Anal. Calcd. for $C_{12}H_{10}O_4N_2$: C, 58.53; H, 4.09; N, 11.39. Found: C, 58.85; H, 3.72; N, 11.30.

The Higher-Boiling Fraction of the Reaction between Allyl Cyanide and Paraformaldehyde in a Sealed Tube at 130–135°.—The high boiling fraction had the following physical constants: $n^{25}D$ 1.4945, d^{25}_4 1.055. The liquid was immiscible with water. It gave the usual tests for unsaturation. It gave off ammonia on boiling with 10% sodium hydroxide. It did not give any test for alcohol or cyclic formal.

Anal. Calcd. for $C_{12}H_{12}ON_2$: C, 68.16; H, 6.86; N, 15.90; *MR*, 48.60. Found: C, 68.90; H, 6.72; N, 15.53; *MR*, 48.72.

Its analysis was not in satisfactory agreement for the dimer (IV) but agreed for a dimer containing one mole of water. This might be the ether of the hydroxy nitrile (I or II) but further work to establish its identity was discontinued.

Isomerization of Allyl Cyanide to a Mixture of *cis*- and *trans*-Crotononitriles.—A mixture of 67 g. of allyl cyanide, 5 g. of phenol and 2 drops of 10% sodium hydroxide was heated on a steam-bath for three hours. The phenol was neutralized with dilute sodium hydroxide. The organic layer was separated, dried over anhydrous sodium sulfate and distilled. The fraction boiling above 107° (60 g.) was collected. This mixture of the two geometrical isomers of crotononitrile had a refractive index $n^{20}D$ 1.4200. The last portion distilling at 119°, which was probably mainly *trans*-crotononitrile, showed $n^{20}D$ 1.4218. The values reported in the literature for the *cis*- and *trans*-isomers are $n^{20}D$ 1.4162 and $n^{20}D$ 1.4216, respectively.

Reaction of Crotononitrile with Paraformaldehyde in a Sealed Tube at 130–135°.—Thirty-four grams of the mixture of geometrical isomers and 15 g. of paraformaldehyde were heated in a sealed tube at 130–135° with shaking. After 24 hours the tube was cooled. The paraformaldehyde remained undissolved. The sealed tube was broken and liquid filtered. On distillation practically the whole of the starting material was recovered unchanged.

NOTRE DAME, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF OREGON]

Ring Scission During Formation of the Grignard Reagent from 3-Methyl-2-(chloromethyl)-thianaphthene. Ring Closure of *o*-(α-Methylallenyl)-thiophenol

BY RUSSELL GAERTNER

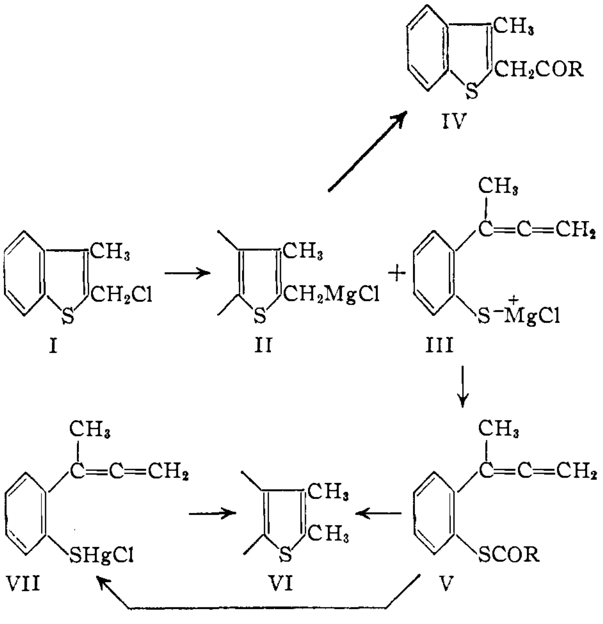
RECEIVED JANUARY 8, 1952

3-Methyl-2-(chloromethyl)-thianaphthene yielded in the cyclic reactor only small amounts of the Grignard reagent, detected by isolation of the expected products in reactions with carbon dioxide, acetyl chloride and ethyl chlorocarbonate. In each case the major product was derived from *o*-(α-methylallenyl)-thiophenol. The free thiophenol was labile, undergoing ring-closure to give 2,3-dimethylthianaphthene under a variety of mild conditions. This is the second example of an equilibrium between acyclic and aromatic anions and the first case in which the carbanion has been detected directly.

Although it had been shown that the furan ring in 2-(chloromethyl)-benzofuran was cleaved during an attempt to form the Grignard reagent,[1] the corresponding thianaphthene derivative was converted in fair yield to a normal reagent,[2] underwent abnormal reactions in the same manner as did 2-thenylmagnesium chloride.[3] Since the thianaphthene nucleus seemed stable to such cleavage and its arylmethyl reagents gave very predominantly abnormal reactions with common reactants,[2,4] the investigation has been extended to 3-methyl-2-(chloromethyl)-thianaphthene (I in Chart A) in the hope of observing products with the "isoaromatic" structure, *i.e.*, in which the reactant attacked the ortho-carbon atom bearing the methyl group. However, only traces of products corresponding to *normal* reactions of this Grignard reagent have been isolated, the mere addition of the methyl group resulting in predominant cleavage of the thiophene ring in a manner analogous to the behavior of the benzofuran derivative.

The halide (I) was best obtained preparatively by chloromethylating 3-methylthianaphthene. Its structure was proved by synthesizing it also by the action of thionyl chloride on the corresponding alcohol.[4] I reacted normally in the cyclic reactor and titration after hydrolysis indicated the presence of magnesium hydroxide equivalent to 83% conversion. However, carbonation of this solution gave only a trace of 3-methyl-2-thianaphthenylacetic acid[4] (IV, R = OH), the major product being 2,3-dimethylthianaphthene (VI). It seemed at first that simple hydrolysis of the reagent had occurred before carbonation; this was shown not to be the case by allowing the "reagent" to react with ethyl chlorocarbonate. Although a trace of the ester (IV, R = OC_2H_5) of the acetic acid was

CHART A



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[1] R. Gaertner, THIS JOURNAL, **73**, 4400 (1951).

[2] R. Gaertner, *ibid.*, **74**, 766 (1952). There was no positive evidence for ring-scission in this case, although polymeric by-products may have represented that side-reaction.

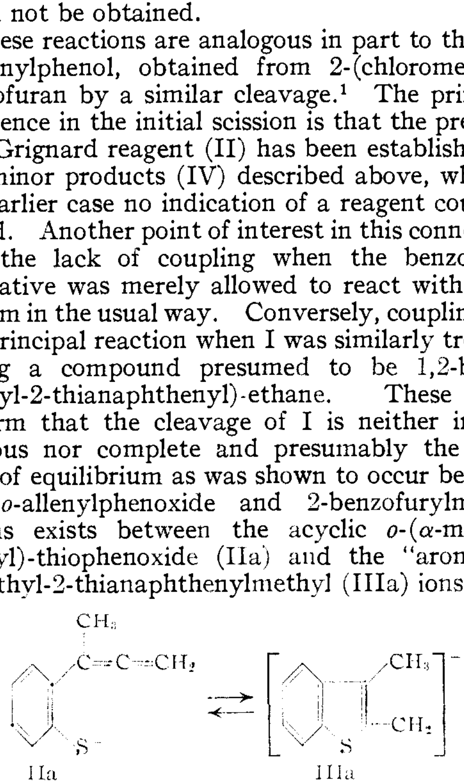
[3] R. Gaertner, *ibid.*, **73**, 3934 (1951).

[4] Concerning 3-thianaphthenylmethylmagnesium chloride, see R. Gaertner, *ibid.*, **74**, 2185 (1952).

present, the isomeric thiolcarbonate (V, $R = OC_2H_5$) predominated. Similarly, with acetyl chloride the corresponding thiolacetate (V, $R = CH_3$) was the major product, appreciable amounts of 3-methyl-2-thianaphthenyl-acetone (IV, $R = CH_3$) being isolated. The latter was identified as the product of normal reaction by desulfurization with Raney nickel to give the known 5-phenyl-2-hexanone, characterized as the semicarbazone; the arylacetone was also reduced to the alcohol by lithium aluminum hydride.

The esters, V, exhibited novel reactions which clarified the nature of the original ring scission. When either the acetate or the carbonate was heated with ethanolic alkali, 2,3-dimethylthianaphthene (VI) was obtained in excellent yield. The acetate was also converted to the same compound by transesterification with methanol containing hydrochloric acid; the carbonate was recovered unchanged from this treatment. The acetate, but not the carbonate, also reacted readily with ethanolic mercuric chloride, forming the insoluble thiophenoxymercuric chloride (VII). When treated with hydrogen sulfide this derivative was converted to impure 2,3-dimethylthianaphthene. Thus attempts to prepare the expected *o*-(α-methylallenyl)-thiophenol failed. Both the acetate and carbonate were unsaturated to hydrogen over platinum oxide but satisfactory quantitative data could not be obtained.

These reactions are analogous in part to those of *o*-allenylphenol, obtained from 2-(chloromethyl)-benzofuran by a similar cleavage.[1] The principal difference in the initial scission is that the presence of a Grignard reagent (II) has been established by the minor products (IV) described above, while in the earlier case no indication of a reagent could be found. Another point of interest in this connection was the lack of coupling when the benzofuran derivative was merely allowed to react with magnesium in the usual way. Conversely, coupling was the principal reaction when I was similarly treated, giving a compound presumed to be 1,2-bis-(3-methyl-2-thianaphthenyl)-ethane. These facts confirm that the cleavage of I is neither instantaneous nor complete and presumably the same type of equilibrium as was shown to occur between the *o*-allenylphenoxide and 2-benzofurylmethyl anions exists between the acyclic *o*-(α-methylallenyl)-thiophenoxide (IIa) and the "aromatic" 3-methyl-2-thianaphthenylmethyl (IIIa) ions. The major differences in the thianaphthene series are the presence of detectable, though minor, amounts of the carbanion (IIIa) and the conditions for ring closure. Theoretically, the first point is understandable in view of the greater aromaticity of the thianaphthene nucleus as compared to benzofuran; thus the anion (IIIa) is more highly stabilized with respect to its cleavage twin (IIa). To illustrate the second difference, acidic, alkaline, or nearly neutral mild conditions (rapid hydrolysis of the "reagent" solution with ice alone) sufficed to effect closure. This behavior is not surprising if the greater acidity of the thiophenol as compared to the phenol is considered. Since an appreciable concentration of the intermediate thiophenoxide (IIa) exists even in acidic media, closure may occur.


IIa IIIa

We are unable to propose a convincing reason for the unexpected effect of the methyl group in promoting cleavage in the thianaphthene series, although the hyperconjugative or inductomeric electron-release of the methyl substituent would operate in the proper direction.

Investigation of other "blocked" reagents continues.

Acknowledgments.—A grant-in-aid by the Graduate School during the 1951–1952 academic year supported this investigation. Continued gifts of thianaphthene by Jefferson Chemical Company were greatly appreciated.

Experimental Part[5]

3-Methyl-2-(chloromethyl)-thianaphthene (I).—3-Methylthianaphthene[6] (14.8 g.) was added dropwise to a rapidly stirred solution of 12 g. of trioxane in 200 ml. of concentrated hydrochloric acid at 60°. After the addition was complete, stirring was continued for 90 minutes, the mixture was cooled, diluted with three volumes of water, and extracted with ether. The extracts were dried first with calcium chloride and then with potassium carbonate. A total of 15.4 g. (79% yield) of the colorless halide distilled principally at 114–117° (0.4 mm.). When the reaction was carried out with a smaller excess of formaldehyde by heating the complete mixture from room temperature to 70°, only a 48% yield was obtained. Both products solidified and melted at 38–40°.

When 11.3 g. of 3-methyl-2-thianaphthenylcarbinol[4] was added in small portions to 15 ml. of thionyl chloride, the mixture heated under reflux one hour and the excess reagent aspirated, a total of 11.4 g. (91%) resulted; b.p. 123–125° (0.8 mm.). Overheating in the presence of thionyl chloride caused resinification; the compound darkened slowly at room temperature and eventually decomposed. The product solidified; m.p. 40.6–41.6°. A middle cut was submitted for analysis. The properties of the supercooled liquid were d^{20}_4 1.254, n^{20}_D 1.6401.

Anal. Calcd. for $C_{10}H_9SCl$: C, 61.06; H, 4.61. Found: C, 61.30; H, 4.74.

From 60 g. of 3-chloromethylthianaphthene, by reaction of the Grignard reagent with ethyl chlorocarbonate,[4] and reduction of the dried ethereal solution of the crude ethyl 3-methyl-2-thianaphthoate with excess lithium aluminum hydride, was obtained 26.7 g. (46%) of the crude distilled alcohol.[4]

3-Methyl-2-thianaphthenylmethylmagnesium Chloride (II) **and Magnesium** ***o*-(α-Methylallenyl)-thiophenoxide** (III). Hydrolysis.—By use of the cyclic reactor with freshly amalgamated magnesium turnings, the halide was smoothly converted in yields as high as 83%, as estimated by titration after hydrolysis. Addition of the ethereal solution containing 0.0229 mole (as hydroxide-equivalent) to excess ice gave, after washing with water (at this stage a small portion of the ether layer was evaporated but the oil did not react with ethanolic mercuric chloride—see below—and had

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(5) Melting points, but not boiling points, are corrected. Properties of previously known compounds agreed satisfactorily with those reported in the references. Microanalyses were by Micro-Tech Laboratories, Skokie, Illinois. Several composite experiments were reported to avoid undue length. The obvious mixture melting points were performed without noticeable depressions.

(6) The reduction of 3-chloromethylthianaphthene with lithium aluminum hydride–lithium hydride in tetrahydrofuran according to the method of J. E. Johnson, R. H. Blizzard and H. W. Carhart, THIS JOURNAL, **70**, 3664 (1948), for benzyl chloride was superior (92% yield) to either of the methods reported previously.[4]

the odor of 2,3-dimethylthianaphthene) and 5% potassium bicarbonate, and drying with potassium carbonate and magnesium sulfate, gave 3.49 g. (94%) of 2,3-dimethylthianaphthene[7]; b.p. 76–77° (0.4 mm), n^{20}_D 1.6170.

Anal. Calcd. for $C_{10}H_{10}S$: C, 74.03; H, 6.21. Found: C, 74.19; H, 6.19.

The picrate[7] formed orange needles from ethanol; m.p. 102.2–102.8°.

Anal. Calcd. for $C_{16}H_{13}N_3O_7S$: C, 49.10; H, 3.35. Found: C, 49.05; H, 3.45.

When 5.0 g. of the chloride (I) in 50 ml. of ether was allowed to react in the conventional manner in an atmosphere of nitrogen with 0.75 g. of magnesium, the mixture heated under reflux for 1 hour, 4 ml. of acetyl chloride added and heating continued for 2 hours, and water added, only 1.2 g. of 2,3-dimethylthianaphthene and traces of higher boiling materials were volatile at 0.2 mm. and 200°. The residual gum failed to crystallize from hexane and was treated with picric acid in ethanol. A total of 1.60 g. of 1,2-bis-(3-methyl-2-thianaphthenyl)-ethane dipicrate separated and was recrystallized from ethanol–benzene; m.p. 168.5–169.5°.

Anal. Calcd. for $C_{32}H_{24}N_6O_{14}S_2$: C, 49.23; H, 3.10. Found: C, 49.22; H, 3.10.

Carbonation.—A solution containing 0.0282 mole of "reagent" was rapidly poured onto about 100 g. of Dry Ice covered with ether. Only 0.1 g. of 3-methyl-2-thianaphthenylacetic acid,[4] m.p. 147–149° after two recrystallizations, was present in the alkaline extracts together with intractable material.

***o*-(α-Methylallenyl)-phenyl Thiolacetate and 3-Methyl-2-thianaphthenylacetone.**—To a solution containing 0.0363 mole of "reagent" cooled in ice under nitrogen was added dropwise with stirring a solution of 10 ml. of reagent acetyl chloride in about 30 ml. of ether. The mixture was heated under reflux 90 minutes and poured onto ice. Rapid distillation of the oily product at 0.25 mm. gave the following cuts: 82–93° (1.81 g., n^{20}_D 1.5960), 93–113° (1.62 g., n^{20}_D 1.5943), 125–130° (principally, 1.75 g., n^{20}_D 1.6063). The last fraction (24% yield) was nearly pure ketone; a subsequent run (0.0543 mole) gave a 31% yield of ketone but a 42% yield of acetate. A sample of the former was distilled for analysis; b.p. 148–150° (1 mm.), n^{20}_D 1.6094. *Anal.* Calcd. for $C_{12}H_{12}OS$: C, 70.55; H, 5.92. Found: C, 70.45; H, 6.08. It was recovered from an attempted hydrolysis with ethanolic alkali and was attacked by hydrogen over platinum oxide at an almost imperceptibly slow rate; 2,3-dimethylthianaphthene was not hydrogenated at all under these conditions. A single attempt to form an oxime failed. When 1.5 g. of the ketone was heated under reflux in ethanol for 30 minutes with about 12 g. of Raney nickel,[8] 0.63 g. of a colorless liquid, b.p. 65–75° (0.4 mm.), was obtained. The semicarbazone melted at 145–147° after two recrystallizations and the compound was therefore 5-phenyl-2-hexanone[9]—formed from 3-methyl-2-thianaphthenylacetone—and not 3-methyl-3-phenyl-2-pentanone[10]—which could have been obtained from the possible product of abnormal reaction, 3-acetyl-3-methyl-2-methylenethianaphthane.

The original ketone (4.4 g.) was also reduced with 1.1 g. of lithium aluminum hydride in ether, giving 3.47 g. (78%) of a viscous colorless liquid, b.p. 123–130° (0.3 mm.). When refractionated, 1-(3-methyl-2-thianaphthenyl)-2-propanol distilled at 120–124° (0.2 mm.), the analytical sample being taken from the 123–124° cut.

Anal. Calcd. for $C_{12}H_{14}OS$: C, 69.86; H, 6.84. Found: C, 69.70; H, 6.79.

The phenylurethan was recrystallized from benzene–hexane; m.p. 119–120°.

Anal. Calcd. for $C_{19}H_{19}NO_2S$: C, 70.12; H, 5.88. Found: C, 70.08; H, 5.74.

The first two fractions (b.p. 82–113°) in the original distillation contained a small amount of 2,3-dimethylthianaphthene, but were mainly *o*-(α-methylallenyl)-phenyl thiolacetate (46% crude yield). The combined material was fractionated in part carefully at 0.6 mm. in a micro-still[11] giving the following cuts: (during flooding and equilibration) 86–89° (0.57 g., n^{20}_D 1.6037), 89–91° (0.80 g., n^{20}_D 1.5930), 91–93° (0.56 g., n^{20}_D 1.5915), 93–98° (column being superheated, 0.41 g., n^{20}_D 1.5921). A portion of the 91–93° cut was submitted for analysis.

Anal. Calcd. for $C_{12}H_{12}OS$: C, 70.55; H, 5.92. Found: C, 70.72; H, 6.23.

The acetate had a pleasant fragrant odor quite unlike the compounds containing the aromatic thianaphthene nucleus; it absorbed overnight only 23% of the theoretical volume of hydrogen over platinum oxide. With excess mercuric chloride in 10 ml. of ethanol, 0.52 g. reacted rapidly, but not instantaneously, at room temperature, precipitating 0.93 g. (73%) of *o*-(α-methylallenyl)-thiophenoxymercuric chloride (VII). It appeared to decompose when recrystallized from ethanol but was pure as formed initially. The compound had no sharp melting point but darkened and evolved a gas at 240–300°.

Anal. Calcd. for $C_{10}H_9ClHgS$: C, 30.23; H, 2.28. Found: C, 30.24; H, 2.38.

2,3-Dimethylthianaphthene was not affected by mercuric chloride under these conditions. When 5.0 g. of the mercury derivative was dissolved in 125 ml. of reagent acetone and treated with hydrogen sulfide for 3 hours, the solution filtered and distilled, a total of 1.84 g. (90% yield, b.p. 72–76° at 0.15 mm., n^{20}_D 1.6117) of colorless mobile, evil-smelling material, principally 2,3-dimethylthianaphthene, which reacted instantly with mercuric chloride in ethanol, resulted. However, 1.47 g. gave only 0.41 g. of an insoluble compound, indicating the presence of only 11% of reactive material (calculated as the thiophenol). Some impurity with a different empirical formula was present; addition of hydrogen sulfide to the unsaturation may have occurred in part.

Anal. Calcd. for $C_{10}H_{10}S$: C, 74.03; H, 6.21; S, 19.76. Found: C, 73.00; H, 6.35; S, 20.82.

A solution of 2.60 g. of the acetate and 2.6 g. of potassium hydroxide in 15 ml. of 95% ethanol and 1.5 ml. of water was heated under reflux for 11 hours, diluted with 30 ml. of water, heated another hour, cooled and extracted repeatedly with petroleum ether (30–60°). Distillation gave 2.03 g. (98%) of 2,3-dimethylthianaphthene.

A solution of 3.08 g. of the acetate in 40 ml. of methanol containing 3 drops of concentrated hydrochloric acid was heated at total reflux under a small Podbielniak column for two hours. The liquid in the head then had the odor of methyl acetate. The solvent was removed by distillation during three hours, while the vapor temperature rose from 53 to 64°. The residue yielded 2.21 g. (90%) of 2,3-dimethylthianaphthene.

Ethyl 3-Methyl-2-thianaphthenylacetate and Ethyl S-*o*-(α-Methylallenyl)-phenyl Thiolcarbonate.—In one run 0.0427 mole of "reagent" was allowed to react with ethyl chlorocarbonate (14.1 ml.) in the previously outlined[3] procedure. Hydrolysis of the crude ester with ethanolic alkali produced a small acidic fraction, which was dissolved in carbon tetrachloride–hexane. The solution deposited 0.25 g. of a tan solid; m.p. 206–210°. After repeated recrystallization from acetone–benzene, the compound formed colorless clumped crystals; m.p. 212.8–213.6°. There was insufficient material for characterization. *Anal.* Calcd. for $C_{11}H_{10}OS$: C, 69.44; H, 5.29. Found: C, 69.44; H, 5.40. The original mother liquors slowly darkened and deposited gummy crystals which were sublimed at 110° (0.1 mm.) and recrystallized from hexane, forming 0.07 g. of leaflets of 3-methyl-2-thianaphthenylacetic acid,[4] m.p. 149–151°. Intractable material remained in the first mother liquors. The neutral fraction in the original saponification yielded only 2,3-dimethylthianaphthene.

In another run, 27.9 g. of the halide (I) was converted in the cyclic reactor, allowed to react with ethyl chlorocarbonate, and the mixture saponified with ethanolic alkali as

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[7] E. G. G. Werner, H. F. Eyhuisen and J. B. de Jonge, *Rec. trav. chim.*, **68**, 509 (1949), reported another synthesis. In subsequent experiments in this work, the compound was identified by boiling point and refractive index.

[8] F. F. Blicke and D. G. Sheets, THIS JOURNAL, **71**, 4010 (1949), have described the desulfurization of other thianaphthenes.

[9] D. Nenitzescu and I. G. Gavăt, *Ann.*, **519**, 260 (1935); J. Colonge and L. Pichat, *Bull. soc. chim. France*, 853 (1949).

[10] A. Favorsky, T. E. Zalesskaja, D. I. Rosanow and G. W. Tchléintzew, *ibid.*, [5] **3**, 239 (1936), described this ketone and its semicarbazone, m.p. 177–178°.

[11] The E. L. Wheeler Co. model GM-145 Micro Column with vapor take-off and heating jacket, for which an efficiency of more than fifty theoretical plates was found with mixtures of *n*-heptane and methylcyclohexane, was used.

usual. After distillation of most of the ethanol, the mixture was diluted with water and extracted with petroleum ether (30–60°). The extracts contained 5.4 g. of 2,3-dimethylthianaphthene. The alkaline layer was acidified with dilute hydrochloric acid in the presence of petroleum ether and extracted repeatedly with the solvent. The combined extracts were dried with magnesium sulfate and concentrated by distillation to a total weight of 31.6 g. When 10.4 g. of this solution was distilled *in vacuo*, only 2,3-dimethylthianaphthene (3.3 g.) was obtained. The solution reacted *instantly* (much more rapidly than the acetate) with ethanolic mercuric chloride, and 10.8 g. of it gave 5.34 g. of *o*-(α-methylallenyl)-thiophenoxymercuric chloride. Dilution of the mother liquors with water and extraction yielded 1.2 g. of 2,3-dimethylthianaphthene. These data indicate the presence of a 15% yield (based on I) of *o*-(α-methylallenyl)-thiophenol and a 28% yield of 2,3-dimethylthianaphthene in the concentrated solution.[12] Neither of the compounds obtained in the earlier run could be isolated in this case. As always, polymeric material remained in the still-pot,

In the best of another series of runs, using 27.3 g. of halide, the mixture after addition of the "reagent" to ethyl chlorocarbonate was heated under reflux for 2 hours, the excess reactant was hydrolyzed, then the ether layer was washed, dried and distilled at 0.4 mm., giving four cuts: 91–102° (5.35 g., $n^{20}_{\rm D}$ 1.5773), 102° (6.81 g., $n^{20}_{\rm D}$ 1.5727), 102–108° (9.24 g., $n^{20}_{\rm D}$ 1.5749), 108–180° (flamed, 1.90 g., dark amber). The first three fractions distilled very largely at 101–103° (a total of 21.4 g., 66%); a sample of ethyl S-*o*-(α-methylallenyl)-phenyl thiolcarbonate was taken from the center cut.

Anal. Calcd. for $C_{13}H_{14}O_2S$: C, 66.63; H, 6.02. Found: C, 66.46; H, 6.06.

The third fraction was light amber and after a day became quite viscous with $n^{20}_{\rm D}$ 1.5834. The center cut did not polymerize noticeably in a week.

The thiolcarbonate very slowly absorbed only 23% of the theoretical amount of hydrogen over platinum oxide in ethanol; it did not react with mercuric chloride in ethanol and was recovered from heating under reflux with either methanol or acetic acid, both containing several drops of concentrated hydrochloric acid.

When 5.26 g. of the ester was heated under reflux for 12 hours with 5 g. of potassium hydroxide in 25 ml. of 95% ethanol, diluted with several volumes of water, and extracted with petroleum ether, 2.98 g. (82%) of 2,3-dimethylthianaphthene was obtained. After reduction of 2.0 g. of ester with 1 g. of lithium aluminum hydride in ether, hydrolysis by pouring the mixture directly on ice, and acidification with sulfuric acid, 1.1 g. (87%) of 2,3-dimethylthianaphthene was isolated.

The last fraction in the original distillation was saponified with ethanolic alkali and the oily acidific material, which deposited only a trace of crystals from hexane, was desulfurized[8] with about 9 g. of Raney nickel in 40 ml. of ethanol; however, the resulting gum could not be resolved by sublimation.

EUGENE, OREGON

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(12) Distillations were carried out in Pyrex ware, which might, of course, have acted catalytically; however, solutions expected to contain the thiophenol were tested routinely with mercuric chloride with negative results except in this experiment. The reason for the stability of the thiophenol under these conditions is obscure in view of the ease of closure under other circumstances which seemed less drastic. Perhaps solvent effects were responsible.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF JOSEPH E. SEAGRAM & SONS, INC.]

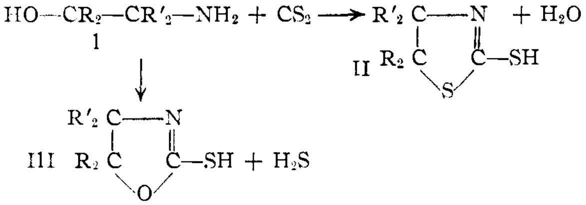
Synthesis of Oxazoline-2-thiols from 2-Aminoalcohols[1]

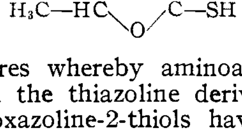
BY A. A. ROSEN[2]

RECEIVED DECEMBER 19, 1951

2-Aminoalcohols are combined with carbon disulfide at low temperature, through the oxidizing action of iodine, to form dialkanol thiuram disulfides. The thiuram disulfides decompose to yield oxazoline-2-thiols. The synthetic method generally employed to prepare these heterocyclic compounds (heating the aminoalcohol with carbon disulfide) results in some instances in the formation of thiazoline-2-thiols. Factors which determine the manner of heterocyclic ring formation by this latter method are considered.

Some 2-aminoalcohols (I), notably ethanolamine, yield thiazoline-2-thiols (II) when heated with carbon disulfide.[3,4] The reaction is usually accomplished in the presence of alkali. Several other 2-aminoalcohols, however, yield the corresponding oxazoline-2-thiols (III) under the same reaction conditions.[5,6] These compounds may be construed either as the thiones or as the tautomeric thiols[7]; the latter basis for nomenclature is the one most frequently encountered in the literature and is accordingly employed in this paper. The analogous 3-aminoalcohol, 4-amino-4-methyl-2-pentanol, yields the corresponding 6-membered oxygen–nitrogen heterocycle, 4,4,6-trimethyl-5,6-dihydro-1,3,4-oxazine-2-thiol[8] (IV).




IV

The procedures whereby aminoalcohols which ordinarily yield the thiazoline derivatives can be converted to oxazoline-2-thiols have been summarized by Ettlinger.[4] The same methods, when applied to primary alkylamines, yield the corresponding alkyl isothiocyanates, R-NCS.[9] Probably

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(1) Portions of this paper were presented before the Division of Organic Chemistry at the St. Louis Meeting of the American Chemical Society, 1941, and at the Boston Meeting, 1951.

(2) This paper is taken in part from a dissertation submitted by the author to the Graduate School of Arts and Sciences of the University of Cincinnati in partial fulfillment of the requirements for the degree of Ph.D., 1938.

(3) (a) L. Maquenne and E. Roux, *Compt. rend.*, **134**, 1589 (1902); (b) L. Knorr and P. Roessler, *Ber.*, **36**, 1278 (1903); (c) E. Roux, *Ann. chim.*, [8] **1**, 72 (1904).

(4) M. G. Ettlinger, THIS JOURNAL, **72**, 4792 (1950).

(5) H. A. Bruson and J. W. Eastes, *ibid.*, **59**, 2011 (1937).

(6) C. Y. Hopkins, *Can. J. Research*, **B20**, 268 (1942).

(7) M. G. Ettlinger, THIS JOURNAL, **72**, 4699 (1950).

(8) H. L. Fisher, U. S. Patent 2,326,732 (1944).

(9) (a) W. Rudneff, *Ber.*, **11**, 987 (1878); (b) J. von Braun, *ibid.*, **33**, 2726 (1900); (c) M. Delépine, *Compt. rend.*, **144**, 1125 (1907).