

CONVERSION OF OXYGEN DERIVATIVES OF HYDROCARBONS INTO BUTADIENE

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I. INTRODUCTION

The present study covers the production of butadiene (i.e., 1,3-butadiene) from oxygen derivatives of hydrocarbons. These derivatives are converted readily into butadiene by processes that involve one or more stages or units of

CHART I
Oxygen derivatives of hydrocarbons directly convertible into butadiene

<p style="text-align: center;">ALKANOLS</p> <p>Ethanol 2-Propanol 1-Butanol 2-Butanol 2-Methyl-1-propanol "Pentanol" ** 3-Methyl-1-butanol 2-Methyl-2-butanol 3-Chloro-1-butanol 3-Chloro-2-butanol</p>	<p style="text-align: center;">CYCLANLALKANOL</p> <p>Cyclopropylcarbinol</p> <p style="text-align: center;">CYCLANOLS</p> <p>Cyclobutanol 1-Methyl-3-cyclopentanol "Dimethylcyclopentanols" Cyclohexanol</p>	<p style="text-align: center;">DIALKYL ETHERS</p> <p>Diethyl ether Ethyl α-chloroethyl ether Ethyl β-chloroethyl ether Ethyl α-hydroxyethyl ether Ethyl β-hydroxyethyl ether Ethyl α-ethoxyethyl ether Methyl α-methoxyethyl ether γ, γ'-Dihydroxydibutyl ether γ-Chlorobutyl γ'-hydroxybutyl ether</p>	<p style="text-align: center;">EPOXYBTANES</p> <p>1,4-Epoxybutane 2,3-Epoxybutane</p> <p style="text-align: center;">DIOXANE</p> <p>4-Methyl-<i>m</i>-dioxane</p> <p style="text-align: center;">ALKANALS</p> <p>Ethanal Butanal 2-Methylpropanal 3-Hydroxybutanal (β-hydroxybutyraldehyde)</p> <p style="text-align: center;">ALKENAL</p> <p>2-Butenal (crotonaldehyde)</p>	<p style="text-align: center;">ALKANOIC ACIDS</p> <p><i>n</i>-Butyric acid Isobutyric acid Isovaleric acid</p> <p style="text-align: center;">ALKENOIC ACIDS</p> <p>Acrylic acid Oleic acid Elaidic acid Calcium $\Delta^{\beta, \gamma}$-dihydromuconate</p> <p style="text-align: center;">ALKADIENOIC ACID</p> <p>2,4-Pentadienoic acid</p> <p style="text-align: center;">MONOESTERS</p> <p>1,3-Butanediol 3-acetate 1,3-Butanediol 1-β-hydroxybutyrate 2-Buten-1-yl acetate 2-Buten-1-yl trichloroacetate</p> <p style="text-align: center;">DIESTERS</p> <p>1,3-Butanediol diacetate 2,3-Butanediol diformate 2,3-Butanediol diacetate 2,3-Butanediol sulfite 1,2,3,4-Butanetetrol diformate 2,3-Butene bis(ethylxanthogenic acid)</p> <p style="text-align: center;">TRIESTERS</p> <p>Natural glycerides</p>
<p style="text-align: center;">ALKANEDIOLS</p> <p>1,3-Butanediol 1,4-Butanediol 2,3-Butanediol</p> <p style="text-align: center;">ALKANETETROL</p> <p>1,2,3,4-Butanetetrol</p> <p style="text-align: center;">ALKENOLS</p> <p>1-Propen-3-ol 1-Buten-3-ol 1-Buten-4-ol 2-Buten-1-ol</p> <p style="text-align: center;">ALKENEDIOL</p> <p>1-Butene-3,4-diol</p>	<p style="text-align: center;">HYDROXYBENZENES</p> <p>Hydroxybenzene 1,2-Dihydroxybenzene 1,3-Dihydroxybenzene 1,4-Dihydroxybenzene</p>	<p style="text-align: center;">ALKYL ALKENYL ETHERS</p> <p>Ethyl vinyl ether Methyl α-vinyl-β-iodoethyl ether Ethyl α-vinyl-β-iodoethyl ether <i>n</i>-Propyl α-vinyl-β-iodoethyl ether Isobutyl α-vinyl-β-iodoethyl ether</p> <p style="text-align: center;">DIALKENYL ETHERS</p> <p>Divinyl ether Di(2-buten-1-yl) ether</p>	<p style="text-align: center;">ALKANOIC ACIDS</p> <p><i>n</i>-Butyric acid Isobutyric acid Isovaleric acid</p> <p style="text-align: center;">ALKENOIC ACIDS</p> <p>Acrylic acid Oleic acid Elaidic acid Calcium $\Delta^{\beta, \gamma}$-dihydromuconate</p> <p style="text-align: center;">ALKADIENOIC ACID</p> <p>2,4-Pentadienoic acid</p> <p style="text-align: center;">MONOESTERS</p> <p>1,3-Butanediol 3-acetate 1,3-Butanediol 1-β-hydroxybutyrate 2-Buten-1-yl acetate 2-Buten-1-yl trichloroacetate</p> <p style="text-align: center;">DIESTERS</p> <p>1,3-Butanediol diacetate 2,3-Butanediol diformate 2,3-Butanediol diacetate 2,3-Butanediol sulfite 1,2,3,4-Butanetetrol diformate 2,3-Butene bis(ethylxanthogenic acid)</p> <p style="text-align: center;">TRIESTERS</p> <p>Natural glycerides</p>	

* "Amylalkohol" in original specification.

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alcohol charged (77). Lebedev claimed that a process utilizing a mixture of zinc oxide and alumina at 400°C. (86, 87) gave an 18 per cent yield of butadiene, and a similar process using a zinc oxide and aluminum hydrosilicate catalyst at 410°C. (88) gave a 15 per cent yield. He also reported a yield of 15 per cent of butadiene from ethanol which was passed at 410°C. through a quartz tube containing zinc dust and floridin (fuller's earth) (92). Subsequent workers generally claimed higher yields but did not disclose the composition of the catalysts used (38, 43, 83, 89, 94, 95, 99, 100, 108, 150, 167, 168, 170).

Table 1 shows the progress made by the butadiene synthetic rubber industry in the U.S.S.R. (37, 170).

Synthetic rubber production in the United States depends largely upon butadiene (derived from ethanol and petroleum fractions) and styrene, which were used for the production of 765,000 long tons of Buna S in the year 1944 (table 2).

TABLE 1
The U.S.S.R. synthetic rubber industry

YEAR	SYNTHETIC RUBBER PRODUCTION	BUTADIENE FROM ETHANOL		SYNTHETIC RUBBER IN PER CENT OF TOTAL NEW RUBBER USED
		<i>per cent by weight</i>	<i>per cent of theory</i>	
	<i>long tons</i>			
1933	5,600			4.7
1934	12,000			18.5
1935	20,000	23.5	40	40.6
1936	24,000			54.1
1937	50,000			73.1
1938	90,000	32.5	56	
1939 (early)		36.3	62	
1939 (late)		41	70	

According to Gilliland (42):

"In the alcohol process, grain alcohol or ethyl alcohol from other sources is used to produce a butadiene fraction of relatively high purity. . . . This type of operation is carried out in three plants designed for the Government program by the Carbide and Carbon Chemical Corporation. These plants will produce 220,000 short tons of butadiene per year. The first, located at Institute, West Virginia, and having a rated annual capacity of 80,000 short tons, has been completed for several months and is operating very successfully. The two other plants, located at Kobuta, Pennsylvania, and Louisville, Kentucky, and having rated annual capacities of 80,000 and 60,000 short tons, respectively, are now producing butadiene. . . .

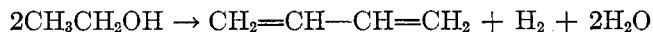
"A different type of process for producing butadiene from alcohol is being constructed by the Bigler Chemical Company, employing the so-called Publicker, or Szukiewicz, process. This alcohol process apparently is fairly similar to the method employed by the Russians for the production of essentially all their butadiene.

"These alcohol processes produce from two to two and a half pounds of butadiene per gallon of 95 percent alcohol."

The quoted yield of butadiene is equivalent to 32-40 per cent by weight based on absolute alcohol.

(b) Lebedev's process

The "ideal" course of butadiene production from ethanol *per se* is given by the following over-all equation:

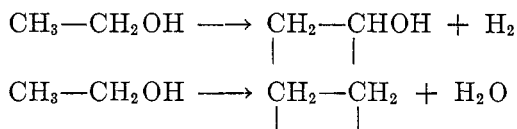


A catalyst mixture having a dehydrogenating component (A) and a dehydrating component (B) is specified. The present authors, however, are of the opinion that an individual catalyst with dehydrogenating and dehydrating properties would function in a similar manner. Lebedev (89) studied the effect of varying the catalyst composition from pure component A to pure component B and concluded that butadiene is formed from active forms of ethenol and of ethene. This theory appears unlikely when viewed in the light of data on ethanol and

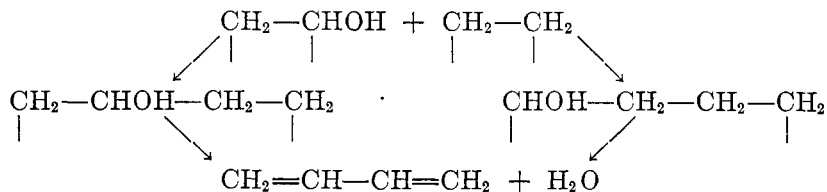
TABLE 2
Production of synthetic rubber in the United States (18)

RUBBER	ACTUAL PRODUCTION 1943	ESTIMATED PRODUCTION 1944
	<i>long tons</i>	<i>long tons</i>
Buna S.....	184,781	765,000
Butyl.....	1,373	26,200
Neoprene.....	33,603	53,200
Buna N.....	14,487	24,500
Total synthetic.....	234,244	868,900

ethanal condensation. The requisite active forms (divalent radicals) were considered to develop through the dehydrogenation and dehydration of ethanol:



Reaction of active forms of ethenol with those of ethene, followed by dehydration of the two intermediates so formed, was considered to give butadiene:



The foregoing formulation was based mainly on phenomena observed in the catalysis of ethanol over various mixtures of components A and B. Gradual addition of the dehydrating component B to dehydrogenating component A was attended by a rapid increase in the amount of butadiene to a maximum value,

corresponding to 25 per cent of B, followed by a rapid decrease to zero (see figure 1).

Lebedev pointed out that the amount of by-product ethanal was sharply diminished almost in proportion to the increase in butadiene content. Corresponding to the maximum on the butadiene curve, there was a sharply defined turn on the ethanal curve, indicating a connection between the processes of butadiene and ethanal formation, and a sharp break in the ethene curve. The content of butadiene diminished rapidly and that of ethene increased markedly as the catalyst composition approached that of the pure B component.

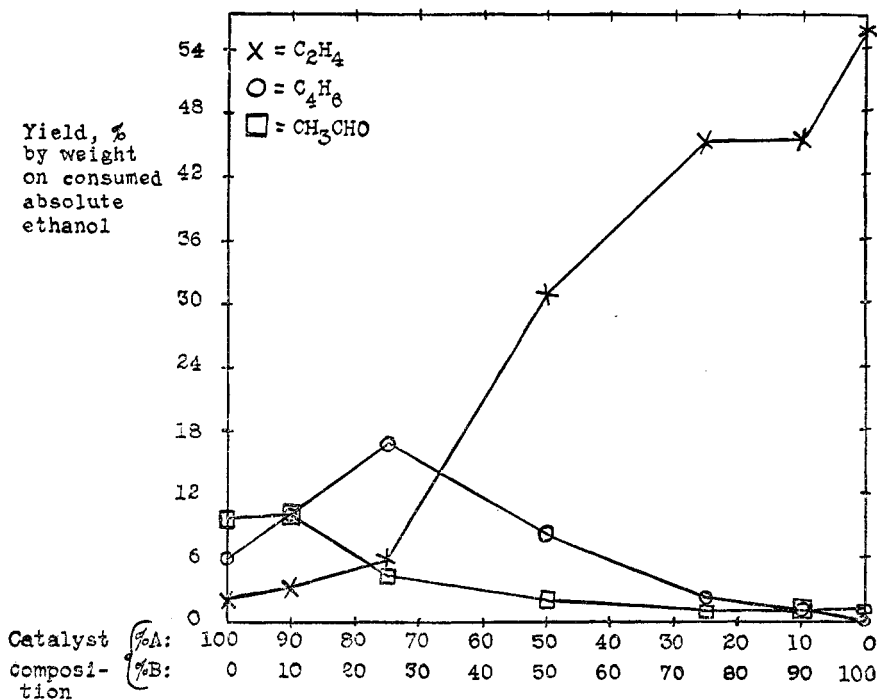


FIG. 1

Lebedev believed that

the reactions of formation of ethanal, ethene and butadiene are connected into a single system, and the assumption . . . highly plausible that butadiene is formed at the expense of the molecules of ethanal and ethene, but during a certain phase of the process preceding the completion of the reaction of formation of these molecules.

In support of the foregoing thesis, tabular and corresponding graphical data were presented covering the conversion of 90 per cent by volume ethanol at 435–445°C. over catalysts containing 0, 10, 25, 50, 75, 90, or 100 per cent of an undisclosed dehydrating component (table 3).

Balandin (1, 2) has applied his multiplet theory of catalysis to Lebedev's reaction and has concluded that the existence of ethenol radicals is impossible

on the basis of energy considerations. According to Balandin, ethanol is first dehydrogenated to ethanal; the latter condenses with ethanol to form butanediol, which loses two molecules of water to form butadiene.

Ostromyslenskii discounted a union between ethene and ethanal (127):

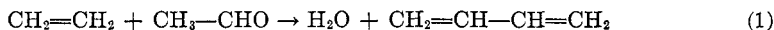
This peculiar reaction [condensation of different alcohols with aldehydes accompanied by elimination of two molecules of water] was first observed in September, 1911. At that time, in private correspondence with O. G. Filippov concerning the new method by which he succeeded in preparing butadiene-1,3, the author indicated its preparation by dehydration of butanediol-1,3 and by condensation of ethene with ethanal. In the last-mentioned

TABLE 3

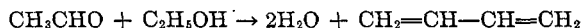
Conversion of ethanol into butadiene at 435-445°C. and approximately atmospheric pressure

	COMPOSITION OF THE CATALYST							
	100% A 0% B	90% A 10% B	75% A 25% B	50% A 50% B	25% A 75% B	10% A 90% B	0% A 100% B	
Grams of ethanol (90% by volume) passed.....	2800	2850	2800	2750	2900	2950	2800	
Per cent of ethanol (90% by volume) recovered.....	68.4	70.5	59.3	25.6	6.9	6.8	0.0	
Per cent of ethanol (90% by volume) consumed.....	31.6	29.5	40.7	74.4	93.1	93.2	100	
Grams of condensate obtained....	2650	2600	2450	1900	1500	1550	1400	
Liters of gas obtained.....	252	230	342	731	1021	1060	1193	
Composition of the gas in per cent by volume	C ₂ H _{2n}	20.2	35.5	43.5	84.5	95.5	99.2	98.0
	H ₂	66.0	60.3	52.6	12.8	3.9	0.45	1.75
	CO.....	4.1	0.28	0.64	0.41	0.0	0.0	0.0
	CO ₂	6.35	3.35	1.92	0.61	0.91	0.0	0.0
	CH ₄	1.58	0.0	0.42	0.40	0.0	0.0	0.0
Grams of butadiene contained in 1 liter of gas.....	0.18	0.32	0.50	0.20	0.05	0.023	0.00	
Yield of products in per cent by weight on con- sumed absolute ethanol	ethene.....	2.25	3.08	5.85	31.0	45.3	45.5	55.7
	ether.....	4.4	7.13	7.25	3.52	0.69	0.52	0.00
	ethanal.....	9.65	10.02	4.36	1.95	1.15	0.89	0.7
	hydrogen.....	1.72	1.57	1.59	0.45	0.14	0.018	0.07
	butadiene....	5.8	10.1	16.6	8.2	2.26	0.99	0.00

case, the author assumed that when a mixture of ethanal and ethanol acts on alumina, the ethanol is first converted into ethene, which further reacts as follows:



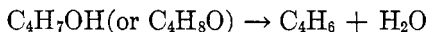
This assumption was quite plausible in view of V. N. Ipatieff's reaction. O. G. Filippov naturally understood the author's communication literally, and replied that he also observed formation of butadiene-1,3 under the action of a mixture of ethanal and ethene on alumina. Thus, O. G. Filippov observed the reaction (1) given above, which, incidentally, the present author so far did not succeed in repeating. Furthermore, in October, 1911, O. G. Filippov definitely stressed in his reply that in his opinion, formation of butadiene-1,3 from a mixture of ethanol and ethanal is impossible. Thus, the reaction



was first observed by the author.

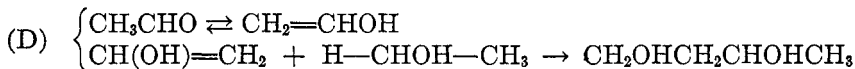
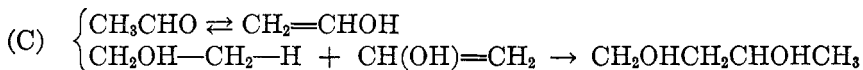
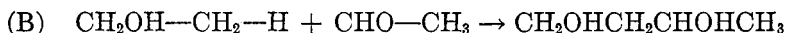
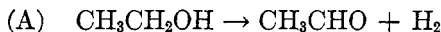
Ostromyslenskii's earlier view, however, was that a mixture of ethene and ethanal may give higher yields of butadiene than does ethanol plus ethanal (133).

The present authors consider the probable function of the dehydration component in the catalyst mixture used in ethanol conversion to be the dehydration of two consecutive intermediary products, i.e., a butanediol and either a butenol or an epoxybutane (see sections on alkanediols, alkenols, and epoxybutanes):

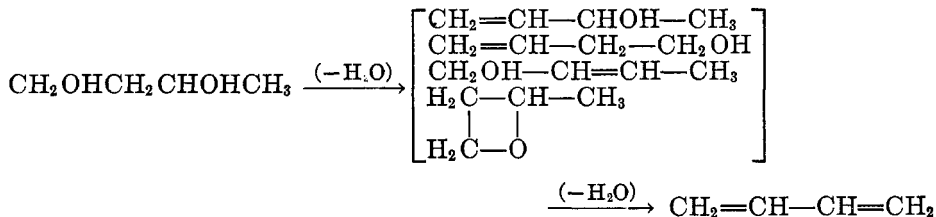


The intermediates to be considered in theories discounting the rôle of ethene include: 1,3- or 1,4- or 2,3-butanediol, 1-buten-3(or 4)-ol, 2-buten-1-ol, 1,3- or 1,4- or 2,3-epoxybutane, ethyl α -hydroxyethyl ether, ethyl α -ethoxyethyl ether, and ethyl vinyl ether. Theoretical formulation is restricted because of unknown rôles of tautomerization and catalytic isomerization among the several butenols *under the conditions* of Lebedev's process. Moreover, the actual or theoretical reaction velocities, activation energies, and heats of reaction for the initial, intermediary, and final steps of Lebedev's process are unknown or unreported.

Several theories can be formulated in place of Lebedev's explanation. The simplest explanation that the authors have devised is dehydrogenation (A) of ethanol, followed by conversion (B, C, or D) into 1,3-butanediol:

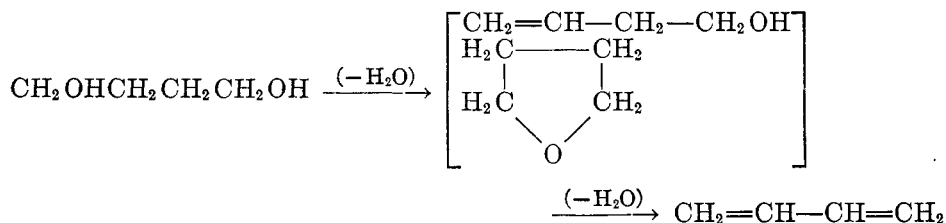
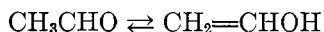
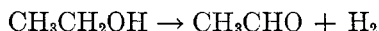


1,3-Butanediol would form 1-buten-3(or 4)-ol, 2-buten-1-ol, or 1,3-epoxybutane, and these, considering the three sources of butanediol and its four monodehydration products, make possible twelve reaction paths, each of which could produce butadiene:



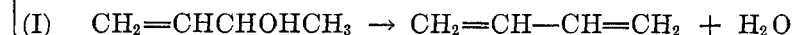
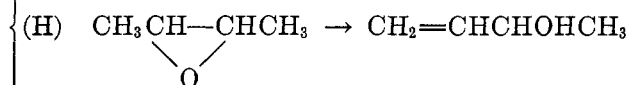
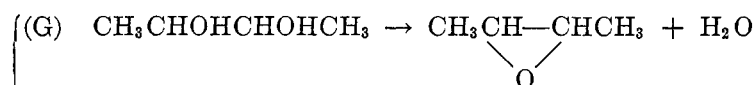
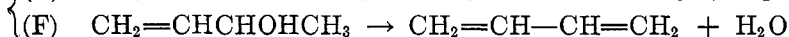
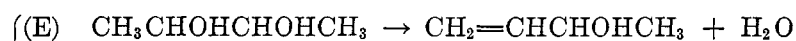
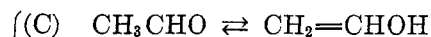
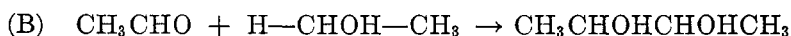
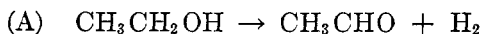
The three reaction paths involving 2-buten-1-ol are related to Ostromyslenskii's explanation of the ethanol and ethanal condensation (page 73), but his intermediary steps are purposely omitted.

Another explanation suggested by the present authors covers conversion through 1,4-butanediol:



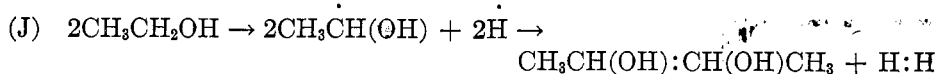
The 1,4-butanediol would form 1-buten-4-ol and 1,4-epoxybutane. Both of these monodehydration intermediates yield butadiene.

The authors postulate also four sequences of reactions (A + B + E + F; A + B + G + H + I; A + C + D + E + F; and A + C + D + G + H + I) proceeding via 2,3-butanediol:

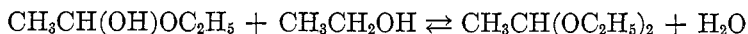
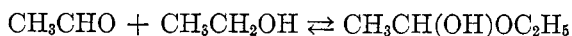
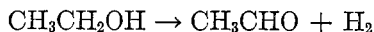


Reactions B and D utilize the keto and enol forms of ethanal, respectively. The final dehydration in all cases is that of 1-buten-3-ol. Since reactions A and B together require two molecular proportions of ethanol to form but one proportion each of 2,3-butanediol and hydrogen, it seems reasonable to include an

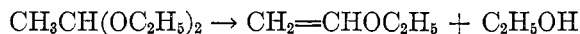
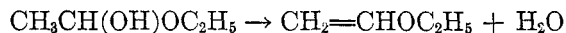
alternative pinaconic type of dehydrogenation to the butanediol rather than to ethanal:



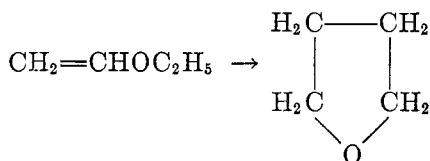
Finally, the authors consider the possibility of hemiacetal and acetal formation in the conversion of ethanol:



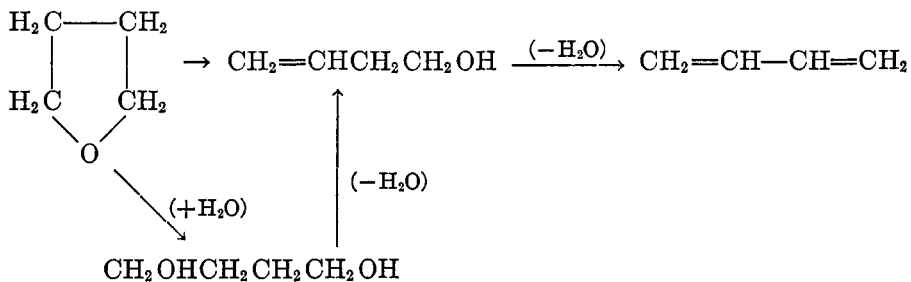
Dehydration rather than reversion of the hemiacetal (i.e., ethyl α -hydroxyethyl ether) and a facile deethanolation (128) of the true acetal would furnish ethyl vinyl ether:



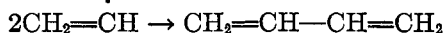
Cyclization of the ether would provide a chain of four methylene groups closed about the oxygen atom:



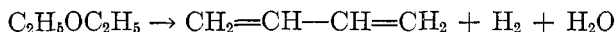
The 1,4-epoxybutane so formed would probably yield butadiene upon isomerization to and dehydration through a 1-buten-4-ol stage and also upon hydration to 1,4-butanediol, followed by an identical stage of dehydration:



In lieu of cyclization, thermal scission of ethyl vinyl ether to form free vinyl radicals can be considered. Union of vinyl radicals through direct electronic coupling and conjugation of double bonds would yield butadiene, formerly called "divinyl":

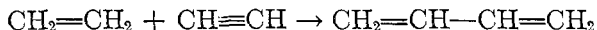


Ipatieff demonstrated that ethanol forms butadiene over heated powdered aluminum (75, 76). At his suggestion, Gdanovitch continued the study of this reaction (39). The explanation finally accepted was formation of diethyl ether over the alumina coating always present on metallic aluminum, followed by conversion of ether into butadiene over the free metal (39, 74):



Filippov, also working under the direction of Ipatieff, investigated the aluminum-catalyzed reaction, finding that diethyl ether gives three times more butadiene than ethanol does (34).

Another theory is that of the dehydration of ethanol into ethene, catalytic dehydrogenation of the latter into ethyne, and subsequent interaction of both hydrocarbons:



In favor of this series of reactions may be cited the presence of a catalyst having dehydrating and dehydrogenating components. Against it can be mentioned the lower yields of butadiene secured from ethene and ethyne mixtures under thermal, catalytic, or electrical conditions (22, 23). The oxidized character of the many by-products (82, 96, 97, 107) in Lebedev's reaction is also against the assumption of a transient conversion of ethanol or ethene into ethyne. Any formation of butadiene from ethene and ethyne via ethanol decomposition over Lebedev-type catalysts can be ascribed to particular reaction conditions. These could be induced by the presence of surplus dehydrogenating component in the catalyst or by excessive carbon deposition because of overheating.

Table 4 contains data on the direct conversion of ethanol into butadiene.

(c) Ostromyslenskii's process

Ostromyslenskii's process is the condensation of ethanol with ethanal:



Its discoverer stated (129) that the interaction of ethanol and ethanal proceeds by formation of a

"hydroxy ether under definite conditions and that this is followed by the formation of butanediol and crotyl alcohol [2-buten-1-ol]. The latter is finally converted into butadiene-1,2 by elimination of water, and isomerization of this diolefin under the action of catalysts results in formation of butadiene-1,3:

1. $\text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{OC}_2\text{H}_5$
2. $\text{CH}_3\text{CH}(\text{OH})\text{OC}_2\text{H}_5 \rightarrow \text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{OH})$
3. $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{CH}_2(\text{OH}) \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CH}=\text{CHCH}_2(\text{OH})$
4. $\text{CH}_3\text{CH}=\text{CHCH}_2(\text{OH}) \rightarrow \text{H}_2\text{O} + \text{CH}_3\text{CH}=\text{C}=\text{CH}_2$
5. $\text{CH}_3\text{CH}=\text{C}=\text{CH}_2 \rightarrow \text{CH}_2=\text{CHCH}=\text{CH}_2$."

TABLE 4
Conversion of ethanol into butadiene

COMPOSITION OF FEED	APPARATUS AND CATALYST USED	TEMPERATURE °C.	PRESSURE <i>atm.</i>	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
Ethanol $2C_2H_5OH \rightarrow C_4H_6 + 2H_2O + H_2$	Catalyst: zinc and pumice	290-335 340-360	1 1	Yields of B were 0.12 and 0.145% by weight on feed at 290-335°C. and 340-360°C., respectively; the reactions were incomplete from the decomposition standpoint	(116)
	Catalyst: Al_2O_3	380		Yield of B was 0.0145% by weight on feed	(72)
	Glass tube charged with powdered aluminum	580-600 660-680		Yields of B were 0.85% by weight on feed	(74, 76)
	Catalyst: $Al_2O_3 + ZnO$			See patent for details; yield of B was "good"	(87)
	Catalyst: $Al_2O_3 + ZnO$	400	0.25	Yield of B was 18% by weight on feed	(86)
	The catalyst had two components (dehydrating and dehydrogenating)			See original article for details	(93)
	Quartz tube containing zinc dust and floridin			See patent for details	(91)
	Catalyst was probably $Al_2O_3 + ZnO$; pressure vessel used	410		Yield of B was 15% by weight on feed	(92)
	Quartz tube containing ZnO + aluminum hydrosilicate ($Al_2O_3 \cdot SiO_2 \cdot xH_2O$) as catalyst	Elevated 410		See patent for details	(90)
				Yield of B was 15% by weight on fully decomposed ethanol; feed was 95% ethanol	(88)

<p>Catalyst of undisclosed composition</p> <p>Quartz tube (10 mm. diameter), or copper tube (28-30 mm. diameter), or copper tube (10 cm. diameter and 1 meter long), or enamelled iron tube (10 cm. diameter and 1 meter long), or copper (?) tube (12 cm. diameter and 3.5 meters long), or six tubes in parallel (copper ? or enamelled iron?) each 10 cm. diameter and 1 meter long; in each case a catalyst was used, but its composition was not revealed</p>	<p>440-450 (28-30 mm. Cu tube) 450 (3.5 meter tube)</p>	<p>0.934 (28-30 mm. Cu tube) 0.934-0.961 (six parallel tubes)</p>	<p>Yield of B was 20-25% by weight on product</p> <p>Yield of B from the "six tubes in parallel" was about 0.5 g. per liter of exit gas; article has much data on furnace construction and on mechanical recovery of B</p>	(89)
<p>Tubes of copper, iron, enamelled iron, aluminum-coated iron, or quartz; each tube contained two-component catalyst (one component clay?)</p>	<p>435 (enamelled iron tube) 435-445 (copper or iron tube) 415-425 (aluminum-coated iron tube) 440 (quartz tube)</p>	<p>1 (iron, enamelled iron, or aluminum-coated iron tube) 0.974 (copper tube) 0.0395-0.526 (quartz tube)</p>	<p>Yield of B from copper tube was 20-23% by weight on fully decomposed ethanol; the enamelled iron tube gave a similar yield; yield of B from aluminum-coated iron tube was 20-22.4% by weight on fully decomposed ethanol; yield of B from plain iron tube was 15% by weight on fully decomposed ethanol; yield of B from quartz tube was 19.4% by weight on fully decomposed ethanol at 0.171 atmosphere pressure; article has data on and considers the significance of feed velocity coefficients, ethanol concentration, preheating of ethanol to reaction temperature, and absolute pressure</p>	(99)

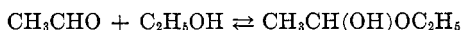
TABLE 4—Continued

COMPOSITION OF FEED	APPARATUS AND CATALYST USED	TEMPERATURE °C.	PRESSURE atm.	REMARKS (B IS 1, 3-BUTADIENE)	REFERENCES
Ethanol $2C_2H_5OH \rightarrow C_4H_6 + 2H_2O + H_2$	Empty iron tube (case A), iron tube containing glass (case B), and copper tube packed with aluminum wire (case C)	600	1?	Yields of B were 0.06, 0.11, and 0.25% by weight on feed in cases A, B, and C, respectively	(99)
	Small laboratory furnace; catalyst was used, but its composition was not disclosed	About 425		No details of process available except on by-products	(167)
	Large-scale laboratory unit; composition of catalyst not disclosed	450		With fresh catalyst, yield of B was 17.9% by weight on feed per pass and 22.3% by weight on fully decomposed feed; with fatigued catalyst, due to carbonization, yield of B was 11.2% by weight on feed per pass and 14.6% by weight on fully decomposed feed	(43)
	Copper tube, 1 meter long and 10 cm. in diameter, containing "well-selected" catalyst	450		With fatigued catalyst, due to repeated regeneration, yield of B was 6-7% by weight on feed per pass and 10-12% by weight on fully decomposed feed	(43)
	Composition of catalyst not disclosed; probably oxides	450	0.974-0.987	Yield of B was over 20% by weight on fully decomposed feed; by-products include ethene, 2-butene, acetaldehyde, diethyl ether, butanol, and hexanol	(94)
				Yield of B was 16% by weight on feed per pass and 24% by weight on fully decomposed feed	(95)

<p>Ethanol and alkanol diluents $2C_2H_5OH \rightarrow C_4H_6 + 2H_2O + H_2$</p>	<p>Silica tube, 1 meter long, in cases A, B, and C; six tubes (copper or enamelled iron) in parallel, each 1 meter long, in case D; diluents were methanol in cases A and B, 2-propanol in case C, and 1-propanol in case D; in all cases the composition of the catalyst was not disclosed, but the dehydrating and dehydrogenating components were 25% and 75%, respectively</p>	<p>425 (case A) 450 (case B) 460 (case C) 450-455 (case D)</p>	<p>0.961-0.974 (all cases)</p>	<p>Yields of B were 1.74, 2.17, 15.2, and 25.15% by weight on absolute ethanol feed per pass in cases A, B, C, and D, respectively</p>	<p>(83)</p>
<p>Ethanol and steam $2C_2H_5OH \rightarrow C_4H_6 + 2H_2O + H_2$</p>	<p>Probably a 1-meter copper tube; the catalyst had two components (one component clay?)</p>	<p>435-445?</p>	<p>1</p>	<p>Yield of B was 17.7% by weight on absolute ethanol feed per pass and 25.1% by weight on fully decomposed absolute ethanol feed</p>	<p>(99)</p>
<p>Ethanol and steam $2C_2H_5OH \rightarrow C_4H_6 + 2H_2O + H_2$</p>	<p>"Laboratory furnace"; feed mixture was "54% by volume ethanol" in cases A and B, "76% by volume ethanol" in cases C and D, and "94.5% by volume ethanol" in cases E and F; catalyst had two components (one component clay?)</p>	<p>440 (cases A, C, E) 500 (cases B, D, F)</p>	<p>1 (all cases)</p>	<p>Yields of B were 15.0, 18.8, 15.3-16.5, 18.0-19.3, 24.0, and 17.7% by weight on fully decomposed absolute ethanol feed in cases A, B, C, D, E, and F, respectively</p>	<p>(99)</p>

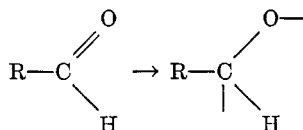
Some of the supposed intermediary products (ethyl α -hydroxyethyl ether and 1,2-butadiene) were isolated; the others were believed to be involved because of their conversion into butadiene in separate reactions. The given set of equations is partly inconsistent with the following statements of Ostromyslenskii (129):

In the general fate of the initial substances in the reaction under discussion, ethyl hydroxyethyl ether plays, apparently, no part. The reaction occurs at 360–440°, while the hydroxyether is easily decomposed on heating into aldehyde and alcohol, especially in the presence of water. . . . Thus, hydroxyether exists only during a short period of time and again virtually completely decomposes into its components. The first phase of the process is a reversible reaction:

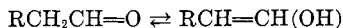


It occurs under definite conditions on mixing acetaldehyde and ethyl alcohol and is apparently not a necessary step in the process.

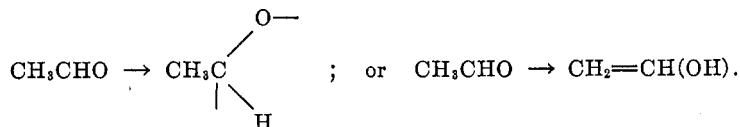
Butadiene-1,3 is actually obtained from the mixture of ethyl alcohol and acetaldehyde and not from the hydroxyether. It was found by experiment that acetaldehyde and ethyl alcohol may be charged into the reaction zone at high temperatures (360–440°) independently of each other and in the presence of water and, furthermore, that acetaldehyde may be substituted by paraldehyde. In all these cases, the reaction produces under identical conditions the same yield of butadiene-1,3 although formation of hydroxyether is entirely prevented. Decomposition of hydroxyether at high reaction temperatures (360–440°) into acetaldehyde and ethyl alcohol is accompanied by condensation of these substances through carbon atoms. Concerning the question which of the carbon atoms of the components are involved in the union, aldehyde possesses an ability to enter into different reactions and add an almost limitless number of different substances in different condensations. All these reactions are due to the aldehyde group —CHO, the carbon atom of which is without exception the most mobile and active. The aldehyde group is rearranged as follows:



The two free bonds determine the effect of each reaction. In rare cases, aldehydes react by their tautomeric form of unsaturated alcohols:

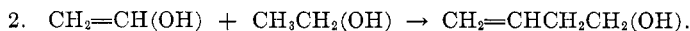
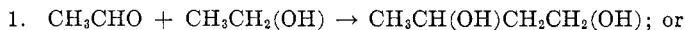


However, in these condensations, only the carbon atom of the aldehyde group is actively involved in the reaction. For this reason, it is beyond doubt that in the reaction described by the present author, condensation also occurs through the carbon atom of this group. The rearrangement of acetaldehyde in the condensation may be described by:

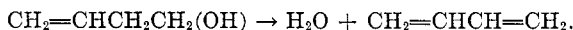


Concerning the carbon atom of ethyl alcohol participating in the union of the molecules, the author succeeded in definitely solving this question by substitution of ethyl alcohol by

one of its homologs, namely, isopropyl alcohol. . . . Experiments showed that a mixture of isopropyl alcohol and acetaldehyde gives under ordinary reaction conditions exclusively pentadiene-1,3 and in good yields (6)¹. Among the by-products of the reaction, not even traces of isoprene or dimethylallene were found. This interesting fact directly indicates that condensation of alcohols and aldehydes involves union of the carbon atom of the aldehyde group with the carbon atom of the methyl group of the alcohols. Consequently, formation of butadiene-1,3 in the author's reaction occurs either through butanediol-1,3 or buten-1-ol-4:

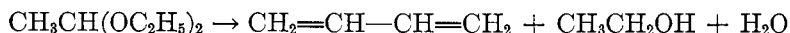
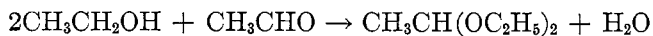


It will be shown later that in this reaction, butadiene-1,3 is formed by isomerization of methylallene; buten-1-ol-4 can give upon dehydration only butadiene-1,3 but not methylallene



The reaction 2 is therefore impossible. Condensation of acetaldehyde and ethyl alcohol occurs, consequently, through butanediol.

Ostromyslenskii and Kelbasinskii postulated a union of ethanol and ethanal to form 1,3-butanediol and 2-buten-1-ol, but admitted the possibility of acetal formation leading to production of butadiene as follows (143):



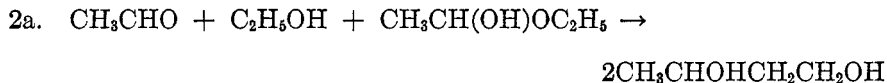
Lebedev (89) regarded Ostromyslenskii's reaction, or the direct condensation of ethanol and ethanal, as a synthesis of butadiene similar to his own process, because ethanal can be regarded as a product in ethanol conversion. Lebedev's last experiments (95) demonstrated that the addition of 10 and 20 per cent of ethene by weight to ethanol affects the amount of butadiene formed to only an insignificant extent. Ethene was evidently very slightly activated on the surface of the particular catalyst used in these tests. However, ethanal in admixture with ethanol participated extensively in the formation of butadiene.

Our discussion of Ostromyslenskii's process begins with a consideration of his statement that the condensation of ethanol and ethanal proceeds through a butanediol. The constitution of this butanediol was formulated *a priori* as 1,3-butanediol from *Zaitsev's rule* (182): the requisite hydrogen atom is split off from the least hydrogenated carbon atom. Because hydroxyl groups split off more easily from secondary than from primary alcohol groups, it follows that the 3-position hydroxyl group and one of the 2-position hydrogen atoms would be eliminated as water.

Ostromyslenskii further assumed that 1,3-butanediol does not split off two molecules of water simultaneously. Intermediary formation of 2-buten-1-ol was given as the first of two dehydrations. 1,2-Butadiene was taken as the final dehydration product, since some was isolated by the expedient of reacting ethanol and ethanal over pure alumina. It gave butadiene when subsequently

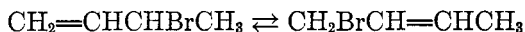
¹ Reference 144 in this paper.

isomerized over impure grades of the same catalyst. In summarizing his own study, Ostromyslenskii formulated (129) a second group of five equations almost identical with the first set (page 73). The second equation of the second group, however, appears to be meaningless:



Ostromyslenskii failed to state which set of equations was most plausible.

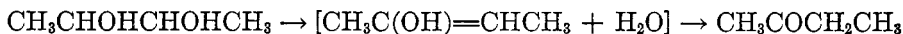
This picture of Ostromyslenskii's process is complicated somewhat by the possibility that at high temperatures 1-buten-3-ol and 2-buten-1-ol may exhibit an interconversion, in the known manner (44, 45, 181) of 3-bromo-1-butene and 1-bromo-2-butene:



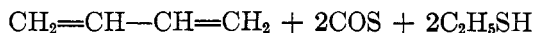
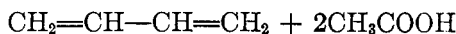
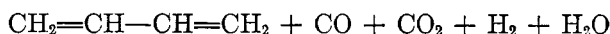
Butadiene has been obtained by individual dehydrations of 1-buten-3-ol, 1-buten-4-ol, and 2-buten-1-ol over catalysts at temperatures probably low enough to avoid significant interconversion. 1-Buten-3-ol yielded butadiene at 140°C. in the presence of trichloroacetic acid (154). 1-Buten-4-ol was similarly dehydrated at 270–290°C. over a fused mixture of ammonium and potassium alums (59). 2-Buten-1-ol gave butadiene at 140–160°C. over toluidine bisulfate (30). These three dehydrations would proceed rapidly at the high temperatures, 360–440°C., used in the ethanol and ethanal condensation. Kinetic studies could establish which of the butenols at the given temperatures is the most stable, probably 2-buten-1-ol, or, the most reactive, e.g., 1-buten-3-ol or 1-buten-4-ol.

Ostromyslenskii's proposition that 1,3-butanediol is an intermediary product rests on firmer ground: related reaction conditions and catalysts for the conversion of this diol into butadiene were already known (84, 109, 134). The dehydration of 1,3-butanediol has been repeatedly studied since 1915, the year of Ostromyslenskii's publication, though not from the instructive standpoint of the kinetics of reaction. 1,3-Butanediol apparently has never been isolated from the reaction products of either an ethanol plus ethanal (129) or an ethanol *per se* (89) condensation. Its presence among the products of the latter type of condensation was inferred from the isolation of 2-buten-1-ol, but one must remember that the last compound is readily obtainable by hydrogenation (9, 106) of 2-butenal from the dehydration of 3-hydroxybutanal. From this point of view, 2-buten-1-ol is a product of the catalytic treatment of ethanal *per se* rather than of ethanol reacting with ethanal. There are several indications that 2,3-butanediol can be the precursor of butadiene. One is the established occurrence (89) of 2-butanone and the probable presence (89) of 2,3-butanedione among the products of the catalytic condensation of ethanol *per se*. Another is the formation of 2,3-butanediol and traces of 2,3-butanedione when a mixture of ethanol and ethanal is exposed to sunlight (14, 146). Dehydration of 2,3-butanediol

into butadiene (48) is competitive with formation of 2-butanone (5, 15, 48, 172):

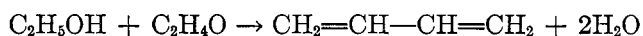
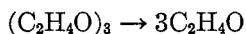


Moreover, derivatives of 2,3-butanediol, such as the diformate (53) and the diacetate (53, 126), and a 2,3-butanedithiol derivative (149) having the structure of 2,3-butene bis(ethylxanthogenic acid) yield butadiene upon decomposition:

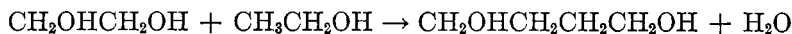
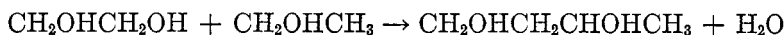


(d) Other ethanol condensations

Paraldehyde can replace part or all of the ethanal in an ethanol condensation (129, 141). It is a trimer of ethanal and presumably would depolymerize prior to reacting with ethanol. The course of the conversion is probably as follows:



1,2-Ethanediol likewise can replace ethanal in Ostromyslenskii's reaction (6). This substitution is expected because of the thermal conversion of this diol into ethanal. However, a conversion proceeding via 1,3- or 1,4-butanediol is to be considered also:



A mixture of ethanol and ethyne is reported (65) to give butadiene, but this reaction can be questioned on grounds similar to those discounting an ethanol and ethene conversion. Any formation of butadiene would be ascribable to a more appropriate ethanol *per se* condensation, to a hydration of ethyne into ethanal, which then reacts with ethanol, or to dehydration of ethanol into ethene prior to a Berthelot condensation between ethene and ethyne. The over-all reaction, of course, in the last two cases is:



TABLE 5
Condensation of ethanal with close derivatives

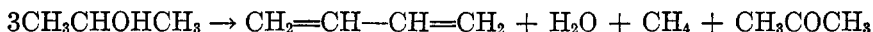
COMPOSITION OF FEED	APPARATUS AND CATALYST USED	TEMPERATURE °C.	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
Ethanol and ethanal $C_2H_5OH + CH_3CHO \rightarrow C_4H_6$ $+ 2H_2O$	Catalyst: Al_2O_3	440-460	0.895-0.934 <i>atm.</i>	Yield of B was 14% by weight on total feed; steam used?; data for 97 experiments given	(143)
	Catalyst: Al_2O_3	360-450		Yield of B = ?	(126)
	Catalysts were red phosphorus; glacial H_3PO_4 ; sulfamic acid; $BaCl_2$; or Al_2O_3 ("argilla pura")	360-440		Yields of B = ?	(129)
	Catalyst was used, but its composition was not disclosed	450	0.974-0.987	Yield of B was 9.5% by weight on total feed and 11% by weight on fully de-composed feed; feed used was ethanal and ethanal in equal amounts by weight	(95)
	Special unit of the plant "Krasnyĭ Bogatyr" in Moscow during 1919-1922			Yield of B was 6% by weight on feed	(94)
	Catalyst was $Al_2(SO_4)_3 \cdot 12H_2O$; feed mixture was ethanol 54, ethanal 33.5, and water 12.5 parts by weight	320-360	1	Yield of B was 19.8% by weight on ethanal and ethanal feed	(78)
	Catalyst was $Al_2(SO_4)_3$ on pumice; feed mixture was ethanol 47, ethanal 23, and water 30 parts by weight	320-360?	1?	Yield of B = ?	(78)
	Catalyst: basic aluminum sulfate	?	1?	Yield of B = ?	(78)

<p>Ethanol, ethanal, and paraldehyde $3C_2H_5OH + (C_2H_4O)_3 \rightarrow 3C_4H_6 + 6H_2O$</p>	<p>Catalyst: Al_2O_3</p>	<p>440-460</p>	<p>Yield of B = ?</p>	<p>(141)</p>
<p>Ethanol and paraldehyde $3C_2H_5OH + (C_2H_4O)_3 \rightarrow 3C_4H_6 + 6H_2O$</p>	<p>Catalyst was used, but its composition was not disclosed</p>	<p>400</p>	<p>Yield of B = ?</p>	<p>(129)</p>
<p>Ethanol and 1,1-dibromoethane $C_2H_5OH + CHBr_2CH_3 \rightarrow C_4H_6 + H_2O + 2HBr$</p>	<p>Catalyst was used, but its composition was not disclosed</p>	<p>400</p>	<p>Yield of B = ?</p>	<p>(126)</p>
<p>Ethanol and 1,2-dibromoethane $C_2H_5OH + CH_2BrCH_2Br \rightarrow C_4H_6 + H_2O + 2HBr$</p>	<p>Catalyst was used, but its composition was not disclosed</p>	<p>400</p>	<p>Yield of B = ? Yield of B was "poor"</p>	<p>(129) (126)</p>
<p>Ethanol and bromoethene (vinyl bromide) $C_2H_5OH + CH_2=CHBr \rightarrow C_4H_6 + H_2O + HBr$</p>	<p>Catalyst: $Al_2O_3 + BaCl_2$</p>	<p>400</p>	<p>Yield of B = ?</p>	<p>(129)</p>
<p>Ethanol and ethyne $C_2H_5OH + CH\equiv CH \rightarrow C_4H_6 + H_2O$</p>	<p>Catalyst was used, but its composition was not disclosed</p>	<p>>350</p>	<p>Yield of B = ?</p>	<p>(65)</p>
<p>Ethanol and 1,2-ethanediol (ethylene glycol) $C_2H_5OH + CH_2OHCH_2OH \rightarrow C_4H_6 + 3H_2O$</p>	<p>Catalyst: Al_2O_3 or aluminum silicate or flortidin</p>	<p>350-450</p>	<p>Yield of B = ?</p>	<p>(6)</p>

Table 5 contains data on condensations of ethanol with close derivatives, including ethanal.

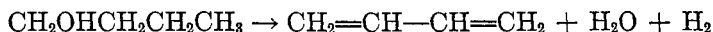
(e) Higher alkanols

2-Propanol, upon passage over pumice (117) at 615–620°C. or through a hard glass tube (71) at 840–850°C., yields small amounts of butadiene. One may assume that two molecules of 2-propanol upon dehydration form propene and eventually two vinyl and two methyl radicals. Also it is possible that another molecule furnishes acetone and the equivalent of two free hydrogen atoms ($\dot{\text{H}}$), which allow the methyl radicals to be removed as methane. The over-all effect, applicable to the relatively few molecules converted and irrespective of any union of vinyl radicals and atomic hydrogen to form ethene, would then be:



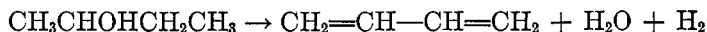
Both 1- and 2-butanol can be converted into butadiene either thermally or catalytically. A mixed alumina and chromia catalyst converts 1-butanol into considerable amounts of butadiene at 575–625°C. and an absolute pressure of 150–128 mm. of mercury (81). Partial oxidation of "butanol" also yields butadiene (33).

1-Butanol undergoes dehydration and dehydrogenation in forming butadiene:



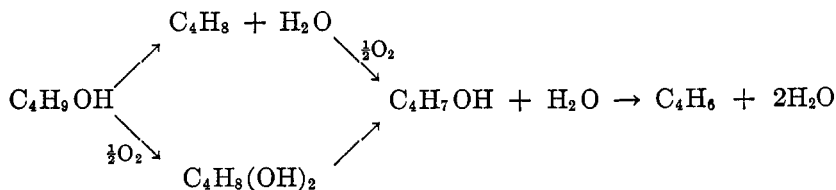
Dehydration presumably precedes dehydrogenation, so that 1-butene rather than 1-buten-4-ol would be the principal intermediate. Questions of (a) an isomerization of 1-butene into 2-butene following dehydration of 1-butanol, and (b) which alkene is dehydrogenated, are left open. This much is certain: the temperatures used in the conversion (32, 81, 149, 169) of 1-butanol into butadiene are considerably higher than those for the isomerization (25) of 1-butene into 2-butene.

2-Butanol, like 1-butanol, undergoes dehydration and dehydrogenation into butadiene (32, 83):



Again assuming the validity of prior dehydration and of Zaitsev's rule governing its course, the intermediate product would be *cis*- or *trans*-2-butene. A 1,4-dehydrogenation of 2-butene would then yield butadiene.

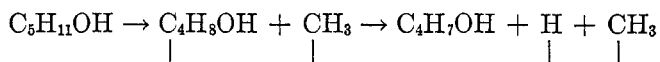
"Butanol" oxidations probably involve competitive initial dehydration and hydroxylation:



In the 1-butanol case, assuming oxidation in the β -position to the hydroxymethyl group, the intermediates would be 1-butene, 1,3-butanediol, 1-buten-3-ol, 1-buten-4-ol, and 2-buten-1-ol. Those for 2-butanol, assuming oxidation in the α -position to the hydroxymethylene group, would be 1- and 2-butenes, 2,3-butanediol, 1-buten-3-ol, and 2-buten-1-ol.

Only a trace of butadiene is formed when 2-methyl-1-propanol is passed over pumice at 600–610°C. under atmospheric pressure (119). The principal products are hydrogen, water, carbon monoxide, methane, ethane, ethene, propene, "butene," ethanal, propanal, and 2-methylpropanal.

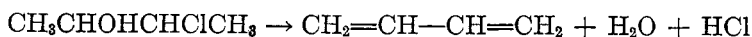
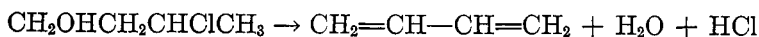
Partial oxidation of "pentanol" yields butadiene (33). A great number of formulations for the partial oxidation of "pentanol" are possible. These depend upon (a) the several orders in which hydroxyl groups can be subtracted or added, (b) the number of hydroxyl groups accumulating in a molecule before dehydrations, (c) the "promptness" with which the terminal methyl groups of 1-, 2-, and 3-pentanol become hydroxymethyl, aldehyde (formyl), and carboxyl groups, (d) the isomerization of intermediary products, and (e) the operation of 1-, 2-, 3-, or 4-hydroxylation. The latter operations are hydroxylations of a carbon atom in the 1-, 2-, 3-, or 4-position to an existing hydroxymethylene, hydroxymethyl, formyl, carboxyl, or 1-alken-1-yl group. A possibility of dehydrogenation without intermediary hydroxylation is a matter of speculation; its existence could be determined only with difficulty. If the velocity of partial oxidation approaches that of rapid combustion or explosion, newly formed hydroxyl radicals cannot become localized about carbon atoms. Upon cooling of the products, definite hydroxy compounds would develop. Their isolation obviously would not solve the question of direct *versus* indirect dehydrogenation at higher temperatures. Another question concerns the extent of demethylation, which would convert pentanols into hydroxybutyls and butenols:



Its operation would be favored by the low activation energy for a carbon-carbon bond scission, but would be extensively superseded by exothermic hydroxylations with or without dehydration of new hydroxyls.

Both 3-methyl-1-butanol and 2-methyl-2-butanol undergo conversions into butadiene over pumice at 600°C., though with small yields (120, 121). Thermal treatment of 3-methyl-1-butanol also yields small amounts of butadiene (7, 71, 130, 169, 171).

At high temperatures over a catalyst, 3-chloro-1-butanol and 3-chloro-2-butanol undergo dehydration and dehydrodechlorination (68, 110):



The two elimination processes, i.e., formation of water and of hydrogen chloride, are favored by the increase in strengths of the 1,2- and 3,4-carbon-carbon linkages and of the C—OH bond in the reactants compared with the H—OH bond

TABLE 6
 Conversion of higher alkanols (C_3H_7OH and above) into butadiene

PROCESS AND ALKANOL USED	APPARATUS AND CATALYSIS USED	TEMPERATURE °C.	PRESSURE <i>atm.</i>	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
Catalysis of 2-propanol (isopropyl alcohol) Probably $3CH_3CHOHCH_3 \rightarrow C_4H_6 + CH_3COCH_3 + 2CH_4 + 2H_2O$	Catalyst: pumice	615-620	1	Yield of B was 0.054% by weight on feed	(117)
	Hard glass tube	840-850	1?	Yield of B = ? (low in value)	(71)
Catalysis of 2-methyl-1-propanol (isobutyl alcohol) Probably $CH_3CH(CH_3)CH_2OH \rightarrow C_4H_6 + H_2O + H_2$	Catalyst: pumice	600-610	1	Yield of B was 0.022% by weight on feed	(119)
	Catalyst: mixture of aluminum silicate and reduced copper	Red heat	<i>In vacuo</i> unless diluents used	Yield of B = ?	(149)
Dehydration and dehydrogenation of 1-butanol $C_4H_9OH \rightarrow C_4H_6 + H_2O + H_2$	Quartz tube	Red heat	1	Yield of B was 11% by weight on feed; if desired, Al_2O_3 or kieselguhr may be used as catalyst	(32)
	Quartz tube containing a 4% Cr_2O_3 and 96% Al_2O_3 catalyst	750	1	Yield of B was 0.41% by weight on feed	(169)
		575 (Expt. 1) 600 (Expt. 2) 625 (Expt. 3)	0.197 (Expt. 1) 0.175 (Expt. 2) 0.168 (Expt. 3)	Yield of B was 1.2-4.8% by weight on gaseous hydrocarbons produced	(124)
				Yields of B were 1.8, 5.1, and 7.4% by weight on feed in experiments 1, 2, and 3, respectively	(81)

<p>Dehydration and dehydrogenation of 2-butanol $C_4H_9OH \rightarrow C_4H_6 + H_2O + H_2$</p>	<p>Quartz tube</p>	<p>Red heat</p>	<p>1</p>	<p>Yield of B was 14.6% by weight on feed; if desired, Al_2O_3 or kieselguhr may be used as catalyst</p>	<p>(32)</p>
<p>Partial oxidation (by air) of "butanol" vaporized by illuminating gas $C_4H_9OH + \frac{1}{2}O_2 \rightarrow C_4H_6 + 2H_2O$</p>	<p>Quartz tube containing 5% of a dehydrating catalyst and 95% of a dehydrogenating catalyst; components of the catalyst not disclosed</p>	<p>440</p>	<p>0.961-0.974</p>	<p>Yield of B was 0.9% by weight on feed per pass and 1.06% by weight on fully decomposed feed</p>	<p>(83)</p>
<p>Partial oxidation (by air) of "pentanol" vaporized by illuminating gas $C_5H_{11}OH + O_2 \rightarrow C_4H_6 + CO_2 + H_2O$</p>	<p>Burner tube was heated to prevent condensation of pentanol vapors</p>	<p>?</p>	<p>1</p>	<p>Yield of B = ?</p>	<p>(33)</p>
<p>Partial oxidation (by air) of "pentanol" vaporized by illuminating gas $C_5H_{11}OH + O_2 \rightarrow C_4H_6 + CO_2 + H_2O$</p>	<p>Porcelain tube</p>	<p>Red heat</p>	<p>1</p>	<p>Yield of B = ?</p>	<p>(7)</p>
<p>Dehydration and demethanation of 3-methyl-1-butanol $CH_2OHCH_2CH(CH_3)CH_3 \rightarrow C_4H_6 + H_2O + CH_4$</p>	<p>Iron tube</p>	<p>Medium red heat</p>	<p>1</p>	<p>Yield of B = ?</p>	<p>(171)</p>
<p>Dehydration and demethanation of 3-methyl-1-butanol $CH_2OHCH_2CH(CH_3)CH_3 \rightarrow C_4H_6 + H_2O + CH_4$</p>	<p>Catalyst: pumice</p>	<p>580-620</p>	<p>1</p>	<p>Yield of B was 0.18% by weight on feed</p>	<p>(120)</p>
<p>Dehydration and demethanation of 3-methyl-1-butanol $CH_2OHCH_2CH(CH_3)CH_3 \rightarrow C_4H_6 + H_2O + CH_4$</p>	<p>Iron tube</p>	<p>660-680?</p>	<p>1?</p>	<p>Yield of B = ?</p>	<p>(71)</p>
<p>Dehydration and demethanation of 3-methyl-1-butanol $CH_2OHCH_2CH(CH_3)CH_3 \rightarrow C_4H_6 + H_2O + CH_4$</p>	<p>Iron tube</p>	<p>750</p>	<p>1</p>	<p>Yield of B was 0.725% by weight on feed</p>	<p>(169)</p>
<p>Dehydration and demethanation of 3-methyl-1-butanol $CH_2OHCH_2CH(CH_3)CH_3 \rightarrow C_4H_6 + H_2O + CH_4$</p>	<p>Iron tube</p>	<p>500-600</p>	<p>1</p>	<p>Yield of B was 0.725% by weight on feed</p>	<p>(130)</p>

TABLE 6—Continued

PROCESS AND ALKANOL USED	APPARATUS AND CATALYSTS USED	TEMPERATURE °C.	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFER- ENCES
Dehydration and demethanation of 2-methyl-2-butanol $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{CH}_3 \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} + \text{CH}_4$	Catalyst: pumice	600–620	<i>atm.</i> 1	Yield of B was 0.071% by weight on feed	(121)
Dehydration and dehydrodechlorination of 3-chloro-1-butanol $\text{CH}_2\text{OHCH}_2\text{CHClCH}_3 \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} + \text{HCl}$	Catalyst: Al_2O_3 , BaCl_2 , or TiO_2	High	1 or <i>in vacuo</i>		(68)
Dehydration and dehydrodechlorination of 3-chloro-2-butanol $\text{CH}_3\text{CHOHCHClCH}_3 \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} + \text{HCl}$	Catalyst: H_3PO_4 (?) on pumice	Over 400	1 or <i>in vacuo</i>	Yield of B = ?	(110)

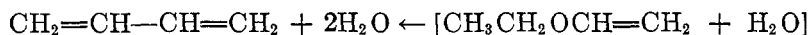
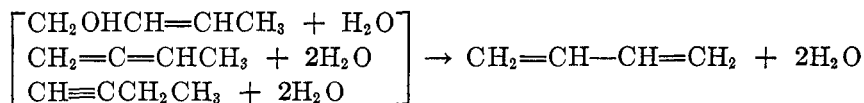
in the product. Dehydration should precede dehydrodechlorination, since water has the higher heat of formation in these reactions. These statements and others on heat of reaction values are based on Pauling's bond energies (147), which are: C—C, 58.6, C=C, 100; C≡C, 123; C—H, 87.3; C—O, 70.0; C=O in CH₂O, 142; C=O in RCHO, 149; C=O in R₂CO, 152; C—I, 45.5; C—Cl, 66.5; H—H, 103.4; O—H, 110.2 kcal. per an Avogadro number of bonds, and on 5.0 kcal. resonance energy per gram-mole of butadiene. When passed over magnesium chloride at 350°C., with or without steam, or at 300°C. over anhydrous magnesium sulfate, 3-chloro-2-butanol forms much more 2-butanone than butadiene (48). These catalysts evidently favor dehydrodechlorination rather than dehydration.

When distilled at an absolute pressure of 16 mm. of mercury, 4-chloro-1-butanol liberates hydrogen chloride and probably forms 1,4-epoxybutane (3, 80). Consequently, butadiene formation by decomposition of the epoxybutane seems possible at higher temperatures.

Table 6 contains data on conversions of 2-propanol and higher alkanols into butadiene.

2. Alkanediols

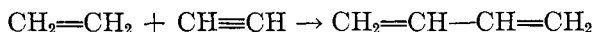
1,2-Ethanediol has not been reported as a direct source of butadiene. However, according to a Russian patent (6), it condenses with ethene or ethanol to form butadiene. The condensation with ethene is explicable on several bases. One explanation developed by the present authors is alkylation to 1,2-butanediol or ethyl β-hydroxyethyl ether, followed by dehydration:



Another explanation depends upon a probable transformation of the ethanediol into ethenol, i.e., vinyl alcohol, and its stabilization product, ethanal. Hydration of ethene into ethanol by water from ethanediol introduces Ostromyslenskii's condensation:



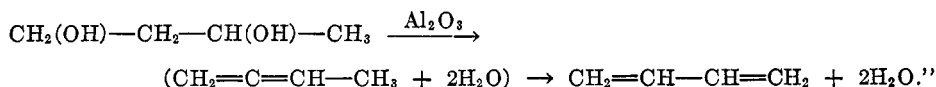
whereas further dehydration of ethenol to form ethyne brings Berthelot's reaction into the picture:



Condensation of ethanal into 3-hydroxybutanal or of ethene into 1- or 2-butene, requiring subsequent reduction (24) of 3-hydroxybutanal and dehydrogenation of the butenes, respectively, are still other mechanisms. Reduction conditions of sufficient potential would probably prevail in the presence of (a) atomic hydrogen traceable to ethene decomposition, (b) ethanol from ethene hydration or ethanal hydrogenation, or (c) ethanal decomposition products, e.g., carbon monoxide plus methane mixture. Dehydrogenation of 1- and 2-butenes would be accelerated by the presence of hydrogen acceptors, including keto compounds and alkenes.

The catalytic bidehydration of 1,3-butanediol is conducted advantageously under reduced pressure (166). Numerous catalysts are available (47, 50, 58, 66, 67, 84, 109, 115, 129, 130, 134, 152, 162, 166, 178). The course of dehydration of 1,3-butanediol probably involves intermediary formation of 1-buten-3-ol, 1-buten-4-ol, 2-buten-1-ol, or 1,3-epoxybutane. Ostromyslenskii's view of the reaction was (135):

"Methylallene in all probability is first formed and this is isomerized to butadiene at the moment of its formation:



This viewpoint was discounted in our discussions on Lebedev's ethanol process and on Ostromyslenskii's ethanol and ethanal juncture. A bond-energy analysis of the over-all reaction,



indicates that its thermal energy requirements, 6.5 kcal. per gram-mole of diol, are very low and practically that of an ordinary alkanol dehydration (5.7 kcal.). This low endothermicity for a bidehydration is due to the usual 5.0 kcal. calorific contribution in the establishment of electronic resonance among butadiene structures. Kyriakides committed himself in part to the following explanation (84):

"The dehydration of 1,3-glycols to hydrocarbons of the divinyl series, would seem to proceed according to the following course:

- (1) $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH} = \text{CH}_3 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2\text{OH} + \text{H}_2\text{O}.$
- (2) $\text{CH}_3 \cdot \text{CH} : \text{CH} \cdot \text{CH}_2\text{OH} = \text{CH}_2 : \text{CH} \cdot \text{CH} : \text{CH}_2 + \text{H}_2\text{O}.$

R. B. Earle [Kyriakides' colleague] has been able to isolate crotonyl alcohol, $\text{CH}_3\text{CH} : \text{CHCH}_2\text{OH}$, among the decomposition products in the formation of divinyl. In fact, β -butylene glycol [1,3-butanediol], if submitted to the action of catalysts at temperatures not exceeding 350° , seems to be dehydrated principally to butenol. The assumption that crotonyl alcohol is an intermediate step in the complete dehydration of the glycol is supported by the discovery that buten-2-ol-1 itself, is readily dehydrated to butadiene-1,3, if subjected to the pyrogenetic action of catalysts. Charon¹ [reference 10 of this paper], furthermore, states that, by heating the bromo-ester of the unsaturated alcohol with potassium formate at $160\text{--}180^\circ$, he obtained the *diene* as the principal product of the reaction. The dehalogenation of bromo-1-butene-2 to divinyl is explained by Charon on the

assumption that methylallene, $\text{CH}_3\cdot\text{CH}:\text{C}:\text{CH}_2$, is the primary reduction product. This substance, however, is immediately isomerized to the more symmetrically constituted divinyl under the influence of the high temperature, the symmetrical configurations being the stablest of all."

1,4-Butanediol produces butadiene when catalytically dehydrated over acidic substances, such as acid phosphates, silicic acid, phosphotungstic acid, phosphomolybdic acid, or boric acid (64). 2,3-Butanediol yields both butadiene and 2-butanone when dehydrated over either magnesium chloride or magnesium sulfate (48).

Mechanisms of the conversion of 1,4-butanediol and 2,3-butanediol have been considered under Lebedev's process. The suggested intermediates are 1-buten-4-ol and 1,4-epoxybutane for the first diol, but 2,3-epoxybutane and/or 1-buten-3-ol for the second diol. Ring strain in 2,3-epoxybutane would hinder its formation and so decrease its stability as to favor production of 1-buten-3-ol (or 3-butanol-1,2-diyl) from the corresponding but-2-yl-3-oxyl:

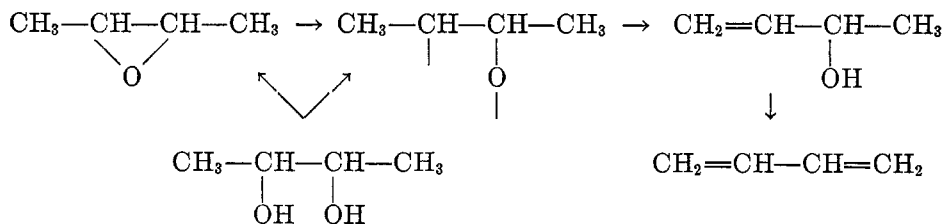
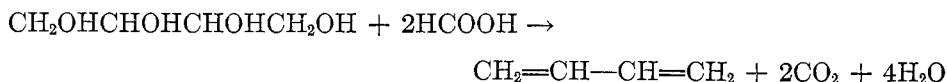


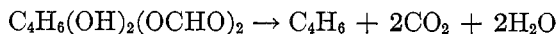
Table 7 contains data on the conversion of butanediols into butadiene.

3. Alkanetetrol

Reduction of 1,2,3,4-butanetetrol by formic acid at temperatures of 100°C. to 230°C. yields butadiene, as illustrated by the following equation (13, 52, 156, 175):



Erythrol monoformin, $\text{CH}_2=\text{CHCHOHCH}_2\text{OCHO}$, is also formed (156). Its structure is such that it should yield butadiene through formation of water and carbon dioxide. One may assume that 1,2,3,4-butanetetrol diformate is also an intermediate product, for it yields butadiene at 210-220°C. (51):



4. Alkenols

1-Propen-3-ol, upon contact with brass at 600°C., yields propenal, hydrogen, carbon monoxide, methane, propene, and butadiene (71, 73).

1-Buten-3-ol dehydrates to butadiene when heated in the presence of trichloroacetic acid, phosphorus pentoxide, or precipitated alumina (154):



TABLE 7
Conversion of butanediols and of butanetetrol into butadiene

PROCESS AND STARTING DERIVATIVE	APPARATUS AND CATALYST USED	TEMPERATURE °C.	PRESSURE atm.	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
Dehydration of 1,3-butanediol $\text{CH}_2\text{OHCH}_2\text{CHOH-CH}_2 \rightarrow \text{C}_4\text{H}_6 + 2\text{H}_2\text{O}$	Catalyst: H_3PO_4 on pumice	Heated	<i>In vacuo</i> if desired	Yield of B = ?; by-products can be recycled	(109)
	Catalyst: ignited kaolin	380-400	1	Yield of B was about 5.5% by weight on feed	(84)
	Catalysts: Al_2O_3 ; red phosphorus; glacial H_3PO_4 ; sulfanilic acid	350-480		Yield of B = ?	(129, 134)
	Catalysts: Al_2O_3 ; caustic alkali; H_3PO_4 ; oxalic acid; KH_2SO_4	450-470 (Al_2O_3 or caustic alkali)		Yield of B was 50-65% (probably on the theoretical, which is 60.0%)	(130)
		300-350 (H_3PO_4)		Yields of B were 36-45% by weight on feed	(152)
	Catalyst: 1% of red phosphorus on pumice	300-330		Yield of B was 39-42% by weight on feed	(67)
	Catalyst: NaH_2PO_4 + red phosphorus	300-330		Yield of B was 80% on the product	(67)
	Catalyst: NaH_2PO_4 + H_3PO_4 on graphite	260	1?	Yield of B = ?	(58)
	Catalyst: $\text{C}_3(\text{H}_2\text{PO}_4)_2$ + H_3PO_4 on lampblack and graphite	260	1?	Yield of B = ?	(58)

Vaporizer for feed mixture of butanediol and water; catalyst was potassium aluminum sulfate predehydrated at 150-180°C.	240-250	1?	Yield of B was 48% by weight on absolute butanediol feed per pass	(66)
Vaporizer for feed mixture of butanediol and water; catalyst was mixture of potassium aluminum sulfate and ammonium aluminum sulfate preoxidized and predehydrated at 180°C. in stream of nitrogen	270-290	1?	Yield of B was 48-49% by weight on absolute butanediol feed	(66)
Catalyst: $\text{AlPO}_4 + \text{H}_3\text{PO}_4$	450	1	Yield of B was 40% by weight on feed	(166)
Catalyst: $\text{AlPO}_4 + \text{H}_3\text{PO}_4$	450	0.25	Yield of B was 52% by weight on feed	(166)
Catalyst was $\text{AlPO}_4 + \text{H}_3\text{PO}_4$; steam and a 17% solution of the butanediol in water used	450?	1	Yield of B was 45% by weight on absolute butanediol feed	(166)
A "complex aluminum phosphate dehydration catalyst" was used in the presence of steam	285	1?	Yield of B was 42-48% by weight on feed without recycling and 54-57% by weight on butanediol with recycling of 1-buten-4-ol, which is a by-product	(178)
Catalyst was H_2SO_4 (1%) in water; an autoclave was used	200	> 15	Yield of B was 48% by weight on feed	(50)
Quartz tube containing the following catalysts: Al_2O_3 from $\text{Al}(\text{NO}_3)_3 + \text{NH}_4\text{OH}$ (expts. 1-3)	250 (expts. 1, 4, 7, 12, 15, 18, 24, 27, 30, 33, 36, 39, 42, 45, 48, 51)	0.934 (all cases)	Yields of B were 4.8, 8.9, 10.6, 4.8, 19.4, 18.1, 8.5, 10.5, 13.3, 14.0, 20.5, 26.8, 27.0, 22.8, 12.0, 20.4, 21.2, 17.0, 26.2, 29.0, 33.8,	(115)

TABLE 7—Continued

PROCESS AND STARTING DERIVATIVE	APPARATUS AND CATALYST USED	TEMPERATURE °C.	PRESSURE <i>atm.</i>	REMARKS (D IS 1,3-BUTADIENE)	REFERENCES	
Dehydration of 1,3-butanediol $\text{CH}_3\text{OHCH}_2\text{CHOH}-\text{CH}_3 \rightarrow \text{C}_4\text{H}_6 + 2\text{H}_2\text{O}$	Al_2O_3 from $\text{NaAlO}_2 + \text{CO}_2$ (expts. 4-6)	300 (expts. 2, 5, 8, 10, 13, 16, 19, 25, 28, 31, 34, 37, 40, 43, 46, 49, 52, 57)		35.1, 37.0, 6.8, 15.9, 16.2, 5.9, 13.7, 14.2, 17.8, 24.6, 23.6, 30.6, 28.6, 23.6, 21.1, 23.9, 25.8, 11.0, 21.0, 18.6, 20.6, 30.4, 29.4, 31.7, 40.1, 31.4, 12.8, 20.1, 19.1, 17.6, 23.0, 24.3, 2.5, 24.0, 22.3, 6.8, and 16.5% by weight on feed for experiments 1-58, respectively		
	Kaolin (Nippon Yakkyokuho) (expts. 10-11)					
	Kaolin (Korea) (expts. 12-14)	350 (expts. 3, 6, 9, 11, 14, 17, 20, 26, 29, 32, 35, 38, 41, 44, 47, 50, 53, 54, 55, 58)				
	Japanese acid clay (Itoigawa) (expts. 15-17)					
	Kaolin (50 parts) + P_2O_5 (50 parts) (expts. 18-23)	400 (expts. 21, 56)				
	Kaolin (50 parts) + Al_2O_3 (50 parts) (expts. 24-26)	450 (expt. 22)				
	Kaolin (49 parts) + Al_2O_3 (49 parts) + KOH (2 parts) (expts. 27-29)	500 (expt. 23)				
	Kaolin (50 parts) + Japanese acid clay (50 parts) (expts. 30-32)					
	Kaolin (50 parts) + FeSO_4 (50 parts) (expts. 33-35)					
	Kaolin (94 parts) + Fe_2O_3 (6 parts) (expts. 36-38)					
	Kaolin (80 parts) + Fe_2O_3 (20 parts) (expts. 39-41)					
	Kaolin (94.7 parts) + Fe_2O_3 (5 parts) + KOH (0.3 part) (expts. 42-44)					
Kaolin (94 parts) + Fe_2O_3 (5 parts) + KOH (1 part) (expts. 45-47)						
Kaolin (92 parts) + Fe_2O_3 (5 parts) + KOH (3 parts) (expts. 48-50)						

<p>Dehydration of 2:1 mixture of 1,3-butandiol and 1,4-butandiol in presence of steam and 1,4-epoxybutane</p> $\text{C}_4\text{H}_{10}\text{O}_2 \rightarrow \text{C}_4\text{H}_6 + 2\text{H}_2\text{O}$	<p>Kaolin (94 parts) + Ni(OH)₂ (5 parts) + KOH (1 part) (expts. 51-53)</p> <p>"Red mud" (i.e., clay after removal of Al₂O₃ with soda lime) (expt. 54)</p> <p>CaSO₄ (expts. 55-56)</p> <p>AlPO₄ (expts. 57-58)</p> <p>Catalyst: triethyl phosphate</p> <p>Catalyst was POCl₃; pumice or charcoal was used for heat transfer purposes</p> <p>Catalyst was NaH₂PO₄ + H₃PO₄ + graphite; steam and <i>n</i>-hexane used as diluents</p> <p>Steam and benzene used as diluents; catalyst was H₃PO₄ on graphite (prepared at 160°C. from sodium phosphate solution, primary <i>n</i>-butylamine phosphatic, and graphite)</p> <p>Catalyst: NaH₂PO₄ + H₃PO₄ on graphite</p>	<p>300-350</p> <p>300-350</p> <p>250</p> <p>280</p> <p>260</p>	<p>1</p> <p>1</p> <p>1?</p> <p>1?</p> <p>1?</p>	<p>Yield of B was 48.6% by weight on feed (47)</p> <p>Yield of B was 45.9% by weight on feed (47)</p> <p>Yield of B was 51% by weight on feed (162)</p> <p>Yield of B was 54% by weight on feed (162)</p> <p>Yield of B was 54% by weight on C₄H₁₀O₂ feed (162)</p>	
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TABLE 7—Continued

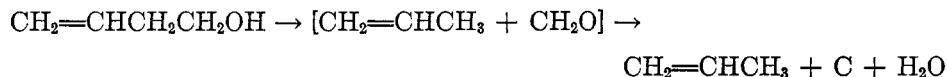
PROCESS AND STARTING DERIVATIVE	APPARATUS AND CATALYST USED	TEMPERATURE °C.	PRESSURE atm.	REMARKS (B IS 1, 3-BUTADIENE)	REFERENCES
Dehydration of 1,4-butanediol $\text{CH}_2\text{OHCH}_2\text{CH}_2\text{OH} \rightarrow$ $\text{C}_4\text{H}_6 + 2\text{H}_2\text{O}$	Catalyst of acid character, such as NaH_2PO_4 , CaHPO_4 , $\text{Ca}(\text{H}_2\text{PO}_4)_2$, Cu_2O , tungsten oxide, molybde- num oxide, silicic acid, phospho- tungstic acid, phosphomolybdic acid, or boric acid	280	1?	See patent for details	(64)
Dehydration of 2,3-butane- diol $\text{CH}_3\text{CHOHCH}-$ $\text{OHCH}_3 \rightarrow$ $\text{C}_4\text{H}_6 + 2\text{H}_2\text{O}$	Catalyst was NaH_2PO_4 ; steam and 1,4-epoxybutane used as diluents Catalysts: MgSO_4 ; MgCl_2 ; MgCl_2 + steam	300-320 (first catalyst) 350 (second and third cata- lysts)		Yield of B was 57% by weight on $\text{C}_4\text{H}_{10}\text{O}_2$ feed	(162)
Reduction of 1,2, 3,4-butanetet- rol (erythrite) $\text{CH}_2\text{OHCHOH}-$ $\text{CHOHCH}_2\text{OH} \rightarrow$ $+ 2\text{HCOOH} \rightarrow$ $\text{C}_4\text{H}_6 + 2\text{CO}_2$ $+ 4\text{H}_2\text{O}$	Vapor-phase catalytic process	?	?	Yield of B = ?	(114)
		230		Yield of B = ?	(52)
		Distillation	1	Yield of B = ?	(13)
		> 100	1	Yield of B was 6.67% by weight on butanetetrol	(156)
		130-150	1	Yield of B = ?	(175)

Isomerization of 1-buten-3-ol into 2-buten-1-ol may occur initially. An incomplete isomerization to 2-buten-1-ol occurs upon prolonged boiling with dilute hydrochloric acid (154). Trichloroacetins may be intermediates when trichloroacetic acid is used as a dehydration catalyst.

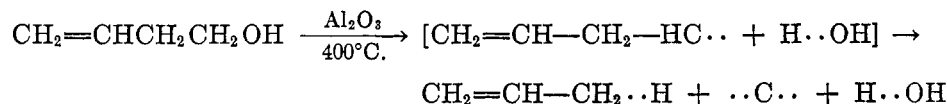
1-Buten-4-ol undergoes dehydration to butadiene when heated with a fused mixture of ammonium and potassium alums or with acid phosphates or pyrophosphates (59):



Alumina as catalyst leads to formation of much more propene and carbon than butadiene. This phenomenon was ascribed to a facile elimination and decomposition of formaldehyde (19):



The present authors suggest that, because of a balanced electronic state of carbon atom 4 and with excessive activity of alumina, the desired 3,4-dehydration is partly replaced by an undesired 4,4-dehydration:



Adsorption of water molecules on the alumina at temperatures around 400°C. is probably strong enough to prevent rehydration of carbon atoms to form formaldehyde. As a consequence, the carbon lattice would be formed.

2-Buten-1-ol forms butadiene when heated with toluidine bisulfate, anhydrous oxalic acid, phosphoric acid, phosphorus oxychloride, alumina, aluminum chloride, aluminum phosphate, or kaolin (30, 47, 84):



If 1,4 loss of water occurs in one step, then the energy-rich *cis*-form of 2-buten-1-ol yields *cis*-butadiene, which enters into equilibrium (113, 158, 159) with the *trans*-alkadiene:

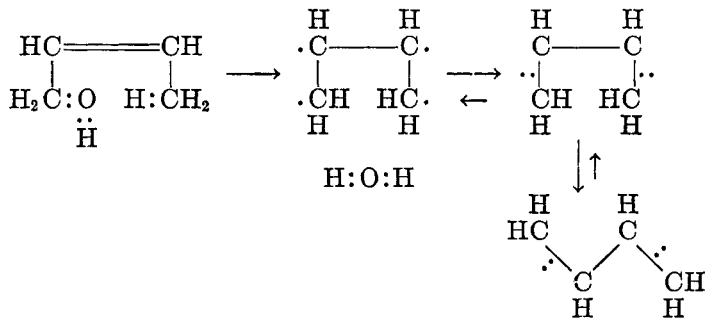


TABLE 8
Conversion of alkenols and alkenediols into butadiene

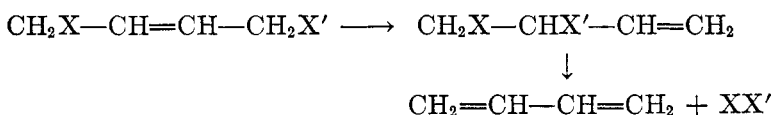
PROCESS AND STARTING DERIVATIVE	APPARATUS, CATALYSTS, AND SPECIAL REACTANTS	TEMPERATURE °C.	PRES- SURE <i>atm.</i>	REMARKS (B IS 1,3-BUTADIENE)	REFER- ENCES
Catalytic treatment of 1-propen-3-ol (allyl alcohol) Probably $2\text{CH}_2=\text{CHCH}_2\text{OH} \rightarrow \text{C}_4\text{H}_6 + 2\text{CO} + 3\text{H}_2$	Brass tube containing brass shavings	600	1?	Yield of B = ? (low in value)	(71)
Dehydration of 1-buten-3-ol (methylvinylcarbinol) $\text{CH}_2=\text{CHCHOHCH}_3 \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O}$	Catalyst of undisclosed composition			Yield of B = ?	(157)
	Catalyst of undisclosed composition	360		Yield of B was about 45-55% on feed per pass and about 56-79% on fully decomposed feed	(156)
Dehydration of 1-buten-3-ol and/or 2-buten-1-ol Probably $\text{CH}_2=\text{CHCHOHCH}_3 \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O}$	Catalyst: trichloroacetic acid	140		Yield of B = ?; product also had two isomeric monoesters	(154)
	Phosphorus pentoxide was used as reactant			Yield of B was slightly above 15% on feed	(154)
	Catalyst: precipitated Al_2O_3	265	1	Yield of B was 20% on feed; Al_2O_3 precipitated on sodium aluminate and placed among layers of pumice was used as catalyst also, but yield of B = ? in this case	(154)

<p>Dehydration of 1-buten-4-ol (allyl carbinol) $\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{OH} \rightarrow \text{C}_4\text{H}_6$ $+ \text{H}_2\text{O}$</p>	<p>Catalyst was prepared by dehydrating and fusing a mixture of ammonium alum (90%) and potash alum (10%) Catalyst: Al_2O_3</p>	<p>270-290</p>	<p>1?</p>	<p>Yield of B was 63.7-67.5% by weight on feed, using one recycle; acid phosphates or pyrophosphates also had a catalytic effect</p>	<p>(59)</p>
<p>Dehydration of 2-buten-1-ol (crotyl alcohol) $\text{CH}_3\text{OHCH}=\text{CHCH}_3 \rightarrow \text{C}_4\text{H}_6$ $+ \text{H}_2\text{O}$</p>	<p>Toluidine bisulfate, anhydrous oxalic acid, KHSO_4, H_3PO_4, Al_2O_3, and AlCl_3 were catalysts named Catalyst: probably kaolin or AlPO_4</p>	<p>140-160 (first catalyst) "Warmed" (second catalyst)</p>	<p>1</p>	<p>Yield of B was 22.5-30% by weight on feed for first catalyst and 30-37.5% by weight on feed for second catalyst; yield of B = ? for other catalysts</p>	<p>(30)</p>
<p>Dehydroxylation of 1-buten-3,4-diol (erythrol) $\text{CH}_2=\text{CHCHOHCH}_2\text{OH} + 2\text{Cu} \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} + \text{Cu}_2\text{O}$</p>	<p>POCl_3 (?) was used as reactant Copper was used as reactant</p>	<p>400-450</p>	<p>1?</p>	<p>Yield of B = ?</p>	<p>(84)</p>
	<p>300-350?</p>	<p>280</p>	<p>1</p>	<p>Yield of B was 32% (?) by weight on feed</p>	<p>(47)</p>
			<p>1</p>	<p>Yield of B was 0.193% by weight on butenediol feed</p>	<p>(176)</p>

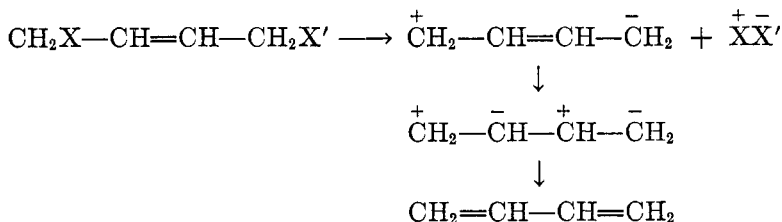
For the given structural formulation, an over-all heat of reaction amounting to about 0.3 kcal. exothermic can be computed on the basis of +1.0, -5.7, and +5.0 kcal., respectively, for available *cis* energy of butenol, heat of simple dehydration, and butadiene resonance energy.

Prévost listed dehydration of 2-buten-1-ol among a group of 1,4-eliminations in which a 2,3 double bond opens to form two conjugated double bonds (153). Two interpretations of the 1,4-eliminations were submitted:

1. Migration of a substituent from carbon atom 4 to carbon atom 2, for example, could give a 3-alkene. This upon loss of adjacent groups in the 1- and 2-positions would form a 1,2 double bond conjugated with the 3,4 double bond:



2. Elimination of oppositely charged substituents from carbon atoms 1 and 4 could give $\overset{+}{\text{C}}\text{H}_2-\text{CH}=\text{CH}-\overset{-}{\text{C}}\text{H}_2$, whose double bond would open simultaneously to form $\overset{+}{\text{C}}\text{H}_2-\overset{-}{\text{C}}\text{H}-\overset{+}{\text{C}}\text{H}-\overset{-}{\text{C}}\text{H}_2$, which is a highly activated state of butadiene:



Interpretation 1 suggests the following course for the dehydration:

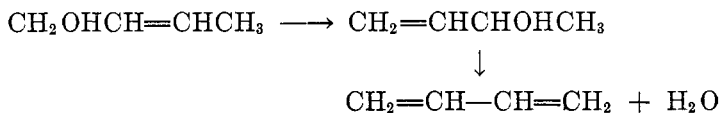
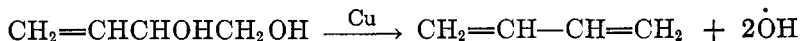


Table 8 contains data on the conversion of alkenols into butadiene.

5. Alkenediol

1-Butene-3,4-diol forms butadiene, propanal, 2-butenal, 2-keto-1-butanol, 3,4-hexanedione, carbon dioxide, and water when heated at 280°C. with copper (175). These products are indicative of extensive electronic changes among butenediol molecules. Urion, investigator of the butenediol conversion, considered butadiene to be formed by a scission of both hydroxyl groups:



Nothing was stated regarding further reactions of the hydroxyl groups. A union of two vinyl fragments was also mentioned. The presence of 2-butenal, i.e., C_4H_6O , as a dehydration plus isomerization product suggests the possibility of its reduction to butadiene. If the latter reaction occurs, it indicates a reductive action of copper comparable with that of zinc in organic synthesis.

B. CYCLIC MEMBERS

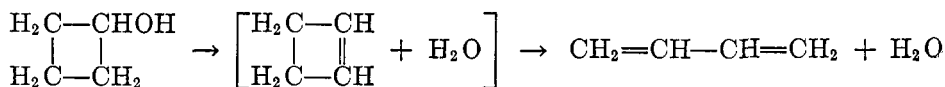
1. *Cyclanyl alkanol*

Cyclopropylcarbinol undergoes a complicated decomposition at 300–400°C. in the presence of alumina (19). The products include much propene, very little butene, butadiene, besides 1-buten-4-ol, 3-butenal, cyclobutanol, cyclobutanone, carbon, carbon monoxide, hydrogen, and water. Formation of propene, carbon, and water was considered to be the main reaction. Butadiene forms instead of methylenecyclopropane, which is the expected dehydration product (19, 20). 1-Buten-4-ol and cyclobutanol are obviously isomerization products, which upon dehydrogenation would yield 3-butenal and cyclobutanone, respectively.

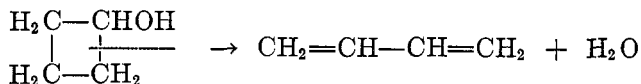
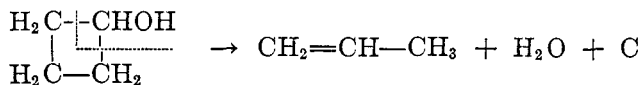
2. *Cyclanols*

Cyclanols generally give high yields of butadiene. This fact recalls the analogous behavior of cyclohexane, cyclohexene, and benzene, in which resonance among valence-bond structures plays an important rôle.

The conversion of cyclobutanol into butadiene was reported by Ostromyslen-skii to occur quantitatively at 300–350°C. over alumina (126, 131):



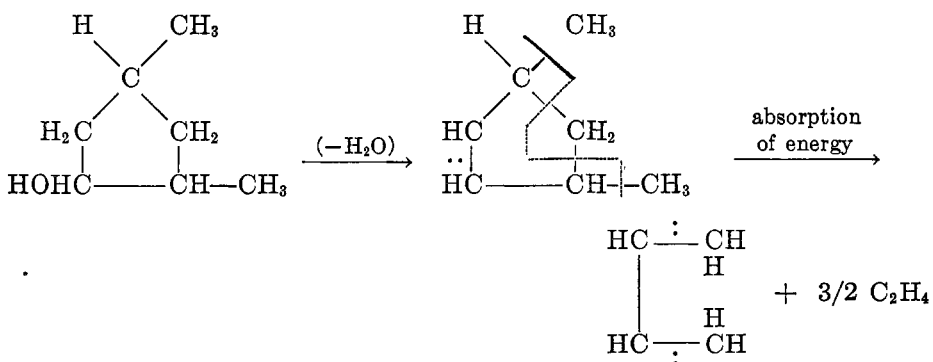
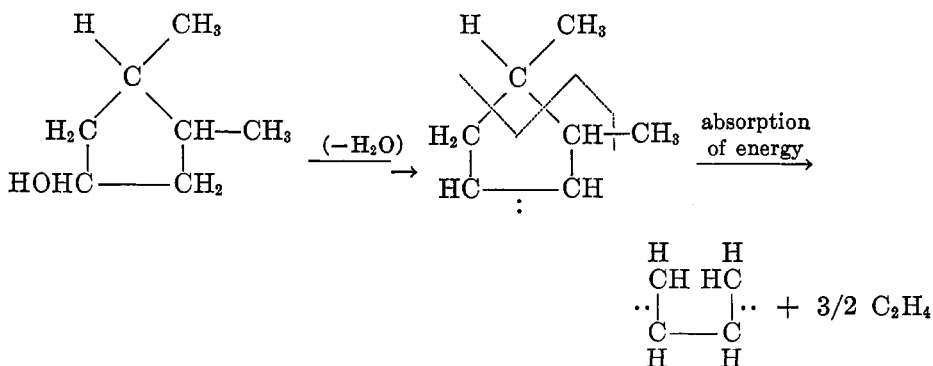
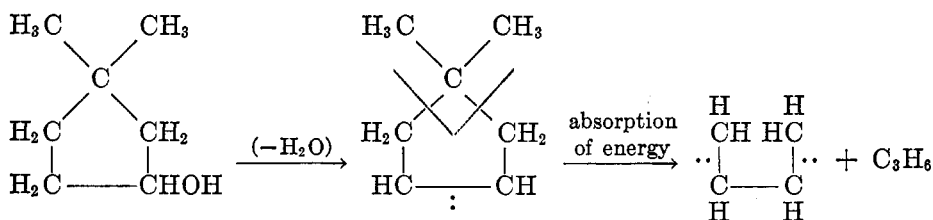
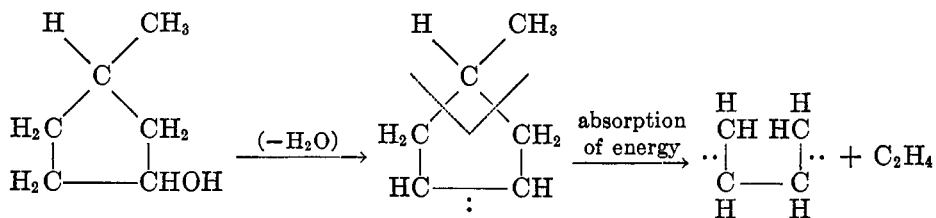
Cyclobutene was assumed to be the intermediate responsible for the reaction. Doyarenko, however, found that the products formed at 360–390°C. included propene, butadiene, cyclobutanone, 2-butenal, carbon, and water (19). "Dehydrations" to propene and butadiene were considered to be the main reactions:



The conversion mechanism was assumed to be formation of unstable, highly energized molecules immediately upon dehydration, such that sufficient excess energy would be present to break a C—C or open a C=C linkage (19, 20).

When passed through a copper tube containing an inner silver gauze at a dark red heat, 1-methyl-3-cyclopentanol and "dimethylcyclopentanol" undergo dehydration and ring scission (29). These conversions into butadiene were not

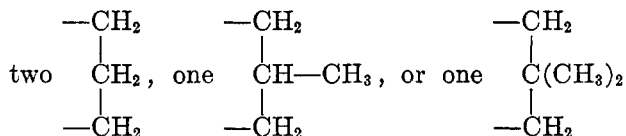
further described, but probably involve formation of ethene and propene as by-products. The present authors suggest that the following reactions occur:



All of the processes given are over-all endothermic. An absorption of external energy occurs in (a) dehydration with double-bond formation, (b) the transforma-

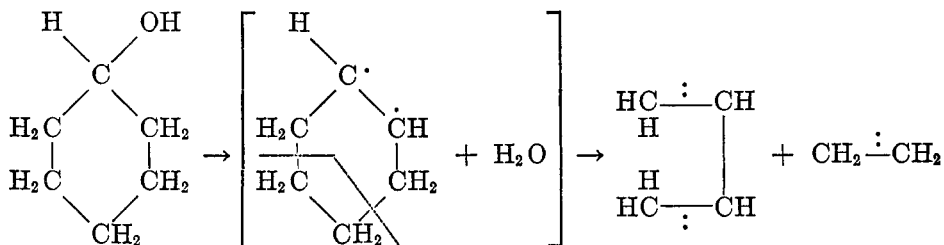
tion of two $\begin{array}{c} | \\ \text{CH}-\text{CH}_3 \\ | \end{array}$ into two $\begin{array}{c} | \\ \text{CH}_2 \\ | \end{array}$ groups plus $\text{CH}_2=\text{CH}_2$, and (c) the conver-

sions of



into $\text{CH}_2=\text{CH}_2$ (or $\text{CH}_2=\text{CH}-\text{CH}_3$) and into the two methylene terminals characteristic of activated butadiene.

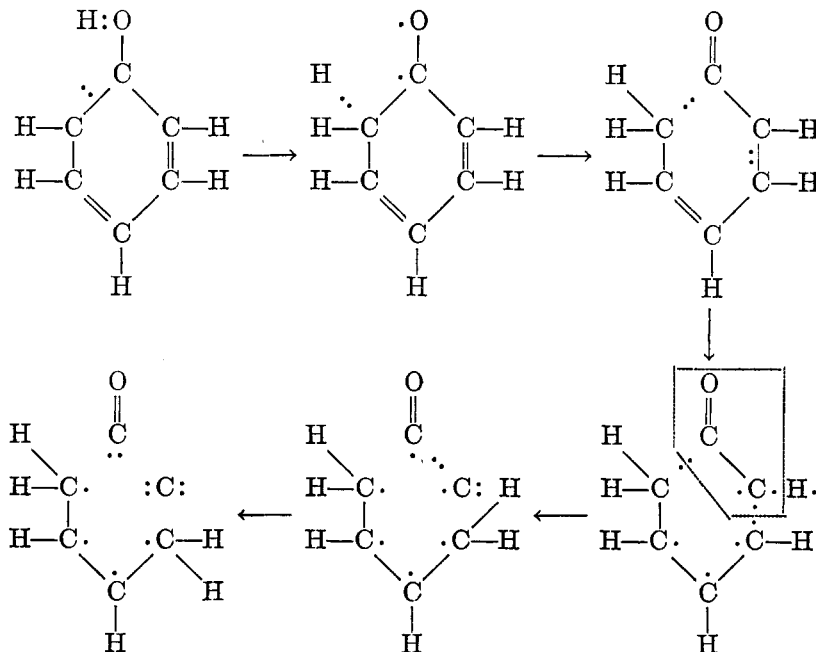
Cyclohexanol gives considerable amounts of ethene and butadiene when passed through tubes of quartz, platinum, silver, or (less favorably) of iron or porcelain, heated to redness (26, 27, 28, 54):



The *cis*-butadiene, of course, would immediately form a large proportion of the *trans*-modification.

3. Hydroxybenzene (phenol)

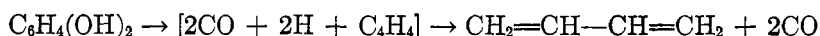
Hydroxybenzene forms hydrogen, carbon, carbon monoxide, carbon dioxide, methane, ethene, ethyne, butadiene, benzene, naphthalene, anthracene, phenanthrene, and chrysene when conducted with nitrogen at 650–750°C. over pumice (49). A direct formation of butadiene from hydroxybenzene seems possible:



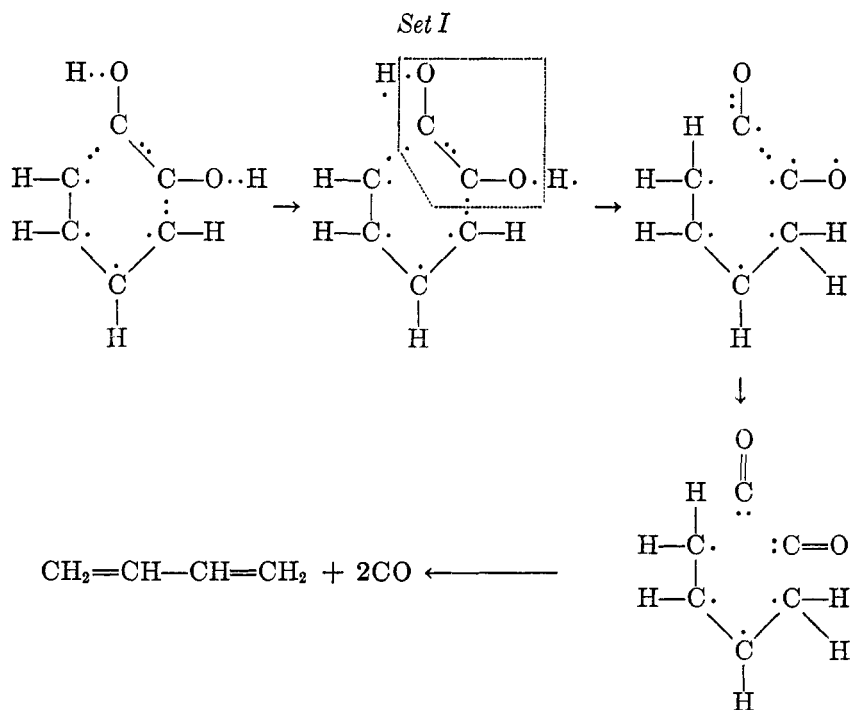
An alternative two-step formulation ending with a similar electronic interpretation is the disproportionation of hydroxybenzene into benzene and the easily convertible 1,2- and 1,4-dihydroxybenzenes. Pumice might exert a splitting action toward the hydroxyl group even at temperatures below 750°C., in which case water should have been formed. Hydroxybenzene also could combine with hydrogen atoms to form cyclohexanol, which dehydrates into cyclohexene and further decomposes into ethene and butadiene.

4. Dihydroxybenzenes

When 1,2-dihydroxybenzene is passed with nitrogen over glass rings at 550°C., large amounts of butadiene and carbon monoxide are produced (49). The assigned course of the reaction was:

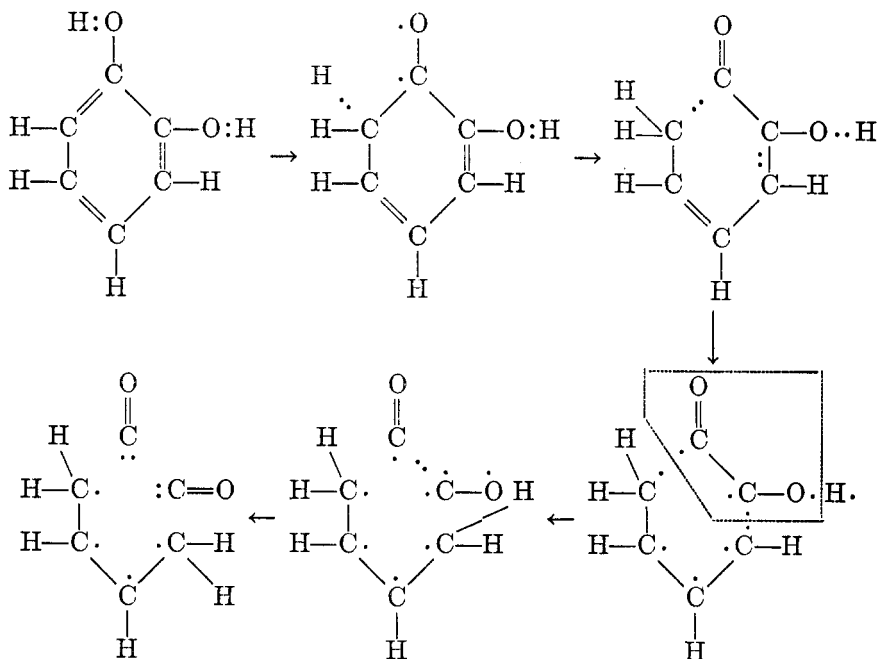


According to the present authors, direct formation of butadiene seems indicated on electronic grounds, as in the case of hydroxybenzene:

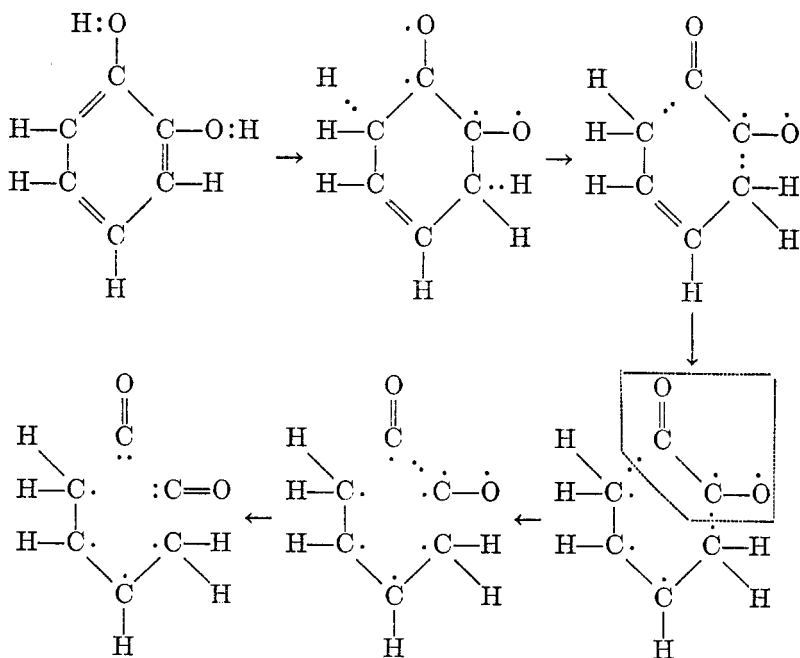


For the case of a prior tautomerization of 1,2-dihydroxybenzene into 2,4-cyclohexadien-1-on-2-ol or to 4-cyclohexene-1,2-dione, a similar formulation can be given:

Set II



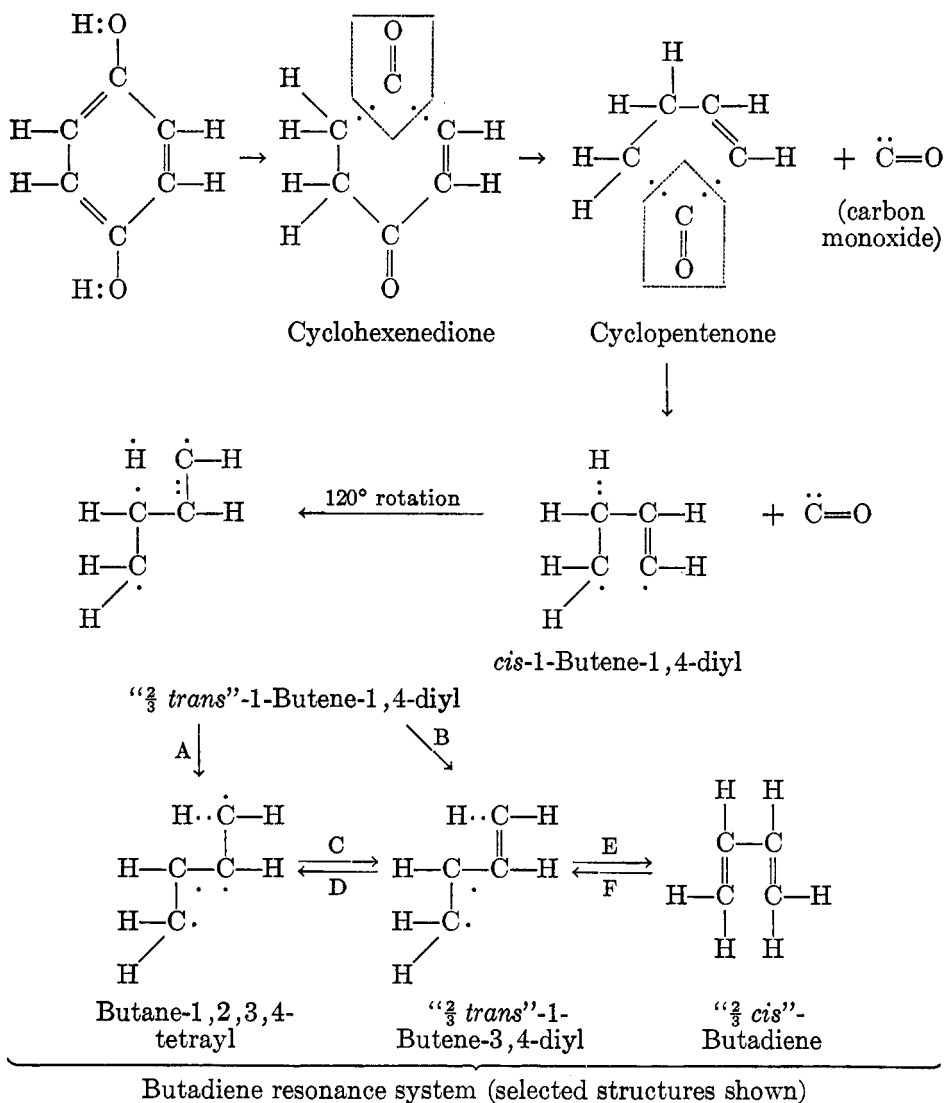
Set III



All three sets of transformations should be 17.4 kcal. endothermic per gram-mole of butadiene produced, assuming 39.4, 5.0, and 2×58 kcal. as the total molal resonance energies of the dihydroxybenzene, butadiene, and carbon monoxide, respectively.

Less butadiene is yielded by 1,3-dihydroxybenzene than by either 1,2- or 1,4-dihydroxybenzene. Upon contact with glass rings at 650°C., 1,3-dihydroxybenzene forms hydrogen, carbon, carbon monoxide, carbon dioxide, methane, ethene, butadiene, and aromatic condensation products (49). At temperatures of 300–380°C., 1,3-dihydroxybenzene begins to lose carbon dioxide and forms aromatic condensation products, some of which are soluble in alkali. Nevertheless, formation of the alkadiene was ascribed to hydrogenation of C_4H_4 as for the case of 1,2-dihydroxybenzene. The present authors cannot accept this version of the mechanism, because no C_4H_4 is directly derivable from 1,3-dihydroxybenzene by formation of two molecules of carbon monoxide. Isomerization to 1,2-dihydroxybenzene is postulated as the probable initial reaction leading to butadiene formation. In favor of this interpretation can be cited the low yield of alkadiene, which corresponds to the expected low extent of isomerization of meta into ortho derivatives. Again a higher yield should be obtained from 1,4- than from 1,3-dihydroxybenzene. This is found to be the case.

Upon passage with some nitrogen over glass rings at 650°C., 1,4-dihydroxybenzene produces large amounts of butadiene and carbon monoxide (49). The equation given for the conversion was identical with that for 1,2-dihydroxybenzene. Since formation of a C_4H_4 residue and *direct* removal of two molecules of carbon monoxide per ring are incompatible, an alternative isomerization to 1,2-dihydroxybenzene is indicated. In lieu of isomerization, tautomerization to 2-cyclohexene-1,4-dione could be postulated. This dione, upon loss of one carbonyl group, might form 2-cyclopenten-1-one, which would require further decarbonylation to give a C_4H_6 fragment (1-butene-1,4-diyl) capable of isomerization to butadiene.



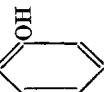
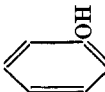
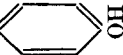
The depicted 1-butene-1,4-diyl would obviously be of *cis* structure at the moment of its formation. Molecular models give further information. A 120° rotation of the ethenediyl group about the ethanedyl group would bring a 3-position hydrogen atom in proximity to the carbon atom in the 1-position, permitting changes A and B to occur. Change A represents a hydrogen migration akin to that of a tautomerization, whereas change B takes advantage of the availability of the lone electron in the 1-position. The similar electronic and spatial configurations of butanetetrayl and 1-butene-3,4-diyl call for arrows C and D. These poly-yls enter into resonance among the other valence-bond structures of butadiene. Change E represents a particularly easy way of ob-

TABLE 9
 Conversion of cyclanols and of hydroxybenzenes into butadiene

PROCESS AND STARTING DERIVATIVE	APPARATUS AND CATALYST	TEMPERATURE °C.	PRES- SURE <i>atm.</i>	REMARKS (B IS 1,3-BUTADIENE)	REFER- ENCES
"Dehydration" of cyclopropylcarbinol $\begin{array}{c} \text{H}_2\text{C} \text{---} \text{CHCH}_2\text{OH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O}$	Catalyst: Al_2O_3	300-400	<i>atm.</i>	Yield of B was 5.6% by weight on feed	(19)
"Dehydration" of cyclobutanol $\begin{array}{c} \text{H}_2\text{C} \text{---} \text{CHOH} \\ \quad \\ \text{H}_2\text{C} \text{---} \text{CH}_2 \end{array} \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O}$	Catalyst: Al_2O_3	?	?	Yield of B = ?	(126)
Dehydration and partition of 1-methyl-3-cyclopentanol $\begin{array}{c} \text{CH}_3 \\ \\ \text{H} \quad \text{C} \\ / \quad \backslash \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \quad \\ \text{H}_2\text{C} \text{---} \text{CHOH} \end{array} \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} + \text{C}_2\text{H}_4$ (Probable reaction is given)	Catalyst: Al_2O_3 Copper tube containing silver gauze inside	300-350 360-390 Dark red heat	1	Yield of B was 75% by weight Yield of B was 5.6% by weight on feed Yield of B = ?	(131) (19) (28)

<p>Dehydration and partition of dimethylcyclopentanol $C_5H_7(CH_2)_2(OH) \rightarrow C_4H_6 + H_2O + C_3H_6$ (Possible reaction is given)</p>	<p>Not described (probably a copper tube containing silver gauze)</p>	<p>Dark red heat?</p>	<p>1?</p>	<p>Yield of B = ?</p>	<p>(29)</p>
<p>Dehydration and partition of cyclohexanol $C_6H_{11}OH \rightarrow C_4H_6 + H_2O + C_2H_4$</p>	<p>Iron tube which can be filled with native Al_2O_3</p>	<p>600</p>	<p>1</p>	<p>Yield of B was "good"</p>	<p>(54)</p>
<p>Dehydration and partition of cyclohexanol $C_6H_{11}OH \rightarrow C_4H_6 + H_2O + C_2H_4$</p>	<p>Iron pipe</p>	<p>600</p>	<p>1</p>	<p>Yield of B = ?</p>	<p>(27)</p>
<p>Dehydration and partition of cyclohexanol $C_6H_{11}OH \rightarrow C_4H_6 + H_2O + C_2H_4$</p>	<p>Quartz tube</p>	<p>Slight red heat</p>	<p>1</p>	<p>Yield of B was 22-28% by weight on feed; tubes of quartz, platinum, or silver are better than those of iron or porcelain</p>	<p>(26)</p>
<p>Catalytic cracking of hydroxybenzene (i.e., phenol) $C_6H_5OH \rightarrow C_4H_6 + CO + C$</p>	<p>Catalyst: pumice</p>	<p>650-750</p>	<p>1?</p>	<p>Yield of B = ?</p>	<p>(49)</p>

TABLE 9—Continued

PROCESS AND STARTING DERIVATIVE	APPARATUS AND CATALYST	TEMPERATURE °C.	PRES- SURE <i>atm.</i>	REMARKS (B IS 1,3-BUTADIENE)	REFER- ENCES
Catalytic cracking of 1,2-dihydroxybenzene (i.e., pyrocatechol)  $\rightarrow \text{C}_4\text{H}_6 + 2\text{CO}$	Quartz tube containing glass rings	650	1?	Yield of B was 21.1% by weight on feed	(49)
Catalytic cracking of 1,3-dihydroxybenzene (i.e., resorcinol)  $\rightarrow \text{C}_4\text{H}_6 + 2\text{CO}$	Quartz tube containing glass rings	650	1?	Yield of B = ?	(49)
Catalytic cracking of 1,4-dihydroxybenzene (i.e., hydroquinone)  $\rightarrow \text{C}_4\text{H}_6 + 2\text{CO}$	Quartz tube containing glass rings	650	1?	Yield of B = ?	(49)

taining strictly covalent butadiene, even if momentarily and, according to molecular models, with only two-thirds orientation toward perfect *cis* configuration.

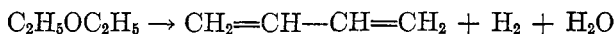
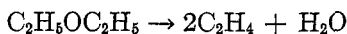
Table 9 gives data on the conversion of cyclanols and hydroxybenzenes into butadiene.

III. OXIDE DERIVATIVES OF HYDROCARBONS

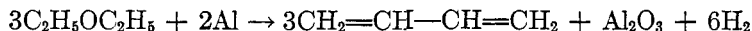
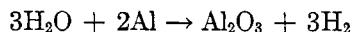
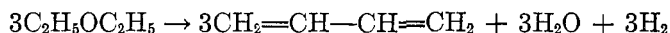
A. ALIPHATIC OXIDES

1. Dialkyl ethers

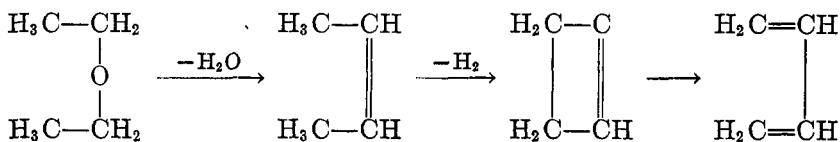
Diethyl ether undergoes a main dehydration to ethene and a lesser dehydration-dehydrogenation to butadiene at 600°C. over initially clean aluminum (34, 35, 95):



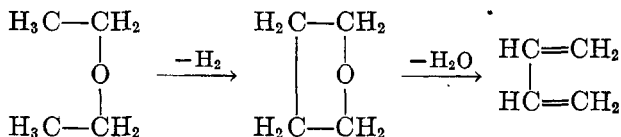
The metal becomes gradually coated with carbon and probably undergoes a certain amount of oxidation through contact with water vapor:



Filippov assumed that ethanal, which is found among the products, participates in butadiene formation. Ostromyslenskii considered the conversion to involve probably dehydration to 2-butene, dehydrogenation to cyclobutene, and isomerization of the latter (136):



A possible dehydrogenation to 1,4-epoxybutane prior to dehydration was not overlooked (137, 142):

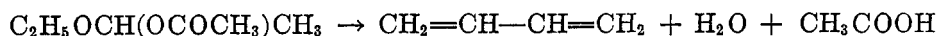
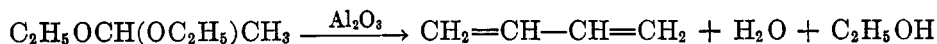
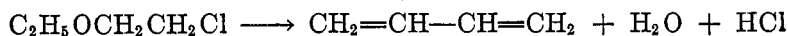


There are several reasons why butadiene should be formed from diethyl ether over aluminum at 300–600°C. First, ethanol and ethene, which are respectively expected and actual products, are each directly convertible into butadiene under similar conditions (21, 23, 72). Ethanal, another product, upon dimerization to 3-hydroxybutanal, with or without dehydration to 2-butenal, would be a further source of alkadiene. However, ethanol probably must be simultaneously

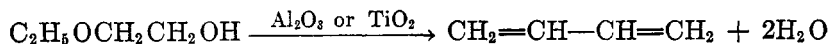
present to effect a reduction to 1,3-butanediol and 2-buten-1-ol, respectively (24).

In formulating a probable course for the conversion of diethyl ether into butadiene, one must take cognizance of the probable preliminary scission into ethoxyl and *ethyl radicals*. The latter, upon loss of two hydrogen atoms apiece, would form vinyl radicals. These upon association form butadiene.

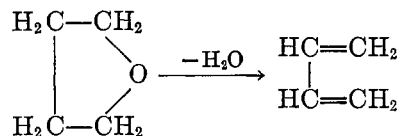
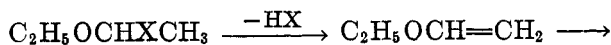
Monosubstituted diethyl ethers undergo vapor-phase catalytic dehydration, forming butadiene as a common product (126). These ethers have the general formula $C_2H_5OC_2H_4R$, in which R may be a halo, hydroxyl, alkoxy, or acyloxy group. The following radicals were utilized: α -chloro, β -chloro, α -hydroxy, α -ethoxy, and α -acetoxy. Five corresponding equations are:



Catalytic conversion of ethyl β -hydroxyethyl ether substantiates the foregoing equations (8):



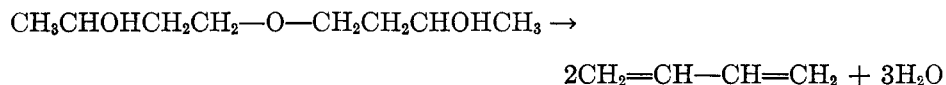
Ostromyslenskii mentioned the mechanism of conversion of substituted diethyl ethers and the equilibrium existing between α -hydroxyethyl ether, ethanol, and ethanal (129). This ether, at 360–440°C., evidently undergoes a complete and facile dissociation into ethanol and ethanal, followed by interaction (condensation) of these components. Although Ostromyslenskii had discovered that ethyl vinyl ether (126) and its isomer, 1,4-epoxybutane (125, 126), both yield butadiene under the same conditions, an interrelationship between these compounds, such as the following equation submitted by the authors, was not considered (X is a halo, hydroxyl, alkoxy, or acyloxy group):



Methyl α -methoxyethyl ether appears to be but slightly convertible into butadiene over alumina-containing catalysts (4, 79). The present authors offer the following mechanisms for the converted portion: (a) an initial demethanolation to methyl vinyl ether, supplemented by scissions affording vinyl radicals which associate; (b-c) an initial removal of dimethyl ether with formation of ethanal,

which is convertible into butadiene by way of aldolization and either reduction to 1,3-butanediol or dehydration followed by reduction to 2-buten-1-ol; and (d) a high-energy barrier "bidehydration" into two methylene radicals plus ethane-1,1,2,2-tetrayl, followed by appropriate combination to butane-1,2,3,4-tetrayl.

When autoclaved at 140–200°C. in the presence of dilute sulfuric or other acids, γ, γ' -dihydroxydibutyl ether dehydrates to butadiene (50):

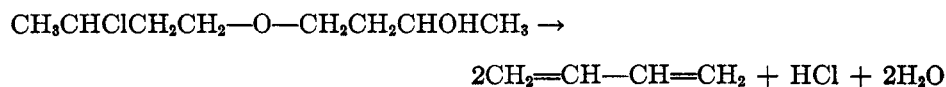


It is desirable to remove the alkadiene from the reaction zone as fast as it is formed. Formation of 2 gram-moles of butadiene from γ, γ' -dihydroxydibutyl ether requires 12.8 kcal., independently of the chosen reaction course. Assuming that C—C scissions requiring 58.6 kcal. need not be considered, the following five interpretations of the reaction can be given:

1. Preliminary formation of γ -hydroxybutyl 2-buten-1-yl ether, followed by further change into one or more related compounds:
 - (a) di(2-buten-1-yl) ether (dicrotyl ether)
 - (b) 1,3-butadiene plus 1,3-butanediol
 - (c) 1-buten-3-ol plus 2-buten-1-ol
2. Initial decomposition to 1,3-butanediol plus 1-buten-3-ol
3. Cyclization to 2,8-dimethyl-1,5-dioxocane, i.e., 2,8-dimethyl-1,5-dioxacycloöctane, followed by decyclization to:
 - (a) 1-butanol-3-yl 3-buten-2-yl ether
 - (b) γ -hydroxybutyl 2-buten-1-yl ether
 - (c) γ -hydroxybutyl 3-buten-1-yl ether
 - (d) di(2-buten-1-yl) ether
 - (e) di(3-buten-1-yl) ether
 - (f) di(3-buten-2-yl) ether
4. Mono- or di-esterification, with deësterification to γ -hydroxybutyl 2-buten-1-yl ether or di(2-buten-1-yl) ether
5. Dissociation to 3-butanol-1-yl and 3-butanol-1-oxyl, followed respectively by disproportionations to:
 - (a) 2-butanol plus 1-buten-3-ol
 - (b) 1,3-butanediol plus 3-hydroxybutanal

A final choice of mechanism for the dehydration of γ, γ' -dihydroxydibutyl ether cannot be made at this time because of lack of experimental data. Conditions favorable to each of the five interpretations given could be devised.

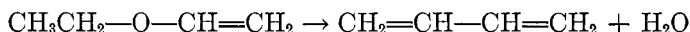
Over barium chloride at 350°C. or over alumina at 450–500°C., under decreased pressure, γ -chlorobutyl γ' -hydroxybutyl ether undergoes a combined hydrodechlorination and bidehydration (31):



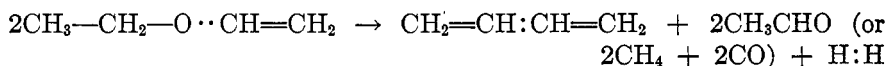
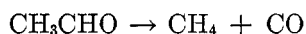
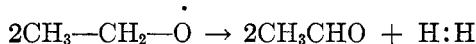
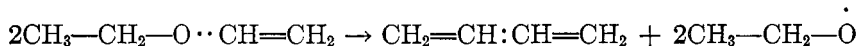
From a mechanism standpoint, the conversion is more complicated in nature than that of γ, γ' -dihydroxydibutyl ether. The location of primary scission probably depends upon relative strengths of bonds other than C—C, the availability or potential of the disrupting energy, and the particular type of catalyst present. It seems probable that the rôles of barium chloride and alumina are, respectively, those of dehydrodechlorination and dehydration catalysts. Hence an active mixture of catalysts to effect both types of catalysis seems desirable.

2. Alkyl alkenyl ethers

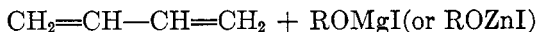
Ethyl vinyl ether undergoes a "catalytic" dehydration to butadiene, ostensibly according to the over-all equation (126):



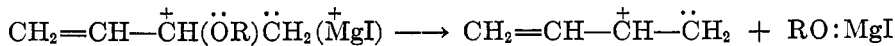
From the reaction mechanism standpoint, it is probable that the radical less firmly attached to the oxygen atom will be mainly eliminated. According to molecular transposition studies (16, 17, 173, 177), the tendency of the vinyl group to split off is greater than that of the ethyl group. This fact introduces for consideration the following equations:



Alkyl α -vinyl- β -iodoethyl ethers readily form butadiene when acted upon by magnesium or zinc dust and ethanol (151). The alkyl group is suitably methyl, ethyl, *n*-propyl, or isobutyl:



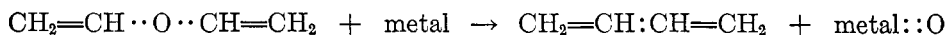
It will be observed that elimination of the alkoxy groups is β to the vinyl group, hence rapid in rate, and that in the fragmentation the normally weak β C—C bond is stronger than the strained C—O bond. The C—I bond is probably the weakest linkage (45.5 kcal.) in the molecule, so that polar alkyl α -vinyl- β -iodomagnesium (or iodozinc) ethyl ethers may be taken as reaction intermediates. Elimination of alkoxy magnesium or alkoxy zinc iodide would occur with simultaneous establishment of resonance among butadiene structures, beginning with 1-butene-3,4-diyl:



All other resonance
forms of butadiene

3. *Dialkenyl ethers*

Divinyl ether forms butadiene when reduced by iron, copper, lead, tin, bismuth, antimony, cadmium, zinc, or aluminum:



The process operates at 100–400°C. (102, 103, 104, 105). One would expect in this reaction a certain amount of dehydration traceable to the metal oxides produced. A dehydration to ethyne or dissociation to ethanal plus ethyne, which would require respectively 48.2 and 9.4 kcal. per gram-mole of divinyl ether, is avoided or minimized presumably by an excess of metal reactant.

Dehydration of di(2-but-en-1-yl) ether was announced by Ostromyslenskiĭ (126):



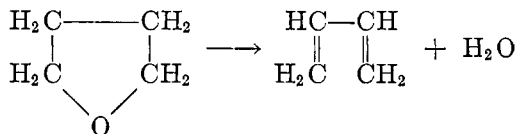
First, 1,4-dehydration would give presumably 2-buten-1-ol plus butadiene and, second, more butadiene by conversion of the butenol. Each step would be only 0.7 kcal. endothermic, making the over-all process theoretically 1.4 kcal. endothermic per two gram-moles of butadiene.

Table 10 gives data on the conversion of the various aliphatic ethers into butadiene.

B. CYCLIC OXIDES

1. *Epoxybutanes*

The catalytic dehydration of 1,4-epoxybutane was discovered by Ostromyslenskiĭ (126):



Catalysts for the conversion include the primary sodium, primary or secondary calcium, other alkaline earth, nickel, cobalt, silver, copper, mercury, and lead orthophosphates, phosphoric acid or boric acid on pumice or other carriers, heteropolyacids of tungsten or of molybdenum, oxides of tungsten or of molybdenum, silica gel, alumina, and chromia (61, 63, 64, 163). The acid phosphates may be used at 250–450°C. in the presence of steam. A later patent cites production of butadiene from 1,3- and 1,4-butanediols over acid phosphates in the presence of 1,4-epoxybutane as an organic diluent that is but slowly decomposed in the reaction (162). Since similar catalysts and temperatures are used in the production (60, 62, 69, 70, 160, 161, 164) of 1,4-epoxybutane from 1,4-butanediol, the possibility of formation of a weak bond between 1,4-epoxybutane and the catalysts is indicated; decomposition of the oxonium salts into butadiene would be the next step.

At 400–500°C. over pumice carrying orthophosphoric acid, 2,3-epoxybutane

TABLE 10
Conversion of ethers into butadiene

PROCESS AND ETHER USED	CATALYSIS OR SPECIAL REACTANTS	TEMPERATURE °C.	PRESSURE <i>atm.</i>	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
<p>"Dehydration" and dehydrogenation of diethyl ether</p> $3(C_2H_5)_2O + 2Al \rightarrow 3C_4H_6 + Al_2O_3 + 6H_2$	Aluminum metal was a reactant	600		Yield of B was small on fully decomposed ether	(34, 35)
<p>...</p>	Aluminum metal was a reactant			Yield of B was 2% on ether	(98)
<p>"Dehydration" and dehydrogenation of ethyl α-chloroethyl ether (mono-α-chlorodiethyl ether)</p> $C_2H_5OCH_2CH_2Cl \rightarrow C_4H_6 + H_2O + HCl$	A catalyst of undisclosed composition was used	450	0.974-0.987	Yields of B were 7% (average) and 10% (maximum) by weight on ether passed and 9-10% (average) by weight on fully decomposed ether	(95)
<p>...</p>	Catalyst: $Al_2O_3 + BaO$	350		Yield of B was 20%	(142)
<p>"Dehydration" and dehydrochlorination of ethyl β-chloroethyl ether (mono-β-chlorodiethyl ether)</p> $C_2H_5OCH_2CH_2Cl \rightarrow C_4H_6 + H_2O + HCl$	Catalyst: Al_2O_3			See patent for possible details	(126, 139)
<p>...</p>	A catalyst was used			See patent for possible details	(126, 139)
<p>"Dehydration" of ethyl α-hydroxyethyl ether</p> $C_2H_5OCHOHCH_3 \rightarrow C_4H_6 + 2H_2O$	Catalyst: Al_2O_3 or ThO_2	400-450		See patent for possible details	(126, 139)
<p>"Dehydration" of ethyl β-hydroxyethyl ether</p> $C_2H_5OCH_2CH_2OH \rightarrow C_4H_6 + 2H_2O$					(8)

Decomposition of methyl α -methoxyethyl ether (1,1-dimethoxyethane) $\text{CH}_3\text{OCH}(\text{OCH}_3)\text{CH}_3 \rightarrow \text{C}_4\text{H}_6 + 2\text{H}_2\text{O}$ <p>...</p>	Catalyst: Al_2O_3	350	Yield of B = ?	(4)
Decomposition of ethyl α -ethoxyethyl ether (acetal or 1,1-diethoxyethane) $\text{C}_2\text{H}_5\text{OCH}(\text{OC}_2\text{H}_5)\text{CH}_3 \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH}$ <p>“Dehydration” and decesterification of ethyl α-acetoxyethyl ether (mono-α-acetoxydiethyl ether) $\text{C}_2\text{H}_5\text{OCH}(\text{OCOCH}_3)\text{CH}_3 \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} + \text{CH}_3\text{COOH}$ </p>	Catalyst: Al_2O_3	300-380	Yield of B was 16%	(142)
Dehydration of γ, γ' -dihydroxydibutyl ether $(\text{CH}_3\text{CHOHCH}_2\text{CH}_2)_2\text{O} \rightarrow 2\text{C}_4\text{H}_6 + 3\text{H}_2\text{O}$	Catalyst was H_2SO_4 (1% in water; an autoclave was used; acid sulfates, sulfonic acids, phosphoric acid, perchloric acid, or mixtures of these compounds may be used as catalysts)	200	Yield of B = ?	(50)
Dehydration and dehydrodechlorination of γ -chlorobutyl γ' -hydroxybutyl ether $\text{CH}_3\text{CHClCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CHOHCH}_3 \rightarrow 2\text{C}_4\text{H}_6 + \text{HCl} + 2\text{H}_2\text{O}$ <p>...</p>	Catalyst: BaCl_2	350	Yield of B was 18% by weight on feed	(31)
“Dehydration” of ethyl vinyl ether $\text{C}_2\text{H}_5\text{OCH}=\text{CH}_2 \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O}$	Catalyst: Al_2O_3	450-500	Yield of B was 24% by weight on feed	(31)
			See patent for possible details	(126, 138)
			See patent for possible details	(126, 138)

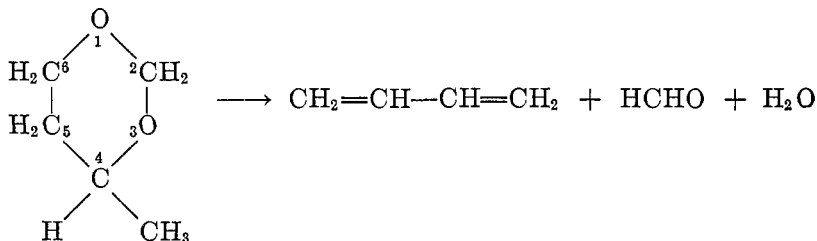
TABLE 10—Continued

PROCESS AND ETHER USED	CATALYSTS OR SPECIAL REACTANT	TEMPERATURE °C.	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
Deiodomethoxylation of methyl α -vinyl- β -iodoethyl ether $\text{CH}_3\text{OCH}(\text{CH}=\text{CH}_2)\text{CH}_2\text{I} + \text{Mg}$ (or Zn) \rightarrow $\text{C}_4\text{H}_6 + \text{CH}_3\text{OMgI}$ (or CH_3OZnI)			<i>atm.</i>		
Deiodoethoxylation of ethyl α -vinyl- β -iodoethyl ether $\text{C}_2\text{H}_5\text{OCH}(\text{CH}=\text{CH}_2)\text{CH}_2\text{I} + \text{Mg}$ (or Zn) $\rightarrow \text{C}_4\text{H}_6 + \text{C}_2\text{H}_5\text{OMgI}$ (or $\text{C}_2\text{H}_5\text{OZnI}$)			1	Yield of B = ?; ethanol was part of the feed	(151)
Deiodopropoxylation of propyl α -vinyl- β -iodoethyl ether $\text{C}_3\text{H}_7\text{OCH}(\text{CH}=\text{CH}_2)\text{CH}_2\text{I} + \text{Mg}$ (or Zn) $\rightarrow \text{C}_4\text{H}_6 + \text{C}_3\text{H}_7\text{OMgI}$ (or $\text{C}_3\text{H}_7\text{OZnI}$)			1	Yield of B = ?; ethanol was part of the feed	(151)
Deiodoisobutoxylation of isobutyl α -vinyl- β -iodoethyl ether $\text{C}_4\text{H}_9\text{OCH}(\text{CH}=\text{CH}_2)\text{CH}_2\text{I} + \text{Mg}$ (or Zn) $\rightarrow \text{C}_4\text{H}_6 + \text{C}_4\text{H}_9\text{OMgI}$ (or $\text{C}_4\text{H}_9\text{OZnI}$)			1	Yield of B = ?; ethanol was part of the feed	(151)
Reduction of divinyl ether $(\text{CH}_2=\text{CH})_2\text{O} + \text{metal} \rightarrow \text{C}_4\text{H}_6 + \text{metal oxide}$	Fe, Cu, Pb, Sn, Bi, Sb, Cd, Zn, and Al are reactants	140–400	?	Yields of B = ?	(102, 103)
Reduction of divinyl ether by zinc $(\text{CH}_2=\text{CH})_2\text{O} + \text{Zn} \rightarrow \text{C}_4\text{H}_6 + \text{ZnO}$	Zn is a reactant	?	?	Yield of B = ?	(104)
Reduction of divinyl ether $(\text{CH}_2=\text{CH})_2\text{O} + \text{metal} \rightarrow \text{C}_4\text{H}_6 + \text{metal oxide}$	Fe, Cu, Pb, Sn, Bi, Sb, Cd, and Zn are reactants	100–400	?	Yields of B = ?	(105)
“Dehydration” of di(2-buten-1-yl) ether $(\text{CH}_3\text{CH}=\text{CHCH}_2)_2\text{O} \rightarrow 2\text{C}_4\text{H}_6 + \text{H}_2\text{O}$?	?	Yield of B = ?	(126, 129)

undergoes dehydration to butadiene (110). Owing to the high temperature range, some question exists concerning the type of dehydration—thermal or catalytic—that is operative.

2. Methyl-dioxane

When 4-methyl-*m*-dioxane, which can be called 1,3-butanediol formal, is conducted over a phosphoric acid on graphite catalyst at 270°C. in the presence of steam, butadiene, formaldehyde, water, and propene are formed (36):



The conversion of 4-methyl-*m*-dioxane can be looked upon as a reversion into 1,3-butanediol and formaldehyde hydrate, followed by dehydration to butadiene:

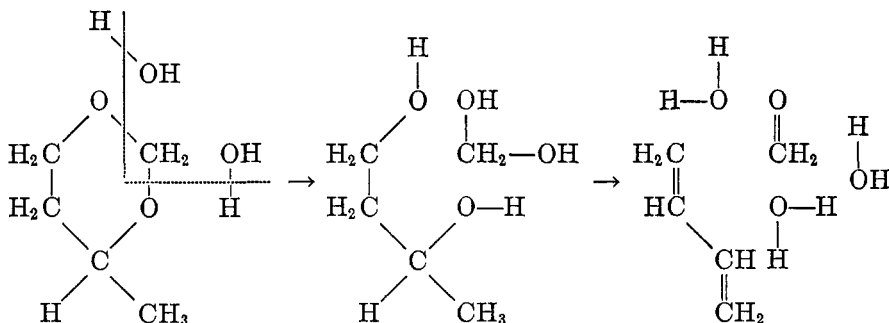
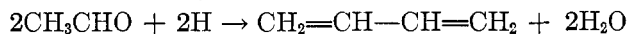


Table 11 contains data on the conversion of cyclic oxides into butadiene.

IV. ALDEHYDES

A. ALKANALS

Considerable theoretical interest lies in an electrolytic reduction and condensation of ethanal, patented twenty-five years ago (145):



The by-products include 1,3-butanediol and butenols, the formation of which was ascribed to hydrogenation of 3-hydroxybutanal and of its dehydration product, 2-butenal, respectively. Abundant evolution of hydrogen at the cathode leads to formation of 1-butanol. From this point of view, butadiene production is dependent on aldolization, hydrogenation, and dehydration. The order

TABLE II
Catalysis of cyclic oxides

PROCESS AND CYCLIC OXIDE	CATALYST	TEMPERATURE °C.	PRESSURE atm.	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
<p>Dehydration of 1,4-epoxybutane (tetrahydrofuran)</p> $ \begin{array}{c} \text{H}_2\text{C}-\text{CH}_2 \\ \quad \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \diagdown \quad / \\ \text{O} \end{array} \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} $	<p>A catalyst was used</p> <p>Catalysts were: (A) mercurous phosphate on pumice; (B) calcium phosphate; (C) W_2O_6 + bleaching earth; (D) NaH_2PO_4 + H_3PO_4 + graphite + nickel acetate</p>	<p>Heated</p> <p>280-290 (case A) 360 (case B) 330-390 (case C) 260-310 (case D)</p>	<p>1 or less (cases A, B, D) Approx. 1 (case C)</p>	<p>See patent for possible details</p> <p>Yields of B were 71, (?), less than 49.4, less than 48.7% by weight on feed in cases A, B, C, and D, respectively</p>	<p>(125)</p> <p>(126, 138)</p> <p>(163)</p>
<p>Dehydration of 2,3-epoxybutane</p> $ \begin{array}{c} \text{CH}_3\text{CH}-\text{CHCH}_3 \\ \diagdown \quad / \\ \text{O} \end{array} \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} $	<p>H_3PO_4 on pumice</p>	<p>400-500</p>	<p><i>In vacuo</i> if desired</p>	<p>Yield of B = ?</p>	<p>(110)</p>
<p>Decomposition of 4-methyl-<i>m</i>-dioxane in presence of steam</p> $ \begin{array}{c} \text{O} \\ / \quad \backslash \\ \text{H}_2\text{C} \quad \text{CH}_2 \\ \quad \\ \text{H}_3\text{C} \quad \text{O} \\ \diagdown \quad / \\ \text{C} \\ \quad \\ \text{H} \quad \text{CH}_3 \end{array} \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} + \text{HCHO} $	<p>H_3PO_4 on graphite (prepared at 160°C. from sodium phosphate solution, primary <i>n</i>-butylamine phosphate, and graphite)</p>	<p>270</p>	<p>1?</p>	<p>Yield of B was 52% by weight on absolute methyldioxane feed</p>	<p>(36)</p>

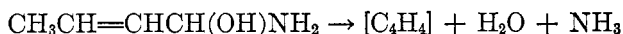
bonyl group is removed by direct elimination and as water (traceable to tautomerization of $\text{HC}-\overset{\cdot}{\text{C}}=\text{O}$ into $\text{C}=\overset{\cdot}{\text{C}}-\text{OH}$ or to carbonyl hydrogenations, $\overset{\cdot}{\text{C}}-\overset{\cdot}{\text{O}} + \overset{\cdot}{\text{H}} \rightarrow \overset{\cdot}{\text{C}}-\overset{\cdot}{\text{O}}:\text{H}$; $\overset{\cdot}{\text{C}}-\overset{\cdot}{\text{O}} + 2\overset{\cdot}{\text{H}} \rightarrow \text{H}:\overset{\cdot}{\text{C}}-\overset{\cdot}{\text{O}}:\text{H}$). Formation of ethane and of ethene indicates a possible butadiene production through dehydrogenation into vinyl radicals and their association. Demethanation of 2-methylpropanal into propenal, followed by decarbonylation or deformylation, is another mechanism that would furnish vinyl radicals.

Ethanol converts 3-hydroxybutanal into butadiene when passed over lumps of aluminum hydroxide at 300°C. (111). Steam is used to minimize resinification of the hydroxybutanal and to keep the catalyst clean.

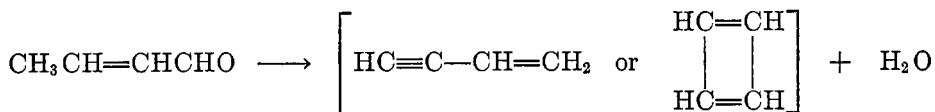
B. ALKENALS

2-Butenal, i.e., crotonaldehyde, is convertible into butadiene by reaction with ethanol (111), ammonia (56), or aniline (55). The conditions for a reaction with ethanol are exposure to temperatures of 250–460°C. in the presence of a "dehydration" catalyst, such as lumps of precipitated aluminum hydroxide (111).

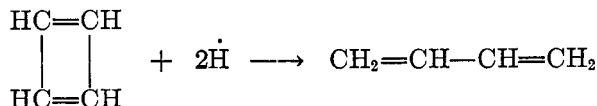
Ammonia reacts with 2-butenal at 390°C. in the presence of alumina, producing ethene, butadiene, benzene, toluene, *o*-xylene, *p*-xylene, ethylbenzene, styrene, naphthalene, acetonitrile, benzonitrile, *o*-tolunitrile, *p*-tolunitrile, pyrrole, and 3-ethyl-4-methylpyridine, i.e., β -collidine (56). Huntenburg pointed out that alumina could act as a catalyst, effecting removal of both ammonia (57) and water from 2-butenalammonia:



and that 2-butenal upon loss of water should form a C_4H_4 member, perhaps butenyne or cyclobutadiene:



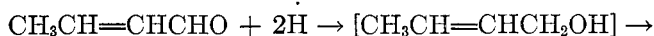
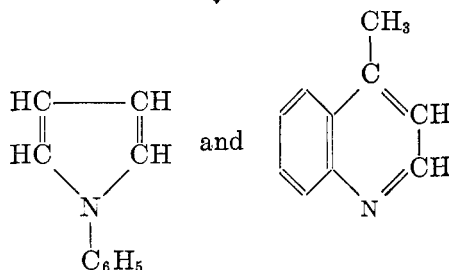
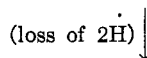
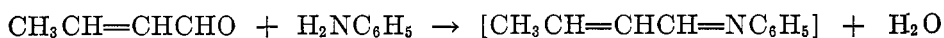
Hydrogenation of cyclobutadiene, which is generally acknowledged to be an unstable molecule, because of ring strain (101, 148, 179, 180), was taken as probably responsible for butadiene production:



Dehydration of the aminohydroxymethyl group of 2-butenalammonia and ethanalammonia, $\text{CH}_3\text{CH}(\text{OH})\text{NH}_2$, would produce aldimines, $\text{RCH}=\text{NH}$, whose dehydrogenation to nitriles could furnish the requisite hydrogen atoms for hydrogenation of C_4H_4 into C_4H_6 . Aldimines were taken as the source of both tolunitriles and acetonitrile. The present authors suggest that ammonia may function also as a source of atomic hydrogen, reducing the 2-butenal car-

bonyl group to the primary alcohol group of 2-buten-1-ol, which would be directly convertible into butadiene.

Aniline reacts with 2-butenal at temperatures above 500°C. in the presence of oxides of aluminum, beryllium, iron, or thorium (55). The products include butadiene, *N*-phenylpyrrole, 4-methylquinoline, and smaller amounts of ethene, benzene, xylene, styrene, naphthalene, hydroxybenzene, *o*-methylbenzaldehyde, quinoline, and 2-methylquinoline. By increasing the proportion of aniline or passing over the catalyst at the same time such hydrogen donors as methanol or tetrahydronaphthalene, the butadiene yield is increased. *N*-Phenylpyrrole production increases if the temperature is above 600°C. and a large amount of aniline is introduced. Consequently, it can be postulated that the *N*-phenylpyrrole, 4-methylquinoline, and butadiene formations are related, with the atomic hydrogen released in 2-butenal and aniline condensations being used to transform 2-butenal into 2-buten-1-ol:



The over-all equation is identical for both the $\text{C}_{10}\text{H}_9\text{N}$ isomers:



Table 12 contains data on the conversion of aldehydes into butadiene.

V. CARBOXYLIC ACIDS AND THEIR ESTERS

A. ALKANOIC ACIDS

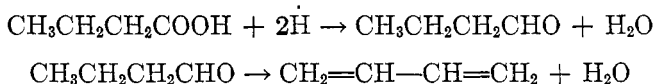
n-Butyric, isobutyric, and isovaleric acids form traces of butadiene upon passage over pumice at 600°C., according to Nef (122). A variety of reactions are operative in these pyrolyses, for the product in each case contains carbon monoxide, carbon dioxide, hydrogen, water, methane, ethane, ethene, propene, butadiene, and a keto compound (dimethyl ketone in the case of isobutyric acid). While butadiene formation could be attributed to an association of vinyl groups or to a polymerization of the ethene or propene with subsequent decomposition, there are other possibilities based on the chemistry of alkanolic acids.

TABLE 12
Conversion of aldehydes into butadiene

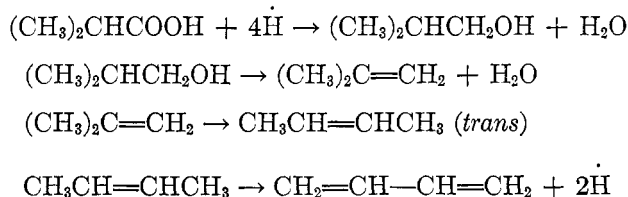
PROCESS AND ALDEHYDE USED	CATALYST	TEMPERATURE °C.	PRES- SURE atm.	REMARKS (B IS 1,3-BUTADIENE)	REFER- ENCES
Electrolytic reduction and condensation of eth- anal (acetaldehyde) $2\text{CH}_3\text{CHO} + 2\text{H} \rightarrow \text{C}_4\text{H}_6 + 2\text{H}_2\text{O}$	Electrolyte had over 20% of H_2SO_4	> 30-35		Yield of B = ?	(145)
"Dehydration" of butanal (butyraldehyde) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHO} \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O}$	Catalyst: aluminum silicate	550	0.00132	Yield of B was 52.5% by weight on feed, using one recycle	(85)
"Dehydration" of 2-methylpropanal (isobuty- raldehyde) $(\text{CH}_3)_2\text{CHCHO} \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O}$	Catalyst: aluminum silicate	Red heat		Yield of B = ?	(149)
Action of ethanol on 3-hydroxybutanal (aldol) $\text{CH}_3\text{CHOHCH}_2\text{CHO} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_4\text{H}_6 +$ $\text{CH}_3\text{CHO} + 2\text{H}_2\text{O}$ $\text{CH}_3\text{CHOHCH}_2\text{CHO} + 2\text{C}_2\text{H}_5\text{OH} \rightarrow 2\text{C}_4\text{H}_6$ $+ 4\text{H}_2\text{O}$ (Probable reactions are given)	Catalyst: pumice	580-590	1	Yield of B was 0.095% by weight on feed	(118)
Action of ethanol on 2-butenal (crotonalde- hyde) $\text{CH}_3\text{CH}=\text{CHCHO} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{C}_4\text{H}_6 +$ $\text{CH}_3\text{CHO} + \text{H}_2\text{O}$ $\text{CH}_3\text{CH}=\text{CHCHO} + 2\text{C}_2\text{H}_5\text{OH} \rightarrow 2\text{C}_4\text{H}_6 +$ $3\text{H}_2\text{O}$ (Probable reactions are given)	Catalyst: lumps of precipi- tated $\text{Al}(\text{OH})_3$	300		Yield of B was 10.8% by weight on aldol feed	(111)

Action of ammonia on 2-butenal (crotonaldehyde)	Catalyst: Al_2O_3	390	Yield of B = ?	(56)
Action of aniline on 2-butenal (crotonaldehyde) $2\text{CH}_3\text{CH}=\text{CHCHO} + \text{C}_6\text{H}_5\text{NH}_2 \rightarrow \text{C}_4\text{H}_6 + \text{C}_{10}\text{H}_9\text{N} + 2\text{H}_2\text{O}$	Catalysts: Al_2O_3 ; BeO ; iron oxide; ThO_2	Above 500	Yield of B was 15% on product	(55)
			1 or less	

The conversion of *n*-butyric acid into butadiene may be dependent on such reactions as:



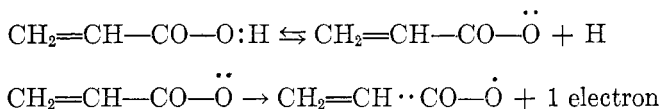
Isobutyric acid might be converted as follows:



Isovaleric acid conversion into butadiene can be explained on the basis of decarboxylation, isomerization, and dehydrogenation.

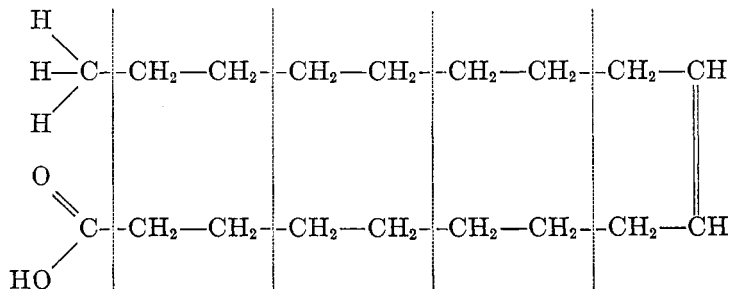
B. ALKENOIC ACIDS

Ostromyslenskii observed that electrolysis of acrylic acid gives small amounts of butadiene at the anode (136). The investigation was discontinued because of unavailability of a commercial supply and no explanation of the reaction course was given. A simple mechanism can be given by assuming that negative acrylate ions become neutralized at the anode, forming unstable acrylate free radicals:



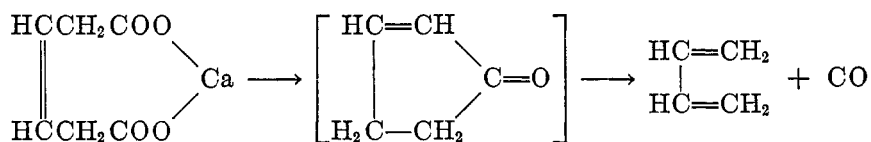
Decarboxylation of the latter would liberate vinyl radicals, some of which would associate to butadiene.

Oleic acid, which is *cis*-9-octadecenoic acid, yields 30 per cent of butadiene when its vapors are passed over a metal spiral heated to a bright red (40). The *trans*-form, or elaidic acid, also produces butadiene. These conversions are probably C_2 and C_4 scissions starting at the carboxyl or terminal methyl group, or in the β -position to the $\text{C}=\text{C}$ group. Other points of weakness in the molecule are located two or four carbon atoms away from the positions of initial scission:

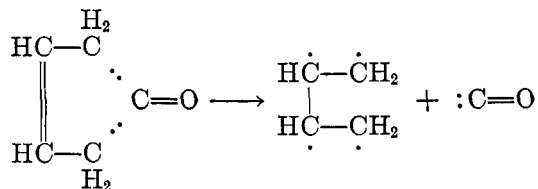


The C₂ and C₄ fragments, except 2-butene-1,4-diyl, require subsequent dehydrogenation to produce butadiene.

Calcium $\Delta^{\beta,\gamma}$ -dihydruconate forms butadiene, carbon monoxide, and 1-cyclopenten-3-one when dry-distilled (112). The theory advanced in explanation of the conversion was decarbonylation of the aforementioned cyclopentenone:



1-Cyclopenten-3-one may have considerable stability, whereas the expected dry-distillation ketone is 1-cyclopenten-4-one. The latter should undergo decarbonylation by β scissions alone:



C. ALKADIENOIC ACID

2,4-Pentadienoic acid yields butadiene when distilled with quinoline (136). This conversion can be considered to involve dissociation of an unstable quinoline compound:

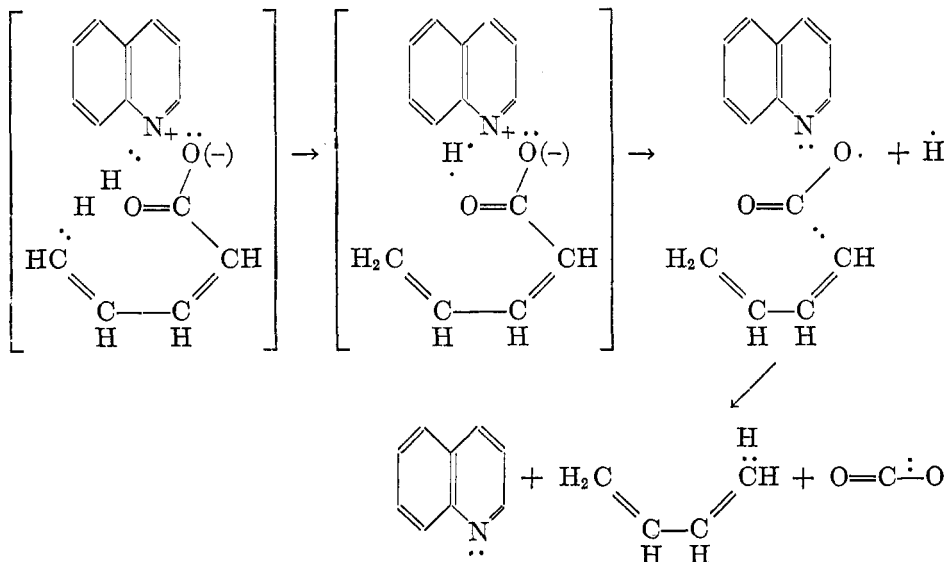


TABLE 13
Conversion of carboxylic acids into butadiene

PROCESS AND CARBOXYLIC ACID	APPARATUS AND CATALYSTS	TEMPERATURE °C.	PRES- SURE	REMARKS (B IS 1,3-BUTADIENE)	REFER- ENCES
Decomposition of <i>n</i> -butyric acid $2\text{C}_4\text{H}_7\text{CH}_2\text{CH}_2\text{COOH} \rightarrow \text{C}_4\text{H}_6 + \text{C}_3\text{H}_6 + \text{CO}_2 + 2\text{H}_2\text{O}$ (Probable reaction is given)	Catalyst: pumice	590-600	<i>atm.</i> 1	Yield of B was 0.22% by weight on feed	(122)
Decomposition of isobutyric acid $2(\text{CH}_3)_2\text{CHCOOH} \rightarrow \text{C}_4\text{H}_6 + \text{C}_3\text{H}_6 + \text{CO}_2 + 2\text{H}_2\text{O}$ (Probable reaction is given)	Catalyst: pumice	600-620	1	Yield of B was 0.029% by weight on feed	(122)
Decomposition of isovaleric acid $(\text{CH}_3)_2\text{CHCH}_2\text{COOH} \rightarrow \text{C}_4\text{H}_6 + \text{CO}_2 + 2\text{H}_2$	Catalyst: pumice	600	1	Yield of B was 0.082% by weight on feed	(122)
Electrolysis of acrylic acid $2\text{CH}_2=\text{CHCOOH} \rightarrow \text{C}_4\text{H}_6 + 2\text{CO}_2 + \text{H}_2$				Yield B of = ?; no details available	(136)
Thermal treatment of vapors of technical oleic acid (olein, stearin oil)	Iron vessel serving as vaporizer; an attached vertical column containing a metal spiral heated by electricity serving as an "isoprene lamp"	Bright red heat	1	Yield of B was 30% by weight on feed	(40)

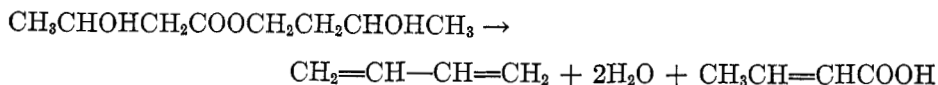
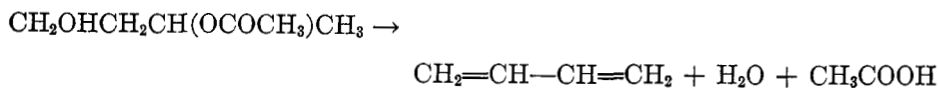
Thermal treatment of elaidic acid (isomer of oleic acid)	Special apparatus with vaporizer; attached porcelain tube containing a platinum wire heated to bright red heat, and fractionator	Bright red heat	<i>In vacuo</i>	(40)
Decarboxylation of 2,4-pentadienoic acid (i.e., β -vinylacrylic acid or 1-carboxy-1,3-butadiene) $\text{CH}_2=\text{CHCH}=\text{CHCOOH} \rightarrow \text{C}_4\text{H}_6 + \text{CO}_2$	Catalyst: quinoline	Distillation temperature	1	(136)

The important feature is formation of the C_5 free radicals, which would readily decarboxylate into 1,3-butadien-1-yl free radicals and then annex an atomic hydrogen.

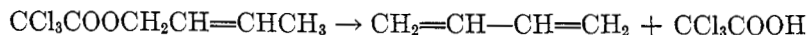
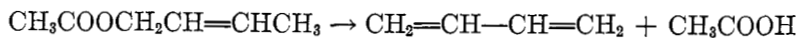
Table 13 gives data on the conversion of carboxylic acids into butadiene.

D. MONOESTERS

Catalytic conversion of esters of 1,3-butanediol was briefly described by Ostromyslenskii (132). The following equations were given for the conversions of 1,3-butanediol 3-acetate and 1,3-butanediol 1- β -hydroxybutyrate, respectively:



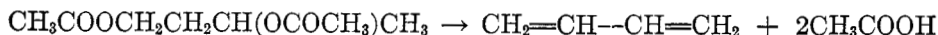
Catalytic elimination of acid from 2-buten-1-yl esters, also, will give butadiene, as demonstrated by conversions of 2-buten-1-yl acetate (126, 132) and 2-buten-1-yl trichloroacetate (155):



Prévost, who investigated the last reaction, maintained that it was a direct breakdown on account of overheating.

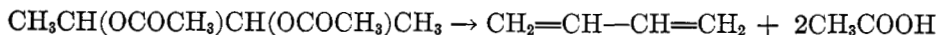
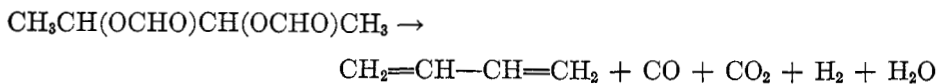
E. DIESTERS

Ostromyslenskii gave the following equation for the catalytic conversion of 1,3-butanediol diacetate (126):



The reaction probably proceeds in two steps, possibly via both 4-acetoxy-1-butene and 1-acetoxy-2-butene. These intermediates would be favored on account of an easier removal of secondary, than primary, acetoxy.

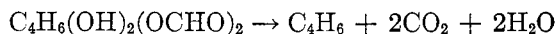
2,3-Butanediol diformate and diacetate form butadiene when passed at 550°C. over quartz chips (53):



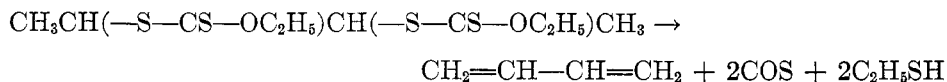
2,3-Butanediol diacetate gives butadiene at 350–575°C. over kaolin (15). The neutral sulfite of 2,3-butanediol forms butadiene at 450–575°C. over the same catalyst (15). 2,3-Butanediol diacetate undergoes an 84.9 per cent conversion into butadiene when treated thermally at about 585°C. in an atmosphere of nitro-

gen (165). Pyrolysis of the same diacetate at 595°C. and substantially atmospheric pressure forms the basis of a commercially operable process developed by the Northern Regional Research Laboratory and the Bureau of Agricultural and Industrial Chemistry of the Agricultural Research Administration, U. S. Department of Agriculture. The diacetate is obtained from 2,3-butanediol by treatment with acetic acid in the presence of sulfuric acid. A butadiene yield of 85.4 per cent of the theoretical based on butanediol charged, or 88 per cent of the theoretical based on diacetate, and a 99 per cent recovery of acetic acid have been secured (123).

Erythrite diformate, i.e., 1,2,3,4-butanetetrol diformate, was converted into butadiene at 210–220°C. by Henninger (51):



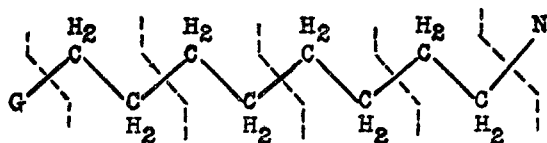
Another diester that gives butadiene is 2,3-butene bis(ethylxanthogenic acid) (174). This compound undergoes 1,2- and 3,4-eliminations without isomerization:



Xanthogenates undergo elimination of an unsaturated hydrocarbon (11, 12) at relatively low temperatures because of the low bond energy of C—S linkages and the practically thermoneutral character of the over-all process. The formation of carbon oxysulfide and ethanethiol, instead of ethylxanthogenic acid, from the 2,3-butene diester, probably changes the character of the conversion from endothermic to slightly exothermic. Development of resonance energy among the various valence-bond structures of butadiene and of carbon oxysulfide is another factor that helps overcome the endothermicity expected in elimination reactions.

F. TRIESTERS

Natural glycerides are converted into butadiene by vaporization followed by contact with a red-hot platinum wire in apparatus reminiscent of the "isoprene lamp." Olive oil, linseed oil, fish oil, and rape-seed oil are suitable (40). No explanation of the conversion of these natural products has been available to date. One can readily be given, however, based on the principle of alteration of C—C bond strengths. In the abbreviated glyceride molecule



G and N represent the glyceryl and non-glyceryl ends, respectively, of a triester and its isolated group of fatty acid ethane-1,2-diyls. Thermal dehydrogenation presumably further connecting the ethanediyls at the points marked by seg-

TABLE 14
Decomposition of esters

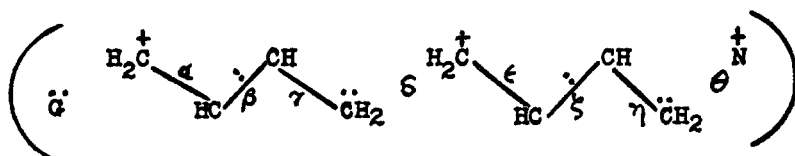
PROCESS AND ESTER DECOMPOSED	APPARATUS AND CATALYST USED	TEMPERATURE °C.	PRES- SURE <i>atm.</i>	REMARKS (B IS 1,3-BUTADIENE)	REFER- ENCES
Dehydration and deesterification of 1,3-butanediol 3-acetate (1-hydroxy-3-acetoxybutane) $\text{CH}_3\text{OHCH}_2\text{CH}(\text{OCOCH}_3)\text{CH}_3 \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} + \text{CH}_3\text{COOH}$	Catalyst of undisclosed composition used; see patent disclosures (138-140) for possible data.	Heated	1?	Yield of B = ?	(126)
Dehydration and deesterification of 1,3-butanediol 1- β -hydroxybutyrate (1- β -oxybutyryloxy-3-hydroxybutane) $\text{CH}_3\text{CH}_2\text{CHOHCH}_2\text{O} \begin{array}{c} \\ \text{O} \\ \\ \text{COCH}_2\text{CHOHCH}_3 \end{array}$ A% $\xrightarrow{\hspace{1.5cm}}$ 100-A% COCH ₂ CHOHCH ₃	Catalyst of undisclosed composition used; see patent disclosures (138-140) for possible data.	Heated	1?	Yield of B was 30.7% by weight on feed	(126)
$\text{C}_4\text{H}_6 + \text{H}_2\text{O} + \text{CH}_3\text{CHOHCH}_2\text{COOH}$ $\text{C}_4\text{H}_6 + 2\text{H}_2\text{O} + \text{CH}_2\text{CH}=\text{CHCOOH}$	Catalyst of undisclosed composition was mentioned in reference 126	Heated	1?	Yield of B = ?; see patent certificate for possible details	(126, 138)
Decomposition of 2-buten-1-yl acetate (crotyl acetate) $\text{CH}_3\text{COOCH}_2\text{CH}=\text{CHCH}_3 \rightarrow \text{C}_4\text{H}_6 + \text{CH}_3\text{COOH}$	Sodium bromide was present; its value = ?	Heated, 140?	1	Yield of B = ?	(155)
Decomposition of 2-buten-1-yl trichloroacetate (crotyl trichloroacetate)	Quartz tube packed with quartz chips	550	1	Yield of B = ?	(63)
Deesterification of 2,3-butanediol diformate (2,3-bisformoxybutane) $\text{CH}_3\text{CH}(\text{OCHO})\text{CH}(\text{OCHO})\text{CH}_3 \rightarrow \text{C}_4\text{H}_6 + \text{CO} + \text{CO}_2 + \text{H}_2 + \text{H}_2\text{O}$					

Deesterification of 1,3-butanediol diacetate (1,3-bisacetoxybutane) $\text{CH}_3\text{COOCH}_2\text{CH}_2\text{CH}(\text{OCOCH}_3)\text{CH}_3 \rightarrow \text{C}_4\text{H}_8 + 2\text{CH}_3\text{COOH}$	Catalyst of undisclosed composition was used; see patent disclosures (138, 140) for possible data	Heated	1?	Yield of B = ?	(126)
		600	0.145	Yield of B was 30% by weight on fully decomposed feed	(46)
Deesterification of 2,3-butanediol diacetate (2,3-bisacetoxybutane) $\text{CH}_3\text{CH}(\text{OCOCH}_3)\text{CH}(\text{OCOCH}_3)\text{CH}_3 \rightarrow \text{C}_4\text{H}_8 + 2\text{CH}_3\text{COOH}$	Quartz tube	600		Yield of B was 30% by weight on fully decomposed feed	(46)
		625		Yield of B was 31% by weight on fully decomposed feed	(46)
	Quartz tube packed with quartz chips	550	1	Yield of B was 30.5% by weight on fully decomposed feed	(46)
		510-515	1	Yield of B was "good" (the theoretical yield is only 31.1% by weight on feed)	(53)
	Glass tube packed with unglazed earthenware rings	510-515	1	Yield of B was 25.2% by weight on feed, corresponding to 28.9% by weight on fully decomposed feed	(53)
		510-515?	1	Yield of B was 25.2% by weight on feed	(53)
	Glass tube packed with stainless-steel turnings Catalyst: kaolin	350-575		Yield of B increased as the temperature approached 575°C.	(15)
		595	1	Yield of B was 27.4% by weight or 88% of the theoretical yield	(123)
	An atmosphere of nitrogen was used	585		Yield of B was 26.4% by weight or 84.9% of the theoretical yield	(165)

TABLE 14—Continued

PROCESS AND ESTER DECOMPOSED	APPARATUS AND CATALYST USED	TEMPERATURE °C.	PRES- SURE	REMARKS (B IS 1,3-BUTADIENE)	REFER- ENCES
Decomposition of the neutral sulfite of 2,3-butanediol $\begin{array}{c} \text{CH}_3\text{CH} \text{---} \text{CHCH}_3 \\ \qquad \\ \text{O} \text{---} \text{SO} \text{---} \text{O} \end{array} \rightarrow \text{C}_4\text{H}_6 + \text{H}_2\text{O} + \text{SO}_2$	Catalyst: kaolin	450-575	atm.	Yield of B was slight at 450° and 8-10% at 575°	(15)
Decomposition of 1,2,3,4-butanetetrol diformates (dihydroxybisformoxybutanes) $\text{C}_4\text{H}_6(\text{OH})_2(\text{OCHO})_2 \rightarrow \text{C}_4\text{H}_6 + 2\text{CO}_2 + 2\text{H}_2\text{O}$		210-220		Yield of B = ?	(51)
Decomposition of 2,3-butene bis (ethylxanthogenic acid) $\text{CH}_3\text{CH}(\text{S}\cdot\text{CS}\cdot\text{OC}_2\text{H}_5)\text{CH}(\text{S}\cdot\text{CS}\cdot\text{OC}_2\text{H}_5)\text{CH}_3 \rightarrow \text{C}_4\text{H}_6 + 2\text{COS} + 2\text{C}_2\text{H}_5\text{SH}$		190-270	1	Yield of B was 5.8% by weight on feed	(174)
Thermal treatment of natural glycerides (olive oil, linseed oil, fish oil, rape-seed oil)	Special apparatus with vaporizer, attached porcelain tube containing a platinum wire heated to red heat, and fractionator	Red heat	1	Yields of B = ?	(40)
Thermal treatment of woolfat (lanolin, <i>Adeps lanae</i>) and of cholesterolin and its derivatives	Vaporizer and "isoprene lamp"	Bright red heat?	?	Yield of B was considerably less than 50% by weight on feed	(41)

mented lines would give a molecule unsaturated at the bonds located β , ζ , κ , ξ , etc., with respect to the first methylene on the glyceryl side:



Subsequent scissions at G, N, and at the ionic bonds labelled δ , θ , μ , etc., would yield butadiene.

Table 14 gives data on the conversion of carboxylic esters into butadiene.

VI. CONCLUSION

Many organic compounds containing carbon, hydrogen, and oxygen produce butadiene under thermal or catalytic conditions. In this respect, the behavior of oxygen derivatives parallels that of the hydrocarbons. Good yields of butadiene are obtainable from ethanol, butanols, butenols, 1,3-butanediol, butanal, oleic acid, 2,3-butanediol diacetate, 4-methyl-*m*-dioxane, cyclohexanol, and 1,2-dihydroxybenzene. Most emphasis in the past has been on the production of butadiene in one stage, as in the cases of ethanol and 3-methyl-1-butanol.

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