induction–period region, is greater than this. The relative increase, therefore, would be less than 10^2, and this probably is not enough to cause a shift in the induction–period reaction from the characteristics of a univalent ion reaction to those of a bivalent ion reaction.

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The Molar Refraction of Sulfonyl Chlorides

BY EDWARD F. LANDAU[1]

Except for the early work of Nasini,[2] there is little published information regarding the molar refraction of tetracovalent compounds of sulfur. In a previous publication,[3] we evaluate the molar refraction of the —SO_2O— group in a series of ethylenesulfonic esters. This value was 9.7 ± 0.2.

In the course of this investigation several liquid aliphatic sulfonyl chlorides were prepared. Their molar refractions were determined and the value of the sulfonyl chloride group compared with two other liquid sulfonyl chlorides. The molar refraction of the sulfonyl chloride group as determined from the five compounds listed, is 15.40 ± 0.07.

TABLE I

MOLAR REFRACTION OF SULFONYL CHLORIDES

Compound	B. p., °C.	Mm.	n^{20}_D	d^{20}_4	M_D[a] (obs.)	M_D-SO_2Cl[b]
2-Bromoethanesulfonyl chloride[c]	82	5	1.5227	1.894	33.44	15.31
2-Chloroethanesulfonyl chloride	68	5	1.4920	1.555	30.72	15.52
Ethylenesulfonyl chloride	52–56	10	1.4686	1.393	25.31	15.45
Benzenesulfonyl chloride			1.5505[e]	1.378[e]	40.73	15.35
i-Butylenesulfonyl chloride[d]	68–70	8	1.4779	1.2704	34.43	15.36

[a] "Landolt–Börnstein Tabellen," Vol. II, p. 986, Bruel values. [b] Evaluated by difference. [c] Marvel, Bailey and Sparberg, THIS JOURNAL, **49**, 1833 (1927). [d] Suter, Malkemus and Archer, *ibid.*, **63**, 1596 (1941). [e] At 23°.

Experimental

Ethylenesulfonyl Chloride.—Powdered phosphorus pentachloride (22 g.) was added in small portions to a rapidly agitated suspension of 12.5 g. ammonium ethylenesulfonate[3] in 100 ml. of chloroform. The temperature of this suspension was maintained at 30–40° for two hours. The chloroform was removed by distillation and the residue dissolved in 50 ml. of ether. After three washings with 50-ml. portions of water, the ethereal solution was dried and distilled. Two fractions were obtained. Fraction I, 4 g.; b. p. 52–56° (1 mm.); n^{20}_D 1.4686; d^{20}_4 1.393.

Anal. Calcd. for $C_2H_3O_2ClS$: S, 25.34; sapn. equiv., 63.3. Found: S, 25.62, 25.51; sapn. equiv., 64.5. Fraction II, 4 g., b. p. 70–72° (5 mm.); n^{20}_D 1.4740; d^{20}_4 1.439; sapn. equiv., 67.7. This fraction was possibly a polymeric vinyl sulfonyl chloride.

CHEMICAL LABORATORY
POLYTECHNIC INSTITUTE OF BROOKLYN
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[1] Present address: Celanese Corporation of America, Newark, New Jersey.

[2] Nasini, *Ber.*, **15**, 2844 (1882).

[3] Whitmore and Landau, THIS JOURNAL, **68**, 1797 (1946).

4-Quinolinemethanol

BY S. F. MACDONALD

As lepidine undergoes a condensation of the Mannich type with an aldehyde and an amine,[1] 4-quinolinemethanol was prepared in the hope that it would do likewise. Unfortunately, we have been unable to condense it with cotarnine or with formaldehyde and piperidine. Such a condensation would have provided an attractive theory as to the biogenesis of the cinchona alkaloids: a Mannich condensation between 4-quinolinemethanols and one[2] of the stereoisomeric aldehydes of meroquinenine; the latter possibly formed from 6-keto-decahydroisoquinoline, by a photolytic reaction analogous to the conversion of cyclohexanone into hexenal.[3]

The preparation of quinoline-4-aldehyde[4] was modified to eliminate difficulties due to bumping and the tedious steam distillation; using acetic acid as solvent we got the same yields with freshly prepared and with year-old selenium dioxide.

Experimental

Quinoline-4-aldehyde (Anhydrous).—A mixture of 40 g. of lepidine, 400 ml. of acetic acid, and 80 ml. of acetic anhydride was stirred at 85–90° and 45 g. of powdered sublimed selenium dioxide added over one and a quarter hours. The mixture was heated one and a half hours longer, cooled and filtered. The filtrate was treated with 70 ml. of concentrated hydrochloric acid, allowed to stand at 10° overnight and filtered. The aldehyde in the filtrate was isolated by steam-distilling off the excess acetic acid, neutralizing the remainder with sodium hydroxide then magnesium oxide, and distilling the aldehyde over in steam. The hydrochloric acid precipitate, containing most of the aldehyde, was dissolved in water, filtered, treated with excess sodium hydroxide and the aldehyde filtered off. The two lots of aldehyde were combined, dehydrated by heating *in vacuo* in the distilling flask and distilled *in vacuo*, collecting at 98–108° (*ca.* 0.1 mm.); yield 50–60%, m. p. 48–49° (uncor.).

Quinoline-4-methanol.—A mixture of 30 g. of quinoline-4-aldehyde, 200 ml. of anhydrous *i*-propyl alcohol, and 6.3 g. of aluminum *i*-propylate was distilled slowly through a Widmer column until the temperature at the top of the column rose to 82°, the volume being kept constant by the occasional addition of *i*-propyl alcohol. Thirty ml. of water was then added to the contents of the flask, and water and *i*-propyl alcohol removed by heating *in vacuo.*

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[1] Heou-Feo, *Bull. soc. chim.*, [5] **2**, 96 (1935).

[2] King, *J. Chem. Soc.*, 523 (1946).

[3] Ciamician and Silber, *Ber.*, **41**, 1071 (1908).

[4] Kwartler and Lindwall, THIS JOURNAL, **59**, 524 (1937); Kaplan, *ibid.*, **63**, 2654 (1941).

The residue was warmed with 20% aqueous potassium hydroxide, cooled, filtered off, washed and dried. Extracting the mother liquor with ether gave more of the product. The quinoline-4-methanol was purified by distilling *in vacuo*, b. p. 145° at 0.2 mm., and crystallizing from benzene; yield 50–60%, m. p. 96–97° (uncor.).

Anal. Calcd. for $C_{10}H_9NO$: C, 75.43; H, 5.70; N, 8.81. Found: C, 75.43, 75.68; H, 5.89, 5.88; N, 9.05, 8.89.

Heating under certain conditions converted the product into a higher melting substance.

Phenylurethan of 4-Quinolinemethanol.—From the components at 100°, crystallized from alcohol, m. p. 159.5–160.5° (uncor.).

Anal. Calcd. for $C_{17}H_{14}N_2O_2$: N, 10.06. Found: N, 9.86, 10.02.

BANTING AND BEST DEPARTMENT OF MEDICAL RESEARCH
UNIVERSITY OF TORONTO
TORONTO, CANADA

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Preparation of Benzaldehyde from Benzene

BY WILLIAM J. KING AND PATRICK T. IZZO

In previous reports from this Laboratory,[1,2] the use of sodium cyanide instead of hydrogen cyanide in the Gattermann synthesis of aldehydes has been shown to be applicable to aromatic hydrocarbons.

In an extension of this investigation it has now been found that contrary to the statements in the literature[3] sodium cyanide can be used satisfactorily to replace hydrogen cyanide even for the preparation of benzaldehyde from benzene. A maximum yield of 14% benzaldehyde has been obtained. Additional quantities of aluminum chloride did not increase the yield of aldehyde beyond this percentage. Augmenting the proportionate amount of sodium cyanide caused the yield of benzaldehyde to drop.

Procedure.—Into a mixture of 400 g. (3 moles) of anhydrous aluminum chloride and 50 g. (1 mole) of sodium cyanide in 200 cc. (2.25 moles) of benzene in a 3-necked flask with a mercury-sealed stirrer and an efficient reflux condenser, dry hydrogen chloride was passed for twenty minutes. The mixture was then boiled on a water-bath and the boiling, stirring and introduction of the hydrogen chloride continued for eleven hours.

At the end of this period, the reaction mixture was cooled and poured on a large amount of ice and hydrochloric acid contained in a three-liter, round-bottom flask. The mixture was refluxed under the hood for about an hour to expel excess hydrogen cyanide and to complete the hydrolysis of the phenylmethyleneformamidine hydrochloride.[4] It was then steam-distilled for two to three hours and the distillate extracted with ether, the extract being dried with anhydrous sodium sulfate. The ether was then distilled off and the residue fractionated. The first fraction, mostly benzene, was collected at 75–100°, the second at 100–160°, the third at 160–185°.

The third fraction was rectified and 20 g. of a liquid boiling at 176–180° was obtained. This compound was characterized by its semicarbazone, m. p. 222° (cor.).

Anal. (benzaldehyde). Calcd.: C, 79.24; H, 5.66. Found: C, 79.07; H, 5.86.

The first fraction (75–100°) was about 30 cc. Assuming this to be mostly benzene, then subtracting this amount from 200 cc., we found that 170 cc. (149 g.) of benzene underwent reaction from which 20 g. of the aldehyde was obtained. On this basis the yield was about 14%.

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[1] Niedzielski and Nord, THIS JOURNAL, **63**, 1462 (1941).

[2] Niedzielski and Nord, *J. Org. Chem.*, **8**, 147 (1943).

[3] J. E. Jones, "Synthetic Organic Chemicals," (Eastman Kodak Company) 15, No. 2 (1943).

[4] Hinkel, Ayling and Morgan, *J. Chem. Soc.*, 339 (1936).

The Purification of Acetone by the Shipsey–Werner Method

BY ROBERT LIVINGSTON

The Shipsey–Werner[1] method of purifying acetone, which involves the formation of the solvate, $NaI\cdot 3C_3H_6O$, is commonly used for small scale laboratory purifications. This method (which was quoted in 1935 by Weissberger and Proskauer[2]) was published before the detailed data on the solubility of NaI and $NaI\cdot 3C_3H_6O$ in acetone[3,4,5] were available. In light of the latter information, the procedure can be improved in respect both to yield and to convenience. The following outline has been tested and proved to be satisfactory.

Saturate acetone with dry sodium iodide at about 25° (between 25 and 30°). Decant the solution from the excess solid. Cool the solution to as low a temperature as can be conveniently maintained during filtration, etc. With ordinary equipment a temperature of about −10° is satisfactory. Filter off the mother liquor on a Buchner or sintered glass filter. Transfer the cold salt to a flask and warm to about 30° (>26°). Decant the liquid into a distilling flask, distill, rejecting the last 10%.

Saturating the acetone with sodium iodide at approximately room temperature (25 to 30°), rather than at the boiling point of the solvent (2), has two advantages. First, it is more convenient; and, second, it results in an increase in the theoretical yield of purified acetone from about 23 to about 35%. The step of warming the solvated salt above its transition point and decanting the liquid into the distilling flask, is introduced largely to avoid the awkward transfer of a moist solid; but it has the additional advantage that the salt cake, remaining in the flask after distillation, is reduced by about 40%.

Precautions: Contamination of the salt, solvent or vessels by acids or by salt of heavy metals (such as iron or copper) should be avoided. Manipulation of the chilled solvent should be planned to

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[1] K. Shipsey and E. A. Werner, *J. Chem. Soc.*, **103**, 1255 (1913).

[2] A. Weissberger and E. Proskauer, "Organic Solvents," Oxford Press, 1935, p. 142.

[3] R. Macy and E. W. Thomas, THIS JOURNAL, **48**, 1547 (1926).

[4] A. E. Wadsworth and H. M. Dawson, *J. Chem. Soc.*, **129**, 2784 (1926).

[5] W. R. G. Gell, C. B. Rowlands, I. J. Bamford and W. J. Jones, *ibid.*, 1930 (1927).