noquinoline.[3] It is also very easily accessible from *p*-nitroaniline.

A mixture of 338 g. of *p*-nitroaniline, 130 g. of glycerol, 84 g. of ferrous sulfate, 150 g. of nitrobenzene and 800 g. of concentrated sulfuric acid was heated until reaction set in and the reaction was then checked by discontinuing the heating. When the reaction subsided the mixture was refluxed for three hours, diluted with water, steam-distilled to remove nitrobenzene, and the solution was decolorized with 34 g. of Norit, filtered and neutralized with sodium hydroxide solution. The crude product was dried and purified by extraction with benzene in a Soxhlet apparatus or by distillation; b. p. 160° (2 mm.). Crystallization from benzene or alcohol gave needles, m. p. 173°; yield 200 g. (46%).

Anal. Calcd. for $C_{12}H_8N_2$: C, 80.0; H, 4.4. Found: C, 79.7; H, 4.5.

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(3) Kaufmann and Radosevic, *Ber.*, **42,** 2612 (1909).

DANIEL SIEFF RESEARCH INSTITUTE
REHOVOTH, PALESTINE
RECEIVED JANUARY 2, 1947

Laboratory Disposal of Mercaptan Vapors

BY HUBERT M. HILL[1] AND M. L. WOLFROM

In the course of many years of work with ethyl mercaptan (ethanethiol), the problem of its reeking odor has been ever present. We have been concerned recently with experiments employing this substance as a solvent and with its subsequent removal by evaporation techniques. We have found that these vapors readily can be adsorbed on a column of carbon impregnated with cupric chloride. This principle is not new and has been employed on a large scale by the chemical engineer.[2] Its adaptation to organic laboratory practice may, however, be of interest.

A good grade of activated carbon (6–14 mesh) of the type used for gas purification or solvent recovery, is impregnated by immersion at room temperature for twenty-four hours in a saturated aqueous solution of cupric chloride. The carbon is then removed by decantation, washed once or twice with water and dried by heating in an open dish to 130° or until hydrogen chloride fumes are evolved. One kilogram of carbon will adsorb 250–300 g. of cupric chloride. This material is then packed in a glass tube which is placed in the directed gas stream containing the volatile mercaptan. The packing converts the thiol to the disulfide with liberation of sufficient heat to require cooling by running water. The packing should be replaced before it is saturated, a condition detectable by the odor of disulfide in the exit gases.

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[1] Bristol Laboratories Research Associate of The Ohio State University Research Foundation (Project 224).

[2] *Cf.* W. L. Nelson, "Petroleum Refinery Engineering," 2nd ed., McGraw-Hill Book Co., New York, N. Y., 1941, p. 586.

DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO
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Preparation of Alkyldichloramines

BY L. K. JACKSON, G. N. R. SMART AND GEORGE F WRIGHT

A method for the preparation of alkyldichloramines which is different from that of Tcherniak[1] and a modification of that of Berg[2] has been devised by close regulation of acidity or, better, by introduction of gaseous chlorine into a cold solution of sodium bicarbonate and the free amine.

The crude oils obtained by this treatment are usually sufficiently pure, on the basis of electropositive chlorine analysis by Chattaway's method,[3] that they can be used for subsequent reaction. When they are handled in this manner, especially with a slight excess of contaminant chlorine, they are fairly stable. Distilled material is relatively less stable and some of the distillations are quite dangerous.

The yield and quality of both *n*-butyldichloramine[2] and N-tetrachloro-1,2-diaminoethane[3] have been improved over those originally reported. In addition a new primary compound, *n*-octyldichloramine, has been prepared as well as three secondary dichloramines. The *n*-octyldichloramine as well as these *i*-propyl, *s*-butyl and cyclohexyl compounds were not sufficiently stable in the pure state to be shipped for elemental analysis, but were analyzed iodometrically for electropositive chlorine content.

Experimental

***n*-Butyldichloramine**.—To a solution of 504 g. (6 moles) of sodium bicarbonate in 3 liters of cold water, was added 110 g. (1.5 moles) of butylamine. The mixture was maintained at 8–12° for six hours while chlorine was passed in over this period until saturation was reached. The yellow-orange oil which settled out (density *ca.* 1.1) was separated, washed with cold 5% sulfuric acid, then cold water, and dried with calcium chloride to weigh 187 g. or 88% of theoretical. When a sample was dissolved in acetic acid, treated with potassium iodide and titrated iodometrically it seemed to contain 103% butyldichloramine. The free chlorine which thus was demonstrated to be present was not removed, since it prevented decomposition to butylammonium chloride. The chlorine could be removed by washing with aqueous sodium thiosulfate. If *n*-butyl monochloramine was suspected to be present (low chlorine analyses) it could be removed by a quick wash with cold 50% sulfuric acid, followed by thorough washing with cold water.

When the molar ratio of bicarbonate to amine was decreased to 2:1 the yield was decreased to 74%; when the ratio was decreased to 3:1, the yield was increased to 92%. Although further purification was not usually necessary, the material could be distilled at 39–40° (17 mm.), (b. p. 46° (30 mm.)) d^{20}_4 1.108, n^{20}_D 1.4553. The electropositive chlorine content was 98% of theoretical.

***n*-Octyldichloramine** was prepared in 76% crude yield when a 3:1 ratio of bicarbonate to amine was used. The chlorine addition time was ten hours. The crude (d^{20}_4 1.007) showed an electropositive chlorine content which was 97% of the calculated value.

***s*-Butyldichloramine** was prepared in 96% yield using a 3:1 ratio of bicarbonate to amine over a ten-hour chlorine addition at 10°. The crude material was pure according to its electropositive chlorine content (d^{25}_4, 1.116).

Cyclohexyldichloramine was obtained in 95% crude yield under conditions identical with those above. A 90% recovery of product was obtained by distillation; b. p. 89–90° (17 mm.), d^{20}_4 1.199.

N-Tetrachloro-1,2-diaminoethane could be obtained in 92% yield only if an 8:1 bicarbonate-amine ratio was used. Chlorine addition over twelve hours at 10° yielded 70 g. of crude product from 30 g. (0.385 mole) of ethylene diamine

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[1] J. Tcherniak, *Bull. soc. chim.*, **24,** 451 (1875); *ibid.*, **25,** 160 (1876); *Ber.*, **9,** 146 (1876).

[2] A. Berg, *Ann. chim. phys.*, [7] **3,** 289 (1905).

[3] F. D. Chattaway, *J. Chem. Soc.*, **87,** 381 (1905).

hydrate. This crude material contained 96% of the theoretical electropositive chlorine content. When it was distilled at 76–78° (10 mm.) this chlorine content was found to be 99% of theoretical. The distilled product melted at 4–4.5° cor., d^{20}_4 1.544. Since the crude material is sufficiently pure for most purposes, the distillation, which is dangerous, ought to be avoided.

i-**Propyldichloramine** was prepared by a modification of the above procedures. To an ice-cooled concentrated aqueous solution of 95 g. (1 mole) of *i*-propylamine hydrochloride (prepared *in situ*) was added slowly 2.25 moles of aqueous sodium hypochlorite (prepared by adding chlorine to cold 15% aqueous sodium hydroxide, 1.6 moles hypochlorous acid per liter). Simultaneously with this addition over two to three hours was added 6 *N* hydrochloric acid at such a rate that the acidity was maintained between *p*H 5.6 and 6.6. Brom cresol green and chlor phenol red papers can be used as criteria if the solution is allowed to creep into the paper so as to give an indicator zone ahead of the bleached zone. After two hours' subsequent stirring in the cold, the heavy oil was separated, washed once with 50 cc. cold water, twice with 50-cc. portions of 5% sodium thiosulfate, once with cold water, twice with cold 50% sulfuric acid and finally twice with cold water. The crude yield (97 g., 76% of theoretical) contained 94% of the theoretical electropositive chlorine content. Distillation at 41–43° (15 mm.) resulted in 70% recovery of yellow oil (d^{20}_4 1.165; n^{23}_D 1.4572) which contained 99.8% of the calculated electropositive chlorine content.

Anal. Calcd. for $C_3H_7NCl_2$: N, 10.9. Found: N, 10.6 (av.).

The authors are grateful for a grant from the National Research Council, Canada, which helped to defray the expenses of this investigation.

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A Modification of Wenker's Method of Preparing Ethyleneimine

BY PHILIP A. LEIGHTON, WILLIAM A. PERKINS AND MELVIN L. RENQUIST

The most convenient method for laboratory preparation of ethyleneimine is that of Wenker.[1] This is a two-step process involving the preparation of β-aminoethylsulfuric acid from monoethanolamine and sulfuric acid followed by treatment of the ester with alkali. An improved technique is suggested for the first step which involves less effort, gives a better quality of the intermediate ester, and leads to higher yields.

Six moles each of ethanolamine (b. p. 169.5–170.1°) and 95% sulfuric acid are separately diluted with half their weight of water and cooled in an ice-bath. The amine is added slowly to the acid with constant stirring in a round-bottom flask also cooled in an ice-bath. The mixture is then boiled under reduced pressure using a water aspirator attached to the flask. Bumping is prevented by the addition of glass beads and the use of a full flame to maintain vigorous boiling.

When the temperature of the liquid reaches 145°, only enough heat is applied to keep the solution boiling, and when a definite turbidity appears, usually between 155 and 160°, heating is stopped unless the temperature begins to fall. Quite suddenly crystallization takes place, causing the temperature to rise sharply to about 185°. After cooling, the cake is softened with 300 cc. of 95% ethanol, removed from the flask and ground with an additional 400 cc. of ethanol followed by filtering and drying.

The yield is 90–95%. The product is white, showing no evidence of charring as was the case when the heating was carried out in an open vessel according to Wenker's directions. Approximately one hour is required to remove the water from the above quantity of material. While Wenker was able to remove only 75% of the theoretical amount of water, in the above method a trap placed between the flask and aspirator collected virtually 100% of the amount expected.

DEPARTMENT OF CHEMISTRY
STANFORD UNIVERSITY
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RECEIVED MAY 5, 1947

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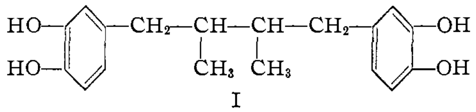
[1] H. Wenker, THIS JOURNAL, **57**, 2328 (1935).

A Synthesis of Nordihydroguaiaretic Acid

BY S. V. LIEBERMAN, GEORGE P. MUELLER AND ERIC T. STILLER

Nordihydroguaiaretic acid or 2,3-*bis*-(3,4-dihydroxybenzyl)-butane [$4,4^1$-(2,3-dimethyltetramethylene)-dipyrocatechol] (I) is of practical interest as an antioxidant used in preserving edible fats and oils.[1] It is obtained for that purpose by the alkaline extraction of dried plants of the species *Larrea divaricata*.[2]

Schroeter and his co-workers first obtained this compound from the dimethyl ether of guaiaretic acid (II) by hydrogenation and subsequent demethylation.[3] The dimethyl ether of guaiaretic acid has since been synthesized by Haworth, *et al.*[4] These two syntheses constitute a proof of the structure of nordihydroguaiaretic acid.



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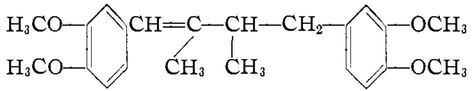

II

The new synthesis described here confirms this structure. The first step involves the coupling of two molecules of 1-piperonyl-1-bromoethane, yielding the corresponding dimethylene ether of nordihydroguaiaretic acid (IV), a compound reported by Orcutt and Bogert as a crystalline solid, m. p. 74°.[5] Apparently a mixture of the diastereoisomers of this compound is produced by the reaction of 1-piperonylethylmagnesium bro-

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[1] U. S. Patent 2,373,192; Higgins and Black, *Oil & Soap*, **21**, 277 (1944).

[2] U. S. Patent 2,382,475.

[3] Schroeter, Lichtenstadt and Irineu, *Ber.*, **51**, 1587 (1918).

[4] Haworth, Mavin and Sheldrick, *J. Chem. Soc.*, 1423 (1934).

[5] Orcutt and Bogert, THIS JOURNAL, **58**, 2057 (1936).