Polycarbonates from the 2,2,4,4-Tetramethylcyclobutane-1,3-diols

*Part I: Preparation and Structure**

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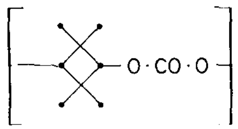
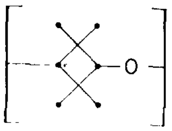
The preparation of a series of polycarbonates of high molecular weight from the cis- *and the* trans-*2,2,4,4-tetramethylcyclobutane-1,3-diols is described. Methods were established for determining the ratio of* trans- *to* cis- *repeat units in the polymers and the nature of an extensive side reaction producing carbon dioxide and 2,2,4-trimethyl-3-pentenal was investigated.*

POLYCARBONATES of aromatic dihydroxy compounds are well known, but very few examples of polycarbonates based entirely on alicyclic diols have been reported. A mixture of the *cis-* and *trans*-2,2,4,4-tetramethylcyclobutane-1,3-diols has recently become available commercially, and this prompted us to prepare polycarbonates, I, from these diols. At the outset of this project, two interesting possibilities were apparent: first polymers of controlled physical properties could be prepared by controlling the ratio of *cis-* to *trans*-cyclobutane units in the chain, which appeared possible because a means of separating the isomeric diols was known[2,3], and secondly polymers containing units of structure, II, might be prepared by thermal decomposition of the polycarbonates, I. There appears to be no well documented example of the preparation of polyethers by these means, but the preparation of cyclic ethers by the base catalysed pyrolysis of the cyclic carbonates or linear polycarbonates of certain 1,3-diols has been reported by Searles *et al.*[4], who have postulated the following mechanism for the reaction:

I





II

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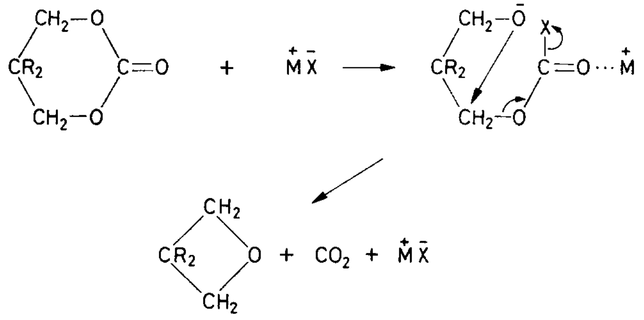
*A preliminary account of this work has been published previously[1].

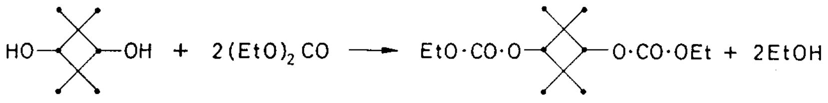


For the case of the polycarbonate, I, intramolecular reaction of the type indicated above would not be possible as too great a distortion of the normal valency angles would be required to produce a cyclic ether, so that the only ether which could be formed would be the polymeric structure, II.

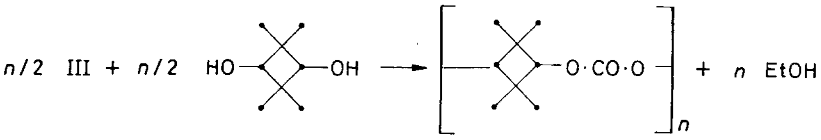
This paper describes the preparation of high melting polycarbonates of known steric composition from these diols, the dependence of the physical properties of the polymers on their steric composition being described in Part II[5]. However, it was not possible to realize the conversion of the polycarbonates, I, to the polyethers, II, although an extensive side reaction producing carbon dioxide was shown to occur.

RESULTS

The polymers were prepared by base catalysed ester interchange between the diols and their bis(ethyl carbonate) esters, III, these latter compounds being prepared in good yield by base catalysed interchange between the diols and a large excess of diethyl carbonate.



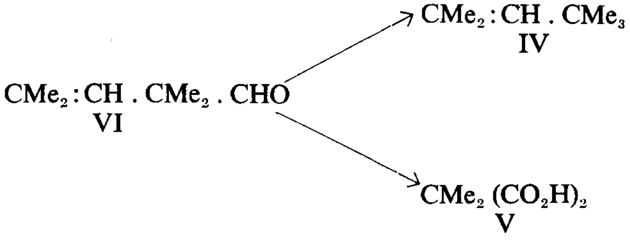
III



Although ester interchange between the diols and their ethyl carbonate esters readily gave polymers of high molecular weight, the yield of polymer was always less than that expected from the quantities of reagents used. It was found that carbon dioxide was evolved during the later stages of the polymerizations and that the liquid distilling from the melt contained a little ethyl carbonate and a liquid boiling at 146°C, as well as ethanol. Some solid products also distilled out of the polymerization vessel and these were shown to be unreacted starting materials.

Carbon, hydrogen and molecular weight determinations carried out on the liquid boiling at 146°C showed that it had the empirical formula

$C_8H_{14}O$. This liquid reduced ammoniacal silver nitrate, and gave a crystalline semi-carbazone and phenylhydrazone. Its infra-red spectrum was similar to that of 2,4,4-trimethylpentene-2, except that it showed a strong absorption at 1 728 cm^{-1} typical of an aldehyde type carbonyl group. Wolff–Kishner reduction of both the hydrazone and the semi-carbazone of the aldehyde gave 2,4,4-trimethylpentene-2, IV, and oxidation of the aldehyde with dichromate or with alkaline permanganate gave a mixture of products from which dimethyl malonic acid, V, was isolated. Thus, the aldehyde is 2,2,4-trimethyl-3-pentenal, VI, and its Wolff–Kishner reduction, and its oxidation occurs as follows:



There are references[6-8] in the older literature to the preparation of an aldehyde thought to have the structure, VI, by dehydration of isobutyraldol, but no sound proof of structure was given and such physical constants that were recorded are not in agreement with ours. Since our work was completed, a new preparation of VI by acid catalysed dehydration of *trans*-2,2,4,4-tetramethylcyclobutane-1,3-diol has been reported[9], proof of structure being provided by i.r. and n.m.r. techniques, together with hydrogenation to the known saturated trimethyl pentanol. The physical constants and melting points of derivatives recorded are in agreement with those noted by us so that the structure, VI, is assigned correctly.

A number of inorganic bases were tried as catalysts and it was found that both the rate of polymerization and the extent to which decarboxylation occurred depended on the basicity of the catalyst. Weak bases, such as butyl titanate or aluminium tertiary butoxide, were poor catalysts and with these extended reaction times were required to produce polymers which were of low molecular weight. However, these catalysts caused little decarboxylation. Metallic magnesium or calcium were somewhat better, but it was not possible to obtain polymers of high molecular weight in a reasonable time without too much decarboxylation. Lithium hydride worked fairly well but tended to give more decarboxylation than did the carbonate. Potassium cyanide and potassium borohydride were powerful catalysts inducing rapid reaction at relatively low temperatures but decarboxylation occurred to such an extent that no polymer was obtained. Lithium carbonate appeared to be the best catalyst and all further polymerization experiments were carried out using this compound.

Polymerizations were carried out in two stages, the first involving reaction between the diol and its bis(ethylcarbonate) ester at atmospheric pressure and a maximum temperature of 260°C, while in the second stage the temperature was gradually raised to 280°C or above while the pressure was reduced to 0·1 mm of mercury. Results obtained by varying both the concentration of catalyst and the final temperature of the second polymerization stage are given in *Table 1*.

Table 1. Polymerizations catalysed by lithium carbonate

10^4 [*catalyst*] (*moles*)	% *Yield*	η*	*Temperature of polymerization (2nd stage)*	*Mole % decarboxylation*
3·1	59	1·52	280–300°	15
6·2	53	1·98	280–290	16
3·1	53	1·92	280–300	16
6·2	50	2·53	280–290	22
12·4	43	2·75	280–290	26
3·1	18·7	1·4	280–330	54

*Specific viscosity for one per cent solution in chloroform at 25°C.

It appears from these results that as the conditions of polymerization become more rigorous, due either to the use of higher catalyst concentrations or higher temperatures, the degree of polymerization increases but loss of reagents due to decarboxylation also becomes greater. Eventually this loss becomes so severe that it is reflected in a decrease in the degree of polymerization. Thus, careful control of polymerization conditions was required to produce satisfactory yields of high molecular weight polymer. However, although extensive decomposition always occurred during polymerization microanalysis of the polymers for carbon and hydrogen gave values as calculated for a polycarbonate with the repeat unit I and quantitative alkaline hydrolysis gave results consistent with a polymer containing 100 ± 1 per cent of these units. The i.r. spectra of the polymers was as expected from structure I and no bands attributable to ether linkages, structure II, could be observed.

Having determined optimum polymerization conditions using intermediates derived directly from the commercially available mixture of isomeric diols, samples of the pure *cis-* and *trans-* diols were separated from the mixture by a known[3] method and their bis(ethyl carbonate) esters prepared. Polymers could then be prepared from intermediates of known steric composition. An assignment of *cis-* or *trans-* structures to the diols has been made[2] on the basis of their n.m.r. spectra. These diols have different i.r. spectra, and we have used this difference to determine the *trans-/cis-* ratios of their mixtures. Methanolysis of mixtures of the *cis-* and *trans-* esters, III, and of the polymers, I, followed by determinations of the *trans-/cis-* ratios of the diol mixtures so obtained provided a simple and convenient method of measuring the ratio of *trans-* to *cis-* repeat units in polymers made from reactants of known steric composition. Sterically pure esters, and polymers prepared from sterically pure reactants gave pure *cis-* or *trans-* diols on methanolysis, showing that no isomerization occurs during their preparation.

Details of some of the polymerizations are given in *Table 2* from which it appears that using reactants containing both *cis-* and *trans-* units, the *trans-/cis-* ratio in the polymers is always less than that in the respective reactants, so that during polymerization *trans-* units are eliminated from the product more readily than *cis*-. The yields of polymers obtained ranged from 40 to 60 per cent of the theoretical, the balance of the reagents appearing either as decarboxylation products (aldehyde plus carbon dioxide) or as unreacted monomers, more diol than di-ester generally being lost in this way. It was found that the molar proportion of carbon dioxide evolved was always a little greater than that of the aldehyde but as the aldehyde was isolated by a fractional distillation procedure, which must involve some loss, it is reasonable to assume that the aldehyde and carbon dioxide are produced in equimolar quantities. This was checked by a separate experiment in which the aldehyde was isolated quantitatively as its semicarbazone, when it was found that the relative molar proportion of aldehyde to carbon dioxide was very close to 1 : 1.

Table 2. Polymerizations with reactants of known steric composition

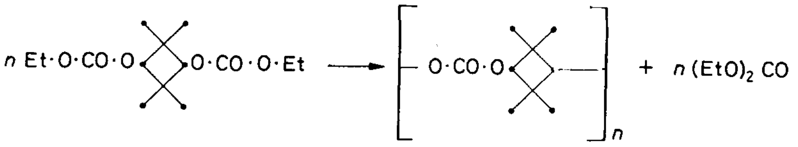
Trans-/cis-*reactant ratio*	Trans-/cis-*ratio in polymer*	η*	*% Yield of polymer*	*% Yield of carbon dioxide*	*% Yield of aldehyde*
0/100	0/100	0·55	56	18	16
0/100	0/100	2·09	43	20	18
25/75	1/99	0·99	43	34	27
—	18/82	0·69	36	—	—
—	29/71	0·88	57	12	11
48/52	32/68	1·42	60	10	9
65/35	49/51	1·14	56	13	12
65/35	50/50	1·16	60	15	16
75/25	61/39	2·58	44	33	—
100/0	100/0	—	43	—	—

*Specific viscosity for a one per cent solution in chloroform at 25°C.

The all *trans*- polymer was insoluble in common solvents, but all the other polymers prepared, that is polymers containing up to 61 per cent of *trans*- units, dissolved in chloroform. Neither the all *trans*- polymer nor the one containing 61 per cent of *trans*- units could be moulded as they decomposed before melting, but all those containing 50 per cent or less of *trans*-units could be moulded at 265°C without reducing their solution viscosities. Thus samples of polymers containing up to 61 per cent of *trans*- units could be fabricated into thin sheet by solvent casting while those containing up to 50 per cent of *trans*- units could be compression moulded.

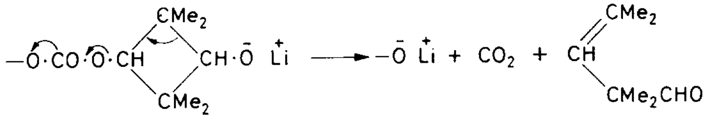
DISCUSSION

The polymerization occurs by base catalysed ester interchange between the diols and their bis(ethyl carbonate) esters, III, with elimination of ethanol. Polymer can also be produced, though more slowly, from the diester alone by the interchange reaction:



This process must occur to some extent during polycondensation of the diol with the diester, as diethyl carbonate occurs in the volatile products of this reaction. Some reactants were always lost from the melt by distillation and the proportion of diol removed in this way was usually greater than that of the diester. This is reasonable as the diol is the more volatile, and the resulting imbalance of reagents does not result in a product of low molecular weight because condensation with elimination of diethyl carbonate can occur between polymers having —O.CO.O.Et end-groups.

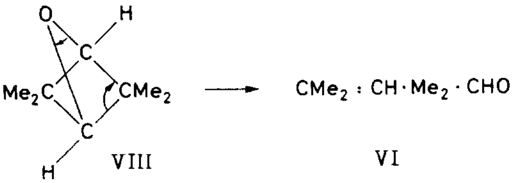
A very considerable loss of reagents occurs with concomitant formation of equimolar quantities of carbon dioxide and 2,2,4-trimethyl-3-pentenal. Formation of these products is considered to occur via the alkoxide ion VII according to the following type of mechanism, which is analogous to that postulated by Searles *et al.*[4] to explain the formation of olefins and aldehydes as side products during the preparation of cyclic ethers by base catalysed decomposition of cyclic carbonates.



VII

Such a reaction involves no loss of functionality so that the surprising observation that polymers of high molecular weight can be formed although an extensive side reaction occurs is explained for this system. No evidence for the formation of ether linkages could be obtained so that the formation of these by an intermolecular analogue of Searle's intramolecular reaction could not be realized.

Formation of carbon dioxide and the pentenal occurs by decomposition of either *cis-* or *trans-* repeat units during the polymerization, and when both steric forms are present, i.e. when mixtures of *cis-* and *trans-* reagents are used, so that the conditions of reaction are identical for each form, the *trans-* structure undergoes reaction much more readily than the *cis-*, and this has the effect of increasing the proportion of *cis-* repeat units in the polymer melt as polymerization proceeds. Hasek *et al.*[9] have observed a similar difference in reactivity between the *cis-* and *trans-*2,2,4,4-tetramethylcyclobutane-1,3-diols, the *trans-* being dehydrated readily to the pentenal, VI, by heating with dilute sulphuric acid, whereas the *cis-*diol is unaffected by such treatment. They consider that these observations can be explained on the assumption that dehydration occurs by a concerted transannular reaction whereby one OH group is displaced by the other to form a bicyclic intermediate VIII, which is possible for the *trans-*isomer but not the *cis-*.



VIII

VI

Decomposition of the alkoxide ion, VII, to give VI could be considered to occur in an analogous manner, provided that the existence of such a highly strained intermediate as VIII can be accepted. Formation of VIII may be less difficult than would at first sight be expected as it appears that in these polymers the cyclobutane ring is puckered[5].

EXPERIMENTAL

Intermediates

Diols—The mixed *cis*- and *trans*-2,2,4,4-tetramethyl-1,3-cyclobutane diols, obtained from Eastman Chemical Products Inc., were purified by recrystallization from toluene to give a product containing 62 per cent of the *trans*- isomer.

Separation of the isomers from the mixture was carried out as described previously[2,3] to give the pure *cis*-diol, m.pt 163° to 164°C and the pure *trans*- m.pt 149° to 150°C (Eastman Kodak report[2,3] m.pts 162·5° to 163·5°C and 148°C respectively).

Bis(ethyl carbonate) esters—These were prepared by ester interchange between the diols (1 mole) and diethyl carbonate (10 moles), the procedure being as follows. A solution of the diol in ethyl carbonate containing *ca.* 0·1 g of lithium hydride was heated to reflux under a short fractionating column and ethanol removed continuously as it was formed. When the reaction was complete, the cooled solution was filtered to remove insoluble lithium salts, and the excess diethyl carbonate distilled off at 25 mm of mercury pressure. The residue was then distilled at low pressure to obtain the *bis(ethyl carbonate)* ester, b.pt 98°/0·2 mm, in 60 to 70 per cent yield, a polymeric residue remaining behind.

Analysis of intermediates

Diols—The *trans-/cis-* ratio in mixtures of the diols was determined by the following method involving a comparison of their i.r. spectra with those of several known mixtures. The spectra of these mixtures (ground in Nujol and spread between rocksalt plates) were obtained and the ratio of the absorbances due to *trans*-diol (at 11·8 μ) and *cis*- (at 12·2 μ) measured in each case. A plot of these absorbance ratios against the *trans-/cis-* ratios gave a straight line calibration from which the *trans-/cis-* ratios of unknown diol mixtures could be determined by measuring their absorbance ratios.

Bis(ethyl carbonate esters)—The *trans-/cis-* ratio in mixtures of the esters was determined by converting them to the diols in almost quantitative yield by the following procedure and measuring the *trans-/cis-* ratio of the product as described above. A solution of the diethyl carbonate ester (2·88 g, 0·01 mole) in methanol (12·5 ml) containing sodium metal (0·030 g) was left to stand at room temperature for 24 h. The solution was then neutralized with 0·13 ml of glacial acetic acid, the methanol removed by distillation from a steam bath, and the residual solid sublimed under vacuum at 0·1 mm of mercury to give the mixed diols (1·3 to 1·4 g, 90 to 100 per cent yield).

The purity of the bis(ethyl carbonate) esters was determined by estimating their 'carbonate' contents by the following procedure.

About 0·3 g of ester was weighed into a Pyrex conical flask and 25 ml of 0·5 N alcoholic potash added. The solution, guarded against atmospheric carbon dioxide, was heated under reflux for one hour. The solution was then diluted to about 100 ml with distilled water, the liberated carbonate precipitated with an extremely small excess of acid-free barium chloride solution, and excess alkali determined by slow titration with standard hydrochloric acid using phenolphthalein as indicator. The strength of the alcoholic potash used was determined beforehand by titrating a 25 ml sample to which 0·5 ml of barium chloride had been added to precipitate any potassium carbonate dissolved in it. From the difference between the two titers, the amount of caustic potash used up, and hence the amount of carbonate present in the sample was calculated.

Polymerizations

Polymerizations were carried out in a cylindrical vessel heated by a 'Wood's metal' bath and fitted with a vertical capillary tube by means of which a slow stream of nitrogen could be forced through the molten reactants. This vessel was connected to a vacuum pump via a water condenser and a set of traps designed to catch the volatile materials distilling from the melt.

To carry out a polymerization, equimolar quantities of the diol, and the bis(ethyl carbonate) ester, together with a small quantity of basic catalyst, were placed in the vessel and all air removed from the apparatus by alternately evacuating and filling it with nitrogen. The reagents were then heated to a predetermined temperature at atmospheric pressure for a given time, after which the pressure was reduced gradually to 0·1 mm of mercury while the temperature was raised to complete the reaction. The polymerizations listed in *Table 2* were carried out by heating the reagents first at 240°C for 1·5 h and then at 290°C for 2 h, using 0·25 wt % of lithium carbonate as catalyst. The quantity of carbon dioxide evolved was estimated either by back-titration of the caustic soda solution in which it had been absorbed, or by measuring the volume of gas and determining its carbon dioxide content from measurements of its i.r. absorption. The liquid products from each reaction were fractionated at atmospheric pressure through a small column of high efficiency to give ethanol, b.pt 77° to 78°C, an intermediate fraction b.pt 78° to 145°C, and 2,2,4-trimethyl-3-pentenal, b.pt 145° to 146°C. Diethyl carbonate, b.pt 126° to 127°C (lit. b.pt 126°C) was separated from the mixed intermediate fractions from several polymerizations by refractionation. The solid products were removed mechanically from the apparatus and triturated with petrol ether. Almost pure diol was then filtered off, and the bis(ethyl carbonate) ester isolated by evaporation of the filtrate.

The polymers

The polymers were isolated by breaking the polymerization vessel, and freed from the catalyst residues by dissolution in chloroform followed by precipitation with methanol, a procedure which always caused some degradation, presumably by methanolysis.

Reduced viscosities $[RV]^{25°}_{1\%} = (t \text{ solution} - t \text{ solvent})/t \text{ solvent} \times C$ were determined for one per cent solutions in chloroform at 25 °C.

Micro-combustion carried out on a sample of purified *polymer* gave C, 63·2; H 8·2 per cent; $C_9H_{14}O_3$ requires C, 63·5; H, 8·3 per cent. Analysis for 'carbonate content' was carried out on several polymer samples as described for the bis(ethyl carbonate) esters, except that as longer periods of heating were required an anhydrous solution of NaOEt in EtOH was used to prevent attack on the glass reaction vessel, and showed the polymers to be 100 ± 0·5 per cent polycarbonates of structure I. The *trans-/cis-* repeat unit ratio for each polymer was determined by hydrolysis to the diols followed by i.r. analysis in a manner analogous to that described for the bis(ethyl carbonate) esters.

2,2,4-Trimethyl-3-pentenal

The fractionated liquid b.pt 146°C/760 mm, n^{20}_D 1·436 (Found: C, 77·4; H, 11·5 per cent. *M* (cryoscopic) 130. Calc. for $C_8H_{14}O$: C, 77·4; H, 11·4 per cent, *M*, 126), reduced ammoniacal silver nitrate solution and gave by conventional methods a *semicarbazone* (Found: C, 58·9; H, 9·9; N, 23·1 per cent. $C_9H_{17}N_3O$ requires C, 58·98; H, 9·35; N 22·9 per cent) m.pt 169° to 172°C and a 2,4-dinitrophenylhydrazone (Found: C, 55·0; H, 6·1; N, 18·2 per cent. Calc. for $C_{14}H_{18}N_4O_4$: C, 55·0; H, 5·9; N, 18·29 per cent) m.pt 143° to 144°C. Hasek *et al.*[9] record n^{20}_D 1·4357 to 1·4361 for the aldehyde and m.pt 142° to 143°C for its 2,4-dinitrophenylhydrazone.

The aldehyde, 6·3 g, was added to a solution of 12·5 g sodium in 250 ml of diethylene glycol containing 25 g of hydrazine hydrate, and this mixture heated to reflux for 20 hours. Then the volatile product was distilled off, washed with water, and dried. Fractionation at atmospheric pressure gave 1·8 g of 2,4,4-trimethylpentene-2, b.pt 104°C, n^{20}_D 1·4160: Egloff[10] records b.pt 104·5°C, n^{20}_D 1·4159.

The semicarbazone of the aldehyde, 9 g, was added to a solution of 10 g sodium in 200 ml diethylene glycol and this mixture heated to reflux for half an hour. The product was diluted with water and extracted with petrol ether (b.pt 40°C). The extract was washed with water, dried and fractionated, to give 2 g of 2,4,4-trimethylpentene-2 b.pt 104°C, n^{20}_D 1·4160.

A few millilitres of the aldehyde was heated to reflux with a solution of potassium dichromate in dilute sulphuric acid for about an hour. Then all the volatile organic products were removed by distillation and the residual aqueous liquid cooled and extracted with ether. Evaporation of the ether layer gave 0·2 g of dimethyl malonic acid m.pt 181° to 185°C decomp., (lit. m.pt 186° to 190°C decomp.) which gave by conventional means a diamide m.pt 273°C (lit. 269°C).

The help of Messrs R. J. G. Miller and B. Stay for measurement of infra-red spectra is acknowledged.

Thanks are also due to Mr D. I. Ritchie for assistance with the experimental work.

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(*Received January 1963*)

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