Insertion of Chloral into Linear and Cyclic Acetals

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Contrary to the known difficulties of synthesizing dialkyl-acetals of chloral, it was found that the latter can be quantitatively inserted into the C–O–C bonds of cyclic, linear, substituted, or unsubstituted acetals at low temperatures in substantially anhydrous, acidic media, providing a variety of novel co-acetals, including a 1,3,5,8-tetraoxecane. The reaction was not applicable to ketals, where an aldol condensation was observed, nor to aldehydes other than chloral. A mechanism which avoids unstable chloral carbonium ion intermediates is discussed. In cases of substituted cyclic acetals or when two chloral units were added, often pure structural isomers were isolated, selectively formed by different Lewis acid catalysts.

The acid-catalyzed cleavage of acetals and ketals into protonated or otherwise complexed oxyalkyl and stabilized hemiacetal carbonium ions has been studied extensively, using hydrolysis for kinetic measurements (3). In anhydrous systems it has been possible to insert alkylene oxides (4) or larger cyclic ethers (5) into the C–O bond, as well as electron-deficient double bond systems, such as vinyl ethers (6), styrene (7), isocyanates (8), and formaldehyde (9).

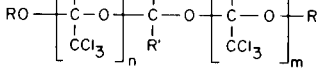
In cases where the products of these reactions were again acetals (3,5,6,9) or aminoacetals (8), often more than one unit could be inserted. When the starting materials were cyclic formals, copolymerizations usually occurred. With aldehydes, such copolymerizations were thought to be restricted to formaldehyde (10) until the disclosure of copolymers of chloral with cyclic formals by the present authors (11). As by-products of these copolymers, cyclic oligomers were noticed, *e.g.*, the dimer formed from chloral and 1,3-dioxolane, the 2-trichloromethyl-1,3,5-trioxepane (**12**). Its synthesis in over 80% yield by depolymerization of the copolymer or directly has been described there.

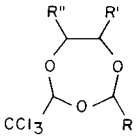
The present paper discusses the general applicability of the addition of chloral to linear and cyclic acetals and ketals in essentially anhydrous media. It was also intended to determine whether the resulting mixed acetals would show enhanced plasticizer and solvent power as one might predict for molecules containing multiple C–O–C and CCl_3 units. It was also of interest to see whether the trichloromethyl group would retain its well established biological activity in these new compositions. Previously two linear alkoxy-terminated coacetals of chloral and formaldehyde had been prepared by the removal of water from alcohol-aldehyde mixtures in conversions of below 40% (12). Cyclic analogues or those derived from chloral and aldehydes other than formaldehyde have not been reported.

In agreement with earlier observations (10) it was found that aromatic and aliphatic aldehydes other than formaldehyde or chloral could not be inserted into 1,3-dioxolane (**7**) under a variety of conditions. Butanal in the presence of dioxolane and acidic catalysts formed a cyclic trimer while benzaldehyde remained unchanged. Poly-1,3-dioxolane isolated from the latter attempt did not contain detectable quantities of benzaldehyde units.

In contrast, chloral could be inserted into all the acetals tested. With cyclic ones ring enlargement occurred accompanied by copolymerization in cases of non-substituted formals. In this respect, chloral differed from formaldehyde, which has been found copolymerizable with substituted cyclic acetals as well (13). The factors favoring ring enlargement over chain formation were not studied beyond what had been reported in the previous paper. Besides the size of the cyclic formal and temperature of reaction, the nature of the catalyst had been found critical there.

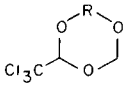
The following products were prepared, starting from different classes of acetals:





2 R = CH_3, R' = H, n = 1, m = 0
3 R = CH_3, R' = H, n = 1, m = 1
4 R = CH_3, R' = H, n = 2, m = 0
6 R = C_2H_5, R' = CH_2Cl, n = 1, m = 0

12 R = H, R' = H, R'' = H
13 R = CH_3, R' = H, R'' = H
14 R = H, R' = H, R'' = CH_2Cl
15 R = H, R' = CH_2Cl, R'' = H



18 R = $(-CH_2-)_4$
19 R = $-(CH_2)_2-O-CH(CCl_3)-$
20 R = $-(CH_2)_2-O-(CH_2)_2-$

TABLE Ia

Reactants

No.	Name	References
1	Formaldehyde, dimethyl acetal	purchased
5	2-Chloroacetaldehyde, diethyl acetal	purchased
7	1,3-Dioxolane	purchased
8	2-Methyl-1,3-dioxolane	purchased
9	4-Chloromethyl-1,3-dioxolane	18
10	2-Trichloromethyl-1,3-dioxolane	19
11	1,3-Dioxepane	purchased
16	2,4-Bis(trichloromethyl)-1,3,5-trioxepane	14
17	1,3,6-Trioxocane	20

The reactants, conditions of reaction and names of the products are listed in Table I; their physical constants in Table II. The proof of the structure of the mixed acetals is based on elementary composition and molecular weight (Table II), the ir spectra (Table III), and nmr spectra (Table IV). The latter two are consistent with the proposed structures and establish the absence of hydroxyl and carbonyl groups.

Visually, the reactions appeared fast even at -78° and were not very exothermic. In the cases of non-substituted formals, the 1:1 insertion compounds were accompanied by products of addition of two or more chloral units besides by polymers. Based on converted starting materials the acetal enlargement reaction appeared quantitative since no by-products were found showing the absence of side reactions (*e.g.*, aldol condensations). It was not attempted to optimize product distribution, conversions, or work-up procedures, except for **12** (11). Therefore, the listed yields represent minimum values and experimental details of preparation and isolation of compounds have been omitted. In all cases, the procedure consisted in mixing of the highly purified components in an inert atmosphere, cold storage for a specified (Table I) period, sometimes neutralization of the catalyst with dry sodium bicarbonate, and fractionation either by distillation or with the solvents listed in Table II.

Interestingly, a catalytic selectivity was noticed when different catalysts were screened, similar to that influencing the ratio of cyclic oligomer to copolymer in the previous work (11). Thus, dimethylformal (**1**) yielded, besides the expected trioxaheptane (**2**), products of addition of more than one chloral molecule to **1**, even when equimolar ratios were used. With phosphorus pentafluoride as the catalyst, the symmetrical di-addition product (**3**) was obtained besides **2** and unreacted formal. When boron trifluoride etherate was the catalyst, the unsymmetrical 2,5-bis(trichloromethyl)-2,4,6,8-tetraoxanonane (**4**) was isolated, free from **3**, according to nmr spectroscopic evidence. Other catalysts such as antimony pentachloride produced inseparable mixtures of **3** and **4**. In addition, small amounts of higher-boiling oils were obtained. They were identified as mixtures of **3** or **4** respectively with higher telomers of chloral, according to their elemental analyses and molecular weights. The reaction of chloral with the diethyl acetal of chloroacetaldehyde (**5**) to yield the expected trioxanonane (**6**) showed that the addition reaction was not restricted to formals.

With one of the cyclic acetals, namely **7**, the addition of two chloral units was also observed, apparently yielding a pure isomer. The structural assignment as the 2,6-bis-(trichloromethyl)-1,3,5,7-tetraoxonane (**19**) rather than as the asymmetrical 2,4-isomer is speculative and based on similarities of its nmr spectrum to that of **3** as compared to **4**. The same holds true for the addition products of

TABLE Ib

Products and Reaction Conditions

No.	Name (a)	Chloral Acetal #	Catalyst,	mole %	Yield %
2	3-Trichloromethyl-2,4,6-trioxaheptane	1:1 (**1**)	BF_3xEt_2O	0.5	85.4
3	3,7-Bis(trichloromethyl)-2,4,6,8-tetraoxanonane	2:1 (**1**)	PF_5	0.04	1.1
4	3-5Bis(trichloromethyl)-2,4,6,8-tetraoxanonane	2:1 (**1**)	BF_3xEt_2O	0.5	12.1
6	4-Chloromethyl-6-trichloromethyl-3,5,7-trioxanonane	1:1 (**5**)	BF_3xEt_2O	2.0	81.0
12	2-Trichloromethyl-1,3,5-trioxepane	1:1 (**7**)	(see 11)		82.5
13	2-Methyl-4-trichloromethyl-1,3,5-trioxepane	1:1 (**8**)	PF_5	0.04	59.6
14 or 15	7-Chloromethyl-2-trichloromethyl-1,3,5-trioxepane (b)	1:1 (**9**)	$SbCl_5$	0.05	62.2
15 or 14	6-Chloromethyl-2-trichloromethyl-1,2,5-trioxepane (c)	1:1 (**9**)	PF_5	0.05	82.3
18	2-Trichloromethyl-1,3,5-trioxonane	1:1 (**11**)	BF_3xEt_2O	0.1	$\leqslant 10$
19	2,6-Bis(trichloromethyl)-1,3,5,7-tetraoxonane	3:1 (**7**)	BF_3xEt_2O	0.1	$\leqslant 10$
20	2-Trichloromethyl-1,3,5,8-tetraoxecane	1:1 (**17**)	BF_3xEt_3O	0.1	$\leqslant 5$

(a) According to an accepted nomenclature recommended by Chemical Abstracts (17). (b) Approx. 90% pure. (c) Approx. 70% pure.

TABLE II

Elemental Analyses and Physical Constants

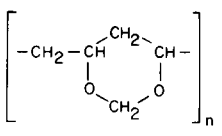
No.	Formula	Calculated %				Found %				n_D^{25}	m.p.	recryst. solvent	b.p.	mmHg
		C	H	Cl	mw	C	H	Cl	mw					
2	$C_5H_9Cl_3O_3$	26.87	4.06		223.5	27.45	4.08		267	1.4568	<-30°	—	108°	27
3	$C_7H_{10}Cl_6O_4$	22.67	2.66		370.9	22.48	2.47		382	--	77-78°	CH_3OH	--	--
4	$C_7H_{10}Cl_6O_4$	22;67	2.66		370.9	22.53	2.65		371	--	59°	CH_3OH	--	--
6	$C_8H_{14}Cl_4O_3$	32.05	4.71	47.28	300.0	32.29	4.70	46.89	302	1.4654	<-30°	--	105°	1.3
12	$C_5H_7Cl_3O_3$	27.10	3.17	48.1	221.5	27.38	3.18	47.9	236	1.4911	29.5°	n-C_6H_{14}	123°	17
13	$C_6H_9Cl_3O_3$	30.59	3.85	45.16	235.5	30.66	3.81	45.1	239	--	59-60°	CH_3OH	59°	0.2
14/15	$C_6H_8Cl_4O_3$	26.70	2.98		269.9	26.85	3.05		268	--	⩾97°	C_2H_5OH	--	--
15/14	$C_6H_8Cl_4O_3$	26.70	2.98	52.54	269.9	26.75	2.94	52.4	267	1.5051	⩾47°	CH_3OH	94-96°	0.1
18	$C_7H_{11}Cl_3O_3$	33.69	4.42		249	34.11	4.53		278	--	55°	CH_3OH	--	--
19	$C_7H_8Cl_6O_4$	22.79	2.17	57.7	369	22.99	2.20	57.6	377	--	147°	CH_3OH	--	--
20	$C_7H_{11}Cl_3O_4$	31.7	4.1	40.06	265	31.7	4.31	39.9	277	--	73°	CH_3OH	--	--

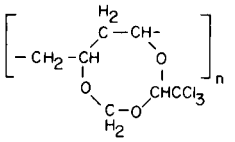
chloral to 4-chloromethyl-1,3-dioxolane (**9**), where two different isomers, (**14**) and (**15**), were obtained, again depending on the catalyst used.

The ten-membered ring (**20**) was isolated as a by-product in the copolymerization of chloral with 1,3,6-trioxocane (**17**). The amount obtained was insufficient for a full characterization.

The known (14) compounds 2-trichloromethyl-1,3-dioxolane (**10**) and 2,4-bis(trichloromethyl)1,3,5-trioxepane (**16**) were prepared for purposes of comparison. An insertion of formaldehyde or of chloral into **10** or **16** which could have resulted in **12**, **16**, or **19**, respectively, or in their corresponding copolymers had been attempted unsuccessfully by previous investigators (15).

The reaction was also used to modify polymeric acetals such as polydivinyl formal (**21**). Since the resulting plastic was soluble, no crosslinking involving acetal belonging to different chain molecules could have taken place, nor could polychloral have formed which is known to be insoluble in all solvents. Chloral apparently enlarged the formal rings without interchain connections according to:





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The reaction was incomplete; only one third of theoretically possible chloral had been added. The modified plastic had a higher softening temperature than the starting material.

The application of this addition reaction to a ketal resulted in a regular aldol condensation of chloral with acetone, liberated in side reactions. When boron trifluoride etherate was added to a 2:1 molar mixture of chloral and acetone, a red-brown discoloration occurred. The mixture solidified after three days standing at 5°, but no identifiable products were found other than the methyl hemiacetal of chloral. A repetition without any added catalyst yielded over 20% of 1,1,1-trichloro-2-hydroxy-4-pentanone which had been obtained previously by base catalyzed aldol condensation of chloral and acetone (16). The condensation, thought to have been catalyzed by traces of acids or of chloral hydrate, must have been preceded by hydrolysis to give acetone and the isolated methyl hemiacetal of chloral. Apparently, the necessary water was supplied by dehydration of aldol condensates, yielding colored by-products, the ir spectra of which showed unsaturation.

The addition of chloral to acetals is known to require a source of protons. This was demonstrated in copolymeri-

TABLE III

I. R. Spectra (a)

No.	Absorptions (microns)
2	3.39-3.42 mdbl; 3.5 w; 6.8-6.9 wdbl; 7.5 w; 8.3 m; 8.65s; 9.45 s; 9.8 s; 10.1s; 10.8 m; 12.3 s; 14.6 m.
3	3.39 m; 3.50 w; 6.88 m; 7.32 m; 7.51 m; 8.30 m; 8.55 sh; 8.93 s; 9.47 m; 9.81 m; 10.10 m; 12.35 s; 14.15 m; 14.95 m.
4	3.38 m; 3.98 wsh; 6.75-6.8-6.9 w. trpl; 7.38 w; 7.6 m; 8.25 m; 8.60 to 10.30 s (showing nine minor bands); 10.80 m; 11.82-12.4 dbl; 14.4 m.
6	3.33 m; 3.39-3.42 wdbl; 6.92 w; 7.30 w; 7.42-7.60 wdbl; 8.3 w; 9.0-9.52 sdbl; 9.85-10.05 sdbl; 11.0 w; 12.0 msh; 12.4 s; 12.95 wsh; 14.9 w.
12	3.4-3.5 wdb.; 6.95 w; 7.5 w; 7.85 m; 8.55-8.8 sdbl; 9.14 m; 9.75-9.9 mdbl; 10.3 m; 10.85 m; 11.95 sh; 12.45 s; 14.1 w.
13	3.4 w; 6.9 w; 7.2 w; 7.45 w; 7.8 m; 7.9 sh; 8.55-8.75 sdbl; 9.0 sh; 9.3 m; 9.6 m; 9.9 m; 10.6 sh; 10.85 m; 11.1 w; 11.4 m; 12.0 m; 12.5 m; 14.0 w.
14/15	3.35-3.4 wdbl; 6.8 w; 7.45 w; 8.1 m; 8.4 m; 8.7-8.85 sdbl; 9.1 sh; 9.45 s; 9.95 s; 10.65-10.85 mdbl; 11.4 m; 12.4-12.7 sdbl; 13.35 s; 14.0 w.
15/14	3.3-3.45 wdbl; 6.9 w; 7.35 w; 7.8 w; 8.5-8.7-8.85 strpl; 9.15 sh; 9.35 m; 9.9 m; 10.9 m; 12.35 s; 12.6 sh; 13.3 m; 15.3 m.
16	3.45 w; 6.95 w; 7.4 w; 7.45 wsh; 7.83 m; 8.0 w; 8.62-8.81 sdbl; 8.91 msh; 9.3 m; 9.7-9.81 mdbl; 10.0 m; 10.0 m; 10.85 w; 11.23 m; 11.9 s; 12.45 s; 14.0 w.
18	3.35-3.45 wdbl; 6.8 w; 7.0 w; 7.55 w; 7.82 m; 8.15 m; 8.6-8.8-9.02 strpl; 9.25 m; 9.4 m; 9.9-10.06 sdbl; 10.28 sh; 10.6-10.7 mdbl; 11.6 w; 12.3-12.5 sdbl; 12.9 sh; 14.4 m.
19	3.35-3.45 wdbl; 6.92; 7.5 w; 7.73 m; 7.9 m; 8.70-8.83 sdbl; 9.01-9.10 sdbl; 9.40 s; 9.7 w; 9.9 m; 10.15-10.25 sdbl; 11.07 w; 11.87-12.0 sdbl; 12.4 s; 14.3 m;
20	No spectrum obtained.

(a) Phase: neat, or potassium bromide pellet, or fluoluble/nujol mulls.

zation studies (11), where it was found that perfectly anhydrous 1,3-dioxolane homopolymerized with Lewis acids in the presence of chloral, while traces of water prompted an alternating copolymerization to take place. Therefore, the addition of chloral to acetals cannot be formulated as an insertion reaction. In agreement with suggestions by Webb and Duke (12) for their preparations from alcohols or hemiacetal, it is assumed that the rather acidic hydroxy group of an intermediate chloral hemiacetal adds to an oxonium-carbonium ion (resulting here from protonation and partial cleavage of acetal):

$$(RO)_2CR'H + Cl_3CCHO \xrightarrow{H^+}$$

$$RO\overset{+}{\cdots\cdots}C(HR') + HOC(CCl_3H)OR \rightarrow$$

$$ROC(HR')\overset{H^+}{O}C(CCl_3H)OR$$

In these authors' system, the yields were limited by unfavorable equilibria which do not exist here, since traces of moisture are thought complexed with the catalyst and thus unavailable for hydrolysis, while providing sufficient protons for catalysis.

As noted by Webb and Duke, this formulation does not require intermediate chloral carbonium ions which are obtainable only under drastic conditions owing to the destabilizing -I effect of the trichloromethyl group. The same effect also causes a reduction of electron density around the oxygen atoms of the protonated chloral acetals **22** thus enabling the proton to shift to the more highly basic starting acetals of other aldehydes.

The above-noted high selectivity of individual Lewis acid catalysts in directing chloral either adjacent to or opposite a substituted alkyloxy or already present chloral unit indicates a strong involvement of the gegen ion in intermediate complexes. A prediction of the direction of addition would require a detailed knowledge of the stability and stereochemistry of these complexes.

In line with initial expectations most of the coacetals showed antimicrobial activity when tested against *Proteus mirabilus* or as pesticides, *e.g.*, controlling the root-knot nematode.

They were also found to be selective solvents and compatible with a number of commercial plastics. Thus, 2-trichloromethyl-1,3,5-trioxepane (**12**) was found miscible with most solvents, except for mineral oils, from which

TABLE IV

NMR Spectra (a)

No.	Group (s)	Position	Proton (s)	Hz (11)	Multiplet
2	CH_3	1	3.0	224	s
	CH	3	3.0	290	s
	CH_2	5		~295	ABq
	CH_3	7	3,0	212	s
3	$2xCH_3$	1 + 9	6.0	229	s
	2xCH	3 + 7	2.15	313	s
	CH_2	5	1.85	300	s
4	CH_3	1	3.0	231	s
	CH	3	3,0	312	s
	CH_2	7		~298	ABq
	CH	5	1.0	318	s
	CH_3	9	3.1	212	s
6	$2xCH_3$	1 + 9	6.0	68 - 86	3t
	$2xCH_3$	2 + 8	8.1	210 - 252	cm
	$C-CH_2Cl$	4		217	d
	2xCH	4 + 6	2.1	294 - 309	cm
12	CH	2	3.0	308	s
	CH_2	4		306	ABq
	$2xCH_2$	6 + 7	4.0	223 - 270	cm
13	CH	2	2.0	322	q
	CH	4		307	s
	$C-CH_3$	2	3.0	85	d
	$2xCH_2$	6 + 7	4.1	220 - 256	cm
14	CH	2	3.0	308	s
	CH_2	4		~310	ABq
	CH_2	6			
	CH	7	5.0	210 - 270	cm
	$C-CH_2Cl$	7			
15	CH	2	3.0	312	s
	CH_2	4		~307	ABq
	CH	6			
	$C-CH_2Cl$	6	5.15	200 - 265	cm
	CH_2	7			
18	CH	2	2.9	292	s
	CH_2	4		~297	ABq
	$2xCH_2$	6 + 9	3.95	60 - 150	cm
	$2xCH_2$	7 + 8	4.0	200 - 265	cm
19	2xCH	2 + 6	2.0	319	s
	CH_2	4	1.95	~304	ABq
	$2xCH_2$	8 + 9	4.0	234 - 265	cm
20	CH	2	3.0	305	s
	CH_2	4		304	s
	$4xCH_2$	6,7,9,10	8.0	200 - 255	cm

(a) Solutions in deuteriochloroform.

it could extract, *e.g.*, aromatic solvents. The materials which dissolve in it at elevated temperatures are nonplasticized polyvinylchloride,-acetate,-butyral, and cellulose acetate, 6,6-nylon, Celcon polyacetal, and swelling was effected in low-density polyethylene. When added in small quantities to the above listed plastics, the acetals as well as their polymeric analogues (11) were effective plasticizers.

EXPERIMENTAL (21)

The purification of chloral and of the acetals was carried out as described previously (11). The reagents were weighed in oven-dried syringes, mixed in moisture-free, two-neck flasks provided with a three-way gas inlet and a magnetic stirrer, and cooled to 0-5°. The catalyst was added from a syringe while purging with inert gas and stirring. The flasks were kept at 0-5° for 1 to 10 days. The products were separated by fractionation at reduced pressures from the reaction mixture directly, or after neutralization with sodium bicarbonate (products containing acetals of acetaldehyde or chloroacetaldehyde). In cases of copolymerizations, the cyclic acetals were separated by extraction with the listed solvents and repeated reprecipitations.

1,1,1-Trichloro-2-hydroxy-4-pentanone.

Anhydrous chloral (b.p. 97.5-97.8° from calcium hydride, 0.5 mole) and 2,2-dimethoxypropane (b.p. 80.3° from sodium benzophenone ketyl, 0.5 mole) were mixed in nitrogen at room temperature which caused a small, sustained exotherm and brown-red discoloration. After 3 days at 5° about 2 g. of sodium bicarbonate were added, the reaction mixture filtered, and fractionated, giving 11.8 g. (20.6%) of the hydroxypentanone: b.p. 101° (0.4 mm.); m.p. (from hexane) 74° (lit. 75-76°) (16); ir, nmr spectra, and elemental analysis were consistent with the structure assigned.

If no cooling is applied to the starting mixture, a violent reaction may occur, resulting in red to black oils besides 2,2,2-trichloro-1-methoxyethanol which was isolated by fractionation at reduced pressure.

Reaction of Chloral with Polydivinylformal.

To a solution of 3 g. (0.03 mole of formal units) of polydivinyl formal, having a number average molecular weight of 3900 in 25 ml. of anhydrous chloral, was added with stirring 2 drops of concentrated sulfuric acid. After standing in a moisture-free atmosphere at 25° for 20 hours, the mixture was poured into a methanol/pyridine solution wherein a solid precipitated. This solid was reprecipitated three times from benzene into methanol to yield 3.95 g. of a light tan powder, softening temperature around 100°; Elemental analysis revealed that the product contained 15.7% by weight chlorine.

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