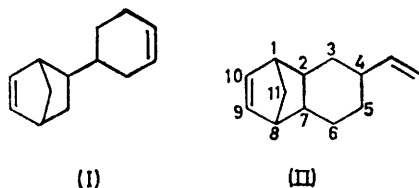


## 4-Vinyltricyclo[6,2,1,0<sup>2,7</sup>]undec-9-ene: a Minor Adduct from the Diels–Alder Reaction of 4-Vinylcyclohexene and Cyclopentadiene

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The endocyclic double bond of 4-vinylcyclohexene can act as dienophile towards cyclopentadiene at 240°. 4-Vinyltricyclo[6,2,1,0<sup>2,7</sup>]undec-9-ene (II) (*ca.* 5%) is formed together with the known 5-cyclohex-3-enylbicyclo[2,2,1]hept-2-ene (I).

5-CYCLOHEX-3-ENYLBICYCLO[2,2,1]HEPT-2-ENE (I), the main product of the reaction between cyclopentadiene and 4-vinylcyclohexene,<sup>1</sup> has been used lately as a termonomer in ethylene-propylene copolymerisations.<sup>2,3</sup> It is accepted<sup>1</sup> that the vinyl group is a more reactive dienophile than the cyclohexene double bond and Diels–Alder additions of the latter to simple dienes are uncommon. However we have found that this second mode of addition also occurs in this reaction and a small amount (*ca.* 5%) of the adduct 4-vinyltricyclo[6,2,1,0<sup>2,7</sup>]undec-9-ene (II) is always formed together with (I).



The structure of (II) was based on its u.v., i.r., and n.m.r. spectra: the n.m.r. data was consistent with the expected *endo*-configuration.

<sup>1</sup> K. Alder and H. F. Rickert, *Ber.*, 1938, **71B**, 373 (*Chem. Abs.*, 1938, **32**, 3368<sup>g</sup>); K. Alder in 'Newer Methods of Preparative Organic Chemistry,' Interscience, New York, 1948, p. 381.

<sup>2</sup> Neth. P. Appl. 6,413,080 (*Chem. Abs.*, 1965, **63**, 18423g); Fr.P. 1,410,455 (*Chem. Abs.*, 1966, **65**, 13923e); U.S.P. 3,487,055 (*Chem. Abs.*, 1970, **72**, 56486s); Ger. Offen. 2,015,855 (*Post P.*, 1971, **8**, 4364).

### EXPERIMENTAL

G.l.c. was carried out with a Varian Autoprep 705 instrument [30% SE-30 Silicone on Chromosorb W column ( $\frac{3}{8}$  in  $\times$  20 ft)]. I.r. spectra were measured for films; peaks are strong unless stated otherwise. U.v. spectra were measured for solutions in hexane, no special precautions were taken for measurement at short wavelength.<sup>4</sup> N.m.r. spectra were measured for solutions in carbon tetrachloride with a 100 MHz instrument (tetramethylsilane as internal standard).

*Reaction of Cyclopentadiene and 4-Vinylcyclohexene.*—The reaction was carried out in a 2-l autoclave under conditions essentially as published.<sup>1,3,5</sup> Cyclopentadiene dimer was used to generate cyclopentadiene<sup>6</sup> and hydroquinone was added as inhibitor. The best yields (95% by g.l.c.) of 5-cyclohex-3-enylnorborn-2-ene (I) were obtained with a 4-vinylcyclohexene to cyclopentadiene dimer ratio of 10 : 1 or 20 : 1 for 0.25–1.0 h at 230–240°. The excess of 4-vinylcyclohexene was distilled off, the adduct fraction was collected between 40–80° at 0.4 mmHg, and then separated by preparative g.l.c. In eight runs, the minor Diels–Alder adduct (II) formed to the extent of 2.9–7.8% (by g.l.c.) of

<sup>3</sup> G. Sartori, N. Cameli, M. P. Lachi, and R. Sudatti, *Chimica e Industria*, 1965, **47**, 1331.

<sup>4</sup> R. A. Micheli and T. H. Applewhite, *J. Org. Chem.*, 1952, **27**, 345; G. M. L. Cragg, C. W. Davey, D. N. Hall, G. D. Meakins, E. E. Richards, and T. L. Whateley, *J. Chem. Soc. (C)*, 1966, 1266.

<sup>5</sup> W. Mack and H. Anselm, Ger.P. 1,227,894 (*Chem. Abs.*, 1967, **66**, 28447n).

<sup>6</sup> J. E. Baldwin, *J. Org. Chem.*, 1966, **31**, 2441.

the main product (I). In addition, 2.8—7.8% of higher-boiling products were obtained. The retention times indicated that the b.p.s of these products at atmospheric pressure would be within 270—300° and the i.r. spectra were similar to that of (I). Thus, it is probable<sup>5</sup> that the higher boiling products consist of adducts of (I) [or (II)] with a second molecule of cyclopentadiene, and they were not examined further.

5-Cyclohex-3-enylbicyclo[2,2,1]hept-2-ene (I).—The i.r. spectra of the main Diels–Alder adduct (I) agreed with published values,<sup>3</sup>  $\lambda_{\max}$  206 nm ( $\log \epsilon$  3.35). In the n.m.r. spectrum, the octet at  $\tau$  4.08 due to the olefinic protons of the bicyclic ring,<sup>7</sup> and the unsymmetrical triplet of the bridgehead protons<sup>8</sup> at  $\tau$  7.22 suggest the *endo*-configuration.

4-Vinyltricyclo[6,2,1,0<sup>2,7</sup>]undec-9-ene (II).—The minor Diels–Alder adduct had  $\lambda_{\max}$  206 nm ( $\log \epsilon$  3.39),  $\nu_{\max}$  700m, 730 (*cis*-CH=CH<sup>9,10</sup>), 910, 995m (vinyl CH=CH<sub>2</sub><sup>9</sup>), 1340m (characteristic of the bicyclo[2,2,1]heptane skeleton<sup>10</sup>),

<sup>7</sup> R. V. Moen and H. S. Makowski, *Analyt. Chem.*, 1967, **39**, 1860.

<sup>8</sup> R. G. Foster and M. C. McIvor, *J. Chem. Soc. (B)*, 1969, 188.

<sup>9</sup> L. J. Bellamy, 'Infrared Spectra of Complex Molecules,' Methuen, London, 1958.

<sup>10</sup> G. Sartori, F. Ciampelli, and N. Cameli, *Chimica e Industria*, 1963, **45**, 1478.

1460m (CH<sub>2</sub>), 1575w (bicyclic C=C stretch<sup>11</sup>), 1640m (vinyl C=C stretch<sup>9</sup>), 2870, 2940 (CH, CH<sub>2</sub>), and 3090m cm<sup>-1</sup> (=C-H stretch<sup>9,10</sup>),  $\tau$  3.98 (2H, t, *J* 2 Hz, 9- and 10-H, multiplicity suggests *endo*-configuration at 2,7-ring junction<sup>7</sup>), 4.12—4.58 (1H, m, CH=CH<sub>2</sub>), 5.21 (2H, q, *J* 8 Hz, CH=CH<sub>2</sub>), 7.33br (2H, s, 1- and 8-H, chemical shift suggests *endo*-configuration at 2,7-ring junction<sup>8</sup>), 7.60br (1H, s, 4-H), 7.8—8.2 (2H, m, 2- and 7-H, chemical shift suggests *endo*-configuration<sup>12</sup>), 8.2—8.85 (6H, m, 3-, 5-, and 6-H), and 8.85—8.95 (2H, m, 11-H). It was eluted before the main adduct (I) on the g.l.c.

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<sup>11</sup> P. v. R. Schleyer and M. M. Donaldson, *J. Amer. Chem. Soc.*, 1956, **78**, 5702; P. v. R. Schleyer, *ibid.*, 1958, **80**, 1700; H. E. Simmons, *ibid.*, 1961, **83**, 1657; H. E. Simmons, E. P. Blanchard, and R. D. Smith, *ibid.*, 1964, **86**, 1347.

<sup>12</sup> P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, 1964, **86**, 1171; D. R. Arnold, D. J. Trecker, and E. B. Whipple, *ibid.*, 1965, **87**, 2596; A. P. Marchand and J. E. Rose, *ibid.*, 1968, **90**, 3724.