Thermal Isomerization of Benzo-(C_9H_{10})hydrocarbons

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Summary Thermal isomerization of 8,9-benzobicyclo-[5,2,0]nona-2,4,8-triene gave *cis*-3a,9b-dihydro-1*H*-benz-[*e*]indene *via* 2,3-benzobicyclo[6,1,0]nona-2,4,6-triene.

IN view of the present interests in the isomerization of C_9H_{10} hydrocarbons,[1] we have studied the isomerization of some benzo-(C_9H_{10})hydrocarbons.

The starting material (I)† was prepared (9·9%) by the reaction of tropylidene with benzenediazonium *o*-carboxylate. Its structure was confirmed by spectral data [mass M^+ (m/e) 168; n.m.r. τ 2·6—3·2 (m, 4H), 3·7—4·35 (m, 4H), 5·7—6·0 (m, 2H), and 7·2—8·0 (m, 2H); λ_{max} (EtOH) 247 (log ϵ 3·69), 258 (infl.) (3·57), 266 (3·47), and 272·5 (3·37)] and by hydrogenation to (II), m.p. 33—34°, which was obtained (6·2%), along with 3-phenylcycloheptene (16%), by reaction of dehydrobenzene with cycloheptene.

Thermolysis of (I) at *ca.* 150° gave two liquid compounds B and C as major products.

Spectral data (mass, n.m.r., and u.v.) for compound B showed that it has no plane of symmetry and contains a *cis*-disubstituted cyclopropane ring and four olefinic

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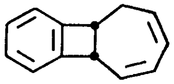
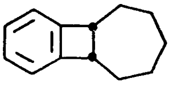
† The n.m.r. spectrum shows that this compound is similar to that isolated by Tabushi *et al.*[3] and assigned structure (VII). It was unstable and gradually formed a hexane-insoluble material when stored for a few days in a refrigerator.

protons, a pair of which are attached to an ethylenic linkage in a 7- or 8-membered ring. Structure (III) was therefore assigned to B..‡


(I)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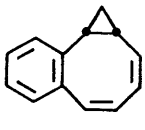
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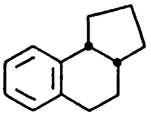
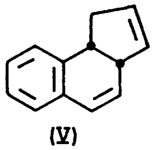
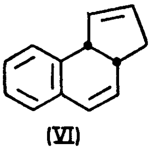
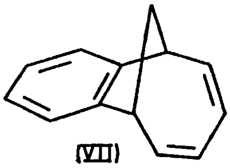

(IV)


(V)


(VI)


(VII)

Catalytic hydrogenation of compound C gave the known *cis*-benz[*e*]indene (IV).[2] Its n.m r. spectrum showed the presence of four aromatic, two allylic (or benzylic) methine, two aliphatic, and four olefinic protons, a pair of which were attached to the phenyl-conjugated olefin. Structures (V) and (VI) could both satisfy the above requirements, but the chemical shift differences between the two methine protons and between the two unconjugated olefinic protons were both too small for structure (VI)§ to be correct; C therefore had structure (V).

Thermolysis of (I) in $(CD)_{32}SO$ in an n.m.r. tube at 150°, monitored by n.m.r. spectroscopy, showed that (V) was formed from (I) in a stepwise manner *via* (III).

The formation of (III) from (I) was surprising, but could be explained as a special case of the thermally allowed [1,5]-sigmatropic shift of a σ-bond of the ring junction of (I) and it is reasonable to assume that bicyclo[6,1,0]nona-2,4,6-triene is an intermediate in the reaction of bicyclo-[5,2,0]nona-2,4,8-triene to *cis*-8,9-dihydroindene.

The reaction (III) → (V) is considered to proceed *via* non-concerted ring opening to an all-*cis* nine-membered intermediate.

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‡ Alternative structures which contain *exo*-methylene groups were eliminated by the absence of strong i.r. band near 890 cm^{-1}.

§ Recently Tanida obtained a compound, which was assigned structures (V) or (VI), by thermolysis of 6,7-benzobicyclo[3,2,2]nona-2,6,8-triene.[4] Although the u.v. spectrum of this compound was similar to that of compound C, the n.m.r. spectra of both compounds were completely different and support the assignments (V) and (VI).

[1] J. A. Berson, R. R. Boettcher, and J. J. Vollmer, *J. Amer. Chem. Soc.*, 1971, **93**, 1540; A. G. Anastassiou and R. C. Griffith, *ibid.*, p. 3083.

[2] R. Muneyuki and H. Tanida, *J. Amer. Chem. Soc.*, 1968, **90**, 656.

[3] I. Tabushi, H. Yamada, Z. Yoshida, and H. Kuroda, *Tetrahedron Letters*, 1971, 4417.

[4] T. Tsuji, H. Ishitobi, and H. Tanida, *Bull. Chem. Soc. Japan*, 1971, **44**, 2447.