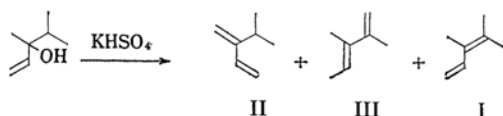


Isolation of 3,4-Dimethylpenta-1,3-diene

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(Received July 29, 1961)

In an attempt¹⁾ to prepare 3,4-dimethylpenta-1,3-diene (I) by dehydrating 3,4-dimethylpent-1-en-3-ol with potassium hydrogen sulfate, it was noticed that the major products were three isomeric dienes, i.e., 2-isopropylbutadiene (II) (53%), 2,3-dimethylpenta-1,3-diene (III) (21%) and I (18%). Although the latter two compounds had not yet been isolated in pure forms, each structure was assigned by chemical transformation of the enriched sample.



Since the separation of I and III was not sufficiently achieved by fractional distillation, gas chromatography (Carbowax 6000 on firebrick) was successfully employed for the complete fractionation of these two isomers, whose structures were confirmed on the basis of spectral evidences.

The compound (n_D^{20} 1.4625), with a shorter retention time, was a colorless liquid, and its ultraviolet absorption maximum at 232 m μ

(ϵ = 22900 in hexane) was in agreement with the calculated value of a trisubstituted butadiene²⁾. Infrared absorption bands at 1640 and 1610 cm^{-1} exhibited the presence of conjugated diene, and strong bands at 880 and 830 cm^{-1} were indicative of unsym-disubstituted and trisubstituted double bonds respectively. Therefore, this compound must be 2,3-dimethylpenta-1,3-diene (III). Independent confirmation of this was provided by the NMR spectrum³⁾ (Fig. 1), which displayed a quartet centered at δ = 5.62 p.p.m. (J = 6.10 c.p.s.) attributable to an olefinic proton having been split by an adjacent methyl group⁴⁾. Two peaks of almost equal intensity at 4.77 and 4.65 p.p.m. were assigned to the two non-equivalent protons of a terminal methylene group. Two peaks at 1.72 and 1.62 p.p.m. can be associated with two methyl groups on double bond, while a doublet (one of which was overlapping on the peak at 1.62 p.p.m.) centered at 1.57 p.p.m. was due to the methyl group having been split by the adjacent olefinic proton.

Another one (n_D^{20} 1.4729), with a longer retention time, was a colorless liquid and had a

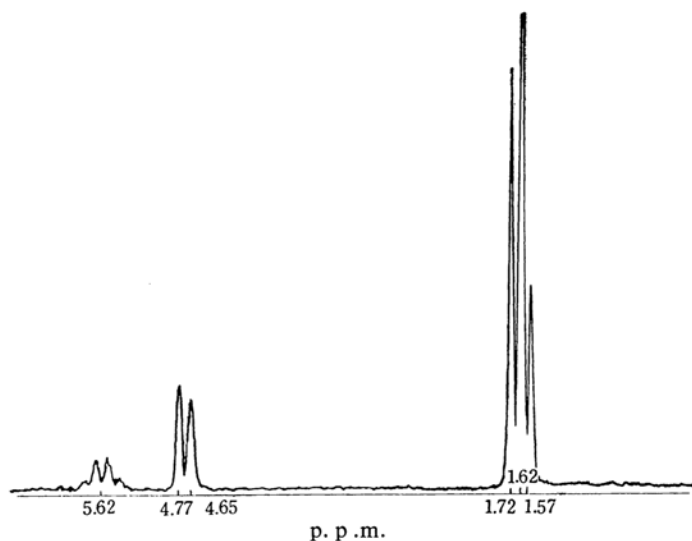


Fig. 1. NMR Spectrum of III.

- 1) A. Arai and I. Ichikizaki, This Bulletin, 35, 45 (1962).
- 2) R. B. Woodward, *J. Am. Chem. Soc.*, **64**, 72 (1942).
- 3) NMR Spectra were determined at 60 Mc. using CCl_4 as solvent and siloxane (δ = 0.10 p.p.m.) as an internal standard. The chemical shifts were recorded in δ -values (C. Djerassi, T. Nakano, A. N. James, L. H. Zalkow, E.

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4) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", Pergamon, London (1959), p. 85.

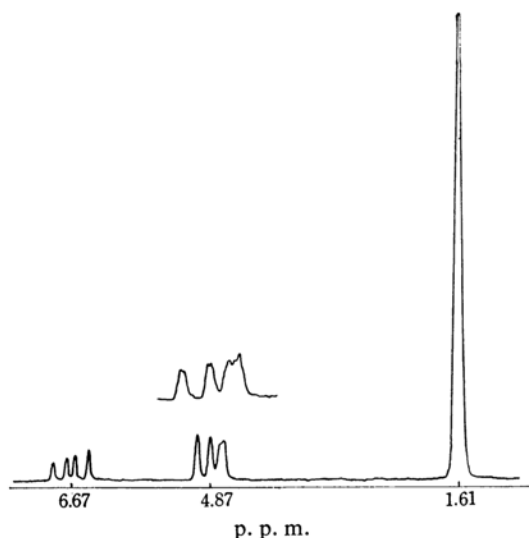


Fig. 2. NMR Spectrum of I.

tendency to polymerize rapidly on standing. Although the ultraviolet absorption spectrum exhibited a bathochromic shift of about $7\text{ m}\mu^{5)}$ (λ_{max} $239\text{ m}\mu$; $\epsilon=27700$ in hexane) from the calculated value²⁾, the infrared spectrum showed conjugated diene absorption bands at 1635 and 1605 cm^{-1} and characteristic bands of the vinyl group at 982 and 888 cm^{-1} . Therefore, these pieces of evidence strongly supported the theory that this compound was 3,4-dimethylpenta-1,3-diene (I). Finally, the NMR spectrum provided an elegant confirmation of the structure. The

spectrum (Fig. 2) showed a typical ABC pattern⁶⁾ attributable to the grouping $-\text{CH}=\text{CH}_2$ with a quartet centered at 6.67 and eight uncompletely resolved lines centered at 4.87 p.p.m. The protons of the methyl groups showed a single peak at 1.61 p.p.m.

As to the mixture of I and III, there was observed a linear relationship between the refractive index and the relative concentration, and the value (1.4729) of our purest sample I was in good agreement with that for I obtained by graphical extrapolation. Although Nazarov and Mavrov⁷⁾ have reported the value (1.4691) for the refractive index of I, graphical estimation of their value shows that their hydrocarbon undoubtedly contains a large amount of III and/or other substances. Furthermore, it is noteworthy that, contrary to some claims^{7,8)}, pure diene I did not afford a Diels-Alder adduct with crotonaldehyde even under conditions so drastic as to cause polymerization or isomerization of the diene. The details of this work will be reported elsewhere.

The authors wish to thank Drs. Yoichiro Mashiko, Kenkichi Nukada and Akio Suzuki of Government Chemical Industrial Research Institute of Tokyo for their measurement of the NMR spectra.

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5) Although it is at present unexplained, this effect can be expected by comparison with the similar bathochromic shift reported in the spectrum of 4-methylpenta-1,3-diene (λ_{max} $234\text{ m}\mu$ in hexane) (I. N. Nazarov and M. V. Mavrov, *Izvest. Akad. Nauk. S. S. S. R., Otdel. Khim. Nauk.*, 1959, 472).

6) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance", McGraw-Hill, New York (1959), p. 241.

7) I. N. Nazarov and M. V. Mavrov, *Zhur. Obshchei Khim.*, 29, 1158 (1959).

8) Y. R. Naves and P. Ardizio, *Helv. Chim. Acta*, 31, 2252 (1948).