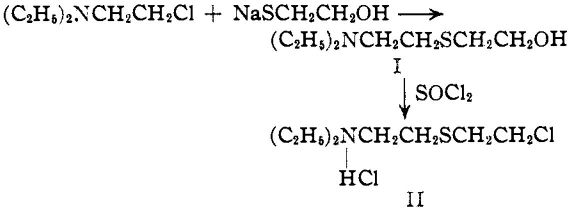
[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF WINTHROP CHEMICAL COMPANY]

The Synthesis of Some Sulfur-Containing Amines

BY R. O. CLINTON, C. M. SUTER, S. C. LASKOWSKI, MARY JACKMAN AND W. HUBER

The literature records the preparation of only a few amines containing alkyl groups interrupted by sulfur. Brighton and Reid[1] have prepared a number of 2-alkylthioethylamines from sodiomercaptides and 2-bromoethylamine, and successfully oxidized these to the corresponding sulfoxides and sulfones. In a similar manner Gabriel and Colman[2] prepared 2-(2-aminoethylthio)-ethanol from 2-chloroethanol and 2-aminoethanethiol. Schneider[3] has prepared a series of 2-alkylthioethylamines by the Gabriel method from 2-bromoethylphthalimide and sodiomercaptides. 2-(2-Chloroethylthio)-triethylamine hydrochloride, II, has been prepared[4] by the following series of reactions



$$(C_2H_5)_2NCH_2CH_2Cl + NaSCH_2CH_2OH \longrightarrow \underset{\text{I}}{(C_2H_5)_2NCH_2CH_2SCH_2CH_2OH}$$

$$\Big\downarrow SOCl_2$$

$$\underset{\text{II}}{(C_2H_5)_2\underset{\substack{|\\ HCl}}{N}CH_2CH_2SCH_2CH_2Cl}$$

Further, 2-(2-diethylaminoethylthio)-ethylamine[5a] III, and 3-(2-diethylaminoethylthio)-propylamine[5b,c] IV, have been mentioned in the patent literature, but were not characterized.

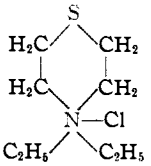
$$\underset{\text{III}}{(C_2H_5)_2NCH_2CH_2SCH_2CH_2NH_2}$$

$$\underset{\text{IV}}{(C_2H_5)_2NCH_2CH_2SCH_2CH_2CH_2NH_2}$$

In general, details of the synthesis of compounds I–IV and of their physical properties are lacking.

The present paper is a report on the preparation of some diethylaminoethylthioalkyl halides and amines, and their corresponding sulfones.

The condensation of 2-chlorotriethylamine with 2-thiolethanol[6] in the presence of sodium ethoxide gave the ethanol, I, in high yields. In spite of the ease with which 2-chlorotriethylamine cyclizes to the piperazine, especially in the presence of basic catalysts, this by-product was not found. It was found that reaction in aqueous media, under conditions analogous to similar reaction in absolute alcohol, gave yields of only 50–54%, as compared to yields of 95–98% in the latter media. This is probably due to competitive reaction of the 2-chlorotriethylamine with the sodium hydroxide present through hydrolysis of the sodio-2-thiolethanol. Treatment of I with thionyl chloride gave the chloride-hydrochloride II; the free base readily cyclized to the 1,4-thiazane, V.

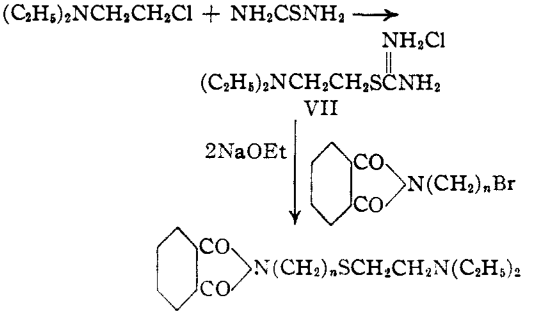


V

$$\underset{\text{VI}}{(C_2H_5)_2NCH_2CH_2SCH_2CH_2SCH_2CH_2OH}$$

Treatment of II, as the free base, with a further mole of 2-thiolethanol gave 2-(2-(2-diethylaminoethylthio)-ethylthio)-ethanol, VI, which was further converted to the chloride-hydrochloride as with II.

The synthesis of the amines III and IV was attempted in a number of ways. The action of ammonia, or of hexamethylenetetramine, on the corresponding alkyl halides did not prove satisfactory. The reaction between an ω-thiolalkylphthalimide and 2-chlorotriethylamine, or between 2-diethylaminoethanethiol[7] and an ω-bromoalkylphthalimide gave low over-all yields. However, it was found that an extension of the method of Snyder and Cannon[8] to the present work, as outlined below, gave excellent results



$$(C_2H_5)_2NCH_2CH_2Cl + NH_2CSNH_2 \longrightarrow \underset{\text{VII}}{(C_2H_5)_2NCH_2CH_2S\overset{\overset{NH_2Cl}{\|}}{C}NH_2}$$

VIII

The amines were prepared from the phthalimido compounds, VIII, by the Ing and Manske modification.[9] 3-(2-Diethylaminoethylthio)-1-propanol was also synthesized from 2-diethylaminoethylisothiouronium chloride, VII, and 3-chloro-1-propanol in a similar manner.

The compound II, as the free base, gave a fair yield of 2-(2-diethylaminoethylthio)-propionitrile upon treatment with potassium cyanide; however, this compound was more readily prepared by the addition of 2-diethylaminoethanethiol to acrylonitrile. Reduction of the nitrile with

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[1] Brighton and Reid, THIS JOURNAL, **65**, 458 (1943).

[2] Gabriel and Colman, *Ber.*, **45**, 1645 (1912).

[3] Schneider, *Ann.*, **386**, 337 (1912).

[4] British patent 286,087.

[5] U. S. Patents (a) 2,082,171, (b) 2,077,249, (c) 2,121,207.

[6] Obtained from Carbide and Carbon Chemicals Corp., New York, N. Y.

[7] Albertson and Clinton, submitted for publication in THIS JOURNAL.

[8] Snyder and Cannon, *ibid.*, **66**, 511 (1944).

[9] Ing and Manske, *J. Chem. Soc.*, 2348 (1926).

sodium and 1-butanol[10] gave a mixture of products which could not readily be separated.

Oxidation of the chloride-hydrochlorides and amines to the corresponding sulfones was effected with 30% hydrogen peroxide either in dilute hydrochloric acid or in acetic acid–acetic anhydride[11] solution in fair yields. The amine sulfones could not be purified.

Experimental[12]

2-(2-Diethylaminoethylthio)-ethanol, I.—To a solution of 103 g. of sodium in 1500 ml. of absolute alcohol was added 363 g. of 2-thiolethanol[6] dropwise with stirring, over a period of one-half hour. To the resulting hot solution was added with stirring 607 g. of 2-chlorotriethylamine, at such a rate as to maintain gentle refluxing (about one and one-half hours). The mixture was stirred under reflux for an additional two hours, cooled and filtered. After washing the salt with absolute alcohol, the combined filtrate and washings were evaporated *in vacuo*. Distillation of the residual oil gave 752 g. (95%) of colorless product, b. p. 104–107° at 2 mm. The pure compound had a b. p. of 91.2° at 1.4 mm., n^{20}D 1.4940 (lit.,[4] b. p. 122° at 6 mm.).

Anal.[13] Calcd. for $C_8H_{19}ONS$: C, 54.19; H, 10.80; N, 7.90. Found: C, 54.00; H, 10.66; N, 7.84.

The 3,5-dinitrobenzoate hydrochloride, prepared by admixture of solutions of equimolecular amounts of the components in cold dry benzene, formed colorless iridescent leaflets from ethyl acetate, m. p. 125–126°.

Anal. Calcd. for $C_{15}H_{22}O_6N_3ClS$: C, 44.17; H, 5.44. Found: C, 44.30; H, 5.47.

2-(2-Chloroethylthio)-triethylamine Hydrochloride, II.—To a solution of 840 g. of I in 1000 ml. of dry chloroform was added dropwise with stirring a solution of 588 g. of pure thionyl chloride in 1000 ml. of dry chloroform during one and one-half hours, with external cooling in an ice-bath. The resulting mixture was stirred for one hour in the ice-bath, and finally heated on the steam-bath for one and one-half hours. The chloroform and excess thionyl chloride were removed *in vacuo* and the residue was poured into a cold mixture of one liter of ethyl acetate and two liters of ether. After cooling and scratching, the crystalline material was filtered, triturated twice with ethyl acetate, and air dried. After working up the mother liquors the combined material was crystallized from ethyl acetate–chloroform. There was thus obtained 861 g. (78%) of product, m. p. 82–84°. Smaller runs, of the order of one-half mole, gave higher yields, up to 97%.

After several recrystallizations the compound formed white prisms, m. p. 83–85°.

Anal. Calcd. for $C_8H_{18}NClS \cdot HCl$: N, 6.03; S, 13.81. Found: N, 6.01; S, 13.69.

N-Ethyl-1,4-thiazane Ethochloride, V.—A cold aqueous solution of II was made alkaline with dilute sodium hydroxide solution and the heavy oil layer was separated and heated on the steam-bath for two hours, during which period it solidified. Several crystallizations from absolute alcohol–ether gave a nearly quantitative yield of product; small white hygroscopic prisms, m. p. 290° (dec.).

Anal. Calcd. for $C_8H_{18}NClS$: C, 49.08; H, 9.27; N, 7.16. Found: C, 49.10; H, 8.82; N, 7.58.

2-(2-Chloroethylsulfo)-triethylamine Hydrochloride.—Prepared from II by oxidation with 30% hydrogen peroxide in glacial acetic acid–acetic anhydride solution,[11] the compound was obtained as long slender white needles, after several crystallizations from absolute alcohol, m. p. 147–148°. The yield of pure material was 82%.

Anal. Calcd. for $C_8H_{18}O_2NClS \cdot HCl$: N, 5.30; Cl, 26.84; N. E., 264.2. Found: N, 5.19; Cl, 26.60; N. E., 264.4.

3-Thiol-1-propanol.—The method of Rojahn and Lemme[14] gave a 17% yield of crude material. Better results were obtained through use of the isothiouronium salt synthesis. A solution of equimolecular amounts of thiourea and 3-chloro-1-propanol in alcohol was refluxed for twenty-four hours. On removal of the solvent *in vacuo* and strong cooling of the residual oil, there was obtained a quantitative yield of crude, crystalline 3-hydroxy-1-propylisothiouronium chloride, m. p. 101–104°, which was sufficiently pure for hydrolysis. One crystallization from absolute alcohol–ethyl acetate gave rosets of white needles, m. p. 105–106°.

Anal. Calcd. for $C_4H_{11}ON_2ClS$: C, 28.15; H, 6.50; N, 16.42. Found: C, 27.87; H, 6.91; N, 16.61.

Hydrolysis with dilute sodium hydroxide solution (one equivalent) gave a 43% over-all yield of 3-thiol-1-propanol, b. p. 75–80° at 7 mm. (lit.,[14] b. p. 85–90° at 15 mm.). The bis-3,5-dinitrobenzoyl derivative (white prisms from acetone–ligroin) had m. p. 139–140°.

Anal. Calcd. for $C_{17}H_{12}O_{11}N_4S$: N, 11.66. Found: N, 11.49.

In both methods of preparation there were obtained substantial amounts of 3-hydroxy-1-propyl disulfide,[14] colorless viscous oil, b. p. 136–140° at 0.5 mm. The bis-3,5-dinitrobenzoyl derivative (white prisms from acetone–ligroin) had m. p. 114–115°.

Anal. Calcd. for $C_{20}H_{18}O_{12}N_4S_2$: N, 9.82. Found: N, 10.20.

3-(2-Diethylaminoethylthio)-1-propanol.—To a solution of 423 g. of 2-diethylaminoethylisothiouronium chloride[7] in 600 ml. of absolute alcohol was added 189 g. of 3-chloro-1-propanol. The mixture was heated under reflux with stirring and treated with a solution of 92 g. of sodium in 2500 ml. of absolute alcohol, added in a thin stream over a period of one and one-half hours. When the addition was complete the pink-colored mixture was refluxed and stirred for six hours, and finally allowed to stand overnight at room temperature. After filtration and washing of the salt with absolute alcohol the combined filtrate and washings were evaporated *in vacuo* and the residual oil was distilled twice *in vacuo*. There was thus obtained 267.5 g. (72.5%) of colorless product, b. p. 125–130° at 5 mm. On redistillation of a middle cut, the pure compound had b. p. 90.5° at 0.4 mm., n^{20}D 1.4955.

Anal. Calcd. for $C_9H_{21}ONS$: C, 56.52; H, 11.07; N, 7.33. Found: C, 56.58; H, 11.12; N, 7.11.

The 3,5-dinitrobenzoate hydrochloride formed small white prisms (from ethyl acetate–ligroin), m. p. 116–117°.

Anal. Calcd. for $C_{26}H_{24}O_6N_3ClS$: C, 45.55; H, 5.73. Found: C, 45.78; H, 5.98.

Preparation of 3-(2-diethylaminoethylthio)-1-propanol from 3-thiol-1-propanol and 2-chlorotriethylamine by the method used for I, above, gave a 92% yield of material boiling at 120–125° at 3 mm.

2-(3-Chloropropylthio)-triethylamine.—The propanol was converted to the chloride-hydrochloride by thionyl chloride as described for II above. The resulting product was an oil, which could not be obtained crystalline. It was dissolved in water, the aqueous solution was made strongly basic with cold 35% sodium hydroxide solution, and the free base was extracted with ether. After working up as usual, there was obtained on distillation a 77.5% yield of light yellow product, boiling at 90–92° at 1 mm. On redistillation of a small center-cut, the pure material was obtained as a light yellow liquid, boiling at 74.0° at 0.3 mm., n^{20}D 1.4886. The compound slowly becomes opaque on standing, probably due to quaternization.

Anal. Calcd. for $C_9H_{20}NClS$: C, 51.53; H, 9.61; N, 6.68. Found: C, 51.36; H, 9.56; N, 6.74.

The picrate had m. p. 74–75° (from dilute acetone).

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(10) Suter and Moffett, THIS JOURNAL, 56, 487 (1934).

(11) Pomerantz and Conner, *ibid.*, 61, 3386 (1939).

(12) All melting and boiling points are uncorrected.

(13) We are indebted to the Misses Alice Rainey and Patricia Curran for the microanalyses.

(14) Rojahn and Lemme, *Arch. Pharm.*, 263, 612 (1925).

Anal. Calcd. for $C_{15}H_{23}O_7N_4ClS$: C, 41.05; H, 5.28. Found: C, 41.18; H, 5.37.

2-(3-Chloropropylsulfo)-triethylamine.—Oxidation of the above sulfide in dilute hydrochloric acid solution with an excess of 30% hydrogen peroxide gave a 42% yield of crude 2-(3-chloropropylsulfo)-triethylamine. The base quaternized when an attempt was made to purify it by distillation. The picrate melted at 112–113°.

Anal. Calcd. for $C_{15}H_{23}O_9N_4ClS$: C, 38.26; H, 4.92. Found: C, 38.28; H, 4.67.

2-(2-(2-Diethylaminoethylthio)-ethylthio)-ethanol, VI.—Treatment of II, as the free base, with a further mole of sodio-2-thiolethanol gave an 80% yield of product: colorless viscous oil, boiling at 154–160° at 1.5 mm. Redistillation of a center-cut gave pure material, boiling at 120.0° at 0.2 mm., $n^{20}\mathrm{D}$ 1.5268.

Anal. Calcd. for $C_{10}H_{23}ONS_2$: C, 50.59; H, 9.76; N, 5.90. Found: C, 50.83; H, 9.90; N, 5.89.

A crystalline derivative of this compound could not be prepared.

2-(2-(2-Chloroethylthio)-ethylthio)-triethylamine.—Treatment of VI with thionyl chloride by the method used to prepare II gave a chloride-hydrochloride melting below room temperature. Conversion to the free base and distillation gave a 62% over-all yield of product: light yellow liquid boiling at 131.0° at 1.0 mm., $n^{20}\mathrm{D}$ 1.5245.

Anal. Calcd. for $C_{10}H_{22}NClS$: C, 46.94; H, 8.68; Found: C, 46.44; H, 8.55.

The free base was accompanied during distillation by a very hygroscopic white crystalline sublimate, from which it could be separated by strong cooling of the distillate and filtration. The sublimate is probably a quaternary salt.

2-(2-(2-Chloroethylsulfoxyl)-ethylsulfoxyl)-triethylamine.—Oxidation of the above thio-compound in dilute hydrochloric acid solution with an excess of 30% hydrogen peroxide gave a crude oily product. The free base was liberated from a methanol–water solution of the hydrochloride by means of aqueous sodium bicarbonate solution, and the resulting solid was crystallized several times from a methylene chloride–acetone mixture. The only compound isolated, in very poor yield, proved to be the disulfoxide. The pure compound formed small white prisms, m. p. 158–159°.

Anal. Calcd. for $C_{10}H_{22}O_4NClS_2$: C, 41.72; H, 7.71; N, 4.87. Found: C, 41.64; H, 7.77; N, 4.82.

ω-Thioalkylphthalimides.—Refluxing an alcoholic solution of thiourea and 2-bromoethylphthalimide for six hours gave a 67% yield of 2-phthalimidoethylisothiouronium bromide, rosets of white needles from absolute alcohol–ethyl acetate, m. p. 229–230°.

Anal. Calcd. for $C_{11}H_{12}O_2N_3BrS$: C, 40.01; H, 3.66; N, 12.73. Found: C, 40.59; H, 3.78; N, 12.70.

Hydrolysis with aqueous sodium hydroxide gave a 24.5% yield of 2-thiolethylphthalimide, m. p. 77–78° (lit.[15] m. p. 78–79°). The compound was also prepared, in 73.5% yield, by the method of Gabriel.[16]

3-Phthalimidopropylisothiouronium bromide, prepared by a method similar to that described for the lower homolog, was obtained in 96% yield. The compound formed short blunt colorless needles from alcohol–ethyl acetate–ligroin, m. p. 231° (dec.).

Anal. Calcd. for $C_{12}H_{14}O_2N_3BrS$: C, 41.86; H, 4.10; S, 9.31. Found: C, 42.03; H, 4.42; S, 9.40.

Basic hydrolysis gave a crude semi-crystalline 3-thiolpropylphthalimide, which could not be obtained sufficiently pure for analysis.

2-(2-Diethylaminoethylthio)-ethylamine, III.—A. To a stirred, refluxing solution of sodio-2-thiolethylphthalimide (from 140 g. of 2-thiolethylphthalimide, 15.6 g. of sodium and 400 ml. of absolute alcohol) was added dropwise 91.4 g. of 2-chlorotriethylamine over a period of twenty minutes. The resulting mixture was stirred under reflux for four hours and filtered while warm. The filtrate on standing (or immediately on seeding) deposited 23 g. of N^1,N^4-diethylpiperazinium diethochloride.[16] The filtrate from the latter compound was evaporated to dryness *in vacuo*, yielding a viscous oil which could not be obtained crystalline. 2-(2-Phthalimidoethylthio)-triethylamine hydrochloride was obtained from a solution of this material in dry benzene by treatment with dry hydrogen chloride. It formed small slender white needles (from absolute alcohol–ligroin) melting at 140–147°.

Anal. Calcd. for $C_{16}H_{22}O_2N_2S\cdot HCl$: C, 56.05; H, 6.76; N, 8.17. Found: C, 56.09; H, 7.26; N, 7.96.

The main portion of the above oil (89 g.) was hydrolyzed by 85% hydrazine hydrate (17.1 g.) in alcohol, followed by treatment with hydrochloric acid.[9] After filtration of phthalhydrazide the filtrate was concentrated to a small volume *in vacuo*, made basic with 35% sodium hydroxide solution and saturated with anhydrous potassium carbonate. The amine was extracted with benzene, the extract was dried over anhydrous potassium carbonate and the benzene was removed *in vacuo*. Distillation of the residual oil gave 26.3 g. (22%) of colorless product, boiling at 84–91° at 1.5 mm. The pure material boiled at 62.0° at 0.4 mm., $n^{20}\mathrm{D}$ 1.4906.

Anal. Calcd. for $C_8H_{20}N_2S$: N, 15.89; S, 18.18. Found: N, 15.72; S, 17.66.

The dithiocarbamate crystallized from dilute alcohol as small white blunt needles in the form of the monoalcoholate. Drying at 60° for four hours *in vacuo* gave the anhydrous compound. Both forms melted at 138–139°.

Anal. Calcd. for $C_9H_{20}N_2S_3\cdot C_2H_5OH$: N, 9.39. Found: N, 9.44. Calcd. for $C_9H_{20}N_2S_3$: C, 42.82; H, 7.99; N, 11.10. Found: C, 42.98; H, 8.03; N, 11.31.

B. The intermediate 2-(2-phthalimidoethylthio)-triethylamine was prepared from 2-diethylaminoethylisothiouronium chloride,[7] 2-bromethylphthalimide and sodium ethoxide in a method analogous to that recorded for 3-(2-diethylaminoethylthio)-1-propanol above. After hydrolysis and isolation of the amine as in A, above, there was obtained a 40% over-all yield of pure amine.

3-(2-Diethylaminoethylthio)-1-propylamine, IV.—A. The reaction between sodio-2-diethylaminoethanethiol (from the pure thiol[7]) and 3-bromopropylphthalimide, carried out by a method analogous to that used in method A under 2-(2-diethylaminoethylthio)-ethylamine, above, gave the pure propylamine in 48% over-all yield. The intermediate 2-(3-phthalimidopropylthio)-triethylamine hydrochloride formed rosets of white needles from absolute alcohol–ligroin, melting at 165°.

Anal. Calcd. for $C_{17}H_{24}O_2N_2S\cdot HCl$: C, 57.20; H, 7.06; N, 7.85. Found: C, 57.10; H, 6.99; N, 7.43.

The pure amine was a colorless oil, boiling at 80.5° at 0.4 mm., $n^{20}\mathrm{D}$ 1.4913 (lit.,[5b,c] b. p. 135–136° at 12 mm.).

Anal. Calcd. for $C_9H_{22}N_2S$: C, 56.79; H, 11.65; N, 14.72; S, 16.84. Found: C, 56.70; H, 11.52; N, 14.70; S, 16.12.

The dithiocarbamate crystallized from dilute acetone as the tetrahydrate and from methanol–chloroform in the anhydrous form. Both products formed short blunt white needles, m. p. 132–133°. The hydrated compound was unstable.

Anal. Calcd. for $C_{10}H_{22}N_2S_3\cdot 4H_2O$: N, 8.28. Found: N, 8.32. Calcd. for $C_{10}H_{22}N_2S_3$: C, 45.07; H, 8.32. Found: C, 44.93; H, 8.47.

B. Use of 2-diethylaminoethylisothiouronium chloride,[7] and 3-bromopropylphthalimide, as outlined for the ethyl homolog above, gave the pure amine in 45% over-all yield.

2-(2-Diethylaminoethylsulfo)-ethylamine and 3-(2-diethylaminoethylsulfo)-1-propylamine were prepared by oxidation of the amines in dilute hydrochloric acid solution with an excess of 30% hydrogen peroxide. Neither com-

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(15) Gabriel, *Ber.*, **24**, 1110 (1891).

(16) Gough and King, *J. Chem. Soc.*, 2437 (1928); Eisleb, *Ber.*, **74**, 1433 (1941).

pound could be obtained sufficiently pure for analysis, since they decomposed readily on heating. Both compounds were viscous yellow liquids.

2-(2-Diethylaminoethylsulfo)-ethylamine.—A derivative of this compound could not be made.

3-(2-Diethylaminoethylsulfo)-1-propylamine dithiocarbamate formed tiny white needles from dilute acetone, melting at 130–132°.

Anal. Calcd. for $C_{10}H_{22}O_2N_2S_3$: C, 40.24; H, 7.43; N, 9.39. Found: C, 40.23; H, 7.11; N, 9.35.

2-(2-Cyanoethylthio)-triethylamine.—To 17.5 g. of acrylonitrile was added, with external cooling, 42.5 g. of 2-diethylaminoethanethiol.[7] The spontaneous exothermic reaction was controlled by frequent cooling in ice. After standing overnight at room temperature the reaction product was distilled *in vacuo*. There was obtained 54.7 g. (92%) of pure colorless product, boiling at 111.0° at 2.5 mm., n^{20}_D 1.4885.

Anal. Calcd. for $C_9H_{18}N_2S$: C, 58.02; H, 9.74; N, 15.04. Found: C, 58.05; H, 9.83; N, 14.76.

The picrate crystallized from absolute alcohol–acetone in yellow needles, melting at 74–75°.

Anal. Calcd. for $C_{15}H_{22}O_7N_5S$: C, 43.37; H, 5.10. Found: C, 43.49; H, 5.23.

2-(2-Cyanoethylthio)-triethylamine was also obtained in 67% yield by the reaction between II, as the free base, and potassium cyanide in aqueous alcohol.

Summary

The preparation of a series of diethylaminoethylthioalkyl chlorides and amines, their corresponding sulfones, and related compounds is described.

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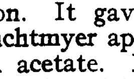
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Grignard Reactions Involving the Naphthalene Nucleus

BY REYNOLD C. FUSON, B. C. MCKUSICK[1] AND FRED W. SPANGLER[2]

Because of the ease with which Grignard reagents reacted with 1-mesitoyl-2-methoxynaphthalene (I),[3] to replace the methoxyl group by an alkyl or aryl group, attempts have been made to condense this type of reagent with the mesitoylnaphthalenes. The present paper is a report of an investigation of the action of methylmagnesium iodide on these ketones. Similar studies with benzoylmesitylene, *p*-toluylmesitylene and benzoylisodurene[4] had indicated that 1,2-addition might be expected with the methyl Grignard reagent. On the other hand, it had been established that phenylmagnesium bromide condensed with 1-mesitoylnaphthalene (II) in the 1,4 manner.[5] Moreover, the fixed nature of the naphthalene bond structure might be expected to facilitate 1,4-addition to naphthyl ketones.



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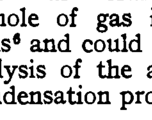
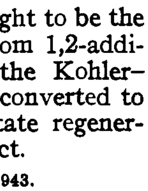


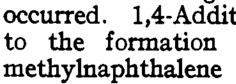
II



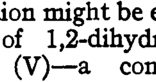
III

In the present work it was found that treatment of 1-mesitoylnaphthalene (II) with methylmagnesium iodide produced a 58% yield of an addition compound. At first it was thought to be the carbinol (III) which would result from 1,2-addition. It gave a mole of gas in the Kohler–Richtmyer apparatus[6] and could be converted to an acetate. Hydrolysis of the acetate regenerated the original condensation product.

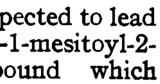
In an attempt to synthesize the carbinol, mesitylmagnesium bromide was condensed with 1-acetonaphthone. Although enolization occurred to the extent of 61%, addition to the carbonyl group did take place. The product, however, was not the carbinol but the corresponding olefin, 1-mesityl-1-(1-naphthyl)-ethylene (IV).



IV



V



VI

This olefin could not be made by dehydration of the supposed carbinol, the latter being unaffected by treatment with dehydrating agents.

Accordingly the carbinol structure had to be abandoned. It seemed likely that conjugate addition involving the naphthalene nucleus had occurred. 1,4-Addition might be expected to lead to the formation of 1,2-dihydro-1-mesitoyl-2-methylnaphthalene (V)—a compound which would possess active hydrogen and would be expected to yield an acetate.

This structure was finally established by dehydrogenation of the compound in the presence of a palladium-charcoal catalyst. The possibility that the addition was 1,6 could not be ignored. For this reason 1-mesitoyl-4-methylnaphthalene as well as 1-mesitoyl-2-methylnaphthalene (VI) was prepared for reference. The dehydrogenation product proved to be identical with the latter (VI). The dihydro structure was confirmed by the identification of the cleavage products of the enol peroxide (VII) prepared by the method of Kohler and Thompson.[7]

The products to be expected from the decomposition of the peroxide are mesitoic acid and 2-

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[3] Fuson and Speck, THIS JOURNAL, 64, 2446 (1942).

[4] Fuson, Armstrong, Wallace and Kneisley, *ibid.*, 66, 681 (1944).

[5] Fuson, Armstrong and Speck, *J. Org. Chem.*, 7, 297 (1942).

[6] Kohler and Richtmyer, THIS JOURNAL, 52, 3736 (1930).

[7] Kohler and Thompson, *ibid.*, 59, 887 (1937).