

THE OLEFIN-ALDEHYDE CONDENSATION

THE PRINS REACTION

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Received August 20, 1952

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I. INTRODUCTION

Under appropriate conditions of temperature, pressure, and in the presence of various catalysts, aldehydes have been found to react with a wide variety of

olefins and their substituted derivatives to form useful synthetic organic chemicals. The first work on the condensation of olefins with aldehydes was done by Kriewitz (74), who, in 1899, found that unsaturated alcohols were produced when pinene or dipentene was heated with paraformaldehyde in a sealed tube. It was not until 1917, however, that Prins (129) carried out the first rather comprehensive study of the reactions of formaldehyde with ethylenic hydrocarbons. Prins investigated the reactions of styrene, pinene, camphene, and anethole with formaldehyde in the presence of sulfuric acid as a catalyst, using water or glacial acetic acid as a solvent. In aqueous media, the formals of 1,3-butanediols or of unsaturated alcohols were produced, whereas esters of acetic acid were usually obtained when this acid was employed in the reaction mixture. Because of this early work, the condensation of olefins with aldehydes is sometimes called the Prins Reaction.

These early studies were primarily of an exploratory nature, however, and the reaction did not receive much attention until about 1937. At that time the olefin-aldehyde condensation was actively investigated both in the United States and abroad for producing diolefins which were required for the manufacture of synthetic rubber. Even though this reaction proved to be less attractive than dehydrogenation or cracking processes for the production of butadiene and isoprene, numerous new chemical products were produced in the course of this work. These compounds were identified and their uses and conversion to other organic chemicals were investigated.

The development of improved petroleum-cracking processes in the late 1930's increased the production of unsaturated hydrocarbons and greatly stimulated the preparation of synthetic organic chemicals. The commercial availability of the lower olefins, coupled with the production of aldehydes by the direct oxidation of the low-boiling paraffins, provided an added incentive for the further investigation of the olefin-aldehyde condensation.

Aldehydes, and more specifically formaldehyde, appear to undergo at least four different reactions with olefins and other unsaturated compounds.

1. An acid-catalyzed reaction.
2. A simple thermal reaction during the course of which the C=C double bond shifts to an adjacent position.
3. A reaction which occurs under substantially anhydrous conditions at room temperature in the presence of "non-acidic" metallic halides.
4. A peroxide-catalyzed reaction.

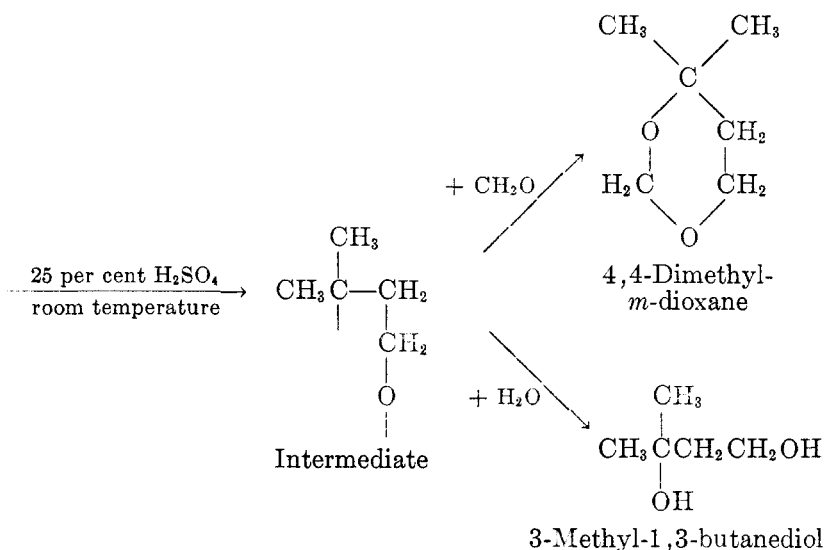
Since the types of chemical compounds produced in the above reactions are different and can be varied by changing the olefin, the aldehyde, the catalyst, and the reaction temperature, this condensation possesses unusual versatility and offers a useful route to the manufacture of synthetic chemicals.

An attempt has been made to review, in the following sections, the work published during the last half-century on the condensation of olefinic compounds with saturated aldehydes. References have been omitted to the use of aldehydes for refining petroleum fractions or for producing resins. The review has been organized on the basis of the compounds produced and does not include refer-

ences to the condensation of aldehydes with aromatic or acetylenic hydrocarbons. The reaction of formaldehyde with hydrocarbons has also been reviewed briefly by Walker (150) and by Ellis (33).

II. ALKYL-*m*-DIOXANES

When olefins and certain other unsaturated compounds are condensed with aldehydes in the presence of aqueous solutions of mineral acid catalysts, alkyl-*m*-dioxanes (cyclic formals or acetals of 1,3-butanediols) and 1,3-butanediols are formed. The distribution between these two products, *m*-dioxane and glycol, can be varied depending on the concentration of the solution of the acid catalyst and the reaction temperature. If the condensation is carried out at 25–65°C. in the presence of a 20–65 weight per cent sulfuric acid solution, alkyl-*m*-dioxanes are formed predominantly, although small amounts of 1,3-butanediols are obtained as byproducts. The following reaction occurs in the case of the isobutylene-formaldehyde condensation:



When the lower-molecular-weight tertiary olefins are employed, the reaction proceeds best at 25–40°C. in the presence of a 25–35 per cent aqueous sulfuric acid solution. Type I or type II olefins¹ and the higher-molecular-weight tertiary olefins (types III, IV, and V²) require, in most cases, higher reaction tempera-

¹ Type I olefin structure: $\text{RCH}=\text{CH}_2$.

Type II olefin structure: $\text{RCH}=\text{CHR}'$.

² Type III olefin structure: $\text{RR}'\text{C}=\text{CH}_2$.

Type IV olefin structure: $\text{RR}'\text{C}=\text{CHR}''$.

Type V olefin structure: $\text{RR}'\text{C}=\text{CR}''\text{R}'''$.

tures, stronger solutions of the acid catalyst, or both. Phosphoric acid solutions or aqueous solutions of boron trifluoride can also be employed, although these catalysts are not as satisfactory as sulfuric acid. Dilute hydrochloric acid also catalyzes the reaction, but a somewhat different product is obtained (see Section VII).

A. SYNTHESIS OF *m*-DIOXANES

1. From acyclic and cyclic olefins

Fitzky (41) and Ritter (133) investigated the preparation of alkyl-*m*-dioxanes through the condensation of formaldehyde with propylene, isobutylene, tri-

TABLE 1
Synthesis of alkyl-m-dioxanes

REACTANTS	CATALYST	CONDITIONS	PRODUCT	YIELD *	REFER- ENCE
				<i>per cent</i>	
Propylene } Formaldehyde }	33% ZnCl ₂ solution; methylene chloride as solvent	12 hr. at 120°C.	4-Methyl- <i>m</i> -dioxane		(41)
	15% phosphotungstic acid solution; benzene as solvent	12 hr. at 100°C.	4, 4-Dimethyl- <i>m</i> -dioxane		(41)
	6% H ₃ PO ₄ solution	1 hr. at 80°C.	4, 4-Dimethyl- <i>m</i> -dioxane	37	(41)
Isobutylene } Formaldehyde }	16% HCl solution	8 hr. at room tem- perature	4, 4-Dimethyl- <i>m</i> -dioxane	34	(41)
	2.6% H ₂ SO ₄ solution	2 hr. at 80°C.	4, 4-Dimethyl- <i>m</i> -dioxane	54	(41)
	40% H ₃ PO ₄ solution	46 hr. at room tem- perature	4, 4-Dimethyl- <i>m</i> -dioxane	58	(133)
	25% H ₂ SO ₄ solution	Room temperature	4, 4-Dimethyl- <i>m</i> -dioxane	60	(133)
2-Pentene } Formaldehyde }	83% H ₂ SO ₄ solution	1 hr. at room tem- perature	4-Ethyl-5-methyl- <i>m</i> - dioxane	95	(133)
Diisobutylene } Formaldehyde }	60% H ₂ SO ₄ solution	4 hr. at 10°C.	C ₁₀ H ₂₀ O ₂ (dioxane)		(133)
Trimethylethylene } Formaldehyde }	10% HCl solution	Reflux for 10 min.	4, 4, 5-Trimethyl- <i>m</i> - dioxane		(41)

* On the basis of the quantity of formaldehyde charged.

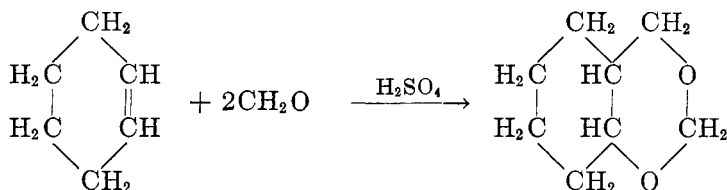
methylethylene, 2-pentene, and diisobutylene in the presence of various acidic catalysts. Specifically, aqueous solutions of zinc chloride, phosphotungstic acid, phosphoric acid, hydrochloric acid, and sulfuric acid were employed as catalysts. Their results are summarized in table 1.

Generally speaking, the highest yields of *m*-dioxanes were obtained with dilute sulfuric acid as catalyst. The concentration of the acid solution could be varied between 3 and 85 per cent, depending on the nature of the olefin feed. For example, primary olefins (types I and II) required a solution containing 50–85 per cent of sulfuric acid. The tertiary olefin isobutylene could be condensed with formaldehyde at 10–40°C. in the presence of a 10–40 per cent acid solution, whereas the condensation of 2-butene with formaldehyde had to be run in the

presence of a 40–60 per cent acid catalyst. Solvents such as benzene or methylene chloride were added to the mixture to improve contact and increase the rate of reaction.

In the case of the lower-molecular-weight olefins, a certain amount of the corresponding saturated secondary or tertiary alcohol was obtained as a by-product, the alcohol being formed through olefin hydration in the presence of the dilute sulfuric acid. When hydrochloric acid was employed as the catalyst, the reaction had to be carried out under mild conditions (i.e., at low temperatures or short contact times) to avoid conversion of the product *m*-dioxanes into chlorohydrins.

Munday and Matuszak (108) obtained a 93 per cent yield of 4,4,5,5-tetramethyl-*m*-dioxane by the reaction of 2,3-dimethyl-2-butene with formaldehyde at 32°C. in the presence of a dilute sulfuric acid solution. Cyclohexene and other cyclic olefins also react with formaldehyde at 60–80°C. in the presence of a 45–55 per cent sulfuric acid catalyst to form cyclopolyethylene-*m*-dioxanes as follows (102):



Higher olefins have also been condensed with paraformaldehyde, using concentrated sulfuric acid as the catalyst. When octadecene was employed as the reactant, the product after caustic neutralization possessed wetting, dispersing, and cleansing properties (60). Apparently the *m*-dioxane or glycol formed in the reaction further reacted *in situ* with the sulfuric acid catalyst to yield a sulfonate or sulfate.

Mottern (107) has employed the reaction with formaldehyde in the presence of sulfuric acid as a means for selectively removing tertiary olefins from refinery distillates. Refinery C₅ cut was treated with formaldehyde at room temperature in the presence of 25 per cent sulfuric acid. The strength of the acid determined the selectivity of the process. *m*-Dioxanes were formed from the tertiary olefins.

Secondary or tertiary alcohols have been employed in place of their corresponding olefins in the formaldehyde condensation. Harvey (57) treated tertiary butyl alcohol with formaldehyde or benzaldehyde in the presence of concentrated sulfuric acid to form products (apparently *m*-dioxanes or glycols) which were found to be solvents for cellulose acetate or nitrate. They also reacted with maleic or phthalic anhydride to form resins. Secondary alcohols (isopropyl, *sec*-butyl, and *sec*-amyl) underwent a similar condensation at 100–165°C. in the presence of 10–94 per cent sulfuric acid, 7–20 per cent hydrochloric acid, nitric acid, or phosphoric acid (58). The products were also solvents for cellulose acetate.

The olefin-aldehyde condensation is also catalyzed by boron trifluoride-water complexes. The mole ratio of boron trifluoride to water must be varied

for different olefin reactants if selectivity to yield *m*-dioxanes is to be achieved. Loder (85, 86) obtained a 52 per cent yield of 4-methyl-*m*-dioxane when condensing propylene with formaldehyde at 0–20°C. in the presence of a catalyst containing 2.7 moles of water per mole of boron trifluoride. Because of the high activity of the catalyst, a portion of the reactants was converted to higher-boiling formals. The yield of lower-boiling formals could be increased, and the amount of higher-boiling byproduct decreased, by conducting the propylene-formaldehyde reaction at 65–75°C. with a catalyst containing 10–18 moles of water per mole of boron trifluoride (136). Tertiary olefins, alcohols, or halides form *m*-dioxanes with aldehydes at substantially room temperature in the presence of catalysts comprising 9–25 moles of water per mole of boron fluoride (135). 1,3-Glycols are obtained as byproducts.

Finally, ion-exchange resins containing sulfonic acid groups have been used to catalyze the condensation of olefins with formaldehyde in aqueous solution (67).

Since dilute sulfuric acid appeared to be the most useful catalyst for the synthesis of *m*-dioxanes, it was applied to the preparation of *m*-dioxanes from other olefins, diolefins, and aldehydes. More definite yield data were also obtained on some of the dioxanes reported earlier. This work, previously unpublished (14), has been summarized below.

The olefin, aldehyde, and acid catalyst solution were charged to a reactor equipped with an agitator. The batch was heated to the required temperature and stirred until the aldehyde had completely reacted. The condensation is exothermic and is usually complete in less than 5 hr., the reaction time depending on the temperature of operation and on the catalyst strength. At the end of the reaction, the acid is neutralized and the organic product dried and fractionated to separate the three reaction products, *m*-dioxane, saturated alcohol, and 1,3-glycol.

4,4-Dimethyl-*m*-dioxane was formed, together with a small amount of tertiary butyl alcohol and 3-methyl-1,3-butanediol, when isobutylene was condensed with formaldehyde in the presence of a 25 weight per cent sulfuric acid solution. The best yield of *m*-dioxane was obtained under the following conditions:

Charge:

Mole ratio isobutylene: formaldehyde.....	0.73
Mole ratio sulfuric acid: formaldehyde.....	0.073
Concentration of sulfuric acid solution.....	25 weight per cent

Conditions:

Temperature.....	32°C.
Contact time.....	5½ hr.
Maximum pressure.....	57 p.s.i.g.
Formaldehyde conversion.....	100 per cent
Mole ratio isobutylene reacted: isobutylene charged.....	0.92

Yields:

4,4-Dimethyl- <i>m</i> -dioxane.....	75 per cent (on CH ₂ O)
3-Methyl-1,3-butanediol.....	9 per cent (on CH ₂ O)
Tertiary butyl alcohol.....	15 per cent (on C ₄ H ₈ reacted)

The glycol and *m*-dioxane which dissolved in the neutralized acid catalyst layer were not recovered in the above experiment. By removing these compounds from the aqueous solution, the above yields should be increased. The byproduct 3-methyl-1,3-butanediol is completely water-soluble and boils at 85–93°C. at 5 mm. pressure.

When isobutylene was caused to react with acetaldehyde in the presence of a 25 per cent sulfuric acid solution, 2,4,4,6-tetramethyl-*m*-dioxane, 1,3-dimethyl-1,3-butanediol, and tertiary butyl alcohol were produced. The following conditions were used:

Charge:

Mole ratio isobutylene: acetaldehyde	0.99
Mole ratio sulfuric acid: acetaldehyde	0.073
Concentration of sulfuric acid solution.....	25 weight per cent

Conditions:

Temperature.....	38–40°C.
Contact time.....	6 hr.
Maximum pressure	70 p.s.i.g.
Acetaldehyde conversion	100 per cent
Mole ratio isobutylene reacted: isobutylene charged.....	0.96

Yields:

2,4,4,6-Tetramethyl- <i>m</i> -dioxane.....	83 per cent (on CH ₃ CHO)
1,3-Dimethyl-1,3-butanediol.....	6 per cent (on CH ₃ CHO)
Tertiary butyl alcohol.....	34 per cent (on reacted isobutylene)

Here again, the products remaining in the neutralized catalyst layer were not recovered. As far as its properties are concerned, this *m*-dioxane is very similar to the 4-methyl- and 4,4-dimethyl-*m*-dioxanes, although it possesses a somewhat lower solubility in water. The solubility of the dioxanes in water or dilute acid solutions decreases as the molecular weight of the olefin or aldehyde reactants is increased. This lower solubility, coupled with the reduced formation of glycol, contributed to the higher yields of *m*-dioxane obtained from acetaldehyde.

The highest yield of 4-methyl-*m*-dioxane (from propylene and formaldehyde) was achieved under the following conditions:

Charge:

Mole ratio propylene: formaldehyde	0.74
Mole ratio sulfuric acid: formaldehyde.....	0.21
Concentration of sulfuric acid solution.....	35 weight per cent

Conditions:

Temperature.....	60°C.
Contact time.....	8 hr.
Maximum pressure	345 p.s.i.g.
Formaldehyde conversion	100 per cent
Mole ratio propylene reacted: propylene charged.....	0.68

Yields:

4-Methyl- <i>m</i> -dioxane.....	65 per cent (on CH ₂ O)
1,3-Butanediol	10 per cent (on CH ₂ O)

Isopropyl alcohol is a byproduct of this reaction. Since this *m*-dioxane is quite volatile and water-soluble, some of the product may have been lost during the isolation process. With improved recovery methods, there is every reason to believe that the yields can be increased.

Other olefins and diolefins were condensed with formaldehyde, acetaldehyde, and benzaldehyde in the presence of aqueous sulfuric acid solutions to form the corresponding *m*-dioxanes. These syntheses, the yields, and boiling points of the products are summarized in table 2.

2. From arylolefins

Under proper conditions, aldehydes can also react selectively with the ethylenic bonds in arylolefins to form phenyl-*m*-dioxanes. Styrene and formaldehyde condense in the presence of dilute hydrochloric acid to yield 4-phenyl-*m*-dioxane (38). Sulfuric acid in acetic acid (34, 129) or dilute aqueous solutions of sulfuric or phosphoric acid (68) are likewise effective catalysts. Under similar conditions, 4-methyl-4-phenyl-*m*-dioxane is obtained through the condensation of α -methylstyrene with formaldehyde. *p*-Dioxane may be used as a mutual solvent for this reaction (37, 124).

Good procedures for preparing substituted *m*-dioxanes from arylolefins, formalin, and sulfuric acid have been contributed by Shortridge (139a) and by Beets and coworkers (23a, 23b, 31a).

ARYLOLEFIN	YIELD OF SUBSTITUTED <i>m</i> -DIOXANE
	<i>per cent</i>
Styrene.....	86
α -Methylstyrene.....	58
Propenylbenzene.....	66
Anethole.....	89
Isosafrole.....	84
1-(4'-Isopropylphenyl)-1-propene.....	96
1-(3',4'-Dimethoxyphenyl)-1-propene.....	68

The arylalkylcarbinols may be substituted for the arylolefins, but the yields of substituted *m*-dioxanes are then 5–20 per cent lower (23a, 23b, 31a). Another modification (139a), using *s*-trioxane with styrene in *p*-dioxane with sulfuric acid at 25°C., gave a 78 per cent yield of 4-phenyl-*m*-dioxane.

3. From terpenes

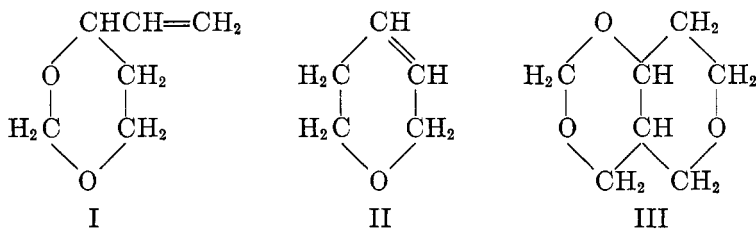
Terpenes such as pinene, *d*-limonene, camphene, cedrene, alloöcimene, and myrcene also react with formaldehyde in the presence of hydrochloric, sulfuric, or *p*-toluenesulfonic acid to form condensation products or resins. The nature of the products obtained under these conditions has not been too clearly defined (56, 59, 109, 127, 128, 129, 137, 148).

4. From diolefins

Gresham and Grigsby (51) obtained 4-vinyl-*m*-dioxane when condensing butadiene with formaldehyde in the presence of an acidic condensation catalyst

and a polymerization inhibitor (hydroquinone) at 100–200°C. Alkylol-substituted hydroxytetrahydropyrans and their cyclic formals were also obtained. Concentrated sulfuric acid in acetic acid has also been studied as a catalyst (30), and the condensation products were characterized by subjecting them to further chemical conversions.

In the presence of an aqueous sulfuric acid catalyst, unsaturated *m*-dioxanes (I), dihydropyrans (II), and trioxaperhydronaphthalenes (III) are produced (65).



5. From substituted olefins

Certain substituted olefins, particularly unsaturated halides and ethers, can also react with aldehydes to form substituted *m*-dioxanes. In the presence of a 50 per cent sulfuric acid solution at 50–70°C., methallyl chloride and isocrotyl chloride form 4-chloromethyl-4-methyl-*m*-dioxane and 5-chloro-4,4-dimethyl-*m*-dioxane, respectively, in 50–80 per cent yields (7). Chloro-1,3-butanediols are obtained as byproducts.

Allyl chloride and formaldehyde condense at 0°C. in the presence of concentrated sulfuric acid and yield 4-chloromethyl-*m*-dioxane (126). Dimethallyl ethyl ether and formaldehyde react quite easily in the presence of a 25 per cent sulfuric acid solution at about room temperature. 5-Ethoxymethyl-4,4-dimethyl-*m*-dioxane is obtained in 73 per cent yield (9).

The reaction of allyl cyanide with formaldehyde in the presence of a concentrated acid catalyst led almost exclusively to the condensation of formaldehyde with the cyanide group rather than with the carbon-carbon double bond. Tris(vinylacetyl)hexahydro-*s*-triazine was produced in the presence of sulfuric acid and methylenebis(vinylacetamide) when phosphoric acid was used as the catalyst (125).

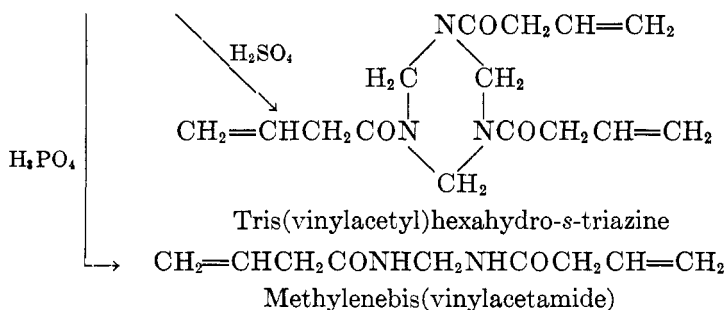
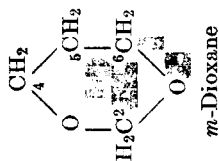


TABLE 2
*Synthesis of alkyl-*m*-dioxanes*



OLEFINIC COMPOUND	ALDEHYDE	CATALYST	REACTION TEMPERATURE °C.	<i>m</i> -DIOXANE FORMED			BYPRODUCT GLYCOL (IF ISOLATED)	
				NAME OR STRUCTURE	BOILING POINT °C.	YIELD* per cent	STRUCTURE AND BOILING RANGE	YIELD* per cent
Isobutylene...	Benzaldehyde	37% H ₂ SO ₄	Room temperature	4,4-Dimethyl-2,6-diphenyl- <i>m</i> -dioxane	163-165/2 mm. 66-68 (melting point)	72		
2-Butene.....	Formaldehyde	50% H ₂ SO ₄	Room temperature	4,5-Dimethyl- <i>m</i> -dioxane	132.5-133	48		
Trimethyl-ethylene....	Formaldehyde	25% H ₂ SO ₄	Room temperature	4,4,5-Trimethyl- <i>m</i> -dioxane	152	80	2,3-Dimethyl-1,3-butanediol 90-96°C./4 mm.	9
Diisobutylene	Acetaldehyde	37% H ₂ SO ₄	Room temperature	2,4,4,5,6-Pentamethyl- <i>m</i> -dioxane	161	70	2,3-Dimethyl-2,4-pentanediol	9
	Formaldehyde	50% H ₂ SO ₄	25-44	5- <i>tert</i> -Butyl-4,4-dimethyl- <i>m</i> -dioxane	203-206 74-78/3 mm.	40		
Cyclohexene...	Formaldehyde	50% H ₂ SO ₄	70		193-195	42		

Styrene	Formaldehyde	50% H ₂ SO ₄	70	4-Phenyl- <i>m</i> -dioxane	99/2 mm.	78
2-Pentene	Formaldehyde	50% H ₂ SO ₄	46	4-Ethyl-5-methyl- <i>m</i> - dioxane	156	48
Isoprene	Formaldehyde	30% H ₂ SO ₄	Room tem- perature	4-Methyl-4-vinyl- <i>m</i> - dioxane	153-154	47
Butadiene	Formaldehyde	60% H ₂ SO ₄	Room tem- perature	4-Vinyl- <i>m</i> -dioxane	144-145	47

* On the basis of the quantity of formaldehyde charged.

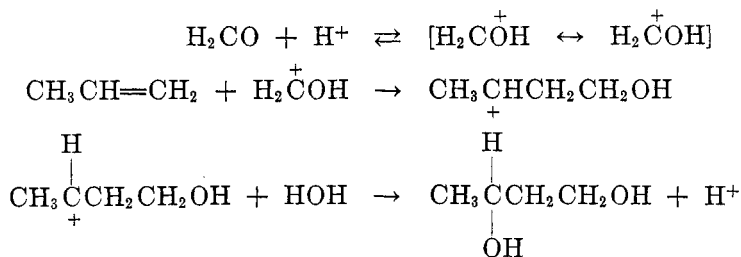
Polymerized

In the presence of a dilute sulfuric acid catalyst, the double bond in methallyl cyanide can also be condensed with formaldehyde (5).

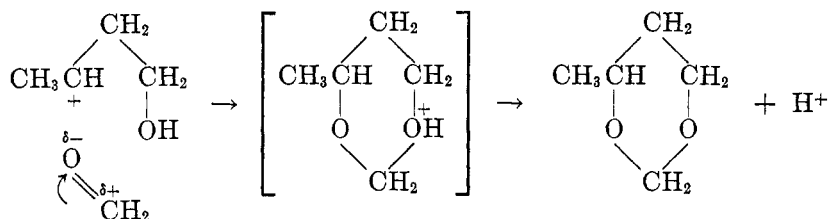
To date, difficulties have been experienced in condensing unsaturated carbonyl compounds (unsaturated acids, ketones, or aldehydes) with formaldehyde to form *m*-dioxanes. Unsaturated alcohols and esters have been reacted with formaldehyde in the presence of acid catalysts but the products were difficult to identify, owing apparently to the further reaction of the aldehyde with the hydroxyl groups in the molecule (see also Section XIII).

B. MECHANISM OF THE REACTION

Several theories (18, 21, 121, 123) have been proposed as to the mechanism of the acid-catalyzed reaction of olefins with formaldehyde to form *m*-dioxanes and 1,3-glycols. At the present time it appears that the reaction proceeds through the formation of an acid-formaldehyde carbonium ion as follows:



or



In the initial reaction, the acid-formaldehyde carbonium ion reacts with a "basic" olefin to form an acid-alcohol carbonium ion. The latter can then react with water to form the glycol or with formaldehyde to yield the *m*-dioxane. The two products are apparently produced simultaneously, the ratio of dioxane to glycol in the product being dependent on the relative "basicity" and the concentrations of formaldehyde and water under the conditions of the synthesis. The authors have concluded that the *m*-dioxane and glycol must form at the same time, since the two compounds are not readily interconverted under the low-temperature conditions of dioxane preparation. For example, when isobutylene and formaldehyde are condensed in the presence of a 25 per cent sulfuric acid solution at room temperature, 4,4-dimethyl-*m*-dioxane and 3-methyl-1,3-butanediol are formed. However, bringing the *m*-dioxane into contact with the 25 per cent acid solution at room temperature does not lead to the formation of 3-methyl-1,3-butanediol to any noticeable extent. Likewise, the reaction of 3-methyl-1,3-butanediol with formaldehyde under the same conditions did not give appreciable yields of 4,4-dimethyl-*m*-dioxane.

The mechanisms involved in the production of unsaturated alcohols and ketones are somewhat different and will be discussed later.

TABLE 3
Properties of alkyl-m-dioxanes

PROPERTIES	4-METHYL- <i>m</i> -DIOXANE	4,4-DIMETHYL- <i>m</i> -DIOXANE	2,4,4,6-TETRAMETHYL- <i>m</i> -DIOXANE
Molecular weight.....	102	116	144
Boiling point, °C. at 760 mm.....	116	133	141-142
Specific gravity, 20°/20°C.....	0.9748	0.9651	0.9050
Refractive index at 20°C.....	1.4202	1.4231	1.4191
Kinematic viscosity (centistokes) at:			
60°F.....	1.012	1.567	1.342
68°F.....	0.951	1.451	1.243
77°F.....	0.887	1.329	1.135
100°F.....	0.757	1.087	0.925
Freezing point, °C.....	-44.5	-88.5	-70
Closed-cup flash point, °F.....	67.1	86.9	93.2
Solubility of dioxane in water (parts/100 parts water by weight) at:*			
30°F.....	57.2	33.5	13.9
40°F.....	53.4	30.7	11.9
50°F.....	50.8	28.2	9.8
60°F.....	49.3	25.6	7.3
70°F.....	47.9	23.5	6.0
80°F.....	46.2	21.4	5.0
90°F.....	43.7	19.6	4.3
100°F.....	40.8	18.2	3.6
110°F.....	38.5	17.4	3.0
Solubility of water in dioxane (parts/100 parts dioxane by weight) at:*			
30°F.....	4.6	2.6	0.73
40°F.....	5.0	2.8	0.78
50°F.....	5.5	3.0	0.82
60°F.....	5.9	3.2	0.89
70°F.....	6.4	3.4	0.98
80°F.....	6.8	3.65	1.09
90°F.....	7.5	3.85	1.20
100°F.....	8.0	4.05	1.32
110°F.....	8.5	4.3	1.46

* Mixtures of known composition were prepared and placed in an A.S.T.M. aniline point apparatus, where they were heated or cooled to effect complete miscibility. The temperatures at which clear solutions were formed are given above.

C. PROPERTIES AND USES OF *m*-DIOXANES

Alkyl-*m*-dioxanes are generally clear, colorless, pleasant-smelling liquids which are miscible with most organic solvents and are incompletely soluble in water. The properties of 4-methyl-, 4,4-dimethyl-, and 2,4,4,6-tetramethyl-*m*-dioxanes are given in table 3. Parachors of *m*-dioxanes have also been reported (2). In addition, the toxicity of certain *m*-dioxanes has been compared with that of *p*-dioxane (111).

Besides their use as raw materials for the synthesis of organic chemicals (see Section II,D), the *m*-dioxanes have been found to be effective as solvents for resins and lacquers, as antiknock agents, and as solvents for dewaxing operations.

1. *m*-Dioxanes as solvents

4-Methyl-, 4,4-dimethyl-, and 2,4,4,6-tetramethyl-*m*-dioxanes have been compared with commercial materials as resin and lacquer solvents (47).

The data on evaporation rate presented in table 4 were obtained on the modified Jolly balance at 35°C. and the following observations were made: (a) The rate of evaporation decreases as the molecular weight of the dioxane increases; (b) the rate of evaporation of 4-methyl-*m*-dioxane approximates that of normal butyl acetate; (c) the rate of evaporation of 4,4-dimethyl-*m*-dioxane is similar to that of both pentacetate and xylol; (d) the rate of evaporation of 2,4,4,6-tetramethyl-*m*-dioxane is considerably slower than that of pentacetate but is much faster than that of the commercial high-boiling solvents such as the Cellosolves.

Qualitative data on solvency were obtained on thirteen different types of resins by agitating 0.5 g. of the resin in 5 ml. of solvent. The results are given in table 5. The following nitrocellulose dilution ratios were also determined:

Data on nitrocellulose dilution ratio
(Regular soluble ½-sec. nitrocellulose, titrating with toluol)

SOLVENT	DILUTION RATIO
4-Methyl- <i>m</i> -dioxane.....	2.06
4,4-Dimethyl- <i>m</i> -dioxane.....	2.22
2,4,4,6-Tetramethyl- <i>m</i> -dioxane.....	Non-solvent
<i>sec</i> -Butyl acetate.....	2.7
<i>n</i> -Butyl acetate.....	3.1
Pentacetate.....	2.5
Cellosolve.....	4.9

The data given above indicate that the 4-methyl- and the 4,4-dimethyl-*m*-dioxanes show more promise as lacquer solvents than does the tetramethyl product. The qualitative results on solvency also indicate that a great many surface-coating materials are soluble in the *m*-dioxanes.

2. *m*-Dioxanes as gasoline blending agents

Alkyl-*m*-dioxanes have been added to motor gasolines to improve the octane number. The results shown in table 6 were obtained on blending various *m*-dioxanes with a 65 octane number gasoline and determining the octane numbers of the blends (10). It appears, therefore, that low-boiling volatile olefins can be converted, through condensation with aldehydes in the presence of acid catalysts, to products boiling in the gasoline boiling range and possessing high octane numbers.

3. *m*-Dioxanes as dewaxing solvents

The ideal dewaxing solvent is one that will show a relatively low solubility for the waxy constituents of an oil, will exhibit a relatively high solubility for the oil itself, and will remain completely miscible with the oily fractions at the low temperatures normally employed in dewaxing operations. *m*-Dioxanes have been investigated in such an application (134).

The desirability of using alkyl-*m*-dioxanes as dewaxing solvents may be seen by reference to table 7, in which the miscibility temperatures and the wax

TABLE 4
Evaporation data on alkyl-*m*-dioxanes at 35°C.

TIME ELAPSED	SOLVESSO TOLUOL	SOLVESSO XYLOL	<i>p</i> -DIOXANE	4-METHYL- <i>m</i> - DIOXANE	4,4-DIMETHYL- <i>m</i> -DIOXANE	2,4,4,6-TET- RAMETHYL- <i>m</i> -DIOXANE
<i>min.</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>	<i>per cent</i>
10	22.5	11.0	25.0	17.5	11.0	8.0
20	44.0	22.0	48.0	33.0	23.0	17.0
30	64.5	33.0	69.0	47.5	34.0	25.5
40	82.0	43.0	87.0	61.5	44.5	33.5
50	98.0	52.5	95.5	74.5	54.0	41.5
60	100	62.0	97.0	86.0	63.0	49.0
70		71.0	97.0	95.5	71.5	56.0
80		79.5		100	79.5	62.5
90		87.0			87.0	69.0
100		93.5			92.5	75.0
110		99.0			97.0	80.0
120		100			100	85.0
130						89.5
140						94.0
150						97.5
160						100

solubilities of the various dioxanes are listed. It can be seen that *m*-dioxanes, particularly the 4,4- and 4,5-dimethyl-*m*-dioxanes, are potential dewaxing solvents. A mixture of these two dioxanes is also effective; such a mixture can be easily prepared by condensing a refinery C₄ cut with formaldehyde in the presence of a 25-60 per cent sulfuric acid catalyst solution.

Other possible uses for the *m*-dioxanes include alcohol denaturants (76), dry-cleaning solvents, antiskinning agents for paints, gasoline solvent oils, fiber-spinning solvents, and disinfectants.

D. REACTIONS OF ALKYL-*m*-DIOXANES

Since alkyl-*m*-dioxanes are the cyclic formals or acetals of 1,3-glycols, they undergo certain chemical reactions common to all acetals. These reactions are discussed separately below.

1. Hydrolysis

Acyclic acetals or formals can be hydrolyzed to the corresponding alcohols by treatment with dilute acids at elevated temperatures. *m*-Dioxanes can also be

TABLE 5
Qualitative data on solubility* of resins in *m*-dioxanes and four other solvents
0.5 g. of resin in 5 ml. of solvent

RESIN	4-METHYL- <i>m</i> -DIOXANE	4,4-DI-METHYL- <i>m</i> -DIOXANE	2,4,4,6-TETRA-METHYL- <i>m</i> -DIOXANE	<i>p</i> -DI- OXANE	<i>sec</i> - BUTYL ACETATE	<i>n</i> - BUTYL ACETATE	PENT- ACETATE	CELLO- SOLVE
Cellulose acetate ^(a)	S (gel)	PS (gel)	I	S	I	I	I	PS
Hercose C (cellulose acetate butyrate) ^(b)	S	PS	I	S	I	I	I	I
Hercose AP (cellulose acetate propionate) ^(b)	S	S	I	S	S	S	I	S
Alvar (polyvinyl acetate-acetal) ^(c)	S	S	PS	S	S	S	S	S
Ethocel (ethyl cellulose) ^(d) ...	S	S	S	S	S	S	S	S
Vynlite (AYAA) (polyvinyl acetate) ^(e)	S	S	PS	S	S	S	S	S
Vynlite (VYNW) (vinyl chloride-acetate) ^(e)	PS	PS	I	S	S	S	S	I
Vynlite (XYNC) (polyvinyl butyral) ^(e)	S (gel)	S (gel)	SW	S	I	I	I	S
Vynlite (XYSG) (polyvinyl butyral) ^(e)	S (gel)	S (gel)	SW	S	I	I	I	S
Chlorinated rubber (125 c.p.s.) ^(b)	S	S	SW	S	S	S	S	PS
Geon (polyvinyl chloride) ^(f) ...	PS	PS	I	PS	I	I	I	I
Geon (polyvinylidene chloride) ^(f)	PS	PS	I	PS	I	I	I	I
½ sec. Nitrocellulose ^(b)	S	S	I	S	S	S	S	S

* S = soluble; I = insoluble; SW = swells; PS = partially soluble.

(a) E. I. du Pont de Nemours and Company.

(b) Hercules Powder Company.

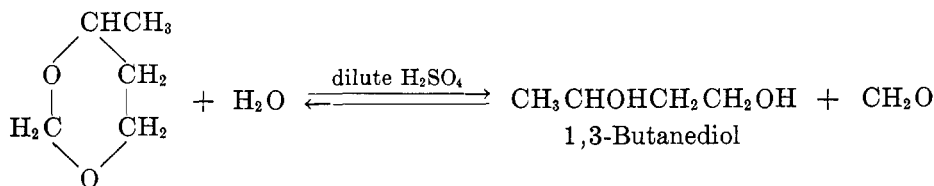
(c) Shawinigan Products Corporation.

(d) Dow Chemical Company.

(e) Carbide and Carbon Chemicals Corporation.

(f) B. F. Goodrich Company.

hydrolyzed under similar conditions to form 1,3-butanediols, as shown by the following equation:



1,3-Butanediol

4-Methyl-*m*-dioxane

Certain *m*-dioxanes, specifically those prepared from type I or type II olefins, can be hydrolyzed to form glycols by stirring the dioxane with a 2 per cent (or lower) sulfuric acid solution at the reflux temperature of the mixture. The yield of glycol varies between 40 and 80 per cent (based on the dioxane reacted), depending on the amount and concentration of the acid catalyst solution. However, the yield based on dioxane charged is only 8–17 per cent, owing apparently to the fact that this hydrolysis is a reversible reaction, as indicated in the above equation.

TABLE 6
Octane numbers of m-dioxanes

<i>m</i> -DIOXANE	<i>m</i> -DIOXANE IN BLEND	A.S.T.M. OCTANE NUMBER* CLEAR	OCTANE-BLENDING VALUE OF <i>m</i> -DIOXANE
	<i>per cent</i>		
4,4-Dimethyl	24.4	73.1	98.2
	50	83.3	102
	10	68.7	102
2,4,4,6-Tetramethyl	25	74.3	102.3
4,4,5-Trimethyl	24.4	72.0	93.7
2,4,4,5,6-Pentamethyl	25	74.4	102.6

* Octane number of base fuel = 65.

TABLE 7
m-Dioxanes as dewaxing solvents

SOLVENT	MISCIBILITY TEMPERATURE (3 VOLUMES OF SOLVENT TO 1 VOLUME OF OIL)	WAX SOLUBILITY (GRAMS OF 140–142°F. MELTING POINT WAX PER 100 ML. OF SOLVENT AT)	
		40°F.	80°F.
	°F.	<i>grams</i>	<i>grams</i>
4,4-Dimethyl- <i>m</i> -dioxane	+7	0.043	0.92
4,5-Dimethyl- <i>m</i> -dioxane	–28		
Mixture of 4,4- and 4,5-dimethyl- <i>m</i> -dioxanes	–13	0.092	1.5
4,4,5-Trimethyl- <i>m</i> -dioxane	–46	0.098	1.60
2,4,4,6-Tetramethyl- <i>m</i> -dioxane	–59	0.165	2.90
2,4,4,5,6-Pentamethyl- <i>m</i> -dioxane	–92		

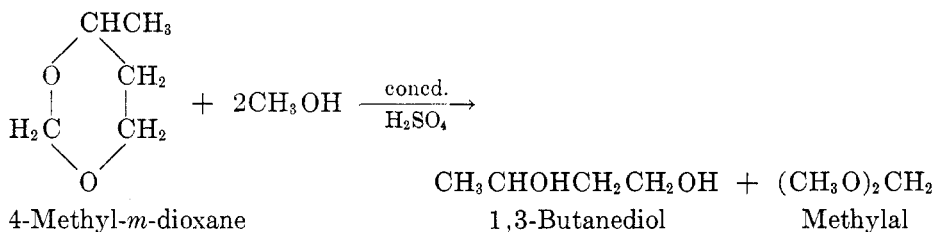
Obviously it was necessary to devise a means for disturbing this equilibrium in order to obtain high conversions of *m*-dioxane to glycol. Since the byproduct formaldehyde could not be easily distilled from the reaction mixture, it had to be removed chemically. This was done without destroying the formaldehyde by adding an olefin and carrying out the hydrolysis reaction under pressure. The olefin condensed with the formaldehyde liberated on hydrolysis of the dioxane to form more *m*-dioxane, which was subsequently converted to the desired glycol (96).

When a mixture of 1.2 moles of 4-methyl-*m*-dioxane and 1.4 moles of propylene was heated at 140–150°C. in the presence of 0.04 mole of sulfuric acid as a 1 per cent aqueous solution, a 200 per cent yield of 1,3-butanediol based on

dioxane reacted (128 per cent yield based on dioxane charged) was obtained. In spite of the satisfactory results obtained with such a procedure, this method of hydrolyzing *m*-dioxanes to glycols may not be considered of commercial interest since, as will be discussed later, it has been found that olefins can be condensed directly with formaldehyde under similar conditions to form the glycols in a single-step process.

2. Alcoholysis

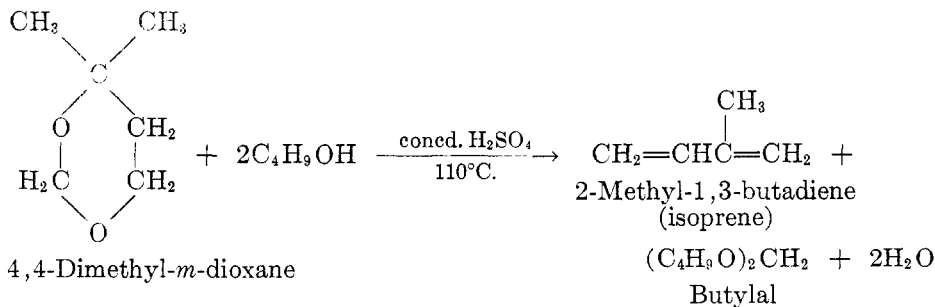
Another method of disturbing the above hydrolytic equilibrium is to treat the byproduct formaldehyde with an organic compound of such a nature that the product will be low boiling and can thus be removed continuously from the hydrolysis mixture. Methyl alcohol has been found particularly satisfactory for this purpose. The reaction, known as alcoholysis, apparently proceeds as shown below:



When a solution containing 1.5 moles of 4-methyl-*m*-dioxane, 4.95 moles of methyl alcohol, and 0.075 mole of concentrated sulfuric acid was heated under a fractionating column at 65–80°C., methylal was taken overhead as it was formed and the desired 1,3-butanediol was left behind. A 92 per cent yield of glycol was obtained (13).

The methylal can be reconverted to methanol and formaldehyde and these compounds recycled (84).

In the presence of methanol, the reflux temperature is low and glycols are the major products. If, on the other hand, higher alcohols are employed, the reflux



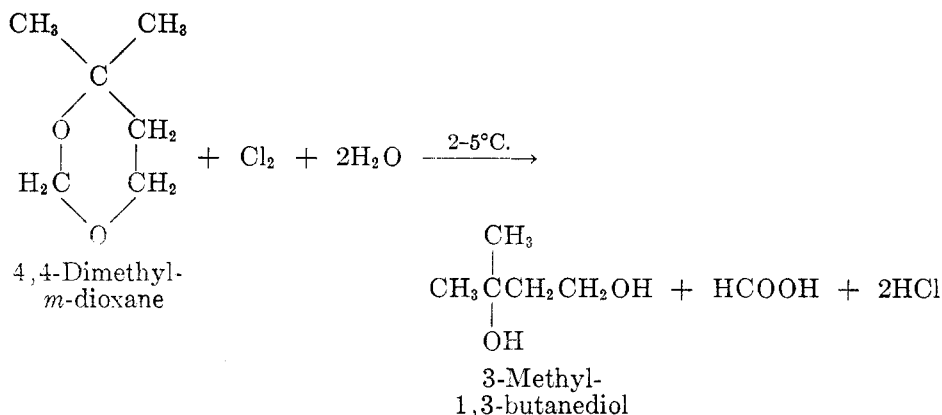
temperature is higher, the byproduct acetal or formal remains in the still, and a diolefin is produced through dehydration of the glycol as soon as the latter is

formed. Under these conditions, the diolefin is taken off overhead in a continuous manner.

This reaction is of particular value in the case of *m*-dioxanes which are formed from tertiary (types III, IV, and V) olefins. As an example, isoprene can be obtained from 4,4-dimethyl-*m*-dioxane by heating a mixture of this dioxane, *n*-butyl alcohol, and concentrated sulfuric acid at 108–110°C. under a fractionating column and taking the diolefin off overhead. Under these conditions, a 50 per cent yield of isoprene and an 88 per cent yield of byproduct butylal were obtained (100).

3. Chlorination

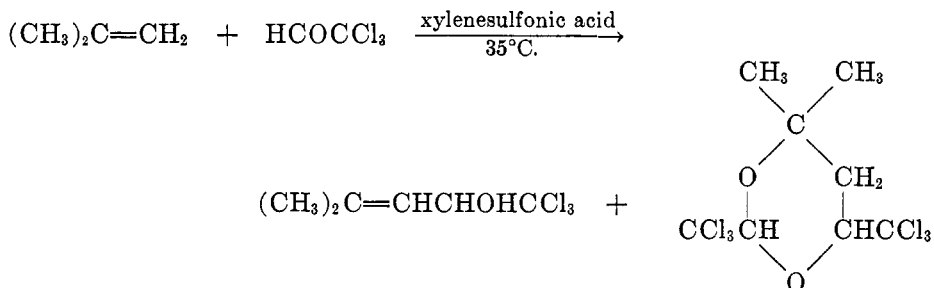
m-Dioxanes prepared from type I or type II olefins and formaldehyde can be converted readily to glycols without appreciable side reactions by the hydrolysis and alcoholysis methods described above. Dioxanes produced from tertiary base olefins (types III, IV, and V), on the other hand, are usually converted to diolefins under these conditions, because the intermediate tertiary-primary glycol which forms from such *m*-dioxanes is unstable in the presence of acids at high temperatures and immediately undergoes dehydration to form the diolefin. However, 4,4-dialkyl-*m*-dioxanes have been hydrolyzed to the corresponding glycols without side reactions or dehydration by chlorinating these dioxanes in the presence of water at low temperatures. Apparently the chlorine replaces one of the hydrogen atoms in the 2-position to form a chloro-*m*-dioxane which is unstable in the presence of water and immediately undergoes hydrolysis to form the glycol, formic acid, and hydrochloric acid. 3-Methyl-1,3-butanediol has been prepared from 4,4-dimethyl-*m*-dioxane in 70 per cent yield by passing chlorine into a stirred mixture of water and the dioxane at 2–5°C. (12).



Chlorination in the absence of water results in the formation of polychloro-dioxanes and related compounds.

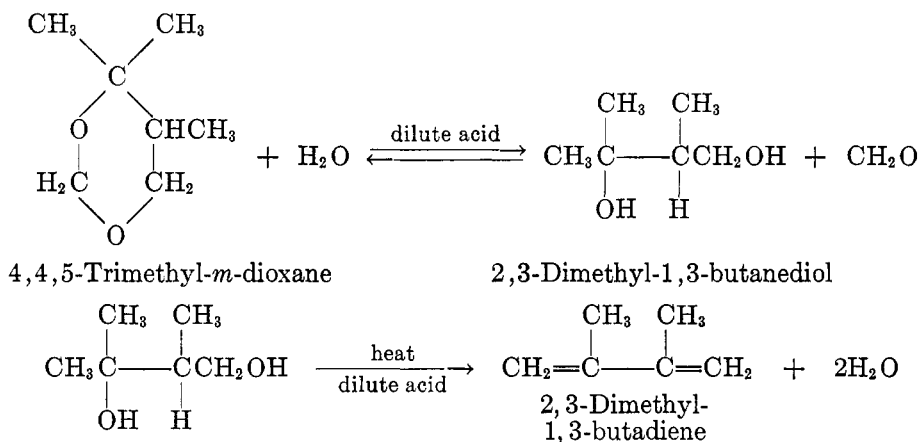
Chlorinated *m*-dioxanes have also been prepared, along with unsaturated tri-

chloromethylcarbinols, by the condensation of olefins with chloral as follows (121a):



4. Dehydratohydrolysis

Alkyl-*m*-dioxanes, particularly those produced from tertiary base olefins and aldehydes, can be converted directly to conjugated diolefins by refluxing them in the presence of very dilute solutions of mineral acids (1-5 per cent concentration) at temperatures above 95°C. The *m*-dioxane is first hydrolyzed to the corresponding glycol, which is immediately dehydrated to a diolefin.

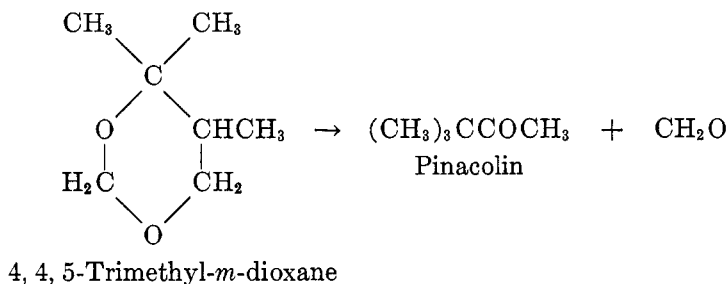


When 2 moles of 4,4,5-trimethyl-*m*-dioxane and 1200 ml. of a 2.5 per cent hydrochloric acid solution were heated at 95°C. in a reactor equipped with a stirrer and fractionating tower, the 2,3-dimethyl-1,3-butadiene could be taken overhead as fast as it was formed. However, the yield obtained in this reaction was only 50 per cent (based on the dioxane charged) and variations in the experimental conditions failed to improve this yield. Apparently, the remainder of the diolefin condensed with the byproduct formaldehyde to form higher-boiling and wide-boiling reaction products, such as hydropyrans or their derivatives (101).

Mottern (106) has prepared diolefins by condensing olefins with formaldehyde in the presence of a dilute sulfuric acid catalyst, subsequently diluting the reac-

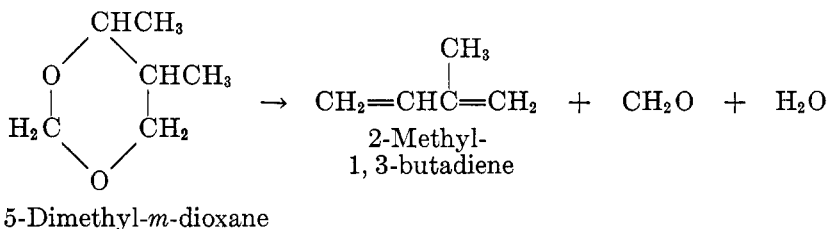
tion mixture further, and subjecting the batch to steam distillation. The hydrocarbon portion of the distillate was further fractionated to isolate the diolefin.

In connection with the dehydrhydrolysis reaction for diolefin preparation, it is of interest to note that ketones can be formed under similar conditions. For example, pinacolin was obtained by adding 4,4,5-trimethyl-*m*-dioxane to a boiling 20 per cent hydrochloric acid solution at such a rate that the pinacolin distilled overhead as formed (43). The following reaction took place:



5. Cracking

Friedrichsen (44, 45, 46) has prepared conjugated diolefins by bringing an alkyl-*m*-dioxane into contact with a solid dehydration catalyst in the vapor phase at 200–300°C.



When a catalyst comprising primary sodium phosphate and primary *n*-butylamine phosphate on graphite was used, the diolefin yields amounted to about 50 per cent, as shown in table 8. Formaldehyde and the parent olefin were by-products.

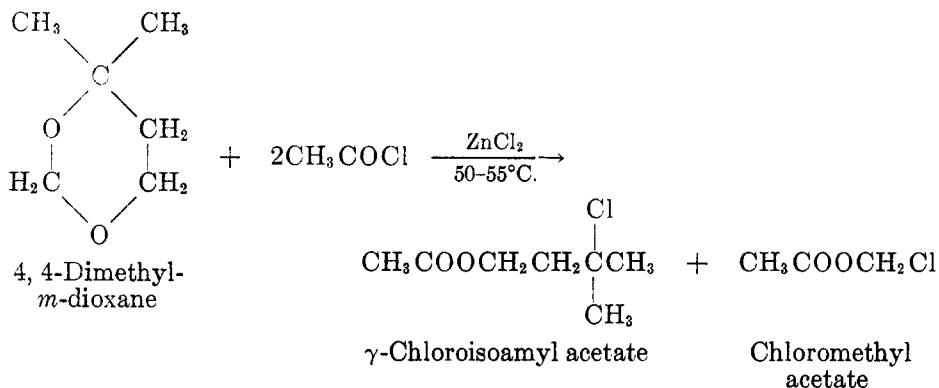
A liquid which is inert under these conditions (e.g., water, hexane, cyclohexane, or carbon tetrachloride) can also be added as a feed diluent. Cracking also occurs in the absence of catalysts at temperatures between 200° and 600°C., but the yields are low (below about 10 per cent), the major portion of the *m*-dioxane being converted to monoolefin, formaldehyde, or carbon monoxide and hydrogen.

Price (124) has indicated that 2-aryl-1,3-butadienes can be synthesized by the pyrolysis of 4-aryl-4-alkyl-*m*-dioxanes.

6. Esterification

When alkyl-*m*-dioxanes are refluxed with small quantities of fatty acid chlorides in the presence of Friedel-Crafts catalysts, solid resins are produced (149).

If, on the other hand, at least 2 moles of acid chloride are reacted with 1 mole of *m*-dioxane, chloroesters are formed.



The above esters were produced when 2 moles of 4,4-dimethyl-*m*-dioxane were slowly added to 4 moles of acetyl chloride and 10 g. of anhydrous zinc chloride at 50–55°C. Both the chloromethyl acetate and the γ -chloroisoamyl acetate

TABLE 8
Cracking of m-dioxanes

<i>m</i> -DIOXANE	CRACKING TEMPERATURE	PRODUCTS	YIELDS	REFERENCE
	°C.		<i>per cent</i>	
4-Methyl- <i>m</i> -dioxane	270	{ Butadiene Propylene	52	(46)
4,5-Dimethyl- <i>m</i> -dioxane	300	{ Isoprene 2-Butene	50	
4,4-Dimethyl- <i>m</i> -dioxane	220	{ Isoprene Isobutylene	70	(44)
4,4,5-Trimethyl- <i>m</i> -dioxane	220	{ 2,3-Dimethylbuta- diene Trimethylethylene	53 26	

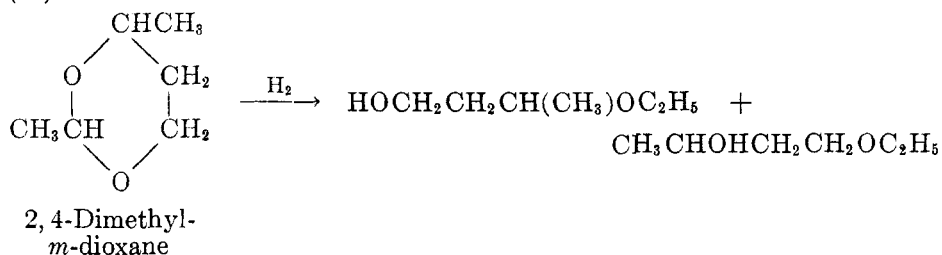
were obtained in almost quantitative yields (5a). The γ -chloroisoamyl acetate can be converted to a chlorohydrin, an unsaturated ester, and an unsaturated alcohol on saponification. The reaction of alkyl-*m*-dioxanes with organic mono- or dibasic acids or their anhydrides to form plasticizers is also possible.

The reaction of *m*-dioxanes with acid anhydrides at 100°C. in the presence of a sulfuric acid catalyst results in the formation of alkyl 2-oxa-1,5-pentanediole diesters (139).

7. Hydrogenolysis

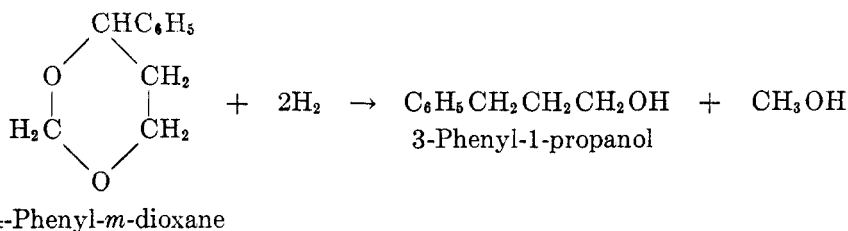
Half-ethers of a 1,3-glycol can readily be obtained by reacting alkyl-*m*-dioxanes with hydrogen in the absence of saponifying media but in the presence

of hydrogenation catalysts (nickel, cobalt, copper, palladium) at 120–210°C. (66).

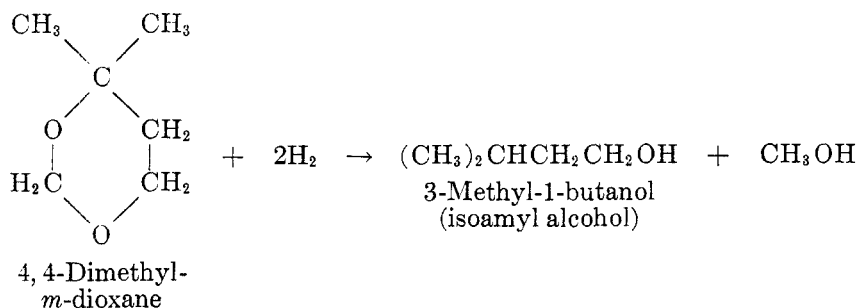


The reaction is carried out in the presence of cyclohexane as a diluent and Raney nickel catalyst at 180–300 atm. pressure. 1-Ethoxy-3-butanol (b.p. 162°C.) was thus obtained in a 34 per cent yield from 2, 4-dimethyl-*m*-dioxane.

Of considerable interest is the conversion of alkyl- or aryl-*m*-dioxanes to primary alcohols by hydrogenolysis (37, 61, 70). Hydrogenation of 4-phenyl-*m*-dioxane in ethanol solution at 200°C. and 1500–2600 p.s.i. in the presence of



copper chromite catalyst yielded 85 per cent of 3-phenyl-1-propanol. 3-Phenyl-1-butanol was similarly obtained in a 68 per cent yield from 4-methyl-4-phenyl-*m*-dioxane. 4,4,5,5-Tetramethyl-*m*-dioxane has thus been converted to 2,2,3-trimethyl-1-butanol and 4,4-dimethyl-*m*-dioxane to isoamyl alcohol (14).



The selective reductive cleavage of 4-aryl-*m*-dioxanes to 3-aryl-1-propanols may also be accomplished by use of sodium and a high-boiling alcohol such as diisobutylcarbinol (23a, 23b, 31a) (see table 9). This reduction with sodium and alcohol was unsatisfactory for 4-aryl-*m*-dioxanes which contained two methoxyl groups or a methylenedioxy group in the 3,4-position.

It is interesting to note the selective character of the reductive cleavage of 4-aryl-*m*-dioxanes. Both catalytic and chemical methods led to cleavage of the

oxygen attached to the benzyl carbon atom,—a behavior paralleling the reductive cleavage of other benzyloxy derivatives such as benzyl carbamates by hydrogen and palladium or *S*-benzyl derivatives by sodium and liquid ammonia.

III. 1,3-GLYCOLS

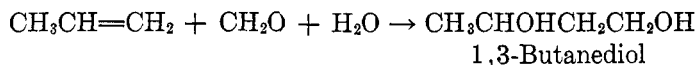
A. GLYCOL SYNTHESIS

As described in Section II, the principal product obtained through the mineral acid-catalyzed condensation of olefins with aldehydes at temperatures below 70°C. is an alkyl-*m*-dioxane. When the *m*-dioxane is subsequently heated in the presence of an olefin and a dilute sulfuric acid catalyst solution, hydrolysis occurs and 1,3-butanediols are produced. At temperatures above 70°C. and with proper control of acid catalyst strength, contact time, and catalyst solution volume, 1,3-glycols can be produced in a one-step operation from type I or type

TABLE 9
Reductive cleavage of 4-aryl-m-dioxanes to 3-aryl-1-propanols

SUBSTITUTED <i>m</i> -DIOXANE	SUBSTITUTED 1-PROPANOL	YIELD <i>per cent</i>
4-Phenyl.....	3-Phenyl-	89
4-Methyl-4-phenyl.....	3-Methyl-3-phenyl-	84
5-Methyl-4-phenyl.....	2-Methyl-3-phenyl-	
5-Methyl-4-(4'-methoxyphenyl).....	2-Methyl-3-(4'-methoxyphenyl)-	92
5-Methyl-4-(4'-isopropylphenyl).....	2-Methyl-3-(4'-isopropylphenyl)-	87
5-Ethyl-4-phenyl.....	2-Ethyl-3-phenyl-	61

II olefins and formaldehyde. In the case of propylene, the following reaction occurs:



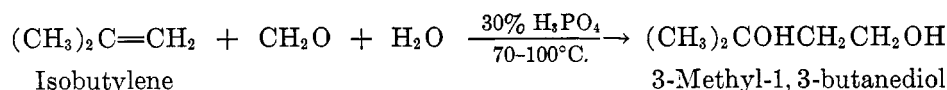
The initial product formed in the condensation is the *m*-dioxane which, on longer heating in the presence of excess olefin, is gradually converted to the glycol.

Fitzky (40) prepared 1,3-butanediol from propylene and formaldehyde at 70–100°C., using a 5 per cent hydrochloric acid solution (in some cases containing zinc chloride) as the catalyst. The yields were not reported. A 70 per cent yield (based on formaldehyde) of 1,3-butanediol was obtained, however, when 1.4 moles of propylene, 1.0 mole of formaldehyde, and 0.2 mole of sulfuric acid (as a 3 per cent aqueous solution) were in contact for 17 hr. at 130–135°C. and 830 p.s.i. pressure (103). After cooling, the acid catalyst was neutralized and the batch filtered and distilled to remove water, isopropyl alcohol, and a small amount of byproduct 4-methyl-*m*-dioxane. The residue was extracted to separate the glycol from inorganic salts and the product was vacuum distilled. When the condensation was carried out under alternate conditions of catalyst strength and temperature, inferior yields of glycol were obtained, owing to the formation of undesirable byproducts.

Hamblet and McAlevy (54) claim that improved yields of glycol can be obtained in shorter periods of time by conducting the synthesis at 150–175°C. and 400–1000 atm. pressure in the presence of added 4-methyl-*m*-dioxane. The *m*-dioxane apparently acts as a mutual solvent, thereby improving contact and increasing the rate of reaction.

In most cases small amounts of polybutylene glycols are obtained as byproducts in the glycol synthesis. These polyglycols can be prepared by heating 1,3-butanediol with small quantities (below 1 per cent) of certain acids or substances having an acidic action (63).

Tertiary olefins (types III, IV, and V) can also be converted to alkylated 1,3-butanediols by a similar one-step process (143). However, lower reaction temperatures (70–100°C.) must be employed and even then the yields are low because the tertiary glycol formed is easily dehydrated to diolefins and other byproducts under the reaction conditions employed. For example, only a 25 per cent yield (based on formaldehyde) of 3-methyl-1,3-butanediol could be obtained when condensing isobutylene with formaldehyde at 70–100°C. in the presence of a 30 per cent phosphoric acid solution as the catalyst. The following reaction takes place:



At higher temperatures, isoprene was obtained (see Section IV).

Glycols and glycol esters have also been synthesized by bringing together olefins, aldehydes, and oxygen in a solvent with a cobalt acetate catalyst (23, 53a).

B. PROPERTIES AND USES OF 1,3-GLYCOLS

The 1,3-glycols are colorless semiviscous liquids of low volatility, mild odor, and high flash point (above 200°F.). Glycols containing three to six carbon atoms are completely soluble in water, whereas the glycols of higher molecular weight have lower solubility. 1,3-Butanediol prepared by the reaction of propylene with formaldehyde was found to possess the following properties: boiling point, 204°C.(92–94°C./3 mm.); specific gravity (20°/20°C.), 1.0045; refractive index at 20°C., 1.4393; kinematic viscosity (centistokes), 160.92 at 60°F., 119.76 at 68°F., 86.88 at 77°F., and 41.63 at 100°F.; freezing point, –39.5°C.

The monobenzyl ether and bis-phenyl urethan of 1,3-butanediol have been prepared by Mayer and Sobotka (93).

1,3-Butanediol is an excellent humectant, approximately 60 per cent as hygroscopic as glycerol. It can therefore be used in printing inks and for softening or moistening tobacco, cork, glue, gelatin, paper, textile fibers, etc. Since it lowers the freezing point of water (see figure 1) it may be a valuable component in non-volatile, non-corrosive antifreeze solutions for automobile engines, ice cream plants, and other cooling systems. Although the data indicate that 1,3-butanediol is of value as an antifreeze, it must be employed in a slightly higher concentration than ethylene or propylene glycol (47). For example, in order to obtain a freezing point of –10°F., the glycol concentration (by volume) in

aqueous solutions of ethylene glycol, propylene glycol, and 1,3-butanediol should be 37.5, 40.5, and 48.5 per cent, respectively, or 40.1, 41.4, and 49 per cent by weight. The refractive indices, freezing points, and viscosities of aqueous solutions of 1,3-butanediol have been reported by Michael and Hopkins (95).

Glycols can also be used in liquid-cooled aircraft engines, as hydraulic fluids, as coupling agents in soluble oils, and as solvents for dyes, inks, essential oils, gums, resins, etc. Glycols, particularly the higher glycols, lend themselves readily to the preparation with mono- and dibasic acids of various esters which are important as plasticizers, synthetic lubricants, emulsifying agents, and resins. For example, the complex ester made by the reaction of 1 mole of 1,3-butanediol with 2 moles of isoöctyl alcohol and 2 moles of adipic acid is a very desirable synthetic lubricating oil and also a plasticizer for vinyl chloride resins.

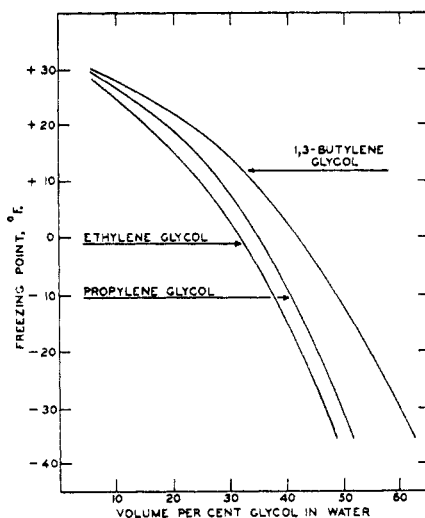


FIG. 1. Freezing-point curves for aqueous solutions of ethylene, propylene, and 1,3-butylene glycols.

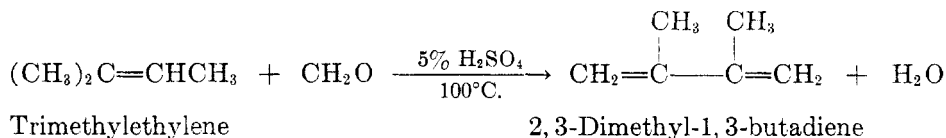
The nitrate esters of glycols are important in low-freezing dynamites and as ignition promoters for Diesel fuels. The glycols themselves can be dehydrated to form conjugated diolefins (32) or dehydrogenated to yield unsaturated aldehydes and ketones. In addition, 1,3-glycols containing one secondary or tertiary hydroxyl group can be partially dehydrated to unsaturated alcohols by heating in the presence of water with zinc chloride (62), iodine, *p*-toluenesulfonic acid (105), phosphoric acid on kaolin (110), or a dilute (5 per cent) sulfuric acid solution (81) as the catalyst. Diolefins are obtained as byproducts.

Heating tertiary-primary glycols with acid anhydrides results in the formation of unsaturated esters (62). The reaction with hydrochloric acid yields unsaturated chlorides or dichlorides.

IV. CONJUGATED DIOLEFINS

As indicated above, when type I and type II olefins are condensed with formaldehyde in the presence of dilute sulfuric acid solutions (1-5 per cent con-

centration) at 100–135°C., 1,3-butanediols are produced (see Section III). However, when tertiary olefins (e.g., isobutylene, trimethylethylene, etc.) are employed under similar conditions, conjugated diolefins are formed. This is probably due to the fact that even though glycols are produced from these tertiary base olefins, they contain a tertiary hydroxyl group and are immediately dehydrated under the reaction conditions. The reaction of trimethylethylene with formaldehyde can be written as follows:



Dilute sulfuric acid solutions appear to be the best catalysts for this reaction (11), although an aqueous solution of boron trifluoride containing approximately 70 moles of water per mole of boron trifluoride may also be employed (135).

In preparing 2,3-dimethyl-1,3-butadiene by this process, 4 moles of formaldehyde, 3.5 moles of trimethylethylene, and 0.1 mole of sulfuric acid (as a 5 per cent aqueous solution) were shaken in a copper-lined reactor for 16 hr. at 100°C. The product was cooled and neutralized, and the organic layer dried and fractionated. The formaldehyde reacted completely and 3 moles of trimethylethylene were consumed. The following yields were obtained:

PRODUCT	YIELD (BASED ON CH ₂ O)
	<i>per cent</i>
2,3-Dimethyl-1,3-butadiene	25
4,4,5-Trimethyl- <i>m</i> -dioxane	31
2,3-Dimethyl-1,3-butanediol	15

In addition, tertiary amyl alcohol was obtained as a byproduct. The yield of diolefin in such a process is low, owing apparently to the fact that, after its formation, this diolefin can condense with formaldehyde to form higher-boiling condensation products. Changes in the type of catalyst, the concentration of the catalyst solution, and the reaction temperature failed to increase the diolefin yield over that given above.

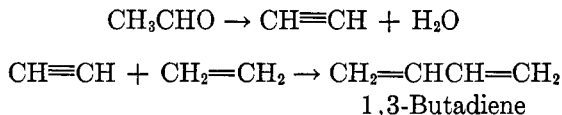
It is also possible to condense tertiary olefins with aldehydes in the presence of a 25 per cent sulfuric acid solution. After the condensation is complete, the catalyst is diluted with water to 1–5 per cent concentration and the diluted batch is distilled to produce the diolefin (106). The diolefin yields obtained under these conditions are, however, no better than those reported above.

Diolefins have also been produced from propylene or isobutylene and formaldehyde by passing the mixture together with steam over an activated alumina catalyst at a temperature of approximately 345°C. The diolefin yields are low (17 per cent on the basis of formaldehyde) and the byproducts include hydrocarbons, hydrogen, and carbon monoxide (from the decomposition of formalde-

hyde) (89). Alcohols can also be employed in place of olefins and the condensation catalyzed by aluminum sulfate deposited on a support (92).

Workman has produced butadiene by the reaction of propylene with formaldehyde under substantially anhydrous conditions at 75–115°F. in contact with a zirconium halide catalyst. The condensation product is subsequently dehydrated to butadiene over a zirconium dioxide catalyst (156).

Butadiene can also be synthesized from ethylene (or ethyl alcohol) and acetaldehyde. The mixed feed in the vapor phase at 200–350°C. is brought into contact with a catalyst comprising a base of aluminum coated with a mixture of silver and copper and the oxides of chromium and molybdenum (104). The following reactions occur:



The ethyl alcohol-acetaldehyde condensation also takes place at 280°C. over alumina to form butadiene (120).

The diolefins find their major outlet in the manufacture of synthetic rubbers and resins although, in view of the low yields, diolefin synthesis by the above method would not appear particularly attractive unless such diolefins could not be produced by other means.

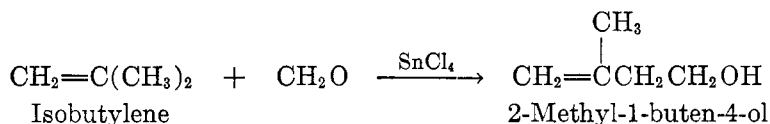
V. UNSATURATED ALCOHOLS AND ESTERS

When the reaction of olefins with formaldehyde is carried out under substantially anhydrous conditions in the absence of acid catalysts or in the presence of "non-acidic" metallic halide catalysts, unsaturated alcohols are produced. It has been demonstrated that olefins, and particularly tertiary base olefins containing from four to eight carbon atoms, can be condensed with formaldehyde (in the form of paraformaldehyde) under either of the following conditions to form such unsaturated primary alcohols: (a) At room temperature under anhydrous conditions in the presence of ether or a halogenated solvent (e.g., chloroform) and with anhydrous stannic chloride, zinc chloride, zinc dichloroacetate, or silicon tetrachloride as the catalyst. The use of aluminum or ferric chlorides as catalysts results primarily in the formation of *m*-dioxanes and not unsaturated alcohols. (b) By heating the olefin and paraformaldehyde at 180–240°C. in the absence of a catalyst.

The synthesis of unsaturated alcohols under either of the above conditions occurs only with tertiary olefins and formaldehyde. Type I or type II olefins or the higher aldehydes such as acetaldehyde react to form alkyl-*m*-dioxanes instead. At higher reaction temperatures the reaction product is of complex composition.

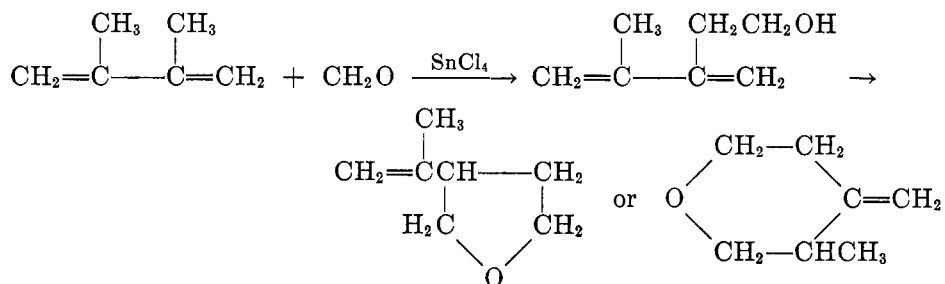
A. REACTION CATALYZED BY METALLIC HALIDES

In the presence of fuming stannic chloride in chloroform as a solvent, paraformaldehyde condenses with isobutylene to yield 2-methyl-1-buten-4-ol (99).



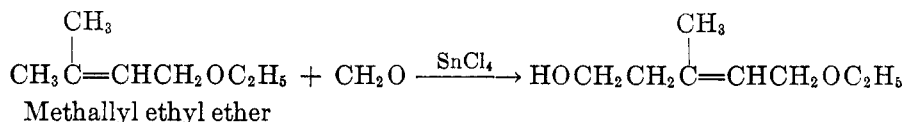
The following experimental conditions were employed (99): Eight moles of formaldehyde (in the form of paraformaldehyde containing 94 per cent of formaldehyde), 8.6 moles of isobutylene, 0.26 mole of fuming stannic chloride, and 600 ml. of dry chloroform were left in contact at room temperature for 16 hr. During this time the formaldehyde reacted completely and 7.3 moles of isobutylene were consumed. The catalyst was then destroyed with ice and water, and the product was neutralized with ammonia, dried, and fractionated. A 30 per cent yield of 2-methyl-1-buten-4-ol was obtained; the product was approximately 90 per cent pure. The impurity was found to be 4,4-dimethyl-*m*-dioxane, which boils about 3°C. above the alcohol itself and forms a constant-boiling mixture therewith. This mixture boiled constantly at 129.5°C. at 763 mm., had a density of 0.8703 at 20°C. and a refractive index of 1.4332 at 20°C., and contained 85 per cent alcohol and 15 per cent *m*-dioxane. The alcohol was purified by esterifying the constant-boiling mixture with acetic anhydride, removing the *m*-dioxane by washing with water, and subsequently saponifying the purified unsaturated acetate. Trioxane is obtained as a byproduct in the alcohol synthesis. This compound can be prepared from paraformaldehyde under similar conditions (98).

Trimethylethylene, 2-methyl-2-pentene, and diisobutylene have also been condensed with paraformaldehyde under similar conditions to yield the corresponding unsaturated alcohols in 20–30 per cent yield. On the other hand, diolefins containing tertiary carbon atoms are apparently converted to unsaturated tetrahydrofurans or pyrans on condensation with formaldehyde, because of the rearrangement of the intermediate diolefinic alcohol under the reaction conditions. The following reaction may occur between formaldehyde and 2,3-dimethyl-1,3-butadiene in the presence of the stannic chloride catalyst (14).



The yields of unsaturated alcohol obtained to date through the stannic chloride-catalyzed reaction of olefins with formaldehyde have been low (25–30 per cent), owing to the fact that the alcohol produced can react further with formaldehyde to form unsaturated formals (which have been isolated), unsaturated glycols, and other side-products. Undoubtedly these alcohol yields could be improved as a result of a comprehensive study of reaction conditions.

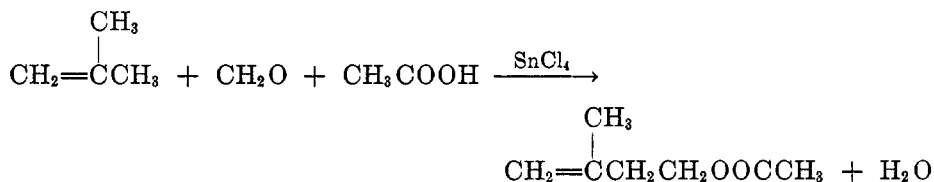
Unsaturated ethers undergo a similar condensation with paraformaldehyde in the presence of stannic chloride to form monoethers of unsaturated dihydric



alcohols (97). 2-(Ethoxymethylisopropenyl)ethyl alcohol has been formed in this way from formaldehyde and methallyl ethyl ether.

Munday and Matuszak (108) tried the reaction of 2,3-dimethyl-2-butene with paraformaldehyde in the presence of mercuric chloride and hydrogen chloride at room temperature. It appears that a chlorohydrin was produced which, on subsequent steam distillation, was converted to 2,3,3-trimethyl-1-buten-4-ol. A 38 per cent yield of this unsaturated alcohol was obtained, along with an 18 per cent yield of byproduct 4,4,5,5-tetramethyl-*m*-dioxane.

If the metallic halide-catalyzed condensation of tertiary olefins with paraformaldehyde is carried out in the presence of an anhydrous organic acid or its anhydride, unsaturated esters are produced as follows:



Again, the reaction is run at room temperature and the yields are about the same as in the case of the synthesis of the unsaturated alcohol (6).

When halogenated organic acids are present in the reaction mixture, no metallic halide catalyst is required. The halogenated organic acid (e.g., dichloroacetic acid) simultaneously acts as (a) a catalyst for the olefin-aldehyde condensation reaction, (b) an esterification reagent, and (c) an esterification catalyst. Thus, at 20–30°C., trimethylethylene, paraformaldehyde, and dichloroacetic acid react to form the dichloroacetate of a C₆ unsaturated alcohol (8).

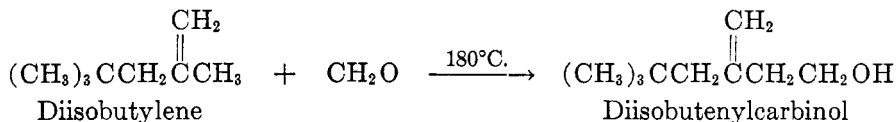
Unsaturated alcohols have also been produced by treating more than 1 mole of isobutylene with 2 moles of formaldehyde in the presence of a strong mineral acid catalyst (141) (see also Section VI).

B. THERMAL CONDENSATION

From the process and economic standpoint, a promising method for producing unsaturated primary alcohols involves the reaction of olefins with anhydrous formaldehyde at elevated temperatures in the absence of added catalysts. On the basis of the limited amount of work which has been done to date on this reaction, tertiary olefins appear to be the most desirable raw materials. The following example will illustrate this method of alcohol synthesis (132).

An equimolar mixture of diisobutylene and formaldehyde (as paraformaldehyde) was heated in a bomb for 18 hr. at 180°C. At the end of this time the reac-

tor contents were cooled, washed with a dilute sodium hydroxide solution, and fractionated. A constant-boiling product was obtained between 192–193°C. at atmospheric pressure (58–63°C./5 mm.). On the basis of analytical data, this appeared to be a mixture of 4,4-dimethyl-5-*tert*-butyl-*m*-dioxane and the C₉H₁₈O unsaturated alcohol, containing about 80 per cent of the latter. The following reaction appears to take place:



The yield on the basis of reacted diisobutylene amounted to approximately 55 per cent. The byproduct *m*-dioxane is probably formed through the condensation of the dimer with 2 moles of formaldehyde in the presence of a trace of formic acid. The latter would be present as a result of the high-temperature Cannizzaro reaction of formaldehyde and could be avoided by changes in the operating conditions or by the addition of formaldehyde stabilizers or buffers. The purified diisobutenylcarbinol was hydrogenated to an alcohol [(CH₃)₃CCH₂CH(CH₃)CH₂CH₂OH] which possessed the following properties: boiling range, 189–191.5°C.; specific gravity at 20°C., 0.8288; refractive index at 20°C., 1.4332; melting point of 3,5-dinitrobenzoate, 60.5°C.; melting point of 3-nitrophthalate, 124.0°C.

The condensation of formaldehyde with the C₆–C₉ tertiary olefins obtained from the polymerization of propylene or isobutylene offers a means of preparing C₇–C₁₀ primary alcohols for use in plasticizer or synthetic lubricant formulations. Hydrogenation of the resulting unsaturated alcohol would permit the synthesis of a saturated alcohol whose structure would be similar to that obtained from a tertiary olefin *via* the “oxo” reaction.

Unsaturated acetates have also been prepared by heating aliphatic olefins with paraformaldehyde in the presence of glacial acetic acid but in the absence of an added catalyst (23c, 48, 82).

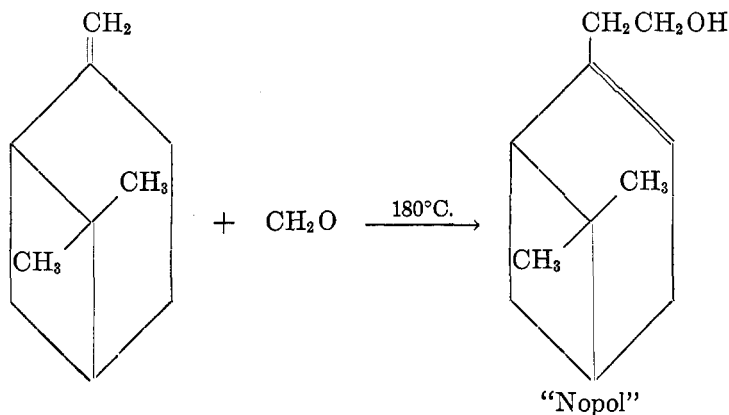
The condensation of diisobutylene with paraformaldehyde in the presence of acetic anhydride and an excess of glacial acetic acid at 200°C. gave a 55–60 per cent yield of the acetate of 2-(2,2-dimethylpropyl)-1-buten-4-ol.

Certain terpenes can be condensed with paraformaldehyde at elevated temperatures to form bicyclic primary alcohols. Kriewitz (74) synthesized a C₁₁H₁₈O alcohol by heating pinene, paraformaldehyde, and ethyl alcohol in a sealed tube for 12 hr. at 170–175°C. Dipentene when treated similarly at 190–195°C. yielded a condensation product of the same empirical formula.

Bain (15, 16) has made a careful study of the condensation of β-pinene with paraformaldehyde to form 6,6-dimethylbicyclo[1.1.3]hept-2-ene-2-ethanol which he named “Nopol” (see also reference 137a).

When the reaction was carried out in ethanol for 12 hr. at 180–200°C., a 51 per cent yield of “Nopol” was obtained. Reaction of the β-pinene and the aldehyde at 100–200°C. in the presence of zinc chloride resulted in a 57 per cent

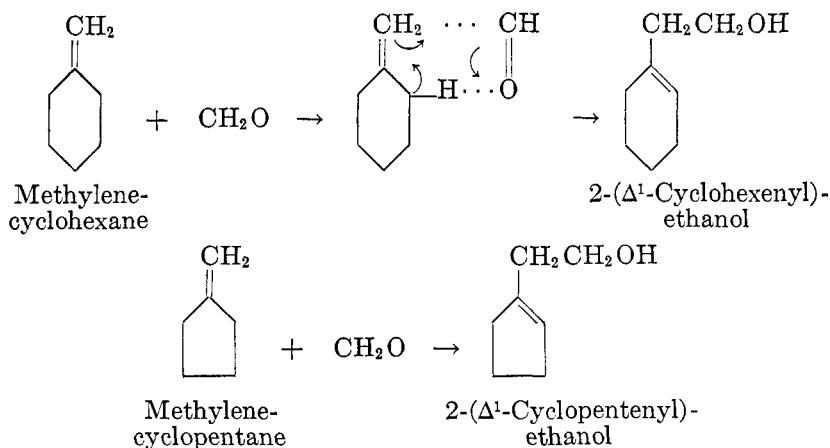
yield of alcohol. The highest yield (95 per cent) was obtained, however, when a mixture of very pure β -pinene and paraformaldehyde was heated in an autoclave at 180°C. for 4 hr. The addition of glacial acetic acid to the reaction mixture resulted in the formation of "Nopol" acetate. The physical properties of the



alcohol and its esters were determined and their conversion to other compounds by hydrogenation, esterification, oxidation, and pyrolysis was studied. It is interesting to note that no pure alcohol could be isolated from the product of the thermal reaction of α -pinene with paraformaldehyde.

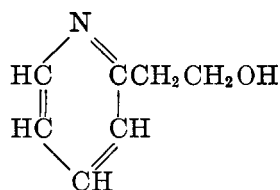
Pyrolysis of "Nopol" at 350–450°C. does not result in dehydration but in the formation of an unsaturated acyclic primary alcohol having the conjugated triene structure of alloöcimene (17). "Nopol" can be dehydrated by refluxing with potassium hydroxide and phenyl- β -naphthylamine in diethyleneglycol diethyl ether. A 75 per cent yield of "Nopadiene" was obtained in this way (73).

Arnold (3, 4) has found that similar reactions occur with methylenecyclohexane and methylenecyclopentane. A 77 per cent yield of 2-(Δ^1 -cyclohexenyl)-ethanol was obtained by heating methylenecyclohexane and paraformaldehyde at 200–205°C. for 4 hr. Under similar conditions, a 38 per cent yield of unsat-



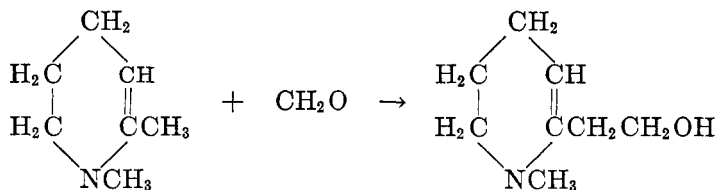
urated alcohol was obtained from methylenecyclopentane. Arnold regards the formation of the adduct as occurring *via* a transient cyclic complex which is formed by a simultaneous attack of the aldehyde at an α -methylene group and a carbon atom at the double bond which is furthest removed from this methylene group. A shift of the double bond is a necessary consequence of this mechanism.

Early literature references also exist on the condensation of formaldehyde with unsaturated compounds other than hydrocarbons. Ladenburg (79, 80) heated 2-methylpyridine (α -picoline) with formalin for 10 hr. at 120°C. to form 2-(1-pyridyl)ethanol.



2-(1-Pyridyl)ethanol

In a similar manner, Lipp (83) caused methyltetrahydropicoline to react with formalin.

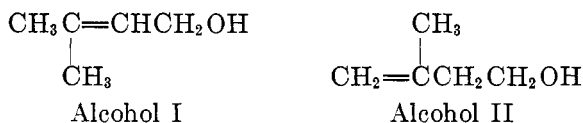


There is some question as to the actual structure of the alcohol which was formed.

Thermal condensation of formaldehyde with allyl cyanide occurs primarily at the active methylene group. After 4 hr. at 150°C., a 28 per cent yield of 2-hydroxy-methyl-3-butenitrile and a 55 per cent yield of the dimer of its dehydration product, 2-cyanobutadiene, were obtained (126a).

C. MECHANISM OF ALCOHOL FORMATION

When the preparation of unsaturated alcohols by the condensation of olefins with formaldehyde in the presence of anhydrous metallic halides was first studied by the authors, it was assumed that the reaction between isobutylene and formaldehyde could result in the formation of either one of the following $\text{C}_5\text{H}_{10}\text{O}$ unsaturated alcohols:



Later experiments indicated that Alcohol I did not have the correct structure for the isobutylene-formaldehyde reaction product. For example, Groll and

Tamele (53) have shown that β -unsaturated alcohols can be readily isomerized to the corresponding saturated aldehydes by refluxing with dilute acids. Since Alcohol I, indicated above, is a β -unsaturated alcohol, it would be expected to isomerize to the aldehyde under these conditions. However, instead of this isomerization taking place in the presence of the dilute acid, the alcohol from the isobutylene-formaldehyde condensation was dehydrated to isoprene, a fact which suggests that the condensation product was not a β -unsaturated alcohol and consequently could not have structure I.

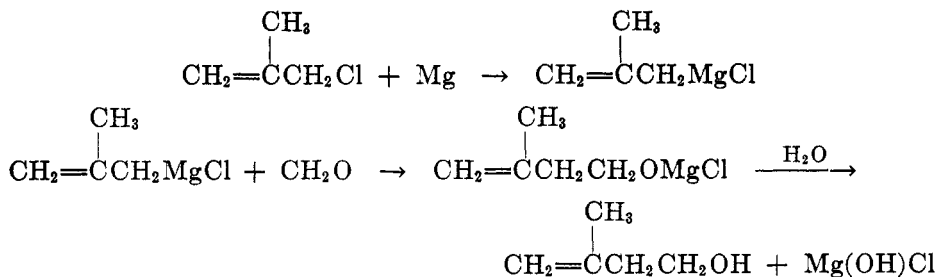
TABLE 10

Comparison of the alcohol obtained from isobutylene and formaldehyde with other alcohols

PHYSICAL PROPERTIES	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{CHCH}_2\text{OH} \end{array}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{CCH}_2\text{CH}_2\text{OH} \end{array}$	ALCOHOL OBTAINED FROM ISOBUTYLENE AND FORMALDEHYDE
Boiling point of alcohol . . .	140°C. (137–139°C.)	130°C.	130.2°C./768 mm.
Boiling point of acetate . . .	152°C.		143–144°C.
Melting point of urethan . . .	65°C.	33°C.	33°C.
Specific gravity at 20°C. . . .	0.863	0.8580	0.8534
Refractive index at 20°C. . . .		1.4329*	1.4347*

* The difference is due to the fact that neither alcohol was absolutely pure.

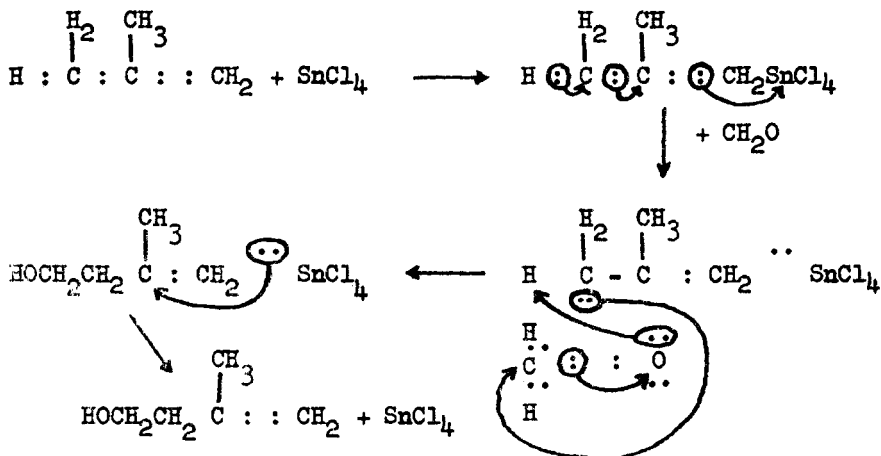
In order to establish definitely the structure of the unknown alcohol, Alcohol II was synthesized by means of the reaction between methallylmagnesium chloride and formaldehyde as follows:



Owing to the difficulty of preparing a Grignard reagent from methallyl chloride because of its olefinic bond, and the difficulty of preventing the coupling reaction between molecules of the Grignard reagent, only a 40 per cent yield of alcohol was obtained. The properties of the alcohol were determined and compared with those reported by Courtot (27) and Groll (53) for Alcohol I and with the properties of the isobutylene-formaldehyde condensation product. The physical properties shown in table 10 demonstrate definitely that the alcohol obtained from isobutylene and formaldehyde is 2-methyl-1-buten-4-ol (Alcohol II). The ethyl ether of the alcohol prepared from isobutylene and formaldehyde boiled at 115–116°C., the formal at 213°C., and the benzoate at 135–151°C./18 mm.

The structure of the product alcohol having been established, it appears that the condensation of isobutylene with formaldehyde under substantially anhy-

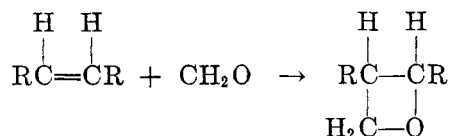
drous conditions in the presence of stannic chloride in an aprotic solvent proceeds as follows:



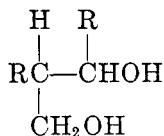
This mechanism has also been reviewed by Baker (21).

VI. 1,3-GLYCOL ESTERS

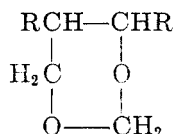
If the reaction of olefins or other unsaturated compounds is carried out at temperatures below 50°C. in the presence of an anhydrous organic acid and concentrated sulfuric acid as the catalyst, diesters of 1,3-glycols are produced. This reaction was discovered by Prins (127, 128, 129), who studied the condensation of formaldehyde with styrene, anethole, camphene, pinene, limonene, and cedrene under the above-mentioned conditions. It was assumed by Prins that the reaction began with the addition of formaldehyde across the double bond to form an epoxide as follows:



This epoxide could then add water to form a 1,3-glycol,

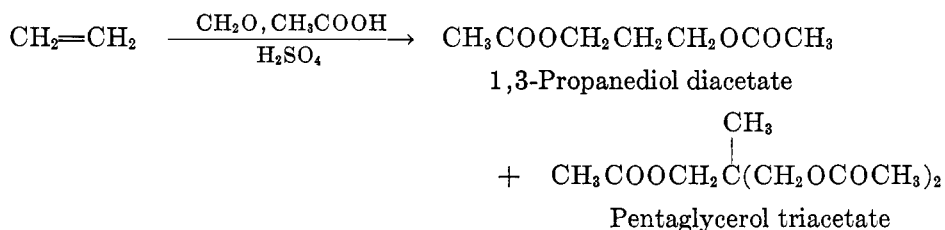


or further condense with another mole of formaldehyde to form a *m*-dioxane



The first two products (I, II) arise from an acid-catalyzed addition to the double bond. The third product (III), which is not formed by the further reaction of the glycol with formaldehyde, apparently results from the direct reaction of the hydrogen of the methyl group of propylene, activated by its conjugation with the olefinic linkage.

Many attempts have been made to condense ethylene with formaldehyde under various conditions to form 1,3-propanediol. However, because of the low order of reactivity of ethylene compared to the higher olefins, such attempts were generally unsuccessful. Baker (19, 20) and Olsen did succeed, however, in obtaining low yields of several condensation products when carrying out the reaction in the presence of glacial acetic acid and concentrated sulfuric acid. In such a system at 130–140°C. and 50–70 atm., Olsen (114, 116) found that ethylene and formaldehyde reacted to yield 1,3-propanediol diacetate and pentaglycerol triacetate:



The 1,3-propanediol diacetate could be converted into allyl acetate by distillation with sulfuric acid or by cracking in the absence of air at 565°C. The above-mentioned di- and triesters were also saponified, and 1,3-propanediol and pentaglycerol were thereby obtained. The reaction of the allyl ester with hypochlorous acid gave glycerol monochlorohydrin, which was then saponified to glycerol (118).

1,3-Glycols and their corresponding diacetates have also been prepared by the condensation of paraformaldehyde with 2-butene (142), cyclohexene (91, 113, 119, 142), octene (142), 2-methylcyclohexene (112), diisobutylene (24), and octadecene (64) in the presence of acetic and sulfuric acids. Boron trifluoride in acetic acid can likewise be employed as a catalyst to prepare diesters (2a).

The reaction between styrene and paraformaldehyde in the presence of an excess of 95 per cent formic acid has been described by Beets (23a). The formate of the glycol was not isolated, but after alcoholysis there was isolated a 51 per cent yield of 1-phenyl-1,3-propanediol and a 15 per cent yield of 4-phenyl-*m*-dioxane.

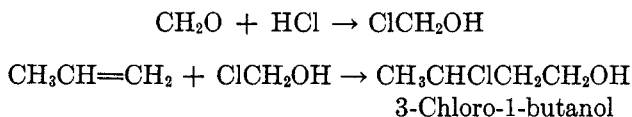
Piel (121a) has likewise found it advantageous to replace the sulfuric-acetic acid catalyst of Prins with 90 per cent formic acid. Direct pyrolysis of the glycol ester fraction gave cinnamyl formate in 64 per cent yield.

Butadiene also reacts with formaldehyde and acetic acid under similar conditions and the products, although uncharacterized, were found to be good plasticizers for cellulose ethers and esters (154).

VII. CHLOROHYDRINS AND DICHLORIDES

As indicated above, hydrochloric acid, like sulfuric acid, is a very active catalyst for the condensation of olefins and other unsaturated compounds with formaldehyde, acetaldehyde, and the like. However, such halogenated acids enter into the reaction, with the result that halohydrins, dihalides, or both are formed depending on the reaction conditions.

Fitzky (39, 71) produced γ -chloro-substituted alcohols when he condensed propylene, ethylene, or vinyl chloride at about 50°C. with formaldehyde solution which had been saturated with hydrogen chloride. The halides of elements in the second group of the periodic table (e.g., zinc chloride, calcium chloride) could also be added as auxiliary catalysts. The reaction apparently took place through the formation of an unstable intermediate (chloromethyl alcohol) which subsequently added to the olefin. With propylene, the condensation took place as follows:



The 3-chloro-1-butanol obtained in this reaction boiled at 170–180°C. It was identified by splitting off the hydrogen chloride and transforming the resulting butanol into butadiene (with dilute acid while applying pressure).

In a similar manner, ethylene (at 70 atm. pressure) was converted to 3-chloro-1-propanol ($\text{ClCH}_2\text{CH}_2\text{CH}_2\text{OH}$). The reaction of vinyl chloride with formaldehyde and hydrochloric acid formed two products: 3,3-dichloro-1-propanol ($\text{CHCl}_2\text{CH}_2\text{CH}_2\text{OH}$) and β -dichlorohydrin ($\text{CH}_2\text{ClCHClCH}_2\text{OH}$). The yields were not given.

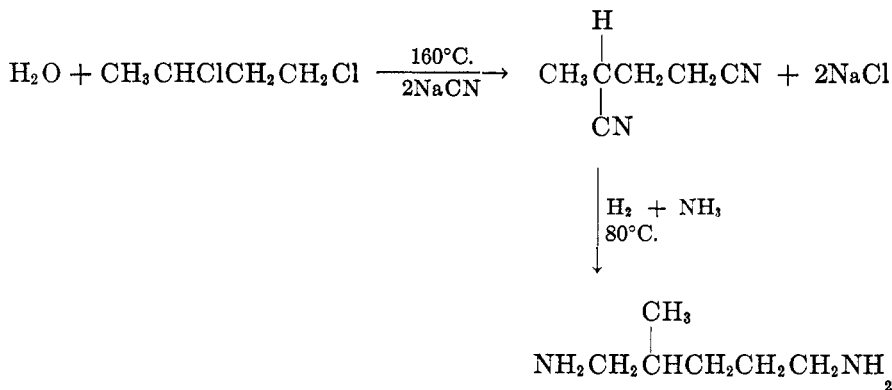
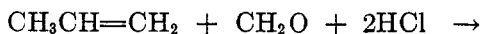
When employing Fitzky's method, Nenitzescu and Przemetzky (112) obtained 2-chlorocyclohexanemethanol and 2-chlorocyclopentanemethanol from cyclohexene and cyclopentene, respectively.

The reaction of the higher olefins (e.g., diisobutylene and "isoheptene") with formaldehyde-hydrogen chloride has also been reported (69).

The use of a catalyst mixture comprising phosphoric acid and zinc or aluminum chloride brings about the reaction of formaldehyde and hydrogen halides with polyhalogenated olefins which are slow to react or are unreactive under other conditions. When a mixture of zinc chloride, syrupy phosphoric acid, trichloroethylene, and paraformaldehyde was heated to 75–80°C., with continuous introduction of dry hydrogen chloride, Londergan (87) obtained a mixture of tetrachloropropanol and the formal of this alcohol. In order to avoid the production of byproducts, the water content of the reaction mass had to be maintained below 5 per cent by weight. The polychlorinated alcohol showed promise as a fungicide and insecticide.

As indicated above, the reaction between an olefin, formaldehyde, and hydrochloric acid under comparatively mild conditions (i.e., below 80°C. and below 450 atm.) tends to yield chlorohydrins and their corresponding formals. If, on

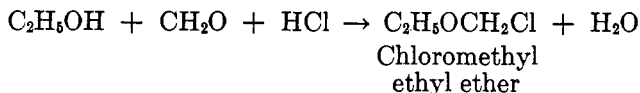
the other hand, the condensation is carried out in a silver reactor at 150–175°C. and 200–900 atm. pressure with a mole ratio of hydrogen halide to formaldehyde between 1 and 3, dihalides are formed in 35–40 per cent yield. Gresham (49) heated propylene with paraformaldehyde, concentrated hydrochloric acid, and dry hydrogen chloride at 150–161°C. under autogenous pressure (200 atm.) to yield 1,3-dichlorobutane. The dihalide was subsequently converted to the corresponding dinitrile and diamine.



Ethylene reacted similarly at 150°C. and 735–925 atm. pressure to form 1,3-dichloropropane.

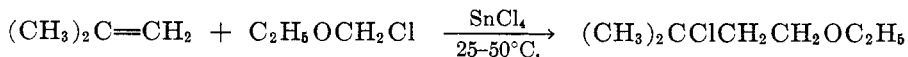
VIII. CHLORO ETHERS

The reaction of formaldehyde and alcohols with hydrogen halides results in the formation of α -halomethyl ethers. For example, chloromethyl ethyl ether is obtained on passing dry hydrogen chloride into a suspension of paraformaldehyde in absolute ethyl alcohol at 0°C., followed by drying over calcium chloride and distillation (25, 90, 152, 153).



Scott (138) has found that such α -chloromethyl ethers can be condensed with olefins at about 25–80°C. in the presence of the chlorides of bismuth, antimony, tin, zinc, iron, or aluminum.

The following reaction occurs between isobutylene and chloromethyl ethyl ether in the presence of anhydrous stannic chloride as the catalyst and chloroform as the reaction solvent.



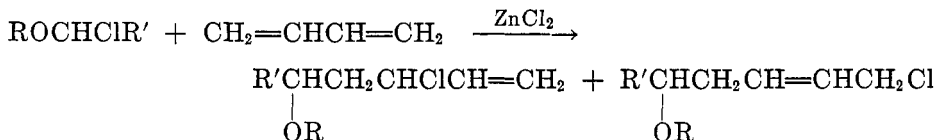
On dehydrohalogenation, such chloro ethers are converted to unsaturated ethers.

The reaction of monochloromethyl ether with propylene, amylene, and ethyl-

ene results in the formation of chlorobutyl methyl ether, chlorohexyl methyl ether, and γ -chloropropyl methyl ether, respectively.

In the above cases, the olefins reacted with preformed α -chloromethyl ethers. However, olefins can be condensed directly with aldehydes, alcohols, and hydrogen chloride, whereby the α -chloromethyl ether is formed *in situ* (146, 147).

Butadiene has likewise been condensed with various α -chloro ethers in the presence of zinc chloride at 0–40°C.; in each case a mixture of the 5-alkoxy-3-chloro-1-pentene and the 5-alkoxy-1-chloro-2-pentene was obtained in 61–86 per cent yield. The isomers had to be separated by distillation at reduced pressure, since they isomerized when heated at atmospheric pressure.



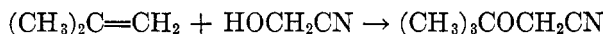
Treatment of the chlorides with boiling aqueous sodium carbonate gave unsaturated alcohols in 52–91 per cent yield (1, 36). Reaction with ammonia yielded amines.

IX. ALKOXYACETONITRILES

Formaldehyde and hydrogen cyanide combine in aqueous solution to form formaldehyde cyanohydrin (glycolonitrile) in 70–80 per cent yield (88). The following reaction occurs:



After its formation, this cyanohydrin can be condensed with tertiary olefins such as isobutylene to yield tertiary alkoxyacetoneitriles.

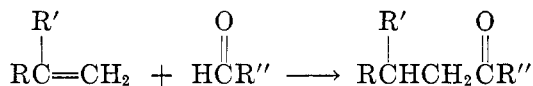


This reaction was discovered by Gresham (50), who obtained an 85 per cent yield of *tert*-butoxyacetoneitrile by the reaction of isobutylene with the cyanohydrin at 80–90°C. and 250 p.s.i. pressure in the presence of a strong inorganic acid, specifically sulfuric acid. Hydrogenation of the alkoxyacetoneitrile resulted in the formation of mono- or di(*tert*-butoxy)ethylamine.

X. KETONES

Because of its high reactivity, formaldehyde has been studied most extensively in the reactions of aldehydes with olefins and other unsaturated compounds. There is one reaction, however, in which the higher-molecular-weight aldehydes are the preferred raw materials. This involves the preparation of ketones by the peroxide-catalyzed addition of aldehydes to olefins. The ketones listed in table 11 can be obtained by condensing various olefins and aldehydes for 40–50 hr. at 70–85°C. in the presence of benzoyl peroxide as the catalyst (77, 145). Other olefinic compounds were also studied (77).

The products listed in table 11 are formed according to the general equation given below:

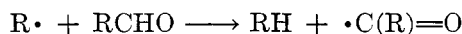
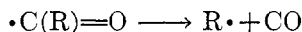
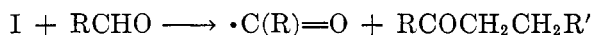
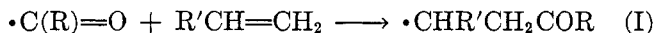
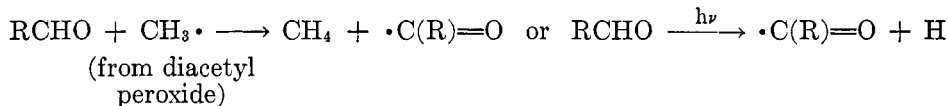


In the case of ethylene and propylene, the higher-molecular-weight byproduct ketones apparently result from the reaction of the aldehyde with dimers or trimers of the olefin, the polymers being formed *in situ*. Very low yields of ketones were obtained when olefins containing non-terminal unsaturated linkages (e.g., 2-butene, 2-octene, cyclohexene, etc.) were employed. Type I olefins are thus to be preferred.

TABLE 11
Ketones from olefins and aldehydes

OLEFIN	ALDEHYDE	PRODUCTS
Ethylene.....	Acetaldehyde	{Methyl ethyl ketone Methyl <i>n</i> -butyl ketone Methyl <i>n</i> -hexyl ketone
	<i>n</i> -Butyraldehyde	{ <i>n</i> -Propyl ethyl ketone <i>n</i> -Propyl <i>n</i> -butyl ketone
Propylene.....	Acetaldehyde	{Methyl propyl ketone Methyl hexyl ketone
	<i>n</i> -Heptaldehyde	Dihexyl ketone
Isobutylene.....	<i>n</i> -Butyraldehyde	Propyl isobutyl ketone
	Acetaldehyde	Methyl octyl ketone
1-Octene.....	<i>n</i> -Butyraldehyde	Propyl octyl ketone
	Isobutyraldehyde	Isopropyl octyl ketone
	<i>n</i> -Heptaldehyde	Hexyl octyl ketone
1-Decene.....	Acetaldehyde	Methyl decyl ketone
1-Dodecene.....	Acetaldehyde	Methyl dodecyl ketone

Kharasch, Urry, and Kuderna (72) have also studied the formation of ketones in the presence of acyl peroxides or light and have proposed the following reaction mechanism:



A less complex reaction mixture was formed when the addition of aldehydes to olefins was initiated photochemically rather than by acyl peroxides.

The best yields of ketones were obtained on adding long-chain aldehydes to long-chain type I olefins. Thus, the addition of acetaldehyde to olefins gave low yields of methyl ketones. Similarly, butyraldehyde and heptaldehyde in reacting with propylene gave low yields of propyl ketones. On the other hand, high yields of ketones were obtained when butyraldehyde or heptaldehyde was added to 1-octene (table 12).

Ladd (78) has also studied the addition of aldehydes to diolefins in the presence of dibenzoyl peroxide. At temperatures of 80–85°C., *n*-butyraldehyde reacted with isoprene to give isopentenyl propyl ketone. Likewise, 1,5-hexadiene and acetaldehyde formed hexenyl methyl ketone, while 4-vinylcyclohexene and *n*-butyraldehyde gave propyl cyclohexenylethyl ketone (77).

TABLE 12
Ketones from olefins and aldehydes

OLEFIN	ALDEHYDE	REACTION INITIATOR	PRODUCT	YIELD <i>per cent</i>
1-Octene.....	Acetaldehyde	Ultraviolet light	2-Decanone	
1-Octene.....	<i>n</i> -Butyraldehyde	Acyl peroxide	4-Dodecanone	57
1-Hexene.....	<i>n</i> -Butyraldehyde	Acyl peroxide	4-Decanone	41
Styrene.....	<i>n</i> -Butyraldehyde	Acyl peroxide	Polymer	
1-Octene.....	<i>n</i> -Butyraldehyde	Visible light	4-Dodecanone	
	Isobutyraldehyde	Acyl peroxide	Polymer	
	<i>n</i> -Heptaldehyde	Acyl peroxide	7-Pentadecanone	75
	<i>n</i> -Heptaldehyde	Visible light	7-Pentadecanone	
Cyclohexene...	<i>n</i> -Heptaldehyde	Visible light	1-Cyclohexyl-1-heptanone*	

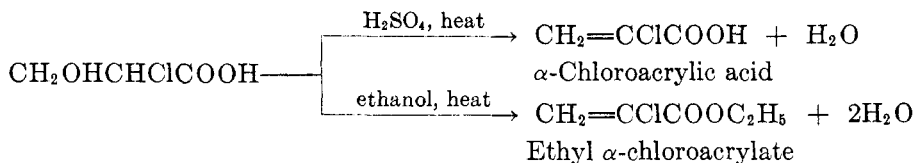
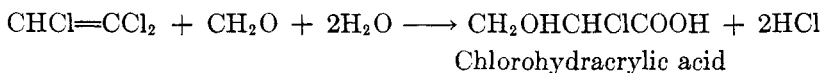
* Cyclohexyl hexyl ketone.

Vinyl acetate reacted with acetaldehyde in the presence of benzoyl peroxide at 140°C. to form condensation products of unknown composition (140). The production of polymeric materials by the condensation of ethylene with formaldehyde at 70–200°C. and 800–1000 atm. pressure has been reported by Hanford (55). The solid polymers contain ethylene:formaldehyde ratios as high as 27.

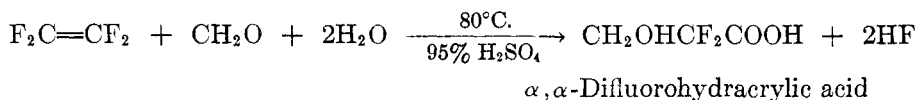
XI. HALOGENATED ACIDS AND ESTERS

As discussed in Section II, the reaction of unsaturated monohalides with formaldehyde in the presence of a dilute sulfuric acid catalyst results in the formation of halogenated *m*-dioxanes and halogenated 1,3-glycols. With polyhalogenated olefins, however, unsaturated acids are produced. This has been demonstrated by Crawford and McLeish (28), who condensed trichloroethylene with formaldehyde at 30–100°C. in the presence of sulfuric acid of at least 80 per cent concentration. Following the reaction, the product was steam distilled to obtain α -chloroacrylic acid. At least one part by weight of water must be present in the mixture for each 10 parts of 100 per cent sulfuric acid. After

condensation of the trichloroethylene with formaldehyde, alcohols can be added to the batch, with the result that the intermediate chlorohydracrylic acid is converted to esters of α -chloroacrylic acid.



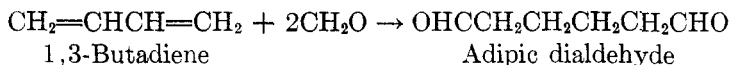
Prins (130) investigated the reaction of formaldehyde with di-, tri-, and tetrachloroethylenes under the influence of concentrated sulfuric acid. Dichloroethylene gave a resinous mass, whereas tetrachloroethylene yielded 2,2-dichlorohydracrylic acid. α, α -Difluorohydracrylic acid has likewise been synthesized by heating paraformaldehyde and oxygen-free tetrafluoroethylene at 80°C. in the presence of 95 per cent sulfuric acid. The subsequent addition of ethyl alcohol gave the corresponding ethyl ester (26, 131).



The reaction has also been applied to the preparation of acrylic acid from vinylidene chloride and formaldehyde (or a polymer thereof) in the presence of aqueous sulfuric acid (94).

XII. DIALDEHYDES

Although the reported data are somewhat limited, Dreyfus (31) claims that the reaction of conjugated and non-conjugated diolefins with formaldehyde results in the formation of dialdehydes. No catalyst is employed. When 2 moles of formaldehyde (as 40 per cent aqueous solution) were stirred with 1 mole of 1,5-hexadiene at 50–80°C. until no more reaction occurred, suberic dialdehyde was formed. Under the same conditions, butadiene and formaldehyde yielded adipic dialdehyde.

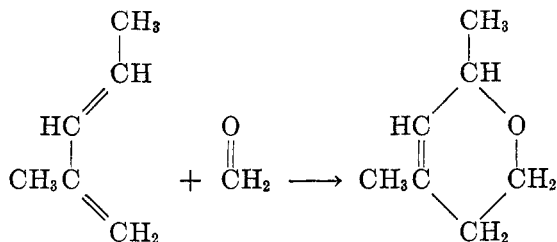


XIII. HYDROPYRANS

The condensation of diolefins or unsaturated alcohols, esters, or acids with aldehydes permits the formation of dihydro- or tetrahydropyrans and their hydroxylated derivatives (see also Section II, A, 4).

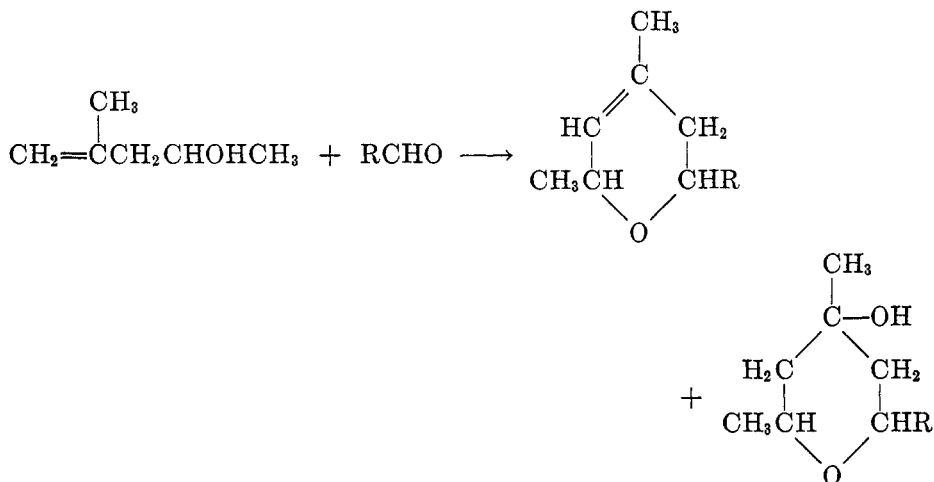
Gresham and Steadman (52) have reported an unusual example of the Diels-Alder reaction in which 2 moles of 2-methyl-1,3-pentadiene and 1 mole of

formaldehyde (as paraformaldehyde) reacted at 185°C. to give a 61 per cent yield of 2,4-dimethyl-5,6-dihydro-1,2-pyran as follows:



Butadiene and piperylene did not react to form pyrans under the above uncatalyzed conditions. However, in the presence of sulfuric acid at 0–10°C., butadiene and methylal condensed to form 3-methoxy-4-(methoxymethyl)tetrahydropyran (13 per cent yield), 3,5-dimethoxy-1-pentene (12 per cent yield), 1,5-dimethoxy-2-pentene (20 per cent yield), and 1,2,5-trimethoxy-3-(methoxymethyl)pentane (3 per cent yield) (29).

On adding a solution of concentrated sulfuric acid in 4-methyl-4-penten-2-ol to acetaldehyde at 10–12°C., Williams and Ballard (155) obtained a 40 per cent yield of 2,4,6-trimethyl-5,6-dihydro-1,2-pyran and a 51 per cent yield of 2,4,6-trimethyl-4-tetrahydropyranol. Other aldehydes also reacted according to the following equation:

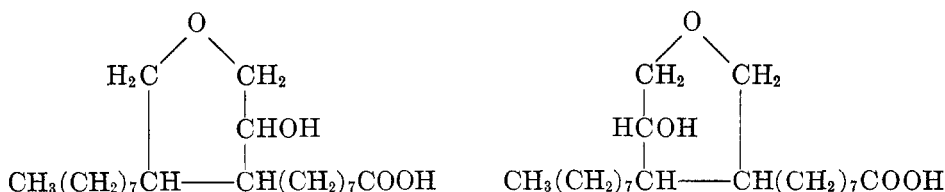


Examples were not given of the use of alternate unsaturated alcohols.

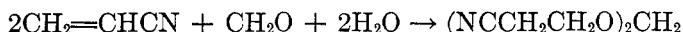
Olsen and Aksnes (117) heated 1,3-butanediol diacetate with *p*-toluenesulfonic acid and obtained 3-buten-1-ol. After esterification of the alcohol with acetic acid, the 3-buten-1-ol acetate was refluxed with paraformaldehyde in acetic acid-sulfuric acid to form 4-acetyxtetrahydropyran, 1,3,5-pentanetriol triacetate, and its 1,3-methylene ether. 3-Buten-1-ol also reacts with formaldehyde.

Under similar conditions allyl acetate reacted (62 per cent) with formaldehyde, and 3-acetoxytetrahydrofuran was obtained. The byproducts were 1,2,4-butanetriol 2,4-methylene ether-1-monoacetate and 1,2,4-butanetriol triacetate. When heated with *p*-toluenesulfonic acid, the triacetate was converted into crotonaldehyde directly and into 3-butene-1,2-diol indirectly through 3-acetoxytetrahydrofuran (115).

Substituted tetrahydropyrans were prepared by condensing oleic acid with formaldehyde in the presence of an 80 per cent sulfuric acid solution for 4 days at 40–50°C. A 4 per cent yield of a solid product (C₂₁H₄₀O₄) was obtained which appeared to be a mixture of the following (122):



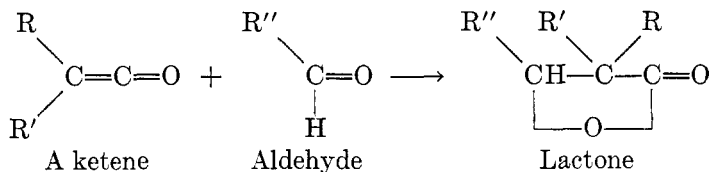
Walker (151) has treated acrylonitrile with formaldehyde in aqueous medium (at least 1 mole of water per mole of formaldehyde) in the presence of an alkaline catalyst (e.g., 0.5 per cent of sodium hydroxide) under reflux to yield the formal and hemiformal of ethylene cyanohydrin as follows:



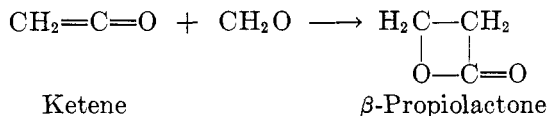
Olefins do not undergo an alkaline-catalyzed reaction with aldehydes.

XIV. β -LACTONES

Küng (75) has developed a process for synthesizing lactones of β -hydroxycarboxylic acids which involves condensing a ketene with a saturated aldehyde at a temperature below 25°C. in the presence of a Friedel-Crafts type of catalyst. The reaction occurs as follows:



This synthesis has also been studied by Steadman and Breyfogle (144), who prepared β -propiolactone through the reaction of ketene and anhydrous formaldehyde. A stream of gaseous anhydrous formaldehyde was mixed with a stream



of gaseous ketene (from acetone pyrolysis) and passed below the surface of a stirred catalyst solution containing 1 part by weight of aluminum chloride and

0.1 part by weight of zinc chloride dissolved in 200 parts of β -propiolactone (or acetone). The catalyst was destroyed with alkali and the reaction mixture distilled to recover the β -propiolactone (b.p. 49–50°C./10 mm.). The above catalyst mixture is claimed to produce improved yields of lactone over those obtained with other Friedel–Crafts catalysts.

β -Lactones containing more than eight carbon atoms have been prepared by Barnett (22). A saturated aliphatic aldehyde containing at least seven carbon atoms was condensed with an aliphatic ketene at 0–200°C. in the presence of a peroxide catalyst. Pelargonyl β -lactone was thus formed when heptaldehyde reacted with an equimolar portion of ketene in the presence of 1–5 mole per cent (on total reactants) of benzoyl peroxide at about 85°C. The yield of saponifiable reaction product was 60 per cent (based on aldehyde charged). In the absence of the peroxide catalyst, the yield was only 16 per cent; this low yield was attributed to the presence of a small amount of peroxide in the feed stocks.

The authors wish to express their appreciation to Dr. C. E. Morrell for his helpful review of the reaction mechanisms and to the Standard Oil Development Company for permission to publish some of the independent work discussed herein. The assistance of Mr. Morris D. Schoengold in the literature search is also gratefully acknowledged.

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THE CRITICAL PROPERTIES OF ELEMENTS AND COMPOUNDS—*Kenneth A. Kobe and R. Emerson Lynn, Jr.*, University of Texas, Austin, Texas.

THE THERMODYNAMIC PROPERTIES OF OXIDES AND THEIR VAPORIZATION PROCESSES—*Leo Brewer*, University of California, Berkeley, California.

REACTIONS OF ALIPHATIC ACID CHLORIDES—*Norman O. V. Sonntag*, Colgate-Palmolive-Peet Company, Jersey City, New Jersey.

RELATIONSHIPS BETWEEN ANALOGOUS ORGANIC COMPOUNDS OF SILICON AND CARBON—*Henry Gilman*, Iowa State College, Ames, Iowa, and *G. E. Dunn*, University of Manitoba, Winnipeg, Canada.

THE SPREADING OF LIQUID METALS ON SOLID SURFACES. THE SURFACE CHEMISTRY OF HIGH-ENERGY SUBSTANCES—*A. Bondi*, Shell Development Company, Emeryville, California.
