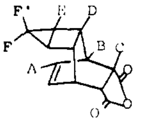
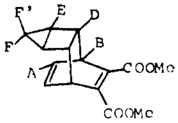
Cyclonona-1,3,5-trienes (**4d**) are also exceedingly prone to undergo valence isomerization,[8] whereas **2** could be heated to its melting point and then be recovered unchanged. More definitive structural evidence for **2** is currently being sought.

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]

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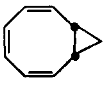
[1] S. J. Rhoads in "Molecular Rearrangements," P. de Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 696.

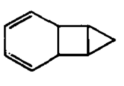
[2] M. Jones and L. O. Schwab, *J. Amer. Chem. Soc.*, 90, 6549 (1968), and references therein; E. Vogel, H. Kiefer, and W. Roth, *Angew. Chem.*, **76**, 432 (1964), and references therein.

[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.

rearrange thermally to *cis*-8,9-dihydroindene,[6] while its molybdenum tricarbonyl complex thermally rearranges to the corresponding complex of bicyclo[4.2.1]nonatriene.[7] However, no observation of the rearrangement of **1** to the tricyclo[4.3.0.0^{7,9}]nona-2,4-diene (**2**) or cyclononatetraene (**3**) tautomers has so far been recorded.[8] We now wish to report that under the appropriate conditions **1** reacts with dienophiles to give derivatives of both **2** and **3**.[9]



1



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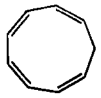
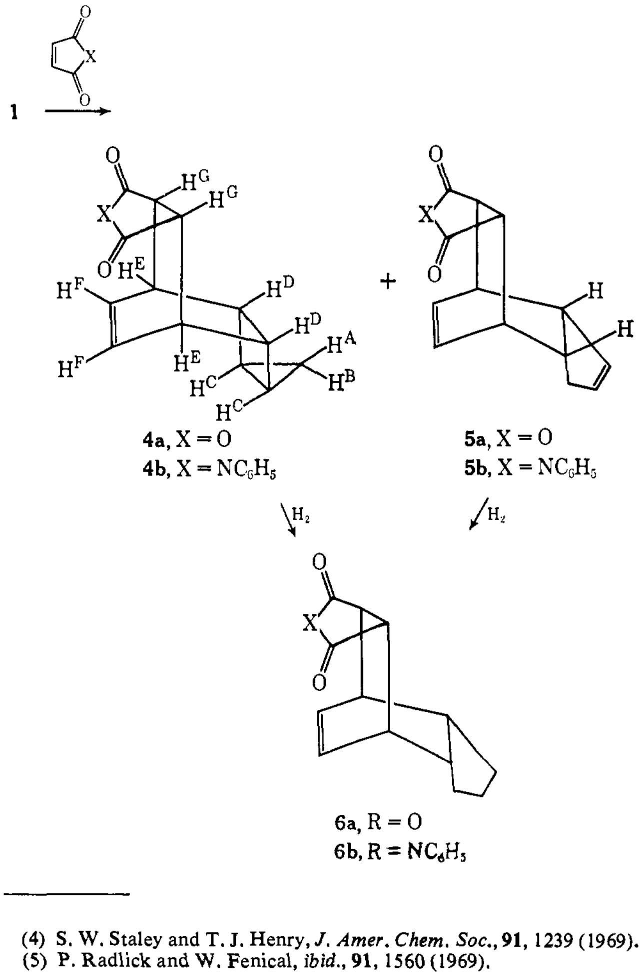


3

An equimolar mixture of **1** and maleic anhydride in benzene was heated under reflux for 3 hr, when a 7:3 mixture (92% yield) of two adducts was obtained. Fractional crystallization (EtOAc, petroleum ether) gave the pure major adduct **4a** (25%, mp 149.5–150°). The mass spectrum (*m/e* 216) and microanalysis[10] demonstrated that **4a** was a 1 : 1 adduct, and the assigned structure is based on the physical and chemical properties. The nmr spectrum (100 MHz, $CDCl_3$) shows resonance signals at τ 3.71 (dd, 2 H, H_F), 6.8 (m, 2 H, H_E), 7.05 (m, 2 H, H_G), 8.10 (m, 2 H, H_D), 8.79 (m, 2 H, H_C), and 9.30 (m, 2 H, H_A, H_B), and the uv spectrum shows no absorption above 230 nm. The nmr spectral assignments were confirmed by double irradiation experiments.



4a, X = O
4b, X = NC_6H_5

5a, X = O
5b, X = NC_6H_5

6a, R = O
6b, R = NC_6H_5

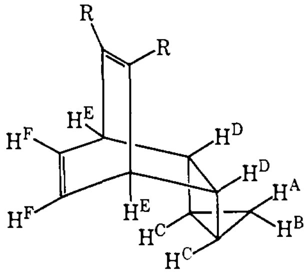
Hydrogenation (PtO_2, EtOAc) of **4a** gave, after the absorption of 1 mol equiv of hydrogen, the known adduct **6a** (83%),[11] identical with an authentic sample.[12]

The corresponding dideuterio adduct was obtained by reacting 9,9-dideuterio-*cis*-bicyclo[6.1.0]nonatriene with maleic anhydride. The absence of the high-field band at τ 9.30 in the nmr spectrum of dideuterio-**4a** further confirmed the assignment of this band to the H_A, H_B protons, and the H_C protons now appeared as a broad singlet.

The assignment of the stereochemistry of **4a** is based on the known stereochemistry of the adduct **6a**, and the coincidental chemical shift of the H_A, H_B cyclopropyl protons. This coincidence might be expected for the isomer in which the cyclopropyl ring is *anti* to the fusion of the four- and six-membered rings,[13] but would be unlikely for the alternative *syn*-fused compound, models of which have one of the cyclopropyl methylene hydrogens close to the double bond.

The minor isomer obtained in these reactions was not purified, but was assigned the structure **5a** on the basis of the comparison of the nmr spectrum of the mixture of isomers with the nmr spectrum of an authentic sample of **5a**.[11]

Reaction of **1** with N-phenylmaleimide gave a similar mixture of adducts from which pure **4b** could be isolated (mp 186–187°). The spectral data support the structure **4b**, showing only the expected differences from the spectra of **4a**. The reaction of **1** with a variety of disubstituted acetylenes gave more complex mixtures of products, but the adducts **7a** and **7b**, prepared from dicyanoacetylene and hexafluorodimethylacetylene, were isolated, and the nmr spectra were found to be similar to those of **4** [**7a**, $CDCl_3$, τ 3.67 (m, 2 H, H_F), 6.12 (m, 2 H, H_E), 8.40 (m, 2 H, H_D), 8.70 (m, 2 H, H_C), 9.14 (m, 2 H, H_A, H_B); **7b**, CCl_4, τ 3.57 (m, 2 H, H_F), 5.96 (m,



7a, R = CN
7b, R = CF_3

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(4) S. W. Staley and T. J. Henry, *J. Amer. Chem. Soc.*, **91**, 1239 (1969).

(5) P. Radlick and W. Fenical, *ibid.*, **91**, 1560 (1969).

(6) E. Vogel, *Angew. Chem.*, **73**, 548 (1961).

(7) W. Grimme, *Chem. Ber.*, **100**, 113 (1967).

(8) A derivative of **2** has been prepared by reaction of 9-acetoxy-9-methylbicyclo[6.1.0]nonatriene with N-phenylmaleimide: T. S. Cantrell and H. Shechter, *J. Amer. Chem. Soc.*, **89**, 5868 (1967). Little evidence was given for this structure.

(9) W. H. Okamura and T. W. Osborn, *ibid.*, **92**, 1061 (1970), have made similar observations. We thank Professor Okamura for informing us of his results, and for suggesting simultaneous publication.

(10) Satisfactory analytical results were obtained for all new compounds.

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

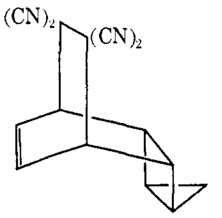
(12) The ease of hydrogenolysis of this type of strained cyclopropane is well known. See R. B. Turner in "Theoretical Organic Chemistry, IUPAC Kekule Symposium," Butterworths, London, 1959, p 67.

(13) The nmr spectrum of bicyclo[2.1.0]pentane shows the methylene cyclopropyl hydrogens as a multiplet centered at τ 9.4 [*cf.* J. P. Chesick, *J. Amer. Chem. Soc.*, **84**, 3250 (1962); J. Meinwald and G. Warren Smith, *ibid.*, **89**, 4923 (1967); P. G. Gassman and K. T. Mansfield, *J. Org. Chem.*, **32**, 915 (1967)]. Substitution at the bridgehead position in some cases causes a separation of these signals [R. Srinivasan and K. H. Carlough, *J. Amer. Chem. Soc.*, **89**, 4932 (1967), and references above], whereas substitution at the 2,3 positions generally does not (see references above).

2 H, H_E), 8.14 (m, 2 H, H_D), 8.78 (m, 2 H, H_C), 9.20 (m, 2 H, H_A, H_B)].

When **1** reacts with tetracyanoethylene (TCNE) the nature of the adduct depends on the experimental conditions. Addition of a solution of TCNE in toluene to an equimolar solution of **1**, followed by subsequent heating at reflux, gave a 1:1 adduct (70%, mp 262–263° dec), assigned the structure of **8** from its physical properties. Addition of **1** in THF to an excess of TCNE in THF, followed by heating to reflux for 48 hr, gave, after purification, the adduct **9** (75%, mp 141–141.5°), identical with that previously reported.[14] The mass spectrum (*m/e* 246) confirmed that **9** was a 1:1 adduct, and the fragmentation pattern differed from those found for the adducts **4** and **8**. These latter adducts had the base peak at *m/e* 66, ($C_5H_6^+$) whereas the base peak in the mass spectrum of **9** is at *m/e* 117 ($C_9H_9^+$). The nmr spectrum (100 MHz, acetone-d_6) shows resonance signals at τ 3.63 (dd, 1 H), 3.9–4.4 (m, 5 H), 5.61 (m, 1 H, H_A or H_B), 6.27 (m, 1 H, H_A or H_B), and 7.30 (dd, 2 H, H_C), indicating that **9** is bicyclic. Irradiation at the frequency of the τ 5.61 signal removes the major coupling (J = 10 Hz) of the τ 6.27 signal (and *vice versa*). Irradiation at the frequency of the signal at *ca.* τ 4.0 causes the high-field double doublet at τ 7.30 to collapse to a broad singlet. The olefinic region is significantly further resolved at 220 MHz, the band at τ 3.9–4.4 now appearing as two multiplets at τ 3.88–4.11 (3 H) and τ 4.16–4.34 (2 H), and the observation was made that the spectrum is temperature dependent.[15] The nmr spectrum of the corresponding adduct from 9,9-dideuteriobicyclo[6.1.0]nonatriene shows the absence of the τ 7.30 signals, and a modified olefinic region.

The structure **9** is in accord with the nmr spectral evidence, although the large chemical shift difference of the bridgehead protons was unexpected.[16] The uv spectrum of **9** shows only end absorption and a shoulder at 230 nm,[14] and is also consistent with the diene structure. The temperature dependence of the spectrum reflects the conformational mobility of the nine-membered ring. Attempted catalytic hydrogenation of **9** (Pt_2O, HOAc) led to the slow uptake of more than the theoretical amount of hydrogen, and gave a complex mixture of products.[17] The compound **9** appears to be thermally stable but is extremely labile to photoirradiation.[18]



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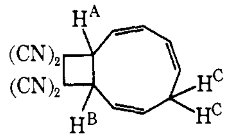

9

The main pathway for dienophile addition to *cis*-bicyclo[6.1.0]nonatriene is *via* the tricyclic tautomer **2**, the preference of the dienophile for the more reactive diene overcoming the strain energy engendered by formation of the cyclopropane ring.[19] The formation of **9** appears likely to arise from the nonconcerted reaction of TCNE with **1**,[21] but further experimental data, including a knowledge of the stereochemistry of the ring junction of **9**, are required for a mechanism to be established. Attempts to prepare **9** from *cis*-cyclononatetraene[22] have so far been unsuccessful.

Acknowledgment. We thank the Badische-Anilin und Sodafabrik, A.G., for a generous gift of cyclooctatetraene, and the Science Research Council for a studentship (C. S. B.). We thank Dr. J. E. Anderson for valuable discussions.

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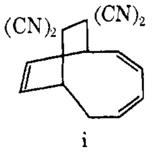
[14] T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.*, **86**, 5194 (1964).

[15] We thank Mr. M. C. McIvor, Imperial Chemical Industries, Ltd., for the 220-MHz spectrum and for the observation that the spectrum is temperature dependent.

[16] A number of alternative bicyclic structures can be considered, and for some time we favored the structure i. However the large coupling constant between the bridgehead protons, together with the temperature dependence of the spectrum, appears to rule out this formulation.



i

[17] Hydrogenation under milder conditions with a variety of catalysts resulted in no hydrogen uptake.

[18] Further chemical support for structure **9** is being sought and the chemistry of the photoproduct is under investigation.

[19] The behavior of **1** resembled that of cycloheptatriene[1] and cyclooctatetraene epoxide.[20]

[20] A. C. Cope, P. T. Moore, and W. R. Moore, *J. Amer. Chem. Soc.*, **80**, 5505 (1958).

[21] For an example of a 1,2-dienophile addition, see P. G. Gassman, H. P. Benecke, and T. J. Murphy, *Tetrahedron Lett.*, 1649 (1969).

[22] E. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.*, **87**, 1941 (1965); V. G. Boche, H. Böhme, and D. Martens, *Angew. Chem. Intern. Ed. Engl.*, **8**, 594 (1969).

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Received October 18, 1969

Carbonium Ion Intermediates and Neighboring Group Participation in the Decomposition of Azo Compounds

Sir:

Although diradical,[1,2] dipolar ion,[3] reverse Diels–Alder,[4] and concerted[5–7] mechanistic pathways have been reported for thermal decomposition of cyclic azo compounds, there never has been a report of a mechanism which involves carbonium ion intermediates. We wish to report that the acetolyses of azo *p*-bromobenzenesulfonates Ia-OBs and IIa-OBs provide the first examples of carbonium ion mechanisms. We also report the first evidence for neighboring group participation by the –N=N– group.

2,3-Dicarbomethoxy-*exo*-2,3-diazabicyclo[2.2.1]heptan-5-ol[8] was converted to *exo*-2,3-diazabicyclo[2.2.1]hept-2-en-5-ol by known procedures.[9,10] Treatment

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[1] R. J. Crawford and A. Mishra, *Can. J. Chem.*, **47**, 1515 (1969); R. J. Crawford and B. H. Al-Sader, *ibid.*, **46**, 3301 (1968); R. J. Crawford and D. M. Cameron, *ibid.*, **45**, 691 (1967); R. J. Crawford and G. L. Erickson, *J. Amer. Chem. Soc.*, **89**, 3907 (1967); R. J. Crawford and L. H. Ali, *ibid.*, **89**, 3908 (1967); R. J. Crawford and A. Mishra, *ibid.*, **88**, 3963 (1966); and other papers in the series.

[2] E. L. Allred and R. L. Smith, *ibid.*, **91**, 6766 (1969).

[3] D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *Can. J. Chem.*, **43**, 1407 (1965).

[4] J. C. Hinshaw and E. L. Allred, *Chem. Commun.*, 72 (1969).

[5] E. L. Allred, J. C. Hinshaw, and A. L. Johnson, *J. Amer. Chem. Soc.*, **91**, 3382 (1969); E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1969).

[6] M. Martin and W. R. Roth, *Chem. Ber.*, **102**, 811 (1969).

[7] J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **91**, 777 (1969).

[8] E. L. Allred, C. L. Anderson, and R. L. Smith, *J. Org. Chem.*, **31**, 3493 (1966).