CONVERSION OF OXYGEN DERIVATIVES OF HYDROCARBONS INTO BUTADIENE

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CONTENTS

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

ALKANOLS
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

ALKANEDIOLS
1,3-Butanediol
1,4-Butanediol
2,3-Butanediol

ALKANETETROL
1,2,3,4-Butanetetrol

ALKENOLS
1-Propen-3-ol
1-Buten-3-ol
1-Buten-4-ol
2-Buten-1-ol

ALKENEDIOL
1-Butene-3,4-diol

CYCLANYLALKANOL
Cyclopropylcar-binol

CYCLANOLS
Cyclobutanol
1-Methyl-3-cyclo-pentanol
"Dimethylcyclo-pentanols"
Cyclohexanol

HYDROXYBENZENES
Hydroxybenzene
1,2-Dihydroxy-benzene
1,3-Dihydroxyben-zene
1,4-Dihydroxyben-zene

DIALKYL ETHERS
Diethyl ether
Ethyl α-chloroethyl ether
Ethyl β-chloroethyl ether
Ethyl α-hydroxyethyl ether
Ethyl β-hydroxyethyl ether
Ethyl α-ethoxyethyl ether
Ethyl α-acetoxyethyl ether
Methyl α-methoxyethyl ether
γ,γ'-Dihydroxydibutyl ether
γ-Chlorobutyl γ'-hydroxy-butyl ether

ALKYL ALKENYL ETHERS
Ethyl vinyl ether
Methyl α-vinyl-β-iodo-ethyl ether
Ethyl α-vinyl-β-iodoethyl ether
n-Propyl α-vinyl-β-iodo-ethyl ether
Isobutyl α-vinyl-β-iodo-ethyl ether

DIALKENYL ETHERS
Divinyl ether
Di(2-buten-1-yl) ether

EPOXYBUTANES
1,4-Epoxybutane
2,3-Epoxybutane

DIOXANE
4-Methyl-m-dioxane

ALKANALS
Ethanal
Butanal
2-Methylpropanal
3-Hydroxybutanal (β-hydroxybutyr-aldehyde)

ALKENAL
2-Butenal (croton-aldehyde)

ALKANOIC ACIDS
n-Butyric acid
Isobutyric acid
Isovaleric acid

ALKENOIC ACIDS
Acrylic acid
Oleic acid
Elaidic acid
Calcium $\Delta^{\beta,\gamma}$-dihydromuconate

ALKADIENOIC ACID
2,4-Pentadienoic acid

MONOESTERS
1,3-Butanediol 3-acetate
1,3-Butanediol 1-β-hydroxybu-tyrate
2-Buten-1-yl acetate
2-Buten-1-yl trichloroacetate

DIESTERS
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(ethylxantho-genic acid)

TRIESTERS
Natural glycerides

64

* "Amylalkohol" in original specification.

(76) DIMROTH, O., AND AICKELIN, H.: Ber. 39, 4390-2 (1906).
(77) DIMROTH, O., AND DIENSTBACH, O.: Ber. 41, 4060-79 (1908).
(78) DIMROTH, O., AND FESTER, G.: Ber. 43, 2222 (1910).
(79) DIMROTH, O., FRISONI, E., AND MARSHALL, J.: Ber. 39, 3920-7 (1906).
(80) DIMROTH, O., AND LETSCHE, E.: Ann. 335, 93-106 (1904).
(81) DIMROTH, O., AND LETSCHE, E.: Ber. 35, 4054-8 (1902).
(82) DIMROTH, O., AND TAUB, L.: Ber. 39, 3912-15 (1906).
(83) EKSTRAND, T.: Svensk Kem. Tid. 54, 257-62 (1942); Chem. Abstracts 38, 5004.
(84) ELBS, K., HIRSCHEL, O., WAGNER, F., HIMMLER, K., TURK, W., HENRICH, A., AND
    LEHMANN, E.: J. prakt. Chem. 108, 209-33 (1924).
(85) EULER, H., AND EULER, A.: Ber. 36, 4256 (1903); 37, 49 (1904).
(86) FIESER, L. F., AND AMES, M. A.: J. Am. Chem. Soc. 49, 2604-17 (1927).
(87) FIESER, L. F., AND HARTWELL, J. L.: J. Am. Chem. Soc. 57, 1479-82 (1935).
(88) FIESSER, L. F., AND MARTIN, E. L.: J. Am. Chem. Soc. 57, 1835-9 (1935).
(89) FIESER, L. F., AND MARTIN, E. L.: J. Am. Chem. Soc. 57, 1840-44 (1935).
(90) FIESER, L. F., AND MARTIN, E. L.: J. Am. Chem. Soc. 57, 1844-9 (1935).
(91) FRANZEN, H.: J. prakt. Chem. 76, 217-8 (1907).
(92) FRIES, K.: Ann. 454, 121-324 (1927).
(93) FRIES, K., AND BILLIG, K.: Ber. 58B, 1128-38 (1925).
(94) FRIES, K., FRANKE, W., AND BRUNS, W.: Ann. 511, 241-67 (1934).
(95) FRIES, K., GUTERBOCK, H., AND KUHN, H.: Ann. 511, 213-40 (1934).
(96) FRIES, K., AND ROTH, E.: Ann. 389, 318-44 (1912).
(97) FRIES, K., WALTER, R., AND SCHILLING, K.: Ann. 516, 248-85 (1935).
(98) GABRIEL, S., AND COLMAN, J.: Ber. 34, 1249 (1901).
(99) GALLOTTI, M.: Gazz. chim. ital. 59, 207-11 (1929).
(100) GATTERMAN, L., AND ROLFES, H.: Ann. 425, 135-61 (1921).
(101) GHIGI, E., AND POZZO-BALBI, T.: Gazz. chim. ital. 71, 228-34 (1941).
(102) GIUA, M.: Gazz. chim. ital. 49, II, 149 (1919); Atti accad. Lincei [5] 28, II, 189 (1919).
(103) GOLDSTEIN, H., AND JAQUET, A.: Helv. Chim. Acta 24, 30-7 (1941).
(104) GOLDSTEIN, H., AND VOEGELI, R.: Helv. Chim. Acta 26, 475-81 (1943).
(105) GRAMANTIERI, P.: Gazz. chim. ital. 65, 102-8 (1935).
(106) GRANDMOUGIN, E.: J. prakt. Chem. [2] 76, 134-5 (1907).
(107) GRIESS, P.: Ber. 2, 436 (1869); Ber. 5, 201 (1872); J. prakt. Chem. [2] 5, 238-9 (1872).
(108) GRIESS, P.: Ber. 15, 1878-82 (1882).
(109) GRIESS, P.: Ber. 15, 2199 (1882).
(110) GUHA, P. C., AND DEY, S. C.: Quart. J. Indian Chem. Soc. 2, 225-39 (1925).
(111) HANN, R. M., AND HUDSON, C. S.: J. Am. Chem. Soc. 66, 735-8 (1944).
(112) HANTZSCH, A., AND CALDWELL, K. S.: Z. physik. Chem. 61, 232 (1908).
(113) HARDEGGER, E., AND EL KHADEM, H.: Helv. Chim. Acta 30, 1478-83 (1947).
(114) HARDEN, A.: Ann. 255, 159 (1889).
(115) HARDEN, A., AND OKELL, J.: Proc. Chem. Soc. 16, No. 230, 229 (1901).
(116) HASKINS, W. T., HANN, R. M., AND HUDSON, C. S.: J. Am. Chem. Soc. 67, 939-41
    (1945).
(117) HASKINS, W. T., HANN, R. M., AND HUDSON, C. S.: J. Am. Chem. Soc. 68, 1766-9
    (1946).
(118) HASKINS, W. T., HANN, R. M., AND HUDSON, C. S.: J. Am. Chem. Soc. 69, 1050-52
    (1947).
(119) HASKINS, W. T., HANN, R. M., AND HUDSON, C. S.: J. Am. Chem. Soc. 69, 1461-3
    (1947).
(120) HEAFIELD, T. G., AND HUNTER, L.: J. Chem. Soc. 1942, 420-2.
(121) HENKEL, K., AND WEYGAND, F.: Ber. 76B, 812-18 (1943).
(122) HINKEL, L. E., RICHARDS, G. O., AND THOMAS, O.: J. Chem. Soc. 1937, 1432-7.
(123) HOFMANN, A. W.: Ann. 115, 251 (1860).
(124) HUTTEL, R.: Ber. 74B, 1680-7 (1941).

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
	long tons	*per cent by weight*	*per cent of theory*	
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:

$$2CH_3CH_2OH \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2 + 2H_2O$$
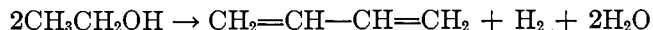
A catalyst mixture having a dehydrogenating component (A) and a dehydrating component (B) is specified. The present authors, however, are of the opinion that an individual catalyst with dehydrogenating and dehydrating properties would function in a similar manner. Lebedev (89) studied the effect of varying 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
	long tons	*long tons*
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:

$$CH_3{-}CH_2OH \longrightarrow CH_2{-}CHOH + H_2$$
$$CH_3{-}CH_2OH \longrightarrow CH_2{-}CH_2 + H_2O$$
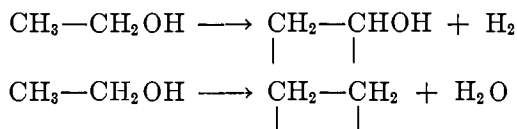
Reaction of active forms of ethenol with those of ethene, followed by dehydration of the two intermediates so formed, was considered to give butadiene:

$$CH_2{-}CHOH + CH_2{-}CH_2$$
$$CH_2{-}CHOH{-}CH_2{-}CH_2 \quad \cdot \quad CHOH{-}CH_2{-}CH_2{-}CH_2$$
$$CH_2{=}CH{-}CH{=}CH_2 + H_2O$$
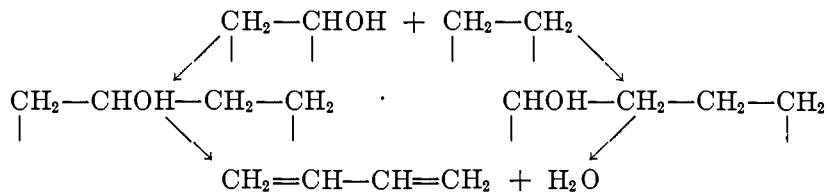
The foregoing formulation was based mainly on phenomena observed in the catalysis of ethanol over various mixtures of components A and B. Gradual addition of the dehydrating component B to dehydrogenating component A was attended by a rapid increase in the amount of butadiene to a maximum value,

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.
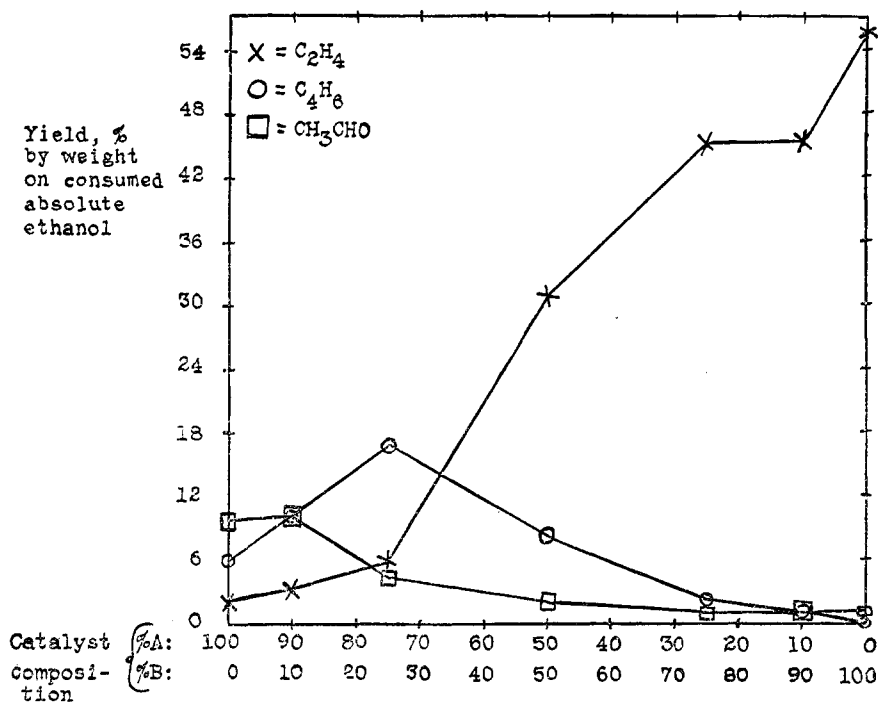
FIG. 1

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.

Ostromyslenskiĭ 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_nH_{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 consumed 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:

$$CH_2=CH_2 + CH_3-CHO \rightarrow H_2O + CH_2=CH-CH=CH_2 \qquad (1)$$
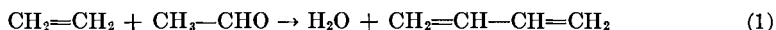
This assumption was quite plausible in view of V. N. Ipatieff's reaction. O. G. Filippov naturally understood the author's communication literally, and replied that he also observed formation of butadiene-1,3 under the action of a mixture of ethanal and ethene on alumina. Thus, O. G. Filippov observed 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

$$CH_3CHO + C_2H_5OH \rightarrow 2H_2O + CH_2=CH-CH=CH_2$$

was first observed by the author.

Ostromyslenskiĭ'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):

$$2C_2H_5OH \rightarrow C_4H_8(OH)_2 + H_2$$

$$C_4H_8(OH)_2 \rightarrow C_4H_7OH(\text{or } C_4H_8O) + H_2O$$

$$C_4H_7OH(\text{or } C_4H_8O) \rightarrow C_4H_6 + H_2O$$
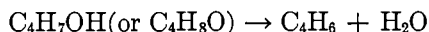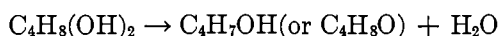
The intermediates to be considered in theories discounting the rôle of ethene include: 1,3- or 1,4- or 2,3-butanediol, 1-buten-3(or 4)-ol, 2-buten-1-ol, 1,3- or 1,4- or 2,3-epoxybutane, ethyl α-hydroxyethyl ether, ethyl α-ethoxyethyl ether, and ethyl vinyl ether. Theoretical formulation is restricted 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:

(A) $CH_3CH_2OH \rightarrow CH_3CHO + H_2$

(B) $CH_2OH—CH_2—H + CHO—CH_3 \rightarrow CH_2OHCH_2CHOHCH_3$

(C) $\begin{cases} CH_3CHO \rightleftarrows CH_2=CHOH \\ CH_2OH—CH_2—H + CH(OH)=CH_2 \rightarrow CH_2OHCH_2CHOHCH_3 \end{cases}$

(D) $\begin{cases} CH_3CHO \rightleftarrows CH_2=CHOH \\ CH(OH)=CH_2 + H—CHOH—CH_3 \rightarrow CH_2OHCH_2CHOHCH_3 \end{cases}$
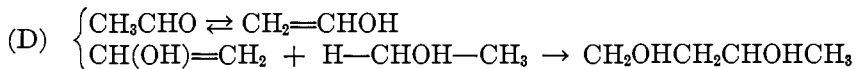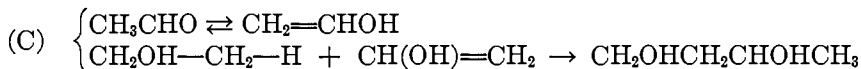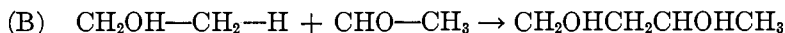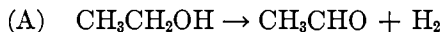
1,3-Butanediol would form 1-buten-3(or 4)-ol, 2-buten-1-ol, or 1,3-epoxybutane, and these, considering the three sources of butanediol and its four monodehydration products, make possible twelve reaction paths, each of which could produce butadiene:

$$CH_2OHCH_2CHOHCH_3 \xrightarrow{(-H_2O)} \begin{bmatrix} CH_2=CH—CHOH—CH_3 \\ CH_2=CH—CH_2—CH_2OH \\ CH_2OH—CH=CH—CH_3 \\ H_2C—CH—CH_3 \\ \quad | \quad\quad | \\ H_2C—O \end{bmatrix}$$

$$\xrightarrow{(-H_2O)} CH_2=CH—CH=CH_2$$

The three reaction paths involving 2-buten-1-ol are related to Ostromyslenskiĭ'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:

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2$$

$$CH_3CHO \rightleftarrows CH_2{=}CHOH$$

$$CH(OH){=}CH_2 + H{-}CH_2{-}CH_2OH \rightarrow CH_2OHCH_2CH_2CH_2OH$$

$$CH_2OHCH_2CH_2CH_2OH \xrightarrow{(-H_2O)} \begin{bmatrix} CH_2{=}CH{-}CH_2{-}CH_2OH \\ H_2C{-\!-\!-\!-}CH_2 \\ \quad | \qquad\quad | \\ H_2C \qquad CH_2 \\ \quad\searrow\quad\swarrow \\ \qquad O \end{bmatrix}$$

$$\xrightarrow{(-H_2O)} CH_2{=}CH{-}CH{=}CH_2$$

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:

(A) $CH_3CH_2OH \rightarrow CH_3CHO + H_2$

(B) $CH_3CHO + H{-}CHOH{-}CH_3 \rightarrow CH_3CHOHCHOHCH_3$

$\big\{$(C) $CH_3CHO \rightleftarrows CH_2{=}CHOH$

$\big\{$(D) $CH_2{=}CHOH + H{-}CHOHCH_3 \rightarrow CH_3CHOHCHOHCH_3$

$\big\{$(E) $CH_3CHOHCHOHCH_3 \rightarrow CH_2{=}CHCHOHCH_3 + H_2O$

$\big\{$(F) $CH_2{=}CHCHOHCH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2O$

(G) $CH_3CHOHCHOHCH_3 \rightarrow CH_3\underset{\diagdown\;O\;\diagup}{CH{-}CH}CH_3 + H_2O$

(H) $CH_3\underset{\diagdown\;O\;\diagup}{CH{-}CH}CH_3 \rightarrow CH_2{=}CHCHOHCH_3$

(I) $CH_2{=}CHCHOHCH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2O$

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:

(J) $2CH_3CH_2OH \rightarrow 2CH_3\overset{.}{C}H(OH) + 2\overset{.}{H} \rightarrow$

$$CH_3CH(OH):CH(OH)CH_3 + H:H$$
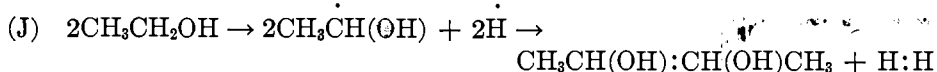
Finally, the authors consider the possibility of hemiacetal and acetal formation in the conversion of ethanol:

$$CH_3CH_2OH \rightarrow CH_3CHO + H_2$$

$$CH_3CHO + CH_3CH_2OH \rightleftarrows CH_3CH(OH)OC_2H_5$$

$$CH_3CH(OH)OC_2H_5 + CH_3CH_2OH \rightleftarrows CH_3CH(OC_2H_5)_2 + H_2O$$
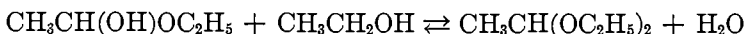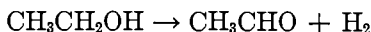
Dehydration rather than reversion of the hemiacetal (i.e., ethyl α-hydroxyethyl ether) and a facile deëthanolation (128) of the true acetal would furnish ethyl vinyl ether:

$$CH_3CH(OH)OC_2H_5 \rightarrow CH_2{=}CHOC_2H_5 + H_2O$$

$$CH_3CH(OC_2H_5)_2 \rightarrow CH_2{=}CHOC_2H_5 + C_2H_5OH$$
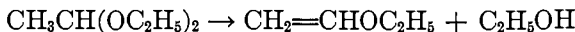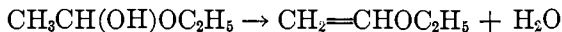
Cyclization of the ether would provide a chain of four methylene groups closed about the oxygen atom:

$$CH_2{=}CHOC_2H_5 \rightarrow \begin{array}{c} H_2C{-}{-}CH_2 \\ |\qquad\quad| \\ H_2C\qquad CH_2 \\ \diagdown\quad\diagup \\ O \end{array}$$
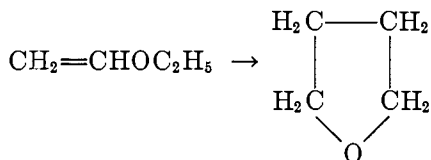
The 1,4-epoxybutane so formed would probably yield butadiene upon isomerization to and dehydration through a 1-buten-4-ol stage and also upon hydration to 1,4-butanediol, followed by an identical stage of dehydration:

$$\begin{array}{c} H_2C{-}{-}CH_2 \\ |\qquad\quad| \\ H_2C\qquad CH_2 \\ \diagdown\quad\diagup \\ O \end{array} \rightarrow CH_2{=}CHCH_2CH_2OH \xrightarrow{(-H_2O)} CH_2{=}CH{-}CH{=}CH_2$$

$$\diagdown{(+H_2O)} \qquad \uparrow{(-H_2O)}$$

$$CH_2OHCH_2CH_2CH_2OH$$
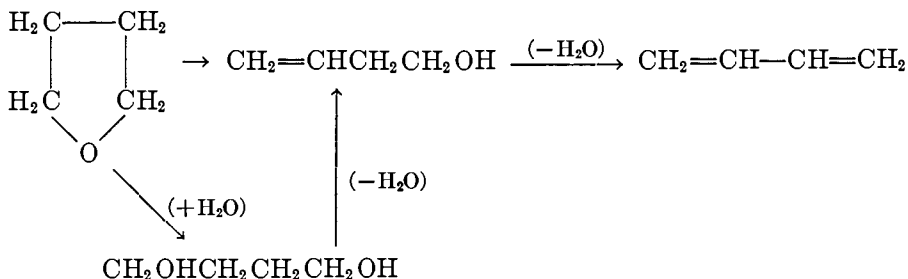
In lieu of cyclization, thermal scission of ethyl vinyl ether to form free vinyl radicals can be considered. Union of vinyl radicals through direct electronic coupling and conjugation of double bonds would yield butadiene, formerly called "divinyl":

$$2CH_2{=}\overset{.}{C}H \rightarrow CH_2{=}CH{-}CH{=}CH_2$$
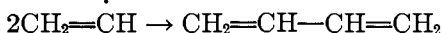
Ipatieff demonstrated that ethanol forms butadiene over heated powdered aluminum (75, 76). At his suggestion, Gdanovitch continued the study of this reaction (39). The explanation finally accepted was formation of diethyl ether over the alumina coating always present on metallic aluminum, followed by conversion of ether into butadiene over the free metal (39, 74):

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O$$

$$C_2H_5OC_2H_5 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2 + H_2O$$
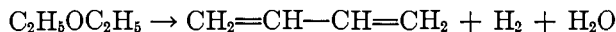
Filippov, also working under the direction of Ipatieff, investigated the aluminum-catalyzed reaction, finding that diethyl ether gives three times more butadiene than ethanol does (34).

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

$$CH_2{=}CH_2 + CH{\equiv}CH \rightarrow CH_2{=}CH{-}CH{=}CH_2$$
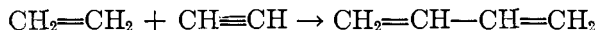
In favor of this series of reactions may be cited the presence of a catalyst having dehydrating and dehydrogenating components. Against it can be mentioned the lower yields of butadiene secured from ethene and ethyne mixtures under thermal, catalytic, or electrical conditions (22, 23). The oxidized character 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) Ostromyslenskiĭ's process

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

$$C_2H_5OH + CH_3CHO \rightarrow CH_2{=}CH{-}CH{=}CH_2 + 2H_2O$$

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. $CH_3CHO + C_2H_5OH \rightarrow CH_3CH(OH)OC_2H_5$

2. $CH_3CH(OH)OC_2H_5 \rightarrow CH_3CH(OH)CH_2CH_2(OH)$

3. $CH_3CH(OH)CH_2CH_2(OH) \rightarrow H_2O + CH_3CH{=}CHCH_2(OH)$

4. $CH_3CH{=}CHCH_2(OH) \rightarrow H_2O + CH_3CH{=}C{=}CH_2$

5. $CH_3CH{=}C{=}CH_2 \rightarrow CH_2{=}CHCH{=}CH_2$."

TABLE 4
Conversion of ethanol into butadiene

COMPOSITION OF FEED	APPARATUS AND CATALYST USED	TEMPERATURE	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
		°C.	atm.		
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)
	. . . .	. . . .	. . . .	See patent for details	(91)
	Quartz tube containing zinc dust and floridin	410		Yield of B was 15% by weight on feed	(92)
	Catalyst was probably $Al_2O_3 + ZnO$; pressure vessel used	Elevated		See patent for details	(90)
	Quartz tube containing $ZnO +$ aluminum hydrosilicate ($Al_2O_3 \cdot SiO_2 \cdot xH_2O$) as catalyst	410	1 or less	Yield of B was 15% by weight on fully decomposed ethanol; feed was 95% ethanol	(88)

Catalyst of undisclosed composition			Yield of B was 20–25% by weight on product	(89)
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	440–450 (28–30 mm. Cu tube) 450 (3.5 meter tube)	0.934 (28–30 mm. Cu tube) 0.934–0.961 (six parallel tubes)	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	(100)
Tubes of copper, iron, enamelled iron, aluminum-coated iron, or quartz; each tube contained two-component catalyst (one component clay?)	435 (enamelled iron tube) 435–445 (copper or iron tube) 415–425 (aluminum-coated iron tube) 440 (quartz tube)	1 (iron, enamelled iron, or aluminum-coated iron tube) 0.974 (copper tube) 0.0395–0.526 (quartz tube)	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	(99)

TABLE 4—*Continued*

COMPOSITION OF FEED	APPARATUS AND CATALYST USED	TEMPERATURE	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
		°C.	atm.		
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)
		About 425		No details of process available except on by-products	(167)
	Small laboratory furnace; catalyst was used, but its composition was 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)
	Large-scale laboratory unit; composition of catalyst not disclosed	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)
	Copper tube, 1 meter long and 10 cm. in diameter, containing "well-selected" catalyst	450		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)
	Composition of catalyst not disclosed; probably oxides	450	0.974–0.987	Yield of B was 16% by weight on feed per pass and 24% by weight on fully decomposed feed	(95)

76

Ethanol and alkanol diluents $2C_2H_5OH \rightarrow C_4H_6 + 2H_2O + H_2$	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	425 (case A) 450 (case B) 460 (case C) 450–455 (case D)	0.961–0.974 (all cases)	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	(83)
	Probably a 1-meter copper tube; the catalyst had two components (one component clay?)	435–445?	1	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	(99)
Ethanol and steam $2C_2H_5OH \rightarrow C_4H_6 + 2H_2O + H_2$	"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?)	440 (cases A, C, E) 500 (cases B, D, F)	1 (all cases)	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	(99)

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 Ostromyslenskiĭ (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:

$$CH_3CHO + C_2H_5OH \rightleftarrows CH_3CH(OH)OC_2H_5$$
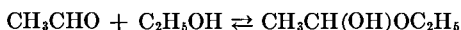
It occurs under definite conditions on mixing acetaldehyde and ethyl alcohol and is apparently not a necessary step in the process.

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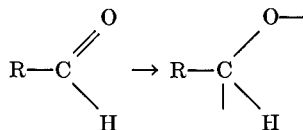
The two free bonds determine the effect of each reaction. In rare cases, aldehydes react by their tautomeric form of unsaturated alcohols:

$$RCH_2CH{=}O \rightleftarrows RCH{=}CH(OH)$$
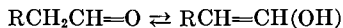
However, in these condensations, only the carbon atom of the aldehyde group is actively involved in the reaction. For this reason, it is beyond doubt that in the reaction described by the present author, condensation also occurs through the carbon atom of this group. The rearrangement of acetaldehyde in the condensation may be described by:
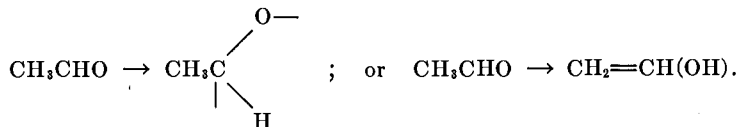
Concerning the carbon atom of ethyl alcohol participating in the union of the molecules, the author succeeded in definitely solving this question by substitution of ethyl alcohol by

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:

1. $CH_3CHO + CH_3CH_2(OH) \rightarrow CH_3CH(OH)CH_2CH_2(OH)$; or

2. $CH_2=CH(OH) + CH_3CH_2(OH) \rightarrow CH_2=CHCH_2CH_2(OH)$.
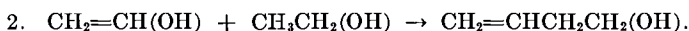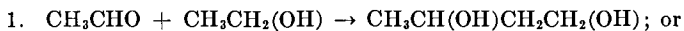
It will be shown later that in this reaction, butadiene-1,3 is formed by isomerization of methylallene; buten-1-ol-4 can give upon dehydration only butadiene-1,3 but not methylallene

$$CH_2=CHCH_2CH_2(OH) \rightarrow H_2O + CH_2=CHCH=CH_2.$$
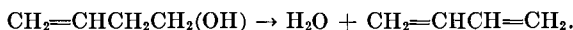
The reaction 2 is therefore impossible. Condensation of acetaldehyde and ethyl alcohol occurs, consequently, through butanediol.

Ostromyslenskiĭ and Kelbasinskiĭ 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):

$$2CH_3CH_2OH + CH_3CHO \rightarrow CH_3CH(OC_2H_5)_2 + H_2O$$

$$CH_3CH(OC_2H_5)_2 \rightarrow CH_2=CH-CH=CH_2 + CH_3CH_2OH + H_2O$$
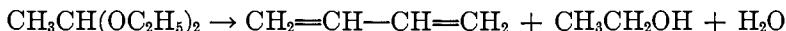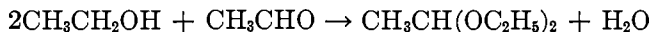
Lebedev (89) regarded Ostromyslenskiĭ's reaction, or the direct condensation of ethanol and ethanal, as a synthesis of butadiene similar to his own process, because ethanal can be regarded as a product in ethanol conversion. Lebedev's last experiments (95) demonstrated that the addition of 10 and 20 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 Ostromyslenskiĭ'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 *Zaĭtsev'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.

Ostromyslenskiĭ 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

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[1] Reference 144 in this paper.

isomerized over impure grades of the same catalyst. In summarizing his own study, Ostromyslenskiĭ 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:

2a. $CH_3CHO + C_2H_5OH + CH_3CH(OH)OC_2H_5 \rightarrow$

$$2CH_3CHOHCH_2CH_2OH$$
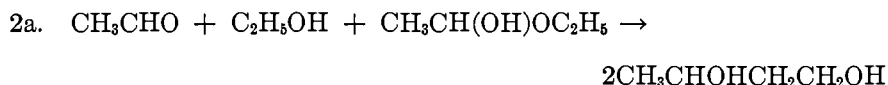
Ostromyslenskiĭ failed to state which set of equations was most plausible.

This picture of Ostromyslenskiĭ'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:

$$CH_2{=}CHCHBrCH_3 \rightleftarrows CH_2BrCH{=}CHCH_3$$
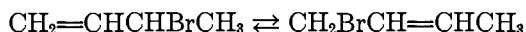
Butadiene has been obtained by individual dehydrations of 1-buten-3-ol, 1-buten-4-ol, and 2-buten-1-ol over catalysts at temperatures probably low enough to avoid significant interconversion. 1-Buten-3-ol yielded butadiene at 140°C. in the presence of trichloroacetic acid (154). 1-Buten-4-ol was similarly 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-ol, or the most reactive, e.g., 1-buten-3-ol or 1-buten-4-ol.

Ostromyslenskiĭ'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 Ostromyslenskiĭ'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):

$$CH_3CHOHCHOHCH_3 \rightarrow CH_2=CH-CH=CH_2 + 2H_2O$$

$$CH_3CHOHCHOHCH_3 \rightarrow [CH_3C(OH)=CHCH_3 + H_2O] \rightarrow CH_3COCH_2CH_3$$
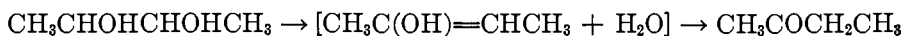
Moreover, derivatives of 2,3-butanediol, such as the diformate (53) and the diacetate (53, 126), and a 2,3-butanedithiol derivative (149) having the structure of 2,3-butene bis(ethylxanthogenic acid) yield butadiene upon decomposition:

$$CH_3CH(O-CO-H)CH(O-CO-H)CH_3 \rightarrow$$
$$CH_2=CH-CH=CH_2 + CO + CO_2 + H_2 + H_2O$$

$$CH_3CH(O-CO-CH_3)CH(O-CO-CH_3)CH_3 \rightarrow$$
$$CH_2=CH-CH=CH_2 + 2CH_3COOH$$

$$CH_3CH(S-CS-OC_2H_5)CH(S-CS-OC_2H_5)CH_3 \rightarrow$$
$$CH_2=CH-CH=CH_2 + 2COS + 2C_2H_5SH$$
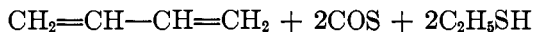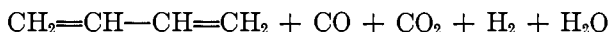
(d) Other ethanol condensations

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:

$$(C_2H_4O)_3 \rightarrow 3C_2H_4O$$

$$C_2H_5OH + C_2H_4O \rightarrow CH_2=CH-CH=CH_2 + 2H_2O$$

$$\overline{3C_2H_5OH + (C_2H_4O)_3 \rightarrow 3CH_2=CH-CH=CH_2 + 6H_2O}$$
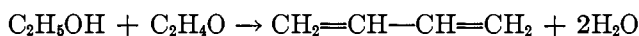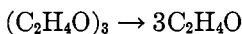
1,2-Ethanediol likewise can replace ethanal in Ostromyslenskiï's reaction (6). This substitution is expected because of the thermal conversion of this diol into ethanal. However, a conversion proceeding via 1,3- or 1,4-butanediol is to be considered also:

$$CH_2OHCH_2OH + CH_2OHCH_3 \rightarrow CH_2OHCH_2CHOHCH_3 + H_2O$$

$$CH_2OHCH_2OH + CH_3CH_2OH \rightarrow CH_2OHCH_2CH_2CH_2OH + H_2O$$
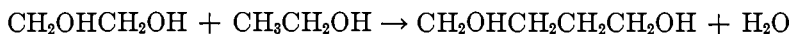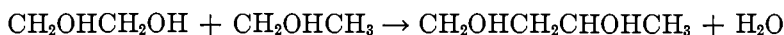
A mixture of ethanol and ethyne is reported (65) to give butadiene, but this reaction can be questioned on grounds similar to those discounting an ethanol and ethene conversion. Any formation of butadiene would be ascribable to a more appropriate ethanol *per se* condensation, to a hydration of ethyne 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:

$$C_2H_5OH + CH\equiv CH \rightarrow CH_2=CH-CH=CH_2 + H_2O$$

TABLE 5
Condensation of ethanol with close derivatives

COMPOSITION OF FEED	APPARATUS AND CATALYST USED	TEMPERA-TURE	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFER-ENCES
		°C.	atm.		
	Catalyst: Al₂O₃	440–460	0.895–0.934	Yield of B was 14% by weight on total feed; steam used?; data for 97 experiments given	(143)
	Catalyst: Al₂O₃	360–450		Yield of B = ?	(126)
	Catalysts were red phosphorus; glacial H₃PO₄; sulfanilic acid; BaCl₂; or Al₂O₃ ("argilla pura")	360–440		Yields of B = ?	(129)
Ethanol and ethanal $C_2H_5OH + CH_3CHO \rightarrow C_4H_6 + 2H_2O$	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 decomposed feed; feed used was ethanol 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 Al₂(SO₄)₃·12H₂O; 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 ethanol and ethanal feed	(78)
	Catalyst was Al₂(SO₄)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)

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

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 (Ḣ), 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:

$$3CH_3CHOHCH_3 \rightarrow CH_2\!\!=\!\!CH\!\!-\!\!CH\!\!=\!\!CH_2 + H_2O + CH_4 + CH_3COCH_3$$

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:

$$CH_2OHCH_2CH_2CH_3 \rightarrow CH_2\!\!=\!\!CH\!\!-\!\!CH\!\!=\!\!CH_2 + H_2O + H_2$$
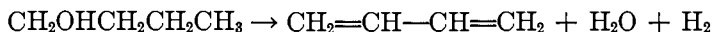
Dehydration presumably precedes dehydrogenation, so that 1-butene rather than 1-buten-4-ol would be the principal intermediate. Questions of (a) an isomerization of 1-butene into 2-butene following dehydration of 1-butanol, and (b) which alkene is dehydrogenated, are left open. This much is certain: 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):

$$CH_3CHOHCH_2CH_3 \rightarrow CH_2\!\!=\!\!CH\!\!-\!\!CH\!\!=\!\!CH_2 + H_2O + H_2$$
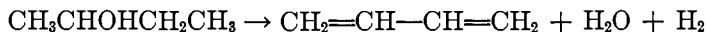
Again assuming the validity of prior dehydration and of Zaĭtsev's rule governing its course, the intermediate product would be *cis-* or *trans-*2-butene. A 1,4-dehydrogenation of 2-butene would then yield butadiene.

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

$$
\begin{array}{ccc}
 & C_4H_8 + H_2O & \\
 \nearrow & & \searrow {\scriptstyle \frac{1}{2}O_2} \\
C_4H_9OH & & C_4H_7OH + H_2O \rightarrow C_4H_6 + 2H_2O \\
 \searrow {\scriptstyle \frac{1}{2}O_2} & & \nearrow \\
 & C_4H_8(OH)_2 &
\end{array}
$$
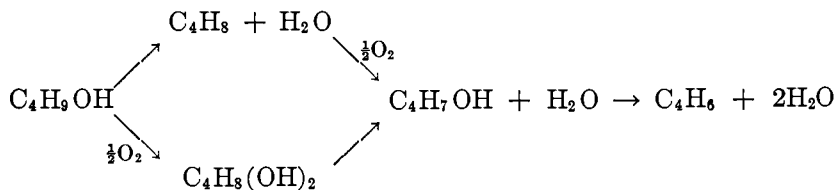
In the 1-butanol case, assuming oxidation in the β-position to the hydroxymethyl group, the intermediates would be 1-butene, 1,3-butanediol, 1-buten-3-ol, 1-buten-4-ol, and 2-buten-1-ol. Those for 2-butanol, assuming oxidation in the α-position to the hydroxymethylene group, would be 1- and 2-butenes, 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-pentanols 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:

$$CH_3 \quad CH_3 \quad CH_3 \quad CH_3$$
$$C_5H_{11}OH \rightarrow C_4H_8OH + CH_3 \rightarrow C_4H_7OH + H + CH_3$$
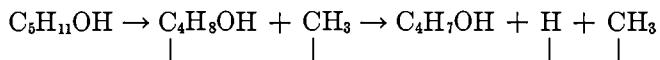
Its operation would be favored by the low activation energy for a carbon-carbon bond scission, but would be extensively superseded by exothermic hydroxylations with or without dehydration of new hydroxyls.

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):

$$CH_2OHCH_2CHClCH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2O + HCl$$

$$CH_3CHOHCHClCH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2O + HCl$$
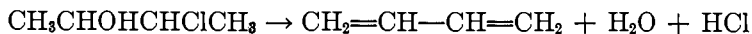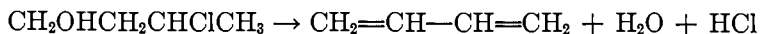
The two elimination processes, i.e., formation of water and of hydrogen chloride, are favored by the increase in strengths of the 1,2- and 3,4-carbon–carbon linkages and of the C—OH bond in the reactants compared with the H—OH bond

TABLE 6

Conversion of higher alkanols (C₃H₇OH and above) into butadiene

PROCESS AND ALKANOL USED	APPARATUS AND CATALYSTS USED	TEMPERATURE	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFER-ENCES
		°C.	atm.		
Catalysis of 2-propanol (isopropyl alcohol) Probably 3CH₃CHOHCH₃ → C₄H₆ + CH₃COCH₃ + 2CH₄ + 2H₂O	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 (iso-butyl alcohol) Probably CH₂CH(CH₃)CH₂OH → C₄H₆ + H₂O + H₂	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	In vacuo unless diluents used	Yield of B = ?	(149)
	Quartz tube	Red heat	1	Yield of B was 11% by weight on feed; if desired, Al₂O₃ or kieselguhr may be used as catalyst	(32)
Dehydration and dehydrogenation of 1-butanol C₄H₉OH → C₄H₆ + H₂O + H₂		750	1	Yield of B was 0.41% by weight on feed	(169)
				Yield of B was 1.2–4.8% by weight on gaseous hydrocarbons produced	(124)
	Quartz tube containing a 4% Cr₂O₃ and 96% Al₂O₃ catalyst	575 (Expt. 1) 600 (Expt. 2) 625 (Expt. 3)	0.197 (Expt. 1) 0.175 (Expt. 2) 0.168 (Expt. 3)	Yields of B were 1.8, 5.1, and 7.4% by weight on feed in experiments 1, 2, and 3, respectively	(81)

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

TABLE 6—*Continued*

88

PROCESS AND ALKANOL USED	APPARATUS AND CATALYSTS USED	TEMPERATURE	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFER-ENCES
		°C.	atm.		
Dehydration and demethanation of 2-methyl-2-butanol $(CH_3)_2C(OH)CH_2CH_3 \rightarrow C_4H_6 + H_2O + CH_4$	Catalyst: pumice	600–620	1	Yield of B was 0.071% by weight on feed	(121)
Dehydration and dehydrodechlorination of 3-chloro-1-butanol $CH_2OHCH_2CHClCH_3 \rightarrow C_4H_6 + H_2O + HCl$	Catalyst: Al_2O_3, $BaCl_2$, or TiO_2	High	1 or *in vacuo*		(68)
Dehydration and dehydrodechlorination of 3-chloro-2-butanol $CH_3CHOHCHClCH_3 \rightarrow C_4H_6 + H_2O + HCl$	Catalyst: H_3PO_4 (?) on pumice	Over 400	1 or *in vacuo*	Yield of B = ?	(110)

BUTADIENE 89

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 CH_2O, 142; C=O in RCHO, 149; C=O in R_2CO, 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:

$$CH_2OHCH_2OH + CH_2=CH_2 \rightarrow CH_2OHCHOHCH_2CH_3$$

$$CH_2OHCHOHCH_2CH_3 \rightarrow \begin{bmatrix} CH_2OHCH=CHCH_3 + H_2O \\ CH_2=C=CHCH_3 + 2H_2O \\ CH\equiv CCH_2CH_3 + 2H_2O \end{bmatrix} \rightarrow CH_2=CH—CH=CH_2 + 2H_2O$$

$$CH_2OHCH_2OH + CH_2=CH_2 \rightarrow CH_3CH_2OCH_2CH_2OH$$
$$\downarrow$$
$$CH_2=CH—CH=CH_2 + 2H_2O \leftarrow [CH_3CH_2OCH=CH_2 + H_2O]$$
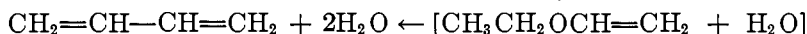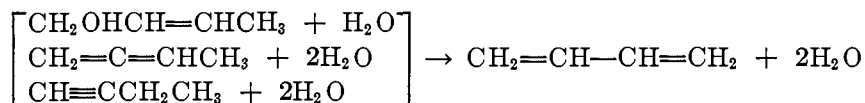
Another explanation depends upon a probable transformation of the ethanediol into ethenol, i.e., vinyl alcohol, and its stabilization product, ethanal. Hydration of ethene into ethanol by water from ethanediol introduces Ostromyslenskiĭ's condensation:

$$CH_3CH_2OH + CH_3CHO \rightarrow CH_2=CH—CH=CH_2 + 2H_2O$$

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

$$CH_2=CH_2 + CH\equiv CH \rightarrow CH_2=CH—CH=CH_2$$
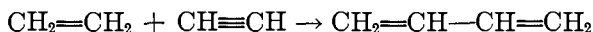
Condensation of ethanal into 3-hydroxybutanal or of ethene into 1- or 2-butene, requiring subsequent reduction (24) of 3-hydroxybutanal and dehydrogenation of the butenes, respectively, are still other mechanisms. Reduction conditions of sufficient potential would probably prevail in the presence of (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. Ostromyslenskiĭ'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:

$$CH_2(OH)\text{---}CH_2\text{---}CH(OH)\text{---}CH_3 \xrightarrow{Al_2O_3}$$

$$(CH_2\text{==}C\text{==}CH\text{---}CH_3 + 2H_2O) \rightarrow CH_2\text{==}CH\text{---}CH\text{==}CH_2 + 2H_2O."$$
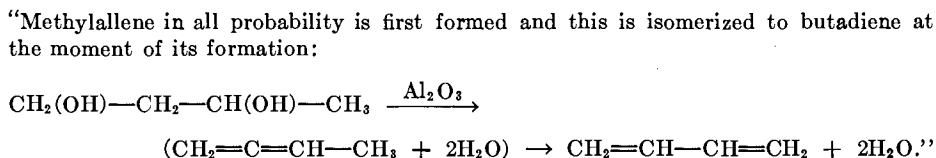
This viewpoint was discounted in our discussions on Lebedev's ethanol process and on Ostromyslenskiĭ's ethanol and ethanal juncture. A bond-energy analysis of the over-all reaction,

$$CH_2OHCH_2CHOHCH_3 \rightarrow CH_2\text{==}CH\text{---}CH\text{==}CH_2 + 2H_2O$$

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) $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CH_2OH = CH_3 \cdot CH:CH \cdot CH_2OH + H_2O.$

(2) $CH_3 \cdot CH:CH \cdot CH_2OH = CH_2:CH \cdot CH:CH_2 + H_2O.$

R. B. Earle [Kyriakides' colleague] has been able to isolate crotonyl alcohol, $CH_3CH:CHCH_2OH$, 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. Charon[1] [reference 10 of this paper], furthermore, states that, by heating the bromo-ester of the unsaturated alcohol with potassium formate at 160–180°, 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, $CH_3 \cdot CH : C : CH_2$, 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:

$$CH_3\!-\!\underset{\diagdown_{O}\diagup}{CH\!-\!CH}\!-\!CH_3 \rightarrow CH_3\!-\!\underset{\mid}{\underset{O}{CH}}\!-\!\underset{\mid}{CH}\!-\!CH_3 \rightarrow CH_2\!=\!CH\!-\!\underset{\mid}{\underset{OH}{CH}}\!-\!CH_3$$

$$CH_3\!-\!\underset{\mid}{\underset{OH}{CH}}\!-\!\underset{\mid}{\underset{OH}{CH}}\!-\!CH_3 \qquad\qquad CH_2\!=\!CH\!-\!CH\!=\!CH_2$$

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):

$$CH_2OHCHOHCHOHCH_2OH + 2HCOOH \rightarrow$$
$$CH_2\!=\!CH\!-\!CH\!=\!CH_2 + 2CO_2 + 4H_2O$$

Erythrol monoformin, $CH_2\!=\!CHCHOHCH_2OCHO$, 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):

$$C_4H_6(OH)_2(OCHO)_2 \rightarrow C_4H_6 + 2CO_2 + 2H_2O$$

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):

$$CH_2\!=\!CHCHOHCH_3 \rightarrow CH_2\!=\!CH\!-\!CH\!=\!CH_2 + H_2O$$

TABLE 7

Conversion of butanediols and of butanetetrol into butadiene

PROCESS AND STARTING DERIVATIVE	APPARATUS AND CATALYST USED	TEMPERATURE	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
		°C.	atm.		
Dehydration of 1,3-butanediol CH_2OHCH_2CHOH-$CH_3 \rightarrow C_4H_6 + 2H_2O$	Catalyst: H_3PO_4 on pumice	Heated	*In vacuo* 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)
				Yield of B was 50–65% (probably on the theoretical, which is 60.0%)	(130)
	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; $KHSO_4$	450–470 (Al_2O_3 or caustic alkali) 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: $Ca(H_2PO_4)_2$ + 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 premixed 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: $AlPO_4$ + H_3PO_4	450	1	Yield of B was 40% by weight on feed	(166)
Catalyst: $AlPO_4$ + H_3PO_4	450	0.25	Yield of B was 52% by weight on feed	(166)
Catalyst was $AlPO_4$ + H_3PO_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 $Al(NO_3)_3$ + NH_4OH (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	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
		°C.	atm.		
Dehydration of 1,3-bu-tanediol $CH_2OHCH_2CHOH-CH_3 \rightarrow C_4H_6 + 2H_2O$	Al_2O_3 from $NaAlO_2 + CO_2$ (expts. 4–6) SiO_2 gel (expts. 7–9) Kaolin (Nippon Yakkyokuho) (expts. 10–11) Kaolin (Korea) (expts. 12–14) Japanese acid clay (Itoigawa) (expts. 15–17) Kaolin (50 parts) + P_2O_5 (50 parts) (expts. 18–23) Kaolin (50 parts) + Al_2O_3 (50 parts) (expts. 24–26) Kaolin (49 parts) + Al_2O_3 (49 parts) + KOH (2 parts) (expts. 27–29) 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)	300 (expts. 2, 5, 8, 10, 13, 16, 19, 25, 28, 31, 34, 37, 40, 43, 46, 49, 52, 57) 350 (expts. 3, 6, 9, 11, 14, 17, 20, 26, 29, 32, 35, 38, 41, 44, 47, 50, 53, 54, 55, 58) 400 (expts. 21, 56) 450 · (expt. 22) 500 (expt. 23)		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 (94 parts) + Ni(OH)₂ (5 parts) + KOH (1 part) (expts. 51–53) "Red mud" (i.e., clay after removal of Al_2O_3 with soda lime) (expt. 54) $CaSO_4$ (expts. 55–56) $AlPO_4$ (expts. 57–58)				
	Catalyst: triethyl phosphate	300–350	1	Yield of B was 48.6% by weight on feed	(47)
	Catalyst was $POCl_3$; pumice or charcoal was used for heat transfer purposes	300–350	1	Yield of B was 45.9% by weight on feed	(47)
	Catalyst was $NaH_2PO_4 + H_3PO_4 +$ graphite; steam and n-hexane used as diluents	250	1?	Yield of B was 51% by weight on feed	(162)
	Steam and benzene used as diluents; catalyst was H_3PO_4 on graphite (prepared at 160 °C. from sodium phosphate solution, primary n-butylamine phosphate, and graphite)	280	1?	Yield of B was 54% by weight on feed	(162)
Dehydration of 2:1 mixture of 1,3-butanediol and 1,4-butanediol in presence of steam and 1,4-epoxybutane $C_4H_{10}O_2 \rightarrow C_4H_6 + 2H_2O$	Catalyst: $NaH_2PO_4 + H_3PO_4$ on graphite	260	1?	Yield of B was 54% by weight on $C_4H_{10}O_2$ feed	(162)

TABLE 7—*Continued*

PROCESS AND STARTING DERIVATIVE	APPARATUS AND CATALYST USED	TEMPERATURE	PRESSURE	REMARKS (B IS 1, 3-BUTADIENE)	REFERENCES
		°C.	atm.		
Dehydration of 1,4-butanediol CH_2OHCH_2-$CH_2CH_2OH \rightarrow$ $C_4H_6 + 2H_2O$	Catalyst of acid character, such as NaH_2PO_4, $CaHPO_4$, $Ca(H_2PO_4)_2$, Cu_2O, tungsten oxide, molybdenum oxide, silicic acid, phosphotungstic acid, phosphomolybdic acid, or boric acid			See patent for details	(64)
	Catalyst was NaH_2PO_4; steam and 1,4-epoxybutane used as diluents	280	1?	Yield of B was 57% by weight on $C_4H_{10}O_2$ feed	(162)
Dehydration of 2,3-butanediol $CH_3CHOHCH$-$OHCH_3 \rightarrow$ $C_4H_6 + 2H_2O$	Catalysts: $MgSO_4$; $MgCl_2$; $MgCl_2$ + steam	300–320 (first catalyst) 350 (second and third catalysts)		Yields of B were 1.60, 2.48, and 1.77% by weight on feed for first, second, and third catalysts, respectively	(48)
	Vapor-phase catalytic process	?	?	Yield of B = ?	(114)
Reduction of 1,2,3,4-butanetetrol (erythrite) $CH_2OHCHOH$-$CHOHCH_2OH$ + $2HCOOH \rightarrow$ $C_4H_6 + 2CO_2$ + $4H_2O$		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)

96

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):

$$CH_2=CHCH_2CH_2OH \rightarrow CH_2=CH-CH=CH_2 + H_2O$$

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):

$$CH_2=CHCH_2CH_2OH \rightarrow [CH_2=CHCH_3 + CH_2O] \rightarrow$$
$$CH_2=CHCH_3 + C + H_2O$$
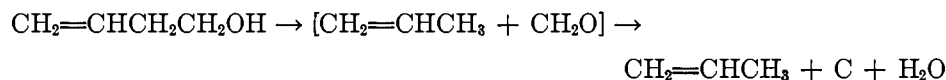
The present authors suggest that, because of a balanced electronic state of carbon atom 4 and with excessive activity of alumina, the desired 3,4-dehydration is partly replaced by an undesired 4,4-dehydration:

$$CH_2=CHCH_2CH_2OH \xrightarrow[400°C.]{Al_2O_3} [CH_2=CH-CH_2-HC\cdot\cdot + H\cdot\cdot OH] \rightarrow$$
$$CH_2=CH-CH_2\cdot\cdot H + \cdot\cdot C\cdot\cdot + H\cdot\cdot OH$$
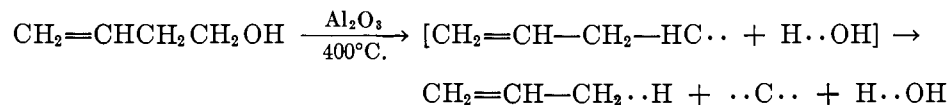
Adsorption of water molecules on the alumina at temperatures around 400°C. is probably strong enough to prevent rehydration of carbon atoms to form formaldehyde. As a consequence, the carbon lattice would be formed.

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):

$$CH_2OHCH=CHCH_3 \rightarrow CH_2=CH-CH=CH_2 + H_2O$$

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:
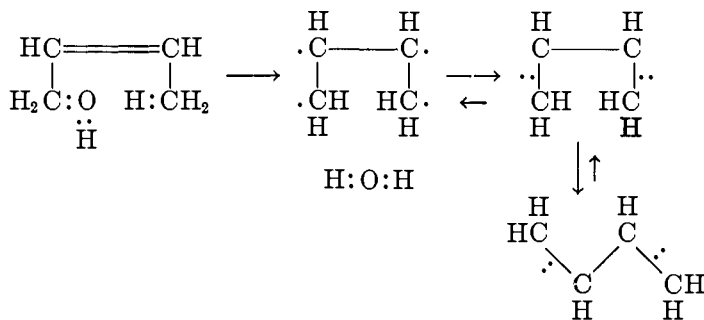
TABLE 8

Conversion of alkenols and alkenediols into butadiene

PROCESS AND STARTING DERIVATIVE	APPARATUS, CATALYSTS, AND SPECIAL REACTANTS	TEMPERATURE	PRES-SURE	REMARKS (B IS 1,3-BUTADIENE)	REFER-ENCES
		°C.	atm.		
Catalytic treatment of 1-propen-3-ol (allyl alcohol) Probably $2CH_2{=}CHCH_2OH \rightarrow C_4H_6 + 2CO + 3H_2$	Brass tube containing brass shavings	600	1?	Yield of B = ? (low in value)	(71)
	Catalyst of undisclosed composition			Yield of B = ?	(157)
Dehydration of 1-buten-3-ol (methylvinylcarbinol) $CH_2{=}CHCHOHCH_3 \rightarrow C_4H_6 + H_2O$	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)
	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)
Dehydration of 1-buten-3-ol and/or 2-buten-1-ol Probably $CH_2{=}CHCHOHCH_3 \rightarrow C_4H_6 + H_2O$	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)

Dehydration of 1-buten-4-ol (allyl carbinol) $CH_2=CHCH_2CH_2OH \rightarrow C_4H_6 + H_2O$	Catalyst was prepared by dehydrating and fusing a mixture of ammonium alum (90%) and potash alum (10%)	270–290	1?	Yield of B was 63.7–67.5% by weight on feed, using one recycle; acid phosphates or pyrophosphates also had a catalytic effect	(59)
	Catalyst: Al_2O_3	400–405	1?	Yield of B was 2.25% by weight on feed	(19)
Dehydration of 2-buten-1-ol (crotyl alcohol) $CH_2OHCH=CHCH_3 \rightarrow C_4H_6 + H_2O$	Toluidine bisulfate, anhydrous oxalic acid, $KHSO_4$, H_3PO_4, Al_2O_3, and $AlCl_3$ were catalysts named	140–160 (first catalyst) "Warmed" (second catalyst)	1	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	(30)
	Catalyst: probably kaolin or $AlPO_4$	400–450	1?	Yield of B = ?	(84)
	$POCl_3$ (?) was used as reactant	300–350?	1	Yield of B was 32% (?) by weight on feed	(47)
Dehydroxylation of 1-butene-3,4-diol (erythrol) $CH_2=CHCHOHCH_2OH + 2Cu \rightarrow C_4H_6 + H_2O + Cu_2O$	Copper was used as reactant	280	1	Yield of B was 0.193% by weight on butenediol feed	(176)

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:

$$CH_2X—CH=CH—CH_2X' \longrightarrow CH_2X—CHX'—CH=CH_2$$
$$\downarrow$$
$$CH_2=CH—CH=CH_2 + XX'$$

2. Elimination of oppositely charged substituents from carbon atoms 1 and 4 could give $\overset{+}{C}H_2—CH=CH—\overset{-}{C}H_2$, whose double bond would open simultaneously to form $\overset{+}{C}H_2—\overset{-}{C}H—\overset{+}{C}H—\overset{-}{C}H_2$, which is a highly activated state of butadiene:

$$CH_2X—CH=CH—CH_2X' \longrightarrow \overset{+}{C}H_2—CH=CH—\overset{-}{C}H_2 + \overset{+}{X}\overset{-}{X}'$$
$$\downarrow$$
$$\overset{+}{C}H_2—\overset{-}{C}H—\overset{+}{C}H—\overset{-}{C}H_2$$
$$\downarrow$$
$$CH_2=CH—CH=CH_2$$

Interpretation 1 suggests the following course for the dehydration:

$$CH_2OHCH=CHCH_3 \longrightarrow CH_2=CHCHOHCH_3$$
$$\downarrow$$
$$CH_2=CH—CH=CH_2 + H_2O$$

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:

$$CH_2=CHCHOHCH_2OH \xrightarrow{\ Cu\ } CH_2=CH—CH=CH_2 + 2\overset{\cdot}{O}H$$

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 Ostromyslenskiĭ to occur quantitatively at 300–350°C. over alumina (126, 131):

$$\begin{array}{c} H_2C\!-\!CHOH \\ |\qquad| \\ H_2C\!-\!CH_2 \end{array} \rightarrow \left[\begin{array}{c} H_2C\!-\!CH \\ |\qquad\| \\ H_2C\!-\!CH \end{array} + H_2O\right] \rightarrow CH_2\!=\!CH\!-\!CH\!=\!CH_2 + H_2O$$
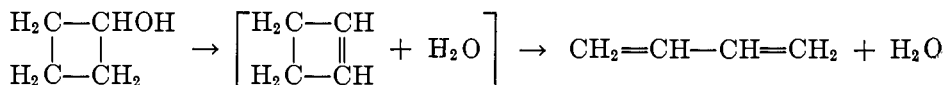
Cyclobutene was assumed to be the intermediate responsible for the reaction. Doyarenko, however, found that the products formed at 360–390°C. included propene, butadiene, cyclobutanone, 2-butenal, carbon, and water (19). "Dehydrations" to propene and butadiene were considered to be the main reactions:

$$\begin{array}{c} H_2C\!-\!CHOH \\ |\qquad| \\ H_2C\!-\!CH_2 \end{array} \rightarrow CH_2\!=\!CH\!-\!CH_3 + H_2O + C$$

$$\begin{array}{c} H_2C\!-\!CHOH \\ |\qquad| \\ H_2C\!-\!CH_2 \end{array} \rightarrow CH_2\!=\!CH\!-\!CH\!=\!CH_2 + H_2O$$
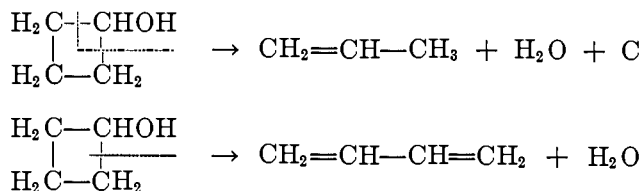
The conversion mechanism was assumed to be formation of unstable, highly energized molecules immediately upon dehydration, such that sufficient excess energy would be present to break a C—C or open a C=C linkage (19, 20).

When passed through a copper tube containing an inner silver gauze at a dark red heat, 1-methyl-3-cyclopentanol and "dimethylcyclopentanols" 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:

$$
\begin{array}{c}
\underset{\text{H}}{\text{C}}\!\!\begin{array}{c}\text{H} \quad \text{CH}_3\\ \diagdown\diagup\\ \text{C}\\ \diagup\quad\diagdown\\ \text{H}_2\text{C}\qquad\text{CH}_2\\ |\qquad\quad|\\ \text{H}_2\text{C}\!\!-\!\!-\!\!-\!\!\text{CHOH}\end{array}
\end{array}
\xrightarrow{(-\text{H}_2\text{O})}
\begin{array}{c}
\text{H}\quad\text{CH}_3\\ \diagdown\diagup\\ \text{C}\\ \diagup\quad\diagdown\\ \text{H}_2\text{C}\qquad\text{CH}_2\\ |\qquad\quad|\\ \text{HC}\!\!-\!\!-\!\!\text{CH}\\ \overset{..}{}\end{array}
\xrightarrow[\text{of energy}]{\text{absorption}}
\begin{array}{cc}
\text{H} & \text{H}\\ \text{CH} & \text{HC}\\ ..| & |..\\ \text{C}\!\!-\!\!-\!\!\text{C}\\ \text{H} & \text{H}\end{array} + \text{C}_2\text{H}_4
$$

$$
\begin{array}{c}
\text{H}_3\text{C}\quad\text{CH}_3\\ \diagdown\diagup\\ \text{C}\\ \diagup\quad\diagdown\\ \text{H}_2\text{C}\qquad\text{CH}_2\\ |\qquad\quad|\\ \text{H}_2\text{C}\!\!-\!\!-\!\!-\!\!\text{CHOH}\end{array}
\xrightarrow{(-\text{H}_2\text{O})}
\begin{array}{c}
\text{H}_3\text{C}\quad\text{CH}_3\\ \diagdown\diagup\\ \text{C}\\ \diagup\quad\diagdown\\ \text{H}_2\text{C}\qquad\text{CH}_2\\ |\qquad\quad|\\ \text{HC}\!\!-\!\!-\!\!\text{CH}\\ \overset{..}{}\end{array}
\xrightarrow[\text{of energy}]{\text{absorption}}
\begin{array}{cc}
\text{H} & \text{H}\\ \text{CH} & \text{HC}\\ ..| & |..\\ \text{C}\!\!-\!\!-\!\!\text{C}\\ \text{H} & \text{H}\end{array} + \text{C}_3\text{H}_6
$$

$$
\begin{array}{c}
\text{H}\quad\text{CH}_3\\ \diagdown\diagup\\ \text{C}\\ \diagup\quad\diagdown\\ \text{H}_2\text{C}\qquad\text{CH}\!-\!\text{CH}_3\\ |\qquad\qquad|\\ \text{HOHC}\!\!-\!\!-\!\!\text{CH}_2\end{array}
\xrightarrow{(-\text{H}_2\text{O})}
\begin{array}{c}
\text{H}\quad\text{CH}_3\\ \diagdown\diagup\\ \text{C}\\ \diagup\quad\diagdown\\ \text{H}_2\text{C}\qquad\text{CH}\!-\!\text{CH}_3\\ |\qquad\qquad|\\ \text{HC}\!\!-\!\!-\!\!\text{CH}\\ \overset{..}{}\end{array}
\xrightarrow[\text{of energy}]{\text{absorption}}
$$

$$
\begin{array}{cc}
\text{H} & \text{H}\\ \text{CH} & \text{HC}\\ ..| & |..\\ \text{C}\!\!-\!\!-\!\!\text{C}\\ \text{H} & \text{H}\end{array} + 3/2\ \text{C}_2\text{H}_4
$$

$$
\begin{array}{c}
\text{H}\quad\text{CH}_3\\ \diagdown\diagup\\ \text{C}\\ \diagup\quad\diagdown\\ \text{H}_2\text{C}\qquad\text{CH}_2\\ |\qquad\quad|\\ \text{HOHC}\!\!-\!\!-\!\!\text{CH}\!-\!\text{CH}_3\end{array}
\xrightarrow{(-\text{H}_2\text{O})}
\begin{array}{c}
\text{H}\quad\text{CH}_3\\ \diagdown\diagup\\ \text{C}\\ \diagup\quad\diagdown\\ \text{HC}\qquad\text{CH}_2\\ ..|\qquad\quad|\\ \text{HC}\!\!-\!\!-\!\!\text{CH}\!-\!\text{CH}_3\end{array}
\xrightarrow[\text{of energy}]{\text{absorption}}
$$

$$
\begin{array}{c}
\text{HC}\!\!-\!\!-\!\!\text{CH}\\ |\qquad\quad\text{H}\\ |\\ |\qquad\quad\text{H}\\ \text{HC}\!\!-\!\!-\!\!\text{CH}\end{array} + 3/2\ \text{C}_2\text{H}_4
$$

All of the processes given are over-all endothermic. An absorption of external energy occurs in (a) dehydration with double-bond formation, (b) the transformation of two $\overset{|}{\underset{|}{\text{C}}}\text{H}\!-\!\text{CH}_3$ into two $\overset{|}{\underset{|}{\text{C}}}\text{H}_2$ groups plus $\text{CH}_2\!\!=\!\!\text{CH}_2$, and (c) the conver-

sions of

$$\text{two } \begin{array}{c} -CH_2 \\ | \\ CH_2 \\ | \\ -CH_2 \end{array} \text{, one } \begin{array}{c} -CH_2 \\ | \\ CH-CH_3 \\ | \\ -CH_2 \end{array} \text{, or one } \begin{array}{c} -CH_2 \\ | \\ C(CH_3)_2 \\ | \\ -CH_2 \end{array}$$
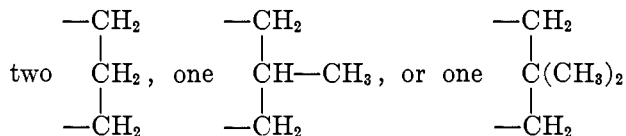
into $CH_2{=}CH_2$ (or $CH_2{=}CH-CH_3$) and into the two methylene terminals characteristic of activated butadiene.
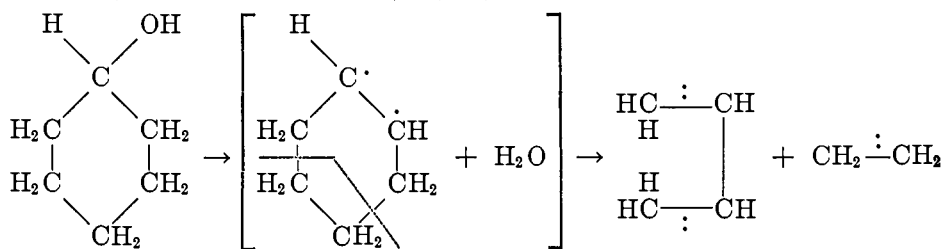
Cyclohexanol gives considerable amounts of ethene and butadiene when passed through tubes of quartz, platinum, silver, or (less favorably) of iron or porcelain, heated to redness (26, 27, 28, 54):

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:
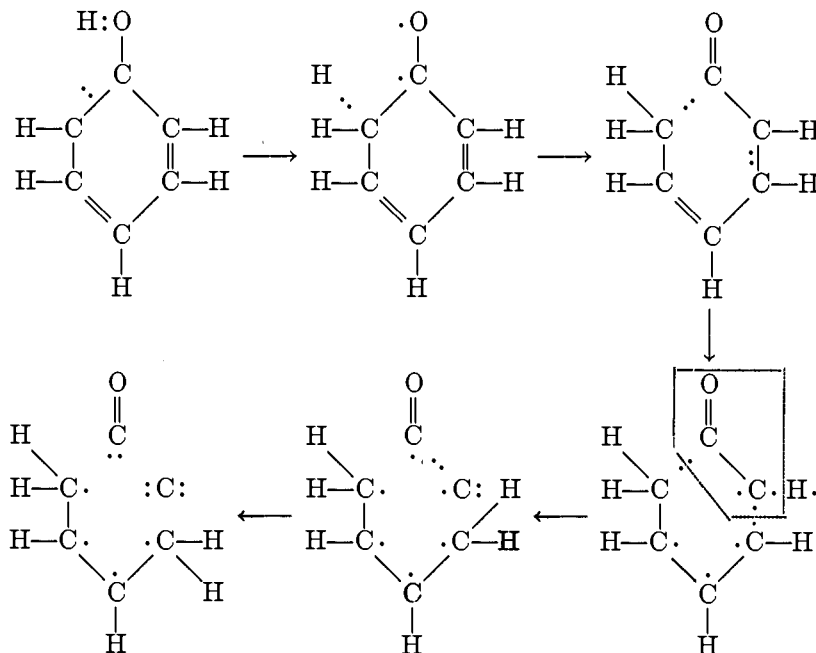
An alternative two-step formulation ending with a similar electronic interpretation is the disproportionation of hydroxybenzene into benzene and the easily convertible 1,2- and 1,4-dihydroxybenzenes. Pumice might exert a splitting action toward the hydroxyl group even at temperatures below 750°C., in 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:

$$C_6H_4(OH)_2 \rightarrow [2CO + 2H + C_4H_4] \rightarrow CH_2{=}CH{-}CH{=}CH_2 + 2CO$$
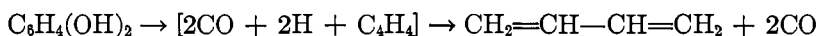
According to the present authors, direct formation of butadiene seems indicated on electronic grounds, as in the case of hydroxybenzene:

Set I

$$CH_2{=}CH{-}CH{=}CH_2 + 2CO \longleftarrow$$
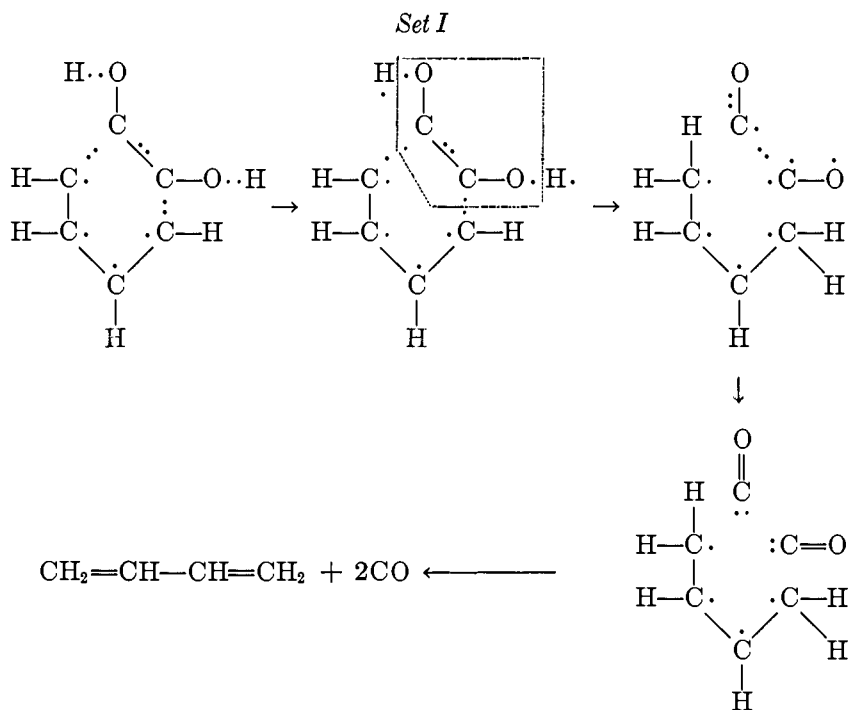
For the case of a prior tautomerization of 1,2-dihydroxybenzene into 2,4-cyclohexadien-1-on-2-ol or to 4-cyclohexene-1,2-dione, a similar formulation can be given:

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, 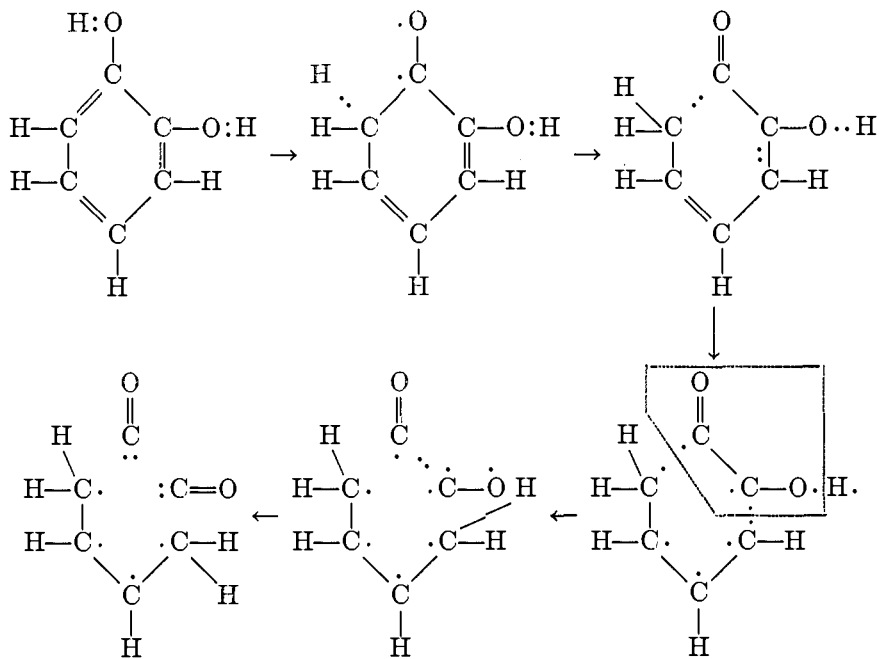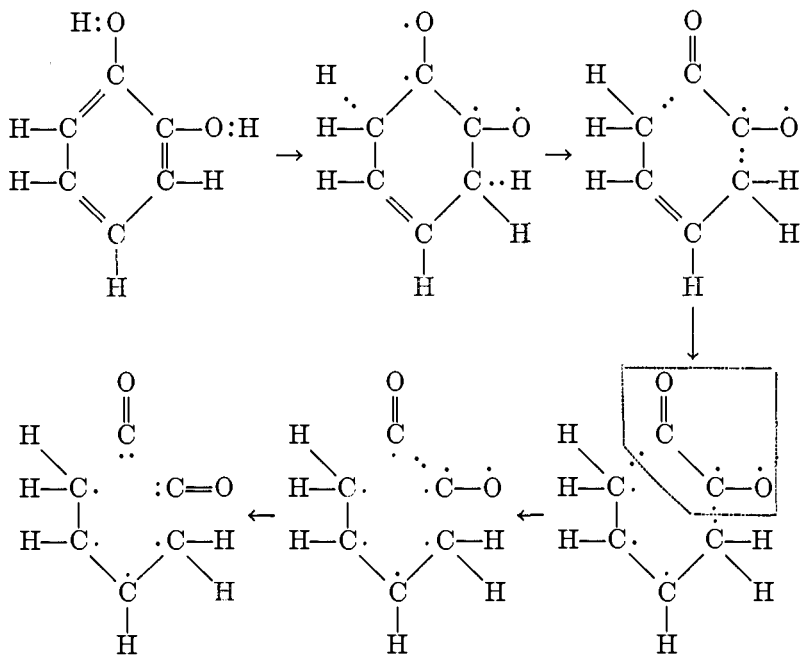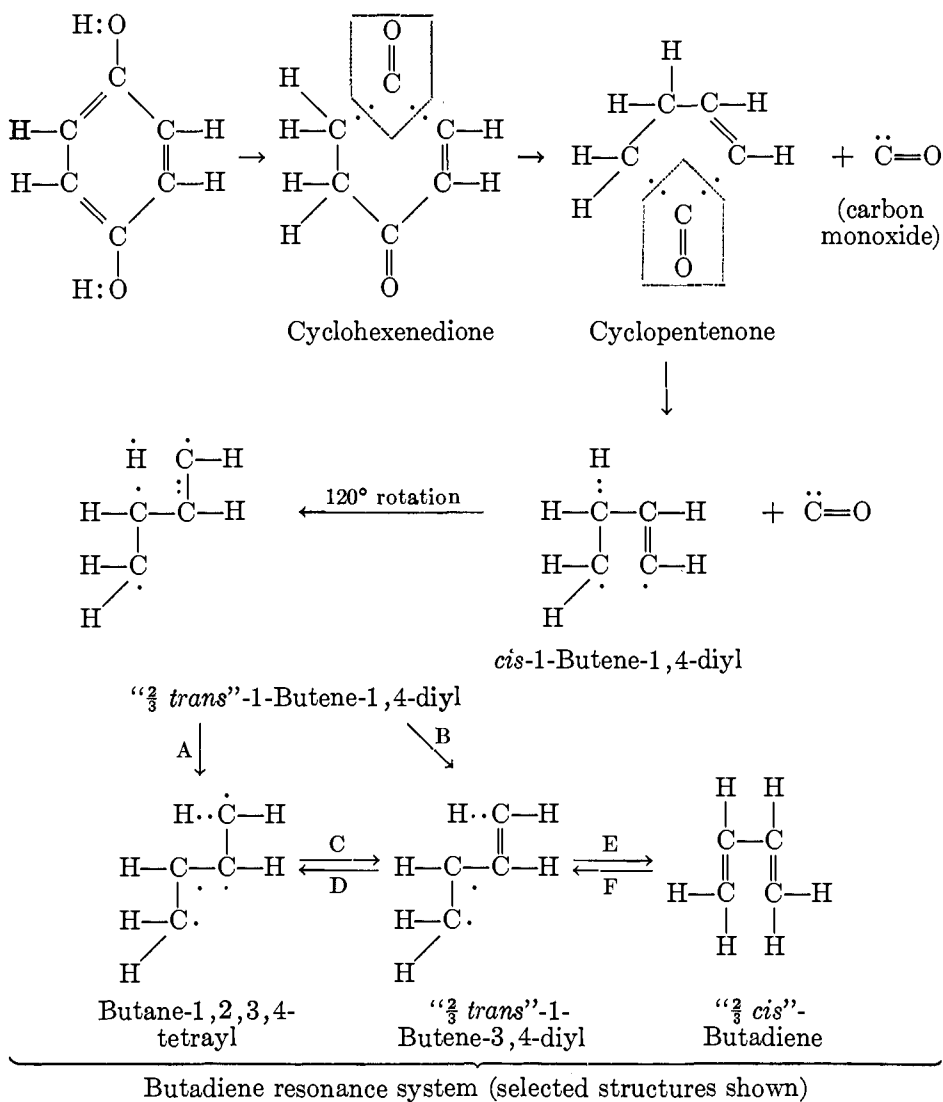and 2×58 kcal. as the total molal resonance energies of the dihydroxybenzene, butadiene, and carbon monoxide, respectively.

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.

Cyclohexenedione   Cyclopentenone   + C=O (carbon monoxide)

120° rotation

cis-1-Butene-1,4-diyl

"⅔ *trans*"-1-Butene-1,4-diyl

A   B

C ⇌ D   E ⇌ F

Butane-1,2,3,4-tetrayl   "⅔ *trans*"-1-Butene-3,4-diyl   "⅔ *cis*"-Butadiene

Butadiene resonance system (selected structures shown)

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 ethanediyl 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	PRES-SURE	REMARKS (B IS 1,3-BUTADIENE)	REFER-ENCES
		°C.	atm.		
"Dehydration" of cyclopropylcarbinol H_2C——$CHCH_2OH \rightarrow C_4H_6 + H_2O$ CH_2	Catalyst: Al_2O_3	300–400		Yield of B was 5.6% by weight on feed	(19)
"Dehydration" of cyclobutanol H_2C—$CHOH$ $\quad \rightarrow C_4H_6 + H_2O$ H_2C—CH_2		?	?	Yield of B = ?	(126)
	Catalyst: Al_2O_3	300–350		Yield of B was 75% by weight	(131)
	Catalyst: Al_2O_3	360–390		Yield of B was 5.6% by weight on feed	(19)
Dehydration and partition of 1-methyl-3-cyclopentanol H CH₃ C H_2C CH_2 $\rightarrow C_4H_6 + H_2O + C_2H_4$ H_2C——$CHOH$ (Probable reaction is given)	Copper tube containing silver gauze inside	Dark red heat	1	Yield of B = ?	(29)
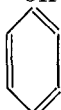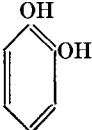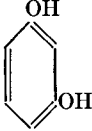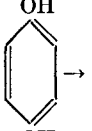
Dehydration and partition of dimethylcyclo-pentanols $C_5H_7(CH_3)_2(OH) \rightarrow C_4H_6 + H_2O + C_3H_6$ (Possible reaction is given)	Not described (probably a copper tube containing silver gauze)	Dark red heat?	1?	Yield of B = ?	(29)
Dehydration and partition of cyclohexanol OH $\rightarrow C_4H_6 + H_2O + C_2H_4$	Iron tube which can be filled with native Al_2O_3	600	1	Yield of B was "good"	(54)
	Iron pipe	600	1	Yield of B = ?	(27)
	Quartz tube	Slight red heat	1	Yield of B was 22–28% by weight on feed; tubes of quartz, platinum, or silver are better than those of iron or porcelain	(26)
Catalytic cracking of hydroxybenzene (i.e., phenol) OH $\rightarrow C_4H_6 + CO + C$ (Probable reaction is given)	Catalyst: pumice	650–750	1?	Yield of B = ?	(49)

TABLE 9—*Continued*

110

PROCESS AND STARTING DERIVATIVE	APPARATUS AND CATALYST	TEMPERATURE	PRES-SURE	REMARKS (B IS 1,3-BUTADIENE)	REFER-ENCES
		°C.	atm.		
Catalytic cracking of 1,2-dihydroxybenzene (i.e., pyrocatechol) OH OH $\rightarrow C_4H_6 + 2CO$	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) OH OH $\rightarrow C_4H_6 + 2CO$	Quartz tube containing glass rings	650	1?	Yield of B = ?	(49)
Catalytic cracking of 1,4-dihydroxybenzene (i.e., hydroquinone) OH $\rightarrow C_4H_6 + 2CO$ OH	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):

$$C_2H_5OC_2H_5 \rightarrow 2C_2H_4 + H_2O$$

$$C_2H_5OC_2H_5 \rightarrow CH_2=CH-CH=CH_2 + H_2 + H_2O$$
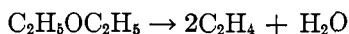
The metal becomes gradually coated with carbon and probably undergoes a certain amount of oxidation through contact with water vapor:

$$3C_2H_5OC_2H_5 \rightarrow 3CH_2=CH-CH=CH_2 + 3H_2O + 3H_2$$

$$3H_2O + 2Al \rightarrow Al_2O_3 + 3H_2$$

$$\overline{3C_2H_5OC_2H_5 + 2Al \rightarrow 3CH_2=CH-CH=CH_2 + Al_2O_3 + 6H_2}$$
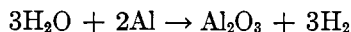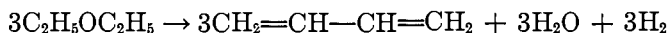
Filippov assumed that ethanal, which is found among the products, participates in butadiene formation. Ostromyslenskiĭ considered the conversion to involve probably dehydration to 2-butene, dehydrogenation to cyclobutene, and isomerization of the latter (136):

$$
\begin{array}{ccccc}
H_3C-CH_2 & & H_3C-CH & & H_2C-C & & H_2C=CH \\
| & \xrightarrow{-H_2O} & \| & \xrightarrow{-H_2} & |\ \ \| & \longrightarrow & | \\
O & & \| & & |\ \ \| & & | \\
| & & H_3C-CH & & H_2C-CH & & H_2C=CH \\
H_3C-CH_2 & & & & & &
\end{array}
$$
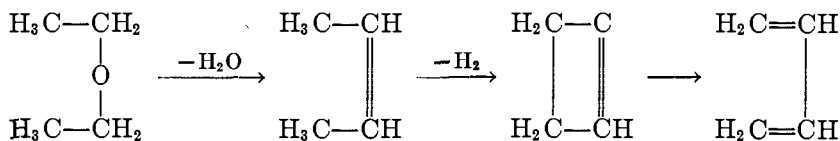
A possible dehydrogenation to 1,4-epoxybutane prior to dehydration was not overlooked (137, 142):

$$
\begin{array}{ccccc}
H_3C-CH_2 & & H_2C-CH_2 & & HC=CH_2 \\
| & \xrightarrow{-H_2} & |\quad\quad| & \xrightarrow{-H_2O} & | \\
O & & O & & HC=CH_2 \\
| & & |\quad\quad| & & \\
H_3C-CH_2 & & H_2C-CH_2 & &
\end{array}
$$
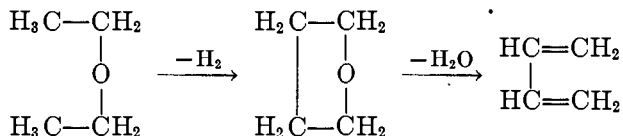
There are several reasons why butadiene should be formed from diethyl ether over aluminum at 300–600°C. First, ethanol and ethene, which are respectively expected and actual products, are each directly convertible into butadiene under similar conditions (21, 23, 72). Ethanal, another product, upon dimerization 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:

$$C_2H_5OCHClCH_3 \xrightarrow{Al_2O_3\ +\ BaO} CH_2{=}CH{-}CH{=}CH_2 + H_2O + HCl$$

$$C_2H_5OCH_2CH_2Cl \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2O + HCl$$

$$C_2H_5OCH(OH)CH_3 \longrightarrow CH_2{=}CH{-}CH{=}CH_2 + 2H_2O$$

$$C_2H_5OCH(OC_2H_5)CH_3 \xrightarrow{Al_2O_3} CH_2{=}CH{-}CH{=}CH_2 + H_2O + C_2H_5OH$$

$$C_2H_5OCH(OCOCH_3)CH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2O + CH_3COOH$$
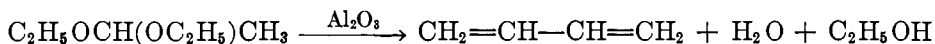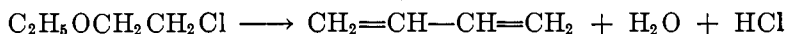
Catalytic conversion of ethyl β-hydroxyethyl ether substantiates the foregoing equations (8):

$$C_2H_5OCH_2CH_2OH \xrightarrow{Al_2O_3\ or\ TiO_2} CH_2{=}CH{-}CH{=}CH_2 + 2H_2O$$
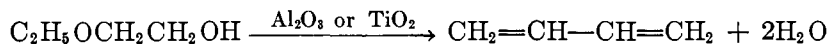
Ostromyslenskiĭ mentioned the mechanism of conversion of substituted diethyl ethers and the equilibrium existing between α-hydroxyethyl ether, ethanol, and ethanal (129). This ether, at 360–440°C., evidently undergoes a complete and facile dissociation into ethanol and ethanal, followed by interaction (condensation) of these components. Although Ostromyslenskiĭ 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):

$$C_2H_5OCHXCH_3 \xrightarrow{-HX} C_2H_5OCH{=}CH_2 \longrightarrow$$

$$\begin{array}{c} H_2C{-}CH_2 \\ | \qquad \diagdown \\ | \qquad \quad O \xrightarrow{-H_2O} \begin{array}{c} HC{=}CH_2 \\ | \\ HC{=}CH_2 \end{array} \\ | \qquad \diagup \\ H_2C{-}CH_2 \end{array}$$
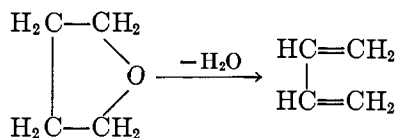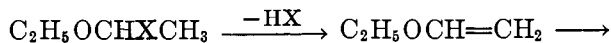
Methyl α-methoxyethyl ether appears to be but slightly convertible into butadiene over alumina-containing catalysts (4, 79). The present authors offer the following mechanisms for the converted portion: (*a*) an initial demethanolation to methyl vinyl ether, supplemented by scissions affording vinyl 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):

$$CH_3CHOHCH_2CH_2—O—CH_2CH_2CHOHCH_3 \rightarrow$$

$$2CH_2{=}CH—CH{=}CH_2 + 3H_2O$$
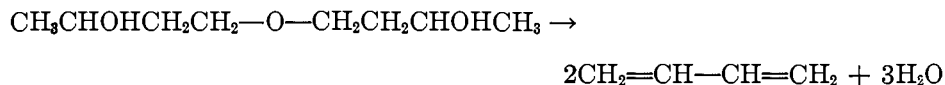
It is desirable to remove the alkadiene from the reaction zone as fast as it is formed. Formation of 2 gram-moles of butadiene from γ,γ'-dihydroxydibutyl ether requires 12.8 kcal., independently of the chosen reaction course. Assuming that C—C scissions requiring 58.6 kcal. need not be considered, the 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 dehydrodechlorination and bidehydration (31):

$$CH_3CHClCH_2CH_2—O—CH_2CH_2CHOHCH_3 \rightarrow$$

$$2CH_2{=}CH—CH{=}CH_2 + HCl + 2H_2O$$
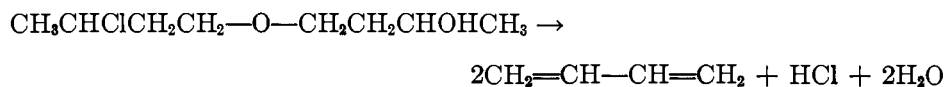
From a mechanism standpoint, the conversion is more complicated in nature than that of γ,γ'-dihydroxydibutyl ether. The location of primary scission probably depends upon relative strengths of bonds other than C—C, the availability or potential of the disrupting energy, and the particular type of catalyst 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):
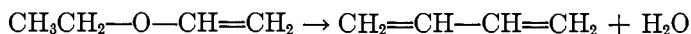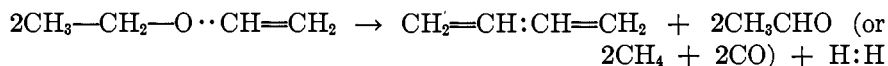
$$CH_3CH_2\text{—}O\text{—}CH\text{=}CH_2 \rightarrow CH_2\text{=}CH\text{—}CH\text{=}CH_2 + H_2O$$

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:

$$2CH_3\text{—}CH_2\text{—}O\cdot\cdot CH\text{=}CH_2 \rightarrow CH_2\text{=}CH{:}CH\text{=}CH_2 + 2CH_3\text{—}CH_2\text{—}\overset{\cdot}{O}$$

$$2CH_3\text{—}CH_2\text{—}\overset{\cdot}{O} \rightarrow 2CH_3CHO + H{:}H$$

$$CH_3CHO \rightarrow CH_4 + CO$$

$$2CH_3\text{—}CH_2\text{—}O\cdot\cdot CH\text{=}CH_2 \rightarrow CH_2\text{=}CH{:}CH\text{=}CH_2 + 2CH_3CHO \text{ (or}$$
$$2CH_4 + 2CO) + H{:}H$$
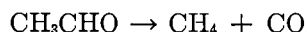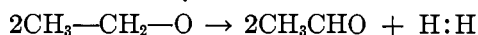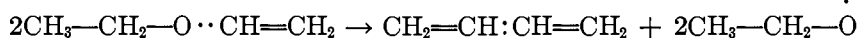
Alkyl α-vinyl-β-iodoethyl ethers readily form butadiene when acted upon by magnesium or zinc dust and ethanol (151). The alkyl group is suitably methyl, ethyl, n-propyl, or isobutyl:

$$ROCH(CH\text{=}CH_2)CH_2I + Mg(or\ Zn) \rightarrow$$

$$CH_2\text{=}CH\text{—}CH\text{=}CH_2 + ROMgI(or\ ROZnI)$$
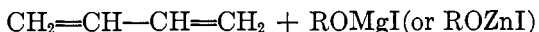
It will be observed that elimination of the alkoxyl groups is β to the vinyl group, hence rapid in rate, and that in the fragmentation the normally weak β C—C bond is stronger than the strained C—O bond. The C—I bond is probably the weakest linkage (45.5 kcal.) in the molecule, so that polar alkyl α-vinyl-β-iodomagnesium(or iodozinc)ethyl ethers may be taken as reaction intermediates. Elimination of alkoxymagnesium or alkoxyzinc iodide would occur with simultaneous establishment of resonance among butadiene structures, beginning with 1-butene-$\overset{+}{3}$,$\overset{-}{4}$-diyl:

$$CH_2\text{=}CH\text{—}\overset{+}{\underset{\cdot\cdot}{C}}H(OR)\overset{+}{C}H_2(\overset{+}{M}gI) \longrightarrow CH_2\text{=}CH\text{—}\overset{+}{C}H\text{-}\overset{\cdot\cdot}{C}H_2 + RO{:}MgI$$

$$\updownarrow$$
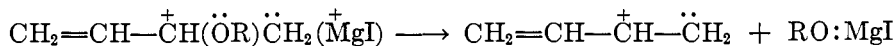
All other resonance
forms of butadiene

3. Dialkenyl ethers

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

$$CH_2{=}CH \cdot\cdot O \cdot\cdot CH{=}CH_2 \ + \ metal \ \rightarrow \ CH_2{=}CH{:}CH{=}CH_2 \ + \ metal{::}O$$
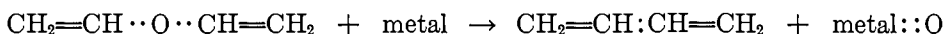
The process operates at 100–400°C. (102, 103, 104, 105). One would expect in this reaction a certain amount of dehydration traceable to the metal oxides produced. A dehydration to ethyne or dissociation to ethanal plus ethyne, which would require respectively 48.2 and 9.4 kcal. per gram-mole of divinyl 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):

$$CH_3CH{=}CHCH_2{-}O{-}CH_2CH{=}CHCH_3 \ \rightarrow \ 2CH_2{=}CH{-}CH{=}CH_2 \ + \ H_2O$$

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):

$$\begin{array}{ccc} H_2C{-\!-\!-\!-}CH_2 & HC{-}CH \\ \ \ | \qquad \ \ | & \ \| \quad \| \\ H_2C \qquad CH_2 \longrightarrow H_2C \quad CH_2 \ + \ H_2O \\ \ \diagdown \ \diagup \\ O \end{array}$$
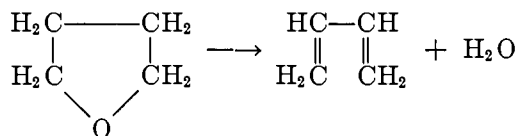
Catalysts for the conversion include the primary sodium, primary or secondary calcium, other alkaline earth, nickel, cobalt, silver, copper, mercury, and lead orthophosphates, phosphoric acid or boric acid on pumice or other carriers, heteropolyacids of tungsten or of molybdenum, oxides of tungsten or 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	CATALYSTS OR SPECIAL REACTANTS	TEMPER-ATURE	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
		°C.	atm.		
"Dehydration" and dehydrogenation of diethyl ether $3(C_2H_5)_2O + 2Al \rightarrow 3C_4H_6 + Al_2O_3 + 6H_2$	Aluminum metal was a reactant	600		Yield of B was small on fully decomposed ether	(34, 35)
	Aluminum metal was a reactant			Yield of B was 2% on ether	(98)
	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)
"Dehydration" and dehydrodechlorination of ethyl α-chloroethyl ether (mono-α-chlorodiethyl ether) $C_2H_5OCHClCH_3 \rightarrow C_4H_6 + H_2O + HCl$	Catalyst: $Al_2O_3 + BaO$	350		Yield of B was 20%	(142)
	Catalyst: Al_2O_3			See patent for possible details	(126, 139)
"Dehydration" and dehydrodechlorination of ethyl β-chloroethyl ether (mono-β-chlorodiethyl ether) $C_2H_5OCH_2CH_2Cl \rightarrow C_4H_6 + H_2O + HCl$	A catalyst was used			See patent for possible details	(126, 139)
"Dehydration" of ethyl α-hydroxyethyl ether $C_2H_5OCHOHCH_3 \rightarrow C_4H_6 + 2H_2O$				See patent for possible details	(126, 139)
"Dehydration" of ethyl β-hydroxyethyl ether $C_2H_5OCH_2CH_2OH \rightarrow C_4H_6 + 2H_2O$	Catalyst: Al_2O_3 or ThO_2	400–450			(8)

	Catalyst: Al_2O_3	350		Yield of B = ?	(4)
Decomposition of methyl α-methoxy-ethyl ether (1,1-dimethoxyethane) $CH_3OCH(OCH_3)CH_3 \rightarrow C_4H_6 + 2H_2O$	Catalysts were (1) Al_2O_3 1, ThO_2 0.045, activated clay 5.225 parts; (2) Al_2O_3 1, $NiCl_2$ 0.01, activated clay 5.05 parts; (3) Al_2O_3 1, ThO_2 0.045, activated clay 5.225 parts	450		Yields of B were 0.051, 0.064, and 0.060% by weight on feed for catalysts 1, 2, and 3, respectively	(79)
Decomposition of ethyl α-ethoxyethyl ether (acetal or 1,1-diethoxyethane) $C_2H_5OCH(OC_2H_5)CH_3 \rightarrow C_4H_6 + H_2O + C_2H_5OH$	Catalyst: Al_2O_3	300–380		Yield of B was 16%	(142)
"Dehydration" and deësterification of ethyl α-acetoxyethyl ether (mono-α-acetoxydiethyl ether) $C_2H_5OCH(OCOCH_3)CH_3 \rightarrow C_4H_6 + H_2O + CH_3COOH$				See patent for possible details	(126, 138)
Dehydration of γ,γ'-dihydroxydibutyl ether $(CH_3CHOHCH_2CH_2)_2O \rightarrow 2C_4H_6 + 3H_2O$	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	>15	Yield of B = ?	(50)
Dehydration and dehydrodechlorination of γ-chlorobutyl γ'-hydroxybutyl ether $CH_3CHClCH_2CH_2OCH_2CH_2$-$CHOHCH_3 \rightarrow 2C_4H_6 + HCl + 2H_2O$	Catalyst: $BaCl_2$	350	0.0395–0.0526	Yield of B was 18% by weight on feed	(31)
	Catalyst: Al_2O_3	450–500	0.0658	Yield of B was 24% by weight on feed	(31)
"Dehydration" of ethyl vinyl ether $C_2H_5OCH=CH_2 \rightarrow C_4H_6 + H_2O$				See patent for possible details	(126, 138)

117

TABLE 10—*Continued*

PROCESS AND ETHER USED	CATALYSTS OR SPECIAL REACTANT	TEMPER-ATURE	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
		°C.	atm.		
Deiododemethoxylation of methyl α-vinyl-β-iodoethyl ether $CH_3OCH(CH=CH_2)CH_2I + Mg$ (or Zn) $\rightarrow$ $C_4H_6 + CH_3OMgI$ (or CH_3OZnI)			1	Yield of B = ?; ethanol was part of the feed	(151)
Deiododeëthoxylation of ethyl α-vinyl-β-iodoethyl ether $C_2H_5OCH(CH=CH_2)CH_2I + Mg$ (or Zn) $\rightarrow C_4H_6 + C_2H_5OMgI$ (or C_2H_5OZnI)			1	Yield of B = ?; ethanol was part of the feed	(151)
Deiododepropoxylation of propyl α-vinyl-β-iodoethyl ether $C_3H_7OCH(CH=CH_2)CH_2I + Mg$ (or Zn) $\rightarrow C_4H_6 + C_3H_7OMgI$ (or C_3H_7OZnI)			1	Yield of B = ?; ethanol was part of the feed	(151)
Deiododeisobutoxylation of isobutyl α-vinyl-β-iodoethyl ether $C_4H_9OCH(CH=CH_2)CH_2I + Mg$ (or Zn) $\rightarrow C_4H_6 + C_4H_9OMgI$ (or C_4H_9OZnI)			1	Yield of B = ?; ethanol was part of the feed	(151)
Reduction of divinyl ether $(CH_2=CH)_2O + metal \rightarrow C_4H_6 + metal$ 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 $(CH_2=CH)_2O + Zn \rightarrow C_4H_6 + ZnO$	Zn is a reactant	?	?	Yield of B = ?	(104)
Reduction of divinyl ether $(CH_2=CH)_2O + metal \rightarrow C_4H_6 + metal$ 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 $(CH_3CH=CHCH_2)_2O \rightarrow 2C_4H_6 + H_2O$		?	?	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. Methyldioxane

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):

$$CH_2{=}CH{-}CH{=}CH_2 + HCHO + H_2O$$
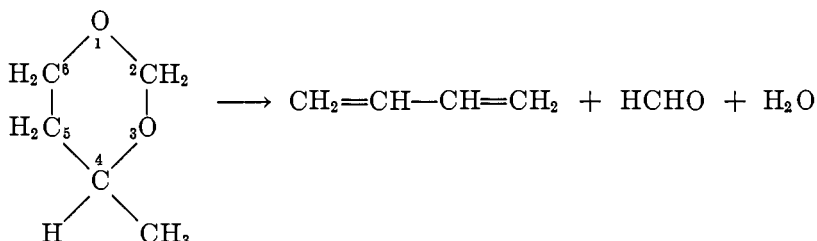
The conversion of 4-methyl-*m*-dioxane can be looked upon as a reversion into 1,3-butanediol and formaldehyde hydrate, followed by dehydration to butadiene:
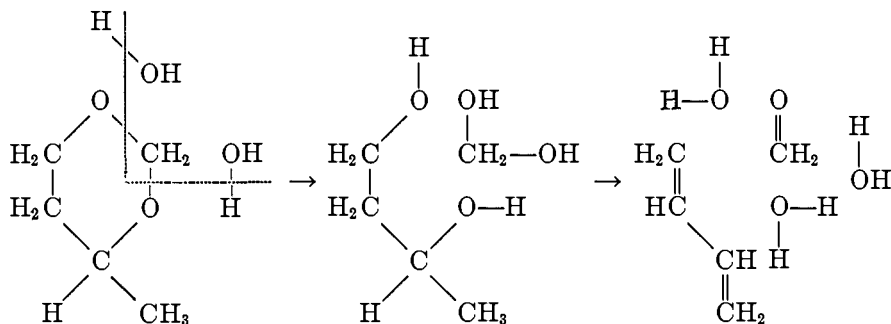
Table 11 contains data on the conversion of cyclic oxides into butadiene.

IV. ALDEHYDES

A. ALKANALS

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

$$2CH_3CHO + 2H \rightarrow CH_2{=}CH{-}CH{=}CH_2 + 2H_2O$$
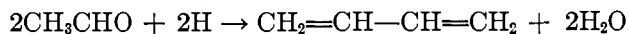
The by-products include 1,3-butanediol and butenols, the formation of which was ascribed to hydrogenation of 3-hydroxybutanal and of its dehydration product, 2-butenal, respectively. Abundant evolution of hydrogen at the cathode leads to formation of 1-butanol. From this point of view, butadiene production is dependent on aldolization, hydrogenation, and dehydration. The order

TABLE 11

Catalysis of cyclic oxides

PROCESS AND CYCLIC OXIDE	CATALYST	TEMPERATURE	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
		°C.	atm.		
	. . . .	. . . .	. . . .	. . . .	(125)
Dehydration of 1,4-epoxybutane (tetrahydrofuran) H_2C——CH_2 | | → $C_4H_6 + H_2O$ H_2C CH_2 \\ / O	A catalyst was used	Heated		See patent for possible details	(126, 138)
	Catalysts were: (A) mercurous phosphate on pumice; (B) calcium phosphate; (C) W_2O_5 + bleaching earth; (D) NaH_2PO_4 + H_3PO_4 + graphite + nickel acetate	280–290 (case A) 360 (case B) 330–390 (case C) 260–310 (case D)	1 or less (cases A, B, D) Approx. 1 (case C)	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	(163)
Dehydration of 2,3-epoxybutane CH_3CH—$CHCH_3$ → $C_4H_6 + H_2O$ \\ / O	H_3PO_4 on pumice	400–500	*In vacuo* if desired	Yield of B = ?	(110)
Decomposition of 4-methyl-*m*-dioxane in presence of steam O / \ H_2C CH_2 | | H_2C O → $C_4H_6 + H_2O$ + HCHO \ / C / \ H CH_3	H_3PO_4 on graphite (prepared at 160°C. from sodium phosphate solution, primary *n*-butylamine phosphate, and graphite)	270	1?	Yield of B was 52% by weight on absolute methyldioxane feed	(36)

of the last two reactions is questionable. An alternative mechanism that warrants attention is a simple type of condensation with a bidehydration. 2,3-Butanediol and 3-butanol-2-oxyl would then be the intermediates:

$$CH_3—\overset{\cdot}{H}C\cdot \ + \ \overset{\cdot}{H} \longrightarrow CH_3—\overset{|}{H}C\cdot \longrightarrow \tfrac{1}{2}CH_3—\overset{|}{H}C\!:\!CH—CH_3$$
$$\underset{O\cdot}{|} \qquad\qquad \underset{O:H}{|} \qquad\qquad \underset{HO}{|}\ \underset{OH}{|}$$

$$(2H_2O\ \text{loss}) \downarrow$$

$$CH_3—CH—CH\!=\!CH_2 \ \xrightarrow[\text{(1H}_2\text{O loss)}]{\overset{\cdot}{H}\ \text{presence}}\ CH_2\!=\!CH—CH\!=\!CH_2$$
$$\underset{\cdot O}{|}$$

$$(1H_2O \diagdown \text{loss}) \qquad\qquad\qquad (2H_2O\ \text{loss}) \uparrow$$

$$CH_3—CH\cdot \ + \ \cdot CH—CH_3 \ \rightarrow \ CH_3—CH\!:\!CH—CH_3 \ \xrightarrow{\overset{\cdot}{H}}\ CH_3—CH—CH—CH_3$$
$$\underset{O\cdot}{|} \quad \underset{OH}{|} \qquad\qquad\qquad \underset{\cdot O}{|}\ \underset{OH}{|} \qquad\qquad \underset{H:O}{|}\ \underset{OH}{|}$$

Since the electrolyte contained over 20 per cent of sulfuric acid and was maintained at temperatures above 30–35°C., a further pinacol type of rearrangement to 2-butanone seems possible. It would decrease the butadiene yield. Isolation of 2-butanol, 2-butanone, or 2,3-butanediol would fortify the foregoing mechanism.

Butanal is readily converted into butadiene by passage over aluminum silicate at 550°C. and an absolute pressure of 1 mm. of mercury (85, 149):

$$CH_3CH_2CH_2CHO \rightarrow CH_2\!=\!CH—CH\!=\!CH_2 + H_2O$$

The catalysis is not that of a simple dehydration. 1-Buten-1-ol, which corresponds to a probably tautomeric form of butanal at high temperatures, and cyclobutanol are hypothetical intermediates for a conversion through cyclobutene. An isomerization of 1-buten-1-ol into 2-buten-1-ol is another possibility; it would permit 1,4-dehydration and avoid cyclization.

When 2-methylpropanal is passed over pumice at 580–590°C. under atmospheric pressure, it yields a trace of butadiene (118). While the desired reaction may be a dehydration with intervening isomerization:

$$CH_3\underset{\underset{CH_3}{|}}{CH}CHO \ \rightarrow \ \left[CH_3\underset{\underset{CH_2}{\diagdown\diagup}}{CH}—CHOH;\ CH_2\!=\!CH\underset{\underset{OH}{|}}{C}HCH_3;\ CH_2\underset{\underset{OH}{|}}{C}H\!=\!CH\underset{\underset{H}{|}}{C}H_2 \right]$$

$$\downarrow$$

$$CH_2\!=\!CH—CH\!=\!CH_2 \ + \ H_2O$$

the other products, i.e., hydrogen, water, carbon monoxide, methane, ethane, ethene, propene, ethanal, and probably 2-butenal, are indicative of a variety of competitive reactions. Demethylation to propanal-α-yl and ethanal-α,α-diyl is expected, accounting for the presence of C_1, C_2, and C_3 products. The car-

bonyl group is removed by direct elimination and as water (traceable to tautomerization of $HC\!\!-\!\!C\!\!=\!\!O$ into $C\!\!=\!\!C\!\!-\!\!OH$ or to carbonyl hydrogenations, $\dot{C}\!\!-\!\!\dot{O} + \dot{H} \rightarrow \dot{C}\!\!-\!\!O\!:\!H$; $\dot{C}\!\!-\!\!\dot{O} + 2\dot{H} \rightarrow H\!:\!C\!\!-\!\!O\!:\!H$). 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.
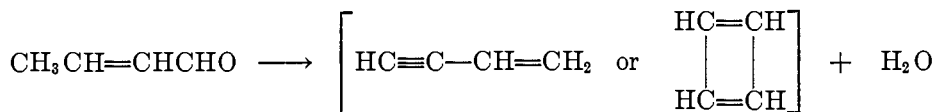
B. ALKENALS

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:

$$CH_3CH\!\!=\!\!CHCH(OH)NH_2 \rightarrow [C_4H_4] + H_2O + NH_3$$
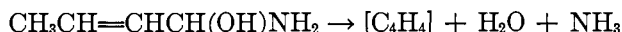
and that 2-butenal upon loss of water should form a C_4H_4 member, perhaps butenyne or cyclobutadiene:

$$CH_3\,CH\!\!=\!\!CHCHO \longrightarrow \left[HC\!\!\equiv\!\!C\!\!-\!\!CH\!\!=\!\!CH_2 \quad \text{or} \quad \begin{matrix} HC\!\!=\!\!CH \\ | \quad\ | \\ HC\!\!=\!\!CH \end{matrix} \right] + H_2O$$

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:

$$\begin{matrix} HC\!\!=\!\!CH \\ | \quad\ | \\ HC\!\!=\!\!CH \end{matrix} + 2\dot{H} \longrightarrow CH_2\!\!=\!\!CH\!\!-\!\!CH\!\!=\!\!CH_2$$
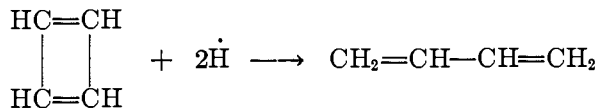
Dehydration of the aminohydroxymethyl group of 2-butenalammonia and ethanalammonia, $CH_3CH(OH)NH_2$, would produce aldimines, $RCH\!\!=\!\!NH$, whose dehydrogenation to nitriles could furnish the requisite hydrogen atoms for hydrogenation of C_4H_4 into C_4H_6. Aldimines were taken as the source of 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-methybenzaldehyde, 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-phenyl-pyrrole, 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:

$$CH_3CH\!\!=\!\!CHCHO \ + \ H_2NC_6H_5 \ \rightarrow \ [CH_3CH\!\!=\!\!CHCH\!\!=\!\!NC_6H_5] \ + \ H_2O$$

(loss of 2$\dot{H}$) $\downarrow$

$$CH_3CH\!\!=\!\!CHCHO + 2\dot{H} \rightarrow [CH_3CH\!\!=\!\!CHCH_2OH] \rightarrow$$

$$CH_2\!\!=\!\!CH\!\!-\!\!CH\!\!=\!\!CH_2 + H_2O$$
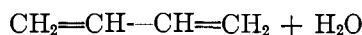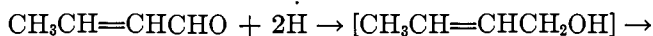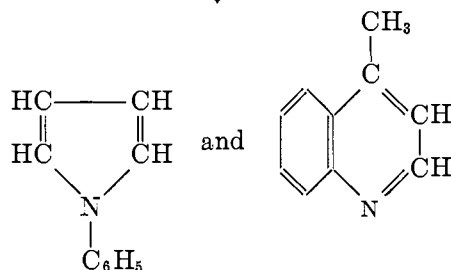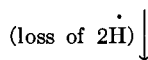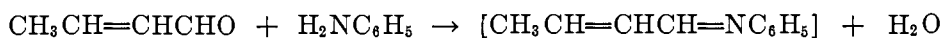
The over-all equation is identical for both the $C_{10}H_9N$ isomers:

$$2CH_3CH\!\!=\!\!CHCHO + C_6H_5NH_2 \rightarrow C_4H_6 + C_{10}H_9N + 2H_2O$$

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 alkanoic acids.

TABLE 12

Conversion of aldehydes into butadiene

PROCESS AND ALDEHYDE USED	CATALYST	TEMPERATURE	PRES-SURE	REMARKS (B IS 1,3-BUTADIENE	REFER-ENCES
		°C.	atm.		
Electrolytic reduction and condensation of ethanal (acetaldehyde) $2CH_3CHO + 2H \rightarrow C_4H_6 + 2H_2O$	Electrolyte had over 20% of H_2SO_4	>30–35		Yield of B = ?	(145)
"Dehydration" of butanal (butyraldehyde) $CH_3CH_2CH_2CHO \rightarrow C_4H_6 + H_2O$	Catalyst: aluminum silicate	550	0.00132	Yield of B was 52.5% by weight on feed, using one recycle	(85)
	Catalyst: aluminum silicate	Red heat		Yield of B = ?	(149)
"Dehydration" of 2-methylpropanal (isobutyraldehyde) $(CH_3)_2 CHCHO \rightarrow C_4H_6 + H_2O$	Catalyst: pumice	580–590	1	Yield of B was 0.095% by weight on feed	(118)
Action of ethanol on 3-hydroxybutanal (aldol) $CH_3CHOHCH_2CHO + C_2H_5OH \rightarrow C_4H_6 + CH_3CHO + 2H_2O$ $CH_3CHOHCH_2CHO + 2C_2H_5OH \rightarrow 2C_4H_6 + 4H_2O$ (Probable reactions are given)	Catalyst: lumps of precipitated $Al(OH)_3$	300		Yield of B was 10.8% by weight on aldol feed	(111)
Action of ethanol on 2-butenal (crotonaldehyde) $CH_3CH=CHCHO + C_2H_5OH \rightarrow C_4H_6 + CH_3CHO + H_2O$ $CH_3CH=CHCHO + 2C_2H_5OH \rightarrow 2C_4H_6 + 3H_2O$ (Probable reactions are given)				Yield of B = ?	(111)

Action of ammonia on 2-butenal (crotonaldehyde)	Catalyst: Al_2O_3	390		Yield of B = ?	(56)
Action of aniline on 2-butenal (crotonaldehyde) $2CH_3CH=CHCHO + C_6H_5NH_2 \rightarrow C_4H_6 + C_{10}H_9N + 2H_2O$	Catalysts: Al_2O_3; BeO; iron oxide; ThO_2	Above 500	1 or less	Yield of B was 15% on product	(55)

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

$$CH_3CH_2CH_2COOH + 2\overset{\cdot}{H} \rightarrow CH_3CH_2CH_2CHO + H_2O$$

$$CH_3CH_2CH_2CHO \rightarrow CH_2{=}CH{-}CH{=}CH_2 + H_2O$$

Isobutyric acid might be converted as follows:

$$(CH_3)_2CHCOOH + 4\overset{\cdot}{H} \rightarrow (CH_3)_2CHCH_2OH + H_2O$$

$$(CH_3)_2CHCH_2OH \rightarrow (CH_3)_2C{=}CH_2 + H_2O$$

$$(CH_3)_2C{=}CH_2 \rightarrow CH_3CH{=}CHCH_3 \ (trans)$$

$$CH_3CH{=}CHCH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + 2\overset{\cdot}{H}$$

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

B. ALKENOIC ACIDS

Ostromyslenskiĭ 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:

$$CH_2{=}CH{-}CO{-}O{:}H \leftrightharpoons CH_2{=}CH{-}CO{-}\overset{\cdot\cdot}{O} + H$$

$$CH_2{=}CH{-}CO{-}\overset{\cdot\cdot}{O} \rightarrow CH_2{=}CH{\cdot\cdot}CO{-}\overset{\cdot}{O} + 1 \text{ electron}$$

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 C=C group. Other points of weakness in the molecule are located two or four carbon atoms away from the positions of initial scission:

The C_2 and C_4 fragments, except 2-butene-1,4-diyl, require subsequent dehydrogenation to produce butadiene.

Calcium $\Delta^{\beta,\gamma}$-dihydromuconate 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	PRES-SURE	REMARKS (B IS 1,3-BUTADIENE)	REFER-ENCES
		°C.	atm.		
Decomposition of n-butyric acid $2CH_3CH_2CH_2COOH \rightarrow C_4H_6 + C_3H_6 + CO_2 + 2H_2O$ (Probable reaction is given)	Catalyst: pumice	590–600	1	Yield of B was 0.22% by weight on feed	(122)
Decomposition of isobutyric acid $2(CH_3)_2CHCOOH \rightarrow C_4H_6 + C_3H_6 + CO_2 + 2H_2O$ (Probable reaction is given)	Catalyst: pumice	600–620	1	Yield of B was 0.029% by weight on feed	(122)
Decomposition of isovaleric acid $(CH_3)_2CHCH_2COOH \rightarrow C_4H_6 + CO_2 + 2H_2$	Catalyst: pumice	600	1	Yield of B was 0.082% by weight on feed	(122)
Electrolysis of acrylic acid $2CH_2{=}CHCOOH \rightarrow C_4H_6 + 2CO_2 + H_2$				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)

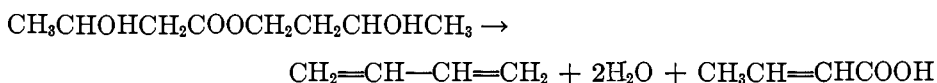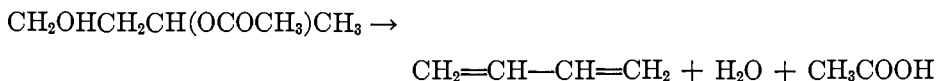|					
Thermal treatment of elaidic acid (isomer of oleic acid)	Special apparatus with vaporizer; attached porcelain tube containing a platinum wire heated to bright red heat, and fractionator	Bright red heat	*In vacuo*	Yield of B = ?	(40)
Decarboxylation of 2,4-pentadienoic acid (i.e., β-vinylacrylic acid or 1-carboxy-1,3-butadiene) $CH_2=CHCH=CHCOOH \rightarrow C_4H_6 + CO_2$	Catalyst: quinoline	Distillation temperature	1	Yield of B = ?	(136)

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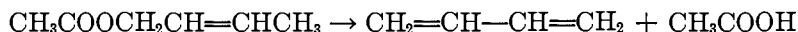
Table 13 gives data on the conversion of carboxylic acids into butadiene.

D. MONOESTERS

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

$$CH_2OHCH_2CH(OCOCH_3)CH_3 \rightarrow$$

$$CH_2{=}CH{-}CH{=}CH_2 + H_2O + CH_3COOH$$

$$CH_3CHOHCH_2COOCH_2CH_2CHOHCH_3 \rightarrow$$

$$CH_2{=}CH{-}CH{=}CH_2 + 2H_2O + CH_3CH{=}CHCOOH$$

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):

$$CH_3COOCH_2CH{=}CHCH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + CH_3COOH$$

$$CCl_3COOCH_2CH{=}CHCH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + CCl_3COOH$$

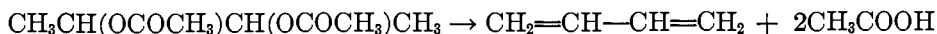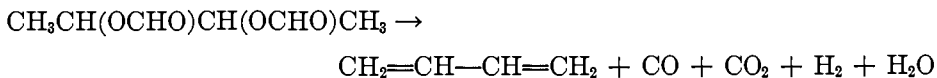Prévost, who investigated the last reaction, maintained that it was a direct breakdown on account of overheating.

E. DIESTERS

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

$$CH_3COOCH_2CH_2CH(OCOCH_3)CH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + 2CH_3COOH$$
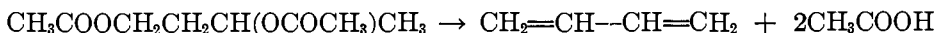
The reaction probably proceeds in two steps, possibly via both 4-acetoxy-1-butene and 1-acetoxy-2-butene. These intermediates would be favored on account of an easier removal of secondary, than primary, acetoxyl.

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

$$CH_3CH(OCHO)CH(OCHO)CH_3 \rightarrow$$

$$CH_2{=}CH{-}CH{=}CH_2 + CO + CO_2 + H_2 + H_2O$$

$$CH_3CH(OCOCH_3)CH(OCOCH_3)CH_3 \rightarrow CH_2{=}CH{-}CH{=}CH_2 + 2CH_3COOH$$

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):

$$C_4H_6(OH)_2(OCHO)_2 \rightarrow C_4H_6 + 2CO_2 + 2H_2O$$
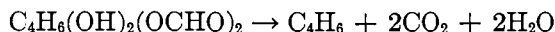
Another diester that gives butadiene is 2,3-butene bis(ethylxanthogenic acid) (174). This compound undergoes 1,2- and 3,4-eliminations without isomerization:

$$CH_3CH(-S-CS-OC_2H_5)CH(-S-CS-OC_2H_5)CH_3 \rightarrow$$

$$CH_2=CH-CH=CH_2 + 2COS + 2C_2H_5SH$$
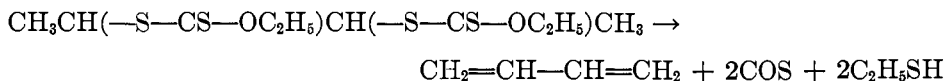
Xanthogenates undergo elimination of an unsaturated hydrocarbon (11, 12) at relatively low temperatures because of the low bond energy of C—S linkages and the practically thermoneutral character of the over-all process. The formation of carbon oxysulfide and ethanethiol, instead of ethylxanthogenic acid, 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
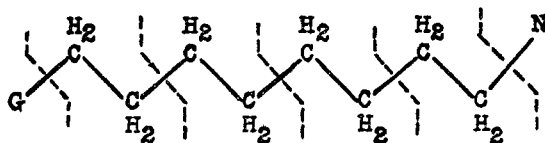
G and N represent the glyceryl and non-glyceryl ends, respectively, of a triester and its isolated group of fatty acid ethane-1,2-diyls. Thermal dehydrogenation presumably further connecting the ethanediyls at the points marked by seg-
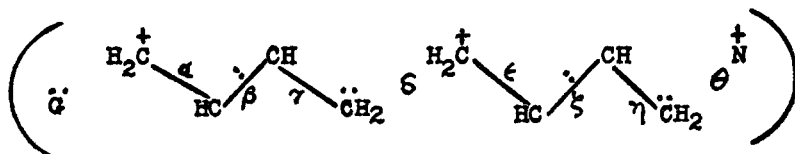
TABLE 14

Decomposition of esters

PROCESS AND ESTER DECOMPOSED	APPARATUS AND CATALYST USED	TEMPERATURE	PRESSURE	REMARKS (B IS 1,3-BUTADIENE)	REFERENCES
		°C.	atm.		
Dehydration and deësterification of 1,3-butanediol 3-acetate (1-hydroxy-3-acetoxybutane) $CH_2OHCH_2CH(OCOCH_3)CH_3 \rightarrow C_4H_6 + H_2O + CH_3COOH$	Catalyst of undisclosed composition used; see patent disclosures (138–140) for possible data	Heated	1?	Yield of B = ?	(126)
Dehydration and deësterification of 1,3-butanediol 1-β-hydroxybutyrate (1-β-oxybutyroxy-3-hydroxybutane) $CH_2CH_2CHOHCH_3$ | O | $COCH_2CHOHCH_3$ $\xrightarrow{A\%}$ $\xrightarrow{100-A\%}$ $C_4H_6 + H_2O + CH_3CHOHCH_2COOH$ $C_4H_6 + 2H_2O + CH_3CH=CHCOOH$	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)
Decomposition of 2-buten-1-yl acetate (crotyl acetate) $CH_3COOCH_2CH=CHCH_3 \rightarrow C_4H_6 + CH_3COOH$	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 trichloroacetate (crotyl trichloroacetate)	Sodium bromide was present; its value = ?	Heated, 140?	1	Yield of B = ?	(155)
Deësterification of 2,3-butanediol diformate (2,3-bisformoxybutane) $CH_2CH(OCHO)CH(OCHO)CH_3 \rightarrow C_4H_6 + CO + CO_2 + H_2 + H_2O$	Quartz tube packed with quartz chips	550	1	Yield of B = ?	(53)

		Heated	1?		
	Catalyst of undisclosed composition was used; see patent disclosures (138, 140) for possible data	Heated	1?	Yield of B = ?	(126)
Deësterification of 1,3-butanediol diacetate (1,3-bisacetoxybutane) $CH_3COOCH_2CH_2CH(OCOCH_3)CH_3 \rightarrow$ $C_4H_6 + 2CH_3COOH$	Sicromal 12 tube used	600		Yield of B was 30% by weight on fully decomposed feed	(46)
	Quartz tube	600	0.145	Yield of B was 30% by weight	(46)
		600		Yield of B was 31% by weight on fully decomposed feed	(46)
		625		Yield of B was 30.5% by weight on fully decomposed feed	(46)
	Quartz tube packed with quartz chips	550	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)
Deësterification of 2,3-butanediol diacetate (2,3-bisacetoxybutane) $CH_3CH(OCOCH_3)CH(OCOCH_3)CH_3 \rightarrow$ $C_4H_6 + 2CH_3COOH$	Glass tube packed with stainless-steel turnings	510–515?	1	Yield of B was 25.2% by weight on feed	(53)
	Catalyst: kaolin	350–575		Yield of B increased as the temperature approached 575°C.	(15)
	See reference 123 for full details	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	PRES-SURE	REMARKS (B IS 1,3-BUTADIENE)	REFER-ENCES
		°C.	atm.		
Decomposition of the neutral sulfite of 2,3-butanediol CH_3CH——$CHCH_3$ | | → $C_4H_6 + H_2O + SO_2$ O—SO—O	Catalyst: kaolin	450–575		Yield of B was slight at 450° and 8–10% at 575°	(15)
Decomposition of 1,2,3,4-butanetetrol diformates (dihydroxybisformoxybutanes) $C_4H_6(OH)_2(OCHO)_2 → C_4H_6 + 2CO_2 + 2H_2O$		210–220		Yield of B = ?	(51)
Decomposition of 2,3-butene bis (ethylxanthogenic acid) $CH_3CH(S\cdot CS\cdot OC_2H_5)CH(S\cdot CS\cdot OC_2H_5)CH_3 →$ $C_4H_6 + 2COS + 2C_2H_5SH$		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, *Adeps lanae*) and of cholesterin and its derivatives	Vaporizer and "isoprene lamp"	Bright red heat?	?	Yield of B was considerably less than 50% by weight on feed	(41)

134

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.

REFERENCES

(1) BALANDIN, A. A.: Acta Physicochim. U.R.S.S. **2**, 345-62 (1935) (in English).
(2) BALANDIN, A. A.: Acta Physicochim. U.R.S.S. **2**, 363-76 (1935) (in English); J. Phys. Chem. (U.S.S.R.) **6**, 357 (1935).
(3) BENNETT, G. M., AND HEATHCOAT, F.: J. Chem. Soc. **1929**, 268-74.
(4) BOITEAU, G.: British patent 15,806 (July 2, 1914) (void).
(5) BOUVEAULT, L., AND LOCQUIN, R.: Bull. soc. chim. [3] **35**, 643-6 (1906).
(6) BUIZOV, B. V.: Russian patent 1101 (September 15, 1925); Chem. Abstracts **22**, 4132 (1928).
(7) CAVENTOU, E.: Compt. rend. **56**, 646-8 (1863); Ann. **127**, 93-7 (1863).
(8) CHALMERS, W.: German patent 599,503 (July 11, 1935); Chem. Zentr. **1935**, II, 2281.
(9) CHARON, E.: Ann. chim. phys. [7] **17**, 217 (1899).
(10) CHARON, E.: Ann. chim. phys. [7] **17**, 234 (1899).
(11) CHUGAEV, L. A.: Ber. **32**, 3332-5 (1899); **33**, 735-6, 3118-26 (1900); **35**, 2473-83 (1902); **37**, 1481-6 (1904); J. Russ. Phys.-Chem. Soc. **31**, 959-61, 961-2 (1899); **32**, 79-80, 358-60 (1900); **35**, 1116-79 (1903); **36**, 988-1052 (1904); Russian dissertation: "Research on Terpenes and Camphor," Moscow (1903).
(12) CHUGAEV, L. A., AND FOMIN, V.: Ann. **375**, 288-97 (1910).
(13) CIAMICIAN, G., AND MAGNAGHI, P.: Ber. **19**, 569-74 (1886).
(14) CIAMICIAN, G., AND SILBER, P.: Ber. **48**, 190-5 (1915).
(15) DENIVELLE, L.: Compt. rend. **208**, 1024-5 (1939).
(16) DEUX, Y.: Compt. rend. **207**, 920-1 (1938).
(17) DEUX, Y.: Compt. rend. **208**, 1090-2 (1939).
(18) DEWEY, COL. B.: "Progress Report No. 5, March 17, 1944," United States of America, War Production Board, Office of Rubber Director, Washington, D. C.
(19) DOYARENKO, M. N.: Ber. **60**, 1536-53 (1927); J. Russ. Phys.-Chem. Soc. **58**, 16-26 (1926).
(20) DOYARENKO, M. N.: J. Russ. Phys.-Chem. Soc. **58**, 27-38 (1926).

(21) EGLOFF, G., AND HULLA, G.: Chem. Rev. **35**, 279–333 (1944).

(22) EGLOFF, G., AND HULLA, G.: Oil Gas J. **41**, No. 29, 127 (1942).

(23) EGLOFF, G., AND HULLA, G.: Oil Gas J. **41**, No. 31, 45–51 (1942).

(24) EGLOFF, G., AND HULLA, G.: Oil Gas J. **41**, No. 32, 36–8 (1942).

(25) EGLOFF, G., HULLA, G., AND KOMAREWSKY, V. I.: *Isomerization of Pure Hydrocarbons*, pp. 55–6, 244–5. American Chemical Society Monograph No. 88. Reinhold Publishing Corporation, New York (1942).

(26) FARBENFABRIKEN VORM. FRIEDR. BAYER AND Co.: British patent 4,076 (October 16, 1913).

(27) FARBENFABRIKEN VORM. FRIEDR. BAYER AND Co.: British patent 27,555 (August 17, 1911).

(28) FARBENFABRIKEN VORM. FRIEDR. BAYER AND Co.: French patent 425,967 (February 18, 1911); French patent of addition 17,873 (June 17, 1913); German patents 241,895 (March 12, 1910) and 262,884 (July 26, 1912).

(29) FARBENFABRIKEN VORM. FRIEDR. BAYER AND Co.: German patent 262,553 (July 11, 1913); Friedlaender's Fortschritte der Teerfarbenfabrikation **11**, 822 (1915).

(30) FARBENFABRIKEN VORM. FRIEDR. BAYER AND Co.: German patent 263,016 (April 14, 1913); Friedlaender's Fortschritte der Teerfarbenfabrikation **11**, 797 (1915).

(31) FARBENFABRIKEN VORM. FRIEDR. BAYER AND Co.: German patent 263,066 (April 14, 1913); Friedlaender's Fortschritte der Teerfarbenfabrikation **11**, 796 (1915).

(32) FARBENFABRIKEN VORM. FRIEDR. BAYER AND Co.: German patent 264,264 (April 28, 1913); Friedlaender's Fortschritte der Teerfarbenfabrikation **11**, 797–8 (1915).

(33) FARBENFABRIKEN VORM. FRIEDR. BAYER AND Co.: German patent 278,647 (June 11, 1914); Friedlaender's Fortschritte der Teerfarbenfabrikation **12**, 564–5 (1917).

(34) FILIPPOV, O. G.: J. Russ. Phys.-Chem. Soc. **42**, 364–5 (1910); Translation S-244, Universal Oil Products Company (J. G. Tolpin) Survey of Foreign Petroleum Literature. [This survey will be designated hereafter as U.O.P. Co. Survey Foreign Petroleum Literature.]

(35) FILIPPOV, O. G.: *Preparation of Butadiene by Contact Pyrolysis*, page 79 (1914); *cf.* reference 95.

(36) FRIEDRICHSEN, W., AND FITZKY, W. (assignors to General Aniline and Film Corporation): U. S. patent 2,218,640 (October 22, 1940).

(37) FULMER, E. I.: Contributions from Iowa Corn Research Institute **3**, No. 1, 62 pp. (1943).

(38) GAMMA, J. A., AND INOUYE, T.: Chem. & Met. Eng. **49**, No. 12, 97–100 (1942).

(39) GDANOVITCH: J. Russ. Phys.-Chem. Soc. **36**, 765 (1904).

(40) GERLACH, A., AND KOETSCHAU, R.: German patent 267,079 (July 21, 1913); Friedlaender's Fortschritte der Teerfarbenfabrikation **11**, 825–7 (1915).

(41) GERLACH, A., AND KOETSCHAU, R.: German patent 267,080 (July 21, 1913); Friedlaender's Fortschritte der Teerfarbenfabrikation **11**, 827 (1915).

(42) GILLILAND, E. R.: Sci. Monthly **58**, 5–15 (1944).

(43) GORIN, YU. A., NEIMARK, O. M., AND KOGAN, F. N.: Sintet. Kauchuk **4**, No. 5, 6–10 (1935); Translation S-199, U.O.P. Co. Survey Foreign Petroleum Literature.

(44) GRÉDY, B., AND PIAUX, L.: Bull. soc. chim. [5] **1**, 1481–9 (1934).

(45) GRÉDY, B., AND PIAUX, L.: Compt. rend. **198**, 1235–7 (1934).

(46) GUGGEMOS, H., AND TREIBS, A. (vested in the Alien Property Custodian): U. S. patent 2,345,113 (March 28, 1944).

(47) GUINOT, H. M. (assignor to Usines de Melle): U. S. patent 2,237,866 (April 8, 1941).

(48) GUTNER, R., AND TISHCHENKO, D.: J. Gen. Chem. (U.S.S.R.) **6**, 1729–36 (1936); Translation S-307A, U.O.P. Co. Survey Foreign Petroleum Literature.

(49) HAGEMANN, A.: Z. angew. Chem. **42**, 355–61 (1929).

(50) HALBIG, P., PLATZER, N., AND TREIBS, A.: U. S. patent 2,229,652 (January 28, 1941). CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE G.M.B.H.: British patent 524,849 (August 15, 1940) and French patent 850,070 (December 7, 1939).

(51) HENNINGER, A.: Ann. chim. [6] 7, 209–33, especially p. 211 (1886).

(52) HENNINGER, A.: Ber. 6, 70–1 (1873).

(53) HILL, R., ISAACS, E., AND IMPERIAL CHEMICAL INDUSTRIES LTD.: British patent 483,989 (April 28, 1938).
HILL, R., AND ISAACS, E.: U. S. patent 2,224,912 (December 17, 1940).

(54) HOFMANN, F., AND TANK, L. (assignors to Farbenfabriken vorm. Friedr. Bayer and Co.): U. S. patent 1,010,405 (November 28, 1911).

(55) HUNTENBURG, W.: German patent 661,902 (June 30, 1938); Chem. Zentr. 1938, II, 2843; Chem. Abstracts 32, 8443–4 (1938).

(56) HUNTENBURG, W.: J. prakt. Chem. [2] 145, 23–30 (1936).

(57) HUNTENBURG, W.: Über die Reaktionsprodukte aus Crotonaldehyd und Ammoniak,'' Dissertation, Hamburg, 1929.

(58) I. G. FARBENINDUSTRIE A.-G.: British patent 326,185 (February 27, 1930).

(59) I. G. FARBENINDUSTRIE A.-G.: British patent 345,270 (March 18, 1931).

(60) I. G. FARBENINDUSTRIE A.-G.: British patent 505,904 (May 17, 1939); Chem. Abstracts 33, 9328 (1939).

(61) I. G. FARBENINDUSTRIE A.-G.: British patent 506,038 (May 18, 1939); Chem. Abstracts 33, 9328 (1939).

(62) I. G. FARBENINDUSTRIE A.-G.: British patent 506,674 (June 2, 1939); Chem. Abstracts 33, 9328 (1939).

(63) I. G. FARBENINDUSTRIE A.-G.: French patent 844,893 (August 3, 1939); Chem. Abstracts 34, 7931 (1941).

(64) I. G. FARBENINDUSTRIE A.-G.: French patent 845,305 (August 18, 1939); Chem. Abstracts 35, 1068 (1941).

(65) I. G. FARBENINDUSTRIE A.-G.: German patent application I. 36212; Friedlaender's Fortschritte der Teerfarbenfabrikation 17, 140 (1932).

(66) I. G. FARBENINDUSTRIE A.-G. (R. Leopold and A. Michael, inventors): German patent 507,995 (September 23, 1930).

(67)' I. G. FARBENINDUSTRIE A.-G. (M. Mueller-Cunradi and E. Ober, inventors): German patent 522,148 (November 14, 1929); Friedlaender's Fortschritte der Teerfarbenfabrikation 16, 2979 (1931).

(68) I. G. FARBENINDUSTRIE A.-G. (F. Runge, and M. Mueller-Cunradi, inventors): German patent 578,038 (June 12, 1933).

(69) I. G. FARBENINDUSTRIE A.-G.: German patent 696,779 (August 29, 1940).

(70) I. G. FARBENINDUSTRIE A.-G.: German patent 700,036 (November 14, 1940); Chem. Abstracts 35, 6982–3 (1941).

(71) IPATIEFF, V. N.: Ber. 35, 1047–57 (1902); J. Russ. Phys.-Chem. Soc. 34, 182–95(1902).

(72) IPATIEFF, V. N.: Ber. 36, 1990–2003 (1903).

(73) IPATIEFF, V. N.: Catalytic Reactions at High Pressures and Temperatures, pp. 20–21. The Macmillan Co., New York (1936).

(74) Reference 73, pp. 119–20.

(75) IPATIEFF, V. N.: Chem.-Ztg. 26, 530 (1902).

(76) IPATIEFF, V. N.: J. prakt. Chem. [2] 67, 420–2 (1903); J. Russ. Phys.-Chem. Soc. 35, 449–52 (1903); Translation S-243, U.O.P. Co. Survey Foreign Petroleum Literature.

(77) IPATIEFF, V. N.: Private communication.

(78) ISTITUTO PER LO STUDIO DELLA GOMMA SINTETICA, MAXIMOFF, A., AND CANONICI, O.: British patent 535,678 (April 17, 1941).

(79) KANBARA, S.: J. Soc. Chem. Ind. Japan 43, Suppl. binding 262b–263b (1940); Chem. Abstracts 35, 4993 (1941).

(80) KIRNER, W. R., AND RICHTER, G. H.: J. Am. Chem. Soc. 51, 2503–6 (1929).

(81) KOMAREWSKY, V. I., AND STRINGER, J. T.: J. Am. Chem. Soc. 63, 921–2 (1941).

(82) KRAUSE, V. P., KOGAN, A. M., AND KOZLOVSKAYA, A. V.: Trudy Gosurdarst. Opyt. Zavoda Sintet. Kauchuka, Litera B, 3, 50–68 (1934); Chem. Abstracts 30, 4810–11 (1936).

(83) KRAUSE, V. P., AND SLOBODIN, YA. M.: J. Applied Chem. (U.S.S.R.) **9**, 1278–89 (1936); Translation S-188, U.O.P. Co. Survey Foreign Petroleum Literature.

(84) KYRIAKIDES, L. P.: J. Am. Chem. Soc. **36**, 980–7 (1914).

(85) KYRIAKIDES, L. P., AND EARLE, R. B.: U. S. patent 1,033,327 (July 23, 1912).

(86) LEBEDEV, S. V.: British patent 331,482 (June 30, 1930).

(87) LEBEDEV, S. V.: French patent 665,917 (December 15, 1928).

(88) LEBEDEV, S. V.: German patent 577,630 (June 3, 1933).

(89) LEBEDEV, S. V.: J. Gen. Chem. (U.S.S.R.) **3**, 698–717 (1933); Trans. Experimental Plant "B" **3**, (1933); "S. V. Lebedev, Life and Works," O.N.T.I. Khimteoret, Leningrad (1938), pp. 491–514; Translation S-183, U.O.P. Co. Survey Foreign Petroleum Literature.

(90) LEBEDEV, S. V.: Polish patent 16,966 (February 12, 1929); Chem. Zentr. **1933**, II, 3916.

(91) LEBEDEV, S. V.: Russian patent 24,393 (September 24, 1931); Chem. Abstracts **28**, 3050 (1934).

(92) LEBEDEV, S. V.: Russian patent 35,182 (March 31, 1934).

(93) LEBEDEV, S. V.: Sotzialist. Rekonstruktziya i Nauka **3**, No. 1, 127–36 (1933); Chem. Abstracts **29** 2390–1 (1935).

(94) LEBEDEV, S. V.: Teknicheskaya Entsiklopediya (Technical Encyclopedia) **20**, 815 ff. (1935); "S. V. Lebedev, Life and Works," O.N.T.I. Khimteoret, Leningrad (1938), pp. 443–61; Translation S-171, U.O.P. Co. Survey Foreign Petroleum Literature.

(95) LEBEDEV, S. V., GORIN, YU. A., KHUTORETSKAYA, S. N., CHARSKAYA, K. N., AND KOGAN, F. N.: Sintet. Kauchuk **4**, No. 1, 8–27 (1935); "S. V. Lebedev, Life and Works," O.N.T.I. Khimteoret, Leningrad (1938), pp. 602–23; Translation S-185, U.O.P. Co. Survey Foreign Petroleum Literature.

(96) LEBEDEV, S. V., KOBLYANSKIĬ, G. G., ANDREEV, N. Z., GORN, I. K., LIVSHITZ, I. A., SIBIRYAKOVA, G. N., AND SLOBODIN, YA. M.: Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka, Litera B, **3**, 41–4 (1934); Chem. Abstracts **30**, 4810 (1936).

(97) LEBEDEV, S. V., KOBLYANSKIĬ, G. G., ANDREEV, N. Z., VOLZHINSKIĬ, I. A., GORIN, YU. A., GORN, I. K., KIBIRKSHTIS, S. S., SIBIRYAKOVA, G. N., AND SLOBODIN, YA. M.: Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka, Litera B, **3**, 44–50 (1934); Chem. Abstracts **30**, 4810 (1936).

(98) LEBEDEV, S. V., AND SKAVRONSKAYA, N. A.: J. Russ. Phys.-Chem. Soc. **43**, 1124–31 (1911); Chem. Abstracts **6**, 855 (1912).

(99) LEBEDEV, S. V., VOLZHINSKIĬ, I. A., GORIN, YU. A., GULYAEVA, A. I., KOGAN, G. M., KIBIRKSHTIS, S. G., KOBLYANSKIĬ, G. G., KRAUSE, V. P., KRUPUISHEV, M. A., LIVSCHITZ, I. A., ORLOV, S. M., SLOBODIN, YA. M., SUBBOTIN, S. A., KHOKHLOVKIN, M. A., RESHETOV, A. N., AND TATARNIKOV, A. M.: Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka, Litera B, **3**, 16–40 (1934); "S. V. Lebedev, Life and Works," O.N.T.I. Khimteoret, Leningrad (1938), pp. 526–53; Translation S-191, U.O.P. Co. Survey Foreign Petroleum Literature.

(100) LEBEDEV, S. V., VOLZHINSKIĬ, I. A., KIBIRKSHTIS, S. G., KOBLYANSKIĬ, G. G., KRAUSE, V. P., KRUPYSHEV, M. A., AND SLOBODIN, YA. M.: Trudy Gosudarst. Opyt. Zavoda Sintet. Kauchuka, Litera B, **3**, 7–16 (1934); "S. V. Lebedev, Life and Works," O.N.T.I. Khimteoret, Leningrad (1938), pp. 515–25; Translation S-192, U.O.P. Co. Survey Foreign Petroleum Literature.

(101) LENNARD-JONES, J. E., AND TURKEVICH, J.: Proc. Roy. Soc. (London) **A158**, 297–305 (1937).

(102) LEYES, C. J.: British patent 329,748 (May 20, 1930).

(103) LEYES, C. J.: French patent 672,210 (December 24, 1929).

(104) LEYES, C. J.: German patent 569,343 (December 3, 1931); Friedlaender's Fortschritte der Teerfarbenfabrikation **18**, 138–40 (1933).

(105) LEYES, C. J.: U. S. patent 1,884,002 (October 25, 1932).

(106) LIEBEN, A., AND ZEISEL, S.: Monatsh. **1**, 823,840 (1880).

(107) LIKHOSHERSTOV, M. V., CHIFINA, L. F., AND KUTEPOV, E. F.: Acta Univ. Voronegiensis **8**, No. 4, 81–5 (1935); Chem. Abstracts **32**, 6616 (1938).

(108) LIVSCHITZ, I. A., AND SINAĬSKIĬ, G. M.: Sintet. Kauchuk **5**, No. 6, 17–21 (1936); Translation S-238, U.O.P. Co. Survey Foreign Petroleum Literature.

(109) MATTHEWS, F. E., STRANGE, E. H., AND BLISS, H. J. W.: British patent 3873 (March 17, 1913).

(110) MATTHEWS, F. E., STRANGE, E. H., AND BLISS, H. J. W.: British patent 12,771 (May 30, 1913).

(111) MAXIMOFF, A. T. (assignor to Naugatuck Chemical Co.): U. S. patent 1,682,919 (September 4, 1928).

(112) MERESHKOVSKIĬ, B. K.: Bull. soc. chim. [4] **37**, 1174–87 (1925).

(113) MULLIKEN, R. S.: J. Chem. Phys. 7, 121–35, 364–73 (1939); Rev. Modern Phys. **14**, 265–74 (1942).

(114) MURPHY, W. J.: Chemical Industries **50**, No. 2, Pt. 1, 172 (1942).

(115) NAGAI, N.: J. Soc. Chem. Ind. Japan **44**, Suppl. binding 64b–66b (1941).

(116) NEF, J. U.: Ann. **318**, 137–230, especially p. 201 (1901).

(117) Reference 116, especially pp. 206–7.

(118) Reference 116, especially p. 208.

(119) Reference 116, especially pp. 208–9.

(120) Reference 116, especially p. 215.

(121) Reference 116, especially p. 218.

(122) Reference 116, especially pp. 223–4.

(123) NORTHERN REGIONAL RESEARCH LABORATORY AND THE BUREAU OF AGRICULTURAL AND INDUSTRIAL CHEMISTRY, AGRICULTURAL RESEARCH ADMINISTRATION, U. S. DEPARTMENT OF AGRICULTURE: "The Development of a Process for the Manufacture of 1,3-Butadiene from 2,3-Butylene Glycol," July 15, 1943.

(124) OBOLENTSEV, R., PAZHITNOV, B., RUTKOVSKIĬ, R., AND TRIFEL, A.: Neftyanaya Prom. (Petrol. Ind. U.S.S.R.) **1941**, No. 1, pp. 93–9; Khim. Referat. Zhur. **4**, No. 9, 119 (1941); abstract translated in July 10, 1942, U.O.P. Co. Survey Foreign Petroleum Literature.

(125) OSTROMYSLENSKIĬ, I. I.: J. Russ. Phys.-Chem. Soc. **46**, 1737–8 (1914).

(126) OSTROMYSLENSKIĬ, I. I.: J. Russ. Phys.-Chem. Soc. **47**, 1472–94 (1915); Translation S-152, U.O.P. Co. Survey Foreign Petroleum Literature.

(127) OSTROMYSLENSKIĬ, I. I.: J. Russ. Phys.-Chem. Soc. **47**, 1472–94 (1915); Translation S-152, p. 7, U.O.P. Co. Survey Foreign Petroleum Literature.

(128) OSTROMYSLENSKIĬ, I. I.: J. Russ. Phys.-Chem. Soc. **47**, 1472–94 (1915); Translation S-152, p. 14, U.O.P. Co. Survey Foreign Petroleum Literature.

(129) OSTROMYSLENSKIĬ, I. I.: J. Russ. Phys.-Chem. Soc. **47**, 1494–1506 (1915); Translation S-157, U.O.P. Co. Survey Foreign Petroleum Literature.

(130) OSTROMYSLENSKIĬ, I. I.: J. Russ. Phys.-Chem. Soc. **47**, 1947–78 (1915); Chem. Abstracts **10**, 1340–1 (1916).

(131) OSTROMYSLENSKIĬ, I. I.: J. Russ. Phys.-Chem. Soc. **47**, 1978–82 (1915); Chem. Abstracts **10**, 1341 (1916); Chem. Zentr. **1916**, II, 307.

(132) OSTROMYELENSKIĬ, I. I.: J. Russ. Phys.-Chem. Soc. **47**, 1991–3 (1915); Chem. Abstracts **10**, 1342 (1916).

(133) OSTROMYSLENSKIĬ, I. I.: "Kauchuk i Ego Analogi," Moscow (1913), pp. 177–80; Translation S-245, U.O.P. Co. Survey Foreign Petroleum Literature.

(134) OSTROMYSLENSKIĬ, I. I.: "Kauchuk i Ego Analogi," Moscow (1913), pp. 195–204; cf. reference 126.

(135) OSTROMYSLENSKIĬ, I. I.: "Kauchuk i Ego Analogi," Moscow (1913); Translation S-201A, p. 44, U.O.P. Co. Survey Foreign Petroleum Literature.

(136) OSTROMYSLENSKIĬ, I. I.: "Kauchuk i Ego Analogi," Moscow (1913); Translation S-201A, p. 47, U.O.P. Co. Survey Foreign Petroleum Literature.

(137) ·Ostromsylenskiĭ, I. I.: "Kauchuk i Ego Analogi," Moscow (1913); Translation
       S-201A, p. 49, U.O.P. Co. Survey Foreign Petroleum Literature.
(138) Ostromyslenskiĭ, I. I.: Russian patent certificate 65,122 (October 16, 1914).
(139) Ostromyslenskiĭ, I. I.: Russian patent certificate 65,391 (December 3, 1914).
(140) Ostromyslenskiĭ, I. I.: Russian privilege 25,590, application of February 29, 1912.
(141) Ostromyslenskiĭ, I. I.: Zemledel'cheskaya Gazeta (Agr. Gaz. Petrograd) **1915**,
       Nos. 25–26, 701–6, 727–8; Monthly Bull. Agr. Intelligence **12**, 1701–3 (1915).
(142) Ostromyslenskiĭ, I. I., and Kelbasinskiĭ, S. S.: J. Russ. Phys.-Chem. Soc. **46**,
       123–33 (1914); Chem. Abstracts **8**, 1965 (1914).
(143) Ostromyslenskiĭ, I. I., and Kelbasinskiĭ, S. S.: J. Russ. Phys.-Chem. Soc. **47**,
       1509–29 (1915); Translation S-166, U.O.P. Co. Survey Foreign Petroleum Litera-
       ture.
(144) Ostromyslenskiĭ, I. I., and Rabinovich, P. N.: J. Russ. Phys.-Chem. Soc. **47**,
       1507–9 (1915); Translation S-158, U.O.P. Co. Survey Foreign Petroleum Literature.
(145) Pascal, P. V. H.: British patent 140,115 (March 25, 1920 (accepted)).
(146) Paternò, E., Chieffi, G., and Perret, G.: Gazz. chim. ital. **44**, I, 151–64 (1914).
(147) Pauling, L.: *The Nature of the Chemical Bond*, 2nd edition, pp. 53, 131. Cornell
       University Press, Ithaca, New York (1940).
(148) Penney, W. G.: Proc. Roy. Soc. (London) **A146**, 223–38 (1934).
(149) Perkin, W. H., and Matthews, F. E.: British patent 17,235 (July 24, 1913 (ac-
       cepted)).
(150) Petrenko, A. V.: Kauchuk i Rezina **1940**, No. 4–5, 1–5; Translation S-230, III, U.O.P.
       Co. Survey Foreign Petroleum Literature.
(151) Petrov, A. A.: Trans. Voronezh State University **10**, No. 2, 101–83 (1938); Transla-
       tion S-165, U.O.P. Co. Survey Foreign Petroleum Literature.
(152) Plauson, H., and Vielle, J. A.: British patent 156,145 (December 31, 1920).
(153) Prévost, C.: Ann. chim. [10] **10**, 113–46 (1928).
(154) Prévost, C.: Ann. chim. [10] **10**, 147–81 (1928).
(155) Prévost, C.: Ann. chim. [10] **10**, 147–81 (1928); *cf.* reference 153.
(156) Prévost, C.: Ann. chim. [10] **10**, 356–439 (1928).
(157) Prévost, C.: Compt. rend. **186**, 1209–11 (1928).
(158) Price, W. C., and Walsh, A. D.: Proc. Roy. Soc. (London) **A174**, 220–34 (1940).
(159) Rasmussen, R. S., Tunnicliff, D. D., and Brattain, R. R.: J. Chem. Phys. **11**.
       432–3 (1943).
(160) Reppe, W. (assignors to General Aniline and Film Corporation): U. S. patent 2,251,
       292 (August 5, 1941); Chem. Abstracts **35**, 6982 (1941).
(161) Reppe, W., Hecht, O., and Steinhofer, A. (assignors to General Aniline and Film
       Corporation): U. S. patent 2,251,895 (August 5, 1941).
(162) Reppe, W., Steinhofer, A., and Daumiller, G.: U. S. patent 2,310,809 (February
       9, 1943).
(163) Reppe, W., Steinhofer, A., and Hecht, O. (assignors to General Aniline and Film
       Corporation): U. S. patent 2,241,792 (May 13, 1941).
(164) Reppe, W., and Trieschmann, H. G. (assignors to General Aniline and Film Corpo-
       ration): U. S. patent 2,251,835 (August 5, 1941); Chem. Abstracts **35**, 7421 (1941).
(165) Schlechter, N., Othmer, D. F., and Brand, R.: Paper presented before the Divi-
       sion of Industrial and Engineering Chemistry, 108th Meeting of the American
       Chemical Society, New York, September 11–15, 1944.
(166) Shilov, E. A.: Sintet. Kauchuk **1**, No. 2, 5–12 (1932); Translation S-234, U.O.P.
       Co., Survey Foreign Petroleum Literature.
(167) Slobodin, Ya. M.: J. Gen. Chem. (U.S.S.R.) **5**, 1415–20 (1935); Translation S-195,
       U.O.P. Co. Survey Foreign Petroleum Literature.
(168) Smirnov, N. I.: Sintet. Kauchuk **3**, No. 1, 13–22 (1934); Translation S-236, U.O.P.
       Co. Survey Foreign Petroleum Literature.
(169) Staudinger, H., Endle, R., and Herold, J.: Ber. **46**, 2466–77 (1913).

(170) TALALAY, A., AND TALALAY, L.: Rubber Chem. Tech. **15**, 403–29 (1942).

(171) THIELE, J.: Ann. **308**, 333–43 (1899).

(172) TIFFENEAU, M., LÉVY, J., AND WEILL, P.: Bull. soc. chim. [4] **49**, 1606–17, especially pp. 1607–8 (1931).

(173) TIFFENEAU, M., AND WEILL, P.: Compt. rend. **204**, 590–92 (1937).

(174) TISCHENKO, V. S., AND KOSTERNAYA, A. F.: J. Gen. Chem. (U.S.S.R.) **7**, 1366–77 (1937).

　　 KOSTERNAYA, A. F.: Uchenye Zapiski Leningrad. Gosudarst. Univ., Ser. Khim. Nauk **3**, 126–56 (1938); Translation S-216A, U.O.P. Co. Survey Foreign Petroleum Literature.

(175) URION, E.: Ann. chim. [11] **1**, 5–87 (1934).

(176) URION, E.: Ann. chim. [11] **1**, 5–87 (1934); *cf.* URION, E.: Compt. rend. **196**, 353–4 (1933).

(177) URION, E., AND BAUM, E.: Compt. rend. **204**, 595–7 (1937).

(178) WELLMAN, V. E. (assignor to The B. F. Goodrich Co.): U. S. patent 2,174,280 (September 26, 1939).

(179) WHELAND, G. W.: J. Chem. Phys. **2**, 474–81 (1934).

(180) WHELAND, G. W.: Proc. Roy. Soc. (London) **A164**, 397–408 (1938).

(181) YOUNG, W. G., AND WINSTEIN, S.: J. Am. Chem. Soc. **57**, 2013 (1935).

(182) ZAĬTSEV, A. M.: Ann. **179**, 296–301 (1875).