

in the case of the trimethylbiphenylsilanes. As in this paper, these workers observed absorption at  $6.47 \mu$  resulting probably from *para*-substitution in unhindered biphenyls. This conclusion is supported by the data of Cannon and Sutherland<sup>14</sup> and others.<sup>25</sup>

Although Young and co-workers<sup>21</sup> noted a symmetrical splitting of the  $8.95 \mu$  band upon diphenyl substitution in polysiloxane chains, there is no such comparable branching in the spectra of diphenylsilanes of the present paper or in 1,1-diphenylalkanes.<sup>26</sup>

Absorption at  $9.91 \mu$  is characteristic of certain biphenyl compounds and seems to be due to stretching vibration in the ring-to-ring C-C bond. It ap-

(25) R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948).

(26) K. T. Serijan, I. A. Goodman and W. J. Yankauskas, National Advisory Committee for Aeronautics, Technical Note 2557, November, 1951.

pears at this wave length in *ortho*- or *para*-substituted biphenyl.<sup>14,24</sup>

The characteristic  $10.05 \mu$  band probably arises from benzene ring C-C stretching, although this mode is infrared inactive in more symmetrical compounds such as benzene itself. The same band has been reported as a characteristic phenyl frequency in trimethylphenylsilane.<sup>27</sup>

The bands at about  $13.5$ – $13.6$  and  $14.3 \mu$  appear to be due to C-H out-of-plane deformations associated with monosubstituted benzenes, whereas such vibrations cause absorption at  $12.0 \mu$  in *p*-disubstituted benzenes.<sup>14,28,29</sup>

(27) C. C. Cerato, J. L. Lauer and H. C. Beachell, *J. Chem. Phys.*, **22**, 5 (1954).

(28) D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 268 (1945).

(29) H. W. Thompson and P. Torkington, *Trans. Faraday Soc.*, **41**, 246 (1945).

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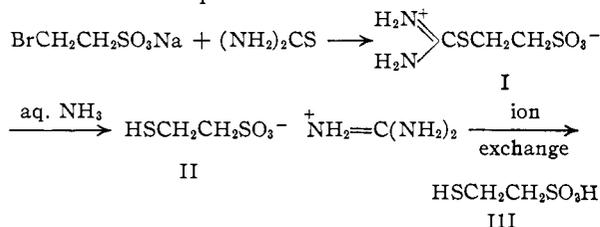
## The Synthesis of Mercaptoalkanesulfonic Acids

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2-Mercaptoethane-, 3-mercapto propane- and 4-mercaptobutanesulfonic acids and several salts of these acids have been synthesized. A series of new betaine-type compounds has been prepared and these products have been found to undergo a novel cleavage reaction with ammonium hydroxide.

The chemical literature describes the preparation of the gold-sodium salt,<sup>1</sup>  $\text{Au}(\text{SCH}_2\text{CH}_2\text{SO}_3\text{Na})_2$ , of 2-mercaptoethanesulfonic acid and an impure sample of the sodium salt,<sup>2</sup>  $\text{HSCH}_2\text{CH}_2\text{SO}_3\text{Na}$ . The use of the sodium salt as a chemical intermediate has been mentioned in two patents.<sup>3</sup> However, there are no published data relative to the preparation of pure  $\omega$ -mercaptoalkanesulfonic acids or their salts. This paper describes the first practical synthesis<sup>4</sup> of these compounds which were prepared by the following reactions, using the ethane derivative as an example



Sodium 2-bromoethanesulfonate<sup>5</sup> was allowed to react under carefully controlled conditions with thiourea to yield the internal salt, 2-S-thiuronium ethanesulfonate (I). The thiuronium compound was

(1) A. Lumiere and F. Perrin, *14me Congr. Chim. Ind. Paris*, (October, 1934); *C. A.*, **29**, 5990 (1935).

(2) I. M. Lipovich, *J. Applied Chem. (U.S.S.R.)*, **18**, 718 (1945).

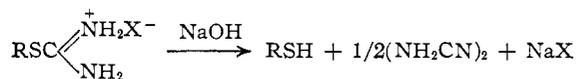
(3) Henkel and Cie, German Patent 619,299 (1935); *C. A.*, **30**, 1386 (1936); A. Kirstahler and W. J. Kaiser, German Patent 644,275 (1937); *C. A.*, **31**, 5383 (1937).

(4) U. S. Patent 2,695,310, Nov. 23, 1954.

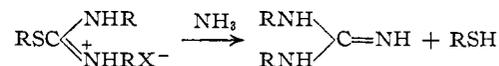
(5) C. S. Marvel and M. S. Sparberg in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 558.

recrystallized from water from which it was obtained as a hard, white crystalline solid. It was insoluble in organic solvents and did not possess a sharp melting point but decomposed slowly upon heating to  $265^\circ$ . These characteristically ionic features helped to verify the above assigned structure of this compound. It appears that this is the first time that compounds of this type have been prepared.

Thiuronium compounds are readily converted into mercaptans by treatment with sodium hydroxide.<sup>6</sup>



Although the betaine-type compounds, the thiuronium alkanesulfonates, can be cleaved readily by this method, a pure product is not obtained since the dicyandiamide (or a product derived therefrom) cannot be removed readily from the reaction mixture. Substituted guanidine compounds have been prepared by the reaction of N-alkyl isothiureas with ammonia,<sup>7</sup> *i.e.*



However, as far as it is known, it seems that this reaction has never been used in the synthesis of mercaptans, nor is there any published record of re-

(6) G. G. Urquhart, J. W. Gates and R. Conmoc, *Org. Syntheses*, **21**, 36 (1941).

(7) B. Rathke, *Ber.*, **14**, 1774 (1881); **17**, 297 (1884); G. Noah *ibid.*, **23**, 2195 (1890); H. Lecher and F. Graf, *ibid.*, **56**, 1326 (1923).



controlled to give a final temperature of 60–65°. The flask was swirled gently during the course of the reaction. After standing for two hours at room temperature, vacuum was applied and the solution was concentrated to dryness. The white guanidinium 2-mercaptoethanesulfonate was obtained in 98% (214 g.) yield. The product after recrystallization from ethyl alcohol melted at 169–172°.

*Anal.* Calcd. for  $C_3H_{11}N_3O_3S_2$ : C, 17.91; H, 5.51; N, 20.89; S, 31.88. Found: C, 18.33; H, 5.67; N, 20.89; S, 31.58.

Pure guanidinium 2-mercaptoethanesulfonate is moderately stable to air oxidation. It can be recrystallized readily and it is possible to obtain a 99% SH value (iodine titration) for material so handled. The presence of guanidinium ion was verified by the precipitation of guanidinium nitrate from solutions of the mercaptoethanesulfonate when nitrate ion was added. A mixed melting point determination with an authentic sample of guanidinium nitrate showed no depression.

**2-Mercaptoethanesulfonic Acid.**—One hundred grams of guanidinium 2-mercaptoethanesulfonate (as a 2 *M* solution) was processed through a column of polystyrene-sulfonate ion exchange resin (Amberlite IR-120) operating in its acid cycle. Vacuum concentration of the aqueous effluate gave 68 g. (96% yield) of the highly viscous 2-mercaptoethanesulfonic acid. This acid proved to be a rather unstable entity and its decomposition was evidenced by the development of a hydrogen sulfide odor on standing. The purity of the material was checked by both acid and mercaptan titrations. Neutralization with guanidinium carbonate reconverted the acid to the guanidinium salt. Other salts (sodium, ammonium, etc.) were readily made by neutralization with the proper base.

**N-Carbamyl 2-S-Thiuronium Ethanesulfonate.**—This compound was isolated from acidic solutions (1–2 *M*) of 2-mercaptoethanesulfonic acid from which it was deposited in 1–4 days. It was recrystallized from water in which it was found to be more insoluble than the thiuronium salt. The compound melted with decomposition at 268–269°.

*Anal.* Calcd. for  $C_4H_9N_3O_4S_2$ : C, 21.14; H, 3.99; N, 18.49; S, 28.22. Found: C, 21.33; H, 4.30; N, 18.29; S, 27.85.

**Guanylurea Salt of 2-Mercaptoethanesulfonic Acid.**—Ten grams of N-carbamyl 2-S-thiuroniumethanesulfonate was heated with 50 cc. of ammonium hydroxide for four hours at 70°. Another 50 cc. of ammonia was added and heating was continued for two hours more. Concentration of the aqueous solution afforded 11 g. of the guanylurea salt which was recrystallized from ethyl alcohol, m.p. 146–148°.

*Anal.* Calcd. for  $C_4H_{12}N_4O_4S_2$ : C, 19.67; H, 4.95; N, 22.94; S, 26.25. Found: C, 19.88; H, 5.18; N, 23.22; S, 26.00.

**3-S-Thiuronium Propanesulfonate.**—One hundred fifty-five grams (0.98 mole) of 1-bromo-3-chloropropane was stirred and refluxed for 1.5 hours with 100 g. (0.79 mole) of sodium sulfite in 1200 cc. of 50% ( $H_2O$ ) ethyl alcohol. The solution was then concentrated to 300 cc. and used directly in the next reaction. To this concentrate there was added 49 g. (0.64 mole) of thiourea and the mixture was refluxed for 0.5 hour. Upon cooling, 74 g. of crystals was obtained. The mother liquors were allowed to stand overnight and this yielded an additional 40 g. of crystals. These were recrystallized from water and combined with the first crop. Recrystallization from water afforded 64 g. (41% yield based on sodium sulfite) of the halogen-free thiuronium salt, m.p. 254–257°.

*Anal.* Calcd. for  $C_4H_{10}O_3S_2N_2$ : C, 24.23; H, 5.08; N, 14.13. Found: C, 24.34; H, 5.15; N, 14.10.

**Guanidinium 3-Mercaptopropanesulfonate.**—This compound was prepared from 3-S-thiuroniumpropanesulfonate by the same method as used for the ethane compound; melting point after recrystallization from chloroform-*n*-propyl alcohol, 112–114°.

*Anal.* Calcd. for  $C_4H_{13}O_3S_2N_3$ : C, 22.31; H, 6.09; N, 19.52. Found: C, 22.47; H, 5.84; N, 19.21.

**Potassium 4-Chlorobutanesulfonate.**—A mixture of 254 g. (2.0 moles) of 1,4-dichlorobutane and 109 g. (0.69 mole) of potassium sulfite in 2.5 liters of ethyl alcohol and 1.4 liters of water was refluxed and stirred for 12.5 hours. The solution was concentrated in vacuum until it weighed 260 g. The precipitate which formed was removed by filtration. The residual solution now weighed 217 g.; yield of potassium 4-chlorobutanesulfonate by organic halogen analysis, 50%.

**4-S-Thiuronium Butanesulfonate.**—Thirty grams (0.39 mole) of thiourea was added to the solution described in the preceding paragraph. The reaction mixture was heated to boiling and the water which distilled was collected (*ca.* 60 cc.). When the solution was cooled, 96 g. of crystals were obtained and these were recrystallized from 90 cc. of water to yield 53 g. of product containing 2.4% potassium chloride; yield 35% based on potassium sulfite, m.p. after three recrystallizations 268–269°.

*Anal.* Calcd. for  $C_5H_{12}O_3S_2N_2$ : C, 28.29; H, 5.70; N, 13.20. Found: C, 28.46; H, 5.89; N, 13.32.

**Guanidinium 4-Mercaptobutanesulfonate.**—4-S-Thiuronium butanesulfonate was converted into guanidinium 4-mercaptobutanesulfonate according to the procedure used for the ethane salt. The compound could be recrystallized from ethylene chloride-*n*-propyl alcohol mixtures but it did not have a sharp melting point.

*Anal.* Calcd. for  $C_5H_{15}O_3S_2N_3$ : C, 26.19; H, 6.59; N, 18.32. Found: C, 26.70; H, 6.57; N, 17.98.

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