dium bicarbonate solution because there seems to be a connection with the "browning reaction" observed in food products which contain both sugars and amino derivatives.

Work is in progress on the formation of acetol in sugar solutions, and the quantitative determinations of acetol and methylglyoxal in mixtures of both.

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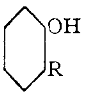
2-Aryl- and 2-Alkoxycyclohexanols[1]

BY B. C. MCKUSICK[2]

As part of a program to find improved insect-repellents, a number of 2-aryl- and 2-alkoxycyclohexanols were prepared from cyclohexene oxide.

The 2-arylcyclohexanols were obtained by condensing cyclohexene oxide with appropriate aryllithiums[3]; Grignard reagents were not used because the products would have been the isomeric arylcyclopentylcarbinols.[3] The postulated cyclohexanol structure was confirmed for one product, 2-(*p*-tolyl)-cyclohexanol, by oxidizing it to the known δ-*p*-toluylvaleric acid. Yields of cyclohexanols were good except in the case of 2-(*p*-methoxyphenyl)-cyclohexanol, where the low yield is understandable in view of the ease with which the side-reaction of *p*-methoxyphenyllithium with *p*-bromoanisole to give anisole and 5-bromo-2-methoxyphenyllithium is known to occur.[4] Since 2-phenylcyclohexanol prepared from cyclohexene oxide and phenyllithium[3] has been shown to have a *trans*-configuration,[5] it is probable that the present 2-arylcyclohexanols are also *trans*.

TABLE I

2-SUBSTITUTED CYCLOHEXANOLS 

R	Boiling point[a] °C.	Mm.	M. p. or n^{25}D	Yield, %	Formula	Analyses, % Calcd. C	H	Found C	H
m-Tolyl	113–114	1.0	1.5396	71	$C_{13}H_{18}O$	82.1	9.5	82.0	9.9
m-Tolyl[b]	85– 86	0.2	1.5113	93	$C_{15}H_{20}O_2$	77.6	8.7	77.4	8.4
m-Tolyl[c]	96–100	0.3	1.5067	97	$C_{16}H_{22}O_2$	78.0	9.0	78.6	9.2
p-Tolyl	109–113	1	72–73°[d]	84	$C_{13}H_{18}O$	82.1	9.5	82.5	9.9
2,5-Xylyl	114–115	2	1.5377	69	$C_{14}H_{20}O$	82.3	9.9	82.7	10.1
p-Methoxyphenyl	135–140	1.5	71–72°[d]	15	$C_{13}H_{18}O_2$	75.7	8.8	75.8	9.0
n-Propoxy[e]	82– 83	9	1.4538	67	$C_9H_{18}O_2$	..	..	..	..
n-Amyloxy	110–113	11	1.4559	77	$C_{11}H_{22}O_2$	70.9	11.9	70.3	11.6
2-Ethylhexyloxy	134–136	8	1.4576	49	$C_{14}H_{22}O_2$	73.6	12.4	73.1	12.5
Benzyloxy	110–112	0.3	1.5290	55	$C_{13}H_{18}O_2$	75.7	8.8	75.6	9.0
β-Phenethoxy	159–162	9	1.5221	48	$C_{14}H_{20}O_2$	76.3	9.2	75.5	9.1
β-Hydroxyethoxy[f,8]	108–110	0.4	1.4797	54	$C_8H_{16}O_3$	..	..	..	..

[a] Fractionations were through a five-inch indented Claisen distillation head. [b] Acetate. [c] Propionate. [d] Recrystallized from hexane. [e] Mousseron and Granger, *Compt. rend.*, **205**, 327 (1937). [f] Miscible with water.

The 2-alkoxycyclohexanols were obtained by heating cyclohexene oxide with an excess of the appropriate alcohol in which a trace of sodium had been dissolved.[6] *trans*-1,2-Cyclohexanediol was a by-product of the preparation of 2-(β-phenethoxy)-cyclohexanol and may have been a by-product in other cases.

Experimental

2-Arylcyclohexanols.—The preparation of 2-(*m*-tolyl)-cyclohexanol can be used to illustrate the general procedure. In a 12-liter three-necked flask, 69 g. (20% excess) of lithium in the form of small strips[7] was stirred vigorously in 3 liters of anhydrous ether under nitrogen while 711 g. of *m*-bromotoluene was added at a rate to maintain gentle refluxing of ether. Once reaction set in, the flask was kept immersed in an ice-bath in order to shorten the time necessary for the addition (about one hour). The mixture was heated under reflux for an hour and 408 g. of cyclohexene oxide[8] was added in the same manner. The mixture was cooled in ice and decomposed by the gradual addition of 3 liters of water with stirring. The ether layer was separated, washed with water, dried over magnesium sulfate, and distilled; 655 g. (71% yield) of 2-(*m*-tolyl)-cyclohexanol was collected at 113–114° (1.0 mm.).

The acetate and propionate were obtained by heating 2-(*m*-tolyl)-cyclohexanol at 100° for two hours with 1.5 molar equivalents of acid anhydride and 2 molar equivalents of pyridine and distilling the reaction mixtures under reduced pressure.

Oxidation of 2-(*p*-Tolyl)-cyclohexanol.—A solution of 23 g. of chromic anhydride in 80 ml. of 80% acetic acid was added to 55 g. of 2-(*p*-tolyl)-cyclohexanol in 80 ml. of acetic acid, the temperature not being allowed to exceed 50°. After twenty-four hours at 25°, the mixture was poured into water and the products were taken up in ether. The ether solution was extracted with a 10%

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[1] This work was performed under Contract NDCrc 136 between Harvard University and the Office of Scientific Research and Development, with Paul D. Bartlett as official investigator.

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[3] Cook, Hewitt and Lawrence, *J. Chem. Soc.*, 71 (1936).

[4] Wittig, Pockels and Droge, *Ber.*, **71**, 1903 (1938).

[5] Price and Karabinos, THIS JOURNAL, **62**, 1159 (1940).

[6] Holt (assigned to E. I. du Pont de Nemours & Co.), U. S. Patent 2,197,105 (1940).

[7] Gilman, Langham and Moore, THIS JOURNAL, **62**, 2327 (1940).

[8] The cyclohexene oxide was kindly furnished by Dr. A. P. Tanberg of the Chemical Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware.

sodium hydroxide solution and distilled; 37 g. of a mixture of starting material and the corresponding ketone was obtained. Acidification of the sodium hydroxide extract caused the precipitation of 7.6 g. of *p*-toluylvaleric acid, m. p. 152.5–154°[9] after recrystallization from a benzene-ethanol mixture; neutralization equivalent, 223 (calcd., 220). δ-Benzoylvaleric acid has been obtained from 2-phenylcyclohexanol under similar conditions.[3]

2-Alkoxycyclohexanols.—In a typical experiment, 2-amyloxycyclohexanol was prepared by refluxing for twenty-two hours a solution of 49 g. of cyclohexene oxide[8] in 200 ml. of *n*-amyl alcohol containing 0.5 g. of dissolved sodium. The reaction mixture was distilled and 72 g. (77%) of 2-amyloxycyclohexanol was collected at 100–113° (11 mm.). When alcohols boiling above 200° were used, the solutions were heated at 180–200°.

In the reaction between 35 g. of cyclohexene oxide and 140 ml. of phenethyl alcohol, the first portion of 2-(β-phenethoxy)-cyclohexanol collected on distillation contained *trans*-1,2-cyclohexanediol, 4 g. of which crystallized out on cooling the mixture. It was recrystallized from hexane and identified by its melting point (102–103°),[10a] dibenzoate melting point (91.5–92°),[10b] and composition.

Anal. Calcd. for $C_6H_{12}O_2$: C, 62.0; H, 10.4. Found: C, 62.1; H, 10.4.

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[9] Brosche, *Ber.*, **52**, 2080 (1919), reports a melting point of 153–154°.

[10] (a) Verkade, Coops, Maan and Verkade-Sandbergen, *Ann.*, **467**, 217 (1928); (b) **477**, 289 (1930).

CONVERSE MEMORIAL LABORATORY
HARVARD UNIVERSITY
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The Solubility of Aminoguanidonium Bisulfate in Water and in Sulfuric Acid Solutions[1]

BY JOHN J. PITHA[2] AND G. B. L. SMITH[3]

In the reduction of nitroguanidine in a sulfuric acid solution, the end-product of the reaction is aminoguanidonium bisulfate. In order better to control the recovery of this salt, some investigations were made into the solubility of aminoguanidonium bisulfate in water and in solutions of various sulfuric acid concentrations.

Experimental

The solubility of aminoguanidonium bisulfate was determined by preparing a saturated solution of the salt in the appropriate solvent at a definite temperature. After equilibrium had been established, a sample of the solution was withdrawn and transferred to a tared volumetric flask and weighed. This solution was then diluted to volume and analyzed for aminoguanidine by the method of Smith and Wheat.[4]

These studies were carried out in a specially constructed three-necked flask of 100 ml. capacity. One neck was used to insert a thermometer into the solution, one neck allowed the entry of an all-glass stirrer, and the third neck was used as an addition port. Ground glass joints were used throughout. Solution temperatures from 5 to 40° were measured with an unjacketed thermometer, but higher temperatures were measured with a thermometer suspended within a glass jacket. The bulb of the flask and the lower third of the necks were immersed in a 7.5-gal. water-bath. This thermostat was equipped with both heating and cooling coils and the temperature of the solution in the reaction flask was controlled to ±0.03°.

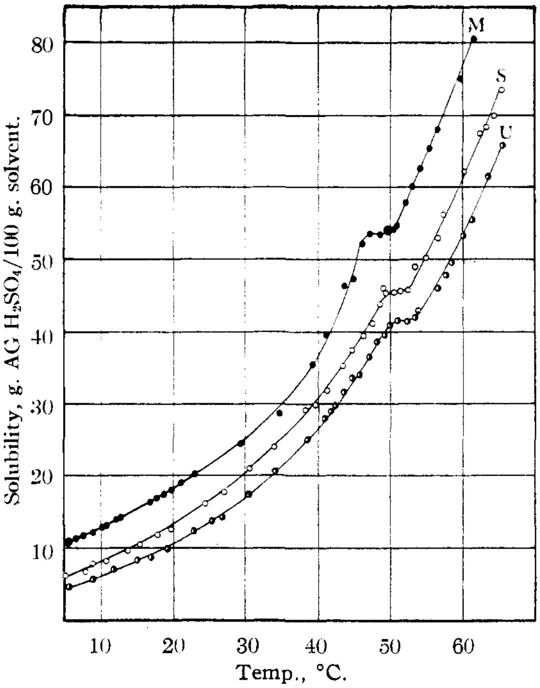

Fig. 1.—M, ●, H_2O; S, O, 0.7419 *N* H_2SO_4; U, ◑, 1.4088 *N* H_2SO_4.

Saturated solutions of the salt at a particular temperature were prepared by adding an excess of the solute to the solvent and stirring the solution until equilibrium had been established. The attainment of equilibrium was proven by successive sampling and analysis at regular intervals of time until three successive values were in agreement. A half-hour lapse of time after the solution had come to temperature was usually sufficient for equilibrium to be reached. In certain portions of these studies, the equilibrium was approached from both directions in order to establish definitely the values reported.

In order to avoid errors that might occur in the removal and transfer of samples due to crystallization of the salt from the saturated solution while in the sampling tube, pipets used for this purpose were kept in an oven and were used warm. The operation was performed with sufficient speed that no difficulty with crystallization was encountered.

At least three determinations of solubility were made at each temperature, and in the cases where abnormalities were observed sufficient determinations were made to establish the points reported. The accuracy of the analytical procedure was such that an error of 0.1% was average. Precision of results on duplicate sets of samples was of the order of 1 part in 1000 parts. The solubility of aminoguanidonium bisulfate in water, 0.7419 *N* sulfuric acid and 1:4088 *N* sulfuric acid was determined. The results of the solubility determinations are summarized in Fig. 1. Crystals obtained by evaporation at temperatures above and below the inflection temperatures in all cases analyzed 99.5% or better for aminoguanidonium bisulfate, and macro observations of these crystals showed no differences in crystalline form. The nature of the inflection observed in each of the curves is not completely understood, but additional information is being sought and will be reported in a subsequent paper.

DEPARTMENT OF CHEMISTRY
POLYTECHNIC INSTITUTE OF BROOKLYN
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[1] This paper is abstracted from the thesis submitted to the Graduate Faculty of the Polytechnic Institute of Brooklyn by Mr. Pitha in June, 1942, in partial fulfillment of the requirements for the degree of Master of Science in Chemistry.

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[4] Smith and Wheat, *Ind. Eng. Chem., Anal. Ed.*, **11**, 200 (1939).