Catalytic Effects in the Valence Isomerizations of Hexamethyltetracyclo[2,2,0,0^{2,6},0^{3,5}]hexane

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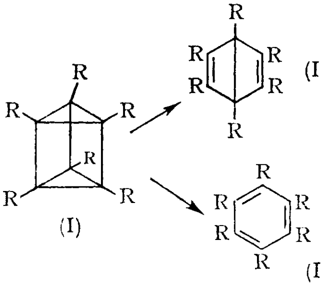
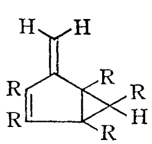
WE have found a remarkable dependency of the ratio of isomers formed, hexamethylbicyclo[2,2,0]hexa-2,5-diene (II) and hexamethylbenzene (III), on the conditions of isomerization of hexamethyltetracyclo[2,2,0,0^{2,6},0^{3,5}]hexane (I).





(IV)
R=Me

These valence isomerizations have been studied in three ways: (i) thermally, (ii) catalysed by HF–BF$_3$, and (iii) catalysed by μ-dichlorodihexamethylbicyclo[2,2,0]hexa-2,5-dienedirhodium. The ratios of isomers formed are:

Ratio of isomers formed in the decomposition of (I)

		(II) : (III)
(i)	Thermally	1 : 30
(ii)	Acid-catalysed	1 : 1
(iii)	Catalysed by transition-metal complex	1 : 0·05

(i) The thermal isomerization was studied in a 0·2 molar solution of (I) in benzene between 90—120°, and followed by integration of the n.m.r. signals. The n.m.r. tubes in which the reactions were carried out were washed thoroughly with ammonia to avoid acid-catalysed decomposition [*cf.* (ii)]. The isomerization of (I) is first-order with $\Delta H^{\ddagger}$ = 34 kcal.mole^{-1} and $\Delta S^{\ddagger}$ = 15 e.u. In contrast to our results Lemal and Lokensgard[1] recently reported for the thermal isomerization of (I) a product distribution of (II) and (III) in a 1 : 0·42 ratio.

(ii) The acid-catalysed reaction was performed in HF–BF$_3$ solution at −80° and −25°. Even at −80° the isomerization was so rapid that only the corresponding carbonium ions[2,3] of (II) and (III) could be observed immediately after the preparation of the n.m.r. samples at −80°.

(iii) The isomerization was carried out in chloroform solution with μ-dichlorodihexamethylbicyclo[2,2,0]hexa-2,5-dienedirhodium[4] as the catalyst at temperatures below 0°. With a 5% molar solution of the catalyst, the half-life of (I) proved to be about 40 minutes at −30°.

The tabulated results clearly show that by suitable choice of reaction conditions either (II) or (III) can be obtained as the predominant isomer, and under the conditions of methods (i), (ii), and (iii), no significant interconversion of (II) and (III) occurs.[3,4]

The thermal isomerization (I) → (II) is a process forbidden by the Woodward–Hoffmann rule for cyclo-addition. According to Mango and Schachtschneider, an isomerization of this type can be made an allowed process by transition-metal catalysis due to a change in symmetry conditions.[5] This is clearly illustrated by the present reaction [method (iii)]; *cf.*, also the conversion of quadricyclene into norbornadiene.[6] The acid-catalysed decomposition of (I) to yield (II) probably involves the opening of a cyclopropane ring as the first step.[3] Hence, this reaction path seems to be excluded for the formation of (III) from (I) under our experimental conditions.[3] Possibly, the first step in the acid-catalysed formation of (III) from (I) is the opening of a cyclobutane bond connecting the cyclopropane rings.

In the photochemical preparation of (I) from (II),[7] an isomer (IV) has been isolated in about 2% yield by preparative g.l.c. The structure was proved by:

(a) the molecular weight was shown to be 162 by mass spectrometry;

(b) the n.m.r. spectrum in CDCl$_3$ showed peaks at 4·71 p.p.m. (=CH$_2$ group), at 1·77 and 1·62 p.p.m. (=C–Me groups), at 1·15 and 1·07 p.p.m. (bridge-head Me groups), at 0·97 p.p.m. (distorted Me doublet with J = 6 c./sec. and at 0·07 p.p.m. (quartet-like absorption with J = 5—6 c./sec. due to the Me–CH proton);

(c) the u.v. spectrum showed an absorption at 225 mμ (ϵ 10,800 l. mole^{-1} cm.$^{-1}$), which is reasonable if the effect of the cyclopropane ring is considered;

(d) the i.r. spectrum revealed the following absorption: 3090 cm.$^{-1}$ ($=CH_2$ stretching), 1705 cm.$^{-1}$ (first overtone of the $=CH_2$ out of plane deformation), 1622 cm.$^{-1}$ (C=C stretching), and 848 cm.$^{-1}$ ($=CH_2$ out-of-plane deformation). The *endo*- or *exo*-configuration of compound (IV) has not been established.

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[1] D. M. Lemal and J. P. Lokensgard, *J. Amer. Chem. Soc.*, 1966, **88**, 5934.

[2] The corresponding carbonium ion of (II) was recently obtained by protonation of hexamethylbicyclo[2,2,0]-hexa-2,5-diene. Results of the isomerization reactions of this carbonium ion will be published shortly (H. Hogeveen and H. C. Volger).

[3] Hexamethylbenzenium ion has previously been reported by E. L. Mackor and C. Maclean, *Pure and Appl. Chem.*, 1964, **8**, 393.

[4] H. C. Volger and H. Hogeveen, *Rec. Trav. chim.*, 1967, **86**, 830.

[5] F. D. Mango and J. H. Schachtschneider, *J. Amer. Chem. Soc.*, 1967, **89**, 2484.

[6] H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, 1967, **89**, 2486.

[7] The irradiation was carried out on a 2% solution of hexamethylbicyclo[2,2,0]hexa-2,5-diene in ether by a Hanovia low-pressure mercury arc for a week (*cf.*, W. Schäfer, R. Criegee, R. Askani, and H. Grüner, *Angew. Chem.*, 1967, **79**, 54).