839. *Acetals and Oligoacetals. Part II.*[1] *Acetals from Chloral, and their Co-oligoacetals with Formaldehyde.*

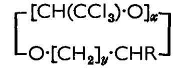
By R. F. Webb and A. J. Duke.

Acetals have been prepared by reaction of chloral and alcohols under azeotropic conditions with perchloric acid as catalyst. They undergo normal alkyl-exchange. Co-oligoacetals incorporating chloral and formaldehyde have also been prepared, and the position of the equilibrium between these compounds and simple oligoformals has been established.

Acetals (I) from chloral have generally[2] been obtained by conversion of chloral hemiacetals into alkyl 1,2,2,2-tetrachloroethyl ethers, and condensation of the latter with alkoxides to give the acetals.[2,3] Compounds containing two hydroxyl groups give cyclic acetals[4] (II a or b) or cyclic diacetals[5] (IIc) on reaction with chloral and sulphuric acid (or zinc chloride[4a]). However, similar treatment of mixtures of chloral and monohydric alcohols usually produces only the chloral hemiacetals,[2,4] although a 26% yield of the diethyl acetal (Ib) has been obtained in this way.[3a]

$Cl_3C\cdot CH(OR)\cdot OR'$

(I) a: $R = R' = Pr^n$
b: $R = R' = Et$
c: $R = R' = CH_2Bu^n$
d: $R = CH_2Bu^n$, $R' = Pr^n$
e: $R = CH_2\cdot CH_2\cdot OEt$, $R' = Pr^n$
f: $R = R' = CH_2\cdot CH_2\cdot OEt$

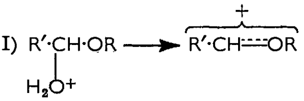


$$\left[\begin{array}{l} [CH(CCl_3)\cdot O]_x \\ O\cdot [CH_2]_y\cdot CHR \end{array}\right]$$

(II) a: $x = 1, y = 1$
b: $x = 1, y = 2$
c: $x = 2, y = 1$

The difficulty encountered in the direct production of acetals from chloral is considered to be due to destabilisation of the required intermediate ion (IVa) by the trichloromethyl group, which renders its formation from the protonated hemiacetal (III) harder than formation of an alkyl-substituted or unsubstituted carbonium-oxonium ion (IVb or c). Since ions of type (IV) are also intermediates in the hydrolysis of acetals,[6] and probably also in their pyrolyses,[7] and since the usual route for pyrolytic degradation of acetals, involving elimination to give vinyl ethers,[7] is not possible from a compound of structure (I), acetals from chloral were expected to be particularly stable, which would be of interest in the synthesis of polymers of high thermal stability. The introduction of the three chlorine atoms might also provide a novel approach to flame-resistant polymers.

(III)



$$\underset{H_2O^+}{R'\cdot CH}\cdot OR \longrightarrow \overset{+}{\overbrace{R'\cdot CH\overset{\ldots}{=}OR}}$$

(IV) a: $R' = Cl_3C$
b: $R' = $ Alkyl. c: $R' = H$

We have found that acetals can be obtained directly from chloral and saturated monohydric primary alcohols by the use of perchloric acid as catalyst and azeotropic removal of the water formed. By this procedure 1,1,1-trichloro-2,2-dipropoxyethane (Ia) has been obtained in 58% yield. Ethyl alcohol does not give the corresponding acetal (Ib) under

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[1] Part I, preceding paper.

[2] Hirwe, *J. Univ. Bombay*, 1937, **6**, Part II, 182.

[3] (*a*) McElvain and Curry, *J. Amer. Chem. Soc.*, 1948, **70**, 3784; (*b*) Magnani and McElvain, *ibid.*, 1938, **60**, 2210.

[4] (*a*) Yoder, *J. Amer. Chem. Soc.*, 1923, **45**, 475; (*b*) Böeseken and Stok, *Kgl. Akad. Wetenschap. Amsterdam, wisk. nat. Afd.*, 1927, **30**, 55; *Chem. Zentr.*, 1927, I, 2987.

[5] Schroeder, U.S.P. 2,595,304 (to G. D. Searle & Co.); *Chem. Abs.*, 1953, **47**, 4377.

[6] O'Gorman and Lucas, *J. Amer. Chem. Soc.*, 1950, **72**, 5489; Kreevoy and Taft, *ibid.*, 1955, **77**, 3146, 5590.

[7] Cf. Copenhaver and Bigelow, "Acetylene and Carbon Monoxide Chemistry," Reinhold Publ. Corp., New York, 1949, p. 32; Celanese Corp. of America, B.P. 681,059 (*Chem. Abs.*, 1954, **48**, 2758); Deschamps, Paty, and Pineau, *Compt. rend.*, 1954, **238**, 2006; Brannock, *J. Amer. Chem. Soc.*, 1959, **81**, 3379.

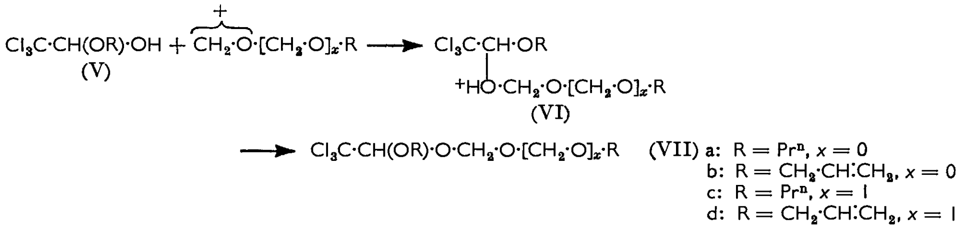
similar conditions, probably because the equilibrium state of the system does not contain sufficient water to cause separation of a second phase in the water entrainer. Under similar conditions, the condensation is also catalysed by sulphuric acid, but its use results in a slower reaction; hydrochloric, fluoroboric, and toluene-*p*-sulphonic acid are not useful as catalysts.

Chloral acetals undergo normal alkyl exchange in the presence of perchloric acid. Heating the acetal (Ia) with pentyl alcohol and perchloric acid in xylene, so that the propanol liberated distils off, gives a mixture of 1,1,1-trichloro-2,2-dipentyloxyethane (Ic) and the mixed acetal (Id).

Compound (Ia) is stable at its boiling point (233°) under atmospheric pressure, but when refluxed in the presence of sulphuric acid it is slowly cleaved in the opposite direction to that observed with acetals of unchlorinated aldehydes,[7] giving chloral n-propyl hemiacetal and an unsaturated gas, presumably propene.

Attempts to produce polymer systems incorporating the chloral acetal grouping have not been successful. The drastic conditions involved in both the direct synthesis and the alkyl exchange result in polymerisation of the unsaturated alcohols, allyl alcohol and 1,2,3,6-tetrahydrobenzyl alcohol, in formation of polybenzyl[8] from benzyl alcohol, and in dehydration of butane-1,4-diol to tetrahydrofuran. Diethylene glycol does not give a linear polymer, possibly owing to dehydration to vinyl ethers since an attempted alkyl exchange between compound (Ia) and 2-ethoxyethanol gave only low yields of the crude acetals (Ie) and (If), accompanied by some chloral propyl hemiacetal.

Because of the difficulties in the production of simple chloral acetals suitable for incorporation into polymeric systems, the co-acetals (VII) of chloral and formaldehyde were examined. In the formation of these compounds, chloral hemiacetals can react by O–H fission [*i.e.*, as an alcoholic component, (V) ⟶ (VI) ⟶ (VII)], which is assisted by the presence of the trichloromethyl group, in contrast to the hindering effect of this group on the formation of simple chloral acetals. Cyclic co-acetals of chloral with other aldehydes have been prepared before.[9] However, reaction of propan-1-ol, formaldehyde, and chloral in the molar ratio 2 : 1 : 1 gave maximum yields of 1,1,1-trichloro-2-propoxy-2-propoxymethoxyethane (VIIa) of only 36—40%, either by simultaneous reaction of all three components, or by reaction of a preformed mixture of dipropyl oligoformals with chloral propyl hemiacetal. This limited yield is due to an " equilibrium " between compounds of type (VII), oligoformals, and free chloral, since a mixture of the same composition is produced from the pure product (VIIa) under similar conditions.



$$\underset{\text{(V)}}{\mathrm{Cl_3C{\cdot}CH(OR){\cdot}OH}} + \overset{+}{\mathrm{CH_2{\cdot}O{\cdot}[CH_2{\cdot}O]_{\mathit{x}}{\cdot}R}} \longrightarrow \underset{\text{(VI)}}{\mathrm{Cl_3C{\cdot}\underset{\overset{|}{+HO{\cdot}CH_2{\cdot}O{\cdot}[CH_2{\cdot}O]_{\mathit{x}}{\cdot}R}}{CH}{\cdot}OR}}$$

$$\longrightarrow \mathrm{Cl_3C{\cdot}CH(OR){\cdot}O{\cdot}CH_2{\cdot}O{\cdot}[CH_2{\cdot}O]_{\mathit{x}}{\cdot}R}$$

(VII) a: $R = Pr^n$, $x = 0$
b: $R = CH_2{\cdot}CH{:}CH_2$, $x = 0$
c: $R = Pr^n$, $x = 1$
d: $R = CH_2{\cdot}CH{:}CH_2$, $x = 1$

The position of " equilibrium " is even less favourable with allyl alcohol, only *ca.* 10% yields of the co-acetal (VIIb) being obtained.

The reaction of more than one mol. of formaldehyde with one of chloral and two of the alcohol gave mixtures in which the presence of at least the second members of the co-oligoacetal series was demonstrated, but the large amounts of oligoformals also produced could not be separated completely from the co-oligoacetals (VIIc) and (VIId) by distillation, so the latter were not obtained pure. These products are believed to have formula

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[8] Shriner and Berger, *J. Org. Chem.*, 1941, **6**, 305.
[9] Pinner, *Ber.*, 1898, **31**, 1926.

(VII) rather than (VIII), both because most of the chloral is present during the reaction as the hemiacetal, and because the infrared spectra of the fractions of product (VIIc) in

(VIII) $RO{\cdot}CH_2{\cdot}O{\cdot}CH(CCl_3){\cdot}O{\cdot}CH_2{\cdot}OR$ $\quad$ $Pr^nO{\cdot}CH(CCl_3){\cdot}O{\cdot}CH_2{\cdot}O{\cdot}CH(CCl_3){\cdot}OPr^n$ (IX)

the 1100—900 cm.$^{-1}$ region are analogous to that of a diformal;[1] structure (VIII) would be expected to give rise to absorption more closely related to that of monoformals, as is found for compounds (VII a) and (VII b).

The use of a propanol–formaldehyde–chloral ratio of 2 : 1 : 2 gave only product (VIIa) and chloral propyl hemiacetal, with no trace of the triacetal (IX).

EXPERIMENTAL

1,1,1-*Trichloro*-2,2-*dipropoxyethane* (Ia).—Chloral (1396 g.), propan-1-ol (1249 g.), benzene (500 ml.), and 60% aqueous perchloric acid (10 ml.) were refluxed under a Dean–Stark water entrainer. Only 15 ml. of water were evolved during 18 hr., so a further 20 ml. of 60% perchloric acid were added, and refluxing was continued for 3 days. The total volume of aqueous phase removed was 245 ml. (calc., 170·5 ml.). The product was distilled rapidly at 15 mm., and fractionally redistilled, giving a forerun, b. p. ~40°/10 mm., n_D^{23} 1·4506 (152 g.), then a small fraction, and next 1,1,1-*trichloro*-2,2-*dipropoxyethane*, b. p. 108°/11 mm. (after refractionation), n_D^{25} 1·4508, d_{25}^{25} 1·166, spec. refraction 0·2309 (calc.,[10] 0·2293) (Found: C, 38·8; H, 5·9; Cl, 42·8. $C_8H_{15}Cl_3O_2$ requires C, 38·5; H, 6·1; Cl, 42·6%) (yield: crude, 1370 g., 58·1%; pure, 1345 g., 57·1%). The apparent consumption of the first-added batch of catalyst was also observed in similar preparations.

Alkyl Exchange by the Acetal (Ia).—The acetal (62·4 g., 0·25 mole), pentan-1-ol (44 g., 0·5 mole), xylene (40 ml.), and 60% perchloric acid (2 ml.) were fractionally distilled until about 35 ml. had passed over, and the head-temperature had risen from 97° to *ca.* 120°. Further distillate then showed no infrared hydroxyl absorption. The residue was distilled, and the fraction boiling in the range 105—160°/11 mm. was redistilled, giving 1,1,1-*trichloro*-2-*propoxy*-2-*pentyloxyethane* (Id) (12·7 g.), b. p. 133·5°/13 mm., n_D^{22} 1·4536, d_{25}^{25} 1·125, spec. refraction 0·2397 (calc., 0·2396) (Found: Cl, 38·4. $C_{10}H_{19}Cl_3O_2$ requires Cl, 38·3%). Further distillation afforded 1,1,1-*trichloro*-2,2-*dipentyloxyethane* (Ic) (7·4 g.), b. p. 154°/13·5 mm., n_D^{24} 1·4543, d_{25}^{25} 1·086, spec. refraction 0·2496 (calc., 0·2480) (Found: C, 47·5; H, 7·6; Cl, 34·3. $C_{12}H_{23}Cl_3O_2$ requires C, 47·2; H, 7·6; Cl, 34·8%).

Pyrolysis of Acetal (Ia).—The acetal (61 g.) containing concentrated sulphuric acid (1 ml.) was distilled very slowly at 1 atm. with partial return. An unsaturated gas was detected at the head of the reflux condenser, and 50·5 g. of distillate were collected during 2 days, mostly of b. p. 97—110°. The infrared spectrum of this distillate was substantially identical with that of chloral propyl hemiacetal (V; R = Pr^n), prepared for comparison by setting aside a mixture of equimolar amounts of propan-1-ol and chloral for a day and then distilling; the latter product had b. p. 118·5° (lit.,[11] 120—122°), n_D^{26} 1·4673.

Preparation of Co-acetals (VII a and b).—(i) *By simultaneous reaction of all three components.* Propan-1-ol (120 g., 2 moles), chloral (147·5 g., 1 mole), paraformaldehyde (30 g., 1 mole as CH_2O), benzene (30 ml.), and toluene-*p*-sulphonic acid (2 g.) were refluxed under a water entrainer for 20 hr., 22·0 ml. of water separating. The product was washed with 10% sodium hydroxide solution (2 × 200 ml.) and water (2 × 200 ml.). Benzene, dipropyl formal, and chloral propyl hemiacetal were removed by distillation, and further distillation then gave 1,1,1-*trichloro*-2-*propoxy*-2-*propoxymethoxyethane* (VIIa) (107·5 g., 38·5%), b. p. 133—134°/10 mm. (after refractionation), n_D^{25} 1·4512, d_{25}^{25} 1·184, spec. refraction 0·2275 (calc., 0·2276) (Found: C, 39·1; H, 6·0; Cl, 37·8. $C_9H_{17}Cl_3O_3$ requires C, 38·7; H, 6·1; Cl, 38·0%).

Yields of 22—40% (based on propanol) were obtained in similar preparations where the proportions of the reactants were varied.

2-*Allyloxy*-2-*allyloxymethoxy*-1,1,1-*trichloroethane* (VIIb) (13·4 g., 4·9%) was prepared similarly, but with magnesium chloride (3 g.) as catalyst, twice as much benzene, and reaction for only 3 hr. It had b. p. 139—141°/15 mm. (after refractionation), n_D^{25} 1·4728, d_{25}^{25} 1·213, spec. refraction 0·231 (calc., 0·236) (Found: C, 39·9; H, 4·9. $C_9H_{13}Cl_3O_3$ requires C, 39·2;

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[10] Denbigh, *Trans. Faraday Soc.*, 1940, **36**, 936.

[11] Gabutti, *Gazzetta*, 1901, **31**, I, 86.

H, 4·8%). Yields of 5—10% were obtained in this case from similar reactions catalysed by toluene-*p*-sulphonic acid, iodine, or titanium tetrachloride (cf. ref. 1).

(ii) *From mixed preformed dipropyl oligoformals.* Propan-1-ol (120 g., 2 moles), paraformaldehyde (60 g., 2 moles as CH_2O), benzene (30 ml.), and toluene-*p*-sulphonic acid (2 g.) were allowed to react as usual until 30 ml. of water had been evolved. Chloral (147·5 g., 1 mole) was then added, and the mixture was heated under simple reflux for 20 hr. The product was washed and distilled as in the preparation above, giving a product, (VIIa), b. p. 128—130°/10 mm., n_D^{25} 1·4510 (89·2 g., 31·9%).

Degradation of Co-acetal (VIIa).—The dry co-acetal (65·8 g.), benzene (20 ml.), and toluene-*p*-sulphonic acid (1 g.) were refluxed for 6 hr., sodium carbonate (3 g.) was then added, and the product was distilled. There were recovered 30·2 g. (46%) of the co-acetal having an infrared spectrum substantially identical with that of the starting material. Lower-boiling fractions showed peaks in the infrared spectrum characteristic of chloral, its propyl hemiacetal, and dipropyl monoformal.

Co-oligoacetals (VII c and d).—Propan-1-ol (120 g., 2 moles), chloral (147·5 g., 1 mole), paraformaldehyde (90 g., 3 moles as CH_2O), benzene (100 ml.), and toluene-*p*-sulphonic acid (1 g.) were caused to react as above, evolving 48 ml. of water during 3·5 hr. The product was washed with 0·5% aqueous sodium hydroxide (2 × 400 ml.) and distilled, removing first benzene and some lower dipropyl oligoformals. The material distilling in the range 85°/15 mm. to 220°/0·2 mm. was fractionally redistilled, giving dipropyl di- and tri-formals (14·3 g.), b. p. 67—126°/13 mm., $n_D^{22\cdot5}$ 1·4128, and the co-acetal (VIIa) (18·1 g.), b. p. 90—92°/0·9 mm., $n_D^{22\cdot5}$ 1·444—1·445, contaminated by some higher dipropyl oligoformals. After a further interfraction, crude co-triacetal (VIIc) (15·0 g.) distilled; it had b. p. 100—105°/0·35 mm., $n_D^{22\cdot5}$ 1·4453—1·4471, with a strong infrared band at 980 $cm.^{-1}$, much weaker absorption at 1020, and no maximum at 1050 $cm.^{-1}$. The spectrum of material (VIIa) contains strong maxima at 1015 and 1050 $cm.^{-1}$.

A similar reaction gave a small fraction of crude material (VIId), b. p. 163—164°/8 mm., n_D^{25} 1·4695, with an infrared spectrum that was poorly defined in the 950—1050 $cm.^{-1}$ region owing to overlapping of the " acetal " bands with those due to the allyl end-groups.

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