Anal. Calcd. for $C_{18}H_{15}N_3O_2S$: C, 64.08; H, 4.48; N, 12.45. Found: C, 64.00; H, 4.48; N, 12.23.

2-(*p*-Acetamidobenzenesulfonimido)-5,6-dihydro-4*H*-thiazolo[5,4,3-*ij*]quinoline (XVI).—A 5.4-g. (0.02 mole) quantity of 2-imino-5,6-dihydro-4*H*-thiazolo[5,4,3-*ij*]quinoline hydrobromide (X) was shaken with 10% aqueous sodium hydroxide and the free base was extracted with ether and dried over magnesium sulfate. It was then filtered into 75 ml. of pyridine. To this mixture was added a solution of 4.7 g. (0.02 mole) of *p*-acetamidobenzenesulfonyl chloride (Eastman) in 25 ml. of pyridine. A solid separated immediately and the liquid phase became orange. The mixture was heated on a steam bath for 1 hr., during which time the ether phase evaporated and the pyridine phase became colorless. It was then cooled and filtered. The solid which separated was the hydrochloride salt of the imine. The filtrate was treated with 10% aqueous sodium hydroxide and the solid which separated weighed 0.7 g. (9%). It was combined with the product obtain by repetition of this reaction, and recrystallized twice from dimethylformamide and water, whereupon it melted at 276–277°.

Anal. Calcd. for $C_{18}H_{17}N_3O_3S_2$: C, 55.77; H, 4.42; N, 10.84. Found: C, 55.55; H, 4.60; N, 10.72.

2-[(N-Benzoylthiocarbamyl)imino]-5,6-dihydro-4*H*-thiazolo[5,4,3-*ij*]quinoline (XVII).—A 15.0-g. (0.055 mole) quantity of 2-imino-5,6-dihydro-4*H*-thiazolo[5,4,3-*ij*]quinoline hydrobromide (X) was slurried with 10% aqueous sodium hydroxide. The base was extracted with ether and dried over magnesium sulfate. This solution was then filtered into a dropping funnel and it was added dropwise to a solution of benzoyl isothiocyanate (0.06 mole) in acetone, prepared as described for the synthesis of XV. The rate of addition was such that a gentle reflux was maintained. After the complete addition of the imine, the mixture was refluxed for 15 min., cooled, and poured onto ice.

The ether layer was separated and retained. The aqueous phase was extracted several times with ether, and all the extracts were combined and diluted with a twofold volume of low boiling petroleum ether. The material which separated was recrystallized twice from benzene as yellow prisms which weighed 3.7 g. (19%) and melted at 182–183° dec.

Anal. Calcd. for $C_{18}H_{15}N_3OS_2$: C, 61.16; H, 4.28; N, 11.89. Found: C, 60.97; H, 4.21; N, 11.67.

2-Dichloroacetimido-5,6-dihydro-4*H*-thiazolo[5,4,3-*ij*]quinoline (XVIII).—A solution of 4.4 g. (0.058 mole) of ammonium thiocyanate in 75 ml. of dry acetone was treated with 8.5 g. (0.058 mole) of dichloroacetyl chloride. A colorless solid separated immediately. This mixture was stirred and treated dropwise with a solution of 11.0 g. (0.058 mole) of 2-imino-5,6-dihydro-4*H*-thiazolo[5,4,3-*ij*]quinoline (X) in 100 ml. of acetone. The reaction mixture warmed only slightly during the addition of the imine. After the addition of the imine was complete, the mixture was refluxed for 15 min., cooled, and poured onto ice. The solid which separated was decolorized and recrystallized twice from ethanol. The colorless product weighed 1.1 g. (6.3%) and melted at 167–168°.

Anal. Calcd. for $C_{12}H_{10}Cl_2N_2OS$: C, 47.85; H, 3.35; N, 9.30. Found: C, 47.70; H, 3.48; N, 9.06.

2-Cyanimino-5,6-dihydro-4*H*-thiazolo[5,4,3-*ij*]quinoline (XIX).—A 7.2-g. (0.027 mole) quantity of 2-imino-5,6-dihydro-4*H*-thiazolo[5,4,3-*ij*]quinoline hydrobromide (X) was slurried in 10% aqueous sodium hydroxide. The free base was extracted with benzene, dried over magnesium sulfate and filtered. The solution was stirred and treated first with 2.6 g. (0.026 mole) of triethylamine and then with 2.7 g. (0.026 mole) of cyanogen bromide (Eastman) in small portions. The mixture was refluxed for 2 hr. after the last addition of the cyanogen bromide, cooled, and filtered. The solid which separated was washed with benzene, dried, and then washed with water and dried. Meanwhile, the benzene filtrate was treated with low boiling petroleum ether and the solid which separated was collected. Both of these solids proved to be identical by a mixture melting point. After recrystallization from ethanol, the product weighed 0.8 g. (15%) and melted at 162–164°.

Anal. Calcd. for $C_{11}H_9N_3S$: C, 61.37; H, 4.21; N, 19.52. Found: C, 61.52; H, 4.25; N, 19.57.

5,6-Dihydro-4*H*-imidazo[4,5,1-*ij*]quinoline.—A solution of 10.0 g. (0.0675 mole) of 8-amino-1,2,3,4-tetrahydroquinoline[1] in 50 ml. of formic acid was refluxed for 17 hr. The solution was cooled and made slightly alkaline with dilute aqueous ammonia. The mixture was extracted with ether, dried over magnesium sulfate, filtered, and the solvent was evaporated. The oil which remained was triturated with petroleum ether (75–90°), whereupon it crystallized. It was filtered and dried for 22 hr. at 40° (0.2 mm.). The product weighed 5.0 g. (44%) and melted at 76–77°.[10]

Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.91; H, 6.37; N, 17.71. Found: C, 76.16; H, 6.72; N, 17.63.

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[10] This product was slightly hygroscopic; thus, the lower melting point previously reported (see ref. 1) may have been due to hydration of the sample.

Reactions of Aromatic Thiols with Oxazolines

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N-Arylmercaptoalkyl amides are obtained in high yield by reaction of aromatic thiols with oxazolines. Structural proof is presented and a reaction mechanism is proposed.

Goldberg and Kelly[1] have shown that N-(2-hydroxyethyl)thiobenzamide results from the reaction of hydrogen sulfide with 2-phenyl-2-oxazoline, the sulfur becoming bonded to what was initially C-2 of the oxazoline ring. Fry[2] and others[3] have reported that thio acids, RCOSH, on reaction with oxazolines yield derivatives resulting from attack at position 5 of the ring. It became of interest to us, as a continuation of our investigation of the chemistry of oxazolines,[4] to determine the behavior of these heterocyclics toward other sulfur compounds. The results of studies with aromatic thiols are reported here.

A reaction occurs on heating a mixture of 2-ethyl-4,4-dimethyl-2-oxazoline and benzenethiol as indicated by a rise in the reflux temperature. Distillation gives a 1:1 product in 98% yield. This was proved to be N-(2-phenylmercapto-1,1-dimethylethyl)propionamide (I). A benzamide derivative II is obtained by the reaction of benzenethiol with 2-phenyl-4,4-dimethyl-2-oxazoline,

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[1] A. A. Goldberg and W. Kelly, *J. Chem. Soc.*, 1919 (1948).

[2] E. M. Fry, *J. Org. Chem.*, **15**, 438 (1950).

[3] E. M. Fry, *ibid.*, **15**, 802 (1950); M. Svoboda, J. Sicher, J. Farkas, and M. Pankova, *Chem. Listy*, **49**, 1351 (1955) [*Chem. Abstr.*, **50**, 5640 (1956)]; J. M. Nys and M. J. Libeer, U. S. Patent 2,823,207 (1958).

[4] H. L. Wehrmeister, *J. Org. Chem.*, **26**, 3821 (1961); **27**, 4418 (1962).

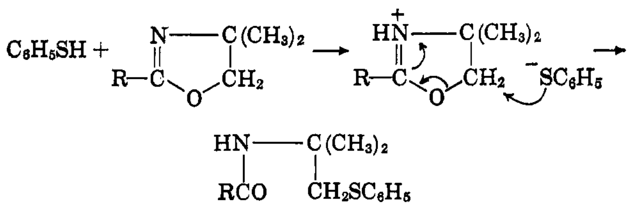
$C_6H_5SCH_2C(CH_3)_2NHCOCH_2CH_3$
I

$C_6H_5SCH_2C(CH_3)_2NHCOC_6H_5$
II

again in nearly quantitative yield. Completely analogous products are obtained by reaction of *p*-chlorobenzenethiol with 2-ethyl-4,4-dimethyl-2-oxazoline and with 2-(8-heptadecenyl)-4,4-dimethyl-2-oxazoline.

Structure assignments were made on the basis of elemental analyses, infrared spectra, and, in two instances, independent synthesis. This independent synthesis involved the acylation of a 2-arylmercapto-1,1-dimethylethylamine obtained by reaction of an arenethiol with 2,2-dimethylaziridine according to a published procedure.[5]

A nucleophilic displacement by the phenylmercaptide ion at position 5 of the oxazoline ring is suggested as a mechanism for this thiol–oxazoline reaction.



Experimental[6]

2-Ethyl-4,4-dimethyl-2-oxazoline was prepared as previously described.[4] 2-Phenyl-4,4-dimethyl-2-oxazoline[7] was prepared by heating benzoic acid with 2-amino-2-methyl-1-propanol with azeotropic removal of water. A product of 99.4% purity (by titration) was obtained, b.p. 77–72° (1.0–0.5 mm.), in a yield of 74%. Alkaterge® A[8] was distilled and a fraction, b.p. 175–180° (0.5–0.3 mm.), was collected as 2-(8-heptadecenyl)-4,4-dimethyl-2-oxazoline [neut. equiv., 335.5 (calcd.), 332.2 (found)]. Benzenethiol and *p*-chlorobenzenethiol were obtained from Distillation Products Industries and were used without further treatment.

N-(2-Phenylmercapto-1,1-dimethylethyl)propionamide (I).—A mixture of 128 g. (1.0 mole) of 2-ethyl-4,4-dimethyl-2-oxazoline and 111.6 g. (1.01 moles) of benzenethiol was heated at reflux under nitrogen at 140–185° for 6 hr. The mixture solidified on cooling. Distillation yielded 231.8 g. (98%) of product, b.p. 148–151° (0.4 mm.). Infrared bands at 3.05 (NH) and 6.05 μ (C═O) are consistent with the assigned structure.

Anal. Calcd. for $C_{13}H_{19}NOS$: N, 5.90; S, 13.50. Found: N, 5.43; S, 13.75.

Recrystallization from hexane yielded material with a melting point of 48–49°.

Anal. Found: N, 5.59; S, 13.22.

N-(2-Phenylmercapto-1,1-dimethylethyl)benzamide (II). *Via* **Oxazoline.**—A mixture of 59 g. (0.33 mole) of 2-phenyl-4,4-dimethyl-2-oxazoline and 37 g. (0.33 mole) of benzenethiol was heated at reflux under nitrogen at 150–180° for 11 hr. Distillation yielded 85 g. (89%) of product A; b.p. 193–188° (0.3–0.2 mm.), m.p. 80–82°; and 9.7 g. of forerun B. Recrystallization of B from hexane yielded 5.8 g. of material, m.p. 78–79°. The total yield was therefore at least 90.8 g. or 95%.

Anal. Calcd. for $C_{17}H_{19}NOS$: N, 4.91; S, 11.23. Found for A: N, 4.36, 4.68; S, 11.16, 11.16.

Recrystallization of A from hexane yielded material with m.p. 80–81°. The infrared spectrum had bands at 3.04 and 6.07 μ.

Anal. Found: N, 4.44, 4.44; S, 11.45, 11.50.

Via **Aziridine.**—2-Phenylmercapto-1,1-dimethylethylamine was prepared from 2,2-dimethylaziridine[9] by the method of Meguerian and Clapp.[5] It was obtained as a water-white liquid boiling at 114° (4 mm.). The reported b.p. is 104–104.5° (4 mm.).

Anal. Calcd. for $C_{10}H_{15}NS$: N, 7.73; S, 17.68; neut. equiv., 181.3. Found: N, 7.69; S, 17.67; neut. equiv., 182.9.

Benzoylation of 2-phenylmercapto-1,1-dimethylethylamine yielded material which, after recrystallization from hexane, melted at 80.5–81°.

This material was identical to that produced *via* the oxazoline as shown by mixture melting point (80.5–81°), infrared spectra, and analysis.

Anal. N, 4.67; S, 11.87, 11.30.

N-(2-*p*-Chlorophenylmercapto-1,1-dimethylethyl)propionamide. *Via* **Oxazoline.**—A mixture of 66.5 g. (0.52 mole) of 2-ethyl-4,4-dimethyl-2-oxazoline and 73.2 g. (0.50 mole) of *p*-chlorobenzenethiol was heated at reflux at 132–181° for 3 hr. The mixture solidified on cooling. Recrystallization from 3 l. of hexane yielded 124.2 g. (91%) of material with m.p. 47–48°. Further recrystallization yielded material for analysis, m.p. 52–53°. The infrared spectrum had bands at 3.06 and 6.10 μ.

Anal. Calcd. for $C_{13}H_{18}NOSCl$: N, 5.15; S, 11.80; Cl, 13.05. Found: N, 4.78; S, 12.03; Cl, 12.81.

Via **Aziridine.**—2-*p*-Chlorophenylmercapto-1,1-dimethylethylamine, b.p. 141–142° (4.0 mm.), was obtained by reaction of *p*-chlorobenzenethiol with 2,2-dimethylaziridine by a procedure analogous to that described for the phenylmercapto derivative.

Anal. Calcd. for $C_{10}H_{14}NSCl$: N, 6.49; neut. equiv., 215.7. Found: N, 6.73; neut. equiv., 218.8.

A solid product, m.p. 86.5–87.5°, also was obtained but not identified.

Propionylation of the amine with propionic anhydride yielded N-(2-*p*-chlorophenylmercapto-1,1-dimethylethyl)propionamide, m.p. 52–53°.

This product was identical to that prepared *via* the oxazoline as shown by mixture melting point (51.5–52.5°) and infrared spectra.

Anal. Found: N, 4.80.

N-(2-*p*-Chlorophenylmercapto-1,1-dimethylethyl)oleamide.—A mixture of 111.5 g. (0.33 mole) of 2-(8-heptadecenyl)-4,4-dimethyl-2-oxazoline and 48.2 g. (0.33 mole) of *p*-chlorobenzenethiol was heated at 160–179° for 6 hr. The residue was neutral. Distillation of a 142.2-g. portion of this residue yielded 121.2 g. (87%) of product, b.p. 227–273° (0.2 mm.). The infrared spectrum had bands at 3.04 and 6.06 μ.

Anal. Calcd. for $C_{28}H_{46}NOSCl$: N, 3.02; S, 6.91. Found: N, 3.09; S, 7.09.

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(5) G. Meguerian and L. B. Clapp, *J. Am. Chem. Soc.*, **73**, 2121 (1951).

(6) Boiling and melting points are uncorrected. Melting points were determined with a Fisher-Johns apparatus.

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(8) Commercial Solvents Corp.

(9) K. N. Campbell, A. H. Sommers, and B. K. Campbell, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p. 148.