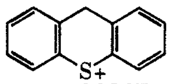

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Hz) with integrated intensities of 12:112:50, respectively. The low-field multiplet and the single line are clearly the spectrum of **3** although two "extraneous" singlets occur within the multiplet. The upfield multiplet is assigned to six of the hydrogens of thioxanthone (**6**), the "extraneous" peaks within the multiplet of **3** account for the remaining two protons. Thus 17 (one-third of 50) of the 112 are assignable to **6**. The resulting ratio of integrated intensities (12:95 and 17:50) is consistent with the assigned structures and indicates the ratio of **3** to **6** to be 1.4:1.

The origin of **6** may rest in the disproportionation of **4** to **6** and to thioxanthene (**8**).[8] This is supported by the nmr spectrum of the (red) solution which results when **8** is dissolved in TFAA; the spectrum is that of **3**. No resonance which could be readily assigned to the methine proton of the trifluoroacetate of **4** was observed in solutions of **4** in TFAA.

Shine[6] has suggested that both **4** and **5** would behave in the same manner in 80% sulfuric acid; however, this was not observed in either TFA or TFAA.

Experimental Section

Nmr Spectra.—All of the nmr spectra that have been cited were obtained on a Varian Model A-60 except for those of **4**, **6**, and **8** in TFAA which, for solubility reasons, were obtained on a Varian Model HA-100. Chemical shifts are reported in hertz at 60 MHz downfield from external TMS. Integrated intensities are consistent with the assigned structures. The nmr spectra (deuteriochloroform) of **1**, **2**, and the corresponding acetates have already been discussed.[4]

Compounds.—The preparation and characterization of all of the compounds employed in this study are extant in the literature.[3,4,6]

Reaction of Thioxanthenol Sulfoxide (1) with TFAA.—A mixture (*ca.* 1:1) of *cis* and *trans* **1** (0.116 g) was dissolved in 0.3 ml of TFAA. The resulting solution soon developed a red-brown color and later deposited a white, crystalline solid.[9] After *ca.* 2 hr, signals characteristic of **6** appeared in the nmr spectrum of the solution.[10] After 4 hr the reaction mixture was diluted with water (35 ml). The resulting solid was removed by filtration and dried (*in vacuo*, sodium hydroxide) to afford 0.085 g of a light yellow solid, mp 188–196° (lit.[11] mp 209°). The ir spectrum (Nujol mull) of this material was almost identical with that of authentic **6**. A tlc[12] of this material indicated that it was essentially pure **6** contaminated with a trace of the corresponding sulfoxide. The thioxanthone sulfoxide may arise from oxidation by oxygen.

Registry No.—**1**, 7605-20-1; **2**, 10445-85-9; **3**, 261-32-5; **4**, 6783-74-0; **5**, 10133-81-0; **6**, 492-22-8; **7**, 17203-18-8; trifluoroacetic acid, 76-05-1; trifluoroacetic anhydride, 407-25-0.

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[8] The disproportionation of **4** to **6** and **8** has been suggested.[6] We have observed that vpc of chloroform solutions of **4** may result in the formation of **6** and **8** (unpublished results).

[9] Thioxanthone (**6**) is relatively isoluble in TFAA.

[10] R. H. Martin, N. Defay, F. Geerts-Evrard, P. H. Given, J. R. Jones, and R. W. Wedel, *Tetrahedron*, **21**, 1833 (1965).

[11] E. G. Davis and S. Smiles, *Trans. Chem. Soc.*, **97**, 1290 (1910).

[12] The thin layer chromatography was performed employing a glass plate coated with silica containing a fluorescent indicator. Development was achieved with chloroform while ultraviolet light was used for visualization.

A Route to Tetraacyl-1,3-dithiacyclobutanes from Carbon Suboxide and Sulfur Dichloride

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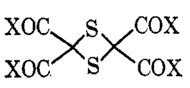
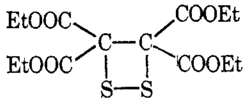
The reaction of carbon suboxide with sulfur dichloride has been found to be a one-step route to the previously unknown 2,2,4,4-tetraacyl-1,3-dithiacyclobutane system. The product, formed from two molecules each of carbon suboxide (C_3O_2) and sulfur dichloride (SCl_2), is the tetraacyl chloride **1**. The direction of addition of the sulfur dichloride, wherein the chlorine adds to the carbonyl carbons, shows that carbon suboxide behaves like ketene in this respect. Ketene has been reported[1] to form thiodiglycolyl chlorides with sulfur dichloride.

Addition of sulfur dichloride to carbon suboxide in a solution of cold ether usually results in the tetraacyl chloride **1** slowly precipitating as orange prisms. Mass spectral analysis shows that the parent ion of **1** has a molecular weight of 340 (theory, 340) and contains four chlorine atoms.[2] The elemental analysis shows the material to be a 2:2 adduct and also shows that no ether was incorporated into the product.

Reaction of the above prisms with ethanol gives a chlorine-free product. The molecular weight and elemental analysis show that this product is also derived from a 2:2 adduct of carbon suboxide and sulfur dichloride and also that it contains four ethyl groups and two sulfur atoms per molecule. The infrared spectrum and nmr spectrum indicate this material to be an ethyl ester and the nmr spectrum shows the four ethyl groups to be in the same environment. These considerations leave only two possible structures, the 1,2- or 1,3-dithiacyclobutane (**4** and **2**, respectively), for these products. Isolation of diethyl malonate upon desulfuration of the ethanol reaction product proves that it is an ester and shows that it possesses the 1,3-dithiacyclobutane structure **2**. Since carbon–carbon cleavage is unlikely under ester formation or the mild conditions of desulfuration, the exclusive formation of diethyl malonate upon desulfuration strongly suggests that the tetraacyl chloride **1** is also a 1,3-dithiacyclobutane. The orange color of the acid chloride, which persists and even intensifies through sublimation and then disappears upon conversion into the ester or amide, is probably due to an intensely colored impurity. Thio ketones, for example, are often highly colored.[3]



1, X = Cl
2, X = OEt
3, X = NEt_2



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[1] D. Harman and C. W. Smith, U. S. Patent 2,514,640 (1950).

[2] J. H. Beynon, "Mass Spectroscopy and its Applications to Organic Chemistry," Elsevier Publishing Co., New York, N. Y., 1960, pp 298–299.

[3] R. Mayer, J. Morgenstern, and J. Fabian, *Angew. Chem. Intern. Ed. Engl.*, **3**, 277 (1964).

The preparation of the tetra(N,N-diethylamide) (**3**) from the tetraacyl chloride is straightforward.

Experimental Section

Sulfur dichloride was obtained from the Hooker Chemical Co. and was distilled from 1% phosphorus trichloride into a refrigerated receiver before use. The fraction distilling at 59° was used in these experiments.

Carbon suboxide was prepared by a method similar to that of Hurd and Pilgrim[4] wherein diacetyl tartaric anhydride[5] was pyrolyzed at 650–700° in a Vycor tube. The product, collected in a Dry Ice trap, was distilled into a clean glass vial and stored at $-25°$. The carbon suboxide was stable for several months under these conditions, but the amount desired for an experiment was distilled (bp 5–7°) prior to use.

1,3-Dithiacyclobutane-2,2,4,4-tetraacyl Chloride.—Into 100 ml of ether cooled to $-5°$ was distilled 4.2 g of carbon suboxide. To this was added 6.2 g of sulfur dichloride and the reaction flask was stoppered and stored at $-20°$ for 24 hr. After this time, the flask contained 3.1 g (30%) of pungent, moisture-sensitive, pale orange crystals of **1**: mp 79–82°; mass spectrum (50 eV), *m/e* (relative intensity, atoms chlorine) 340 (1,4), 277 (100,3), 249 (37,3), 207 (16,1), 179 (31,1), 170 (20,2), 135 (32,1), 107 (63,1), 63 (72,1); ir (Nujol), 1790 (C=O), 1740 (C=O), 1075, 1000, 882, 825, 725 (neat), 610, 580, 520, and 482 cm^{-1}.

Anal. Calcd for $C_6Cl_4O_4S_2$: C, 21.07; H, 0.00; Cl, 41.46; S, 18.75. Found: C, 21.50; H, 0.30; Cl, 41.54; S, 18.09.

The mother liquor was concentrated under vacuum to a deep orange paste that reacted vigorously with ethanol and gave, upon concentration and recrystallization, 1.5 g of the tetraethyl ester 2 (see below). In subsequent preparations, sublimation of the deep orange paste at 50° (0.1 mm) gave additional amounts of the acyl chloride 1.

Tetraethyl 1,3-Dithiacyclobutane-2,2,4,4-tetracarboxylate.—Admixture of 0.25 g of the acid chloride 1 with 3 ml of ethanol resulted in a vigorous reaction and formation of a yellow solution. Upon removal of excess ethanol, 0.28 g (100%) of a crystalline material formed that was free of chlorine but contained sulfur. The crystals were dissolved in hexane, decolorized with charcoal, and recrystallized to give white prisms: mp 59.5–60°; ir (halocarbon, Nujol), 1740 (ester C=O), 1220, 1095, 1025, 858, 838, 810, 745, 710, and 652 cm^{-1}; nmr ($CDCl_3$), 4.30 (q, 2.0, J = 7 Hz, CH_3**CH_2**—O—) and 1.28 ppm (t, 3.0, J = 7 Hz, **CH_3**—CH_2—O—). This material was homogeneous upon tlc in three solvent systems (acetone, benzene, 40:60 ether–Skellysolve B).

Anal. Calcd for $C_{14}H_{20}O_8S_2$: C, 44.20; H, 5.30; S, 16.86; mol wt, 380.4. Found: C, 44.26; H, 5.68; S, 16.56; mol wt (osmometry, $CHCl_3$), 386.

1,3-Dithiacyclobutane-2,2,4,4-tetra-(N,N-diethyl carboxamide).—A solution of 0.5 g of the acid chloride 1 in 50 ml ether was added with stirring to a solution of 1 g of diethylamine in 50 ml of ether. A solid precipitated, and, after 15 min, the mixture was filtered and the filtrate was treated with charcoal, refiltered, and concentrated under vacuum to an orange crystalline paste. This was triturated with hexane and the residue was recrystallized from hexane–acetone (6:1) to give 0.25 g of glistening white prisms: mp 194.5–195° (turns purple at melting point); ir (halocarbon, Nujol), 1640 (amide C=O), 1270, 1220, 1145, 1082, 1070, 810, 640, and 610 cm^{-1}.

Anal. Calcd for $C_{22}H_{40}N_4O_4S_2$: C, 54.08; H, 8.25; N, 11.46; S, 13.10. Found: C, 54.37; H, 8.37; N, 11.46; S, 13.08.

In another run, 0.154 g of the orange prisms were dissolved in 5 ml of ether and diethylamine was cautiously added until the solution was basic. Diethylammonium chloride, mp 219–221°, was formed in 94% (0.186 g) yield.

Desulfuration of the Ester.—One teaspoonful of W. R. Grace active Raney nickel was rinsed with ethanol and suspended in 50 ml of absolute ethanol. To this was added 0.3 g of the tetraethyl ester **2**, and the mixture was stirred with a spatula at room temperature for 5 min. A tlc plate (benzene) showed that none of the starting material remained; so the mixture was filtered and concentrated. The reaction product was found to have the same retention time as diethyl malonate upon gas chromatography on a nonpolar (OV-1) and polar (OV-17) column. Thin layer chromatography (Skellysolve B) showed the product to be a single component with the same R_f value as diethyl malonate. In addition, the reaction product had the odor of diethyl malonate. Addition of aqueous sulfuric acid to the Raney nickel resulted in the vigorous liberation of a gas with the odor of hydrogen sulfide.

Registry No.—Carbon suboxide, 504-64-3; sulfur dichloride, 10545-99-0; **1**, 17255-70-8; **2**, 17239-56-4; **3**, 17255-71-9.

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[4] C. D. Hurd and F. D. Pilgrim, *J. Amer. Chem. Soc.*, **55**, 757 (1933).

[5] Wohl and Oesterlin, *Ber.*, **34**, 1144 (1901).

Free-Radical Addition of Hydrogen Bromide to 1,5-Cyclooctadiene

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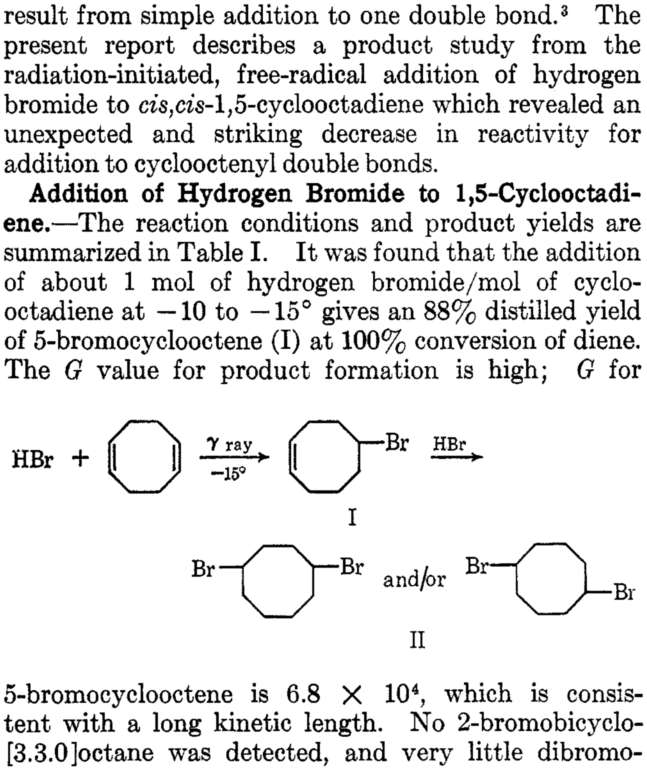
Free-radical addition reactions with *cis,cis*-1,5-cyclooctadiene usually lead to substituted bicyclo[3.3.0]octane derivatives as a result of transannular cycloaddition.[1,2] A number of free-radical addends yield this type of product at 135° including carbon tetrachloride, chloroform, N,N-dimethylformamide, N-*t*-butylformamide, and acetaldehyde. In contrast to these results, the free-radical additions of thiolacetic acid, thiolbenzoic acid, and benzenethiol to *cis,cis*-1,5-cyclooctadiene at ambient temperature give high yields of 5-substituted cyclooctenyl derivatives, which result from simple addition to one double bond.[3] The present report describes a product study from the radiation-initiated, free-radical addition of hydrogen bromide to *cis,cis*-1,5-cyclooctadiene which revealed an unexpected and striking decrease in reactivity for addition to cyclooctenyl double bonds.

Addition of Hydrogen Bromide to 1,5-Cyclooctadiene.—The reaction conditions and product yields are summarized in Table I. It was found that the addition of about 1 mol of hydrogen bromide/mol of cyclooctadiene at -10 to $-15°$ gives an 88% distilled yield of 5-bromocyclooctene (I) at 100% conversion of diene. The G value for product formation is high; G for 5-bromocyclooctene is 6.8×10^4, which is consistent with a long kinetic length. No 2-bromobicyclo[3.3.0]octane was detected, and very little dibromocyclooctane (II) was found. The 5-bromocyclooctene



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[1] R. Dowbenko, *J. Amer. Chem. Soc.*, **86**, 946 (1964); *Tetrahedron*, **20**, 1843 (1964).

[2] L. Friedman, *J. Amer. Chem. Soc.*, **86**, 1885 (1964).

[3] J. M. Locke and E. W. Duck, *Chem. Commun.*, 151 (1965).