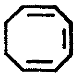
Addition of Dibromocarbene to Cyclo-octa-1,3,5-triene. Preparation of Bicyclo[6,1,0]nona-2,6-diene and Derivatives

By M. S. BAIRD and C. B. REESE*

(*University Chemical Laboratory, Lensfield Road, Cambridge* CB2 1EW)

Summary The previously undescribed hydrocarbons, bicyclo[6,1,0]nona-2,6-diene (**5**) and tricyclo[6,1,0,0^{4,9}]-nona-2,6-diene (**11**) have been prepared; the former compound (**5**) slowly isomerizes at room temperature to give bicyclo[5,2,0]nona-2,5-diene (**7**).

REACTION between cyclo-octa-1,3,5-triene[1] (**1**) and an excess of dibromocarbene gave both possible mono-adducts (**2** and **3**), and two bis-adducts. The two mono-adducts were isolated as pure oils in yields of 36 and 10·5% respectively; they were characterized on the basis of their elemental composition and of their mass, u.v., and n.m.r. spectra.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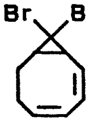

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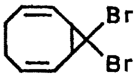

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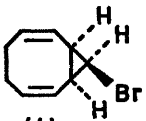
Reduction of (**3**) with Zn–AcOH[2] at 65° gave *endo*-9-bromo-bicyclo[6,1,0]nona-2,6-diene (**4**) [n.m.r. spectrum:† τ 4·2—4·9 (m, 4H), 6·82 (t, *J* 7·5 Hz, 1H), 7·1—7·6 (m, 2H), 7·8—8·5 (m, 4H)] in 59% yield. Reduction of (**3**) with Na–NH$_3$–Et$_2$O[3] at −70° and work-up at room temperature gave a high yield of a hydrocarbon mixture, the principal component (*ca.* 75%) of which was identified as the previously undescribed bicyclo[6,1,0]nona-2,6-diene (**5**). A purer sample of (**5**) was obtained by the Na–NH$_3$–Et$_2$O reduction of (**4**), under the same conditions.



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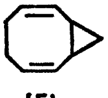
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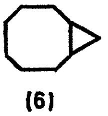
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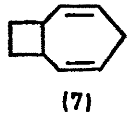
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The structure assigned to (**5**) is based on mass, i.r., and n.m.r. spectral evidence (see Figure for n.m.r. spectrum) and on its conversion, by hydrogenation in the presence of 10% Pd–C at 20°, into bicyclo[6,1,0]nonane (**6**).‡ When bicyclo[6,1,0]nona-2,6-diene (**5**) was heated at 60° for 1 hr it was converted into a product, the i.r. and n.m.r. spectra of which were identical with those reported by Roth[4] for bicyclo[5,2,0]nona-2,5-diene (**7**).

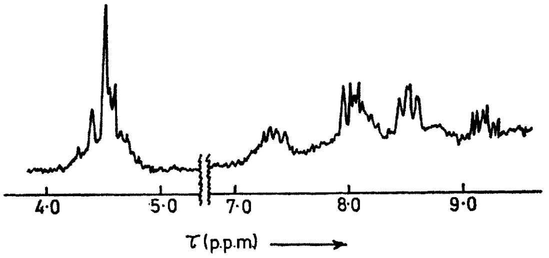
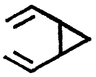


FIGURE. 100 *MHz n.m.r. spectrum of bicyclo*[6,1,0]*nona*-2,6-*diene* (**5**) *in* CCl$_4$ *solution.*

Roth[4] obtained (**7**) as one of the products of methylene addition to cyclo-octa-1,3,5-triene (**1**) at 20°, and concluded that the isomerization of (**5**) to (**7**) had occurred rapidly at room temperature. We now report that (**5**), which may be considered to be a derivative of *cis*-1,2-divinylcyclopropane (**8**), was virtually unchanged after it had stood at −15° for 3 days, and that it was found to have a half-life of *ca.* 1 day at 25°. Doering and Roth[5] showed that *cis*-1,2-divinylcyclopropane (**8**) itself was unstable with respect to its valence tautomer cyclohepta-1,4-diene at −45°, and there is no evidence[6] for the existence of norcaradiene (**9**) even below −150°. As the next higher homologue, bicyclo-[5,1,0]octa-2,5-diene (**10**) has been shown[5] to undergo a rapid degenerate Cope rearrangement at room temperature, bicyclo[6,1,0]nona-2,6-diene (**5**) appears to be the simplest known example of a stable *cis*-1,2-divinylcyclopropane system.§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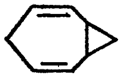
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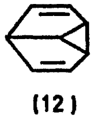
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As anticipated from the behaviour of the related 9,9-dibromobicyclo[6,1,0]non-2-ene,[8] when (**3**) was treated with an excess of methyl-lithium in ether solution at 25°, tricyclo-[6,1,0,0^{4,9}]nona-2,6-diene (**11**) was obtained. The latter

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† N.m.r. spectra of CCl$_4$ solutions were measured at 100 MHz with a Varian HA 100 spectrometer. Me$_4$Si was used as internal standard, and chemical shifts are given in p.p.m. on a τ scale.

‡ Authentic (**6**), prepared by the Na–liq. NH$_3$ reduction[3] of 9,9-dichlorobicyclo[6,1,0]nonane, and the hydrogenation product of (**5**) had identical i.r. and n.m.r. spectra, and identical g.l.c. properties.

§ *endo*-6-Vinylbicyclo[3,1,0]hex-2-ene, another derivative of *cis*-1,2-divinylcyclopropane, has also been found[7] to have moderate stability at room temperature. An example of a stable monocyclic *cis*-1,2-divinylcyclopropane derivative has recently been reported (G. Ohloff and W. Pickenhagen, *Helv. Chim. Acta*, 1962, **52**, 880,): *cis*-1-(*cis*-1-hexenyl)-2-vinylcyclopropane was found to be stable at room temperature, but was completely converted into 6-n-butylcyclohepta-1,4-diene when heated at 75° for 5 h.

compound was isolated in 89% yield and, like (**3**) and (**4**), was stable for a long period at room temperature. This contrasts with the properties of its next lower homologue semibullvalene (**12**), which is reported[9] to undergo a degenerate Cope rearrangement more rapidly than any other known system.

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