Tetrahedron Letters No. 5, pp. 313-315, 1963. Pergamon Press Ltd.
Printed in Great Britain.

# *o*-QUINODIMETHANE AS AN INTERMEDIATE IN THE ISOMERIZATION OF *cis*-4-OCTENE-1,7-DIYNE

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(Received 27 December 1962)

WE have found that isomerization of *cis*-4-octene-1,7-diyne (I) [b.p. 49-50° (26 mm.), $n_D^{26}$ 1.4689; from *cis*-1,4-dichloro-2-butene and ethynylmagnesium bromide][1] with potassium *t*-butoxide in *t*-butyl alcohol at 60-65° for 15 minutes gives rise to two aromatic dimers, besides conjugated linear monomeric products. These dimers, isolated by chromatography on alumina, proved to be the spiro-compound IV[3,4] [25% yield; unstable colorless liquid, b.p. 155° (bath temp.) (0.2 mm.), $n_D^{25}$ 1.5989; $\lambda_{max}^{isooctane}$ 303 mμ (ε 6770); infrared spectrum apparently identical with that published[3]][5] and 1,2,5,6-dibenzocycloöctadiene (V) (2% yield; m.p.

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[1] This substance on gas-liquid chromatography was found to be contaminated with *ca.* 5% of the corresponding *trans*-isomer[2]

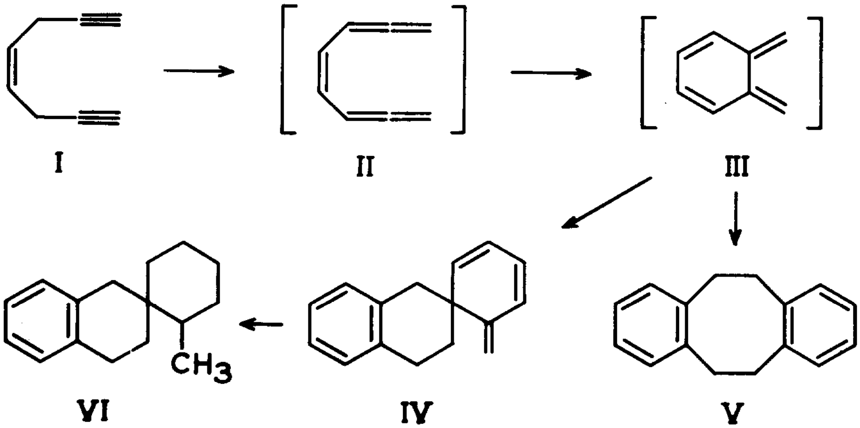
[2] F. Sondheimer and Y. Gaoni, *J. Amer. Chem. Soc.* **83**, 4863 (1961).

[3] L. A. Errede, *J. Amer. Chem. Soc.* **83**, 949 (1961).

[4] L. A. Carpino, *J. Amer. Chem. Soc.* **84**, 2196 (1962).

[5] Reported:[3] $n_D^{26}$ 1.5998; $\lambda_{max}^{isooctane}$ 304 mμ (ε 2560).

111-112°; identified with an authentic sample by mixture m.p. determination and infrared comparison).



Hydrogenation of the spiro-compound IV in dioxane over a 10% palladium-charcoal catalyst yielded the hexahydro-compound VI[3] [colorless liquid, b.p. 100° (bath temp.) (0.1 mm.), $n_D^{25}$ 1.5486], exhibiting infrared and ultraviolet spectra identical with those of an authentic sample.[3] Our specimen of VI gave a single peak on gas-liquid chromatography (5% silicone SE-30 on Chromsorb-W at 124°), but thin-layer chromatography (Kieselgel-G) gave rise to two spots; the authentic sample of VI behaved identically. The two components of VI are presumably the two possible diastereoisomers, and this assignment was supported by the fact that the individual components, separated by preparative thin-layer chromatography, showed virtually identical infrared and ultraviolet spectra. Surprisingly, hydrogenation of IV in pentane, ethyl alcohol or ethyl acetate, over the same catalyst used previously, yielded in each case only one stereoisomer of VI.

It has been shown previously that the two dimers IV and V are obtained from o-quinodimethane (o-xylylene) (III).[3] This intermediate is clearly involved in the present reaction, presumably being formed from I via the bis-allene II (or an equivalent species).[6] The formation of a relatively large amount of spiro-compound IV compared with V, as well as the fact that no benzocyclobutene or o-xylene was obtained (as shown by gas-liquid chromatography), is in accord with the previously observed behavior of o-quinodimethane at relatively low temperatures.[3]

The above-described isomerization of I represents the first example of the generation of o-quinodimethane (III) from an acyclic precursor, this intermediate having previously been formed only from benzenoid substances.[3,4,7] By contrast with the cis-compound I, the corresponding trans-isomer,[2] which does not possess the favorable configuration for the formation of o-quinodimethane, yielded only linear conjugated products[8] on isomerization under the conditions used with I.

We are indebted to Dr. L. A. Errede and to Dr. M. P. Cava for kindly providing comparison samples.

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[6] For a related rearrangement, see G. Eglinton, R. A. Raphael and R. G. Willis, Proc. Chem. Soc. 247 (1960).

[7] F. G. Mann and F. H. C. Stewart, J. Chem. Soc. 2826 (1954); M. P. Cava and A. A. Deana, J. Amer. Chem. Soc. 81, 4266 (1959); W. Baker, J. F. W. McOmie and D. R. Preston, J. Chem. Soc. 2971 (1961).

[8] Unpublished experiments of Dr. Y. Gaoni.