 79.97; H, 5.75; N, 6.67. Found: C, 79.65; H, 5.60; N, 6.70.

Strain<sup>4</sup> 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.

The authors express their thanks to Dr. Francine Schwartzkopf for the micro analyses.

(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

By ROBERT W. SHORTRIDGE

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,<sup>1</sup> in his original study of this reaction, erroneously formulated the products as derivatives of 2-phenyl-1,3-propanediol. Later, Fourneau, Benoit and Firmenich<sup>2</sup> proved their correct struc-

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

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

ture as derivatives of 1-phenyl-1,3-propanediol. Recently the structure of these compounds has been discussed by Emerson<sup>3</sup> 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<sup>4</sup> 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

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

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

with dilute sodium carbonate solution, dilute sodium bisulfite solution and water. It was then dried by azeotropic distillation with 100 ml. of benzene.<sup>7</sup> Further distillation yielded 144 g. (88%) of 4-phenyl-*m*-dioxane, b. p. 121–123° at 11 mm.

In several repetitions of the preceding preparation, the yields varied from 84 to 88%. The combined products were fractionated through a Vigreux column. A center cut from this distillation had these physical properties: b. p. 95° at 2 mm.,  $n_D^{25}$  1.5288,  $d_4^{25}$  1.101. Prins<sup>1</sup> reported b. p. 128–30° at 13 mm.,  $n_D^{25}$  1.53063,  $d_4^{25}$  1.1111.

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### The Vapor Pressures of Solutions of Sodium and Potassium Bisulfates at 25°

By R. H. STOKES

As part of a general study of the vapor pressure-concentration curves of a number of mono-sodium and mono-potassium salts of dibasic acids which is in progress in this Laboratory, isopiestic vapor pressure measurements have been made on sodium and potassium bisulfates. Owing to the relatively large second dissociation constant<sup>1</sup> of sulfuric acid ( $K_2 = 0.012$  at 25°) these two salts have little in common with the others being investigated and are therefore reported separately.

Stock solutions of the two bisulfates were prepared by dissolving the calculated amount of the anhydrous normal sulfate in sulfuric acid which was previously analyzed by weight-titration against sodium carbonate. The resulting solutions were equilibrated (in platinum dishes) against sodium chloride as reference substance by the usual technique,<sup>2</sup> the molalities of pairs of solutions of equal vapor pressure being given in Table I. From these results and the standard values<sup>3</sup> for sodium chloride the vapor pressures

TABLE I

(a) Isopiestic solutions of sodium bisulfate and sodium chloride at 25°

$m_{NaHSO_4}$	0.1041	0.1237	0.1482	0.1529	0.2039	
$m_{NaCl}$	0.1190	0.1400	0.1664	0.1713	0.2255	
$m_{NaHSO_4}$	0.2823	0.4272	0.6425	0.7774	1.084	1.174
$m_{NaCl}$	0.3078	0.4573	0.6763	0.8119	1.119	1.210
$m_{NaHSO_4}$	1.340	1.382	1.632	2.398	3.065	4.067
$m_{NaCl}$	1.376	1.420	1.671	2.456	3.138	4.140
$m_{NaHSO_4}$	4.191	5.112	5.240	5.610	6.320	
$m_{NaCl}$	4.265	5.122	5.228	5.555	6.147	

(b) Isopiestic solutions of potassium bisulfate and sodium chloride at 25°

$m_{KHSO_4}$	0.1068	0.1277	0.1361	0.1445	0.2423	0.4216
$m_{NaCl}$	0.1199	0.1425	0.1505	0.1595	0.2584	0.4311
$m_{KHSO_4}$	0.5287	0.7233	0.7538	1.002	1.156	1.502
$m_{NaCl}$	0.5300	0.7038	0.7307	0.9471	1.074	1.359
$m_{KHSO_4}$	1.664	1.827	2.259	2.653		
$m_{NaCl}$	1.485	1.614	1.943	2.235		

(1) W. J. Hamer, *THIS JOURNAL*, **56**, 860 (1934).

(2) R. A. Robinson and D. A. Sinclair, *ibid.*, **56**, 1830 (1934).

(3) R. A. Robinson, *Trans. Roy. Soc. New Zealand*, **75** (11), 203 (1946); see also appendix to R. H. Stokes and B. J. Levien, *THIS JOURNAL*, **68**, 333 (1946).

at round concentrations were computed and are given in Table II in the form of  $(p_0 - p)/mp_0$ . A

TABLE II

RELATIVE MOLAL VAPOR PRESSURE LOWERINGS  $(p_0 - p)/mp_0$  OF SODIUM AND POTASSIUM BISULFATES AT 25° (CALCULATED RELATIVE TO  $p_1 = 23.756$  MM.)

$m$	$NaHSO_4$	$KHSO_4$	$m$	$NaHSO_4$	$KHSO_4$
0.1	0.03838	0.03775	1.2	0.03425	0.03074
.125	.03778	.03722	1.4	.03435	.03035
.15	.03737	.03669	1.6	.03456	.03000
.2	.03671	.03589	1.8	.03482	.02977
.3	.03590	.03469	2.0	.03508	.02957
.4	.03537	.03384	2.5	.03582	.02916
.5	.03502	.03316	3.0	.03658	
.6	.03477	.03266	3.5	.03731	
.7	.03460	.03223	4.0	.03795	
.8	.03445	.03188	4.5	.03847	
.9	.03436	.03156	5.0	.03882	
1.0	.03432	.03129	6.0	.03912	

graph of this relative molal vapor pressure lowering against  $m$  shows a rapid rise below 1M as is to be expected in consequence of the increasing dissociation of the bisulfate ion with dilution. There seems, however, to be little justification for attempting a quantitative estimate of the amounts of the various ionic species present. The calculation of activity coefficients is also complicated by this dissociation which makes extrapolation to infinite dilution difficult. Consequently, though the data are of good accuracy (0.1–0.2%) no solute activity data derived from them are included in Table II.

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### Quinazolines. IV. Synthesis and Hydrolysis of 3-(4'-Quinazolyl)-4-quinazolone<sup>1</sup>

By ARTHUR J. TOMISEK AND BERT E. CHRISTENSEN

In the attempts to prepare 4-cyanoquinazoline by fusion of 4-chloroquinazoline with either silver or cuprous cyanide<sup>2</sup> only small amounts of a fibrous material were isolated. This product appeared to be pure, and analysis suggested that it might be a diquinazolyl ether. Since 4-chloroquinazoline is easily hydrolyzed by traces of water, it is possible to account for diquinazolyl ether as resulting from the condensation of the 4-chloroquinazoline with small amounts of hydroxyquinazoline impurity.

There is no record in the literature of a diquinazolyl ether. Bogert and May attempted the syn-

(1) Published with the approval of the Monographs Publication Committee, Oregon State College, as Research Paper No. 115, School of Science.

(2) Tomisek and Christensen, *THIS JOURNAL*, **67**, 2114 (1945).