

Reaction of Bicyclo[6,1,0]nona-2,4,6-triene with Dimethyl Acetylenedicarboxylate

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Summary The reaction of bicyclo[6,1,0]nona-2,4,6-triene (I) and dimethyl acetylenedicarboxylate (II) is described; the Diels-Alder adduct (III) from (I) and (II) is stable under the reaction conditions and does not cleave to bicyclo[2,1,0]pent-2-ene.

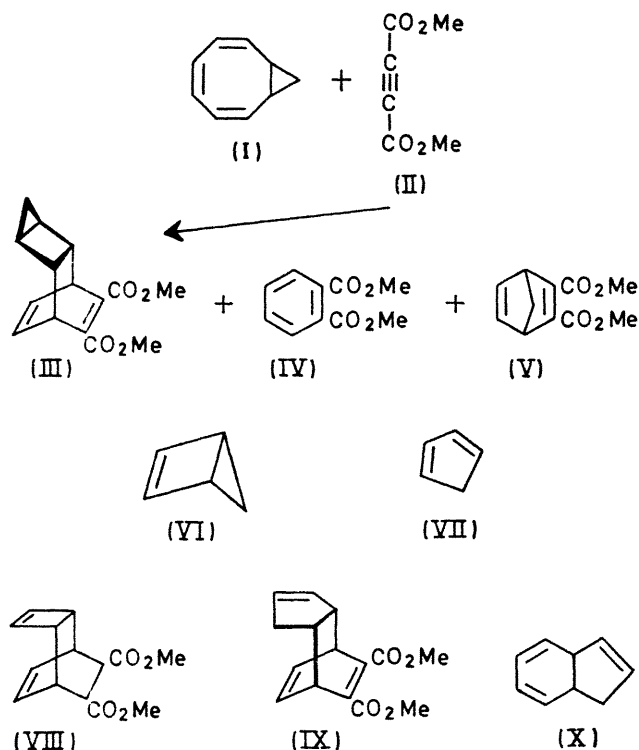
cis-BICYCLO[6,1,0]NONA-2,4,6-TRIENE (I) and dimethyl acetylenedicarboxylate (II) give the tetracyclic adduct (III) and the dimethyl esters (IV) and (V) when heated under reflux in tetrahydrofuran.¹ This could be rationalized by assuming that the adduct (III) fragments under the reaction conditions giving (IV) and bicyclo[2,1,0]pent-2-ene (VI).² The diene would then isomerize to cyclopentadiene (VII) which would give the adduct (V) with (II).³

If the initially generated olefin could be removed from the solution to a cold trap faster than it rearranged, this

reaction could serve as an alternative synthesis of bicyclopentene (VI);⁴ a conversion of various known and easily prepared 9-substituted bicyclo[6,1,0]nona-2,4,6-trienes to 5-substituted bicyclo[2,1,0]pent-2-enes would also be most useful.

We prepared the tetracycle (III) both from (I) and (II) as described and from the Diels-Alder adduct (VIII)⁵ of bicyclo[4,2,0]octa-2,4,7-triene and (II) through a Simmons-Smith reaction,⁶ thus confirming the structural and stereochemical assignment.¹ The adduct (III) was purified by chromatography (silica gel) and vacuum distillation, δ (CCl₄) 6.39 (2H, dd, *J* 3.8 and 4.0 Hz), 3.98 (2H, m), 3.66 (6H, s), 1.88 (2H, m), 1.23 (2H, m), and 0.76 p.p.m. (2H, m);¹ λ_{\max} (EtOH) 218 (log ϵ 3.8). The adduct (III) was fairly stable; neither heating as a neat liquid at 118° for 3 h nor attempted decomposition in the presence of a ten-fold excess

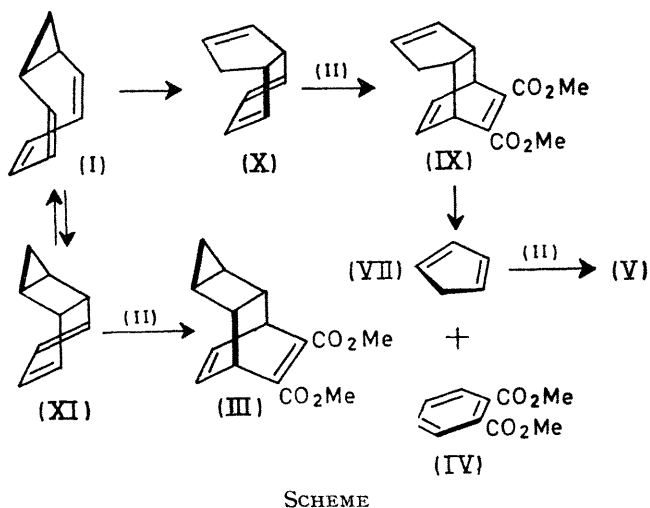
of (II) in tetrahydrofuran under reflux for 2 h gave any (IV), (V), or (VII).†



By contrast, the adduct (IX) [from the reaction of dihydroindene (X)⁸ and diester (II) at room temperature] [δ (C_6D_6) 6.05 (2H, m), 5.34 (1H, dm, J 5.9 Hz), 5.21 (1H, dm, J 5.9 Hz), 3.88 (2H, m), 3.47 (6H, s), 2.97 (1H, dm, J ca. 8 Hz), 2.48 (1H, tt, J ca. 3.5 and ca. 9 Hz), 2.08 (1H, ddm, J 17 and 9.5 Hz), and 1.52 p.p.m. (1H, dm, J 17 Hz);

λ_{\max} (EtOH) 222 nm ($\log \epsilon$ 3.8)] is comparatively labile, being converted, in the presence of (II), into phthalate (IV) and diene (V) in 1.5 h at 70° (90%).

It seems that bicyclopentene may not be involved in the reaction of (I) and (II) to give the esters (IV) and (V). A more plausible scheme is the thermal rearrangement of (I) to (X), which has been intensively investigated but whose mechanism is still unclear,^{8,9} followed by reaction with (II) as outlined in the Scheme. The sequence (I) \rightleftharpoons (XI) \rightarrow (III) is competitive and separate.¹¹



Exploratory attempts to obtain useful quantities of bicyclopentene from (III) photochemically have not been successful.

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† Gas phase pyrolysis in a flow tube at 250–330° was needed to achieve partial decomposition of (III). Competition experiments showed (III) to be somewhat less stable than (VIII) to pyrolysis.⁷ At such temperatures (VII) rather than the unstable (VI) was the low boiling product.

¹ W. H. Okamura and T. W. Osborne, *J. Amer. Chem. Soc.*, 1970, **92**, 1061. No reaction was observed using dilute solutions of (I) and (II) in tetrahydrofuran. When the solvent was reduced to 40% of the mixture, the boiling point increased 15–20% and the reaction proceeded to ca. 50% completion in 2 h to give III, IV, and V in a ratio of 5:9:9; a 60% yield of III was achieved by heating I in excess II without solvent at 90° for 10 h.

² J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Amer. Chem. Soc.*, 1966, **88**, 846; J. I. Brauman and D. M. Golden, *ibid.*, 1968, **90**, 1920; D. M. Golden and J. I. Brauman, *Trans. Faraday Soc.*, 1969, **65**, 464; J. E. Baldwin and R. K. Pinschmidt, jun., *J. Amer. Chem. Soc.*, 1970, **92**, 5247; J. E. Baldwin, R. K. Pinschmidt, jun., and A. H. Andrist, *ibid.*, 1970, **92**, 5249; S. L. Hsu, A. H. Andrist, T. D. Gierke, R. C. Benson, W. H. Flygare, and J. E. Baldwin, *ibid.*, 1970, **92**, 5250; J. E. Baldwin and A. H. Andrist, *Chem. Comm.*, 1970, 1561; S. McLean and D. M. Findlay, *Canad. J. Chem.*, 1970, **48**, 3107; J. E. Baldwin and R. K. Pinschmidt, jun., *Tetrahedron Letters*, 1971, 935.

³ O. Diels and K. Alder, *Annalen*, 1931, **490**, 236.

⁴ A. H. Andrist, J. E. Baldwin, and R. K. Pinschmidt, jun., *Org. Synth.*, submitted for publication.

⁵ W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Annalen*, 1948, **560**, 1.

⁶ E. LeGoff, *J. Org. Chem.*, 1964, **29**, 2048.

⁷ M. Avram, C. D. Nenitzescu, and E. Marica, *Chem. Ber.*, 1957, **90**, 1857.

⁸ T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, 1964, **86**, 5194; E. Vogel, *Angew. Chem.*, 1961, **73**, 548; K. Alder and F. H. Flock, *Chem. Ber.*, 1954, **87**, 1916.

⁹ See J. C. Barborak, T.-M. Su, P. v. R. Schleyer, G. Boche, and G. Schneider, *J. Amer. Chem. Soc.*, 1971, **93**, 279 and J. E. Baldwin and A. H. Andrist, *ibid.*, in the press, for leading references on this rearrangement.

¹⁰ Cf. C. S. Baxter and P. J. Garratt, *J. Amer. Chem. Soc.*, 1970, **92**, 1062.

¹¹ A derivative of the previously postulated^{1,10} intermediate (XI) has recently been reported (W. P. Lay and K. Mackenzie, *Chem. Comm.*, 1970, 398).