Methanesulfenyl Chloride. IV. The Reaction of Sulfenyl Chlorides with Alkyl Xanthates and Trimethyl Thionophosphate[1]

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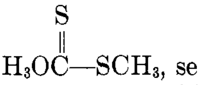
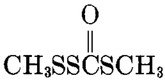
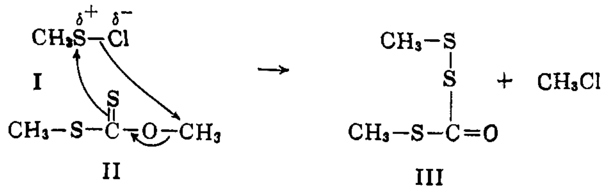
Methanesulfenyl chloride (I) reacts with O,S-dimethyl xanthate (II) by a mechanism which is apparently an electrophilic attack at the thiocarbonyl sulfur atom to form 2,3,5-trithiahexanone-4 (III) and methyl chloride. I also reacts with S-methyl O-*n*-propyl xanthate to form III and *n*-propyl chloride. Benzenesulfenyl chloride and trichloromethanesulfenyl chloride react with II to form methyl chloride and, respectively, 1-phenyl-1,2,4-trithiapentanone-3 and 1,1,1-trichloro-2,3,5-trithiahexanone-4. I reacts with trimethyl thionophosphate to liberate methyl chloride and to form S-methylsulfenyl O,O-dimethyl thiolphosphate.

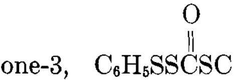
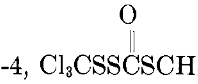
The ability of methanesulfenyl chloride (I) to react with various types of organic molecules in a manner suggesting electrophilic attack has been reported in previous publications.[3] In considering other types of molecules to use as substrates for reaction with I, O,S-dimethyl xanthate (II),  $CH_3O\overset{S}{\overset{\|}{C}}{-}SCH_3$, seemed of interest since it has three different sites at which electrophilic attack might occur—the alkoxy oxygen, the thiono sulfur, and the thiol sulfur.

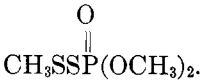
Reaction between I and II took place readily with the liberation of methyl chloride and the formation of a yellow oil. Purification of the latter gave a colorless product, the analysis of which corresponded to 2,3,5-trithiahexanone-4 (III),  $CH_3SS\overset{O}{\overset{\|}{C}}SCH_3$, suggesting that attack had occurred at the thiono sulfur atom, according to the following equation.

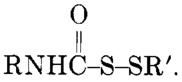


The reaction between I and S-methyl O-*n*-propyl xanthate also took place readily with the formation of III and 1-chloropropane. There seems little doubt concerning the structure of III since it shows a strong infrared absorption in the carbonyl region whereas the spectra of both II and S-methyl O-*n*-propyl xanthate showed none. In addition, both xanthate esters show strong absorption in the 1220-cm.$^{-1}$ region indicative, according to Bellamy,[4] of a thiocarbonyl in dimethyl thiocarbonate and dithioacetic acid. This thiocarbonyl absorption band is missing in III and in the trithia ketones formed when trichloromethanesulfenyl and benzenesulfenyl chlorides react with II.

Special mention should be made of the absence of a carbonyl absorption band in the xanthate esters studied, for II was found to isomerize readily into S,S-dimethyl dithiolcarbonate in the presence of methyl sulfate. Preparations of II made with the latter reagent showed carbonyl adsorption. The conversion of xanthate esters to dithiolcarbonates had been reported previously,[5] but no reference has been found to the problem the isomerization causes in preparing pure xanthate esters.

Benzenesulfenyl chloride and trichloromethanesulfenyl chloride react with II in an analogous manner forming methyl chloride and, respectively, 1-phenyl-1,2,4-trithiapentanone-3,  $C_6H_5SS\overset{O}{\overset{\|}{C}}SCH_3$, and 1,1,1-trichloro-2,3,5-trithiahexanone-4,  $Cl_3CSS\overset{O}{\overset{\|}{C}}SCH_3$. The latter compound is isomeric with the product prepared by the reaction of trichloromethanesulfenyl chloride with an alkali salt of methyl xanthate.[6,7]

One extension of the reaction to other types of thiono esters was carried out. Trimethyl thionophosphate reacted readily with I to yield methyl chloride and a product the analysis of which corresponded to O,O-dimethyl S-methylsulfenyl thiolphosphate,  $CH_3SS\overset{O}{\overset{\|}{P}}(OCH_3)_2$.

The reaction of sulfenyl chlorides with compounds containing thiocarbonyl groups to form disulfido products is not entirely new. Margot and Gysin[8] treated benzenesulfonylthioureas with trichloromethanesulfenyl chloride (V) and obtained compounds of the type $RSO_2NHC(SSCCl_3)NR'$. In an analogous reaction, Harris[9] found that alkyl thionocarbamate esters react with sulfenyl chlorides to split out alkyl chlorides and form alkyl or aryl carbamoyl disulfides of the type  $RNH\overset{O}{\overset{\|}{C}}{-}S{-}SR'$. When the reaction was carried out in the presence of a tertiary amine, like pyridine, the product was a dithioformamidic ester, $RN{=}C(OR')$-SSR''.

Experimental

Preparation of Xanthate Esters.—O,S-Dimethyl xanthate (II) was prepared by treating a methanol solution of potassium methyl xanthate with methyl iodide below 40°. After standing overnight the reaction mixture was diluted with water and the crude xanthate ester was separated, dried, and distilled. The purified

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[1] Taken from the Master's thesis of William J. Evers, 1962.

[2] National Defense Education Act, Title IV Fellow, 1960-1962.

[3] I. B. Douglass and D. A. Koop, *J. Org. Chem.*, **27**, 1398 (1962), and prior publications.

[4] L. J. Bellamy in "Organic Sulfur Compounds," Vol. I, N. Kharasch, Ed., Pergamon Press, London, 1961, p. 52.

[5] E. Biilmann and J. Bjerrum, *Ber.*, **50**, 503 (1917).

[6] R. S. Hawley and A. R. Kittleson, U. S. Patent 2,553,777 (May 22, 1951); *Chem. Abstr.*, **45**, 7742*i* (1951).

[7] V. Ettel and M. Zbirovsky, *Chem. Listy*, **50**, 670 (1956); *Chem. Abstr.*, **50**, 8513*f* (1956).

[8] A. Margot and H. Gysin, U. S. Patent 2,813,902 (November 19, 1957); *Chem. Abstr.*, **52**, 7349*f* (1958).

[9] J. F. Harris, Jr., *J. Am. Chem. Soc.*, **82**, 155 (1960).

product boiled at 66–68° (21 mm.) and had $n^{25}\mathrm{D}$ 1.5655 and d^{0}_{4} 1.2045, d^{24}_{4} 1.1804. The compound showed no infrared absorption in the carbonyl region but absorbed strongly at 1070, 1090, 1160, 1220, and 1435 cm.$^{-1}$, and more weakly at 975 cm.$^{-1}$. Earlier attempts to prepare the compound from equivalent amounts of methyl sulfate and potassium methyl xanthate led to a product contaminated with unchanged methyl sulfate from which it could not be separated by distillation. The methyl sulfate also catalyzed the conversion of the xanthate to the isomeric S,S-dimethyl dithiolcarbonate. Such preparations always showed infrared absorption in the carbonyl region and slowly formed glistening crystals on standing.

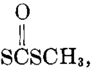
A preparation of II containing residual methyl sulfate was refluxed for 28 hr. at atmospheric pressure and was completely converted to S,S-dimethyl dithiolcarbonate boiling at 169° (760 mm.) or 75–76° (29 mm.) and having $n^{24}\mathrm{D}$ 1.5461 and d^{0}_{4} 1.2128, d^{24}_{4} 1.1878 [lit.[10] b.p. 169° (760 mm.), $n^{17.5}\mathrm{D}$ 1.5504, and $d^{17.5}_{4}$ 1.1913]. Its infrared spectrum showed strong absorption at 870, 970, and 1640 cm.$^{-1}$ and moderately strong absorption at 1045, 1310, 1420, 1740, and 2900 cm.$^{-1}$. The spectrum was identical with that of a specimen prepared by the reaction of methyl chlorothiolformate with methyl mercaptan.

S-Methyl O-*n*-propyl xanthate was prepared by the action of methyl iodide on a solution of potassium *n*-propyl xanthate. The product boiled at 92–94° (15 mm.) and had $n^{20}\mathrm{D}$ 1.5375 [lit.[11] b.p. 201–203° (760 mm.), $n^{20}\mathrm{D}$ 1.53789]. Its infrared spectrum showed strong absorption peaks at 1065 and 1220 cm.$^{-1}$ and weak absorption at 925, 970, 1110, 1145, 1320, 1345, 1380, 1420, 1465, and 2950 cm.$^{-1}$, but no absorption in the region 1500–2000 cm.$^{-1}$.

Methanesulfenyl chloride was prepared by the method previously described.[12]

Benzenesulfenyl chloride was prepared by the method of Morrison.[13] The trichloromethanesulfenyl chloride was a sample of "perchloromethyl mercaptan," obtained from the Stauffer Chemical Company, and was used as received.

Reaction of Sulfenyl Chlorides with Xanthate Esters.—A pure sample of O,S-dimethyl xanthate (II, 48.4 g., 0.4 mole), contained in a three-necked reaction flask equipped for stirring and fitted with reflux condenser and outlet leading to a Dry Ice trap, was treated slowly with I (34.2 g., 0.4 mole) at −40° to −50°. When addition was complete, the mixture was allowed to warm to room temperature and was then heated to 80° to drive off volatile matter. The residue consisted of 41 g. of yellow liquid. From the cold trap 19 g. of colorless liquid was recovered which, after bubbling through sodium hydroxide solution and recondensing, gave an infrared spectrum identical with that of methyl chloride. The recovered yield was 95%.

A thin layer chromatograph of the yellow residue in the reaction flask indicated three substances were present. Two, which moved more rapidly on the plate, were present only in minor proportions and remain unidentified. The principal product was isolated by column chromatography on silicic acid using *n*-hexane as eluent. Chromatography of a 6.0-g. portion of the yellow liquid residue gave 4.2 g. (46% over-all yield) of 2,3,5-trithiahexanone-4,  $\mathrm{CH_3SS\overset{\overset{O}{\|}}{C}SCH_3}$, having $n^{28}\mathrm{D}$ 1.5934.

Anal. Calcd. for $C_3H_6OS_3$: C, 23.36; H, 3.92; S, 62.36. Found: C, 23.62; H, 3.95; S, 62.46.

The infrared spectrum showed strong absorption of 840, 885, 1640, and 1705 cm.$^{-1}$ and moderate absorption at 960, 1310, and 1415 cm.$^{-1}$.

In similar manner the reaction between I and S-methyl O-*n*-propyl xanthate yielded *n*-propyl chloride (identified by its boiling point, refractive index, and infrared spectrum, which was identical with Sadtler Standard Spectrogram 193) and 30 g. of a yellow, liquid residue. Chromatography of a 3.5-g. portion of the latter gave 1.6 g. of colorless product having $n^{24}\mathrm{D}$ 1.5914 and an infrared spectrum identical with that of the 2,3,5-trithiahexanone-4 previously obtained.

Benzenesulfenyl chloride (14.5 g., 0.1 mole) was added dropwise with stirring to 12.2 g. (0.1 mole) of O,S-dimethyl xanthate at −20°. Further treatment, as previously described, led to the recovery and identification of methyl chloride in 57% yield and 21.6 g. of a liquid residue. Chromatography of a 4.0-g. portion of the latter gave 3.06 g. of colorless product, which after rechromatographing had $n^{25}\mathrm{D}$ 1.6478, d^{0}_{4} 1.315, and d^{25}_{4} 1.294, and showed strong absorption peaks at 685, 745, 835, 885, 1640, and 1705 cm.$^{-1}$ and weaker absorption peaks at 975, 1025, 1315, 1440, and 1480 cm.$^{-1}$. The over-all yield was 76%.

Anal. Calcd. for $C_8H_8OS_3$: C, 44.41; H, 3.72; S, 44 47. Found: C, 44.73; H, 4.24; S, 44.53.

Trichloromethanesulfenyl chloride (18.6 g., 0.1 mole) reacted with II (12.2 g., 0.1 mole) at 30° over a 30-min. period to yield methyl chloride (3.4 g., 67%), isolated and identified as described above, and 25.8 g. of liquid residue. Chromatography of 4.0 g. of residue yielded 3.5 g. of material which thin layer chromatography indicated to be a single component. The recovered pure product corresponded to an 87% over-all yield. Rechromatographing gave an analytical sample having $n^{25}\mathrm{D}$ 1.6118, d^{0}_{4} 1.563 and d^{25}_{4} 1.532, and showing strong infrared absorption at 750, 770, 790, 830, 880, 1650, and 1720 cm.$^{-1}$ and much weaker bands at 970, 1315, and 2350 cm.$^{-1}$. The analysis corresponds to 1,1,1-trichloro-2,3,5-trithiahexanone-4.

Anal. Calcd. for $C_3H_3Cl_3S_3O$: C, 13.98; H, 1.17; S, 37.34; Cl, 41.29. Found: C, 14.30; H, 1.43; S, 37.50; Cl, 41.20.

The Reaction of I with Trimethyl Thionophosphate.—Trimethyl thionophosphate (31.2 g., 0.2 mole), prepared by the reaction of trimethyl phosphite with sulfur after the method of Pistschimuka,[14] was treated with I (17.1 g., 0.2 mole) in the usual manner at −20°. Methyl chloride in 53% yield was isolated and identified as described, and the residue was chromatographed on silicic acid, using 2:1 petroleum ether–benzene as eluent. When the fast-moving yellow band had been removed from the column the main product was purified, using as eluent a mixture of 8% ether in benzene. Rechromatographing gave an analytical sample having $n^{30}\mathrm{D}$ 1.5103 and corresponding on analysis to S-methylsulfenyl O,O-dimethyl thiolphosphate.

Anal. Calcd. for $C_3H_9O_3PS_2$: C, 19.15; H, 4.82; S, 34.07; P, 16.46. Found: C, 19.32; H, 4.75; S, 34.08; P, 16.52.

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[10] M. Delepine, *Ann. chim. phys.*, [8] **25**, 529 (1912).

[11] M. Delepine, *Bull. soc. chim. France*, **7**, 404 (1910); *Chem. Abstr.*, **4**, 2302 (1910).

[12] I. B. Douglass, *J. Org. Chem.*, **24**, 2004 (1959).

[13] D. C. Morrison, *J. Am. Chem. Soc.*, **77**, 181 (1955).

[14] P. Pistschimuka, *Russ. J. Phys. Chem. Soc.*, **44**, 1406 (1913); *Chem. Abstr.*, **7**, 987 (1913).