α-Acetamido-N-benzylsuccinamic Acid (V, R′ = CH_3CO).—When either α-acetamino-N-benzylsuccinimide (VI) or α-acetamido-α-carbethoxysuccinbenzylimide was refluxed for three hours with 10% sodium carbonate and the solution made acid to congo paper with hydrochloric acid there was obtained an acid which, on crystallization from a large volume of ethyl acetate, melted at 153–155°. This proved to be α-acetamido-N-benzylsuccinamic acid.

Anal. Calcd. for $C_{13}H_{16}N_2O_4$: N, 10.60; neut. equiv., 264.3. Found: N, 10.43; neut. equiv., 266.5.

When about 15–20 mg. of this acid was warmed above its m. p. it evolved water and gave an oil. Upon trituration with water to which several drops of ammonium hydroxide had been added a white solid, m. p. 169–172°, was obtained. This proved to be VI.

One gram of V (R′ = CH_3CO) was refluxed with 15 ml. of 10% alcoholic potassium hydroxide for two hours. The alcohol was removed *in vacuo*, the residue dissolved in water and made just acid with hydrochloric acid. The solution was then brought to *p*H 8 with ammonium hydroxide to precipitate an amino acid. This was recrystallized from water and identified as α-amino-N-benzylsuccinamic acid by mixed m. p. and nitrogen analysis.

1-Acetyl-2-thiohydantoin-5-(N-benzyl)-acetamide.—A mixture of 4 g. of α-acetamido-N-benzylsuccinamic acid, 3 g. of ammonium thiocyanate, 18 ml. of acetic anhydride and 2 ml. of acetic acid was warmed for one and one-half hours on the steam-bath. The solution was poured onto 100 g. of ice and water and stirred to induce crystallization of 4.1 g. of product. Two recrystallizations from butanol gave a solid melting at 162–164°. It dissolved in ammonium hydroxide, but not in sodium bicarbonate. The same product was obtained by starting with α-amino-N-benzylsuccinamic acid.

Anal. Calcd. for $C_{14}H_{15}N_3O_3S$: N, 13.78; S, 10.50. Found: N, 13.21; S, 10.23.

α-Phenylureido-N-benzylsuccinamic Acid (VII).—Prepared by treating 2.2 g. of α-amino-N-benzylsuccinamic acid with 1.9 ml. of phenyl isocyanate in basic solution in the usual manner; m. p. 180–181.5° from aqueous ethanol.

Anal. Calcd. for $C_{18}H_{19}N_3O_4$: N, 12.31; neut. equiv., 341.3. Found: N, 12.16; neut. equiv., 337.5.

3-Phenylhydantoin-5-(N-benzyl)-acetamide (VIII).—A suspension of 1.7 g. of VII was refluxed with 45 ml. of 12% hydrochloric acid for forty-five minutes. It was then cooled, filtered, washed with dilute bicarbonate and then with water. Recrystallization from aqueous ethanol gave a product melting at 166–167°, dec.

Anal. Calcd. for $C_{18}H_{17}N_3O_3$: N, 13.00. Found: N(K), 12.77.

3-Phenylhydantoin-5-acetic Acid (IX).—One-half gram of VIII was refluxed with 60 ml. of hydrochloric acid for two hours, evaporated *in vacuo* and the residue recrystallized from water to give a compound melting at 218–220°. A sample prepared from aspartic acid melted at 223–224°,[9] and the mixture melted at 219–221°.

***dl*-Aspartic Acid.**—Condensation of ethyl chloroacetate (0.52 m.) with acetamidomalonic ester (0.48 m.) and hydrolysis of the condensation product in the manner employed by Galat for the corresponding formamidomalonic ester,[10] gave a 53% yield of *dl*-aspartic acid melting above 300°.

Anal. Calcd. for $C_4H_8NO_4$: N, 10.52. Found: N, 10.52.

Acknowledgment.—The authors are indebted to Mr. Morris E. Auerbach and his staff for the analytical results.

Summary

1. Diethyl N-benzyl-*dl*-aspartate was synthesized from maleic anhydride and benzylamine, and from diethyl *dl*-chlorosuccinate and benzylamine.

2. The reaction of benzylamine with diethyl fumarate at 150° gave the dibenzylamide of N-benzyl-*dl*-aspartic acid, and a compound melting at 62.5° which was identified as N,N′-dibenzyl-α-aminosuccinimide. These results differ from those of Warren and Grose who reported that the reaction gave N,N′-dibenzyl-α-aminosuccinimide melting at 205°.

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[9] Gaunt and Wormall, *Biochem. J.*, **30**, 1915 (1936).

[10] Galat, This Journal, **69**, 965 (1947).

Rensselaer, New York Received March 2, 1948

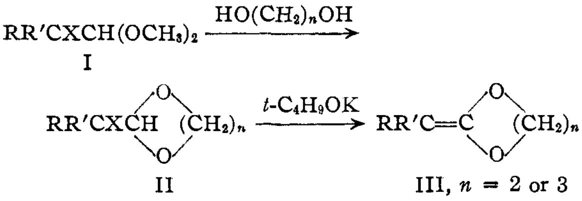
[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

Ketene Acetals. XIX. 2-Methylene-1,3-dioxolanes and 1,3-Dioxanes

By S. M. McElvain and Michael J. Curry[1]

As an extension of previous work on the ketene acetals in This Laboratory, the preparation of a variety of ketene cyclic acetals derived from ethylene and trimethylene glycols was undertaken. The rather unusual properties of these compounds are now reported.

The ketene cyclic acetals, 2-methylene-1,3-dioxolanes and 1,3-dioxanes (III), were obtained by the dehydrohalogenation of the corresponding halogenated cyclic acetals (II). The latter compounds, with the exception of the chloral cyclic acetals, were prepared by an alcohol exchange between the glycol and the methyl (or ethyl) acetals (I).



It was found advantageous to prepare the ethylene glycol acetals from the methyl rather than the ethyl acetals (I) because of the proximity of the boiling points of the latter to those of the cyclic acetals (II, *n* is 2). The trimethylene glycol acetals, because of their higher boiling points, could be prepared from either the methyl or ethyl acetals. Chloral diethyl acetal did not undergo this type of alcohol exchange; instead higher boiling products, which appeared to have the structures

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[1] Wisconsin Alumni Research Foundation Research Assistant, 1947–1948.

TABLE I

2-METHYLENE-1,3-DIOXOLANES AND -1,3-DIOXANES AND SOME CORRESPONDING KETENE DIMETHYLACETALS, $\mathrm{RR'C{=}\underline{CO(CH_2)_nO}}$

No.	R is	R' is	n is	B. p. °C.	B. p. Mm.	$n^{25}\mathrm{D}$	Formula	Analyses, % Calcd. C	Calcd. H	Calcd. X[a]	Found C	Found H	Found X[a]
1	H	H	2	120–124	735	1.4465	$C_4H_6O_2$	..	...	..[b]	..	..	..
2	H	H	3	147–155	740	1.4304	$C_5H_8O_2$	60.0	8.1	..	56.4	9.4[c]	..
3	C_6H_5	H	2	108–112	0.8[d]	1.6075	$C_{10}H_{10}O_2$	74.1	6.2	..	73.7	6.3	..
4	C_6H_5	H	3	124–126	0.6[e]	1.5840	$C_{11}H_{12}O_2$	75.0	6.9	..	74.0	6.6[f]	..
5	Cl	H	2	89–93	23[g]	1.4874	$C_4H_5ClO_2$	..	...	29.4	..	..	28.1
6	Cl	H	3	132–135	23	1.4780	$C_5H_7ClO_2$	..	...	26.4	..	..	27.3
7	Br	H	2	118–119	24	....	$C_4H_5BrO_2$	..	...	48.5	..	..	47.6
8	Br	H	3	73–75	2	1.5007	$C_5H_7BrO_2$	..	...	44.6	..	..	44.0
9	Cl	Cl	2	118–121	21[h]	....	$C_4H_4Cl_2O_2$	31.0	2.6	45.8	30.5	2.8	45.5
10	Cl	Cl	3	105–106	8[i]	....	$C_5H_6Cl_2O_2$	..	...	42.0	..	..	42.5
						$RCH{=}C(OCH_3)_2$							
11	H	..	..	89–91	740[j]	....	....	..	...	..	..	..	..
12	C_6H_5	..	..	81–82 235–238	1.0[k] 735	1.5620	$C_{10}H_{12}O_2$	73.1	7.4	..	73.3	7.7	..
13	Cl	..	..	140–141	730	1.4460	$C_4H_7ClO_2$	..	...	28.9	..	..	29.3[l]
14	Br	..	..	171–172	732	1.4880	$C_4H_7BrO_2$	..	...	47.9	..		7.7

[a] Halogen. [b] This compound polymerized so rapidly that no analyses were obtained. [c] These analyses indicate absorption of water by the ketene acetal; in fact γ-hydroxypropyl acetate was isolated from the ketene acetal after a short storage. [d] M. p., 38–40°. [e] M. p., 25–27°. [f] These analyses were performed on a sample that had been weighed by difference from a tightly stoppered weighing bottle within fifteen minutes after the ketene acetal had been distilled; after two and four hours, respectively, this material showed the following analyses: C, 73.3 and 72.5; H, 6.6 and 6.7. [g] This ketene acetal was completely polymerized within two hours. [h] M. p., 55.5–57°. [i] M. p., 67–69°. [j] B. p. reported by McElvain, Anthes and Shapiro, THIS JOURNAL, **64**, 2525 (1942). [k] d^{25}_4, 1.0592; this material contained 36.6% methoxyl (calcd. 37.8); it was a colorless liquid in contrast to the pale yellow product, b. p. 240–245°, $n^{25}\mathrm{D}$ 1.5390, reported in ref. 8. [l] Calcd.: OCH_3, 50.6. Found: OCH_3, 49.2.

$CCl_3CH(OC_2H_5)OCH_2CH_2OH$ and $CCl_3CH(OCH_2CH_2OH)_2$, were obtained. The acetals of chloral, corresponding to II, were prepared directly from the aldehyde and the glycols.

The dehydrohalogenations of the cyclic acetals (II) to the ketene acetals (III) were accomplished in 50–80% yields by potassium *t*-butoxide in *t*-butyl alcohol.[2] The physical properties and analyses of the methylenedioxolanes and dioxanes so prepared are summarized in Table I. Also listed in this table are some of the corresponding ketene dimethylacetals. It is of interest to note that the dioxolanes (*n* is 2) generally boil much higher than these related methyl acetals, to which they are comparable in molecular weight.

The most striking property of most of these ketene cyclic acetals is their marked tendency to undergo spontaneous polymerization. Only those containing a phenyl or two chlorine substituents in the methylene group (nos. 3, 4, 9 and 10, Table I) were relatively resistant to polymerization. The other ketene cyclic acetals listed in Table I are obtained pure only with the greatest difficulty because of the polymerization that occurs during their isolation. The use of alkali-washed glassware minimized but did not prevent this polymerization; varying amounts of a voluminous white precipitate generally were present in all freshly distilled samples. The extent of this polymerization appeared to be related to the purity of the ketene acetal, *i.e.*, the purer the acetal the more rapidly it polymerized.[3]

When the polymerization was slight, the ketene acetal was generally found to be contaminated with the ester resulting from the reaction of water with the acetal. These acetals have an extraordinary affinity for moisture as shown by a drop in the refractive index toward that of the ester when exposed to air.[4]

Two types of polymers resulted from these spontaneous polymerizations. Those obtained from the unsubstituted methylenedioxolanes and dioxanes were solids, which melted over a relatively narrow range and which were readily hydrolyzed by dilute hydrochloric acid to red, alkali-soluble oils similar to that obtained from the cadmium chloride-polymerized ketene diethylacetal.[5] The polymers obtained from the monohalogenated ketene cyclic acetals (nos. 5 and 7) were talc-like

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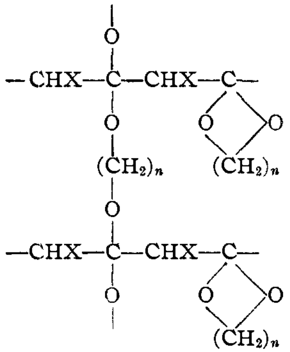
(2) McElvain and Kundiger, "Organic Syntheses," **23**, 45 (1943).

(3) In one instance a freshly prepared sample of 2-methylene-1,3-dioxane polymerized with such rapidity and evolution of heat within a few minutes after it was placed in a stoppered container that the stopper was blown out and the solid white polymer scattered over the desk.

(4) This great affinity for water is also shown by the ketene dimethylacetals; for example, when a sample of the phenylketene dimethylacetal (no. 12, Table I) was placed in one arm of an inverted U-tube that contained water in the other arm, the acetal was completely converted to a mixture of the normal and orthoesters in a few hours. That this change is not related to the oxygen of the atmosphere was shown by the refractive index of a sample of this ketene acetal remaining quite constant after being treated with a stream of dry oxygen.

(5) Johnson, Barnes and McElvain, THIS JOURNAL, **62**, 964 (1940).

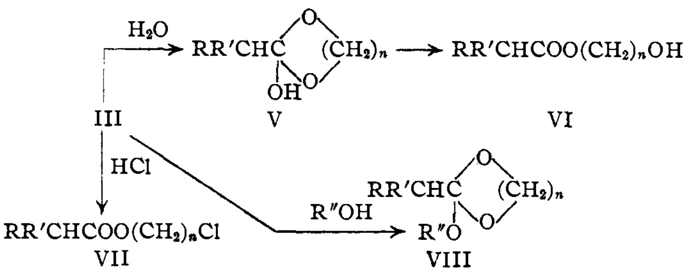
powders that did not melt, but sintered in the range of 290–350°. They were insoluble in all solvents except concentrated sulfuric acid (from which they could not be recovered by dilution), and remained unaffected after heating for several hours with concentrated hydrochloric acid. Both types of polymers usually gave the same analytical data as those calculated for the monomers. These properties lead to the conclusion that the polymers formed from the methylene dioxolane and dioxane (nos. 1 and 2) are the relatively simple straight chains, which yield red poly-1,3-diketones on hydrolysis, that have been postulated for the polymers of ketene diethylacetal.[5] The more refractory character of polymers of the monohalogenated ketene cyclic acetals suggests that in these the polymer chains are cross-linked through the bifunctional glycol moieties to give the more complex structure shown in part in IV



IV

Qualitatively, the dioxolanes of Table I appear to polymerize somewhat more readily than the dioxanes and the chloro compounds more readily than the bromo compounds. In fact, there is no noticeable difference in the ease with which the chloromethylene dioxolane (no. 5) and the methylene dioxolane (no. 1) undergo spontaneous polymerization. In contrast to this behavior the ketene dimethylacetals listed in Table I show no more tendency to polymerize than do the ketene diethylacetals. The polymerization of the unsubstituted ketene dialkyl acetals may be induced by acidified glass surfaces, cadmium chloride, aluminum ethoxide and other agents that can coördinate with the anionoid center of the ketene acetal. Chloroketene dimethylacetal shows a similar resistance to polymerization as has previously been noted[5] for the corresponding diethylacetal.

The phenyl- and dichloroketene cyclic acetals (nos. 3, 4, 9 and 10), which are relatively stable toward polymerization, show an affinity for water similar to that of the other cyclic acetals. The reaction of these compounds with water may be readily followed by the change in refractive index and may be prevented only by a rigid exclusion of the acetals from contact with the atmosphere of the laboratory. When these acetals (III) react with water they are converted to the hydroxyalkyl esters (VI), probably *via* the intermediate ortho acid–ester (V), as the reaction of III with an alcohol produces the stable mixed orthoester[6] (VIII).



With the exception of 2-methylene-1,3-dioxolane, which undergoes a rapid exothermic polymerization when treated with hydrogen chloride, the ketene cyclic acetals react with this acid to yield the chloroalkyl esters VII.

2-Methylene-1,3-dioxolane, when heated with benzyl bromide yielded 43% of the monobenzylation product, β-bromoethyl hydrocinnamate, and 42% of the polymer of the ketene acetal. There was no evidence of any dibenzylated product, which was one of the major products in the benzylation of ketene diethylacetal.[7]

Phenylketene dimethylacetal has been prepared[8] by the pyrolysis of methyl orthophenylacetate and reported to be a yellow liquid. As the phenylketene cyclic acetals (nos. 3 and 4) listed in Table I were water white liquids, it seemed desirable to prepare the corresponding dimethylacetal by dehydrohalogenation of the bromoacetal and compare its properties with those of the product obtained from the orthoester. The dimethylacetal prepared from phenylbromoacetaldehyde dimethylacetal in the present work is perfectly colorless and has the properties listed in Table I. Since this product has a significantly higher refractive index than that obtained from the orthoester and gives a practically quantitative yield of phenylacetamide when treated successively with water and aqueous ammonia, it appears that the previously reported phenylketene dimethylacetal was a relatively impure compound.

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(6) It is of interest to note in this connection that Hibbert and Grieg (*Can. J. Research*, **4**, 254 (1931), found the mono-ethylene glycol esters of acetic and chloroacetic acids to exist as the open chain structures corresponding to VI, but claim that the corresponding esters of dichloro- and trichloroacetic acid exist in the form of V. Meerwein and Sonke (*Ber.*, **64**, 2375 (1931); *J. prakt. Chem.*, **137**, 295 (1933)) believe the latter esters to exist as an equilibrium mixture of forms V and VI and in support of this conclusion they isolated the methyl esters corresponding to VIII after treating such equilibrium mixtures with diazomethane. The mixed orthoester, 2-dichloromethyl-2-methoxy-1,3-dioxolane (VIII, R = R' = Cl; R″ = CH_3; n = 2) obtained in the present work from the reaction of 2-dichloromethylene-1,3-dioxolane (no. 9, Table I) with methanol corresponds in properties with the ester reported by Meerwein and Sonke from the reaction of β-hydroxyethyl dichloroacetate with diazomethane.

(7) McElvain and Kundiger, THIS JOURNAL, **64**, 254 (1942).

(8) McElvain and Stevens, *ibid.*, **68**, 1917 (1946).

Experimental

α,β,β,β-Tetrachloroethyl Methyl and Ethyl Ethers.—Chloral methyl alcoholate was prepared by mixing 100 g. (0.68 mole) of chloral and 22 g. (0.69 mole) of absolute methyl alcohol. An ether solution of this alcoholate was added, with vigorous stirring, to a cooled solution of 54 g. (0.68 mole) of pyridine and 81 g. (0.68 mole) of thionyl chloride in 500 ml. of anhydrous ether. An ice-salt mixture was used to keep the temperature of the mixture at 10-15° during the addition. After the alcoholate was added, the mixture was stirred for an additional hour and then water was added to dissolve the precipitated pyridine hydrochloride. The ether layer was separated, washed with sodium carbonate solution, dried over anhydrous sodium sulfate and distilled to yield 110 g. (82%) of α,β,β,β-tetrachloroethyl methyl ether, b. p. 72-75° (22 mm.), b. p. 173-174° (735 mm.); $n^{25}\text{D}$ 1.4820.

In a similar experiment α,β,β,β-tetrachlorodiethyl ether, b. p. 188° (740 mm.); $n^{25}\text{D}$ 1.4735 was prepared in 74% yield from the ethyl alcoholate.

α,β,β,β-Tetrachloroethyl methyl ether has been prepared[9] by treatment of chloral methyl alcoholate with phosphorus pentachloride and α,β,β,β-tetrachlorodiethyl ether has been prepared[10] by the same procedure. In the present work these two ethers were prepared in only 28% and 67% yields, respectively, with this reagent.

β,β-Dichlorovinyl Methyl Ether.—This ether, b. p. 128-131° (740 mm.); $n^{25}\text{D}$ 1.4603, was prepared in 68% yields by treatment of α,β,β,β-tetrachloroethyl methyl ether with zinc in methyl alcohol solution at 15° according to the procedure used by Neher and Fleece[10] for the ethyl homolog.

Anal. Calcd. for $C_3H_4Cl_2O$: OCH_3, 24.4; Cl, 55.9. Found: OCH_3, 23.7; Cl, 55.7.

Denaro[11] reported that β,β-dichlorovinyl methyl ether boiled at 109-110°. However, subsequent work[12] has shown that the reaction used by Denaro yields the isomeric α,β-dichlorovinyl methyl ether.

Dichloroacetaldehyde Dimethylacetal. (a) **From α,β,-β,β-Tetrachloroethyl Methyl Ether.**—The addition of 85 g. of 20-mesh zinc metal to a mixture of 198 g. of α,β,β,β-tetrachloroethyl methyl ether and 128 g. of absolute methyl alcohol was made at such a rate that the solution refluxed gently. After the solution had cooled, it was decanted from the excess zinc and heated in a distilling flask until approximately 60% of the alcohol had been removed. The residual dark-colored liquid was poured over cracked ice and the oily layer separated, dried over anhydrous calcium sulfate and distilled to yield 89 g. (56%) of dichloroacetaldehyde dimethylacetal.

(b) **From β,β-Dichlorovinyl Methyl Ether.**—A 30-g. sample of β,β-dichlorovinyl methyl ether was saturated with hydrogen chloride and then diluted to 100 ml. with absolute methanol. The solution was placed in a glass-lined reaction bomb and heated at steam-bath temperature for three hours. After cooling the bomb was opened (no pressure), the alcoholic solution poured into water, and the oily layer separated. The aqueous layer was extracted twice with ether and the ether and oil layers were combined and dried over anhydrous sodium sulfate. Distillation yielded 29 g. (76%) of dichloroacetaldehyde dimethylacetal.

This dichloroacetal has been prepared[13] by treatment of α,β,β-trichloroethyl methyl ether with methyl alcohol in a sealed tube. The method described above is a modification of the method of Neher and Foster[10] for the preparation of dichloroacetaldehyde diethylacetal.

The properties of this dichloroacetal and the other acetals used in the present work are summarized in Table II.

Table II

Acetals, $RCH(OR')_2$

R is	R′ is	B. p. °C.	B. p. Mm.	$n^{25}\text{D}$
CH_3	CH_3	58-62	732[a]	1.3660
CH_3	C_2H_5	101-103.5	760[b]	
CH_2Cl	CH_3	127-128	740[c,d]	1.4189
CH_2Cl	C_2H_5	151-154	740[c,e]	1.4160
CH_2Br	CH_3	145-147	740[d]	1.4440
CH_2Br	C_2H_5	167-170	760[f]	
C_6H_5CHBr	CH_3	110-114	1.7[g]	1.5390
$CHCl_2$	CH_3	161-163	740[h]	1.4405
$CHCl_2$	C_2H_5	176-178	732[i,j]	1.4360
$CHBr_2$	CH_3	185-187	732[k]	1.5006
$CHBr_2$	C_2H_5	190-200	740[l]	1.4802
CCl_3	CH_3	178	740[m]	
CCl_3	C_2H_5	193-195	740[i,n]	1.4586

[a] Clarke, *J. Chem. Soc.*, 101, 1804 (1912). [b] Adkins and Nisson, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N.Y., p. 1. [c] Filachione, This Journal, **61**, 1705 (1939). [d] Prepared according to the procedure of Bedoukian, *ibid.*, **66**, 651 (1944). [e] Redistilled technical grade from Niacet Chemical Co. [f] Hartung and Adkins, This Journal, **49**, 2520 (1927). [g] Bedoukian, *ibid.*, **66**, 1324 (1944). When this acetal was distilled slowly through a 20-plate Fenske column in the absence of potassium carbonate it yielded **β-bromo-β-phenylvinyl methyl ether**, b. p. 139-141° (13 mm.); $n^{25}\text{D}$ 1.5892. *Anal.* Calcd. for C_9H_9BrO: OCH_3, 14.5, Br, 37.5. Found: OCH_3, 14.0; Br, 38.9. [h] See experimental section. [i] Magnani and McElvain, This Journal, **60**, 2212 (1938). [j] This acetal was also prepared in 55% yield from chloral diethylacetal by the method of Meldrum and Vad, *J. Indian Chem. Soc.*, **13**, 118 (1936). [k] Prepared by the procedure of Hartung and Adkins (This Journal, **49**, 2520 (1927)); $d^{25}{}_4$ 1.877. *Anal.* Calcd. for $C_4H_8Br_2O_2$: OCH_3, 25.0. Found: OCH_3, 24.9. [l] Beyerstedt and McElvain, This Journal, **59**, 2266 (1937). [m] B. p. reported by Magnani, *Gazz. chim. ital.*, **16**, 332 (1886). [n] This acetal was also prepared in 26% yield from chloral and ethyl alcohol in the presence of sulfuric acid according to the procedure of Böeseken, *C.A.*, 21, 1962 (1927).

Preparation of the Cyclic Acetals (II).—The ethylene and trimethylene glycol cyclic acetals of the aldehydes listed in Table III, with the exception of those of chloral, were prepared in 75-90% yields by an alcohol exchange between the dimethyl or diethylacetal of the appropriate aldehyde and the glycol.[14]

The procedure consisted of heating equimolar quantities of these reactants with a few drops of concentrated sulfuric acid and allowing the liberated methyl or ethyl alcohol to distil out. The remaining liquid was fractionated in the presence of a small amount of anhydrous potassium carbonate. When the theoretical quantity of alcohol did not distil from the reaction mixture, the excess glycol distilled with the cyclic acetal and formed an immiscible layer in the distillate. In such cases the reaction mixture was washed with water and dried over anhydrous sodium sulfate before distillation.

2-Trichloromethyl-1,3-Dioxolane.—A mixture of 38 g. (0.26 mole) of chloral, 16 g. (0.26 mole) of ethylene glycol and 25 ml. of concentrated sulfuric acid was heated at 70° for two hours. After cooling, the black solution was poured over cracked ice and the resulting mixture extracted with chloroform. The chloroform extract was washed with water, dried over anhydrous sodium sulfate, and distilled to yield 31 g. (63%) of 2-trichloromethyl-1,3-dioxolane, b. p. 85-86° (12 mm.), m. p. 41-42°.

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(9) Magnani, *Gazz. chim. ital.*, **16**, 332 (1886).

(10) Neher, *et al.*, This Journal, **31**, 412 (1909); **48**, 2416 (1926).

(11) Denaro, *Gazz. chim. ital.*, **14**, 117 (1884).

(12) Crompton and Vanderstichele, *J. Chem. Soc.*, **117**, 691 (1920).

(13) Oddo and Mamelli, *Gazz. chim. ital.*, **33** (II), 414 (1903).

(14) Hallonquist and Hibbert, *Can. J. Research*, **8**, 129 (1933); these workers used no catalyst but Delépine (*Compt. rend.*, **132**, 970 (1901)) used a few drops of hydrochloric acid as a catalyst.

TABLE III

2-SUBSTITUTED-1,3-DIOXOLANES AND -1,3-DIOXANES, $\mathrm{R}\underbrace{\mathrm{CHO(CH_2)}_n\mathrm{O}}$

R is	n is	B. p. °C.	B. p. Mm.	$n^{25}D$	d^{25}_4	Formula	Halogen Analyses, % Calcd.	Halogen Analyses, % Found
CH_2Cl	2	155–159	740[a]	1.4465	1.2337			
CH_2Cl	3	67–69	12[b]	1.4519	1.1893			
CH_2Br	2	172–175	745[c]	1.4805	1.6358			
C_6H_5CHBr	2	162–165	9[d]	1.5628		$C_{10}H_{11}BrO_2$	32.9	33.2
C_6H_5CHBr	3	120–125	0.8[e]	1.5602		$C_{11}H_{13}BrO_2$	31.1	30.7
$CHCl_2$	2	186–188	732[f]	1.4695	1.3861			
$CHCl_2$	3	210–212	740	1.4796	1.3471	$C_5H_8Cl_2O_2$	41.4	40.9
$CHBr_2$	2	101–104	9	1.5351	2.0617	$C_4H_6Br_2O_2$	65.0	64.9
$CHBr_2$	3	116–118	9	1.5300	1.9345	$C_5H_8Br_2O_2$	61.5	61.5
CCl_3	2	198–200	740[g,h,i]					
CCl_3	3	105-112	12[i,j]			$C_5H_7Cl_3O_2$	51.9	51.5

[a] Delépine, *Compt. rend.*, **132**, 970 (1901). [b] Hallonquist and Hibbert, *Can. J. Research*, **8**, 129 (1933). [c] Otto, THIS JOURNAL, **59**, 1590 (1937). [d] M. p. 37–39°. [e] M. p. 46–48°. [f] Tellegen, *Rec. trav. chim.*, **57**, 667 (1938). [g] M. p. 41–42°. [h] Meldrum and Vad, *J. Indian Chem. Soc.*, **13**, 118 (1936). [i] See experimental section for preparation. [j] M. p. 66.5–68.5°.

This compound has been prepared[15] by mixing one mole of ethylene glycol and two moles of chloral and then distilling the crystalline product. In the present work it was found that this crystalline material formed very slowly over a period of one week; distillation of this material gave ethylene glycol and chloral in approximately 85% yields.

2-Trichloromethyl-1,3-Dioxane.—The reaction between chloral and trimethylene glycol in the presence of sulfuric acid in a procedure similar to that outlined above gave a 55% yield of this acetal.

Ketene Acetals. 2-Methylene-1,3-dioxolanes and 1,3-Dioxanes (III) and Certain Ketene Dimethylacetals.—These compounds, which are listed in Table I, were obtained in 50–80% yields by the action of potassium *t*-butoxide in *t*-butyl alcohol[2] on the corresponding halo-aldehyde acetals of Tables II and III. For the preparation of those ketene acetals which contained no halogens, the halogenated acetal was treated with a slight excess of the potassium *t*-butoxide. Inasmuch as these ketene acetals do not react with the base, the excess served to remove the last traces of the halogenated acetals. However, in the preparation of the halo-ketene acetals it was found that 1.6 moles of potassium *t*-butoxide reacted with one mole of the dihalogenated acetal and that additional base was not used up during longer periods of refluxing. Some of the original base had reacted with the halogenated-ketene acetal, as it was found that when equimolar quantities of potassium *t*-butoxide and chloroketene diethylacetal were refluxed in *t*-butyl alcohol for ten minutes one-third of the base was consumed, but that no further reaction occurred during prolonged refluxing. This observation is contrary to that reported by McElvain and Walters,[16] who found that dibromoacetaldehyde diethylacetal reacted readily with one equivalent of potassium ethoxide but was very resistant to further action of the reagent. In the present work no attempts were made to isolate the reaction products or determine the course of the reaction. Because of the reaction of the potassium *t*-butoxide with the product as well as with the starting material, the use of an excess of base gives lower yields of the haloketene acetals and does not yield a product entirely free from the starting dihalogenated acetal. As the boiling points of these compounds are usually very close together, separation was accomplished only by distillation through an efficient column.

Reactions of the Ketene Cyclic Acetals.—Some illustrative reactions of certain of these ketene acetals are given in this section. For brevity the acetals are indicated by their numbers in Table I.

2-Methylene-1,3-dioxolane (1).—Water converted 1 quantitatively to β-hydroxyethyl acetate; methanol gave a 96% yield of **2-methyl-2-methoxy-1,3-dioxolane**, b. p. 132–134° (745 mm.), $n^{25}D$ 1.4060; d^{25}_4 1.0424.

Anal. Calcd. for $C_5H_{10}O_3$: C, 50.8; H, 8.5. Found: C, 50.3; H, 8.4.

Similarly, ethyl alcohol converted 1 to **2-methyl-2-ethoxy-1,3-dioxolane**, b. p. 144–145° (745 mm.), $n^{25}D$ 1.4079, d^{25}_4 1.0038.

Anal. Calcd. for $C_6H_{12}O_3$: C, 54.6; H, 9.2. Found: C, 53.9; H, 9.2.

When 4 g. (0.047 mole) of 1 and 9 g. (0.053 mole) of benzyl bromide were mixed there was only a slight heat of reaction so the mixture was heated at 150° for two hours. Distillation yielded 2.6 g. of recovered benzyl bromide and 5.0 g. (43%) of **β-bromoethyl hydrocinnamate**, b. p. 165–168° (12 mm.); $n^{25}D$ 1.5295; d^{25}_4 1.3453.

Anal. Calcd. for $C_{11}H_{13}BrO_2$: Br, 31.1; sapn. equiv., 129. Found: Br, 29.3; sapn. equiv., 126.

In addition there remained in the flask 3 g. of an oily residue 1.7 g. of which was insoluble in ethyl alcohol and was a polymer of the ketene acetal, m. p. 245–249°.

The white polymer that formed in samples of 1 on standing was dried in vacuum for eight hours. The resulting white powder melted at 285–290°. The same white polymer was formed rapidly and with the evolution of sufficient heat to cause the acetal to boil when 1 was exposed to a trace of hydrogen chloride.

Anal. Calcd. for $(C_4H_6O_2)_x$: C, 55.8; H, 7.0. Found: C, 54.8; H, 8.4.

When 1 was added to dilute acid a white powder, m. p. 120–125°, was precipitated in 50% yield. The remaining material was β-hydroxyethyl acetate.

Each of these polymers was rapidly converted by dilute hydrochloric acid to an insoluble red oil, which dissolved in 10% sodium hydroxide solution.

2-Methylene-1,3-dioxane (2).—Dry hydrogen chloride converted a sample of 2 to γ-chloropropyl acetate, b. p. 166–172°. Another sample of 2, which had polymerized, was dried in a vacuum for eight hours. The dried product melted at 194–206°.

Anal. Calcd. for $(C_5H_8O_2)_x$: C, 60.0; H, 8.0. Found: C, 59.6; H, 7.9. This polymer showed the same behavior with dilute acid as did that of 1.

2-Benzal-1,3-dioxolane (3).—A solution of 11 g. of 3 in 15 ml. of methanol was treated with a drop of glacial acetic acid and then distilled to yield 9.6 g. (73%) of **2-methoxy-2-benzyl-1,3-dioxolane**, b. p. 75–77° (0.8 mm.); $n^{25}D$ 1.5060; d^{25}_4 1.1140.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.3; *M*D 51.1. Found: C, 67.8; H, 7.5; *M*D 51.8.

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(15) Meldrum and Vad, *J. Indian Chem. Soc.*, **13**, 118 (1936).

(16) McElvain and Walters, THIS JOURNAL, **64**, 1963 (1942).

2-Benzal-1,3-dioxane (4).—The reaction of 4 with water gave an 85% yield of **γ-hydroxypropyl phenylacetate**, b. p. 161–165° (7 mm.); n^{25}_{D} 1.5161; d^{25}_{4} 1.1017.

Anal. Calcd. for $C_{11}H_{14}O_3$: C, 68.0; H, 7.3; sapn. equiv., 194. Found: C, 67.4; H, 7.3; sapn. equiv., 195.

2-Chloromethylene-1,3-dioxolane (5).—Hydrogen chloride quantitatively converted 5 to β-chloroethyl chloroacetate,[17] b. p. 198–201°, n^{25}_{D} 1.4619. Methanol and 5 gave a 95% yield of **2-chloromethyl-2-methoxy-1,3-dioxolane**, b. p. 60–63° (6 mm.), n^{25}_{D} 1.4449; d^{25}_{4} 1.2630.

Anal. Calcd. for $C_5H_9ClO_3$: Cl, 23.3; sapn. equiv., 76.3. Found: Cl, 24.2; sapn. equiv., 79.3.

A freshly distilled sample of 5 set to a solid mass within a few hours. Heating this material at 100° in a vacuum, washing with water or ether, or boiling with concentrated hydrochloric acid left approximately 72% of the original ketene acetal as a white polymer, which sintered at 280–340° but did not melt.

Anal. Calcd. for $(C_4H_5ClO_2)_x$: C, 39.9; H, 4.2; Cl, 29.4. Found: C, 39.3; H, 4.5; Cl, 28.7.

This polymer is insoluble in all of the common laboratory solvents, but dissolves in concentrated sulfuric acid. Dilution of this solution with water, however, does not produce any precipitate.

2-Bromomethylene-1,3-Dioxolane (7).—The oily white polymer that formed in the receiver after redistillation of 7 was heated at 100° for six hours *in vacuo*.

Anal. Calcd. for $(C_4H_5BrO_2)_x$: C, 29.1; H, 3.1. Found: C, 27.7; H, 3.9.

This polymer showed the same solubility behavior as that from 5.

2-Bromomethylene-1,3-dioxane (8).—The reaction of 8 with water gave a 75% yield of **γ-hydroxypropyl bromoacetate**, b. p. 127–132° (7 mm.); n^{25}_{D} 1.4830; d^{25}_{4} 1.5760.

Anal. Calcd. for $C_5H_9BrO_3$: Br, 40.6. Found: Br, 41.0.

2-Dichloromethylene-1,3-dioxolane (9).—When 16.5 g. of 9 was added to 15 ml. of water there was no apparent reaction until two drops of concentrated hydrochloric acid was added to the mixture. The temperature rose to 45° and two layers formed. The oily layer was separated immediately and the aqueous layer was saturated with sodium chloride and extracted with ether. The ether and oil layers were combined, dried over anhydrous sodium sulfate, filtered and distilled to yield 9.2 g. (49%) of β-hydroxyethyl dichloroacetate,[6] b. p. 77–78° (0.4 mm.); n^{20}_{D} 1.4735; n^{25}_{D} 1.4720 and 6.8 g. of a higher boiling product, b. p. 144–149° (0.4 mm.), the chlorine content of which (41.2%) approximated that of 2-dichloromethyl-2-(β-dichloroacetoxyethoxy)-1,3-dioxolane (calcd. for $C_8H_{10}Cl_4O_5$: Cl, 43.3).

Methanol reacted with 9 to give an 83% yield of **2-dichloromethyl-2-methoxy-1,3-dioxolane**, b. p. 69–70° (1.7 mm.); n^{20}_{D} 1.4700; n^{25}_{D} 1.4680; d^{20}_{4} 1.400. Meerwein and Sonke[6] prepared this compound by the action of diazomethane on β-hydroxyethyl dichloroacetate and report the following properties: b. p. 66–69° (1.35 mm.); n^{20}_{D} 1.4703: d^{20}_{4} 1.387. The same authors report the preparation of the isomeric ester, β-methoxyethyl dichloroacetate, b. p. 60° (1.3 mm.); n^{20}_{D} 1.4516; d^{20}_{4} 1.309, by treatment of methyl cellosolve with dichloroacetyl chloride.

Phenylketene Dimethylacetal (12).—A 1.2-g. sample of 12 was treated with 5 ml. of water and then shaken with 10 ml. of aqueous ammonia until a homogeneous solution was obtained. Evaporation of this solution left 0.94 g. (100%) of phenylacetamide, m. p. 150–154°.

Summary

Several ketene cyclic acetals containing the 1,3-dioxolane and 1,3-dioxane rings have been prepared from the corresponding halogenated acetals by dehydrohalogenation. The dichloroketene and phenylketene cyclic acetals show little or no tendency to polymerize. The unsubstituted, as well as the monohaloketene cyclic acetals polymerize so readily that their isolation in the monomeric form was difficult.

The polymers of the unhalogenated ketene cyclic acetals are readily hydrolyzed by dilute acid, but the polymers of the monohalogenated compounds are resistant to hydrolysis and appear to have a cross-linked structure.

The ketene cyclic acetals react vigorously with water to yield the normal esters and with alcohols to yield mixed orthoesters. With the exception of 2-methylene-1,3-dioxolane, which rapidly polymerizes in the presence of hydrogen chloride, the ketene cyclic acetals and hydrogen chloride react to form chloroalkyl esters.

Phenylketene dimethylacetal has been prepared as a colorless liquid by the dehydrohalogenation of phenylbromoacetaldehyde dimethylacetal and found to have physical properties significantly different from those of the yellow product obtained from the pyrolysis of methyl orthophenylacetate.

Some new ketene dimethylacetals have been prepared.

MADISON, WISCONSIN RECEIVED JULY 9, 1948

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[17] Henry, *Bull. soc. chim.*, [2] **42**, 260 (1884).