

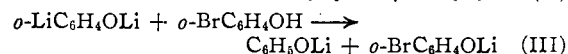
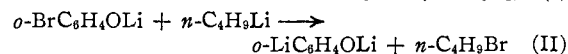
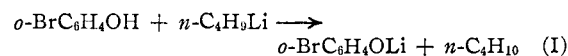
TABLE I
 REACTIONS OF RX COMPOUNDS WITH *n*-C₄H₉Li

| RX | RX in mole | ether, cc. | <i>n</i> -C ₄ H ₉ Li mole | ether, cc. | Temp. of <i>n</i> -C ₄ H ₉ Li sol., °C. | Time of addition, min. | Stirring period, min. | Product | Yield, g. | Yield, % |
|---|------------------|---------------|--|---------------|--|------------------------------|-----------------------------|--|--------------|-------------------|
| <i>o</i> -BrC ₆ H ₄ OH | 0.041 | 25 | 0.082 | 250 | Room | Rapidly | 40 | <i>o</i> -HOC ₆ H ₄ COOH ^a | 3.77 | 67 |
| <i>p</i> -BrC ₆ H ₄ OH | .05 | 50 | .1 | 200 | Room | | | <i>p</i> -HOC ₆ H ₄ COOH ^b | | 35 ^c |
| <i>p</i> -IC ₆ H ₄ OH | .0437 | 50 | .0875 | 190 | Room | 4 ^d | 3 | <i>p</i> -HOC ₆ H ₄ COOH | | 50 ^e |
| <i>o</i> -BrC ₆ H ₄ COOH | .05 | 100 | .1 | 200 | -75 | 2 | 10 at -75° | <i>o</i> -C ₆ H ₄ (COOH) ₂ | 2.9 | 35 ^f |
| <i>o</i> -IC ₆ H ₄ COOH | .05 | 125 | .1 | 150 | -75 | 4 | 6 at -75° | <i>o</i> -C ₆ H ₄ (COOH) ₂ | 1 | 12 ^g |
| <i>p</i> -IC ₆ H ₄ COOH | .05 ^h | | ca. .1 | 200 | -75 | | 4 at -75° | <i>p</i> -C ₆ H ₄ (COOH) ₂ | | 62 ^{i,j} |
| <i>p</i> -IC ₆ H ₄ SO ₂ N(C ₂ H ₅) ₂ | .02 | 60 | ca. .02 | 100 | -75 ^k | 2 ^k | 1 | <i>p</i> -HOCC ₆ H ₄ SO ₂ N(C ₂ H ₅) ₂ ^m | 3.7 | 78 |

^a Identified by mixed melting point. ^b Refluxed without stirring for two hours. ^c When *p*-bromophenol was allowed to react with *n*-butyllithium for one and one-half hours, the yield of *p*-hydroxybenzoic acid was 41% (studies by R. W. Leeper). ^d The mode of addition was reversed in this experiment, the *n*-butyllithium being added to the RX compound. This is the preferred order of addition. ^e When *p*-iodophenol was allowed to react with *n*-butyllithium for twenty minutes, the yield of acid was 48% (studies by R. K. Abbott). ^f Also obtained here was 9 g. of an oil containing neutral components which was not investigated further. ^g Weight of neutral oil obtained was 11 g. ^h Powdered *p*-iodobenzoic acid was added in one portion to the *n*-butyllithium solution. ⁱ Weight of neutral oil obtained was 9 g. ^j In addition to the terephthalic acid formed (identified as the dimethyl ester by mixed melting point) there was recovered 7% of *p*-iodobenzoic acid. The separation was accomplished by extraction with acetone. Recovery of starting material indicates that an insufficient quantity of *n*-butyllithium was used. The experiment was carried out before the precise method for determining the titer of alkyl lithium compounds was completed (see Gilman and Haubein, THIS JOURNAL, **66**, 1515 (1944)). Also the yield would probably have been improved by the reverse method of addition. ^k A bright yellow precipitate formed immediately. ^l When the interconversion was carried out at room temperature, a tar was obtained. ^m Melting point 192–194° (with turbidity). Recrystallization from ethanol or acetic acid did not raise the melting point. *Anal.* Calcd. for C₁₁H₁₅O₄NS: N, 5.44; neut. equiv., 257. Found: N, 5.38 and 5.41; neut. equiv., 253.

some organolithium compounds in which were contained a functional group, like hydroxyl or carboxyl. One of the better ways for the synthesis of such types is the halogen-metal interconversion reaction^{1a}: RX + R'Li → RLi + R'X. Some of the yields by this reaction are quite satisfactory. For example, the RLi compound from *o*-bromophenol is formed to an extent of at least 67%, because carbonation after interconversion gives a 67% yield of salicylic acid. By a corresponding procedure it was shown that the yields of RLi compounds from *p*-iodobenzoic acid and *p*-iodo-*N,N*-diethylbenzenesulfonamide were 62 and 72%, respectively.

In those cases where the functional group has an active hydrogen it is preferable to add the *n*-butyllithium to the RX compound so that the primary product is not consumed in a secondary halogen-metal interconversion with RX. This is illustrated by the sequence of reactions



Reaction (I) generally proceeds at a much more rapid rate than reaction (II). When (II) is under way, there are contained in the mixture two RLi compounds which can participate in the interconversion reaction: *o*-LiC₆H₄OLi and *n*-C₄H₉Li. The extent to which the *o*-LiC₆H₄OLi contributes to the interconversion results essentially in the destruction of a corresponding amount of the substituted RX compound [Reaction (III)].

(1a) For general references, see pp. 538–539 of Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943.

Accordingly the addition of *n*-butyllithium to the RX compound ensures a maximum initial replacement of the active hydrogen.

Experimental

General Procedure.—The solution of the RX compound in ether was added, in the first experiments, over a short period of time to an ether solution of butyllithium. After stirring the mixture, it was carbonated by pouring over solid carbon dioxide. The product was obtained by acidification of the sodium hydroxide extract. From *p*-iodophenol and from *o*- and *p*-bromophenol, the hydroxybenzoic acids obtained as products were separated from the phenols by saturating the alkaline extract with carbon dioxide and extracting with ether. Details are given in the accompanying table.

***p*-Iodo-*N,N*-diethylbenzenesulfonamide.**—*p*-Iodobenzenesulfonyl chloride was prepared from iodobenzene in accordance with the directions of Baxter and Chattaway.² Then, to a solution of 8 g. (0.026 mole) of the sulfonyl chloride in 100 cc. of ether was added 3.8 g. (0.052 mole) of diethylamine. After one hour, the diethylamine hydrochloride was removed by filtration and the ether solution washed with dilute hydrochloric acid followed by dilute potassium hydroxide. The yield of *p*-iodo-*N,N*-diethylbenzenesulfonamide, melting at 57–58.5° after crystallization from ethanol, was 7 g. (80%).

Anal. Calcd. for C₁₀H₁₄O₂NIS: N, 4.13. Found: N, 4.05.

(2) Baxter and Chattaway, *J. Chem. Soc.*, **107**, 1814 (1915).

CHEMISTRY DEPARTMENT
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RECEIVED DECEMBER 2, 1946

4,7-Phenanthroline

BY L. HASKELBERG

4,7-Phenanthroline has been prepared from *p*-phenylenediamine,¹ 6-nitroquinoline,² and 6-ami-

(1) Smith, THIS JOURNAL, **52**, 397 (1930); see Wibaut and co-workers, *Rec. trav. chim.*, **56**, 1219 (1937).

(2) Kuczynski and Sucharda, *C. A.*, **31**, 3921 (1937).

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 C₁₂H₈N₂: C, 80.0; H, 4.4. Found: C, 79.7; H, 4.5.

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

DANIEL SIEFF RESEARCH INSTITUTE

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Laboratory Disposal of Mercaptan Vapors

BY HUBERT M. HILL¹ 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.

(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

RECEIVED MARCH 3, 1947

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 Tcherniak¹

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

and a modification of that of Berg² 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 gaseous.

The yield and quality of both *n*-butyldichloramine² and *N*-tetrachloro-1,2-diaminoethane³ 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*₄²⁰ 1.108, *n*_D²⁰ 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*₄²⁰ 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*₄²⁰, 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*₄²⁰ 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

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

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