[Contribution from Shell Development Company]

Cyclic Acrolein Acetals

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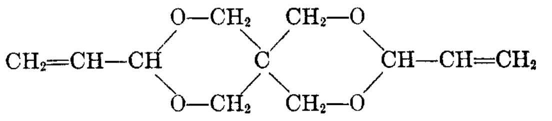
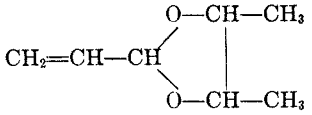
Acetals have been made in 70–98% yields by reaction of acrolein and various alcohols, largely 1,2- and 1,3-glycols. β-Chloro-, hydroxy-, cyano-, and α,β-epoxy-derivatives otherwise difficultly accessible are readily prepared from the acetals derived from 2-methyl-2,4-pentanediol or pentaerythritol.

Acrolein contains two highly reactive groups, an aldehyde and an ethylenic linkage. Numerous examples of addition to both the carbonylic and ethylenic functions are known.[1] Early attempts to form unsaturated acetals led to mixtures in which extensive addition to the double bond occurred.[2] Recently, however, a number of publications have indicated that in acidic media the carbonylic function is slightly more reactive toward alcohols than is the ethylenic group and in particular that substituted 1,2- and 1,3-glycols tend to form cyclic acetals. Schulz and Wagner[3] prepared 3,9-divinyl-2,4,8,10-tetroxaspiro-(5,5)-undecane (diallylidene-pentaerythritol), I, from pentaerythritol and a large excess of acrolein,



I

while Neish and MacDonald[4] produced *l*-2-vinyl-4,5-dimethyl-1,3-dioxolane II

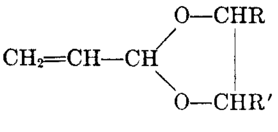


II

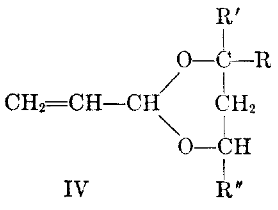
from *l*-2,3-butanediol. A recent patent[5] discloses that by means of very low catalyst concentrations (0.001 to 0.010 mole percent *p*-toluenesulfonic acid) and removal of water at temperatures below 50° for 24–36 hours, lower aliphatic acrolein acetals can be prepared in 50–80% yields.

We have found, however, that three factors can be controlled to maximize acetal formation while minimizing addition to the ethylenic link: 1) catalyst concentration should be reduced to the lowest value consistent with a practical rate while minimizing addition to the olefinic bond; 2) 1,2- or 1,3-glycols should be used, as they lead to the more stable cyclic acetals; 3) glycols substituted on the hydroxyl-bearing carbons are preferred, as such substitution favors ring formation while hindering addition to the ethylenic bond.

A number of representative acrolein cyclic acetals have been prepared in 70–98% yield. In most cases distillation without fractionation from the reaction mixture has given products with analyses in agreement with the theoretical values. The products from 1,2-glycols are 2-vinyl-1,3-dioxolanes, III, while from 1,3-glycols one obtains 2-vinyl-1,3-dioxanes, IV. Table I summarizes the products

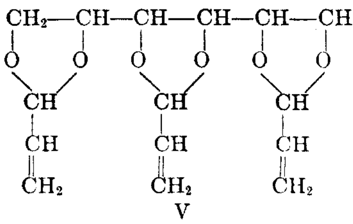


III



IV

obtained and reaction conditions employed for the best yields obtained from various alcohols. Many of the compounds in Table I have not been described in the literature (marked with an asterisk), and except for the pentaerythritol and 2,3-butanediol acetals, none has been prepared previously in good yield. For cyclic acetals two-five times as much catalyst as for noncyclic acetals could be used and the reaction temperature could be raised to 80°. This reduced the reaction time to as little as 50 minutes when using the efficient drying solvent, benzene. Under these conditions, the yield of I was increased to 80% while reducing the excess acrolein from 300%[2] to 20%. To illustrate the generality of the reaction, allyl alcohol and crotonaldehyde have also been included. The more complex polyol, sorbitol, however, gave only 33% yield of triallylidene sorbitol, probably V, in addition to much polymer.



V

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[1] S. A. Ballard, H. de V. Finch, B. P. Geyer, G. W. Hearne, C. W. Smith, and R. R. Whetstone, "Chemicals from Acrolein," Proceedings of the Fourth World Petroleum Congress, Section IV C, Rome, Italy, 1955.

[2] *Org. Syntheses* II, **17**, 137 (1943).

[3] H. Schulz and H. Wagner, *Angew. Chem.* **62**, 105 (1950).

[4] A. C. Neish and F. J. MacDonald, *Can. J. Research* **25B**, 70 (1947).

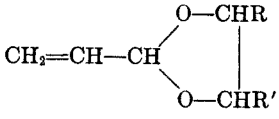
[5] D. R. Myers, B. J. Magerlein, and G. W. Staffen, U. S. Patent **2,678,950** (1954) to Upjohn Co.

TABLE I

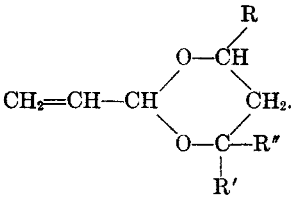
SYNTHESIS OF ACROLEIN ACETALS

Alcohol	Product[a]	Conversion of Alcohol to Product	Yield on Alcohol	Excess Acrolein Present	Solvent	Mole % of Catalyst[b] Present	Reaction Time
Allyl alcohol	Acrolein diallyl acetal	72%	75%	None	Petroleum ether	0.0010	24 hr.
2,3-Butanediol	III, $R=R'=CH_3$	86%	86%	10%	Benzene	0.020	3 hr.
2-Methyl-2,4-pentanediol	IV, $R=R'=R''=CH_3$[c]	98.5%	98.5%	10%	Benzene	0.026	2.5 hr.
Glycerine	III, $R=H$, $R'=CH_2OH$	78.5%	88%	20%	Benzene	0.023	50 min.
1,2,6-Hexanetriol	III, $R=H$[c] $R'=CH_2CH_2CH_2CH_2OH$	88%	88%	50%	Benzene	0.020	50 min.
Glycerol α-monochlorohydrin	III, $R=H$, $R'=CH_2Cl$	75%	75%	None	Benzene	0.056	1.5 hr.
Trimethylene glycol	IV, $R=R'=R''=H$	78%	78%	None	67% Benzene 33% Ether	0.043	3 hr.
Ethylene glycol	III, $R=R'=H$[c]	58%	58%	10%	67% Benzene 33% Ether	0.025	9 hr.
Pentaerythritol	Diallylidenepentaerythritol, I	86%	86%	20%	Benzene	0.070	2.5 hr.
Sorbitol	Triallylidenesorbitol, V[c]	33%	33%	10%	Benzene	0.059	8 hr.
Pentaerythritol (with crotonaldehyde)	Dicrotonylidenepentaerythritol[c]	95%	95%	10%	Benzene	0.048	3 hr.

[a] "III" is the generalized 2-vinyl-1,3-dioxolane,



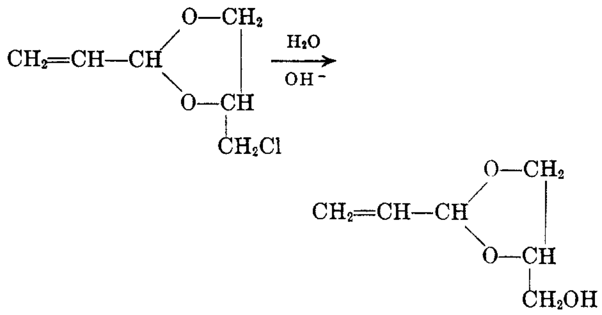
"IV" is the generalized 2-vinyl-1,3-dioxane,



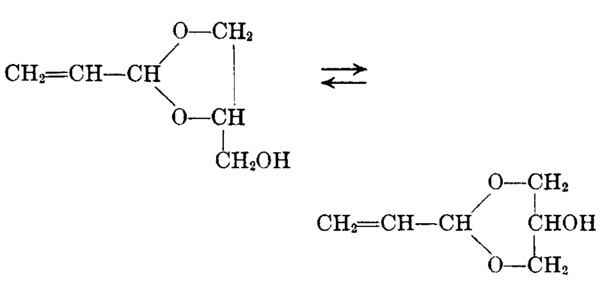
[b] p-Toluenesulfonic acid. [c] Apparently new compounds.

In two cases which gave relatively low yields under the usual conditions, catalysis with sulfuric acid adsorbed on silica gel has given marked improvements. Thus unsaturated acetals were prepared from ethylene glycol and glycerine in 70 and 83% yields. Corresponding yields with p-toluenesulfonic acid were 58 and 54% (for large runs).

Although two structures are possible for the glycerine acetal, the isomer containing the five-membered ring predominates. Hibbert and Whelan,[6] who prepared an acetal (10% yield) by thermal reaction of glycerine and acrolein, methylated their product and then hydrolyzed it to the known glycerol α-methyl ether. The main product obtained by alkaline hydrolysis of the glycerol α-monochlorohydrin acetal has substantially the same infrared absorption spectrum as does the glycerine acetal obtained directly. The boiling range of the compound is generally taken as 65–70° (1 mm.), but there is usually a small forecut starting at 55°. As it was desired in one case to obtain a very pure sample, a large composite which had previously boiled in the range 65–70° (1 mm.) was fractionated through a 20-tray bubble plate, Oldershaw, column.



(The isomers may be in equilibrium, however.)



At a reflux ratio of 60:1, the head temperature remained at 54–55°, n_D^{20}, 1.4680. When 20% of the material had been taken overhead, the reflux ratio was changed to 20:1, whereupon the head temperature rose gradually to 65°. Here 33% of

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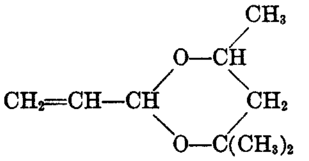
(6) H. Hibbert and M. Whelan, *J. Am. Chem. Soc.* **51**, 3115 (1939).

the material was taken, b.p. 65–67° (1 mm.) n_D^{20} 1.4612. It is possible that under the very high reflux ratio, time was available for slow transformation of the common high-boiling isomer to a low-boiling one.

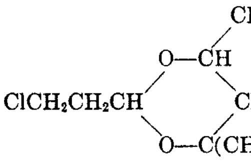
The acetal from glycerol α-monochlorohydrin, 2-vinyl-4-chloromethyl-1,3-dioxolane has also been obtained from acrolein and epichlorohydrin in the presence of stannic chloride. This is apparently the first unsaturated acetal obtained from acrolein and an epoxide.

The nearly quantitative yield of the acrolein acetal of 2-methyl-2,4-pentanediol is especially noteworthy and has led to the study of some of the reactions of the product, 4,4,6-trimethyl-2-vinyl-1,3-dioxane, VI.

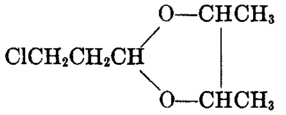


VI

Dry hydrogen chloride simultaneously adds to the double bond of acrolein and catalyzes acetal formation. From 2-methyl-2,4-pentanediol, 2-(2-chloroethyl)-4,4,6-trimethyl-1,3-dioxane, VII, was obtained in 94% yield, while 2,3-butanediol afforded 2-(2-chloroethyl)-4,5-dimethyl-1,3-dioxolane, VIII.



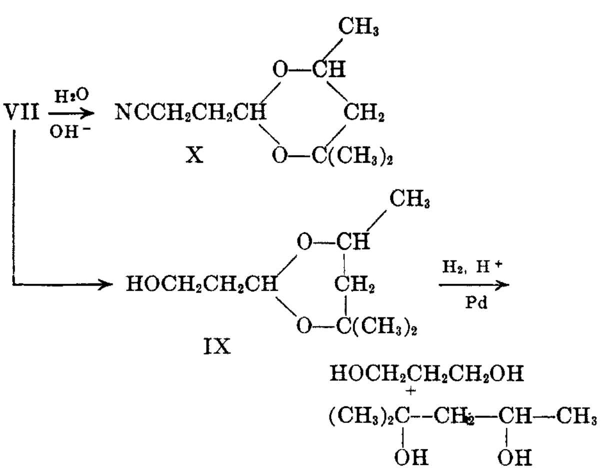
VII

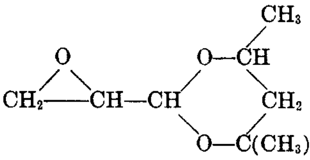


VIII

This general type of compound has been obtained previously only in poor yield.[7]

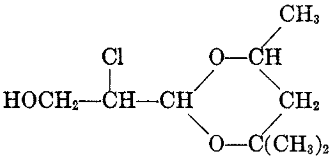
Reaction of the chloride, VII, with aqueous alkali at 160° gave the cyclic β-hydroxypropionaldehyde acetal, IX, (80% yield), and hydrogenolysis of this compound yielded trimethylene glycol in 50% yield. When VII is treated with sodium cyanide, the acetal of β-cyanopropionaldehyde, X, is obtained in 95% yield. The epoxide XI was prepared in fair purity





XI

by epoxidation of VI with peracetic or peroxytrifluoroacetic acid, but preparation *via* chlorohydrination proved to be a better route. Two chlorohydrination procedures were used; in one, carbon dioxide was passed into an emulsion of VI in aqueous calcium hypochlorite. The product probably consisted largely of 2-(1-chloro-2-hydroxyethyl)-4,4,6-trimethyl-1,3-dioxane, XII, but may have contained the 1-hydroxy -2-chloro isomer.

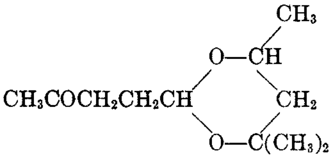


XII

Dehydrochlorination of the chlorohydrin gave XI in 90% purity in good yield. Overall yields from acrolein were 55%. The chlorohydrin was acetylated, but failed to react with ammonia or potassium phthalimide.

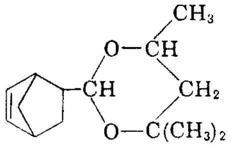
When chlorohydrin samples were prepared from hypochlorous acid generated from chlorine and sodium hydroxide the epoxide ultimately obtained was persistently contaminated with unidentified chlorine-containing impurities.

Mondon[8] has described the peroxide-catalyzed reaction of aldehydes with simple acrolein acetals, and we have found that VI reacts similarly to give the cyclic levulinic aldehyde acetal.

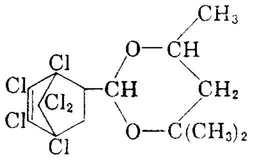


XIII

The acetal VI has also given adducts with cyclopentadiene and hexachlorocyclopentadiene.



XIV



XV

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(7) M. Bergmann, A. Miekeley, and E. V. Sippmann, *Ber.* **62B,** 1467 (1929).

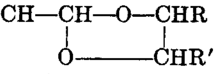
(8) A. Mondon, *Angew. Chem.* **64,** 224 (1952).

TABLE II

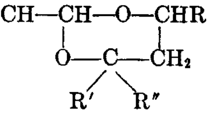
PROPERTIES OF ACROLEIN ACETALS

Starting Alcohol	Product[a]	B.P.	n_D^{20}	Analyses, %
Allyl alcohol	Acrolein diallyl acetal	75°/28 mm.	1.4380	Calcd.: C, 70.2; H, 9.2; Br_2 No., 312 g./100 g. Found: C, 70.0; H, 9.2; Br_2 No., 315 g./100 g.
2,3-Butanediol	III. R=R'=CH_3	56–58°/42 mm.	1.4282	Calcd.: C, 65.6; H, 9.4; Br_2 No., 124 g./100 g. Found: C, 65.4; H, 9.5; Br_2 No., 118 g./100 g.
2-Methyl-2,4-pentanediol	IV. R=R'=R''=CH_3	62–64°/18 mm.	1.4381	Calcd.: C, 69.3; H, 10.2; Br_2 No., 102 g./100 g. Found: C, 69.1; H, 10.3; Br_2 No., 100 g./100 g.
Glycerine	III. R=H R'=CH_2OH	70–72°/2 mm.	1.4647	Calcd.: C, 55.4; H, 7.7; OH value, 0.77 eq./100 g. Found: C, 55.4; H, 8.0; OH value, 0.76 eq./100 g.
1,2,6-Hexanetriol	III, R=H R'=$CH_2CH_2CH_2CH_2OH$	95–105°/0.2 mm.	1.4641	Calcd.: C, 62.7; H, 9.4; OH value, 0.58 eq./100 g. Found: C, 62.3; H, 9.4; OH value, 0.63 eq./100 g.
Glycerol α-monochlorohydrin	III. R=H R'=CH_2Cl	60°/9 mm.	1.4611	Calcd.: C, 48.5; H, 6.1; Cl, 23.9 Found: C, 48.6; H, 6.3; Cl, 24.2
Trimethylene glycol	IV, R=R'=R''=H	65–66°/44 mm.	1.4438	Calcd.: C, 63.1; H, 8.8 Found: C, 62.9; H, 8.8
Ethylene glycol	III, R=R'=H	114–116°/ atm.	1.4327	Calcd.: C, 60.0; H, 8.0 Found: C, 60.6; H, 8.1
Pentaerythritol	Diallylidenepentaerythritol I	93–4°/1 mm.	M.P. 42°	Lit.,[8] 43°
Pentaerythritol-crotonaldehyde	Dicrotonylidene pentaerythritol	130–132°/ 0.5 mm.	M.P. 50–52°	Calcd.: C, 65.1; H, 8.3; Br_2 No., 133 g./100 g. Found: C, 64.9; H, 8.4; Br_2 No., 131 g./100 g.
Sorbitol	Triallylidene sorbitol V	149–151°/ 0.9 mm.	1.4865	Calcd.: C, 60.8; H, 6.8; Br_2 No., 162 g./100 g. Found: C, 60.9; H, 6.9; Br_2 No., 158 g./100 g.

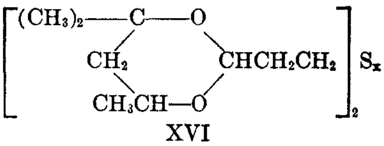
[a] "III" is the generalized 2-vinyl-1,3-dioxolane,



"IV" is the generalized 2-vinyl-1,3-dioxane,

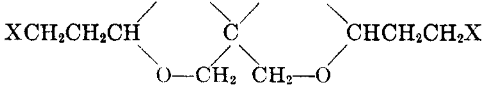


Attempts to add hydrogen sulfide to VI in the presence of cobalt polysulfide[9] led largely to the disulfide (XVI,x = 2) and trisulfide (XVI,x = 3). The disulfide may have arisen from the thiol during the workup but was also obtained from β-chloropropionaldehyde acetal and sodium sulfide.



XVI

The diacetal I from pentaerythritol and acrolein has served as the precursor of a series of bifunctional derivatives. Addition of hydrogen chloride gave the bis(β-chloropropionaldehyde acetal) XVIIa in 80% yield, and reaction of XVIIa with sodium cyanide has given the dinitrile XVIIb in 50% yield.



XVII a. X = Cl b. X = CN

Epoxidation of I with peracetic acid gave mainly monoepoxide, along with small amounts of diepoxide.

EXPERIMENTAL[10]

Acrolein Acetals. General. Benzene soluble glycols were mixed with a small excess of acrolein, 1–3 volumes of an azeotroping solvent (usually benzene) and a small quantity of p-toluenesulfonic acid and then refluxed vigorously under a phase separating head until water evolution had ceased. After excess acrolein and some benzene had been removed through the head, the residue was cooled and an excess of calcium oxide was stirred into the solution. After filtration (sometimes omitted) the solvent was removed and the residue was distilled at reduced pressure. When benzene-insoluble glycols were used, a stirred three-necked flask was employed. Conditions were listed in Table I and the products are described in Table II.

2-Vinyl-4-hydroxymethyl-1,3-dioxolane. Solid Catalyst. In a 2-l., three-necked flask equipped with stirrer and phase-separating head were placed 228 ml. (3.2 mol.) of 96% acrolein, 276 g. (3.0 mol.) of glycerine, 600 ml. of benzene and 0.15 × 10^{-4} mol. of sulfuric acid adsorbed on 0.3 g. silica gel.[11] After 3 hr. under reflux, 62 ml. of water layer had been removed. The clear solution was decanted and the solvent removed at reduced pressure. Distillation from a Claisen flask gave 327 g. (83%) of crude 2-vinyl-4-hydroxymethyl-1,3-dioxolane b.p. 70–125° (2 mm.) (90% between 75° and 85°). The residue weighed 56 g.

Several such preparations were combined and distilled through a 20-tray bubble plate column at reflux ratios varying from 20:1 to 60:1. The following fractions were taken at 1 mm.

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(9) A. M. Alvarado, U. S. Patent 2,402,586 (to E. I. du Pont de Nemours and Co.) (1946).

(10) Melting points corrected; boiling points not corrected.

(11) Prepared by addition of 40 ml. of water containing 0.5 g. of sulfuric acid to 100 g. of dry silica gel (Davison, grade 9–12, 28–200 mesh), followed by stirring on a hot plate until the silica is free-flowing. We are indebted to Dr. L. C. Fetterly of these laboratories for this material.

Fraction	B.P.°	Weight, g.	$n_{\rm D}^{20}$	Yield, %
1	54–58	224	1.4680	26
2	58–65	106	1.4639	12
3	65–67	338	1.4612	39
4	67–75	101	1.4620	12
5	75–78	43	1.4650	5
residue	—	64	—	6

Fractions 1 and 3 may be respectively the isomeric dioxane and dioxolane. Fractions 4 and 5 are probably merely less pure dioxolane. Numerous earlier fractionations had shown only a very small low-boiling fraction, and it is therefore possible that conversion was occurring during the distillation.

Several attempts to prepare large amounts of this acetal with *p*-toluenesulfonic acid catalysis gave relatively poor yields. For example, from 3.1 mol. of glycerine, 4.15 mol. of acrolein and 0.2 g. of *p*-toluene-sulfonic acid, only 1.7 mol. (54%) of crude monomer was obtained. On redistillation through a 2-foot helices-packed column an analytically pure sample was taken as 2-vinyl-4-hydroxymethyl-1,3-dioxolane, b.p. 67° (0.6 mm.).

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.4 H, 7.7; OH, 0.77 eq./100 g.; Br$_2$No., 123 g./100 g. Found: C, 55.1; H, 7.9; OH, 0.78 eq./100 g.; Br$_2$No., 123 g./100 g.

Several redistillations of the high boiling residue gave 36 g. (32 ml.) of pure material, b.p. 129° (0.10 mm.), $n_{\rm D}^{20}$ 1.4733. Its analysis was in agreement with a linear dimer of the acrolein–glycerine acetal from addition of the hydroxyl group of one molecule to the ethylenic linkage of another.

Anal. Calcd. for $C_{12}H_{20}O_6$: C, 55.4; H, 7.7; OH, 0.38 eq./100 g., Br$_2$No., 61.5 g./100 g., acetal-bound acrolein, 21.6%;[12]) (acetal + ether) bound acrolein, 43.1%.[13] Found: C, 55.5; H, 7.7; OH, 0.40 eq./100 g., Br$_2$No., 61 g./100 g.; acetal-bound acrolein, 23%; (acetal + ether) bound acrolein 45%.

Reaction of Acrolein and Epichlorohydrin. A solution of 156 ml. (2.2 mol.) of acrolein and 189 g. (2.0 moles) of epichlorohydrin in 500 ml. of benzene was dried by refluxing under a phase separating head. The solution was cooled to 20° and 1.4 g. of stannic chloride in 20 ml. of benzene was added with stirring. The temperature was held at 35° (ice cooling) for 1.5 hr., then 0.7 g. of stannic chloride in benzene was added, and the mixture was allowed to stand overnight.

Five grams of calcium oxide was added with stirring, after which the benzene and excess acrolein were removed at reduced pressure. The residue was distilled (Claisen still). After 8 g. of forcut b.p. 45–53° (10 mm.), probably largely recovered epichlorohydrin, the bulk of the product boiled in the range 55–67° (10 mm.) $n_{\rm D}^{20}$ 1.4603; yield 210 g. (71%, based on epichlorohydrin used).

2-(2-Chloroethyl)-4,4,6-trimethyl-1,3-dioxane (VII). Dry hydrogen chloride was bubbled with stirring into a solution of 236 g. (2.0 mole) of 2-methyl-2,4-pentanediol and 142 ml. (2.0 mole) of 96% acrolein in 350 ml. of chloroform at −15° to −10°. When hydrogen chloride was no longer absorbed, the aqueous layer which had formed was separated, the organic layer was washed with water and bicarbonate solution, dried, filtered, and relieved of solvent in vacuo. Distillation of the residue from a Claisen flask gave 360 g. (94% yield) of product, b.p. 69–77° (5 mm.). A center cut b.p. 71° (5 mm.) gave analyses in agreement with 2-(2-chloroethyl)-4,4,6-trimethyl-1,3-dioxane.

Anal. Calcd. for $C_8H_{17}O_2Cl$: C, 56.2; H, 8.8; Cl, 18.4. Found: C, 56.1; H, 8.9; Cl, 18.5.

2-(2-Chloroethyl)-4,5-dimethyl-1,3-dioxolane (VIII). This was prepared similarly from acrolein, 2,3-butanediol, and hydrogen chloride gas. The product, b.p. 72–88° (20 mm.) was obtained in 77% yield; a heart cut, b.p. 85° (20 mm.) $n_{\rm D}^{20}$ 1.4419 was analyzed.

Anal. Calcd. for $C_7H_{13}O_2Cl$: C, 51.1; H, 8.0; Cl, 21.5. Found: C, 51.0; H, 8.0; Cl, 22.0.

2-(2-Hydroxyethyl)-4,4,6-trimethyl-1,3-dioxane (IX). A mixture of 112 g. (0.5 mole) of the cyclic β-chloropropionaldehyde acetal VII, 300 ml. of water, and 16 g. of sodium carbonate were placed in a stirred 1-1 autoclave. No apparent reaction occured at 140°, but at 160° 27% sodium hydroxide had to be pumped into the autoclave to maintain the *p*H at 8–9. In 6 hr., 61 ml. (94% of theory) was consumed, after which no further reaction occurred. The cooled product was taken up in ether, dried, filtered, and relieved of solvent. Distillation of the residue (Claisen) gave 82 g. (82% yield), b.p. 82–92° (3 mm.). Redistillation through a 2-foot helices-packed column gave a complete recovery; b.p. 69° (1 mm.), $n_{\rm D}^{20}$ 1.4485.

Anal. Calcd. for $C_9H_{18}O_3$: C, 62.1; H, 10.4; OH value, 0.58 eq./100 g. Found: C, 62.1; H, 10.4; OH value, 0.58 eq./100 g.

Hydrogenolysis of 2-(2-hydroxyethyl)4,4,6-trimethyl-1,3-dioxane. A solution of 55 g. (0.316 mole) of the acetal (IX) in 100 ml. of 20% acetic acid was hydrogenated at 100° and 1000 p.s.i.g. in a stainless steel vessel over 5 g. of 10% palladium on charcoal. After filtration the water and acetic acid were removed in vacuo, leaving 58 g. of residue. Twenty-six grams (45%) of this residue was distilled in a Piros-Glover spinning band column. There was obtained a 94% recovery of 2-methyl-2,4-pentanediol, b.p. 114.5° (35 mm.), $n_{\rm D}^{20}$ 1.4274, and 4.7 g. (48% yield) of trimethylene glycol, b.p. 130° (35 mm.) $n_{\rm D}^{20}$ 1.4388.

Anal. Calcd. for $C_3H_8O_2$: C, 47.4; H, 10.6; OH value, 2.63 eq./100 g. Found: C, 46.9; H, 10.6; OH value, 2.63 eq./100 g.

The actual yield of trimethyl glycol was doubtless higher, as the kettle and still drainings amounted to 3 g. probably largely trimethylene glycol.

2-(2-Cyanoethyl)-4,4,6-trimethyl-1,3-dioxane (X). A mixture of 95 g. (0.5 mole) of 2-(2-chloroethyl)4,4,6-trimethyl-1,3-dioxane and 26.5 g. (0.52 mole) of sodium cyanide was refluxed with stirring in 300 ml. of methyl cellosolve for 19 hr. After cooling, 1.5 g. of water was added and the mixture was extracted four times with chloroform. The extracts were washed with water, dried, filtered, and freed of solvent. Distillation from a flask equipped with a Claisen head gave 87 g. (95% yield) of the nitrile, b.p. 85–7° (2 mm.).

Anal. Calcd. for $C_{10}H_{17}NO_2$: C, 65.5; H, 9.4; N, 7.6. Found: C, 65.3; H, 9.4; N, 7.2.

2-(1,2-Epoxyethyl)-4,4,6-trimethyl-1,3-dioxane (XI). *With peracetic acid.* Forty-nine grams of 45% peracetic acid was added with stirring to 39 g. (0.25 mole) of VI in 150 ml. of chloroform. The temperature rose to 27°, whereupon cooling water was applied. After standing overnight, titration indicated no more peracetic acid was present. The solution was washed with water and bicarbonate, dried, and relieved of solvent. Distillation and redistillation through a 2-foot helices-packed column gave 18 g. of starting acetal, b.p. 65–70°C. (17 mm.), $n_{\rm D}^{20}$ 1.4355, and 12 g. of 2-(1,2-epoxyethyl)-4,4,6-trimethyl-1,3-dioxane, b.p. 96–99° (15 mm.), $n_{\rm D}^{20}$ 1.4461.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.8; H, 9.4; epoxide value, 0.58 eq./100 g Found: C, 63.3; H, 9.3; epoxide value, 0.60 eq./100 g.

2-(3-Ketobutyl)-4,4,6-trimethyl-1,3-dioxane (XIII). A mixture of 78 g. (0.5 mole) of VI, 66 g. (1.5 mole) of acetaldehyde and 4 g. of azobisisobutyronitrile was held at 80° for 40 hr. in a Hastelloy vessel. After removal of excess acetaldehyde the product was distilled from a Claisen flask and then through a 2-foot helices-packed column. There was obtained 10 g. of VI b.p. 39° (1 mm.) and 41 g. (40% conversion, 47% yield of the desired aldehyde acetal, b.p. 99° (1 mm.), $n_{\rm D}^{20}$, 1.4430.

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(12) *p*-Phenylenediamine method.

(13) Dinitrophenylhydrazine – potassium hydroxide method. Both methods developed by Analytical Research Groups, Shell Development Company, and performed under the supervision of Mr. J. L. Jungnickel.

Anal. Calcd. for $C_{11}H_{20}O_3$: C, 66.0; H, 10.0; carbonyl value, 0.50 eq./100 g. Found: C, 65.7; H, 10.0; carbonyl value, 0.50 eq./100 g.

Reaction of VI *with Hexachlorocyclopentadiene.* A mixture of 30 g. (0.1 mole) of hexachlorocyclopentadiene (Hooker Electrochemical Co.) and 16 g. (0.1 mole) of VI was heated to 180°, whereupon an exothermic reaction set in. Distillation of the partly charred product gave 12 g. of recovered diene, b.p. 57–60° (1 mm.), followed by 29 g. (60%) of viscous yellow products, b.p. 160–168° (0.5 mm.). Redistillation gave 21 g. of a product, analyses of which indicate that it may contain 2,3,4,5,7,7-hexachloro-1,2,5,6-tetrahydro-2,5-methanobenzaldehyde, 2-methyl-2,4-pentanediol acetal, b.p. 157–160° (0.5 mm.).

Anal. Calcd. for $C_{14}H_{26}Cl_6O_2$: C, 39.2; H, 3.8; Cl, 49.5. Found: C, 40.3; H, 3.8; Cl, 49.9.

Reaction of VI *with Cyclopentadiene.* Twenty-one grams (0.32 mole) of freshly distilled cyclopentadiene and 18 g. (0.12 mole) of VI were heated for 4 hr. at 180° in a stainless steel vessel. Distillation and redistillation through a 2-foot helices-packed column gave 12 g. of recovered VI, b.p. 60–70° (3 mm.), and 19 g. (50% conversion, 70% yield based on VI of 1,2,5,6-tetrahydro-2,5-methanobenzaldehyde, 2-methyl-2,4-pentanediol acetal, b.p. 93–4° (3 mm.), n_D^{20} 1.4747.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.8; H, 10.0. Found: C, 75.7; H, 10.0.

3,9-Bis(2-chloroethyl)-2,4,8,10-tetroxaspiro[5.5]undecane. Dry hydrogen chloride was passed into a stirred solution of 278 g. (1.3 mole) of I in 350 ml. of chloroform at −15° to −10°. When hydrogen chloride was no longer absorbed the solution was stirred for 1 hr. with solid sodium carbonate. After filtration and removal of solvent, the residue was distilled from a flask equipped with a Claisen head. The first cut, b.p. 113–144° (0.6 mm.), 31 g., was redistilled, b.p. 118–122° (1 mm.) and gave analyses in agreement with 3(2-chloroethyl)-9-vinyl-2,4,8,10-tetroxaspiro[5.5]undecane.

Anal. Calcd. for $C_{11}H_{17}ClO_4$: C, 53.2; H, 6.9; Cl, 14.3. Found: C, 53.3; H, 7.2; Cl 14.1.

Analyses indicate that the main cut, b.p. 140–150° (0.2 mm.), contains 3,9-bis(2-chloroethyl)-2,4,8,10-tetroxaspiro[5.5]undecane, XVIIa, apparently contaminated with the mono-chloro derivative.

Anal. Calcd. for $C_{11}H_{18}Cl_2O_4$: C, 46.5; H, 6.3; Cl, 24.8. Found: C, 47.3; H, 6.5; Cl, 24.0.

3,9-Bis(2-cyanoethyl)-2,4,8,10-tetroxaspiro[5.5]undecane. This was prepared from 0.5 mole of crude XVIIa in the manner described above. Simple distillation of the product gave a large (62 g.) unidentified forecut, b.p. 46–178° (0.14 mm.) and 65 g. (49%) of dinitrile, b.p. 187–199° (0.14 mm.). Redistillation gave a product, b.p. 180–181° (0.2 mm.), with analyses in agreement with 3,9-bis(2-cyanoethyl)-2,4,8,10-tetroxaspiro[5.5]undecane.

Anal. Calcd. for $C_{13}H_{18}N_2O_4$: C, 58.2; H, 6.8; N, 10.1. Found: C, 58.5; H, 7.0; N, 10.1.

Epoxidation of (I).[14] A mixture of 53 g. (0.25 mole) of the bisacetal, 150 ml. of chloroform, and 92 g. (0.56 mole) of freshly prepared peracetic acid was stirred gently at room temperature. Titration after 16 hr. showed 57% consumption of active oxygen, and after 40 hr., 90% consumption. The solution was stirred with sodium bicarbonate solution, dried over magnesium sulfate, filtered, and relieved of solvent.

The 55 g. of residue was distilled and redistilled from a Claisen still, giving 10 g. of recovered acetal, b.p. 102–110° (2 mm.), and 10 g. of a fraction containing mainly the mono epoxide, b.p. 138° (1 mm.).

Anal. Calcd. for $C_{11}H_{16}O_5$: C, 57.9; H, 7.1; epoxide value, 0.44 eq./100 g. Found: C, 58.0; H, 7.1; epoxide value, 0.37 eq./100 g.

A third fraction contained the bisacetal of glycidaldehyde, b.p. 176° (1 mm.) 11 g.

Anal. Calcd. for $C_{11}H_{16}O_6$: C, 54.2; H, 6.6; epoxide value 0.82 eq./100 g. Found: C, 55.1; H, 6.7; epoxide value, 0.67 eq./100 g.

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[14] Fischer, R. F., U. S. Patent 2,895,962 (1959) to Shell Development Co.

[CONTRIBUTION NO. 1051 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Reaction of Benzyne With An Allylic Olefin

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An attempted Diels-Alder condensation of benzyne with 2,5-dimethyl-2,4-hexadiene produced 2,5-dimethyl-3-phenyl-1,4-hexadiene (II), the first example, to our knowledge, of alkylation by an olefin through the benzyne intermediate. It is suggested that the reaction follows the mechanism that has been well established for the addition of allylic olefins to other dienophiles at high temperatures. At this point the reaction we have observed appears to offer little promise of having general synthetic value.

In the past several years considerable interest[1–4] has developed in the synthesis of the unknown hydrocarbon *o*-di-*t*-butylbenzene and varying estimates have been made of its strain energy. An attractive path to its synthesis that would avoid the difficult step of forcing two bulky groups into *ortho*- positions through substitution on the benzene nucleus would be through the Diels-Alder condensation of the benzyne intermediate[5] with 2,5-dimethyl-2,4-hexadiene to give the unknown 1,1,4,4-tetramethylnaphthalene (I) which could then be oxidized to *o*-phenylenebis(α-isobutyric acid)[6] and hence by suitable reduction to the desired hydrocarbon.

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