EXPERIMENTAL

2-Fluoroethanol was prepared in 50% yield from ethylene chlorohydrin and potassium fluoride by ultraviolet irradiation as described by Oláh and Pavláth.[13]

2-Fluoroethyl chloroformate was prepared in 72% yield by the method of Oláh and Pavláth.[4]

General procedures for the preparation of the 2-fluoroethylurethan derivatives. (A). A 0.1-mole portion of the amine was dissolved in 40 ml. of absolute ethyl ether in a three-necked round-bottomed flask fitted with a reflux condenser, a mechanical stirrer, and a dropping-funnel; then 6.32 g. (0.05 mole) of 2-fluoroethyl chloroformate was slowly dropped on to the ice cooled solution. The stirring was continued for an hour after which time the precipitated amine hydrochloride was filtered. The ether was removed by distillation and the remaining oil was fractionated *in vacuo.* If crystalline the product was recrystallized from hexane.

(B). A 0.1-mole portion of the amine was dissolved in a solution of 4.8 g. (0.12 mole) of sodium hydroxide in 25 ml. of water. The resultant solution was cooled in an ice-water bath and efficiently stirred while 12.65 g. (0.1 mole) of 2-fluoroethyl chloroformate was dropped into the mixture. Stirring was continued without further cooling for 2 hr. The 2-fluoroethylurethan formed was extracted with ether, the ether was evaporated, and the residue was fractionated *in vacuo.* In the case of crystalline products the substances were recrystallized from hexane.

(C). A 0.1-mole portion of the amine was dissolved in 25 ml. of benzene and 6.32 g. (0.05 mole) of 2-fluoroethyl chloroformate was added; the reaction then was continued and worked up as under (A).

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[13] G. Oláh and A. Pavláth, *Acta Chim. Acad. Sci. Hung.*, 3, 199 (1953) [*Chem. Abstr.*, 48, 7533 (1954)].

Synthesis from Thiolacetates. I. Synthesis of Alkanesulfonyl Chlorides[1]

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Received September 11, 1956

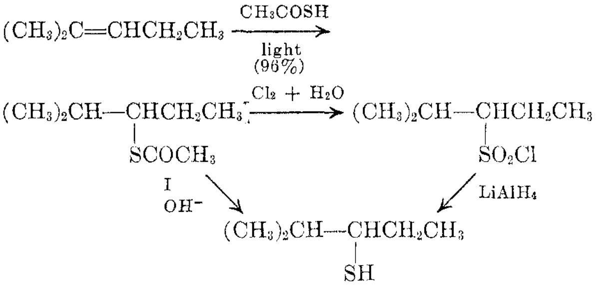
The reaction of thiolacetic acid with olefins has been found to be generally applicable, and to give high yields of thiolacetates.[2] Hydrolysis of these thiolacetates provides an excellent route for the synthesis of thiols.[2] Oxidative chlorination of thiolacetates is utilized herein as a route to the preparation of alkanesulfonyl chlorides from olefins.

Douglass and Johnson included two thiolesters in their general study of the oxidative chlorination of divalent sulfur compounds.[3] They obtained a 71% yield of ethanesulfonyl chloride from ethyl thiolacetate and a mixture of benzyl disulfide, benzyl phenylmethanethiosulfonate, and phenylmethanesulfonyl chloride from benzyl thiolacetate.

In the present study the thiolacetates were prepared in yields of 92–96% from 4-methyl-1-pentene, 2-methyl-2-pentene, and cyclohexene. Oxidative chlorination of these thiolacetates by the method of Douglass and Johnson[3] gave 77%, 62%, and 72% yields of the corresponding sulfonyl chlorides.

The method is, therefore, applicable to the preparation of primary, secondary, and cycloalkanesulfonyl chlorides from the olefins in overall yields of 58–71%. Compounds in which the sulfur atom is attached to a secondary carbon atom appear not to have been subjected to oxidative chlorination of this type before.

The addition of thiolacetic acid to olefins occurs exclusively in an anti-Markownikoff manner,[2b] so the sulfonyl chlorides prepared from them should be of high purity. Their structures should correspond to those of the thiolacetates. However, to make certain that rearrangement does not accompany the oxidative chlorination of thiolacetates to sulfonyl chlorides, the sulfonyl chloride from 1-ethyl-2-methylpropyl thiolacetate (I) was reduced with lithium aluminum hydride to the thiol. The 2,4-dinitrophenyl sulfide derivative of this thiol was found to be identical with that obtained from the thiol prepared from the original thiolacetate. Since rearrangement is more likely to occur with a secondary thiolacetate having a tertiary hydrogen on an alpha carbon, such as I, than for other types of thiolacetates it seems safe to conclude that rearrangements will not often occur in this reaction.



2-Phenyl-1-propanesulfonyl chloride was prepared by oxidative chlorination of 2-phenylpropyl thiolacetate with the purpose of synthesizing 2-methyl-2,3-dihydrobenzothiophene-1-dioxide from it by ring closure. This is potentially a route to cyclic sulfones of this type from styrenes, but Friedel-Crafts type ring closures were unsuccessful in our hands in this instance.

EXPERIMENTAL[4]

1-Ethyl-2-methylpropyl thiolacetate Thiolacetic acid (Eastman Kodak Co., practical grade) was purified by distillation prior to use. One hundred fifty-two and two-tenths

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[1] This investigation was carried out as part of American Petroleum Institute Research Project 48B, given in part at the 126th Meeting of the AMERICAN CHEMICAL SOCIETY, New York, N. Y., September 1954 (p. 6-0 of Abstracts).

[2] (a) The first report of this reaction was B. Holmberg, *Arkiv. Kemi, Mineral Geol.*, 12B, No. 47, 3 (1938). (b) The literature concerning this reaction, together with numerous further examples, may be found in the Ph.D. dissertation of W. A. Hewett, Northwestern University, August 1955.

[3] I. B. Douglass and T. B. Johnson, *J. Am. Chem. Soc.*, 60, 1486 (1938).

[4] Microanalyses were by Miss Hilda Beck.

grams (2 moles) of thiolacetic acid was added slowly with stirring to 336.6 g. (4 moles) of 2-methyl-2-pentene (95% mol. % minimum, Phillips Petroleum Co , Special Products Division, Bartlesville, Okla.). The reaction mixture was irradiated during the addition with light from a 100 watt bulb,[5] and irradiation and stirring were continued for 1 hr. after addition of the thiolacetic acid was complete. Distillation of the reaction mixture yielded 308.5 g. (96.2%) of 1-ethyl-2-methylpropyl thiolacetate, b.p. 70° (13 mm.), n_D^{25} 1.4603.

Anal. Calcd. for $C_8H_{16}OS$: C, 59.95; H, 10.06. Found: C, 60.46; H, 10.12.

1-Ethyl-2-methylpropanethiol. Three hundred five grams (1.92 moles) of 1-ethyl-2-methylpropyl thiolacetate was refluxed for 1 hr. in 2.5 l. of 10% aqueous-alcoholic (50% by volume) potassium hydroxide solution. The solution was neutralized with glacial acetic acid and the non-aqueous phase separated. The aqueous portion was extracted three times with pentane and the pentane extracts were dried over anhydrous magnesium sulfate. The combined non-aqueous phase and pentane extracts were distilled giving 203 g. (90.5%) 1-ethyl-2-methylpentanethiol, b.p. 135°, n_D^{25} 1.4467.

Anal. Calcd. for $C_6H_{14}S$: C, 60.95; H, 11.93. Found: C, 61.46; H, 11.75.

The 2,4-dinitrophenyl sulfide derivative of the pure thiol was prepared according to the method of Bost, Turner, and Morton.[6] The sulfide melted at 60–60.5° after crystallization from absolute alcohol.

Anal. Calcd. for $C_{12}H_{16}O_4N_2S$: N, 9.85. Found: N, 10.13.

4-Methyl-1-pentyl thiolacetate. Starting with 200 g. (2.38 moles) of 4-methyl-1-pentene (95% mol. % minimum, Phillips Petroleum Co., Special Products division, Bartlesville, Okla.) and 121.2 g. (1.59 moles) of thiolacetic acid, 238 g. (93.5%) of 4-methyl-1-pentyl thiolacetate, b.p. 89° (16 mm.), n_D^{25} 1.4575, was obtained by the procedure described above.

Anal. Calcd. for $C_8H_{16}OS$: C, 59.95; H, 10.06. Found: C, 60.55; H, 9.56.

Cyclohexyl thiolacetate. This compound was prepared in 92.5% yield by the method described above. The boiling point of this compound was 77° (5.8 mm.). Cunneen[7] reported b.p. 90° (14 mm.).

2-Phenyl-1-propyl thiolacetate. This compound was prepared in 90% yield by the method described above. The boiling point of this compound was 105–107° (1.8 mm.). Brown, Jones, and Pinder[8] reported b.p. 105° (4 mm.).

1-Ethyl-2-methylpropanesulfonyl chloride. Twenty grams (0.12 mole) of 1-ethyl-2-methylpropyl thiolacetate, suspended in water, was chlorinated at 0°, and the product processed according to the procedure of Douglass and Johnson.[3] Distillation through a 3-plate Vigreux column yielded 14.8 g. (62%) of 1-ethyl-2-methylpropanesulfonyl chloride, b.p. 70–75° (2 mm.), n_D^{25} 1.4651.

Anal. Calcd. for $C_6H_{13}O_2SCl$: C, 39.23; H, 7.13. Found: C, 39.03; H, 6.72.

Lithium aluminum hydride reduction of 2-methyl-3-pentanesulfonyl chloride. Nine grams (0.05 mole) of 1-ethyl-2-methylpropanesulfonyl chloride in 25 ml. of dry ether was added slowly with stirring to a slurry of 5.7 g. (0.15 mole) of lithium aluminum hydride in 200 ml. of dry ether. After stirring and heating on the steam bath for an additional 2 hr., the excess lithium aluminum hydride was destroyed by addition of 250 ml. of 10% sulfuric acid. The non-aqueous layer was separated and the aqueous layer was extracted three times with 50 ml. portions of ether. The ether extracts and the non-aqueous layer combined and the ether distilled. Steam distillation of the residue gave 2 g. (30%) of crude 2-methyl-3-pentanethiol. The 2,4-dinitrophenyl sulfide derivative, prepared according to the method of Bost, Turner, and Morton,[6] melted at 60–61° after crystallization from alcohol. The melting point of a mixture with a comparable derivative, prepared from the thiol resulting from hydrolysis of 2-methyl-3-pentyl thiolacetate, was not depressed.

Other alkanesulfonyl chlorides. In a manner similar to that described above 17.5 g. (77%) of *4-methyl-1-pentanesulfonyl chloride*, b.p. 84° (2.5 mm.), n_D^{25} 1.4550, was obtained from 20 g. of 4-methyl-1-pentyl thiolacetate.

Anal. Calcd. for $C_6H_{13}O_2SCl$: C, 39.23; H, 7.13. Found: C, 38.97, 38.79; H, 6.63, 6.74.

A 72% yield of cyclohexanesulfonyl chloride, b.p. 70° (0.5 mm.), n_D^{25} 1.4958, was obtained from cyclohexyl thiolacetate. Borsche and Lange[9] reported a b.p. of 127–128° (15 mm.), and an anilide melting at 87°. The anilide prepared from our sulfonyl chloride melted at 85–85.5° (uncorr.).

A 54% yield of *2-phenyl-1-propanesulfonyl chloride*, b.p. 126° (2 mm.), was obtained from 2-phenyl-1-propyl thiolacetate.

Anal. Calcd. for $C_9H_{11}O_2SCl$: C, 49.42; H, 5.07. Found: C, 50.05, 50.07; H, 4.91, 5.03.

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(5) In most cases visible light is sufficient to initiate the reaction; in some cases, however, peroxides and heating on a water bath or in a bomb are required to increase the yield. Ref. (2) (b) in text.

(6) R. W. Bost, J. O. Turner, and R. D. Morton, *J. Am. Chem. Soc.*, **54**, 1985 (1932).

(7) J. I. Cunneen, *J. Chem. Soc.*, 134 (1947).

(8) R. Brown, W. E. Jones, and A. R. Pinder, *J. Chem. Soc.*, 2123 (1951).

(9) W. Borsche and W. Lange, *Ber.*, **38**, 2767 (1905).

Conversion of Steroidal Alkaloids, Tomatidine and Solasodine into Dihydrosapogenins

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Received January 2, 1957

The elegant work of White[1] on the deamination of aliphatic amines prompted us to apply his method to the deamination of the steroidal alkaloids, tomatidine (I) and solasodine (II).

Accordingly, I and II were converted to their respective *O,N*-diacetyl-22,*N*-dihydro and *O,N*-diacetyl-5,6,22,*N*-tetrahydro derivatives[2] (Ia), (IIa) and treated with nitrogen tetroxide to give the corresponding *N*-nitrosoamides, Ib and IIb. Upon subjecting these crude *N*-nitroso derivatives to thermal deamination and hydrolyzing the resulting diacetates with methanolic alkali, nitrogen free products were obtained. Chromatography on alumina yielded dihydroneotigogenin[3] (Ic) (from tomatidine) and dihydrotigogenin (IIc)(from solasodine) in moderate yields. The deaminated prod-

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(1) E. H. White, *J. Am. Chem. Soc.*, **77**, 6008, 6011, 6014 (1955).

(2) Y. Sato and H. G. Latham, Jr., *J. Am. Chem. Soc.*, **78**, 3150 (1956).

(3) The authors are indebted to Dr. Callow of the National Institute for Medical Research, London, for a generous gift of neotigogenin acetate.