terphenyl in the reaction of biphenyl-d_{10} seems to contain one benzene ring derived from biphenyl and two from phthalic anhydride. In the reaction of phthalic anhydride-d_4 with unlabeled biphenyl a small amount of terphenyl, about 3% of the total, contains 6 and 7 deuterium atoms and thus may be formed in the same fashion.

Almost all phenylnaphthalene comes *via* benzyne addition to biphenyl. Naphthylbiphenyl similarly should arise from benzyne and terphenyl. Terphenyl-d_{13} and -d_{14} would be expected to give $C_{22}(H + D)_{16}$ containing 12 deuterium atoms as well as 13 and 14, as a result of intramolecular scrambling in the 1,4 adduct before it loses acetylene; however, as the first column in Table IV shows, there was an appreciable amount of d_{15} and d_{16} species as well. Correspondingly, terphenyl-d_0 with benzyne-d_4 gave not only the expected d_3 and d_4 species, but also an appreciable amount of the d_0 and d_1. In both reactions these species suggest hydrogen transfer from biphenyl to benzyne and formation of phenylbenzyne (Scheme IV), paralleling the formation of thiophyne from thiophene and benzyne.[5]

SCHEME IV

The ratios of addition to insertion products in the reaction of benzyne with biphenyl-d_{10} and benzyne-d_4 with biphenyl in this study were 5.1 and 3.8, respectively.[6] Although benzyne in solution reacts as a dienophile,[7] the ratio of addition to insertion products in the reactions of benzyne from phthalic anhydride with different reagents varies over a wide range.[8] See Table V.

TABLE V

Reagent	Ratio, addition to insertion products
Benzene-d_6	7.0
Naphthalene	3.4
Phenanthrene	2.4
Hexafluorobenzene	0.21
Hexachlorobenzene[a]	
Hexamethylbenzene[a]	
Pyridine	1.9
Thiophene	1.5
Thianaphthene	2.5
Dibenzothiophene	2.0

[a] All addition, no insertion product.

From the table, the factors influencing benzyne addition *vs.* insertion are not clear. We are examining the reactions of phthalic anhydride with additional aromatic and heterocyclic compounds at 700°.

Experimental Section

Reactions were run in a Vycor tube filled with Vycor beads, in an electric furnace maintained at 700 ± 1° under pure dry nitrogen. Phthalic anhydride and biphenyl were separately sublimed from heated bulbs and swept by nitrogen through a Y junction into the heated tube. The vapors were condensed in a bulb at −10°. The condensate was distilled to recover unreacted material and the residue was analyzed.

Analyses were performed with a Consolidated Model 21-103 mass spectrometer with the inlet system at 250°; with a directly coupled gas chromatograph–mass spectrometer combination[9] also employing a 21-103 instrument with an electron multiplier in place of the Faraday-cup detector; and by gas chromatography on a column of polyethylene glycol sebacate on Chromosorb W. Mass spectra were measured at the conventional 70 ionizing V and at low voltage, 7.5 V, uncorrected. For the low-voltage measurements, the repellers were maintained at an average potential of 3 V, the exact values being selected to give maximum sensitivity.

The reagents and standards for gas chromatography were purchased from Aldrich Chemicals and used as received. Where purity was critical, the reagent was analyzed and, if necessary, purified by distillation, crystallization, and gas chromatography. Biphenyl-d_{10} was prepared from biphenyl, deuterium oxide, and platinum in a shaking bomb at 185°.[10] Phthalic anhydride-d_4 was prepared by oxidation of naphthalene-d_8 (from naphthalene, deuterium oxide, and platinum at 185°[9]) with calcium permanganate[11] in 45% yield.

Registry No.—Phthalic anhydride, 85-44-9; biphenyl, 92-52-4.

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(5) E. K. Fields and S. Meyerson, "Organosulfur Chemistry," M. J. Jannsen, Ed., Interscience Publishing Co., New York, N. Y., 1967, p 143.

(6) Because of the shorter contact time used to minimize thermal scrambling, some of the products listed in Table I such as anthracene, phenanthrene, and binaphthyl were formed in concentrations too low to list as significant in Table IV. This omission may introduce some error into the addition to insertion ratios; however, they are consistent with the figures in the last table, and demonstrate a marked preference for addition over insertion, except in the reaction with hexafluorobenzene.

(7) G. Wittig, *Angew. Chem.*, **69**, 245 (1957); T. G. Corbett and A. N. Porter, *Aust. J. Chem.*, **18**, 781 (1965); W. L. Dilling, *Tetrahedron Lett.*, 939 (1966).

(8) E. K. Fields and S. Meyerson, unpublished data.

(9) R. S. Gohlke, *Anal. Chem.*, **31**, 535 (1959); L. P. Lindeman and J. L Annis, *ibid.*, **32**, 1742 (1960); J. T. Watson and K. Biemann, *ibid.*, **36**, 1135 (1964).

(10) G. E. Calf and J. L. Garnett, *Aust. J. Chem.*, **21**, 1221 (1968), and references cited therein.

(11) F. Ullmann and B. Uzbacher, *Ber.*, **36**, 1797 (1903).

Thiols and Sulfides from Xanthogenic Acid Ester

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Previous work on the preparation of thiol from xanthogenic acid ester (I) was carried out with a water-soluble thiol such as thioglycolic acid.[1] Although Maneli[2] obtained the derivatives of thiocarbaminic acid ester and thiol on the reaction of I with amine such as liquid ammonia, monoethanolamine, or pyrolidine, little attention was paid to this reaction as a convenient synthetic method for thiols. Furthermore, any attempt to prepare sulfides through the reaction of alkyl chlorides with thiols or I in the presence of ethylenediamine had not been tried. In this paper, it has been demonstrated that even water-insoluble I decomposes under mild conditions in ethylenediamine to afford thiols in good yield, and that the reaction of I or thiol with alkyl chlorides in ethylenediamine affords sulfides directly.

This procedure, as well as the thiuronium salt method has given good results with a wide variety of halides.

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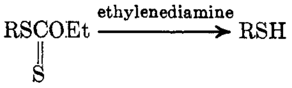
(1) E. E. Reid, "Organic Chemistry of Bivalent Sulfur," Vol. I, Chemical Publishing Co., Inc., New York, N. Y., 1958, p 31.

(2) E. Maneli, *Chem. Abstr.*, **49**, 186 (1955).

TABLE I

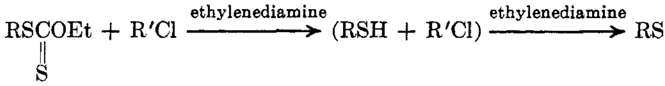


$$\mathrm{RS}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{OEt} \xrightarrow{\text{ethylenediamine}} \mathrm{RSH} \tag{1}$$

				RSH			
				Yield,	SH, %		
Registry no.	R, eq 1	Amine	pK_a	%	Calcd	Found	Bp, °C (mm)
112-55-0	n-$C_{12}H_{25}$–	$NH_2C_2H_4NH_2$	9.97	85	16.3	16.2	54–55 (0.04)
111-88-6	n-C_8H_{17}–	$NH_2C_2H_4NH_2$	9.97	80	22.5	21.9	71–72 (10
6338-61-0	$C_4H_9(OC_2H_4)_2$–	$NH_2C_2H_4NH_2$	9.97	80	18.5	18.1	97–98 (14)
22003-66-3	$C_4H_9(OC_2H_4)_3$–	$NH_2C_2H_4NH_2$	9.97	81	14.8	15.0	84–85 (0.1)
100-53-8	$C_6H_5CH_2$–	$NH_2C_2H_4NH_2$	9.97	85	26.6	26.9	80–81 (15)
540-63-6	–C_2H_4–[a]	$NH_2C_2H_4NH_2$	9.97	78[b]	70.2	70.1	46–47 (16)
2150-02-0	–$C_2H_4OC_2H_4$–[a]	$NH_2C_2H_4NH_2$	9.97	84[b]	47.8	47.5	55–56 (1)

[a] $\mathrm{EtO}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SRS}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{OET}$. [b] HSRSH.

TABLE II



$$\mathrm{RS}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{OEt} + \mathrm{R'Cl} \xrightarrow{\text{ethylenediamine}} (\mathrm{RSH} + \mathrm{R'Cl}) \xrightarrow{\text{ethylenediamine}} \mathrm{RSR'} \tag{2}$$

					RSR'			
				RSH	Yield,	S, %		Bp,
Registry no.	R, eq 2	R'	Amine	yield, %	%	Calcd	Found	°C (mm)
16900-07-5	C_8H_{17}–	n-C_4H_9–	$NH_2C_2H_4NH_2$	Trace	80	15.8	16.1	125 (14)
16900-08-6	$C_{12}H_{25}$–	n-C_4H_9–	$NH_2C_2H_4NH_2$	Trace	75	13.1	13.0	77–78 (0.4)
638-74-9	$C_6H_5CH_2$–	$C_6H_5CH_2$–	$NH_2C_2H_4NH_2$	Trace	95	14.9	14.8	47–48
22037-97-4	–C_2H_4–[b]	n-C_3H_7–	$NH_2C_2H_4NH_2$	Mixture[c]	73[d]	36.0	35.8	76–77 (15)
22003-70-9	–$C_2H_4OC_2H_4$–[b]	n-C_4H_9–	$NH_2C_2H_4NH_2$	Mixture[c]	68[d]	29.3	28.9	90–91 (0.02)

[a] Melting point; [b] $\mathrm{EtO}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SRS}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{OEt}$. [c] Mixture of mono- and dithiol; [d] R'SRSR'.

Principal steps in these reactions are outlined in eq 1 and 2.

The reaction as shown in eq 1 does not take place in tertiary amine solution,[3] but in primary or secondary amine. Yields of thiol in this reaction generally depend upon the basicities of monoamine. However, I has been found to afford thiol in higher yield in ethylenediamine solution than in monoamines which generally have stronger basicities than the former (Table I). In addition, the reactions of I with alkyl chlorides have been found to afford sulfides as shown in Table II in ethylenediamine solution and not to form sulfides in monoamines or N-substituted diamines such as N-dimethylpropanediamine. Both monoamines and N-substituted diamines accelerate the formation of thiol from I. However, they have less of an accelerating effect on the condensation of thiols with alkyl chlorides and do not react with alkyl chloride under our conditions. Under the same conditions, ethylenediamine has been found to accelerate sulfide formation from alkyl chloride and thiols in good yield. Therefore the principal step of sulfide formation from I and alkyl chloride in the presence of ethylenediamine is considered as the condensation of an alkyl chloride with the thiol which is formed by decomposition of I. In addition, dodecyl sulfide was prepared directly from dodecyl chloride and potassium ethylxanthogenate in the presence of ethylenediamine at 30°. The accelerating effect of ethylenediamine on the sulfide formation was also observed on other aliphatic primary diamines. From the ultraviolet spectra, it was found that the thiol band of n-dodecylthiol determined in ethylenediamine is at a longer wavelength (λ_{max} 281 mμ, ϵ_{max} 450) than that in n-hexane (λ_{max} 252 mμ, ϵ_{max} 42). This shift may suggest the formation of an activated charge transfer complex between the thiol group and ethylenediamine. In view of the above results, such a complex seemed to accelerate sulfide formation as a strong nucleophilic agent to alklychloride as well as an acid acceptor. However, more careful studies are desired to confirm this mechanism.

Experimental Section

The reagents were obtained by fractional distillation of commercial reagents. The final compounds were confirmed by infrared spectra. The presence of the thiol group and of sulfur was determined by means of the iodine and Schöniger methods, respectively. Spectra were determined by means of Hitachi EPU II spectrometer using 10-mm fused silica cells at the concentration of 3.75 × 10^{-3} mol/l.

Preparation of Xanthogenic Acid Ester.—Xanthogenic acid esters were prepared by a method similar to that described by F. C. Whitmore.[4] A solution of 0.1 mol of alkyl chloride and 0.15 mol of potassium ethylxanthogenate in 200 ml of acetone was refluxed for 8 hr and the precipitated potassium chloride was then filtered from the solution. After the filtrate was evaporated under reduced pressure, the residue was washed with water several times to remove unreacted potassium xanthogenate. Xanthogenic acid ester, recovered in 90–95% yields as an oil, was dried over anhydrous sodium sulfate and used in the next reaction without distillation because of the decomposition of the ester on heating.

Preparation of Thiol from Xanthogenic Acid Ester.—A solution of 0.1 mol of xanthogenic acid ester in 30 ml of ethylenediamine was stirred for 3 hr in a nitrogen current at 30° and then poured into an ice–water solution of sulfuric acid. The mixture was extracted three times with 50 ml of benzene. The benzene extracts were washed with a 5% solution of sulfuric acid and dried over anhydrous sodium sulfate. The solution was then

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(3) H. Yoshida and S. Inokawa, *Nippon Kagaku Zasshi*, **86**, 956 (1956).

(4) F. C. Whitmore and C. T. Simpson, *J. Amer. Chem. Soc.*, **55**, 3809 (1933).

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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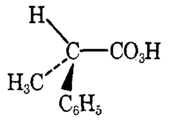
Dissymmetric peracids have been widely used as oxidants in the asymmetric synthesis of various sulfoxides,[1] epoxides,[2] and oxaziridines,[3] and recently this route has been used in the preparation of an optically active azoxy compound.[4] Three of the more accessible peracids which have been employed 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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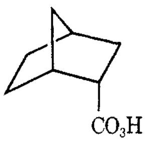
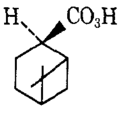


3



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%, $[\alpha]^{18}\mathrm{D}$ +54° (*c* 2.6, ethanol) (lit.[5] mp 49-50°, $[\alpha]\mathrm{D}$ +52°.

(+)-Perhydratropic Acid (2).—(+)-Hydratropic acid[6] (6.0 g), $[\alpha]^{18}\mathrm{D}$ +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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(1) (a) A. Mayr, F. Montanari, and M. Tramontini, *Gazz. Chim. Ital.*, **90**, 739 (1960); (b) A. Maccioni, F. Montanari, M. Secci, and M. Tramontini, *Tetrahedron Lett.*, 607 (1961); (c) U. Folli, D. Larossi, F. Montanari, and G. Torre, *J. Chem. Soc., C*, 1317, 1372 (1968).

(2) (a) H. B. Henbest, Special Publication No. 19, The Chemical Society of London, 1965, p 83; (b) R. C. Ewins, H. B. Henbest, and M. A. McKervey, *Chem. Commun.*, 1085 (1967); (c) R. M. Bowman, J. F. Collins, and M. F. Grundon, *ibid.*, 1131 (1967); (d) R. M. Bowman and M. F. Grundon, *J. Chem. Soc., C*, 2368 (1967); (e) F. Montanari, I. Moretti, and G. Torre, *Chem. Commun.*, 135 (1969).

(3) (a) D. R. Boyd, *Tetrahedron Lett.*, 4561 (1968); (b) U. Folli, D. Larossi, and F. Montanari, *Chem. Commun.*, 1694 (1968).

(4) F. D. Greene and S. S. Hecht, *Tetrahedron Lett.*, 575 (1969).

(5) N. A. Milas and A. McAlevy, *J. Amer. Chem. Soc.*, **55**, 349 (1933).

(6) D. J. Cram and F. A. Abd Elhafez, *ibid.*, **74**, 5846 (1952).

(7) (a) J. A. Berson and D. A. Ben-Efraim, *ibid.*, **81**, 4083 (1959); (b) J. A. Berson, J. S. Walla, A. Remanik, S. Suzuki, P. Warnhoff, and D. Willner, *ibid.*, **83**, 3986 (1961).

(8) G. W. Eigenmann and R. T. Arnold, *ibid.*, **81**, 3440 (1959).

(9) H. C. Brown and G. Zweifel, *ibid.*, **83**, 2544 (1961).

(10) L. S. Sibert, E. Siegel, and D. Swern, *J. Org. Chem.*, **27**, 1336 (1962).

(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.