evaporated to recover the crude thiol, which was fractionated under reduced pressure in a nitrogen current. Results are summarized in Table I.

Preparation of Sulfide from Xanthogenic Acid Ester and Alkyl Chloride.—Alkyl chloride (0.15 mol) was added dropwise into the solution of 0.1 mol of xanthogenic acid ester in 30 ml of amine at a rate that did not cause the temperature to rise above 30°. The mixture was stirred for 5 hr in a nitrogen current at 30°. The reaction mixture was treated as in the above described procedure. The results are summarized in Table II.

Preparation of Sulfide from Octylthiol and Butyl Chloride.—To a solution of 0.1 mol of octylthiol in 30 ml of ethylenediamine was added 0.15 mol of butyl chloride. The reaction mixture was stirred for 5 hr in a nitrogen current at 30°. The mixture was treated as in the above described procedure. Octylbutyl sulfide was obtained in 85-89% yields, bp 125° (14 mm).

Anal. Calcd for $C_8H_{17}SC_4H_9$: S, 15.84. Found: S, 16.11.

Preparation of Dodecyl Sulfide from Dodecyl Chloride and Potassium Xanthogenate.—To a solution of 0.1 mol of potassium ethylxanthogenate in 30 ml of ethylenediamine was added 0.1 mol of dodecyl chloride. The mixture was stirred for 8 hr in a nitrogen current at 30°. The reaction mixture was treated as in the above described procedure. Removal of benzene from the benzene extract left a yellow liquid which, on distillation in a nitrogen current, gave 1.1 g of dodecylthiol, bp 50-54° (0.04 mm). *Anal.* Calcd for $C_{12}H_{25}SH$: SH, 16.3. Found: SH, 16.0. The residue was recrystallized from acetone to give 15 g of dodecyl sulfide, mp 41-41.5°, 81% yield. *Anal.* Calcd for $(C_{12}H_{25})_2S$: S, 8.13. Found: S, 8.40.

Registry No.—Dodecyl sulfide, 2469-45-6.

Acknowledgment.—The authors thank Koei Chemical Co., Ltd., and Seitetsu Chemical Co., Ltd., for supplying amines, and Nihon Emulsifier Co., Ltd., for supplying glycols.

The Preparation of Some Optically Active Peracids

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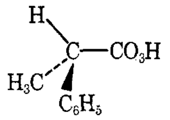
Received June 17, 1969

Dissymmetric peracids have been widely used as oxidants in the asymmetric synthesis of various sulfoxides,[1] epoxides,[2] and oxaziridines,[3] and recently this route has been used in the preparation of an optically active azoxy compound.[4] Three of the more accessible peracids which have been employed in asymmetric synthesis are (+)-*cis*-monopercamphoric acid (**1**), (+)-perhydratropic acid (**2**), and (−)-*endo*-2-pernorbornanecarboxylic acid (**3**). These peracids are not easily obtained in crystalline form in a high state of purity (*i.e.*, a high active oxygen content) and many of the methods previously described suffer from this disadvantage. This note describes the preparation of these three compounds, and a new peracid, (−)-*cis*-permyrtanic acid (**4**), with active oxygen contents in the range of 85-98%.

1



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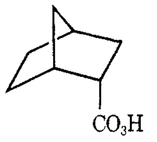

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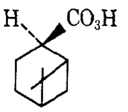

4

cis-Monopercamphoric acid was prepared by a simplified version of the procedure described by Milas and McAlevy[5] in which camphoric anhydride was treated with sodium peroxide. The product was usually obtained as an oil or a semisolid, although crystals could be obtained by the procedure described in the Experimental Section. Hydratropic acid[6] and *endo*-2-norbornanecarboxylic acid[7] were prepared and resolved by the literature methods, and (−)-*cis*-myrtanic acid[8] was obtained by oxidation of (−)-*cis*-myrtanol, a compound readily available from hydroboration of (−)-α-pinene.[9] Conversion into the peracids was achieved using the Swern[10] method, in which 85% hydrogen peroxide was cautiously added to a solution of the acid in methanesulfonic acid while the temperature was maintained in the range of 10-20° for compounds **2** and **3**, and 20-30° for compound **4**. At temperatures above 20°, the perhydratropic acid preparation was violently exothermic, and, at temperatures below 20°, myrtanic acid was recovered largely unchanged from the reaction. All three peracids were obtained as crystalline solids.

Experimental Section[11]

(+)-*cis*-**Monopercamphoric Acid (1).**—A suspension of camphoric anhydride (80.0 g) in ether (1 l.) was added during 2 hr to a well-stirred solution of sodium peroxide (34.4 g) in water (2 l.) at 0-5°. After the solution was stirred for an additional 1 hr, the layers were separated and the aqueous layer was acidified with ice-cold 6 *N* hydrochloric acid. Ether (1 l.) was added and the mixture was shaken twice. The organic layer was separated, washed with cold saturated ammonium sulfate solution, and dried ($MgSO_4$) at 0°. Removal of the solvent at reduced pressure at 0° gave an oil which was dissolved in benzene (200 ml). Petroleum ether (bp 60-80°) was added until two layers separated and ether was then added until the mixture became homogeneous. Storage of the solution at −20° overnight gave crystals, mp 40-45° (54 g, 57%). A sample recrystallized in the same way had mp 51°, active oxygen content 85-90%, $[\alpha]^{18}\text{D}$ +54° (*c* 2.6, ethanol) (lit.[5] mp 49-50°, $[\alpha]\text{D}$ +52°.

(+)-**Perhydratropic Acid (2).**—(+)-Hydratropic acid[6] (6.0 g), $[\alpha]^{18}\text{D}$ +80° (*c* 0.65, benzene), optical purity 83.7%, methanesulfonic acid (24.0 g), and a magnetic stirrer were placed in an open beaker immersed in a water bath at 10°; 85% hydrogen peroxide (5.0 g) was added dropwise to the stirred solution while the temperature was maintained between 10 and 20°. Stirring was continued for 1 hr; the solution was then cooled to 0°. Ice and cold saturated ammonium sulfate were added and the mixture

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[11] Melting points were determined on a hot-stage apparatus and are uncorrected. All solvents used in the extraction and purification of the peracids were rendered olefin free by standard procedures. Experiments involving the use of 85% hydrogen peroxide were conducted from behind a safety screen.

was extracted with cold benzene (three 20-ml portions). The benzene solution was washed with cold water and dried ($MgSO_4$). Removal of the solvent at reduced pressure at 20° gave a white solid. Crystallization from petroleum ether (bp 40–60°) at −20° gave (+)-perhydratropic acid (5.0 g, 75%), mp 65–67°, $[\alpha]^{18}\mathrm{D}$ +108.8° (*c* 2.27, $CHCl_3$), active oxygen content 97–98%. A sample of (±)-perhydratropic acid, prepared in the same way, had mp 44.5–45.5°.

Anal. Calcd for $C_9H_{10}O_3$: C, 65.1; H, 6.0. Found: 64.9; H, 6.2.

(−)-2-*endo*-Pernorbornanecarboxylic Acid (3).—Application of the above procedure to (−)-2-*endo*-norbornanecarboxylic acid[7] (10.0 g), $[\alpha]^{18}\mathrm{D}$ −15° (*c* 1.0, $CHCl_3$), gave (−)-*endo*-2-pernorbornanecarboxylic acid (7.8 g, 71%), mp 64–66° after recrystallization from pentane at −80°, $[\alpha]^{18}\mathrm{D}$ −12.3°, active oxygen content *ca.* 98%.

Anal. Calcd for $C_8H_{12}O_3$: C, 61.54; H, 7.69. Found: C, 61.69; H, 7.76.

(−)-*cis*-Myrtanic Acid.—(−)-*cis*-Myrtanol[9] (15.0 g) was dispersed by means of a high-speed stirrer in a solution of concentrated sulfuric acid (50 ml) in water (400 ml). Powdered potassium permanganate (21.0 g) was added while the temperature was maintained at 20–30°. Sodium metabisulfite was added until the color was discharged and the mixture was extracted with ether. The ether extract was shaken twice with 50% aqueous sodium hydroxide and the resulting aqueous solution deposited a solid on acidification with concentrated hydrochloric acid. Crystallization from acetic acid gave (−)-*cis*-myrtanic acid (7.0 g, 43%), mp 110–111° (lit.[8] mp 111–112°), $[\alpha]^{18}\mathrm{D}$ −38.6° (*c* 2.77, $CHCl_3$). The ether solution contained unreacted *cis*-myrtanol.

(−)-*cis*-Permyrtanic Acid (4).—(−)-*cis*-Myrtanic acid (32.0 g) in methanesulfonic acid (183 g) was treated with 85% hydrogen peroxide (21.3 g) at 20–30°. The solution was stirred for an additional 2 hr at 20°. Work-up as described for perhydratropic acid gave white crystals (32.0 g), mp 45–52°. Crystallization from ether–petroleum ether (bp 40–60°) at −20° gave *cis*-permyrtanic acid (25.0 g, 70%), mp 55–56°, $[\alpha]^{18}\mathrm{D}$ −53.3° (*c* 2.72, $CHCl_3$), active oxygen content >96%.

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.2; H, 8.7. Found: C, 65.5; H, 9.0.

Acknowledgment.—We thank Professors H. B. Henbest and M. F. Grundon for their advice and encouragement. This work was supported in part by The Northern Ireland Ministry of Education.

Registry No.—**1**, 16211-85-1; **2**, 19773-77-4; **3**, 21643-88-9; **4**, 21643-89-0.

The Chemistry of Trifluorothiolacetic Acid and Its Derivatives. I[1]

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Received May 5, 1969

Trifluorothiolacetic acid (CF_3COSH) was first prepared by Sheppard and Muetterties[3] by allowing $(CF_3CO)_2O$ and H_2S to react together at 200° in 45% yield.

The chemistry of CF_3COSH has received very little attention, and only one paper[3] has appeared in the literature. The presence of the -SH group offered a way to prepare new sulfenyl halides and sulfides which contained the highly reactive trifluoroacetyl group.

CF_3COSH reacts readily with chlorine or bromine, giving the corresponding trifluoroacetylsulfenyl halide.

$$CF_3COSH + Cl_2 \xrightarrow{-78^\circ} CF_3COSCl + HCl \qquad (1)$$

$$CF_3COSH + Br_2 \xrightarrow[\text{room temperature}]{-78^\circ\text{ to}} CF_3COSBr + HBr \qquad (2)$$

With iodine monochloride, the corresponding disulfide was formed. The equations for this reaction are

$$CF_3COSH + ICl \longrightarrow [CF_3COSI] + HCl \qquad (3)$$

$$2[CF_3COSI] \longrightarrow (CF_3COS)_2 + I_2 \qquad (4)$$

Water reacts according to the following equation.

$$CF_3COSH + H_2O \longrightarrow CF_3COOH + H_2S \qquad (5)$$

After 6 days, only 88% of the thioacid had reacted. This behavior could account for the instability of the fluoroalkanethiolcarboxylic acids in water, as noted by Sheppard and Muetterties.[3] In a sodium hydroxide solution, the acid slowly evolved H_2S with the formation of sodium trifluoroacetate. Organic bases (pyridine and aniline) react to form solid complexes, with the aniline complex, being unstable, evolving H_2S as one of its decomposition products.

The trifluoroacetylsulfenyl halides react readily with mercury at room temperature, giving the white solid mercurial $(CF_3COS)_2Hg$ and the disulfide (eq 6). The

$$4CF_3COSX + 3Hg \longrightarrow (CF_3COS)_2Hg + 2HgX_2 + (CF_3COS)_2 \qquad (6)$$

$$X = Cl \text{ or } Br$$

mercurial is unstable at room temperature, slowly decomposing, giving quantitatively HgS. It is unstable in water, again producing HgS. The disulfide is also unstable in water and reacts according to eq 7. When

$$(CF_3COS)_2 + 2H_2O \longrightarrow H_2S + S + 2CF_3COOH \qquad (7)$$

heated with mercury, $(CF_3COS)_2$ formed mainly HgS and not $(CF_3COS)_2Hg$. With AgF_2 in freon-113 ($CClF_2$–$CFCl_2$) at room temperature, CF_3COF, SF_4, and SOF_2 were formed.

The reaction of CF_3COSCl with aqueous sodium hydroxide can be represented by eq 8. The (S_3O^{2-}) represents S, S^{2-}, S_2, and $S_2O_3{}^{2-}$. Free sulfur was formed during the basic hydrolysis, and upon acidification H_2S was noted. Evaporation of the above solution left a white solid identified as sodium trifluoroacetate *via* its infrared spectrum.

$$3CF_3COSCl + 8OH^- \longrightarrow 3CF_3COO^- + 3Cl^- + 4H_2O + (S_3O^{2-}) \qquad (8)$$

The infrared spectra for these compounds are listed in Table I. All, except the aniline and pyridine salts, show characteristic carbonyl stretching frequencies at 1670–1780 cm^{-1}. The stretching vibration frequencies for the carbonyl group in thiol esters of perfluorocarboxylic acids are on the average 1695 cm^{-1}.[4] The bands at 1285–1136 cm^{-1} are due to the asymmetric and symmetric stretching vibration of the C–F bond.[5] The bands at 750–736 cm^{-1} are due to CF_3 deformation.[5]

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[1] Presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., 1969.

[2] To whom inquiries should be addressed.

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