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ISOMERIZATION OF BUTADIENE DIMER

3-METHYL 1,4,6-HEPTATRIENE

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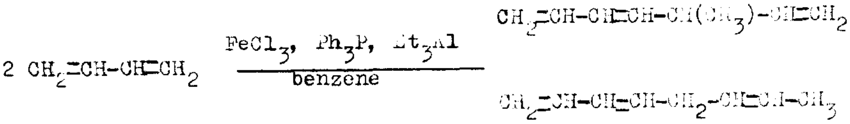
Synthesis of 3-methyl 1,4,6-heptatriene upon dimerization of butadiene has been carried out with catalysts of cobalt compounds-trialkylaluminum by several workers (1). Recently, the authors had conveniently synthesized a mixture of 3-methyl 1,4,6-heptatriene and 1,3,6-octatriene upon dimerization of butadiene with a novel catalyst of ferric chloride-triphenylphosphine-trialkylaluminum systems (2). Present communication deals with isomerization of 3-methyl 1,4,6-heptatriene with a dimethyl sulfoxide solution of potassium tert-buthoxide.

Butadiene linear dimers were prepared as follows. To a mixture of anhydrous ferric chloride and one mole of triphenylphosphine, a benzene solution of 4 moles of triethylaluminum was added and treated with butadiene in an autoclave at room temperature. Distillation of the reaction product gave a dimer fraction in 85%

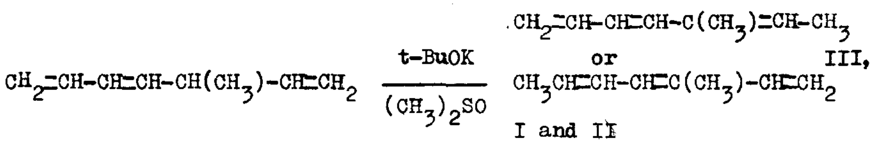
yield. The fraction consisted of a mixture of 3-methyl 1,4,6-heptatriene boiling at 115 °C (about 30%) and 1,3,6-octatriene boiling at 129 °C (about 70 %). This method gave 1,3,6-octatriene in better yield than other methods.



$$2\ CH_2{=}CH{-}CH{=}CH_2 \xrightarrow[\text{benzene}]{FeCl_3,\ Ph_3P,\ Et_3Al} \begin{array}{l} CH_2{=}CH{-}CH{=}CH{-}CH(CH_3){-}CH{=}CH_2 \\ \\ CH_2{=}CH{-}CH{=}CH{-}CH_2{-}CH{=}CH{-}CH_3 \end{array}$$

A solution of 40 g. of 3-methyl 1,4,6-heptatriene and 30 ml. of dimethyl sulfoxide was added to a solution of 2 g. of potassium tert-buthoxide in 40 ml. of tert-buthanol in nitrogen atmosphere under ice-cooling whithin 20 minutes and stirred at 60 °C for one hour. After cooling, 200 ml. of ether was added and washed with water. The ether layer was dried over anhydrous sodium sulfate and the solvent was removed, giving 12 g. of a fraction boiling at 115-125 °C. By gas chromatograph using a TCP column of 3 m., the fraction gave a peak of a small amount of 3-methyl 1,4,6-heptatriene and an asymmetrical peak at retention time ratio of 3 to 3-methyl 1,4,6-heptatriene at 120 °C and carrier gas pressure of 0.4 kg./cm^2. Polyethylene glycol column of 20 m. was used for separation and collection of the asymmetrical fraction and gave three peaks (I, II, III) as Fig. I. For an amount of the fractions polymerized in the column, yields of each fraction were very poor. The fractions had the following properties; fraction I, n_D^{25} 1.4791; fraction II, n_D^{25} 1.5340, λ_{max} 257 mμ (ε_{max} 2.0x10^5), λ_{max} 267 mμ (ε_{max} 2.4x10^5), λ_{max} 278 mμ (ε_{max} 1.5 10^5); fraction III, n_D^{25} 1.5357,

λ_{max} 256 mμ (ε_{max} 2.1×10^5), λ_{max} 267 mμ (ε_{max} 2.7×10^5), λ_{max} 275 mμ (ε_{max} 2.3×10^5).



$$CH_2{=}CH{-}CH{=}CH{-}CH(CH_3){-}CH{=}CH_2 \xrightarrow[(CH_3)_2SO]{t\text{-}BuOK} \begin{array}{l} CH_2{=}CH{-}CH{=}CH{-}C(CH_3){=}CH{-}CH_3 \\ \qquad\qquad \text{or} \qquad\qquad\qquad \text{III,} \\ CH_3CH{=}CH{-}CH{=}C(CH_3){-}CH{=}CH_2 \\ \text{I and II} \end{array}$$

Ultraviolet spectrum of the fraction (III) showed that all of three double bonds conjugated and its NMR spectrum showed three peaks of methyl groups at τ = 8.21, 8.23, 8.28 and many peaks of double bonds ($=CH-$, $=CH_2$) at τ = 3.6-5.5 ,(60 mc.). From these facts, the fraction is 3-methyl 2,4,6-heptatriene or 3-methyl 1,3,5-heptatriene. The fraction (II) gave similar infrared spectrum with that of the fraction (III) as Fig. II but more analytical data were not obtained.

1,3,6-Octatriene was treated with potassium tert-buthoxide in dimethyl sulfoxide, giving a fraction boiling at 125-135 °C, but gas chromatogram of the fraction gave only a peak of the starting material.

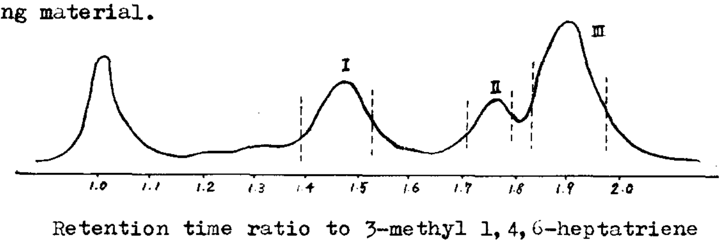


Figure I. Gas chromatogram of a fraction boiling at 115-125 °C that obtained from 3-methyl 1,4,6-heptatriene. The broken lines indicate the portions of the peaks collected. Polyethylene glycol, 170 °C.

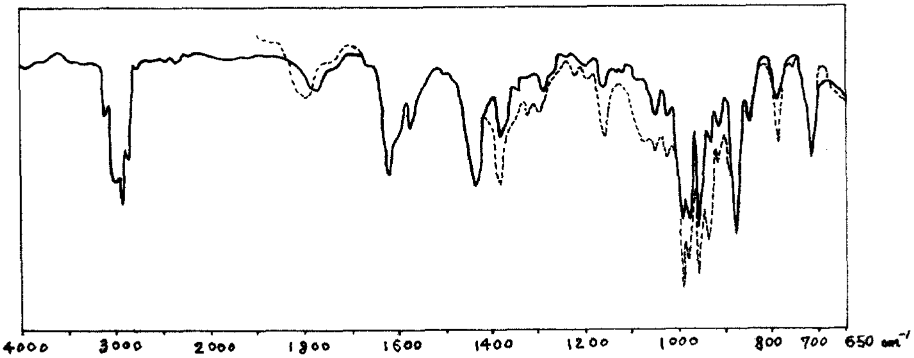


Figure II.

IR spectra of the fraction III (——) and II (----).

Analytical data of the fraction III.

Found: C, 89.05; H, 11.21. Calcd for C_8H_{12}: C, 88.82; H, 11.18.

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Reference

(1) S. Otzuka, T. Taketomi and T. Kikuchi, J. Chem. Soc. Japan (Industrial Section), 66, 1094 (1963); T. Saito, T. Ono, Y. Uchida and A. Misono, ibid., 1099 (1963); D.W. Wittenberg, Angew. Chem., 75, 1124 (1963).

(2) H. Takahasi and M. Yamaguchi, unpublished.