

Preparation and Polymerisation of Some 3:3-Disubstituted Oxacyclobutanes.

By A. C. FARTHING.

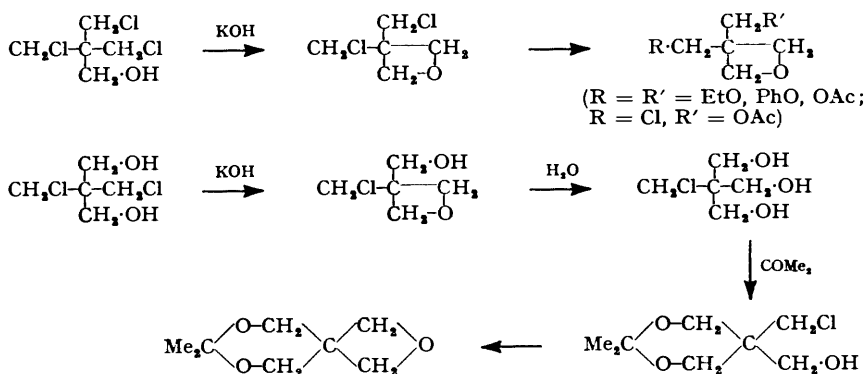
[Reprint Order No. 6428.]

The preparation of some 3:3-disubstituted oxacyclobutanes, mainly derived from pentaerythritol, and an improved preparation of pentaerythritol monochloride are described. The oxacyclobutanes are polymerised by powerful electrophilic catalysts to yield linear polyethers. The properties of the polymers are correlated with the nature of the substituent group. Solution polymerisation below room temperature gives the highest molecular weights. The boron trifluoride-catalysed polymerisation of 3:3-bis(chloromethyloxy)oxacyclobutane does not proceed in the absence of water: admission of traces of water results immediately in polymerisation.

THE preparation of a number of substituted oxacyclobutanes, in particular some derived from pentaerythritol, was undertaken as a preliminary to a study of their polymerisation (a preliminary communication to the XIII International Congress of Pure and Applied Chemistry was published in *J. Polymer Sci.*, 1954, **12**, 503). The literature on oxacyclobutanes from pentaerythritol has been reviewed by Marrian (*Chem. Rev.*, 1948, **43**, 149).

Oxacyclobutanes are made by the dehydrohalogenation of the appropriate 1:3-halogenohydrins. Because of the unfavourable steric factors, oxacyclobutane itself can be obtained in this way only in very poor yield (Derrick and Bissell, *J. Amer. Chem. Soc.*, 1916, **38**, 2478), though by treatment of the acetate of the chlorohydrin with solid potassium hydroxide Searles (*ibid.*, 1951, **73**, 124) was able to improve the yield to 45%. We have obtained 3:3-dimethyloxacyclobutane from the chlorohydrin in only 19% yield. When the central carbon atom bears two more bulky substituents the reacting groups are brought closer together, and good yields of the oxacyclobutanes are obtained. Thus Govaert and Beyaert (*Natuurw. Tijdschr.*, 1940, **22**, 73), obtained 3:3-bis(chloromethyloxy)oxacyclobutane in 70–80% yield from pentaerythritol trichloride, and using substantially their conditions we have obtained it in high yield.

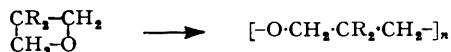
We have now carried out the annexed syntheses from pentaerythritol di- and trichloride, prepared as described by Mooradien and Cloke (*J. Amer. Chem. Soc.*, 1945, **67**, 942).



Replacement of the chlorine atoms in 3:3-bis(chloromethyloxy)oxacyclobutane by other groups required very vigorous conditions, as might be expected from the neopentyl-type structure of the compound. The preparations of pentaerythritol monochloride and of 3:3-bis(acetoxymethyloxy)oxacyclobutane are more convenient than those hitherto reported.

It is well known that boron trifluoride and other powerful electrophilic compounds polymerise many ethenoid compounds and also some strained three- and five-membered heterocycles. The mechanism is undoubtedly ionic and has been widely investigated in

recent years (for a review see Hamann, *Angew. Chem.*, 1951, **63**, 231). The polymerisation of oxacyclobutanes to polyethers has, however, not hitherto been studied. The work now reported is the subject of B.P. 723,777.



Linear polyethers have been made by extension of the classical methods for ether preparation; but such reactions rarely proceed quantitatively and the molecular weight of the polymer is accordingly limited. Thus, heating glycols with acid catalysts does give polyethers, but if the terminal hydroxyl group is lost by olefin formation the growth of the macromolecule ceases. This method has succeeded in the case of 2 : 3 : 5 : 6-tetramethyl-*p*-xylylene glycol (Rhoad and Flory, *J. Amer. Chem. Soc.*, 1950, **72**, 2216) where the peculiar structure of the glycol does not allow side-reactions. The Williamson reaction, using dihalides and disodium derivatives of glycols, has also been used to make polyethers (U.S.P. 2,060,715). The polymerisation of cyclic ethers is more attractive because the moiety which would require to be eliminated in a condensation reaction (water or sodium halide) is removed before the polymerisation. This can prove an advantage on purely manipulative grounds. In polymerisation of ethylene oxide (see Hamann, *loc. cit.*, for references) the molecular weight of the product is again limited by side-reactions, including isomerisation to acetaldehyde. As a general method the ring opening of cyclic ethers is of course limited by the stability of the ring.

However, for oxacyclobutanes we have found that the polymerisation can proceed to high molecular weight. Thus in the case of 3 : 3-bischloromethyloxacyclobutane, the monomer principally studied, it has been possible to polymerise to such molecular weight that the polymer could be spun to fibres which exhibit the property of "cold-drawing."

The polymerisation is very exothermic and consequently difficult to control when monomer alone is used. Thus conditions of bulk polymerisation were not suitable for a detailed study of the reaction. However, this method affords a rapid way of making polymers on a small scale in order that some structure-property relations may be established. The following Table summarises results so far obtained.

Structure-property relations in oxacyclobutane polymers, viz., $\left[-\text{O}-\text{CH}_2-\underset{\text{CH}_2\text{R}'}{\overset{\text{CH}_2\text{R}}{\text{C}}}-\text{CH}_2- \right]_n$

| R | R' | M. p. | | Solubility in H ₂ O |
|-----|-----|-------|-----------|--------------------------------|
| Cl | Cl | 180° | Cryst. | Insol. |
| Cl | OAc | 72 | Amorphous | Insol. |
| OAc | OAc | — | Amorphous | Sol. |
| OH | OH | >280 | Cryst. | Insol. |
| Me | Me | 47 | Cryst. | Insol. |
| OEt | OEt | 75—83 | Cryst. | Insol. |
| OPh | OPh | 85 | Amorphous | Insol. |

The polymer where R = R' = OH could not be made directly. It was prepared by polymerising 7 : 7-dimethyl-2 : 6 : 8-trioxaspiro[3 : 5]nonane, which gave an amorphous polymer freely soluble in benzene. The protecting ketal group was removed by hydrolysis to yield a range of polymers. As the hydroxyl groups were freed the polymer became insoluble in non-polar solvents and soluble only in highly polar solvents, and after acid hydrolysis at 100° it became insoluble even in highly polar solvents such as formic acid. This change in properties is due probably to progressively increasing hydrogen-bonding between the polymer chains, and may be compared to that in analogous derivatives of cellulose. Attempts to prepare linear polymers from oxacyclobutanes containing free hydroxyl groups resulted in cross-linked polymers, as would be expected.

The properties of the other polymers in the Table are governed by the symmetry, polarity, and size of the substituent groups and may be correlated with these factors.

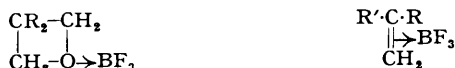
The polymerisation of 3 : 3-bischloromethyloxacyclobutane has been studied in more detail. The molecular weights of the polymers from 3 : 3-bischloromethyloxacyclobutane were compared by melt-viscosity measurements. An absolute measure of molecular weight has not yet been made because solution-viscosity measurements were anomalous, probably

because the high intra- and inter-molecular forces do not allow the molecules of dissolved polymer to separate and open out completely. This explanation is consistent with the high crystallinity and low solubility of the polymer at room temperature.

It was found that the polymerisation is generally catalysed by powerful electrophilic substances. For most of the work boron trifluoride-diethyl ether complex ($\text{BF}_3 \cdot \text{Et}_2\text{O}$) was selected because it was easier to handle and purify.

Bulk polymerisation did not give really high molecular weights, probably owing to lack of temperature control and consequent decomposition of the "geggenion." Accordingly polymerisation in solution, under reflux, was examined. Solvents boiling above room temperature gave lower molecular weights than did bulk polymerisation. The use of lower-boiling solvents such as methyl chloride gave much higher molecular weights. Thus bulk polymerisation yielded polymer of melt viscosity ~ 200 poises at 197° , polymerisation in methyl chloride ~ 200 poises at 277° . In all the work attention was paid to the conditions of dryness of the reagents and apparatus, with the precautions commonly used for water-sensitive organic reactions. However, about 30 experiments revealed that experimental results (yield and viscosity of polymer) could not be accurately reproduced, nor could these results be correlated with any of the experimental conditions. It was apparent that some critical factor had not been brought under control. In view of the work of A. G. Evans (see, e.g., Hamann, *loc. cit.*) on the importance of co-catalysis in *isobutene* polymerisation it appeared likely that co-catalytic effects were responsible for this lack of reproducibility, and suspicion was directed to variable traces of water (cf. Norris and Russell, *Trans. Faraday Soc.*, 1952, **48**, 91). An apparatus was accordingly devised in which the polymerisation could be carried out in the presence of controlled, minute amounts of water. It was then shown unequivocally that a co-catalyst is necessary for reaction. Under rigorously dry conditions, reaction did not take place until admission of traces (of the order of 0.01%) of water. The influence of the proportion of co-catalyst has not yet been determined accurately, but when the proportion of water was kept to such a low level it was possible to make polymer of considerably higher molecular weight than hitherto.

An analogy with the cationic polymerisation of ethenoid compounds immediately suggests itself. It is certain now in both cases that the monomer-"catalyst" adduct, which may be written:



is not capable of inducing polymerisation. On admission of water protons are generated, which initiate polymerisation through oxonium or carbonium ions:



It has been shown that the triethyloxonium ion is capable of polymerising *oxacyclobutanes*.

Whether ether can function as a co-catalyst, as with polymerisation of *isobutene* (Evans and Meadows, *J. Polymer Sci.*, 1949, **4**, 359), has not yet been established. When the boron trifluoride-ether complex was used, as described above, traces of water would certainly also be present.

EXPERIMENTAL

3 : 3-Bischloromethyloxacyclobutane.—Potassium hydroxide (70% K_2O ; 435 g., 1 mol.) was dissolved in 98% ethanol ($2\frac{1}{2}$ l.). Then were added pentaerythritol trichloride (1240 g., 1 mol.) and also trichloride (285 g.) recovered from a previous preparation, slightly contaminated with the *oxacyclobutane*. The solution was boiled under reflux, with stirring, for 15 min., and left to cool. Potassium chloride (483 g.) was filtered off and washed with ethanol. The combined liquors were concentrated, filtered, and fractionated, to yield **3 : 3-bischloromethyloxacyclobutane** (925 g.), b. p. $80^\circ/10$ mm., and trichloride (370 g.), b. p. $130^\circ/12$ mm. containing a little *oxacyclobutane*. With allowance for recovered trichloride the yield was $\sim 90\%$. The **3 : 3-bischloromethyloxacyclobutane**, purified by drying (CaH_2), followed by distillation at 0.05 mm., had m. p. 18.7° , d_{25}^{25} 1.2951, n_D^{20} 1.4858.

3 : 3-Bisacetoxymethyl- and 3-Acetoxyethyl-3-chloromethyl-oxacyclobutane.—3 : 3-Bis-chloromethyloxacyclobutane did not react with potassium acetate in boiling ethanol or acetic acid. Consequently it was heated alone with anhydrous potassium acetate (2 mols.) for 4 hr. at 180°. The product was filtered and washed with dry ether. After removal of the ether the residue was fractionally distilled, to yield two main fractions, b. p. 42—44°/0.05 mm. and 68°/0.05 mm. The former, when redistilled (b. p. 120—121°/13 mm.; 30% yield) was 3-acetoxy-methyl-3-chloromethyloxacyclobutane (Found : C, 46.7; H, 5.7; Cl, 18.65. $C_7H_{11}O_3Cl$ requires C, 47.0; H, 6.15; Cl, 18.9%). The second fraction, b. p. 152°/21 mm. (60% yield), was 3 : 3-bis-acetoxymethyloxacyclobutane (Found : C, 52.9; H, 7.0. Calc. for $C_9H_{14}O_5$: C, 52.4; H, 6.9%) as described by Govaert and Bayaert (*Proc. Acad. Sci. Amsterdam*, 1939, 42, 790).

3-Chloromethyl-3-hydroxymethyloxacyclobutane.—Pentaerythritol dichloride (1015 g.) in ethanol (700 c.c.) was stirred in a 5-l. flask under reflux, with gentle heating to dissolve the dichloride. Potassium hydroxide (325 g.; 1 mol.) in ethanol (1.3 l.) was then added during 5 min., with stirring. Next morning the solution was boiled for 5 min. Potassium chloride was filtered off and washed with ethanol. The liquors were concentrated and the residue fractionated, to yield a syrup, b. p. 120—130°/10 mm. (585 g.), and a mixture of syrup and crystals, b. p. 130—148°/10 mm. (139 g.). The latter fraction was largely unchanged starting material; the former (86% yield) was redistilled at 64°/0.09 mm. and was 3-chloromethyl-3-hydroxymethyloxacyclobutane (Found : C, 43.5; H, 6.6; Cl, 26.0. $C_5H_9O_2Cl$ requires C, 44.0; H, 6.6; Cl, 26.2%).

Pentaerythritol Monochloride.—3-Chloromethyl-3-hydroxymethyloxacyclobutane (400 g.) in water (2 l.) containing concentrated sulphuric acid (3.0 c.c.) was boiled under reflux for 6 hr. After partial concentration the acid was precipitated with barium hydroxide and removed by filtration. After total removal of the water the residue was distilled, to give pentaerythritol chloride, b. p. 160°/0.09 mm. (368 g.; 81%).

5-Chloromethyl-5-hydroxymethyl-2 : 2-dimethyl-1 : 3-dioxan.—The preceding product was dissolved in pure acetone (2 l.) containing dry hydrogen chloride (20 g.). The solution was left overnight and then stirred with excess of anhydrous potassium carbonate until neutral. After removal of acetone the residue was distilled, to yield 374 g. (80%) of 5-chloromethyl-5-hydroxy-methyl-2 : 2-dimethyl-1 : 3-dioxan, b. p. 80°/0.1 mm. (Found : C, 49.6; H, 7.6; Cl, 18.7. $C_8H_{13}O_3Cl$ requires C, 49.4; H, 7.7; Cl, 18.3%). A sample with 2 : 4-dinitrophenylhydrazine in 2N-hydrochloric acid gave acetone 2 : 4-dinitrophenylhydrazine.

7 : 7-Dimethyl-2 : 6 : 8-trioxaspiro[3 : 5]nonane.—The chloride from the preceding preparation was dehydrochlorinated in the same manner as the pentaerythritol chlorides, to yield 66% of 7 : 7-dimethyl-2 : 6 : 8-trioxaspiro[3 : 5]nonane, b. p. 40°/0.15 mm., 91°/13 mm. (Found : C, 60.8; H, 8.7. $C_8H_{14}O_3$ requires C, 60.75; H, 8.85%).

3 : 3-Bisphenoxyethyloxacyclobutane [Prepared by Mr. J. M. PHILLIPSON].—3 : 3-Bis-chloromethyloxacyclobutane was heated with dry potassium phenoxide (2 mols.) at 120—125° for 2 hr. and the mixture directly distilled, to yield 40% of 3 : 3-bisphenoxyethyloxacyclobutane, b. p. 143°/0.05 mm., m. p. 68° (from methanol) (Found : C, 75.6; H, 6.6. $C_{17}H_{18}O_3$ requires C, 75.5; H, 6.6%).

3 : 3-Bisethoxymethyloxacyclobutane [Prepared by Dr. P. C. JOHNSON].—3 : 3-Bischloro-methyloxacyclobutane (31.0 g.) was added to a solution of potassium (25.0 g.) in dry ethanol (150 c.c.). The solution was boiled under reflux for 20 hr. and cold filtered from potassium chloride. Ethanol was removed, finally at the water pump. The distillate was fractionated, to give 3 : 3-bisethoxymethyloxacyclobutane, b. p. 81.5—82°/19 mm. (23 g., 68%) (Found : C, 62.2; H, 9.9. $C_9H_{18}O_3$ requires C, 62.0; H, 10.3%).

3-Chloro-2 : 2-dimethylpropan-1-ol.—2 : 2-Dimethylpropan-1 : 3-diol was treated with 1 mol. each of pyridine and thionyl chloride under the conditions used by Mooradien and Cloke (*loc. cit.*) for pentaerythritol. The mixture was taken up in water (1 l.) and acidified with concentrated hydrochloric acid, then extracted three times with ether; the extract was dried ($MgSO_4$) and the ether removed. The residue was fractionated, to yield the chloride, b. p. 78—80°/10 mm. (240 g., 54%).

3 : 3-Dimethyloxacyclobutane.—The preceding chlorohydrin (248 g.) was slowly added to potassium hydroxide (250 g.) with stirring, at such a rate that the temperature of the distillate did not exceed 80°. When reaction ceased the remaining volatile matter was distilled off at room temperature to a condenser at -70° by application of water-pump vacuum. The total condensate was dried with potassium hydroxide and fractionated, to yield 3 : 3-dimethyloxacyclobutane, b. p. 79.5—80° (33 g., 19%) (cf. Bennett and Phillip, *J.*, 1928, 1937).

Polymer from 3 : 3-Bischloromethyloxacyclobutane.—The molecular weights of the various

preparations of the polymer were compared by measurement of melt viscosity, which is given in poises at the temperature of measurement. There being no solvent available which dissolved the polymer at 25°, the following solution viscosities were determined at 100° and 0.5 g./100 c.c. in *o*-dichlorobenzene:

| | | | | |
|--------------------------------|------|------|------|------|
| Logarithmic viscosity no. | 18.0 | 23.8 | 19.0 | 16.0 |
| Melt viscosity at 197° | 390 | 150 | 25 | 210 |

On one polymer sample the following results were obtained:

| | | | | |
|--------------------------------|------|------|------|------|
| Logarithmic viscosity no. | 27.0 | 23.8 | 18.6 | 23.2 |
| Concn. (g./100 c.c.) | 0.25 | 0.5 | 1.0 | 2.0 |

Another sample of logarithmic viscosity no. 16.0 at 0.5% was capable of forming oriented fibres, whereas all the samples above were of too low a molecular weight to be cold-drawn.

Bulk polymerisations. Portions of 3:3-bischloromethyloxacyclobutane (60 g.) were treated with boron trifluoride-diethyl ether complex (redistilled; 0.15 c.c. and 0.3 c.c.). After 3 min. and 1 min. respectively the two mixtures became very hot and viscous. On being kept overnight the polymers became opaque. Each was heated at 197°/15 mm. for 50 min.; 21.3% and 20.8% respectively of monomer was thus removed, leaving polymer of melt viscosity 390 and 150 at 197°.

Solution polymerisation above room temperature. Monomer (10 c.c.) in pure dry solvent (10 c.c.) was treated with boron trifluoride-diethyl ether (redistilled; 2.0 c.c.). After *ca.* 2 min. the solution was boiled under reflux for *ca.* 30 sec. and set to a pale pink paste. The solid polymer was filtered off, washed with dry ether, and dried at 100°, to give the following results:

| Solvent | Yield (g.) | η (at 197°) | Softening point |
|----------------------------|------------|------------------|-----------------|
| Methylene dichloride | 12 | 24 | 178° |
| Benzene | 9 | 26 | 180 |
| Ether | 11 | 24 | 178 |

Many other solvents were examined, *o*f b. p. above room temperature, with various monomer and catalyst concentrations, but the viscosity of the products remained at 20–60 at 197°.

Solution polymerisation below room temperature. A flask fitted with (i) a cold-finger type of reflux condenser carrying a calcium chloride tube, (ii) a stirrer, sealed with rubber tubing, and (iii) an aperture for addition of reagents, was assembled hot from components dried at 100° for at least 1 hr. The condenser was charged with solid carbon dioxide and ethanol, and a known volume of solvent distilled in from the cylinder, through several drying towers of sodium hydroxide or calcium chloride. The flask was cooled and a known volume of monomer added, followed by boron trifluoride-diethyl ether. The reaction was left to proceed at the temperature of reflux. A wide range of conditions was covered, solvents being methyl chloride, sulphur dioxide, and dichlorofluoromethane. Monomer concentration varied from 50 to 30% and catalyst proportion from 1.5 to 5% (on monomer). The melt viscosities obtained were from 60 to 240 at 277°, much higher than those obtained above room temperature; but the results were not reproducible nor could the influence of experimental conditions be discerned.

Properties of the polymer. The polymer was a tough solid, softening point 180° (penetrometer method, Edgar and Ellery, *J.*, 1952, 2633). It was highly crystalline. Fibres could be spun from the molten polymer and these could readily be cold-drawn to yield highly oriented specimens of identity period 4.8 Å (calc. 4.92 Å for the fully extended repeating unit). It had very high X-ray absorption, no doubt due to the high chlorine content (Found: Cl, 45.35. Calc. for $[C_5H_8OCl_2]_n$: Cl, 45.6%). It was insoluble generally at room temperature, but freely soluble at 100° in chlorinated hydrocarbons, esters, and amines.

Polymers from 3-Chloromethyl-3-hydroxymethyl- and 3:3-Bishydroxymethyl-oxacyclobutane, and 2:6-Dioxaspiro[3:3]heptane.—Each of these compounds rapidly polymerised with traces of boron trifluoride-diethyl ether. Polymer was formed round the drop of catalyst and often stopped further reaction. The polymers were insoluble and infusible without decomposition. The last two monomers were made by recorded methods (Marrian, *Chem Rev.*, 1948, 43, 149).

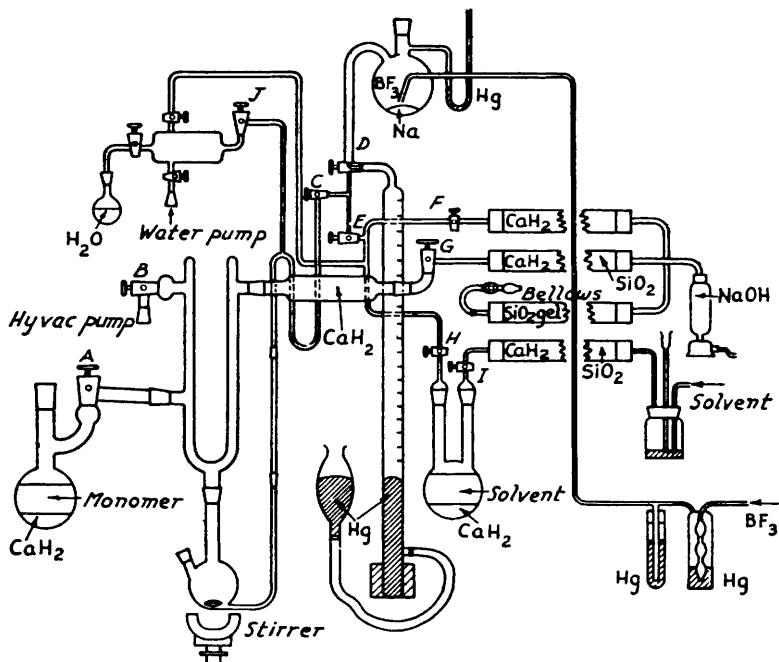
Polymer from 3:3-Bisacetoxymethyl-oxacyclobutane.—The monomer (5 g.) with boron trifluoride-diethyl ether (0.05 c.c.) reacted slowly compared with the bischloromethyl derivative. The temperature of the mixture did not rise above 35°. On storage overnight there was left a soft colourless and clear resin, hygroscopic, and freely soluble in hot and cold water.

Polymer from 3-Acetoxymethyl-3-chloromethyl-oxacyclobutane.—The monomer (25 g.) was treated with boron trifluoride-diethyl ether (0.3 c.c.). Overnight the mixture became a hard brittle resin, softening point (copper block) 72°, insoluble in water.

Polymer from 3:3-Dimethyloxacyclobutane.—The monomer was extremely sensitive to

boron trifluoride-diethyl ether. Thus monomer (2 c.c.) and catalyst (0.05 c.c.) reacted immediately with evolution of heat. Polymerisation occurred immediately at -70° with the same mixture. In all cases the viscous polymer set to a white wax, m. p. 47° (capillary), giving a sharply defined X-ray diffraction pattern. It was insoluble in water and ethanol, soluble in benzene.

Polymer from 7 : 7-Dimethyl-2 : 6 : 8-trioxaspiro[3 : 5]nonane and its Conversion into lin-Polypentaerythritol.—The spiran (20 g.) was treated with boron trifluoride-diethyl ether (0.2 c.c.). Overnight the mixture set to a tough translucent solid, m. p. 102° (capillary), soluble in benzene. The polymer was cut into flakes and immersed in water for 2 days. The flakes became brittle and the water contained acetone (identified as 2 : 4-dinitrophenylhydrazone). The flakes were ground in a mortar and covered with *N*-hydrochloric acid for 1 hr. The polymer was collected, washed with water, and dried over sodium hydroxide. It then had m. p. 220 – 250° , and was insoluble in benzene and soluble in *m*-cresol to give a viscous solution. Further treatment



with 0.2*N*-hydrochloric acid at 100° for 1.5 hr. gave a polymer, m. p. $>280^{\circ}$, insoluble in formic acid, *m*-cresol, and cupriethylenediamine reagent, and giving an X-ray photograph characteristic of a crystalline compound. Treatment of the above *m*-cresol solutions with traces of concentrated hydrochloric acid resulted in immediate gelation. Infrared analysis of the polymers showed the formation of hydrogen-bonded hydroxyl groups as hydrolysis proceeded.

Polymer from 3 : 3-Bisethoxymethyloxacyclobutane.—Boron trifluoride-diethyl ether (0.1 c.c.) was added to monomer (1 c.c.) in boiling methyl chloride (1 c.c.). After the solution had boiled under reflux for 5 hr. methanol (1 c.c.) was added. The mixture was diluted with ether, and the polymer filtered off and dried [0.5 g.; m. p. 75 – 83° (capillary), softening at $\sim 45^{\circ}$]. X-Ray examination showed it to be highly crystalline. It was insoluble in water.

Polymer from 3 : 3-Bisphenoxy-methyloxacyclobutane.—Boron trifluoride-diethyl ether (0.05 c.c.) was added to a solution of monomer (1.0 g.) in dichlorofluoromethane (1 c.c.). After the solution had boiled under reflux for 3 hr. methanol (1 c.c.) was added and the polymer isolated by decantation and dried. It was a clear glassy resin, m. p. $\sim 85^{\circ}$ (capillary).

Other Catalysts in Oxacyclobutane Polymerisations.—Bentonite, trifluoroacetic acid, and tris-2-chloroethyl borate were without effect. Boron trifluoride-acetic acid complex ($\text{BF}_3 \cdot 2\text{AcOH}$) and triethyloxonium fluoroborate were active catalysts, stannic chloride was less active, and concentrated sulphuric acid least active, on the basis of qualitative test-tube experiments with various monomers.

"Dry" Apparatus.—The apparatus is reproduced, roughly to scale except for the long drying tubes, in the Figure. The central part, bounded by taps *A*, *B*, *C*, *D*, *E*, *G*, and *J* could

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be evacuated to 0.02 mm. and then heated to $\sim 200^\circ$ to remove water and other volatile materials. Other parts were kept dry by calcium hydride. Monomer and solvent were dried over calcium hydride, and boron trifluoride over flakes of sodium. Exits from the apparatus were protected by tubes 3 ft. long and $1\frac{1}{2}$ in. in diameter packed with silica gel and calcium hydride. These long tubes were themselves protected from the atmosphere. The condenser and its attached calcium hydride tube up to tap *G* were wound with "Nichrome" wire connected to a 25-v transformer for heating the glass. The rest of the apparatus was heated with a free flame. The reaction mixture was stirred magnetically.

The use of the apparatus may largely be inferred from inspection of the Figure. Solvent was distilled into the solvent reservoir at least 24 hr. before use and stored there over calcium hydride. Monomer, already dried by calcium hydride, was added to the monomer reservoir as required and kept at least 24 hr. over calcium hydride before use. The apparatus was dried by heating and evacuation and left to cool whilst connected to the pump. Monomer was then distilled up to a mark on the reaction vessel with solid carbon dioxide to cool the condenser, the vacuum was discharged with solvent, and tap *G* opened. Solvent was next distilled up to a second mark. Then, with stirring, boron trifluoride was added, being forced through the tube by use of the hand bellows. After some time water was added from the chamber to initiate reaction. The chamber was of 97 c.c. capacity. It was evacuated at the water pump and left for *ca.* 30 min. to come to equilibrium with the water in the flask. The water vapour was then transferred to the reaction mixture with the aid of a small amount of solvent. It is doubtful whether all the water (2.26 mg. at 25°) reached the reaction mixture, as some would probably be adsorbed by the dry glass after tap *J*.

Reaction flasks of up to 500 c.c. capacity were used, in which 100 c.c. samples of monomer could be polymerised. The polymer was precipitated from the solution, and after 2—3 days the solvent was allowed to evaporate through tap *G*. The flask was immediately replaced by a fresh one, with a fresh stirrer capsule. Any solvent vapour was removed at the water pump, and the apparatus was ready for re-use.

Silicone grease was adequate for taps not in contact with boron trifluoride. After trial, taps *C*, *D*, and *E* were lubricated satisfactorily with a chlorofluorocarbon grease kindly supplied by Imperial Chemical Industries Limited, General Chemicals Division. Other greases were degraded by boron trifluoride (except Silicone grease, which was converted into a cement) Tap *C* was added to the apparatus because tap *D* tended to leak slightly except when it was freshly greased.

Boron trifluoride was selected as catalyst because it could be easily manipulated under dry conditions.

Results. In an experiment with monomer (20 c.c.), methyl chloride (60 c.c.), and boron trifluoride (1.93% w/w on monomer), there was no polymerisation after 3 hr. In a similar experiment with 3.92% of boron trifluoride there was a very slight haze in the mixture after 22 min. The reaction vessel was lowered by the length of the joint for 5 sec. and replaced. There was an immediate precipitate of white clots of polymer. To monomer 10 c.c., methyl chloride (20 c.c.), and boron trifluoride (90 c.c.) (at $21^\circ/765$ mm.; 0.252 g., 1.95% on monomer) there was added the contents of the water-vapour chamber (97 c.c. of water vapour at $21^\circ/18.6$ mm.; 1.77 mg.). There was an immediate precipitate of polymer. After 22 hours' reaction the reaction flask was detached and some methanol added. There were recovered 13 g. of polymer (100% yield).

The melt viscosities of the polymer obtained varied between 300 and 3000 poises at 277° .

In a higher-boiling solvent, dichlorofluoromethane (b. p. $+8.9^\circ$; cf. methyl chloride -24.22°), and similar amounts of reagents, melt viscosities of 200—300 poises at 277° were obtained. However, these figures were obtained during early experiments with the apparatus and the lower viscosities may be a consequence of a somewhat higher adventitious moisture content.

The author thanks Dr. H. Gudgeon for advice and encouragement, Mr. A. M. Jones for valuable experimental assistance throughout the whole of the work, Dr. C. J. Brown for X-ray measurements, and Mr. J. S. F. Gill for melt-viscosity determinations.

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[Received, May 13th, 1955.]