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Abstract

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TWO METHODS FOR THE TECHNICAL SYNTHESIS OF METHYLPENTADIENE

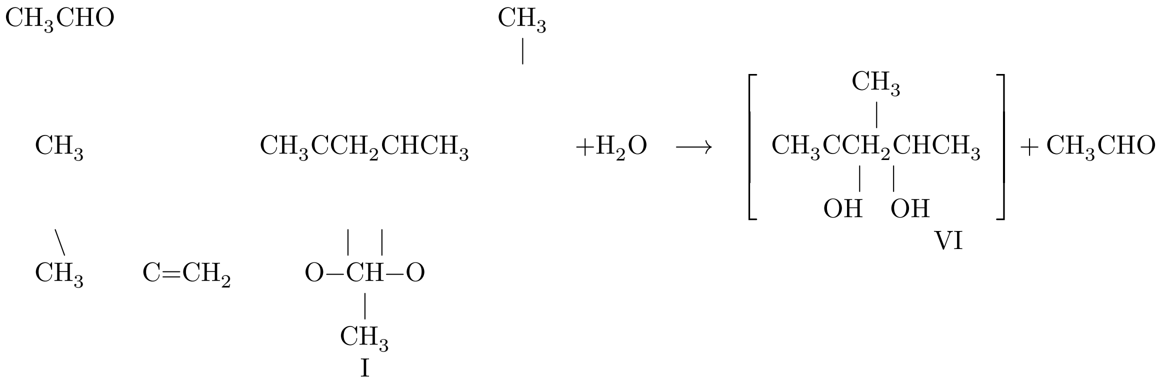
(Presented by Academician I. N. Nazarov, 15 I 1957)

Methylpentadiene has until now been a diene of little technical accessibility. The only method that may have some industrial significance is the method proposed by American authors for obtaining methylpentadiene from acetone through a series of stages ([1]). Meanwhile, methylpentadiene is of definite technical interest because of the properties of its polymers and copolymers ([2]). The present article describes two methods developed by us for the technical synthesis of methylpentadiene.

1. In our laboratory, the reactions of olefins with aldehydes have been studied in detail ([3]). When isobutylene reacts with acetaldehyde in the presence of 1-2% sulfuric acid, the main product of the reaction, obtained in a yield of 90% based on the reacted aldehyde, is 2,4,4,6-tetramethyldioxane-1,3 (TMD (I)). There are indications in the literature that alkyldioxanes-1,3 may serve as starting materials for the synthesis of dienes ([4]).

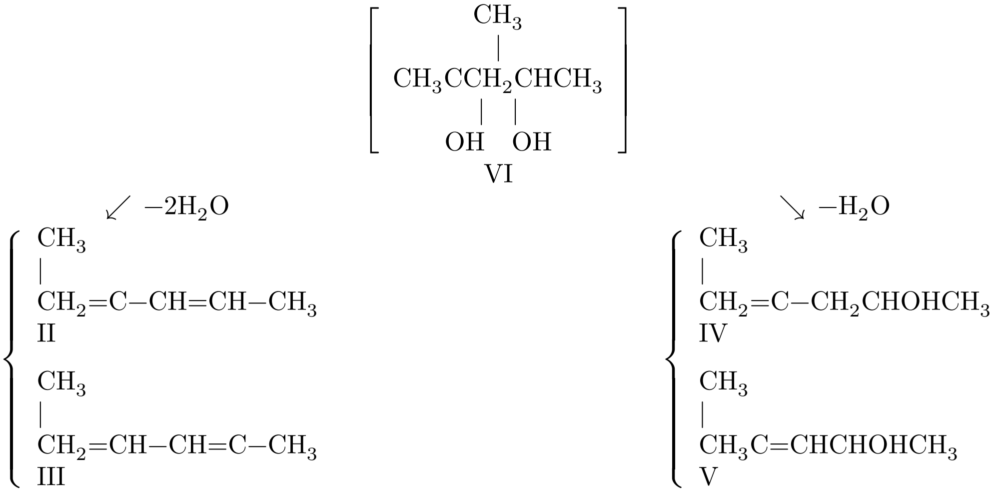
Our experiments showed that, when TMD (I) is passed in admixture with steam at a temperature of 300—325° over a catalyst, methylpentadiene is obtained in a yield of up to 75 mole % based on decomposed I. In this process two isomeric dienes are formed–2-methylpentadiene-1,3 (II) and 4-methylpentadiene-1,3 (III). The two isomers are very close in physical properties. Their quantitative determination in the mixture is based on their different behavior toward maleic anhydride: II forms an adduct, while III forms a copolymer ([5]). In the presence of inhibitors, the tendency of III to polymerize can be suppressed, and it will be separated from II. II and III were obtained in a ratio of 45 : 55.

In addition to methylpentadiene, in the contact cleavage of I there is formed, in small amount (3% based on I passed through), a mixture of two isomeric methylpentenols (IV and V). There also occurs a cracking reaction of I to the original acetaldehyde and isobutylene. The following scheme for the contact cleavage of TMD (I) into diene appears probable to us:



$$\begin{array}{llc} \mathrm{CH_3CHO} & & \mathrm{CH_3} \\ & & | \\ \mathrm{CH_3} & & \mathrm{CH_3CCH_2CHCH_3} \\ \diagdown & & |\quad | \\ \mathrm{CH_3} & \mathrm{C{=}CH_2} & \mathrm{O{-}CH{-}O} \\ & & | \\ & & \mathrm{CH_3} \\ & & \mathrm{I} \end{array} + \mathrm{H_2O} \longrightarrow \left[\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{CH_3CCH_2CHCH_3} \\ |\quad | \\ \mathrm{OH}\quad \mathrm{OH} \end{array}\right] + \mathrm{CH_3CHO}$$

VI



$$\left[\begin{array}{c} \mathrm{CH_3} \\ | \\ \mathrm{CH_3CCH_2CHCH_3} \\ |\quad | \\ \mathrm{OH}\quad \mathrm{OH} \end{array}\right]$$

VI

$$\swarrow -2\mathrm{H_2O} \qquad\qquad \searrow -\mathrm{H_2O}$$

$$\left\{\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH_2{=}C{-}CH{=}CH{-}CH_3} \\ \mathrm{II} \\ \mathrm{CH_3} \\ | \\ \mathrm{CH_2{=}CH{-}CH{=}C{-}CH_3} \\ \mathrm{III} \end{array}\right. \qquad \left\{\begin{array}{l} \mathrm{CH_3} \\ | \\ \mathrm{CH_2{=}C{-}CH_2CHOHCH_3} \\ \mathrm{IV} \\ \mathrm{CH_3} \\ | \\ \mathrm{CH_3C{=}CHCHOHCH_3} \\ \mathrm{V} \end{array}\right.$$

Water, apparently, participates in the reaction and promotes the hydrolysis of I on the surface of the catalyst to the intermediate diol (VI). At the moment of its formation, VI is dehydrated with the elimination of one or two molecules of water and with the formation, respectively, of a mixture of two isomeric methylpentenols IV, V or of the dienes II, III.

Table 1 gives the data from one of the typical balance experiments on the contact decomposition of I. Reaction conditions: temperature 325°, space velocity 2.63, dilution with steam 1 : 3. A total of 47.67 g of I was fed to the contact zone.

Table 1

	Yield in g per feed I	Yield in mol. %, based on feed I	Yield in mol. %, based on decomposed I
Methylpentadiene	18.6	68.6	74.4
Isobutylene	3.28	17.7	19.2
Butylenes and propylene	0.27	1.4	1.5
Carbon on the catalyst	0.052	0.2	0.2
"Recycle" dioxane	2.3	4.8	–
Methylpentenol	1.01	3.0	–
Resin and losses	2.16	4.3	4.7
Total . . .	**47.67**	**100.0**	**100.0**

Table 2

	Yield in g per VII consumed	Yield in mol. %, based on feed VII	Yield in mol. %, based on decomposed VII
Methylpentadiene	24.152	37.0	71.4
Isoprene	1.160	1.8	3.4
Isobutylene	2.210	3.4	6.5
Propylene	0.880	1.3	2.5
"Recycle" dimer	31.260	–	–
Higher hydrocarbons	0.930	1.4	2.7
Carbon on the catalyst	1.725	2.6	5.0
Losses	2.883	4.4	8.6
Total . . .	**65.2**	**–**	**100.0**

II. Another possible technical method for the synthesis of methylpentadiene is the dehydrogenation of propylene dimer–2-methylpentene-1 (VII). This dimer can be obtained in yields close to quantitative by dimerization of propylene according to Ziegler [6] in the presence of trialkylaluminum as catalyst.

Experiments on the catalytic dehydrogenation of VII showed that in this way methylpentadiene can be obtained (here also a mixture of isomers II and III is formed in approximately equal proportions) in a yield of 35–38% based on the feed and 70–75% based on the decomposed VII.

Fig. 1. Distillation curve of "reverse" tetramethyldioxane: 1 —boiling temperature, 2 —n_D^{20}

Figure 1: Fig. 1. Distillation curve of "reverse" tetramethyldioxane: 1 —boiling temperature, 2 —n_D^{20}

It is interesting to note that, in this process, substantial isomerization of VII occurs, with migration of the double bond within the molecule and conversion into 2-methylpentene-2 (VIII). Along with this, some side cracking reactions of VII and VIII take place, with the formation of isoprene (demethylation), propylene, isobutylene, and ethylene:

$$2\,CH_3{-}CH{=}CH_2 \xrightarrow[220^\circ]{Al(C_2H_5)_3} CH_3{-}CH_2{-}CH_2{-}C(CH_3){=}CH_2 \quad VII$$

$$\left.\begin{array}{ll} CH_3{-}CH{=}CH{-}C(CH_3){=}CH_2 & II \\ CH_2{=}CH{-}CH{=}C(CH_3){-}CH_3 & III \end{array}\right\} \xleftarrow[-H_2]{500^\circ\ cat.} CH_3{-}CH_2{-}CH_2{-}C(CH_3){=}CH_2$$

$$CH_3{-}CH_2{-}CH_2{-}C(CH_3){=}CH_2 \xrightarrow{isomerization} CH_3{-}CH_2{-}CH{=}C(CH_3){-}CH_3$$

We give a typical balance experiment for the dehydrogenation of 2-methylpentene-1 (VII) (Table 2). Experimental conditions: temperature 500°, space velocity 0.6; dilution with water vapor 1 : 1.75. Fed into the reaction—65.2 g of VII.

Experimental Part

The contact reactions were carried out in a block-type electric furnace with a quartz tube (d = 17 mm, l = 900 mm). The temperature was measured by thermocouples above and below the contact layer and was maintained within ±2°. The starting products I and VII were fed by automatic dispensers in the required ratios first into an evaporator-preheater, where the vapors were brought to the reaction temperature. The contact gas passed through a condenser, where a considerable part of it condensed; the noncondensed gas entered a gas meter. The resulting catalyzate was distilled into fractions on a semilaboratory column (33 theoretical plates). In the 50–80° fraction, the content of dienes was determined by reaction with maleic anhydride in sealed ampoules (^{7}). Analysis of the noncondensed gas was carried out on an Orsat apparatus, and the content of diene hydrocarbons in it on a Bushmarin apparatus (^{8}).

Fig. 1. Distillation curve of "reverse" tetramethyldioxane: **1** —boiling temperature, **2** —n_D^{20}

Fig. 2. Distillation curve of the condensate from dehydration of 2-methylpentan-1: 1 —boiling temperature, 2 —n_D^{20}

Figure 2: Fig. 2. Distillation curve of the condensate from dehydration of 2-methylpentan-1: 1 —boiling temperature, 2 —n_D^{20}

In carrying out balance experiments, the catalyzate was thoroughly dried and distilled on a precision column (60 theoretical plates).

2,4,4,6-Tetramethyldioxane-1,3 (I) was used with b.p. 139-141°; d_4^{20}0.9039; n_D^{20}1.4192 (^{3}); 2-methylpentene-1 (VII) with b.p. 60-62°; d_4^{20}0.6813, n_D^{20}1.3920 (^{9}). In the contact cleavage of I, a selective catalyst was used for the conversion of alkyldioxanes into dienes (developed by one of us jointly with T. I. Kishinskii). In the dehydration of VII, the standard catalyst for the dehydration of butylene to divinyl was used (zinc oxide based).

Fig. 2. Distillation curve of the condensate from dehydration of 2-methylpentan-1: **1** —boiling temperature, **2** —n_D^{20}

The space velocity was determined in milliliters of liquid product I and VII fed per 1 ml of catalyst per hour. Dilution with steam was expressed in volume ratios of the starting products (I and VII) in liquid form. A mixture of isomeric methylpentadienes with b.p. 75.5-76°, d_4^{20}0.7215, n_D^{20}1.4462, hydrogen number found 538-542, C_6H_{10} calculated 546. Literature data for the mixture of isomers: b.p. 72.5-75.5°, n_D^{20}1.4474 (^{10}).

Quantitative determination of II and III. Into a cooled ampoule containing a weighed amount of maleic anhydride in 5-7 ml of toluene was introduced a sealed ampoule containing a weighed amount of diene (0.5-0.7 g) and charged with hydroquinone, and it was broken inside. After three days' standing at room temperature, the ampoule was opened. The toluene and unreacted III were removed under vacuum to constant weight. M.p. of the adduct of II with maleic anhydride 57.8-58.2; literature data 57° (^{5}).

A mixture of the isomeric methylpentenols IV, V was found in the fraction 128-130° upon distillation of the "reverse" TMD (Fig. 1). Literature data: b.p. 130-130.5° $^{(11)}$. The content of IV and V in the fraction, determined both by acetylation and by unsaturation (bromide-bromate method), coincides, namely (respectively): 75.5 and 76.4%. An acetate was obtained with b.p. 142-143° at 742 mm, d_4^{20} 0.8852, n_D^{20} 1.4160, MR_D 40.2, calculated 40.48. Literature data for acetate IV $^{(11)}$: b.p. 150.1° at 763 mm, d_4^{20} 0.8852, n_D^{20} 1.4167.

2-Methylpentene-2 (VIII) was found upon distillation of the reverse dimer (Fig. 2); b.p. 67-67.5° at 760 mm, n_D^{20} 1.4008, d_4^{20} 0.6896. Literature data: b.p. 67.25° at 760 mm, n_D^{20} 1.4005, d_4^{20} 0.6904 $^{(9)}$.

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CITED LITERATURE

1. C. H. Staatsman, R. S. Morris, R. M. Stager, G. J. Pierotti, Chem. Engin. Progr., **43**, 148 (1947).
2. F. M. McMillan, E. F. Bishop, K. E. Marple, T. W. Evans, Ind. Rubber World, No. 2, 663 (1946).
3. M. I. Farberov, DAN, **110**, 1005 (1956).
4. E. Arundale, R. A. Mikeska, Chem. Rev., **51**, 505 (1952); Uspekhi Khimii, **23**, 223 (1954).
5. G. Bachman, G. Goebel, J. Am. Chem. Soc., **64**, 787 (1942).
6. K. Ziegler, Angew. Chem., **64**, 323 (1952).
7. I. D. Volzhinskii, V. N. L' vov, V. O. Reikhfel' d, *Guide to Practical Laboratory Work in Synthetic Rubber*, 1955, p. 66.
8. A. I. Gulyaeva et al., *Analysis of By-products from Divinyl Production from Ethyl Alcohol*, V. Lebedev, 1952, p. 262.
9. C. G. Schmitt, C. E. Boord, J. Am. Chem. Soc., **54**, 754 (1932).
10. R. Ya. Levina, A. A. Fainzil' berg, V. M. Tatevskii, E. G. Treshchova, ZhOKh, **23**, 223 (1951).
11. P. H. Williams, G. G. Ecke, S. A. Ballard, J. Am. Chem. Soc., **72**, 5738 (1950).

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