**548.** *Some Polyoxymethylene Compounds. Part I.*

By Frank S. H. Head.

The reaction between paraformaldehyde and thionyl chloride gives di-(chloromethyl) ether and di(chloromethoxy)methane together with higher αω-polyoxymethylene dichlorides, two of which have been identified as their 2,4,6-tribromophenyl derivatives.

Di(chloromethyl) ether (I; $n = 1$) has been prepared by many methods, including a variety of procedures in which formaldehyde solution or paraformaldehyde was treated with hydrogen chloride or a source of it, a recent variation being the use of thionyl chloride in the presence of zinc chloride.[1] The formation of methylene chloride [2] and di(chloromethoxy)methane [3] as by-products has been reported. The latter was also made by heating di(chloromethyl) ether with paraformaldehyde under pressure,[3] and was accompanied by a fraction of higher b. p. [possibly the dichloride (I; $n = 3$)].

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

The presence of small amounts of higher dichlorides (I; $n > 1$) in crude preparations of di(chloromethyl) ether has been demonstrated by the isolation of bis(trimethylammonium hexachloroplatinates) [4] and dimethyl polyacetals [5] (II; R = Me) derived from the di-chlorides (I; $n = 2$ and 3). The yields of the dimethyl compounds were 10% and 1·2%, respectively; they were also isolated as by-products in the preparation of di(methoxy-methyl) ether from dimethoxymethane heated with formaldehyde in the presence of an acid catalyst.[6]

Di(aryloxymethyl) ethers (II; R = aryl; $n = 1$) have recently been made by treating phenols in the presence of pyridine or dilute alkali,[7] or as dry potassium salts in ether or benzene,[5] with di(chloromethyl) ether.

When paraformaldehyde was treated with thionyl chloride at the b. p., or in 90% sulphuric acid at room temperature, a mixture containing the dichloro-compounds (I; $n = 1$—4) was obtained, but the two higher polyoxymethylene dichlorides ($n = 3$ or 4) could not be distilled from it without decomposition. The relative yields of the dichloro-compounds (I; $n = 1$ and 2) and of the undistillable residue varied considerably, but the reaction at room temperature was more reliable for the preparation of di(chloro-methoxy)methane.

Gas chromatography of several distillation residues, and of a crude reaction mixture, provided evidence of the presence of the compounds (I; $n = 1$, 2, and 3), but not of (I; $n = 4$). The last-named was, however, detected by examination at 200° of a mixture of phenyl derivatives (II; R = Ph, $n = 1$, 2, 3, and 4) prepared from a residue. The presence of the last two compounds in this mixture was established by the excellence of the fit of their $V_g$ values on the linear relation observed between $\log V_g$ and $n$ for the known compounds in which $n = 0$, 1, and 2.

The polyoxymethylene dichlorides (I; $n = 1$ or 2) and the undistillable residues reacted readily with sodium 2,4,6-tribromophenoxide in alcohol–ether mixtures, giving crystalline polyacetals (II; R = $C_6H_2Br_3$). The pure dichlorides gave compounds

[1] Rohland, G.P. 849,102; *Chem. Abs.*, 1958, **52**, 11,889.
[2] Schneider, *Angew. Chem.*, 1931, **51**, 274.
[3] Descudé, *Bull. Soc. chim. France*, 1906, **35**, 958.
[4] Litterscheid and Thimme, *Annalen*, 1904, **334**, 1.
[5] Rieche and Gross, *Chem. Ber.*, 1960, **93**, 259.
[6] Gresham and Brooks, B.P. 603,872; *Chem. Abs.*, 1949, **43**, 1051.
[7] Kohana, *J. Pharm. Soc. Japan*, 1953, **73**, 1061.

identical with two obtained earlier during unsuccessful attempts to convert 2,4,6-tri-bromophenol into its chloromethyl ether (by reaction in chloroform solution with para-formaldehyde and hydrogen chloride) and thence into 2,4,6-tribromophenoxymethoxy-methane by reaction with sodium methoxide.[8] In this case the polyacetals may have arisen from interaction of polyoxymethylene dichlorides, formed during the first step, and sodium 2,4,6-tribromophenoxide formed in the second. The undistillable residues gave rise to variable mixtures of products from some of which the polyacetals (II; $R = C_6H_2Br_3$; $n = 3$ or 4) were isolated; the lower compounds in which $n = 1$ or 2 were obtained in some instances. An intractable mixture remained which may have contained higher members of the series. This confirms the earlier indications [4,5] that the reaction between formaldehyde and hydrogen chloride affords mixtures of $\alpha\omega$-polyoxymethylene dichlorides, an additional member of the series having been detected.

Bis-(2,4,6-tribromophenoxymethyl) ether (II; $R = C_6H_2Br_3$; $n = 1$) was highly resistant to hydrolysis by hot aqueous acid or alkali, or by alcoholic potassium hydroxide, but gave 2,4,6-tribromophenol rapidly and almost quantitatively when warmed with hydrogen bromide in acetic acid. The related polyacetals (II; $R = C_6H_2Br_3$; $n = 2, 3$, or 4) behaved similarly. The infrared spectra of all four compounds differed considerably in detail, as did those of the corresponding phenyl and pentachlorophenyl polyacetals (II; $R = Ph$ or $C_6Cl_5$; $n = 1$ or 2) derived from di(chloromethyl) ether and di(chloro-methoxy)methane.

With the two dichloro-compounds, quinol gave intractable products, probably polymers, which decomposed at high temperatures. Resorcinol behaved similarly with di(chloro-methyl) ether, but pyrocatechol gave 1,3,5-benzotrioxepan (III), a steam-volatile solid, whereas with di(chloromethoxy)methane it gave a mixture which was freed from phenolic



(III)                                   (IV)
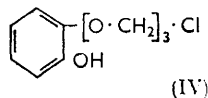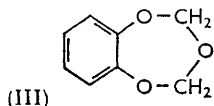
substances (including much pyrocatechol) only by numerous extractions with alkali. This effect could have been caused by gradual decomposition of the intermediate substance (IV), but an attempt to demonstrate its presence in the reaction mixture, by bringing about further reaction with sodium 2,4,6-tribromophenoxide, was unsuccessful, only unidentified products being obtained. Successive reaction of di(chloromethoxy)methane with the sodium salts of 2,4,6-tribromophenol and pyrocatechol also failed to give the mixed polyacetal, the principal product being bis-(2,4,6-tribromophenoxymethoxy)-methane. Similarly, di(chloromethyl) ether, treated successively with sodium phenoxide and sodium 2,4,6-tribromophenoxide, gave only the symmetrical polyacetals (II; $R = Ph$ or $C_6H_2Br_3$; $n = 1$).

*trans*-Cyclohexane-1,2-diol failed to react with di(chloromethyl) ether in pyridine or under Schotten–Baumann conditions, but when heated with the dipyridinium salt of the dichloro-compound it gave a moderate yield of *trans*-hexahydro-1,3,5-benzotrioxepan.[9]

### EXPERIMENTAL

Infrared absorption spectra of liquids were measured on films between rock-salt plates; solids were examined as Nujol mulls. The spectra of all the substances were free from hydroxyl and carbonyl absorption; for spectra see Documentation of Molecular Spectroscopy, numbers 10,400 onwards. References to purity are to gas–liquid chromatography, where the possibility of non-volatile impurities is ignored. Unless otherwise stated, gas-chromatography was carried out by a special procedure at 27° [10] to avoid decomposition on the column.

*Polyoxymethylene Dichlorides.*—(*a*) A mixture of paraformaldehyde (100 g.) and thionyl

[8] Cf. Head and Williamson, *J.*, 1961, 2578.
[9] Head, *J.*, 1960, 1778.
[10] Sagar, unpublished work.

chloride (205 g.) was heated gently under reflux for 6 hr. The homogeneous product was roughly fractionated under reduced pressure, giving fractions A, b. p. up to 45°/30 mm., and B, b. p. up to 80°/18 mm. Fractionation of A at atmospheric pressure gave di(chloromethyl) ether (30—55%; 99% pure), b. p. 101—103°. Fractionation of B under reduced pressure gave di(chloromethoxy)methane (0—40%; 95% pure), b. p. 58—61°/16 mm., 160—162°/760 mm. (slight decomp.) (lit.,[3] b. p. 65—67°/15 mm., 166°/760 mm.), $n_D^{20}$ 1·4511 (Found: C, 25·0; H, 4·3; Cl, 48·9; O, 22·3. Calc. for $C_3H_6Cl_2O_2$: C, 24·8; H, 4·2; Cl, 48·9; O, 22·1%).

(b) Thionyl chloride (160 g.) was added gradually to a stirred suspension of paraformaldehyde (120 g.) in 90% sulphuric acid (100 c.c.) and stirring was continued for 0·5 hr. after all the solid had dissolved. The upper layer was separated, cooled to below 0°, and stirred with potassium hydroxide pellets for 15 min. The filtered liquid was fractionated, as under (a), and gave di(chloromethyl) ether (10—40%) and di(chloromethoxy)methane (20—30%), together with a residue containing higher dichloro-compounds (ca. 20 g.). Reduction of the amount of thionyl chloride to 125 g. favoured the production of the residual substances. On distillation at 0·3 mm. a portion (28 g.) decomposed giving a further quantity (16 g.) of di(chloromethoxy)methane, b. p. 38—40°/0·3 mm., 51·5—52·5°/12 mm. identified by infrared and gas liquid chromatographic examination.

The infrared spectra of di(chloromethyl) ether and di(chloromethoxy)methane differ considerably in the " finger-print " region. Both exhibit strong bands between 1150 and 1060 cm.[-1] indicative of ether groupings. The spectra of the undistillable residues usually, but not always, contained additional bands at 860 and 790 cm.[-1]. Gas–liquid chromatography of several residues and of a crude reaction mixture, before distillation, showed that they contained di(chloromethyl)ether and di(chloromethoxy)methane together with a less volatile compound with $V_g$ value similar to that predicted for the compound (I; $n = 3$); occasionally this third component was not detected.

*General Procedure for Preparation of Diarylpolyacetals (II; R = aryl).*—To a solution of the phenol in dry ether (usually 5 c.c. per g.) was added a warm solution of sodium ethoxide, prepared from the theoretical amount of sodium dissolved in the minimum amount of alcohol (14 c.c. per g.). A solution of the appropriate dichloro-compound (I) in ether (4 c.c. per g.) was then added and the whole was heated on the steam-bath for 6 hr., cooled, and filtered. Ether-insoluble products were washed successively with ether, acetone, and water, and dried. Soluble products were recovered from the ethereal filtrate by evaporation.

*Specific Cases.*—(a) Phenol (9·4 g.) with di(chloromethyl) ether (5·8 g.) gave di(phenoxymethyl) ether as an ether-soluble product which was dissolved in alcohol and poured into water containing potassium carbonate. The precipitated solid (8·9 g., 77%), collected and recrystallised from alcohol, gave needles, m. p. 82—83° (pure by gas–liquid chromatography at 200°) (lit., m. p. 80—80·5°;[7] 82·5°[5]).

(b) Phenol (18·6 g.) with di(chloromethoxy)methane (14·4 g.) gave a reaction mixture which was washed with dilute alkali and with water, dried ($K_2CO_3$), and evaporated, yielding crude *di(phenoxymethoxy)methane* (19·5 g., 75%) as an oil. Three fractionations gave the compound, b. p. 165—169°/0·25 mm., $n_D^{21}$ 1·5444 [purity (at 200°) 99%] [Found: C, 68·4; H, 6·0; O, 25·8%; M (in camphor), 247. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2; O, 24·6%; M, 260]. Its infrared spectrum differed in the " finger-print " region from that of di(phenoxymethyl) ether.

(c) 2,4,6-Tribromophenol (22 g.) with di(chloromethyl) ether (3·9 g.) gave an ether-insoluble powder (18 g., 72%), m. p. 204—205°. Recrystallisation from pyridine gave *bis-(2,4,6-tribromophenoxymethyl) ether* (II; R = $C_6H_2Br_3$; $n = 1$), needles, m. p. 205—206° (Found: C, 24·3; H, 1·1; Br, 68·3; O, 6·6; tribromophenol, 93·6. $C_{14}H_8Br_6O_3$ requires C, 23·9; H, 1·1; Br, 68·1; O, 6·8; tribromophenol, 94·0%). The same compound was obtained in 81% yield when 2,4,6-tribromophenol (6·6 g.) was treated under Schotten–Baumann conditions with di(chloromethyl) ether (3·0 g.).

(d) 2,4,6-Tribromophenol (22 g.) with di(chloromethoxy)methane (5·1 g.) gave an ether-insoluble powder (20·3 g., 83%), m. p. 160—161°. Recrystallisation from pyridine gave *bis-(2,4,6-tribromophenoxymethoxy)methane* (II; R = $C_6H_2Br_3$; $n = 2$), needles, m. p. 163—164° (Found: C, 24·7; H, 1·1; Br, 65·4; O, 8·9; tribromophenol, 89·8. $C_{15}H_{10}Br_6O_4$ requires C, 24·6; H, 1·4; Br, 65·4; O, 8·7; tribromophenol, 90·2%).

(e) 2,4,6-Tribromophenol (33·1 g.) with an undistillable residue (8·8 g.) containing higher polyoxymethylene dichlorides gave an ether-insoluble powder (27·8 g.; m. p. ca. 159—163°).

Crystallisation from pyridine (530 c.c.) gave *bis*-[(2,4,6-*tribromophenoxymethoxy*)*methyl*] *ether* (II; R = $C_6H_2Br_3$; $n = 3$) (17·6 g.) as tiny hair-like crystals, m. p. 170—171° [depressed on admixture with (II; R = $C_6H_2Br_3$; $n = 2$)], unchanged by several recrystallisations from pyridine [Found: C, 25·2; H, 1·7; Br, 62·4; O, 10·6; tribromophenol, 86·6%; $M$ (in camphor), 727. $C_{16}H_{12}Br_6O_5$ requires C, 25·2; H, 1·6; Br, 62·8; O, 10·5; tribromophenol, 86·7%; $M$, 764].

Addition of water to the mother-liquor from the first crystallisation from pyridine gave a precipitate (8·9 g.; m. p. 137—142°) which on crystallisation from pyridine (90 c.c.) gave *bis*-[(2,4,6-*tribromophenoxymethoxy*)*methoxy*]*methane* (II; R = $C_6H_2Br_3$; $n = 4$) (5·9 g.) as needles, m. p. 143—145°, raised by repeated recrystallisation from pyridine and from acetone to 153—154° [depressed on admixture with either of the corresponding compounds (II; $n = 2$ or 3)] [Found: C, 25·9; H, 1·7; Br, 60·6; O, 12·2; tribromophenol, 82·5%; $M$ (in camphor), 761. $C_{17}H_{14}Br_6O_6$ requires C, 25·7; H, 1·8; Br, 60·4; O, 12·1; tribromophenol, 83·4%; $M$, 794].

Another preparation of the undistillable residue (4·4 g.) gave a crude derivative (12·2 g.), m. p. *ca.* 130—150°, which on crystallisation from pyridine (100 c.c.) gave the product (II; R = $C_6H_2Br_3$; $n = 3$) (4·4 g.), m. p. 169—170°.

The compounds in which $n = 1$ or 3 are very sparingly soluble in acetone, but those with $n = 2$ or 4 dissolve rather more readily.

(*f*) Pentachlorophenol (21·3 g.) with di(chloromethyl) ether (4·8 g.) gave, after a reaction time of 10 hr., *bis*(*pentachlorophenoxymethyl*) *ether* (16·2 g., 70%), m. p. 220—221°, which separated from benzene as needles, m. p. 221·5—222° (Found: C, 29·7; H, 1·0; Cl, 61·4; O, 8·0. $C_{14}H_4Cl_{10}O_3$ requires C, 29·3; H, 0·7; Cl, 61·7; O, 8·3%).

(*g*) Pentachlorophenol (21·3 g.) with di(chloromethoxy)methane (6·0 g.) gave, after a reaction time of 2 hr., *bis*(*pentachlorophenoxymethoxy*)*methane* (12·3 g., 51%), m. p. 200—201°, which on recrystallisation from benzene formed needles, m. p. 205—206° (Found: C, 30·1; H, 1·3; Cl, 58·4; O, 10·5. $C_{15}H_6Cl_{10}O_4$ requires C, 29·8; H, 1·0; Cl, 58·6; O, 10·6%).

(*h*) The disodium salt from pyrocatechol (11 g.) with di(chloromethyl) ether (11·4 g.) gave a mixture of ether-soluble products, which on steam-distillation in the presence of alkali gave 1,3,5-*benzotrioxepan* (III) (5·6 g., 37%), colourless plates (from 25% aqueous ethyl alcohol), m. p. 69—70° (pure; at 200°) [Found: C, 63·1; H, 5·3; O, 31·4%; $M$ (in camphor), 154. $C_8H_8O_3$ requires C, 63·2; H, 5·3; O, 31·6%; $M$, 152]. This compound was also obtained in 32% yield by the treatment of pyrocatechol (22 g.) with di(chloromethyl) ether (45·4 g.) under Schotten–Baumann conditions.

*Attempts to Prepare Mixed Polyacetals of Type* (II).—(*a*) A mixture of sodium 2,4,6-tribromophenoxide, from tribromophenol (16·6 g.), with di(chloromethoxy)methane (7·2 g.) in ether (60 c.c.) was heated on the steam-bath for 1 hr. The monosodium salt from pyrocatechol (5·5 g.) in ether (50 c.c.) was added, and heating continued for a further 3 hr. The ether-insoluble product, worked up as usual, consisted of bis-(2,4,6-tribromophenoxymethoxy)-methane (5·1 g.), m. p. and mixed m. p. 161—162°. Evaporation of the ethereal filtrate gave a solid residue (19·5 g.) which was dissolved in hot carbon tetrachloride (50 c.c.); pyrocatechol (3·7 g.) separated on cooling. Evaporation of the mother-liquor and extraction of the residue with dilute sodium hydroxide gave an insoluble solid (A) (3·0 g.). Acidification of the alkaline extract gave 2,4,6-tribromophenol (8·3 g.). The solid A, purified by dissolution in acetone, filtration, and precipitation with water, followed by recrystallisation from methanol, was ethyl 2,4,6-tribromophenoxymethyl ether, m. p. 58—59° (not depressed on admixture with an authentic specimen [8]) (Found: C, 27·6; H, 2·5; Br, 62·0; O, 8·4. OEt, 11·2. Calc. for $C_9H_9Br_3O_2$: C, 27·8; H, 2·3; Br, 61·7; O, 8·2; OEt, 11·6%).

(*b*) A mixture of sodium phenoxide [from phenol (4·7 g.)] with dichloromethyl ether (5·8 g.) in ether (70 c.c.) was heated on the steam-bath for 2 hr. Sodium 2,4,6-tribromophenoxide, from tribromophenol (16·6 g.) in ether (50 c.c.), was added, and heating continued for a further 6 hr. The ether-insoluble product consisted of bis-(2,4,6-tribromophenoxymethyl) ether (8·3 g.), m. p. and mixed m. p. 204·5—206°. Evaporation of the ethereal filtrate, extraction of the residue with acetone, and filtration gave a further quantity of the above product (2·5 g.). Precipitation of the acetone filtrate with dilute alkali gave crude di(phenoxymethyl) ether (5·1 g.; m. p. 66—76°), needles (from alcohol), m. p. and mixed m. p. 82—83°.

*Determination of Tribromophenol Content of the Tribromophenyl Derivatives* (II; R = $C_6H_2Br_3$; $n = 1$—4).—The substance (*ca.* 0·5 g.), suspended in a 25% w/v solution of hydrogen

bromide in acetic acid (10 c.c.), was heated on the steam-bath for 2 hr., poured into water (100 c.c.), and stirred with sodium hydroxide (10 g.). Tribromophenol was precipitated from the clear solution with a slight excess of concentrated hydrochloric acid, filtered off next day in a sintered-glass crucible (grade 2), washed, dried *in vacuo* over phosphoric oxide, weighed, and identified by m. p., mixed m. p., and infrared examination. In control experiments with pure tribromophenol the amount recovered was 96·9%; results for the tribromophenyl derivatives were corrected on this basis.

trans-*Hexahydro-1,3,5-benzotrioxepan.*—A mixture of pyridine (63·2 g.) in ether (160 c.c.) and di(chloromethyl) ether (46 g.) in ether (160 c.c.) was stored at room temperature for 3 days and distilled to dryness. The solid residue was broken up, *trans*-cyclohexane-1,2-diol (23·2 g.) was added, and the mixture was heated at 140—150° (oil-bath) for 5 hr., cooled, mixed with water, and extracted with chloroform. The extract was washed thoroughly with dilute hydrochloric acid and with water, dried ($K_2CO_3$), and evaporated. Distillation of the residue in steam gave *trans*-hexahydro-1,3,5-benzotrioxepan (13·4 g.), b. p. 85—86°/12 mm., $n_D^{19}$ 1·4701 (lit.,[9] b. p. 97°/20 mm., $n_D^{21}$ 1·4686), identified by comparison of its infrared spectrum with that of an authentic specimen.

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