been obtained on very small amounts of material, and it is the sign of the rotation and not its exact magnitude that is significant.

Acknowledgment. The authors express their gratitude to Professor M. Nakajima of Kyoto University for samples of *cis*- and *trans*-1,2-dihydro-1,2-dihydroxybenzene, to Dr. K. Kirk of this laboratory for a sample of 9,10-phenanthrene oxide, and Dr. J. Holtzman, NIH, for a sample of *trans*-1,2-dihydro-1,2-dihydroxynaphthalene. In addition we thank Dr. Bernhard Witkop for his continued interest and encouragement.

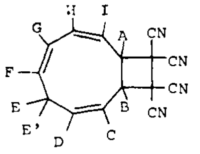
Communications to the Editor

Cycloaddition Reactions of Bicyclo[6.1.0]nona-2,4,6-triene

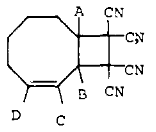
Sir:

There has been considerable interest recently in establishing the mechanism of the thermal reorganization of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) based on orbital symmetry considerations.[1] The cycloaddition reactions of **1**, however, have received little attention.[2] Since orbital symmetry is inherently related to electrocyclic, sigmatropic, and cycloaddition reactions,[3] we felt it important to obtain information regarding the mode of cycloaddition of **1** with several dienophiles.

Tetracyanoethylene (TCNE) reacts with **1** (refluxing tetrahydrofuran, 2 hr)[4] in a remarkable way to produce the adduct, tentatively assigned structure **2**. Even a cursory examination of the nmr spectrum of the adduct, mp 140.5–141.0° (56%),[4] indicates the presence of six olefinic protons and four other protons. The structure of the adduct corresponds *formally* to an adduct produced by the cycloaddition of TCNE to a cyclononatetraene.[5] The uv spectrum (in ethanol) of the adduct reveals a shoulder at 225 mμ (log ϵ 3.86) with end absorption, which suggests the presence of a conjugated diene in an eight- or nine-membered ring.[6] The infrared spectrum appears to lack *trans* double bond absorption.



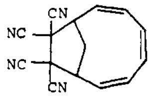
2



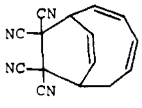
3

The nmr spectrum (60 MHz; $CDCl_3$) of **2** shows six olefinic protons at τ 3.59 (1 H, d, $J \sim 12.3$ Hz), 3.9–4.3 (4 H, m), and 4.36 (1 H, dd, $J \sim 11.1$, 2.6 Hz) and four other protons at τ 6.09 (1 H), 6.36 (1 H), and 7.3–7.6 (2 H). On the assumption that **2** is correctly assigned, the resonances at τ 6.36 and 6.09 can be assigned to H_A and H_B, respectively, and on more careful examination, they appear to constitute an AB pattern ($|J_{AB}| \sim 10.7$ Hz). The double doublet at τ 4.36 is assigned to H_C, because irradiation of H_B, but not H_A, causes its smaller coupling ($|J_{BC}| \sim 2.6$ Hz) to disappear. The irradiation of the low-field doublet (τ 3.59) assigned to H_I produces only slight sharpening of H_A, but no other changes in the high-field resonances. Conversely, irradiation of H_A produces only slight sharpening of H_I. Careful irradiation of the highest field resonances (H_E, $H_{E'}$) produces considerable sharpening, but no interpretable changes, in the region τ 3.9–4.3, which presumably contains the resonances due to H_D, H_F, H_G, and H_H. Furthermore, H_E does not appear to be coupled to H_A or H_B. The ABC pattern in the spectrum of **2** is similar to that of **3**, which was kindly communicated to us by Dr. J. J. Bloomfield.[7] The coupling constants for **3** observed by Bloomfield were $|J_{AB}| \sim 9.5$ Hz, $|J_{CD}| \sim 11$ Hz, and $|J_{BC}| \sim 4$ Hz, and the protons H_A, H_B, and H_C appeared (in dimethyl sulfoxide) at τ 6.2, 5.7, and 4.4, respectively.

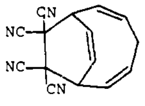
Besides **2**, other structures, **4a–d**, were also considered. The symmetrical structures **4a** and **4c** are ruled out by the lack of symmetry in the observed nmr spectrum. **4a** and **4d** appear inconsistent with the uv spectrum. **4b** and **4d** appear to be ruled out, because the observed methylene protons appeared not to be coupled (nmr) to either of the methine protons, whereas such a coupling might be expected, especially in the case of **4b**.



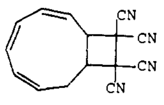
4a



4b



4c



4d

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[1] S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239 (1969), and P. Radlick and W. Fenical, *ibid.*, **91**, 1560 (1969), for leading references. We thank Professor Staley for providing us with the details of his excellent method for synthesizing **1**.

[2] Several adducts of bicyclo[6.1.0]nona-2,4,6-trienes have been reported. See (a) T. J. Katz and P. J. Garratt, *ibid.*, **86**, 5194 (1964); (b) E. A. LaLancette and R. E. Benson, *ibid.*, **87**, 1941 (1965); (c) T. S. Cantrell and H. Schechter, *ibid.*, **89**, 5868 (1967); (d) A. C. Cope, P. T. Moore, and W. R. Moore, *ibid.*, **80**, 5505 (1958); (e) D. Schoenleber, *Chem. Ber.*, **102**, 1789 (1969).

[3] (a) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395, 2511 (1965); (b) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4388, 4389, (1965); (c) H. C. Longuet-Higgins and E. W. Abrahamson, *ibid.*, **87**, 2045 (1965); (d) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); (e) R. B. Woodward, Special Publication No. 21, The Chemical Society, London, 1967, pp 217–249.

[4] We thank Professor Katz for some comparison data.[2a]

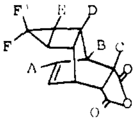
[5] The *all-cis*-cyclonona-1,3,5,7-tetraene has been prepared [P. C. Radlick and G. Alford, *J. Amer. Chem. Soc.*, **91**, 6529 (1969)]. See also, A. G. Anastassiou, *Chem. Eng. News*, **47** (39), 48 (1969); V. G. Boche, H. Böhme, and D. Martens, *Angew. Chem.*, **81**, 565 (1969); and S. Masamune, P. M. Baker, and K. Hojo, *Chem. Commun.*, 1203 (1969).

[6] Cyclonona-1,3-diene: λ_{max} 213 mμ (ϵ 2300); P. D. Gardner, private communication. Cyclonona-1,3,6-triene: λ_{max} 223 mμ (log ϵ 3.61); W. R. Roth, *Ann.*, **671**, 10 (1964). Cycloocta-1,3-diene: λ_{max} 228 mμ (log ϵ 3.75); "Organic Electronic Spectral Data," Vol. III, Wheeler and L. A. Kaplan, Ed., Interscience Publishers, New York, N. Y., 1966, p 165.

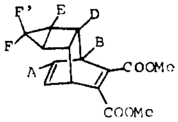
[7] The Monsanto Co., St. Louis, Mo.

Cyclonona-1,3,5-trienes (**4d**) are also exceedingly prone to undergo valence isomerization,[8] whereas **2** could be heated to its melting point and then be recovered unchanged. More definitive structural evidence for **2** is currently being sought.

A 1:1 mixture of **1** and maleic anhydride (MA) in refluxing tetrahydrofuran (THF) produces, after 36 hr, a ~3:1 mixture (~quantitative yield) of **5** (major) and **6** (minor), which were separated by fractional recrystallization from carbon tetrachloride. Adduct **6** was discovered to be identical with the known MA adduct of *cis*-8,9-dihydroindene.[9] Adduct **5**, mp 128–130°, was a new substance, assigned as the formal 2 + 4, presumably *endo*,[3] cycloaddition adduct of MA with tricyclo[4.3.0.0^{7,9}]nona-2,4-diene (**7**). The nmr spectrum (60 MHz; $CDCl_3$) of **5** exhibited resonances with equal areas at τ 3.63 (H_A, dd, $J \sim 3.3, 4.5$ Hz), 6.74 (H_B, m), 7.06 (H_C, t, $J \sim 1.7$ Hz), 8.07 (H_D, m), 8.78 (H_E, m), and 9.30 ($H_{F,F'}$, m). Double-resonance experiments appear to support the indicated assignments.[10]



5



10

A 1:1 mixture of **1** and dimethyl acetylenedicarboxylate (DMA) in refluxing THF (2 hr) produces a mixture of substances, from which dimethyl phthalate (**8**)[11] and 2,3-dicarbomethoxybicyclo[2.2.1]hepta-2,5-diene (**9**)[12] can be isolated. The nmr spectrum of the crude reaction mixture, even if the reaction is carried out to partial completion, or run at lower temperatures, clearly shows (in varying proportions) the presence of **8**, **9**, DMA, **1**, and another component, which appears to be **10**. If the reaction mixture is carefully distilled to remove most of **8**, **9**, and starting materials, the nmr spectrum (60 MHz; CCl_4) of the remaining residue, containing mainly **10**, appears strikingly similar to that of **5** with the expected differences: τ 3.64 (H_A, dd, $J \sim 3, 4$ Hz), 6.1 (H_B, m), 6.36 (CH_3, s), 8.1 (H_D, m), 8.8 (H_E, m), and 9.3 ($H_{F,F'}$, m) in ratio 1:1:3:1:1:1.

The reverse Diels–Alder reaction of **10** could conceivably account for the production of **8** and bicyclo[2.1.0]pent-2-ene.[13] The latter, or its isomerization product (cyclopentadiene), can react with DMA to produce **9**. It is also possible to rationalize the formation of **8** and **9**, if **10** reacts with another DMA molecule across the C_E–C_E bond in **10**,[14] to give a bis adduct, which produces **8** and **9** directly on undergoing a reverse Diels–Alder reaction. The reaction of **1** with benzoquinone, ethyl azidoformate, or dimethyl azodicarboxylate lead to mixtures, from which pure products have not yet been obtained.[15]

The mode of cycloaddition of DMA or MA with **1** is readily understandable on the basis of the now well known[16] cycloocta-1,3,5-triene ⇄ bicyclo[4.2.0]octa-2,4-diene equilibrium. The addition of TCNE to **1**, however, appears novel. Compound **1** has been referred to as a "homo" derivative of cyclooctatetraene (COT).[17] It is possible that the TCNE addition is related to the 2 + 2 (or 2 + 8) cycloaddition reaction reported for COT.[18] It could also be related to the nonstereospecific 2 + 2 cycloaddition reaction of bicyclo[4.2.0]oct-7-ene or *cis,trans*-cycloocta-1,3-diene.[19] Thus, *cis,cis,trans,cis*-cyclonona-1,3,5,7-triene could be an intermediate.[1,5]

The mechanistic features of these cycloadditions require further studies.[20,21]

Acknowledgment. It is a pleasure to acknowledge financial support from the Petroleum Research Fund (Grant No. 3369-Al), administered by the American Chemical Society, the Research Corporation (Frederick G. Cottrell Grant), and the Intramural Fund of the University of California at Riverside. The author is also grateful to Professor Phillip Radlick for stimulating discussions and to Badische-Anilin und Sodafabrik, A. G., for a most generous gift of cyclooctatetraene.

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(8) D. S. Glass, J. W. H. Watthey, and S. Winstein, *Tetrahedron Lett.*, 377 (1965); E. Vogel, W. Grimme, and E. Dinne, *ibid.*, 391 (1965).

(9) K. Alder and F. H. Flock, *Chem. Ber.*, 87, 1916 (1954).

(10) The ABC pattern of **5** is similar to other MA adducts of cyclohexa-1,3-diene derivatives (R. Klem and P. Radlick, private communication). The DEF pattern of **5** was compared to that of 2,3-*exo,exo*-dideuterobicyclopentane (Professor P. G. Gassman, private communication), but the latter appears to be a poor model even though some similarities were apparent. The cyclopropane ring of **5** is presumed to be *exo*.[2d]

(11) Sadtler Standard Spectra.

(12) O. Diels and K. Adler, *Ann.*, **490**, 236 (1931).

(13) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Amer. Chem. Soc.*, **88**, 847 (1966).

(14) (a) P. G. Gassman and G. D. Richmond, *ibid.*, **90**, 5637 (1968); (b) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *ibid.*, **90**, 4746 (1968); (c) P. G. Gassman and K. T. Mansfield, *ibid.*, 90, 1517, 1524 (1968).

(15) The crude reaction mixture from the benzoquinone experiment exhibited a nmr spectrum, which appeared similar to that of **5**.

(16) A. C. Cope, A. C. Haven, F. L. Ramp, and R. E. Trumbull, *ibid.*, **74**, 4867 (1952). For a recent discussion and leading references, see R. Huisgen, G. Boche, A. Dahmen, and W. Hechtl, *Tetrahedron Lett.*, 5215 (1968).

(17) (a) R. Rieke, M. Ogliaruso, R. McClung, and S. Winstein, *J. Amer. Chem. Soc.*, **88**, 4729 (1966); (b) M. Ogliaruso and S. Winstein, *ibid.*, **89**, 5290 (1967); (c) M. Ogliaruso, R. Rieke, and S. Winstein, *ibid.*, **88**, 4731 (1966).

(18) G. Schröder and Th. Martini, *Angew. Chem. Intern. Ed. Engl.*, **6**, 806 (1967).

(19) (a) P. G. Gassman, H. P. Benecke, and T. J. Murphy, *Tetrahedron Lett.*, 1649 (1969); (b) Dr. J. J. Bloomfield[15] has communicated similar results[19a] to us.

(20) C. S. Baxter and P. J. Garratt have obtained results similar to ours. See C. S. Baxter and P. J. Garratt, *J. Amer. Chem. Soc.*, **92**, 1062 (1970).

(21) Correspondence should be directed to W. H. O.

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Reaction of Dienophiles with *cis*-Bicyclo[6.1.0]nonatriene

Sir:

Intricate interconversions have been observed to occur within the $(CH)_6CH_2$,[1] $(CH)_8$,[2] and $(CH)_{10}$[3] groups of hydrocarbons. Similar valence tautomerisms might be expected for the $(CH)_8CH_2$ hydrocarbons, and considerable interest has recently been shown in the mechanism of the electrocyclic rearrangement of *cis*-bicyclo[6.1.0]nonatriene (**1**).[4,5] This compound is known to

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(1) S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 696.

(2) M. Jones and L. O. Schwab, *J. Amer. Chem. Soc.*, **90**, 6549 (1968), and references therein; E. Vogel, H. Kiefer, and W. Roth, *Angew. Chem.*, **76**, 432 (1964), and references therein.

(3) S. Masamune, R. T. Seidner, H. Zenda, M. Wiesel, N. Nakatsuka, and G. Bigam, *J. Amer. Chem. Soc.*, **90**, 5286 (1968), and references therein.