with dilute sodium carbonate solution, dilute sodium bisulfite solution and water. It was then dried by azeotropic distillation with 100 ml. of benzene. 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^{25}_D 1.5288, d^{25} 1.101. Prins[1] reported b. p. 128–30° at 13 mm., n^{18}_D 1.53063, d^{18}_4 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[1] 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,[2] the molalities of pairs of solutions of equal vapor pressure being given in Table I. From these results and the standard values[3] for sodium chloride the vapor pressures at round concentrations were computed and are given in Table II in the form of $(p_0 - p)/mp_0$. A graph of this relative molal vapor pressure lowering against m shows a rapid rise below 1*M* 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.

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		

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	

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CHEMISTRY DEPARTMENT
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[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** (II), 203 (1946); see also appendix to R. H. Stokes and B. J. Levien, THIS JOURNAL, **68**, 333 (1946).

Quinazolines. IV. Synthesis and Hydrolysis of 3-(4'-Quinazoyl)-4-quinazolone[1]

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[2] 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-

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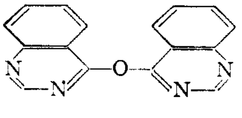
[1] Published with the approval of the Monographs Publication Committee, Oregon State College, as Research Paper No. 115, School of Science.

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

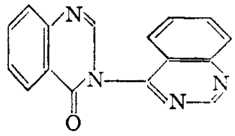
thesis by refluxing sodium 4-quinazolonate with 4-chloroquinazoline in a benzene medium.[3] Attributing their failure to the insolubility of sodium 4-quinazolonate in benzene, the work was repeated in this laboratory using a dry dioxane solvent. This modified procedure gave a product which was found to be identical with that resulting from the cyanide fusions.

A diquinazolyl ether synthesized as above could have either of two possible structures: di-4-quinazolyl ether (I) or 3-(4'-quinazolyl)-4-quinazolone (II). Among the alkylquinazolyl ethers, O-ethers (I) or N-ethers[4] (II) are synthesized depending on which radical contains the halide and which the —ONa group (Fig. 1). When both radicals are quinazolyl, analogy to the alkylquinazolyl ethers fails to distinguish between the two possible isomers.

O-Ethers are very easily cleaved by acid in contrast to N-ethers which are stable.[3] The diquinazolyl ether prepared above reacted very readily with dilute hydrochloric acid to yield almost quantitatively a product ($C_{15}H_{13}N_3O$) which contained a quinazoline unit bound apparently to a degraded quinazoline nucleus. The failure to obtain 4-hydroxyquinazoline as the hydrolysis product, together with the fact that the two nuclei remain attached after hydrolysis, suggests an N-ether type of linkage. The stability of the ether toward boiling alcohol or water and to dry heat (m. p. 232° without decomposition or rearrangement) lends additional support to this point of view. The O-ethers are generally unstable under these conditions.[5]



I



II

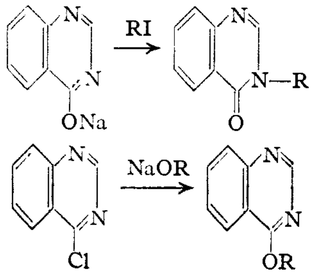


Fig. 1.

Experimental[6]

3-(4'-Quinazolyl)-4-quinazolone.—Twelve and seventenths grams of 4-hydroxyquinazoline was added to a solution containing 4.5 g. of potassium hydroxide (0.08 mole) in 75 ml. of absolute alcohol. The solvent was then removed on a steam-bath and the quinazolinate throughly dried under high vacuum. One hundred milliliters of dry dioxane and 14.6 g. of 4-chloroquinazoline (0.088 mole) were added to the pulverized residue and the mixture was refluxed for three days. Potassium chloride was removed by filtration while the reaction mixture was still hot. 3-(4'-Quinazolyl)-4-quinazolone separated from the liquors on cooling. Additional product was obtained by evaporating the mother liquors to dryness. The combined fractions were then triturated with dilute sodium hydroxide solution. The crude product (16.1 g., 74%), purified by charcoal treatment of a hot alcohol solution, yielded 14.1 g. (64%) of pure 3-(4'-quinazolyl)-4-quinazolone. The product recrystallized from alcohol as thin, wool-like fibers, m. p. 232.5°, was insoluble in water, soluble in both dioxane and hot benzene. It was stable to long boiling in water.

Anal. Calcd. for $C_{16}H_{10}N_4O$: C, 70.06; H, 3.68; N, 20.43: Found, C, 70.02; H, 3.85; N, 20.43.

Acid Hydrolysis Product of 3-(4'-Quinazolyl)-4-quinazolone.—The 3-(4'-quinazolone)-4-quinazolone (10.6 g.) was dissolved in hot dilute hydrochloric acid. In a few seconds the hydrochloride of the cleavage product precipitated. The mixture was cooled and filtered. The solid material and liquors were separately treated with excess sodium bicarbonate. The free base was then filtered, washed with water and dried. Combined fractions amounted to 9.3 g. (96%) of the crude product. After recrystallization from pyridine–water, fine, white, needle-like crystals melting at 244–225° were obtained.

Anal. Calcd. for $C_{15}H_{13}N_3O$; C, 71.69; H, 5.21; N, 16.72; mol. wt., 251. Found: C, 71.69; H, 5.23; N, 16.87; mol. wt.,[7] 255, 232, 257.

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[3] Bogert and May, This Journal, **31**, 507 (1909).

[4] For other examples of this terminology, see ref. 3, p. 508.

[5] Bogert and Seil, This Journal, **29**, 526 (1907).

[6] All melting points are corrected. All N-analyses are by the Dumas method.

[7] Niederl and Niederl, "Micromethods of Quantitative Organic Analysis," 2d ed., John Wiley & Sons, New York, N. Y., 1942, p. 217.

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Investigation of the Oxidative Condensation of 2-Methoxy-4-nitrotoluene. The Use of Oxidative Catalysts

BY GINO R. TREVES

The oxidation of various substituted 4-nitrotoluenes to stilbenes was described by Green and Baddiley.[1] They also prepared 2,2'-dimethoxy-4,4'-dinitrostilbene by a two stage air oxidation of 2-methoxy-4-nitrotoluene. Recently Ashley and Harris[2] repeated the work of Green and Baddiley but were unable to obtain the stilbene. They report that the reaction ceased at the bibenzyl stage. When we carried out the reaction only minute quantities of condensation products were obtained. It was then decided to run the reaction with oxygen instead of air under more carefully controlled conditions.

The reaction mixture was shaken in the Adams shaker and the rate of oxygen consumption observed. The contact was continued for twenty-two hours and the product consisted of a mixture of the bibenzyl and the stilbene in 30% yield.

Compounds of high oxidation potential were tried in the hope that they would catalyze the reaction by functioning as hydrogen carriers. Results are shown in Fig. 1. Of special interest was the fact that cyclohexanol was almost as effective as cyclohexanone. This indicates that cyclo-

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[1] Green and Baddiley, *J. Chem. Soc.*, **93**, 1721 (1908).

[2] Ashley and Harris, *ibid.*, 567 (1946).