180. *Some Polyoxymethylene Compounds. Part II.*[1]

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The series of αω-polyoxymethylene dichlorides [1] has been extended by the isolation of di[(chloromethoxy)methyl] ether. With sodium cyclohexyl oxide the first two members of the series yielded the corresponding dicyclohexyl derivatives together with higher polyacetals, but other procedures gave mainly dicyclohexyloxymethane.

Di[(CHLOROMETHOXY)METHYL] ETHER (I; $n = 3$) and the homologue (I; $n = 4$) have been shown previously (Part I) to be formed as by-products in the preparation of di(chloromethyl) ether (I; $n = 1$) and di(chloromethoxy)methane (I; $n = 2$) from thionyl chloride and paraformaldehyde, but attempts to isolate them directly were unsuccessful.

(I) $Cl\cdot[CH_2\cdot O]_n\cdot CH_2Cl$ $\quad$ $RO\cdot[CH_2\cdot O]_n\cdot CH_2\cdot OR$ (II)

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[1] Part I, Head, *J.*, 1963, 2972.

Subsequently, when a quantity of crude di(chloromethoxy)methane was redistilled it yielded a small proportion of di[(chloromethoxy)methyl] ether which was identified by analysis, conversion into di[(phenoxymethoxy)methyl] ether (II; R = Ph, $n = 3$) and bis-[(2,4,6-tribromophenoxymethoxy)methyl] ether (II; R = $C_6H_2Br_3$, $n = 3$), and hydrolysis with cold water [2] to give the expected amounts of hydrochloric acid and formaldehyde.

When cyclohexanol was heated at 140—150° with the dipyridinium salt of di(chloromethyl) ether or treated at room temperature with di(chloromethyl) ether in dimethylformamide,[3] the principal product was the formal (II; R = C_6H_{11}, $n = 0$), but in the latter case a small amount of the expected di(cyclohexyloxymethyl) ether (II; R = C_6H_{11}, $n = 1$) was also isolated. Its properties agreed with those reported by Rieche and Gross [4] who made the compound from di(chloromethyl) ether and the alkoxide prepared from cyclohexanol and sodium powder in ether; any excess of cyclohexanol led to formation of the formal. In accordance with this, cyclohexanol pre-treated with sodium hydride in dimethylformamide gave a 50% yield of di(cyclohexyloxymethyl) ether. Some higher polyacetals ($n > 1$) were also present but the formal was not isolated.

Similarly, when cyclohexanol was treated with di(chloromethoxy)methane in dimethylformamide the formal was produced, together with the polyacetals (II; R = C_6H_{11}, $n = 1$, 2, 3, and 4), but when sodium cyclohexyl oxide was used there was a 60% yield of crude di(cyclohexyloxymethoxy)methane (II; R = C_6H_{11}, $n = 2$) together with higher polyacetals ($n = 3$, 4, and 5) and very little of the compounds in which $n = 0$ or 1. The presence of the higher polyacetals was indicated by gas–liquid chromatography (g.l.c.); their specific retention volumes (V_g) fitted excellently on the linear relation observed between log V_g and n for the known compounds in which $n = 0$, 1, and 2. Fractions rich in the compounds in which $n = 3$ and 4 were obtained but complete purification was not achieved.

The cyclohexyl polyacetals (II; R = C_6H_{11}) exhibit strong infrared (i.r.) absorption at 1105—1110 cm.$^{-1}$ and also at 990, 965, 952, and 947 cm.$^{-1}$ respectively, for values of n from 1 to 4. The compounds in which $n = 1$ and 2 also displayed moderate absorption at 935 cm.$^{-1}$ and all four exhibited shoulders at 1020—1010 cm.$^{-1}$. These figures are in fair agreement with the results of Webb, Duke, and Smith [5] who showed that in the 1200—900 cm.$^{-1}$ region a number of aliphatic polyacetals of this type absorb at about 1120 cm.$^{-1}$ and also at a lower frequency dependent only upon the value of n. The i.r. spectra of the aromatic polyacetals described in Part I do not show this correlation. The formal (II; R = C_6H_{11}, $n = 0$) absorbs strongly at 1035 cm.$^{-1}$ and there are weaker absorptions at 1187, 1157, 1131, 1094, and 930 cm.$^{-1}$ in the 1200—900 cm.$^{-1}$ region.

EXPERIMENTAL

With one indicated exception i.r. absorption spectra were measured on liquid films between rock-salt plates, and all were consistent with the formulæ ascribed to the compounds; for spectra see Documentation of Molecular Spectroscopy (Butterworths), Numbers 12,235 onwards. References to purity are to g.l.c. Di[(chloromethoxy)methyl] ether was examined at 27°; the dicyclohexyl compounds (II) were examined at 125° for $n = 0$ and 1, and at 150° for $n = 2$, 3, 4, and 5.

Di[(chloromethoxy)methyl] Ether (I; $n = 3$).—Crude di(chloromethoxy)methane which had been stored for several months was stirred with potassium hydroxide pellets, filtered, and fractionated at atmospheric pressure to remove di(chloromethyl) ether until a thermometer at the base of the column registered 152°. Fractionation under reduced pressure then gave di(chloromethoxy)methane and a smaller amount of *di[(chloromethoxy)methyl] ether* b. p. 90—97°/14 mm., which after further fractionation was obtained as a colourless liquid (99% pure) b. p.

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[2] Descudé, *Bull. Soc. chim. France*, 1906, **35**, 958.
[3] Ames, Blackmore, and King, *J. Appl. Chem.*, 1964, **14**, 503.
[4] Rieche and Gross, *Chem. Ber.*, 1960, **93**, 259.
[5] Webb, Duke, and Smith, *J.*, 1962, 4307.

91°/11 mm., n_D^{18} 1·4543 (Found: C, 27·8; H, 4·7; Cl, 39·6; O, 28·0. $C_4H_8Cl_2O_3$ requires C, 27·5; H, 4·6; Cl, 40·5; O, 27·4%). On hydrolysis with water (see below) it yielded Cl^-, 40·7, and H•CHO, 66·4 (Calc. 68·6%). Its i.r. spectrum exhibits strong bands between 1150 and 1060 cm.$^{-1}$ consistent with the presence of ether groupings, and differs considerably from those of di(chloromethyl) ether and di(chloromethoxy)methane. The relation between log V_g and n is linear for the three dichloro-compounds. A compound the V_g value of which corresponded to (I; $n = 4$) was present in the residue from the above distillation.

Diarylpolyacetals (II; R = aryl, $n = 3$).—The general procedure described in Part I was followed. (*a*) Phenol (6·3 g.) with the dichloro-ether (I; $n = 3$) (5·8 g.) gave an ethereal reaction mixture which was washed with dilute sodium hydroxide and with water, dried (K_2CO_3), and evaporated, giving crude *di*[(*phenoxymethoxy*)*methyl*] *ether* (8·6 g., 89%) as an oil which slowly solidified (m. p. 25—27°). Crystallisation from methanol and drying *in vacuo* gave crystals, m. p. 28° (Found: C, 66·0; H, 6·1; O, 27·7. $C_{16}H_{18}O_5$ requires C, 66·2; H, 6·2; O, 27·6%). Its i.r. spectrum resembled that of di(phenoxymethoxy)methane.

(*b*) 2,4,6-Tribromophenol (11·0 g.) with the dichloro-compound (2·9 g.) gave bis-[(2,4,6-tribromophenoxymethoxy)methyl] ether (9·7 g., 76%) as an ether-insoluble powder, m. p. 168—169° raised to 170·5—171·5° on crystallisation from pyridine. Its m. p., mixed m. p., and i.r. spectrum (Nujol mull) showed that it was identical with the compound already described in Part I.

Hydrolysis of Di[(*chloromethoxy*)*methyl*] *Ether*.—A weighed portion of the dichloro-compound was hydrolysed with cold water [2] and the hydrochloric acid liberated was titrated with 0·1N-sodium hydroxide (Methyl Red). Formaldehyde was determined as the dimedone derivative.

Di(*cyclohexyloxy*)*methane*.—A mixture of cyclohexanol (40 g.) and the dipyridinium salt of di(chloromethyl) ether (55 g.; prepared as described in Part I) was heated at 140—150° for 6½ hr. (oil bath), cooled, diluted with water, acidified with hydrochloric acid, and extracted with chloroform. The extract was washed with dilute hydrochloric acid and with water, dried (K_2CO_3), and evaporated. Fractionation of the residue gave di(cyclohexyloxy)methane (26·4 g.), b. p. 108—109°/0·3 mm., which on redistillation gave a fraction (99% pure), b. p. 110°/0·3 mm., n_D^{20} 1·4709, identical in i.r. spectrum with an authentic specimen (99·5% pure) prepared from cyclohexanol and formaldehyde [6] b. p. 270—272° (slight decomp.), 131°/9 mm., n_D^{20} 1·4707 (lit., b. p. 279—280°; [7] 241—242°; [6] 139—140°/14 mm.; [8] n_D^{20} 1·4710; [6] n_D^{21} 1·4702 [8]) (Found: C, 74·1; H, 11·1; O, 15·1. Calc. for $C_{13}H_{24}O_2$: C, 73·5; H, 11·4; O, 15·1%). Its i.r. spectrum exhibited strong absorption at 1035 cm.$^{-1}$ and a somewhat weaker band at 930 cm.$^{-1}$.

Dicyclohexylpolyacetals (II; R = C_6H_{11}).—(*a*) Di(chloromethyl) ether (47 g.; 0·41 mole) was added to a solution of cyclohexanol (40 g.; 0·4 mole) in dimethylformamide (200 c.c.) and stored for 4 days. The mixture was poured into water (500 c.c.) containing sodium hydroxide (40 g.), left for 2 hr., and extracted with ether. The extract was washed with dilute sodium hydroxide and with water, dried (K_2CO_3), and evaporated. Fractionation of the remaining oil *in vacuo* gave crude di(cyclohexyloxy)methane (20 g.), b. p. 99—107°/0·8 mm., n_D^{21} 1·4697, and a residue (5 g.) of higher b. p. which had n_D^{20} 1·4672 and absorbed strongly in the i.r. region at 990 cm.$^{-1}$. Redistillation of several such residues yielded di(cyclohexyloxymethyl) ether (>95% pure), m. p. 3·5—4·5°, b. p. 126—128°/0·5 mm., n_D^{20} 1·4668 (lit.,[4] b. p. 100—103°/0·1 mm., n_D^{20} 1·4670) (Found: C, 69·3; H, 10·7; O, 20·4. Calc. for $C_{14}H_{26}O_3$: C, 69·4; H, 10·8; O, 19·8%). It absorbed strongly at 990 cm.$^{-1}$; there was a weaker band at 935 cm.$^{-1}$ and a shoulder at 1020 cm.$^{-1}$.

(*b*) Cyclohexanol (40 g.) was added to a suspension of sodium hydride (50% dispersion in mineral oil; 40 g.) in dimethylformamide (200 c.c.), and freshly redistilled di(chloromethyl) ether (46 g.; 100% excess) was added gradually with cooling. The mixture was stored at room temperature for 24 hr., treated with methanol (10 c.c.), and poured into water (500 c.c.) containing sodium hydroxide (2 g.). After a further 2 hr. the mixture was extracted with ether and the extract was washed with dilute sodium hydroxide and with water, dried (K_2CO_3), and evaporated. Distillation of the remaining oil (54·5 g.) gave the following fractions: (i) b. p. 28—100°/0·15 mm. (mostly at 52—54°), n_D^{18} 1·4592 (6·8 g.); (ii) b. p. 102—109°/0·15 mm., n_D^{18} 1·4560 (1·6 g.); (iii) b. p. 109—114°/0·1 mm., n_D^{18} 1·4652 (18·6 g.); (iv) b. p. 117—129°/0·15 mm., n_D^{18} 1·4653 (4·2 g.); (v) b. p. 130—160°/0·15 mm., n_D^{17} 1·4658 (6·6 g.); and a residue

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[6] Vinokurov, *Izvest. Vysshikh Uchebn. Zavedenii, Khim. i Khim. Tekhnol.*, 1960, **3**, 190.

[7] Murat and Cathala, *J. Pharm. Chim.*, 1912, (7), **6**, 289.

[8] Sabetay and Schving, *Bull. Soc. chim. France*, 1928, (4), **43**, 1341.

(containing mineral oil), n_D^{18} 1·4710 (14·4 g.). The infrared spectrum of (i) indicated that it was mainly cyclohexanol (no formal peak at 1035 cm.$^{-1}$, but considerable absorption at 990 cm.$^{-1}$), and those of (ii), (iii), and (iv) closely resembled that of di(cyclohexyloxymethyl) ether (except that (ii) exhibited slight hydroxyl absorption at 3400 cm.$^{-1}$), the total yield being 51%. Fraction (v) absorbed more strongly at 965 cm.$^{-1}$ than at 990 cm.$^{-1}$, and the residue absorbed at 952 cm.$^{-1}$. After further fractionations the main product (94% pure) had b. p. 122—124°/0·35 mm., n_D^{19} 1·4659 (Found: C, 70·4; H, 10·8; O, 18·9%). Its i.r. spectrum and V_g value agreed with those of the compound described under (*a*).

(*c*) Di(chloromethoxy)methane (36 g., 100% excess) was added to a solution of cyclohexanol (25 g.) in dimethylformamide (125 c.c.), and the mixture was stored for 24 hr. at room temperature and worked up as described under (*a*). Distillation of the oily product gave the following fractions: (i) b. p. 32—94°/0·15 mm., $n_D^{21·5}$ 1·4644 (3·6 g.); (ii) b. p. 94—101°/0·15 mm., $n_D^{21·5}$ 1·4689 (6·0 g.); (iii) 101—124°/0·15 mm., $n_D^{21·5}$ 1·4682 (3·3 g.); (iv) b. p. 124—150°/0·15 mm., $n_D^{21·5}$ 1·4658 (5·3 g.); and (v) b. p. 150—161°/0·15 mm., $n_D^{21·5}$ 1·4642 (1·6 g.). Infrared examination indicated that (i) was mainly cyclohexanol, (ii) was mostly the formal (but there was moderate absorption at 990 cm.$^{-1}$ as well as at 1035 cm.$^{-1}$), (iii) was a mixture of the formal and di(cyclohexyloxymethyl) ether, (iv) was mostly di(cyclohexyloxymethyl) ether whilst (v) contained much di(cyclohexyloxymethoxy)methane ($\nu_{max.}$ 970 cm.$^{-1}$). The presence of the formal and the dicyclohexylpolyacetals (II; $R = C_6H_{11}$, n = 1, 2, 3, and 4) in fractions (iii), (iv), and (v) was confirmed by g.l.c.

(*d*) As (*b*) but with di(chloromethoxy)methane (58 g., 98% pure) instead of di(chloromethyl) ether. Before distillation the crude oil was dissolved in methanol, separated from mineral oil, and recovered by evaporation of the methanol. Fractional distillation gave the following fractions: (i) b. p. 36—117°/0·15 mm., n_D^{18} 1·4568 (3·4 g.); (ii) b. p. 120—133°/0·1 mm., n_D^{18} 1·4596 (2·6 g.); (iii) b. p. 133—136°/0·1 mm., n_D^{18} 1·4636 (22·3 g.); (iv) b. p. 137—150°/0·1 mm., n_D^{18} 1·4636 (7·6 g.); and a residue, n_D^{18} 1·4661 (10·6 g.). The i.r. spectrum of (i) indicated that it was mainly cyclohexanol (no formal peak at 1035 cm.$^{-1}$ and very weak absorption only at 990 cm.$^{-1}$) and those of (ii), (iii), and (iv) exhibited strong absorption at 965 cm.$^{-1}$ [broadened to 945 cm.$^{-1}$ in the case of (iv)] with very faint shoulders only at 1035 and 990 cm.$^{-1}$. The residue absorbed strongly at 952—945 cm.$^{-1}$. Repeated fractionations of the main product (32·5 g., 60%) gave *di(cyclohexyloxymethoxy)methane* (II; $R = C_6H_{11}$, $n = 2$) (94% pure), b. p. 131—133°/0·015 mm., n_D^{21} 1·4639 (Found: C, 66·0; H, 10·2; O, 24·1. $C_{15}H_{28}O_4$ requires C, 66·1; H, 10·4; O, 23·5%). Its i.r. spectrum resembled that of di(cyclohexyloxymethyl) ether, but it absorbed strongly at 965 cm.$^{-1}$ (instead of 990 cm.$^{-1}$) and less strongly at 935 cm.$^{-1}$. There was a shoulder at 1010 cm.$^{-1}$.

Repeated fractional distillations of fraction (iv) and the distillation residue gave a fraction (m. p. 0—1°; b. p. 148—151·5°/0·06 mm., $n_D^{19·5}$ 1·4632) which was shown by g.l.c. to contain compound (II; $R = C_6H_{11}$; $n = 3$) and another (m. p. 9—10°; b. p. 160—162·5°/0·02 mm., $n_D^{20·5}$ 1·4630) which contained the corresponding ($n = 4$) compound. Both were about 80% pure and absorbed strongly in the i.r. region at 952 and 947 cm.$^{-1}$, respectively (no other maxima between 1035 and 930 cm.$^{-1}$). G.l.c. also revealed the presence of the polyacetal in which $n = 5$ in some of the higher-boiling fractions.

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