plete, the acid mixture was added with stirring to 30 g. of 105% sulfuric acid at 120–130°. The hot acid solution was then allowed to stir at 120° for 10 min. The mixture was cooled in an ice bath and neutralized with concentrated ammonia at a temperature of 25° or below. One hundred milliliters of chloroform was added to the neutral mixture. After agitation for 10 min., the mixture was filtered and the filter cake washed with chloroform. The organic layer was separated, the aqueous phase extracted with chloroform, and the combined chloroform solution dried. The solvent was removed from the extract by distillation to leave 18.5 g. of crude semi-solid ε-caprolactam. The crude lactam was distilled under vacuum to yield 17 g. (68%) of ε-caprolactam (b.p.$_{10}$ 138°). The infrared spectrum of the product was identical with the spectrum of an authentic sample of ε-caprolactam.

WILMINGTON, DEL.

[CONTRIBUTION FROM THE PIONEERING RESEARCH DIVISION, TEXTILE FIBERS DEPARTMENT, E. I. DU PONT DE NEMOURS AND CO., INC.]

Some Reactions of 3,3-Bis(chloromethyl)oxetane

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The neopentyl type halides in bis(halomethyl)oxetanes are readily displaced by nucleophilic reagents. A number of such reactions have been studied, and the products characterized.

In comparison to the tremendous amount of research which has been devoted to a study of the chemistry of ethylene oxides, the chemistry of trimethylene oxides (oxetanes) has been overlooked under quite recently. Reviews of certain phases of earlier work have appeared[1] and in the past few years, a number of workers, notably Searles[2-8] have contributed to the field. In this paper some work carried out in these laboratories will be presented.

In general, the preparation of trimethylene oxides is carried out by removing the elements of HX from a 1,3-halohydrin, or better, a halohydrin acetate by treatment with alkali at elevated temperatures.[2,9-11] The yields may be poor because of competing elimination reactions, resulting in the formation of open chain, unsaturated derivatives.[2] If the central carbon atom is substituted with negative groups, for example with two chloromethyl groups,[12] the ring closure by alkali can be carried out at low temperatures, thus minimizing side reactions. A convenient source of an appropriately substituted trimethylene oxide which has been recognized[12] and exploited[13-15] recently is pentaerythritol. This inexpensive raw material reacts readily in glacial acetic acid with hydrogen chloride at elevated temperatures (ca. 160°) to give tris(chloromethyl) ethyl acetate in high yield:

$$C(CH_2OH)_4 + 3HCl + HOAc \xrightarrow[\text{solvent}]{\text{HOAc}} (ClCH_2)_3CCH_2OAc$$

The corresponding bromo derivative may be made in the same fashion.

Ring closure in refluxing methanol with two equivalents of alkali yields the trimethylene oxide easily, despite the fact that the halogen displaced during ring closure is of the neopentyl type.[16]

The product, 3,3-bis(chloromethyl)oxetane, is quite stable under normal conditions, although it is quite sensitive to acidic reagents, and under proper conditions can be converted to a high molecular weight polyether, as reported by several workers.[13,14,17,18] We find the halogen atoms are surprisingly reactive[19] considering that they are still nominally neopentyl halides. They can be displaced by a variety of nucleophilic reagents under mild conditions. This enhanced reactivity undoubtedly arises from the altered geometry of the

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(1) S. F. Marrian, *Chem. Revs.* **43**, 149 (1948).

(2) S. Searles and M. J. Gortakowski, *J. Am. Chem. Soc.*, **75**, 3030 (1953).

(3) S. Searles and V. F. Butler, *J. Am. Chem. Soc.*, **76**, 56 (1954).

(4) S. Searles, M. Tamres, and E. R. Lippincott, *J. Am. Chem. Soc.*, **75**, 2775 (1953).

(5) S. Searles and V. P. Gregory, *J. Am. Chem. Soc.*, **76**, 2789 (1954).

(6) S. Searles, *J. Am. Chem. Soc.*, **76**, 2313 (1954).

(7) H. S. Gutowsky, R. L. Rutledge, M. Tamres, and S. Searles, *J. Am. Chem. Soc.*, **76**, 4242 (1954).

(8) S. Searles and M. Tamres, *J. Am. Chem. Soc.*, **73**, 3704 (1951).

(9) C. Derick and D. D. Bissell, *J. Am. Chem. Soc.*, **38**, 2485 (1916).

(10) G. Bennett and W. Philip, *J. Chem. Soc.*, 1938 (1928).

(11). J. Rose, *J. Chem. Soc.*, 542, 546 (1956).

(12) F. Govaert and M. Beyaert, *Natuurw. Tijdschr Belg.*, 22, 73 (1940).

(13) A. C. Farthing and W. J. Reynolds, *J. Polymer Sci.*, 12, 503 (1954).

(14) A. C. Farthing, *J. Chem. Soc.*, 3648 (1955).

(15) H. K. Boardman, paper presented before Delaware section of the AMERICAN CHEMICAL SOCIETY, Symposium Feb. 18, 1956.

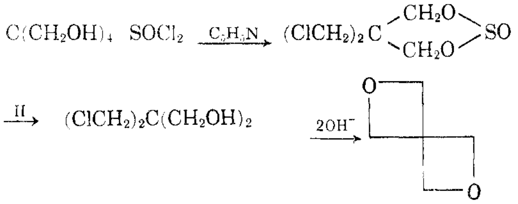
(16) S. Winstein and R. B. Henderson, *Heterocyclic Compounds*, Vol. 1, R. Elderfield, ed., J. Wiley and Sons, Inc., New York, 1950, p. 60.

(17) U.S. Patents **2722340, 2722492, 2722493, 2722520,** issued Nov. 1, 1955 and assigned to Hercules Powder Co.

(18) British Patent **723,777** assigned to Imperial Chemical Industries.

(19) Compare Ref. 14.

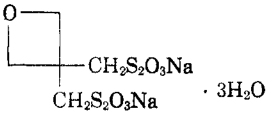
quaternary carbon atom, imposed by the four membered ring, which should force the halogen atoms into a more available position in space, where they may be displaced more easily.[20] Despite this reactivity, it becomes more difficult to close a second ring onto the first; thus pentaerythritol dichloride[21] prepared by the acid hydrolysis of its cyclic sulfite,[21c] yields only small amounts of dioxaspiroheptane[22] under similar conditions.



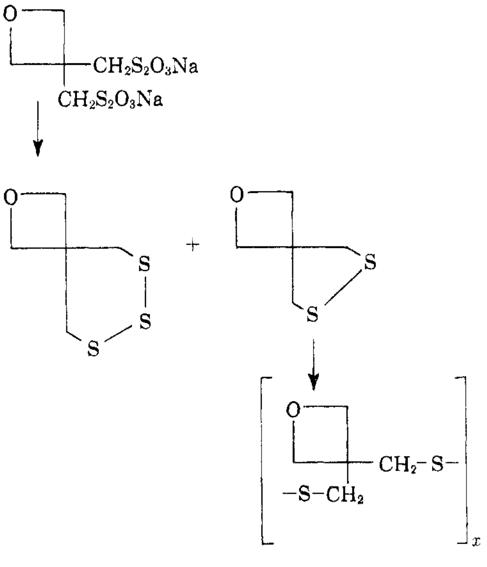
In the present study, a number of displacements have been carried out on bischloromethyloxetane without disrupting the oxetane ring. Thus with iodide ion, cyanide ion, and liquid ammonia the previously reported 3,3-bis(iodomethyl)oxetane,[12] 3,3-bis(cyanomethyl)oxetane,[23] and 3,3-bis(aminomethyl)oxetane[24] were prepared. The physical constants reported in *Chemical Abstracts* for 3,3-bis(aminomethyl)oxetane do not agree with the values we have observed, hence, the preparations are described in the Experimental Section. The diamine was further characterized by the preparation of derivatives with benzoyl chloride and phenyl isocyanate, and a study of the infrared spectra of the compounds.

With thiocyanate ion, it was found possible to isolate from the reaction mixture (preferably in acetone) both the mono and the dithiocyano derivatives. The former was a liquid, the latter a well-defined crystalline solid. The reaction mixture tended to polymerize spontaneously to dark, undefined solid tars during preparation.

Sodium thiosulfate reacted rapidly with 3,3-bis(chloromethyl)oxetane in aqueous ethanol to give a good yield of a crystalline, water soluble di-Bunte salt (I) which crystallized from 85% ethanol with 3 molecules of water of crystallization.



The di-Bunte salt (I) was hydrolyzed under different conditions and the products isolated. Two substances were obtained: The first, a colorless, crystalline material, was probably 2,3,4-trithia-8-oxaspiro[5,5]nonane, produced by reaction of the intermediate dithio compound with sulfur produced in the acid hydrolysis of excess sodium thiosulfate.[25] The other product, a yellow oil, stable in benzene solution, polymerized on distillation to a rubbery polymer, probably a linear polymeric disulfide such as that obtained from trimethylene disulfide.[26,27]



Reaction of 3,3-bis(chloromethyl)oxetane with sodium sulfide or thiourea under a variety of conditions gave 2-oxa-6-thiaspiroheptane, which was

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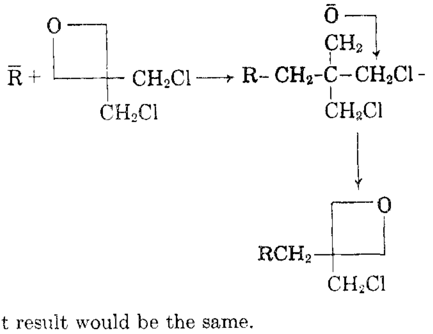
[20] An alternative mode of displacement would involve a cyclic mechanism, in which the *ring* is attacked by the entering group, displacing $-\bar{O}$, which then eliminates the halogen:



The net result would be the same.

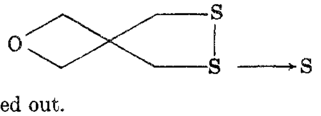
[21] (*a*) A. Mooradian and J. B. Cloke, *J. Am. Chem. Soc.*, **67**, 942 (1945). (*b*) H. Rapoport, *J. Am. Chem. Soc.*, **68**, 341 (1946). (*c*) H. Pietsch and H. Nagel, German Patent **875,804**.

[22] H. J. Backer and K. J. Kenning, *Rec. trav. chim.*, **53**, 812 (1934).

[23] R. Fonteyn, P. Cornand, and M. Ticket, *Natuurw. Tijdschr.* **25**, 67 (1943).

[24] M. Beyaert and F. Govaert, *Proc. Acad. Sci. Amsterdam*, **42**, 776 (1939) [*Chem. Abstr.*, **34**, 5414 (1940)].

[25] A stucture such as

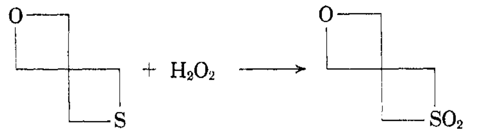


cannot be ruled out.

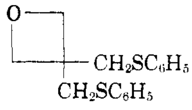
[26] J. A. Barltrop, P. M. Hayes, and M. Calvin, *J. Am. Chem. Soc.*, **76**, 4348 (1954).

[27] J. A. Affleck and A. Dougherty, *J. Org. Chem.*, **15**, 865 (1950).

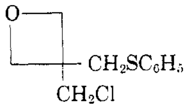
oxidized with hydrogen peroxide to an unusual cyclic sulfone.



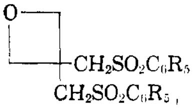
Sodium thiophenolate reacted rapidly with 3,3-bis(chloromethyl)oxetane to give both 3,3-bis-(phenylthiomethyl)oxetane (II), and 3-chloromethyl-3-phenylthiomethyloxetane (III). The former was oxidized with hydrogen peroxide in acetic acid to the crystalline disulfone (IV).



II

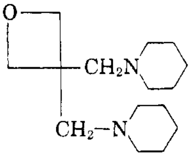


III



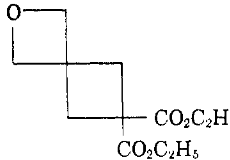
IV

Similarly, piperidine gave bispiperidinomethyloxetane VI, which yielded a crystalline dipicrate.



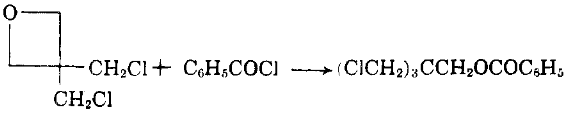
VI

Sodiomalonic ester was allowed to react with bischloromethyloxetane under a variety of conditions. It is interesting to note that even under conditions specifically designed to favor monoalkylation, the internal displacement is so favored[28] that the only product isolated was 2,2-biscarboxyethyl-5-oxaspiroheptane (VII).



VII

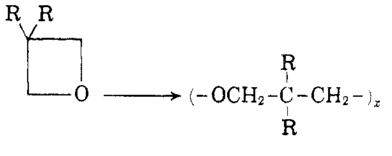
It was observed earlier[9] that trimethylene oxide itself reacts explosively with acetyl chloride to give *gamma*-chloropropyl acetate. Similarly, bischloromethyloxetane and bisbromomethyloxetane react readily with benzoyl chloride or benzoyl bromide to give respectively *β,β,β*-trischloromethylethylbenzoate and *β,β,β*-trisbromomethylethylbenzoate.



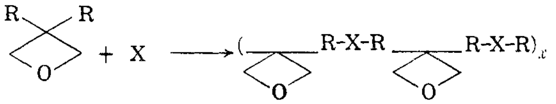
This reaction probably proceeds by a nucleophilic attack of the oxide ring on the acid chloride. The similarity of this reaction to the reaction of acid halides with aldehydes[29,30] and epoxides[31] to give haloesters is noteworthy.

POLYMERS FROM OXETANES

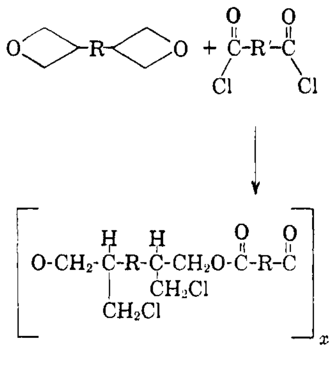
Three ways can be visualized for the conversion of oxetanes to polymers. In the first, a Lewis acid catalyst opens the trimethylene oxide ring to give a linear polyether.[13-15]



In the second, a reactive group R on the oxetane nucleus is caused to condense with a second difunctional molecule X.



In the third, a diacid chloride is added to a bisoxetane to give a polyester.



In the first category, the most interesting example is the polymer from 3,3-bis(chloromethyl)oxetane, described in detail in the recent literature by Farthing and Reynolds[13,14] and by Boardman.[15] Polymers of this type which have not been described in the literature previously have been prepared, in the hope of finding some other useful and unique polymers. Thus 3,3-bis(bromomethyl)oxetane gave a polymer with a melting point in the range of 220°, while 3,3-bis(iodomethyl)oxetane gave a polymer *stable up to its melting point* (290°) which was unusual in that it was 75.2% by weight iodine. In addition, 2-oxa-5-thiaspiro-(3,3)heptane-5,5-dioxide and 3,3-bis(phenylthiomethyl)oxetane di-

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[28] This is to be expected from the work of Cason and Allen, *J. Org. Chem.*, **14**, 1036 (1949), on the reaction of trimethylene dibromide and sodiodiethylmalonate.

[29] R. Adams and E. H. Volweiler, *J. Am. Chem. Soc.*, **40**, 1732 (1918).

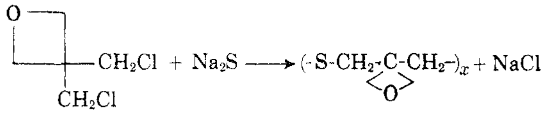
[30] H. E. French and R. Adams, *J. Am. Chem. Soc.*, **43**, 657 (1921).

[31] E. L. Gustus and P. G. Stevens, *J. Am. Chem. Soc.*, **55**, 374 (1933).

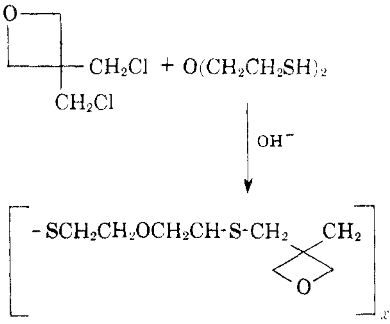
sulfone gave polymers by ring-opening polymerization and 2,5-dioxaspiroheptane gave an infusible, cross-linked polymeric powder.

Copolymers of 3,3-bis(chloromethyl)oxetane and 3,3-bis(iodomethyl)oxetane were prepared. These showed a minimum melting point at a composition corresponding to about 85 mole % of 3,3-bis-(chloromethyl)oxetane.

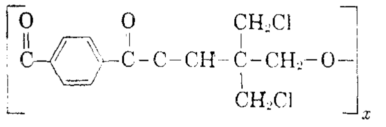
Polymers which were presumably of the second type were obtained as by-products of the reaction of 3,3-bis(chloromethyl)oxetane and sodium sulfide:



They were viscous oils which cross-linked when treated with boron fluoride etherate. A similar, low-molecular weight oil was obtained from 3,3-bis-(chloromethyl)oxetane and bis(mercaptoethyl)-ether:



Polymers of the third type were investigated only briefly. Thus terephthaloyl chloride and 3,3-bis(chloromethyl)oxetane gave a polymer presumed to be



It was, however, cross-linked, and contained less than the calculated amount of chlorine.

INFRARED SPECTRA OF OXETANES

All of the compounds described in this article as being oxetane derivatives have been examined in the infrared. The position of the characteristic bands are shown in Table 1. Previous workers[32] have observed bands characteristic of oxetanes at about 8.1 and 10.2 μ. The intense 10.2 μ band showed up consistently as might be expected from its assignment as an antisymmetric stretching vibration. A splitting of this band may be observed with KBr pellet spectra. There was also usually a weaker, less definite band at 10.5–10.6 μ. The 8.1 μ band, which has been assigned to a methylene wagging motion[32] seems rather variable, and was at times obscured. It is therefore not considered to be a reliable criterion of structure.

EXPERIMENTAL

Preparation of 3,3-bis(chloromethyl)oxetane.[12–15] This compound was made by the action of alkali in refluxing methanol on pentaerythritol trichlorohydrin acetate, which was obtained by the action of gaseous hydrogen chloride on pentaerythritol in acetic acid at 100°. Bis(chloromethyl)-oxetane boiled at 101°/27 mm., 65°/5 mm.

Preparation of 3,3'-bis(bromomethyl)oxetane.[12] This substance was made in the same way as the bischloro compound. It boiled at 125°/23 mm.

Anal. Calcd. for $C_5H_8OBr_2$: C, 24.62; H, 3.30. Found: C, 24.67, 24.85; H, 3.28, 3.58.

Bis(bromomethyl)oxetane was polymerized in a manner similar to that described in the literature for the bischloro compound.[13–17] The product was a solid melting at about 220°.

Anal. Calcd. for $(C_5H_8OBr_2)_n$: C, 24.62; H, 3.30. Found: C, 24.98, 25.04; H, 3.28, 3.58.

Preparation of 3,3-bis(iodomethyl)oxetane.[12] A mixture of 15.5 g. of 3,3-bis(chloromethyl)oxetane, 150 cc. of methyl ethyl ketone and 35 g. of dry sodium iodide was refluxed for 24 hr. The solution was cooled, filtered, and the solvent partially removed by distillation. The residue solidified on standing and was recrystallized from cyclohexane. The yield was 30 g. (89%) of coarse, colorless, very dense crystals with a melting point of 50°.

Anal. Calcd. for $C_5H_8OI_2$: C, 17.75; H, 2.37. Found: C, 17.97, 18.09; H, 2.41, 2.40.

The polyether, prepared as described under the bisbromo derivative, melted at 290° with decomposition. However, it was stable up to this temperature.

Anal. Calcd. for $(C_5H_8OI_2)_n$: C, 17.75; H, 2.37. Found: C, 17.87, 17.84; H, 2.24, 2.28.

Copolymers of 3,3-bis(iodomethyl)oxetane and 3,3-bis-(chloromethyl)oxetane. A series of copolymers of these two monomers, prepared in quantitative yields by polymerizing various mixtures of the monomers as in preceding experiments, is described in Table II.

TABLE II

COPOLYMERS OF BIS(IODOMETHYL)OXETANE AND BIS(CHLOROMETHYL)OXETANE

Molar Ratio $\frac{Cl_2 \text{ monomer}}{I_2 \text{ monomer}}$	M.P.	Observed Analysis C	H	Analysis Calcd. on Basis of Monomer Ratio C	H
3.05	163°	29.94	4.12	30.0	4.0
1.00		30.39	4.05		
1.02	240°	21.81	2.92	21.7	2 9
2.00		21.90	2.90		
2.00	185°	28.11	3.88	27.8	3.7
1.00		28.18	3.98		
1.08	210°	24.88	3.57	24.8	3.3
1.00		25.00	3.66		

Preparation of 3,3-bis(cyanomethyl)oxetane. A mixture of 10 g. of 3,3-bis(chloromethyl)oxetane, 7 g. of sodium cyanide, and 25 ml. of 95% ethanol was refluxed for 24 hr. The dark brown mixture was filtered hot and the filtrate was then

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(32) G. M. Barrow and S. Searles, *J. Am. Chem. Soc.*, **75**, 1175 (1953).

cooled in ice. The crystalline product was filtered, dried, and recrystallized from benzene. The pure 3,3-bis(cyanomethyl)oxetane melted at 76.5° and was obtained in about 40% yield. 3,3-Bis(cyanomethyl)oxetane is soluble in water, insoluble in ether and petroleum ether, soluble in hot benzene and cold methylene chloride.

Anal. Calcd. for $C_7H_8ON_2$: C, 61.76; H, 5.92; N, 20.51. Found: C, 62.01, 62.33; H, 6.08, 5.99; N, 20.31, 20.19.

It was polymerized to low molecular weight oils by ionic catalysts.

Reaction of sodiomalonic ester with 3,3-bis(chloromethyl)-oxetane. Sodiomalonic ester was prepared from 53 g. of malonic ester, 7.6 g. of sodium, and 200 ml. of ethyl alcohol. This mixture was added dropwise with stirring and refluxing to 50 g. of 3,3-bis(chloromethyl)oxetane mixed with 100 g. of excess malonic ester and 100 ml. of ethyl alcohol. The reaction mixture was worked up as above and distilled from a simple Claisen Flask rapidly to minimize thermal decomposition. The desired product was obtained at about 120° at 3 mm. This temperature is probably not reliable, however, because the distillation was carried out quite rapidly. The distillate weighed 63 g. and consisted of the tailings of malonic ester as well as the spiro condensation product. This material was fractionated through a spinning band column to give 31 g. of product, boiling point 105–107°/1.1 mm.

Anal. Calcd. for $C_{12}H_{18}O_5$: C, 59.47; H, 7.49; Cl, 0.0. Found: C, 58.9, 58.9; H, 7.16, 7.03; Cl, 0.0, 0.0.

Reaction of 3,3-bis(chloromethyl)oxetane with liquid ammonia.[12] Fifty grams of 3,3-bis(chloromethyl)oxetane was mixed with 250 ml. of liquid ammonia in a stainless steel bomb and heated at 80° for 8 hr. The bomb was cooled to room temperature, the excess ammonia was carefully vented, and the solid product was removed from the reaction vessel. The white crystalline solid consisted of a mixture of ammonium chloride and the mono-hydrochloride of 3,3-bis(aminomethyl)oxetane. The mixture was dissolved in 50% aqueous methanol and sufficient hydrogen chloride was added to convert the diamine monohydrochloride to the dihydrochloride. The solution was cooled and the solid crystalline product was filtered. It was then recrystallized twice from aqueous methanol. The product, 3,3-bis(aminomethyl)-oxetane dihydrochloride, was obtained in large, coarse, non-hygroscopic crystals, stable up to the melting point of 249°. The yields ran from 55 to 75%.

Anal. Calcd. for $C_5H_{12}ON_2 \cdot 2HCl$: C, 31.75; H, 7.46; N, 14.71. Found: C, 31.77, 31.47; H, 7.10, 7.45; N, 14.73, 14.87.

Liberation of free 3,3-bis(aminomethyl)oxetane from its dihydrochloride. The free diamine was prepared by treating the dihydrochloride with saturated potassium carbonate solution. The mixture was then separated and distilled rapidly. The diamine was obtained as a thick liquid, b.p. 97–99°/2 mm.; 71°/0.5 mm., 90°/1.5 mm. Redistillation through a spinning band column gave constant boiling material, b.p. 75.5/0.5 mm.

Anal. Calcd. for $C_5H_{12}ON_2$: C, 51.64; H, 10.41. Found: C, 51.46, 51.49; H, 10.20, 10.31.

3,3-Bis(benzamidomethyl)oxetane. The diamine was dibenzoylated by the usual Schotten-Bauman procedure. The solid product was filtered, washed, and dried. The solid was nearly pure as shown by its analysis. The dibenzamide was difficult to recrystallize, since it came out of most solvents as a gum. It was finally dissolved in ethyl acetate, treated with Norite, and filtered. The filtrate was placed in the refrigerator at −20° for one week. The crystals were filtered and dried, m.p. 168–169°.

Anal. Calcd. for $C_{19}H_{20}O_3N_2$: C, 70.34; H, 6.21. Found: C, 70.03, 70.05; H, 6.47, 6.40.

Reaction of 3,3-bis(aminomethyl)oxetane with phenylisothiocyanate. One gram of the diamine in dimethyl formamide (15 ml.) was mixed with 2 g. of phenylisothiocyanate in 15 ml. of the same solvent. The mixture became warm. After one hour it was poured into water and the solid was filtered. The solid was recrystallized from ethanol, m.p. 164–165°.

Anal. Calcd. for $C_{19}H_{22}OS_2N_4$: C, 59.07; H, 5.73. Found: C, 59.25, 59.09; H, 6.11, 6.36.

2,6-Dioxaspiro[3,3]heptane.[21] Dichloropentaerythritol[21] was made in over-all yields of above 80% by the conversion of pentaerythritol to the dichlorocyclic sulfite[22] followed by acid hydrolysis in aqueous methanol. A mixture of 50 g. of pentaerythritol dichloride, 48 g. of potassium hydroxide, and 200 ml. of 95% ethanol was refluxed 6 hr. and then allowed to stand at room temperature overnight. The mixture was brought to pH 7 with dilute hydrochloric acid and filtered. The filtrate was distilled through a spinning band column at atmospheric pressure. In this manner 10 g. of 2,6-dioxaspiro[3,3]heptane was obtained as a crystalline solid boiling at 170–172°. It was recrystallized twice from hexane to give a white crystalline solid melting sharply at 90°.

Anal. Calcd. for $C_5H_8O_2$: C, 60.06; H, 8.06. Found: C, 60.02, 59.85; H, 8.22, 8.26.

Polymerization with boron fluoride etherate gave a white, infusible, insoluble cross-linked polyether.

Reaction of 3,3-bis(chloromethyl)oxetane with sodium thiosulfate. A mixture of 99 g. (0.4 mole) of sodium thiosulfate pentahydrate in 100 ml. of water and 31 g. (0.2 mole) of bis(chloromethyl)oxetane in 150 ml. of ethanol was refluxed with stirring overnight. Two liquid phases of about equal volume were present initially, but merged to one after about 1–2 hr. refluxing, indicating that the reaction was probably complete. The reaction mixture was diluted with an equal volume of alcohol, and allowed to stand overnight again. The fine needle-like crystals were filtered and dried. The solid was boiled with 85% ethanol, which dissolved most of the product. The hot solution was filtered, and allowed to cool. After several hours, the needle-like crystals were filtered, recrystallized once more from the minimum amount of 85% ethanol and dried at room temperature. The yield was 57 g.

Anal. Calcd. for $C_5H_8O_6S_4Na_2 \cdot 3H_2O$: C, 15.32; H, 3.5; S, 32.5. Found: C, 15.61, 15.58; H, 3.1, 3.0; S, 31.1, 31.1.

In another experiment 15.5 g. of 3,3-bis(chloromethyl)-oxetane was dissolved in 150 ml. of ethanol and 49.6 g. of sodium thiosulfate pentahydrate in 30 ml. of hot water was added. This two-phase mixture was heated gently until the two layers became one. The mixture was then refluxed for an additional 48 hr. in the presence of a trace of dilute acid. Water was added and the oily precipitate was extracted into chloroform. Distillation of the chloroform gave about equal amounts of 3,3-bis(chloromethyl)oxetane, b.p., 6.52° at 2.5 mm. and a yellowish crystalline compound, b.p. 115–120° at 2.5 mm. This latter material was recrystallized twice from methylene chloride-hexane mixture. The product was a colorless crystalline compound melting at 90–91°.

Anal. Calcd. for $C_5H_8OS_3$: C, 33.30; H, 4.47; S, 53.36. Found: C, 33.52, 33.62; H, 4.55, 4.79; S, 53.9, 54.0.

The recrystallized di-Bunte salt was hydrolyzed by refluxing with dilute hydrochloric acid. The bright yellow product was extracted into dichloromethane and distilled. The distillate was a bright yellow liquid, b.p. 100–110°/2.5 mm. However, it could not be isolated since it polymerized rapidly in the receiving vessel to a rubbery polymer.

Reaction of 3,3-bis(chloromethyl)oxetane with sodium thiocyanate. A mixture of 20 g. of sodium thiocyanate and 250 ml. of acetone was heated to boiling to give a homogeneous solution. To this solution was added 31 g. of bis(chloromethyl)oxetane in an additional 100 ml. of acetone. The mixture rapidly assumed a yellow color which did not change with time. The mixture was refluxed over the weekend after which the precipitated sodium chloride was filtered. The filtrate was distilled to yield two compounds, after removal of the residual solvent and unreacted bis(chloromethyl)oxetane. The first (5.9 g.) b.p. 115°/1.5 mm., n_D^{25} 1.5298 was 3-chloromethyl-3-thiocyanomethyloxetane.

Anal. Calcd. for C_6H_8OSNCl: N, 7.88. Found: N, 7.60, 7.65.

The second, a solid (2.5 g.) pot residue, was recrystallized twice from absolute ethanol, using decolorizing carbon.

The product was obtained readily in the form of fine needles, m.p. 81.8–82.1.°

Anal. Calcd. for $C_7H_8OS_2N_2$: C, 42.0; H, 4.0; N, 14.0. Found: C, 42.0, 42.0; H, 4.0, 3.9; N, 13.8, 13.9.

Using a higher ratio of thiocyanate to oxetane, 6.3 g. of pure dithiocyano compound was obtained from 15.5 g. of 3,3-bis(chloromethyl)oxetane. Attempts to distil the dithiocyanate caused it to polymerize spontaneously to a dark tar. This tar also formed occasionally during the initial reaction with sodium thiocyanate in acetone, for no apparent reason, usually with such vigor as to eject the contents of the flask through the condenser.

Reaction of 3,3-bis(chloromethyl)oxetane with sodium thiophenoxide. A mixture of 31 g. of 3,3-bis(chloromethyl)oxetane, 200 ml. of absolute ethanol, and 11 g. of thiophenol was treated with a solution of 2.3 g. of sodium in 50 ml. of ethyl alcohol. The mixture was refluxed and stirred for 3 hr. at which time the solution was neutral. The precipitated sodium chloride was filtered and the filtrate was distilled. After a forerun of about 11 g. consisting of unreacted bis(chloromethyl)oxetane, the main product, 3-chloromethyl-3-phenylthiomethyloxetane was obtained, b.p. 144°/1.3 mm. The yield was 23 g.

Anal. Calcd. for $C_{11}H_{13}OSCl$: C, 57.6; H, 5.68. Found: C, 58.0, 57.8; H, 5.6, 5.7.

The undistillable pot residue appeared to be 3,3-bis(phenylthiomethyl)oxetane.

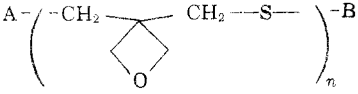
Anal. Calcd. for $C_{17}H_{18}OS_2$: S, 21.2.

Found: S, 21.08, 21.56, 21.30.

In another experiment employing a different ratio of reactants, 15.5 g. of bis(chloromethyl)oxetane was allowed to react with 22 g. of thiophenol in the presence of 4.6 g. of sodium in a manner described above. After 3 hr. the mixture was filtered and volatile materials removed. The pot residue which was a light straw-colored, viscous liquid was taken into 100 ml. of acetic acid and the mixture was filtered. Fifty ml. of 30% hydrogen peroxide was added to the acetic acid solution and the exothermic reaction was controlled by external cooling. After 3 hr. at room temperature the mixture was heated for an additional 2 hr. on a steam bath, then poured into water. The heavy oil which precipitated soon crystallized. The solid was filtered and dried. It was recrystallized from boiling ethyl alcohol to give 19.5 g. of product melting at 154–157°. An additional 8.5 g. of product melting at 140–147° was obtained from the filtrate by concentration. This product had a mixed melting point with the first fraction of 144–150°. Recrystallization of the first fraction from absolute ethanol gave a product melting at 159–159.5°.

Anal. Calcd. for $C_{17}H_{18}O_5S_2$: C, 55.8; H, 4.91; S, 17.46. Found: C, 56.2, 56.5; H, 4.9, 5.0; S, 17.47, 17.41.

2-Oxa-6-thiaspiro[3.3]heptane. A mixture of 38 g. of 3,3-bis(bromomethyl)oxetane, 38 g. of $Na_2S \cdot 9H_2O$, and 100 ml. of 95% ethanol was refluxed for 24 hr. and then cooled. Several grams of white solid which was incompletely soluble in water was filtered. This product was insoluble in alcohol, acetone, and ether but was soluble in chloroform. It was considered to be mainly



of unknown chain length and end groups.

Anal. Found: C, 45.33, 45.37; H, 6.23, 6.23; S, 21.3, 21.4, 21.2.

None of the desired spiro[3,3]heptane could be obtained from the nonpolymeric fraction.

Metallic sodium (11.5 g.) was added under nitrogen to 500 cc. of absolute ethanol. Hydrogen sulfide was passed into this solution until no more was absorbed. At this point another 11.5 g. of sodium was added. To the resulting solution of sodium sulfide was added 77.5 g. of bis(chloromethyl)oxetane and the mixture was refluxed for 24 hr. The reaction was stopped and the precipitate was filtered. The precipitate was washed repeatedly with ether and the combined filtrates were distilled, giving 10.3 g. (20%) of 2-oxa-6-thiaspiro[3.3]heptane, b.p. 60°/3 mm.

Anal. Calcd. for C_5H_8OS: S, 27.5. Found: S, 26.9, 26.3.

The filter cake, which was similar to that obtained above, was leached with water and dried at 90° at 1 mm. The solid polymer was broken up and extracted in a Soxhlet extractor with methylene chloride. The undissolved portions, consisting of approximately half of the total, was organic since it burned completely. However, it was infusible at 350°. The methylene chloride extract was evaporated to remove the solvent and was dried at 1 mm. The product was a very viscous oil which on standing became a wax. Solutions in methylene chloride on treatment with boron trifluoride etherate immediately gave insoluble, infusible polymer.

Anal. Found: C, 45.15, 45.27; H, 6.69, 6.81; S, 25.9, 25.9, 26.2.

2-Oxa-6-thiaspiro[3.3]heptane-6,6-dioxide. A sample of oxathiaspiroheptane, weighing 7.5 g., was treated with a mixture of 12.5 g. of 30% hydrogen peroxide and 12 ml. of glacial acetic acid. An exothermic reaction occurred which was moderated with ice water. When the reaction was complete, the residue was evaporated to dryness, recrystallized twice from methanol, and once from toluene. The product was obtained in a yield of 4.7 g. with a melting point of 161–162°.

Anal. Calcd. for $C_5H_8O_3S$: C, 40.54; H, 5.44. Found: C, 40.32, 46.62; H, 5.37, 5.46.

Polymerization of 2-Oxa-6-thiaspiro[3.3]heptane-6,6-dioxide. A sample of monomer weighing 1.90 g. was dissolved in about 5 ml. liquid sulfur dioxide at −50°. The solution was treated with a trace of BF_3 catalyst and allowed to stand overnight without external cooling. Next day the solid polymer was ground with alcohol and dried. The polymer melted at about 220°.

Anal. Calcd. for $(C_5H_8O_3S)_x$: C, 40.54; H, 5.40; S, 21.6. Found: C, 39.56, 39.60; H, 5.42, 5.40; S, 20.9, 20.8, 21.1.

The rather poor analyses reported above were probably the result of unknown end groups. The polymer was not of very high molecular weight.

Condensation of 3,3-bis(chloromethyl)oxetane and β,β′-dimercaptodiethyl ether. Ten grams of the dithiol and 11.2 grams of 3,3-bis(chloromethyl)oxetane were mixed with 25 ml. of 80% ethyl alcohol, treated with excess alkali, and refluxed under N_2. After 3 hr., the mixture was diluted with cold water and extracted with methylene chloride. This was in turn extracted with water, then dried and evaporated. The gummy residue was rubbed with methanol and the methanol extract was discarded. This procedure was repeated twice and the methanol-insoluble residue was dried in a high vacuum over P_2O_5.

Anal. Found: S, 28.0, 28.0, 27.9; Mol. wt. 1200 (ebullioscopic in benzene).

Reaction of piperidine with 3,3-bis(chloromethyl)oxetane. A mixture of 15.5 g. of 3,3-bis(chloromethyl)oxetane and 34 g. of piperidine was heated on a steam bath without solvent for 20 hr. The crystalline mush so obtained was treated with alkali and the liberated amines were taken into benzene. The benzene layer was washed with water, dried, and distilled. After considerable forerun the desired product, 3,3-bis(piperidinomethyl)oxetane was obtained in a yield of 8 g. with a b.p. 145°/3 mm.

Anal. Calcd. for $C_{15}H_{28}ON_2$: C, 71.39; H, 11.18; N, 11.09. Found: C, 71.49, 71.72; H, 10.81, 11.42; N, 10.59, 10.81.

A dipicrate, m.p. 180–185°, was prepared by mixing alcoholic solutions of picric acid and the diamine.

Anal. Calcd. for $C_{27}H_{34}O_{15}N_8$: N, 15.6. Found: N, 15.45, 15.90.

Reaction of 3,3-bis(chloromethyl)oxetane with benzoyl chloride. A mixture of 0.5 g. of 3,3-bis(chloromethyl)oxetane and 0.45 g. of benzoyl chloride was warmed at 110° for 16 hr. in a stoppered tube. The product, which solidified on cooling, was recrystallized from aqueous methanol, then from hexane. The yield was 0.86 g. of fine needles, melting point 77°.

Anal. Calcd. for $C_{12}H_{13}O_2Cl_3$: C, 48.76; H, 4.43. Found: C, 49.08, 48.83; H, 4.34, 4.45.

An authentic specimen of β,β,β-tris(chloromethyl)ethyl benzoate was prepared by benzoylating pentaerythritol trichloride with benzoyl chloride and pyridine. The product was recrystallized from hexane and had a melting point of 77° which was not depressed by a mixture of the reaction product of benzoyl chloride with 3,3-bis(chloromethyl)oxetane.

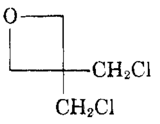
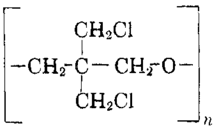
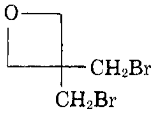
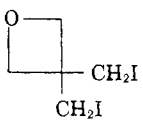
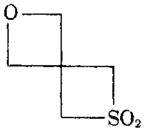
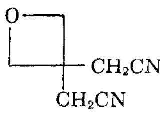
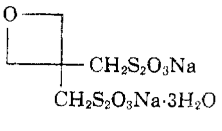
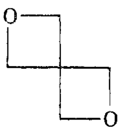
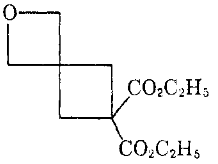
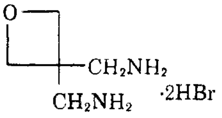
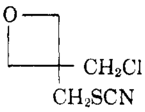
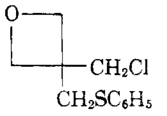
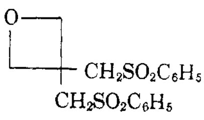
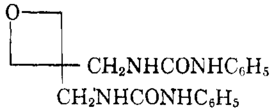
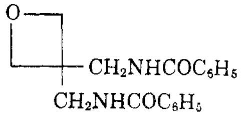
Reaction of bis(bromomethyl)oxetane with benzoyl bromide. Benzoyl bromide (3.70 g.) was added to 4.88 g. of 3,3-bis-(bromomethyl)oxetane. Reaction was rapid and exothermic in contrast to the slow reaction of benzoyl chloride reported above. β,β,β-Tris(bromomethyl)ethyl benzoate was obtained in a yield of 77% after recrystallization from hexane, m.p. 99.5–100°.

Anal. Calcd. for $C_{12}H_{13}O_2Br_3$: C, 33.58; H, 3.05. Found: C, 33.77, 33.73; H, 3.10, 3.12.

Condensation of terephthaloyl chloride with 2,5-dioxaspiro heptane. Equivalent amounts of terephthaloyl chloride (0.2 g.) and dioxaspiroheptane (0.1 g.) were mixed and the mixture was heated at about 150° for several hours. The reaction mixture gradually thickened and finaly solidified. The final product appeared to be cross-linked since it was not soluble in any solvents tested. Residual monomer was removed by swelling the polymer with dimethyl formamide. The swollen polymer was then triturated with ethanol and the resulting powder was washed repeatedly with more ethanol.

TABLE I

INFRARED BAND CHARACTERISTIC OF OXETANE RING

Structure Assigned to Compound	Position of Characteristic Band, μ	Remarks
	10.15 10.48	Band at 8.1 μ.
	9.0 (broad)	Measured as thin film. Bands at 10.15 and 10.48 completely absent.
	10.20 10.57	
	10.20 10.60 10.20 10.42 10.60	In chloroform solution. As a KBr pellet.
	10.05 10.30 10.65	Strong bands in —SO₂— stretching vibration region. (7.6–8.5 μ)
	10.22 10.42	Shows also characteristic —CN band at 4.48 μ.
	10.35 10.52 (10.85)	Sharp bands at 2.85–6.17 μ. Indicate water of crystallization.
	10.31 10.88	
	10.28 10.57	Ester band at 5.8 + 8.0 μ.
	10.45 10.68	Nothing in 8 μ region.
	10.18 10.50	Intense split band at 4.65–4.75 (—SCN). Band at 8.16.
	10.2 10.53	Bands assigned to mono substituted benzene rings present. These overlap and make uncertain presence of C—Cl band.
	10.13 10.52	—SO₂— vibrations at 7.7 and 8.8 μ. Nothing at *ca.* 8.0 μ. 10.13 band did not split in solid state.
	10.28	KBr pellet.
	10.55 10.15 10.35	In chloroform solution In KBr pellet.

Anal. Calcd. for $(C_{13}H_{12}O_4Cl_2)_n$: Cl, 23.4. Found: Cl, 17.9, 18.2.

The same reaction was carried out in nitrobenzene solution at 150°. The solution rapidly became thick and finally set to a stiff gel in approximately 0.5 hr. The polymer was washed free of solvent and unreacted monomer as in the preceding experiment.

Anal. Calcd. for $(C_{13}H_{12}O_4Cl_2)_n$: C, 51.5; H, 3.96. Found: C, 52.60, 52.52; H, 4.12, 4.25.

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