Paper Chromatography of the Amine.—A portion of the amine solution which was obtained by the hydrolysis of the original DNP derivative was chromatographed on Whatman No. 1 filter paper, using butanol saturated with 1% (v./v.) ammonium hydroxide as the developer. Ninhydrin treatment of the chromatograph showed a spot at R_f 0.58. A similar chromatograph was treated with acidified potassium permanganate[3] before development with the solvent. After chromatographic development no ninhydrin reactive material was observed.

Synthesis of 1-Amino-2-methyl-2-propanol.—This compound was prepared from isobutylene oxide and ammonia.[11] The isobutylene oxide was prepared from isobutylene chlorohydrin[12] which was obtained by hydration of methallyl chloride.[13] The latter compound was donated by the Shell Chemicals Corp.

1-Dinitrophenylamino-2-methyl-2-propanol.—This compound was prepared from the amine by the method of Porter and Sanger.[8] The derivative was crystallized twice from benzene–ligroin (7:3). The yellow orange crystals melted at 107–108°.

Comparison of the Isolated and Synthetic Compounds.—A mixture of the isolated and synthetic materials melted at 106–108°. These derivatives were chromatographed on alumina impregnated paper using 10% ether in ligroin as the solvent, both moved to R_f 0.71. The rates of movement on silicic acid–celite columns were the same. The free bases were chromatographed on Whatman No. 1 paper, and both moved with the following R_f's: in butanol saturated with 1% ammonium hydroxide, 0.54; in isobutyric acid saturated with water, 0.87.

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[11] T. L. Cairn and J. H. Fletcher, THIS JOURNAL, **63**, 1034 (1941).

[12] C. E. Wilson and H. J. Lucas, *ibid.*, **58**, 2396 (1936).

[13] J. Burgin, G. Hearns and F. Rust, *Ind. Eng. Chem.*, **33**, 385 (1941).

THE KERCKHOFF LABORATORIES OF BIOLOGY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIF.

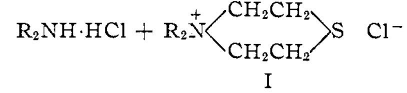
Reactions of Long-chain Amines. III. Preparation of N,N-Dialkylthiamorpholinium Chlorides[1]

BY JOHN G. ERICKSON

RECEIVED MARCH 25, 1954

Lawson and Reid[2] have studied the reactions of mustard gas with several secondary amines in the presence of sodium carbonate. They found that diethylamine, dipropylamine, dibutylamine and piperidine react to form bis-(2-dialkylaminoethyl) sulfides, $(R_2NCH_2CH_2)_2S$. A similar product is apparently formed with dimethylamine but the only products isolated in this case were divinyl sulfide and 2-vinylmercaptoethyldimethylamine, $CH_2{=}CHSCH_2CH_2N(CH_3)_2$. Apparently they obtained no compounds containing thiamorpholine rings.

We have found that long-chain dialkylamines react with mustard gas, forming N,N-dialkylthiamorpholinium chlorides (I)



$$2R_2NH + (ClCH_2CH_2)_2S \longrightarrow R_2NH\cdot HCl + R_2\overset{+}{N}\left\langle\begin{matrix}CH_2CH_2\\CH_2CH_2\end{matrix}\right\rangle S \quad Cl^-$$

I

When 2-chloroethyl sulfone is used, the product is the 1,1-dioxide of I. The most suitable reaction conditions appear to require somewhat more than two moles of amine for each mole of mustard gas, the mixtures being heated at about 130°. Compounds similar to I, differing only in the nature of the anion, have been prepared by Niederl, McGreal and Hart,[3] and Hart, McGreal and Camilli.[4] These workers alkylated long-chain N-alkylthiamorpholines with long-chain dialkyl sulfates.

The difference between our results and those of Lawson and Reid is due presumably to the relative success of two competing reactions. The initial reaction products, $R_2NCH_2CH_2SCH_2CH_2Cl$, may cyclize or they may react with a second mole of amine. The long-chain amines are apparently sufficiently unreactive in this case so that the second reaction cannot easily occur and cyclization takes place instead. The reverse is true with the more reactive amines used by Lawson and Reid.

Acknowledgments.—We wish to thank the Chemical Corps for a generous gift of mustard gas. Microanalyses were performed by James Kerns of these laboratories.

Experimental[5]

4,4-Didodecylthiamorpholinium Chloride.—A mixture of didodecylamine (53.0 g., 0.15 mole), mustard gas (90% pure, 10.6 g., 0.06 mole) and butyl alcohol (20 ml.) was heated at 130° for 27 hours. It was then dissolved in hot methanol (300 ml.) and an aqueous solution of 2.5 g. of sodium hydroxide was added. The mixture was chilled and filtered, giving 42.8 g. of unreacted amine. The filtrate was evaporated to dryness and the residue was recrystallized from ethyl acetate to give 5.6 g. (20% yield) of white solid, m.p. 160–200° dec. A second recrystallization gave iridescent white flakes, same m.p.

Anal. Calcd. for $C_{28}H_{58}ClNS$: C, 70.60; H, 12.27; Cl, 7.44; N, 2.94; S, 6.73. Found: C, 71.05; H, 12.50; Cl, 7.55; N, 2.46; S, 6.42.

4,4-Dioctadecylthiamorpholinium Chloride.—A mixture of dioctadecylamine (349.7 g., 0.67 mole), mustard gas (90% pure, 48.2 g., 0.27 mole) and butyl alcohol (25 ml.) was heated at 130–140° for 33 hours. It was poured into hot methanol (2 l.) containing 12.0 g. of sodium hydroxide. The mixture was heated to boiling, cooled, filtered and the filter cake washed with methanol. The combined filtrate and washings were evaporated *in vacuo*. The residue was extracted with hot ethyl acetate (400 ml.) which, after cooling and filtration, gave 41.1 g. of cream-colored product, m.p. 190–198°; m.p., after recrystallization from ethyl acetate, 202–204.5° dec. Further extraction of the crude amine fraction gave an impure product. This was recrystallized from ethyl acetate to give an additional 16.1 g. of product.

Anal. Calcd. for $C_{40}H_{82}ClNS$: C, 74.52; H, 12.82; Cl, 5.50; S, 4.97. Found: C, 74.58; H, 12.65; Cl, 5.32; S, 5.05.

The 1,1-Dioxide of 4,4-Dioctadecylthiamorpholinium Chloride.—This was prepared in two ways. In the first, dioctadecylthiamorpholinium chloride (12.9 g., 0.02 mole) was dissolved in warm (50–60°) acetic acid (60 ml.) and 30% hydrogen peroxide (5.4 g., 0.048 mole) was added dropwise. After 18 hours the mixture was evaporated on the steam-bath and the residue was recrystallized four times from ethyl acetate, giving 6.3 g. (46%) of white solid, m.p. 197–199°.

Anal. Calcd. for $C_{40}H_{82}ClNO_2S$: C, 71.00; H, 12.22; Cl, 5.24; N, 2.07; S, 4.74. Found: C, 71.07; H, 12.63; Cl, 5.17; N, 2.94; S, 5.18.

In the second method, a mixture of dioctadecylamine (62.5 g., 0.12 mole), 2-chloroethyl sulfone (9.5 g., 0.05 mole) and *n*-butyl alcohol (20 ml.) was heated at 130° for 14 hours, mixed with one liter of hot methanol and neutralized with NaOH (2.0 g.). The mixture was cooled, filtered and evaporated to dryness. Recrystallization of the residue

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[1] Paper No. 164, Journal Series, General Mills, Inc., Minneapolis, Minn.

[2] W. R. Lawson and E. E. Reid, THIS JOURNAL, **47**, 2821 (1925).

[3] J. B. Niederl, M. E. McGreal and W. F. Hart, *J. Org. Chem.*, **14**, 579 (1949).

[4] W. F. Hart, M. E. McGreal and C. F. Camilli, THIS JOURNAL, **71**, 3569 (1949).

[5] M.p.'s are corrected.

from ethyl acetate containing some methanol gave 12.1 g. (36%) of product.

CHEMICAL LABORATORIES
GENERAL MILLS, INC.
MINNEAPOLIS, MINN.

Some Aromatic and Heterocyclic Dialkylarsines

BY HENRY GILMAN AND SOUREN AVAKIAN

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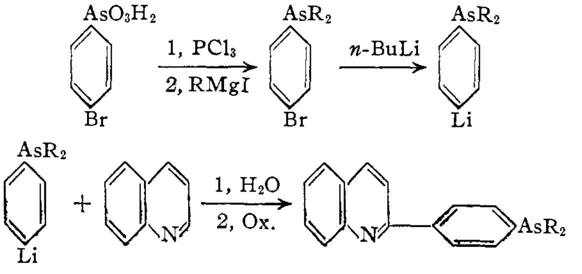
In connection with studies on the preparation and properties of aromatic and heterocyclic organolithium compounds derived from reactions of metalation and halogen–metal interconversion, it was considered worthwhile to synthesize some selected dialkylarsine types easily derived from the corresponding organometallic compounds. These arsenic containing compounds were of interest primarily for evaluation of their biological activities.

A typical reaction sequence is



A second route for introduction of the dialkylarsino groups involved the coupling of a dialkyliodoarsine with an organometallic compound as

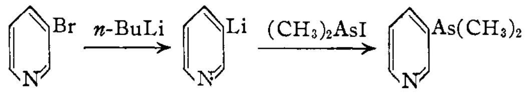


TABLE I

DIALKYLARSINO COMPOUNDS

Compound	M.p., °C.	B.p. °C.	B.p. Mm.	Yield, %	Arsenic, % Calcd.	Arsenic, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
p-Dimethylaminophenyldimethylarsine[a]		136–137	15	73			6.22	6.31
1,4-Bis-(dimethylarsino)-benzene[b]		146–148	16	91	52.41	52.28		
2-Pyridyldimethylarsine		90–91	14	81			7.65	7.72
3-Pyridyldimethylarsine		105–107	16	58			7.65	7.76
p-Bromophenyldiallylarsine[c]		105–106	0.06	73	23.80	23.92		
p-Bromophenyldipropylarsine[d]		106–107	0.05	94	23.64	23.79		
8-Methyl-2-(*p*-di-*n*-propylarsinophenyl)-quinoline[e]	84–85			79			3.69	3.76
6-Methoxy-2-(*p*-di-*n*-propylarsinophenyl)-quinoline[e]	95–96			76			3.54	3.61

[a] The picrate derivative melts at 159–160°. [b] Prepared from *p*-dimethylarsinophenylmagnesium bromide and dimethyliodoarsine. [c] Prepared from *p*-bromophenyldichloroarsine and allylmagnesium bromide. [d] Prepared from *p*-bromophenyldichloroarsine and *n*-propylmagnesium bromide. [e] Recrystallized from ethanol.

Experimental[1]

***p*-Bromophenylarsonic Acid.**[2]—A mixture of 34.0 g. (0.2 mole) of *p*-bromoaniline and 1.5 l. of 1 *N* hydrochloric acid was diazotized and the resulting solution added slowly with stirring to 7.0 l. of a cold aqueous solution of 30 g. of sodium arsenite, 0.5 g. of copper sulfate and 300 g. of sodium carbonate. Stirring was continued for five hours after which the reaction mixture was allowed to stand at room temperature for 12 hours. Filtration followed by concentration to 1.5 l. and acidification of the filtrate precipitated 45 g. (80%) of *p*-bromophenylarsonic acid, melting above 310°.

Anal. Calcd. for $C_6H_6AsBrO_3$: As, 26.75. Found: As, 26.92.

***p*-Bromophenyldichloroarsine.**—A solution of 20 ml. of phosphorus trichloride in 30 ml. of acetic acid was added slowly to a suspension of 20.0 g. (0.072 mole) of *p*-bromophenylarsonic acid in 100 ml. of boiling acetic acid. The mixture was heated under reflux for 30 minutes, cooled and 200 ml. of concentrated hydrochloric acid added. The precipitated oil was separated, dissolved in benzene, washed with water, dried over sodium sulfate and distilled to yield 17 g. (80%), b.p. 90–91° (3.0 mm.).

Anal. Calcd. for $C_6H_4AsBrCl_2$: As, 21.50. Found: As, 21.21.

***p*-Bromophenyldimethylarsine.**—A solution of 54 g. (0.18 mole) of *p*-bromophenyldichloroarsine in 300 ml. of ether was added slowly with stirring and ice-bath cooling to a solution of 0.46 mole of methylmagnesium iodide in ether. The mixture was stirred for 30 minutes after completion of the addition, hydrolyzed with water and the ether layer separated and dried. Distillation gave 91% of *p*-bromophenyldimethylarsine boiling at 130–131° (17 mm.), n^{20}_D 1.6105, d^{20}_4 1.6082. This compound has been reported by Jones,[3] b.p. 134–136° (9 mm.), and Blicke,[4] b.p. 120–125° (11 mm.).

Anal. Calcd. for $C_8H_{10}AsBr$: As, 28.71. Found: As, 28.82.

***p*-Carboxyphenyldimethylarsine.**—A solution of 13.0 g. (0.05 mole) of *p*-bromophenyldimethylarsine in 200 ml. of ether was converted to the Grignard reagent with 2.3 g. (0.1 g. atom) of magnesium. Treatment with solid carbon dioxide and work-up in the usual manner gave the carboxylic acid in 80% (9.0 g.) yield. The acid melted at 143–144°.

The compound was also prepared in 63% yield by carbonation of the product of halogen–metal interconversion of *n*-butyllithium and *p*-bromophenyldimethylarsine.

Anal. Calcd. for $C_9H_{11}AsO_2$: As, 33.15. Found: As, 33.38.

Dimethyliodoarsine.—This compound was prepared by a combination and modification of the procedures of Wigren[5] and McKenzie.[6] Methyl iodide (350 g.) was added to a solution of 110 g. of arsenious oxide and 194 g. of sodium hydroxide in 2 l. of 80% ethanol in water. After 20 hours the alcohol was removed by distillation, the residue acidified with hydrochloric acid and then saturated with sulfur dioxide. During passage of the sulfur dioxide, 210 g. of sodium iodide was added in small portions. The precipitated methyldiiodoarsine was separated, dissolved in 800 ml. of ethanol and treated with a solution of 208 g. of sodium hydroxide in 300 ml. of water and 85 ml. of methyl iodide. After standing overnight the alcohol was removed by distillation, the residue acidified with hydrochloric acid and saturated with sulfur dioxide. The product was dissolved

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[1] All melting and boiling points are uncorrected.

[2] A. Mouneyrat, English Patent 142,947 (1919) [*C. A.*, **14**, 2802 (1920)].

[3] W. J. Jones, *et al.*, *J. Chem. Soc.*, 2287 (1932).

[4] F. F. Blicke and S. R. Safir, THIS JOURNAL, **63**, 575 (1941).

[5] N. I. Wigren, *Ann.*, **437**, 285 (1924).

[6] A. McKenzie and J. K. Wood, *J. Chem. Soc.*, **117**, 406 (1920).