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THE REACTION OF *CIS*-BICYCLO[6.1.0]NONATRIENE WITH DIENOPHILES AND DIENES[1]

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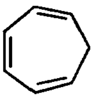
Abstract—*cis*-Bicyclo[6.1.0]nonatriene normally reacts with dienophiles as if it were the valence isomer. tricyclo[4,3,0,0^{7,9}]nona-2,4-diene, but with tetracyanoethylene and benzyne adducts are also obtained which are formally derived from cyclononatetraene. *cis*-Bicyclo[6.1.0]nonatriene is unreactive towards dienes. only products derived from *cis*-8,9-dihydroindene being obtained. A related addition of cyclopentadiene to cyclooctatetraene is described.

THE structure of cycloheptatriene (1) and its derivatives was, for a long time, a subject of controversy, since many of these compounds behave as if existing as the bicyclic, norcaradiene isomers (2). The classic example of this isomerism was believed to occur in the Buchner acids,[2] and it was only quite recently that von Doering *et al.*[3] showed that there were only the four isomeric monocyclic acids (3). Cycloheptatriene (1) has also been shown to be a monocyclic, nonplanar system,[4] but while it has not been possible to detect the presence of 2 by NMR spectroscopy,[4a,c,d] a considerable 1,6-interaction has been invoked on the basis of a number of physical measurements.[5] A number of substituted cycloheptatrienes are now known, however, to exist in the norcaradiene form,[6] while 7-cyano-7-trifluoromethylcycloheptatriene has been shown to be a tautomeric mixture of **4a** and **4b**.[7]



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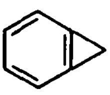

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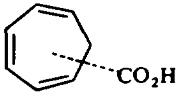

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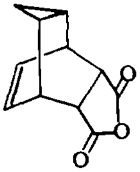
4a **4b**

When cycloheptatriene reacts with dienophiles, the resulting Diels-Alder adducts are formally derived from the norcaradiene tautomer **2**; thus maleic anhydride gives the adduct **5**.[8] However, in the case of the addition of fumaryl chloride to **1** it has been shown that norcaradiene (**2**) is not involved, and a norcaradiene-like transition state has been suggested.



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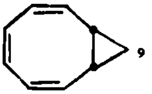
cis-Bicyclo[6.1.0]nonatriene (**6**), the higher vinologue of norcaradiene, is a well characterised molecule.[10, 11] It is thermally transformed into a mixture of *cis*- and *trans*-8,9-dihydroindane (**7**),[12, 13] and it does not appear to be in equilibrium with the open form, cyclononatetraene. When our research was initiated, cyclononatetraene was not known, having only been implicated as the initial product derived by hydrolysis of the cyclononatetraenyl anion.[14] However, all-*cis*-cyclononatetraene (**8**) and a stereoisomer have subsequently been prepared.[15,*] Only one adduct derived from the reaction of **6** with dienophiles had been reported,[11] that resulting from



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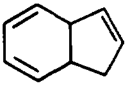

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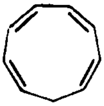

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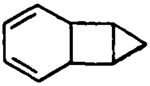

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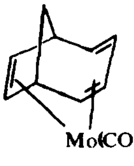
reaction with tetracyanoethylene (TCNE), and its structure was unknown. A derivative of 9-acetoxy-9-methylbicyclo[6.1.0]nonatriene with N-phenylmaleimide had also been prepared,[16] and this had been postulated to have a structure derived from a substituted tricyclo[4.3.0.0^{7,9}]nona-2,4-diene (**9**), but little evidence was given for this assignment.

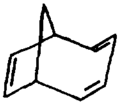
It therefore appeared of interest to examine the relationship of **6** to its valence isomers, and the reaction of **6** with both dienes and dienophiles was therefore studied. The results of these investigations are described in this paper.

Reaction of cis-*bicyclo*[6.1.0]*nonatriene* (**6**) *with dienophiles*

Reaction of **6** with maleic anhydride in refluxing benzene for 3 hr gave a 92% yield of a mixture of 1:1 adducts, from which **10** (mp 149·5–150°) was isolated by fractional crystallisation. The structure **10** was assigned on the basis of the spectroscopic properties and chemical behaviour. The mass spectrum (*m/e* 216) indicated that it was a 1:1 adduct, the UV spectrum showed no maximum above 220 nm. and the



(i)



(ii)

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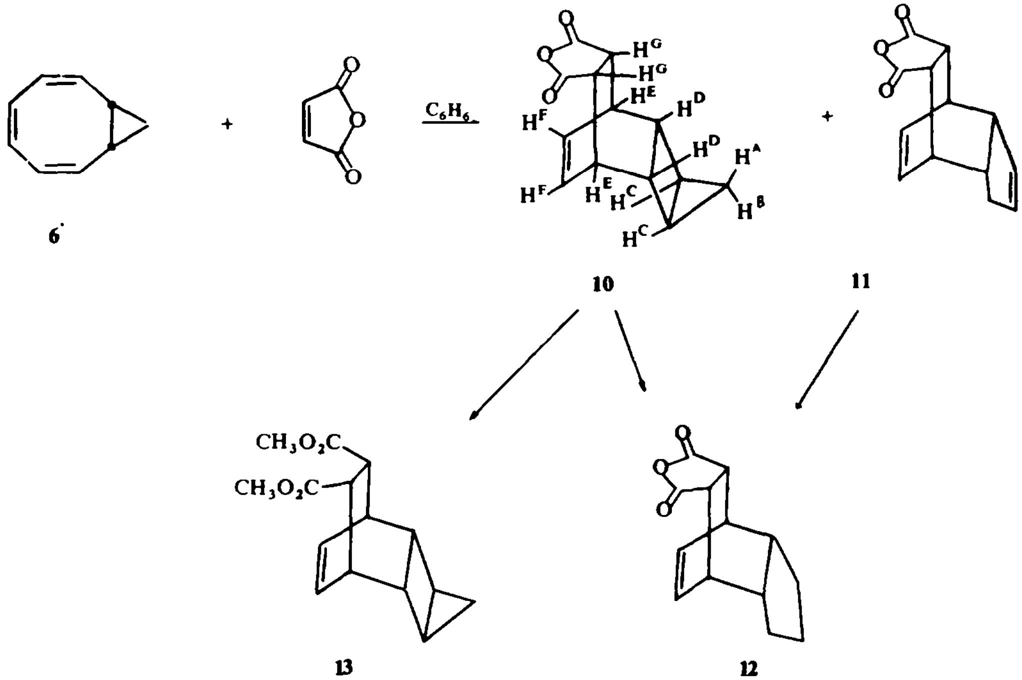
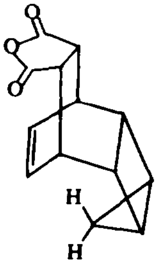
[*] A further valence isomer (ii) of **6** was prepared by removal of the metal from (i).



NMR spectrum showed six signals of equal intensity at τ 3·71 (dd, H^F) 6·80 (m, H^E), 7·05 (m, H^O), 8·10 (m, H^D), 8·79 (m, H^C) and 9·30 (m, H^A, H). The proton assignments are supported by double irradiation experiments: irradiation at the frequency of the τ 9·30 signal (H^A, H^B) causes collapse of the τ 8·79 multiplet (H^C) to a broad singlet, and irradiation at the frequency of the τ 8·79 multiplet causes collapse of the τ 9·30 signal to a singlet; irradiation at the frequency of the τ 3·71 signal (H^F) causes a change only in the signal at τ 6·80 (H^E); irradiation at the frequency of the τ 7·05 signal (H^E) causes a change only in the τ 6·80 signal (H^E); irradiation at the frequency of the τ 6·80 signal (H^E) causes the collapse of the τ 3·71 signal (H^F) to a doublet ($J = 2·5$ Hz) and the τ 8·10 signal (H^D) to a sharp singlet. The coupling between H^C and H^D thus appears to be *ca* zero.

Hydrogenation of **10** in EtOAc over Pt gave **12**, identified by comparison with an authentic sample.[17] The ease of hydrolysis of strained cyclopropane rings is well known.[18] Alkaline hydrolysis of **10**, followed by subsequent treatment with diazomethane, gave the dimethyl ester **13**, which had the expected spectroscopic properties.



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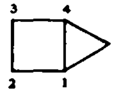

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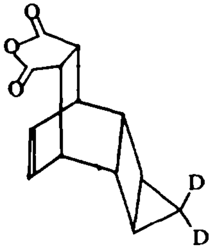
The stereochemistry shown for **10** was assigned on the basis of the known stereochemistry of **12**, and the co-incidental chemical shift of the H^A, H^B protons. Models of the *syn*-isomer **14** have one of the methylene protons on the cyclopropyl ring close to the double bond, whereas in **10** both protons are remote from this bond. The NMR spectrum of bicyclo[2.1.0]pentane (15) shows the methylene cyclopropyl hydrogens as a multiplet centred at τ 9·4,[19a] and 2,3-substituted bicyclo[2.1.0] pentanes do not generally show a separation of these protons.[19] The position and similarity of the chemical shifts of the methylene protons are thus consistent with the stereochemistry shown for **10** and not that for **14**.

The second adduct obtained in the reaction of **6** with maleic anhydride was not obtained pure, being contaminated with **10**. However, a comparison of the NMR spectrum with that of the known adduct **11**[17] clearly indicated that it was identical with this compound.

Repetition of the reaction with 9,9-dideuterio-*cis*-bicyclo[6.1.0]nonatriene, (prepared from the cyclooctatetraenyl dianion and dideuteriomethylene chloride) gave the corresponding dideuterio adducts, **16** and **17**. In the NMR spectrum of **16** the signal at τ 9·30 is absent, and the signal at τ 8·79 is simplified (broad singlet), both observations supporting the previous assignments. The NMR spectrum of **17** shows that all of the deuterium is in the methylene group, which demonstrates that **17** arises from Diels-Alder addition to 8,9-dihydroindene rather than from rearrangement of **16**. This evidence is supported by the finding that **10** is recovered unchanged after heating at 150° for several hours.



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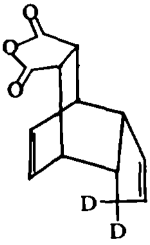

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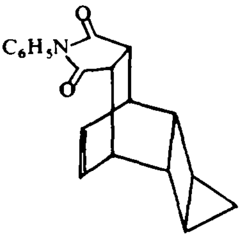
Reaction of **6** with N-phenylmaleimide in refluxing THF gave a 1:1 adduct (mp 186–187°) assigned the structure **18**, together with a small amount of the adduct **19**. The spectroscopic properties of **18** and **19** show only the expected differences from those of **10** and **11**, respectively.



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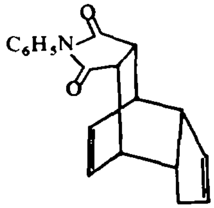

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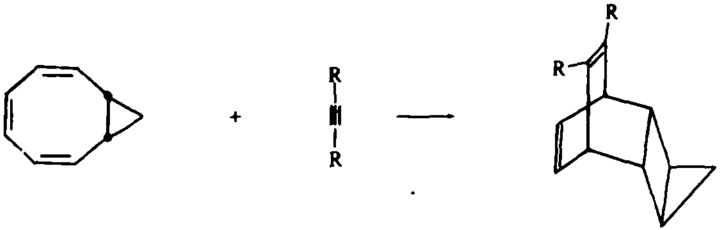
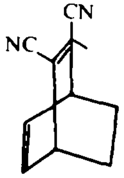
The reaction of **6** with substituted acetylenes was found to take a similar course to that with maleic anhydride. Hexafluoro-2-butyne (**20a**) gave the adduct **21a**, and dicyanoacetylene (**20b**) gave the adduct **21b**. The NMR spectra of these adducts show only the expected differences from the spectrum of the maleic anhydride adduct **10**, and the UV spectrum of **20b** [238 nm (ε 8500) 274 (650)] was very similar to that of the known adduct **22** [237 nm (ε 8700) 266 (700)].[20]



6

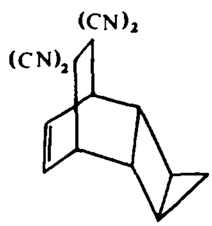
20a: R = CF_3
20b: R = CN

21a: R = CF_3
21b: R = CN



22

The products of the reaction of **6** with tetracyanoethylene (TCNE) was found to depend upon the experimental conditions. Reaction in refluxing toluene gave a 5:1 mixture of adducts, of which the major product, (m.p. 262–263°) was assigned the structure **23**. The mass spectrum molecular ion (*m/e* 246) indicates that it is a 1:1 adduct, the UV spectrum shows no maximum above 220 nm, and the NMR spectrum was similar to that of the adduct **10**. The minor adduct was shown to have the structure **24** by comparison with an authentic sample.[12]



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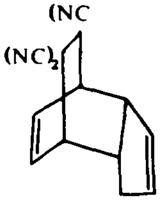

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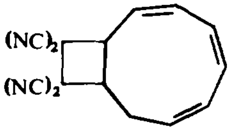
Refluxing **6** with excess TCNE in THF gave a different adduct (m.p. 141·5°–142°), identical to the adduct previously reported,[11] to which no structure had been assigned. The mass spectrum molecular ion (*m/e* 246) showed that this was also a 1:1 adduct, and the UV spectrum showed no maximum above 220 nm. The NMR spectrum in

$(CD_3)CO$ at 35° showed the presence of six olefinic (τ 3·63, dd, 1H; 3·9–4·4, m, 5H) and four saturated (τ 5·61, m, 1H; 6·27, m, 1H; 7·30, dd, 2H) protons, thus indicating that the adduct was bicyclic. Six possible bicyclic adducts have to be considered, as shown in structures **25–30** (no stereochemistry is implied). Structures **25** and **26** formally arise from 2 + 2 addition to cyclononatetraene, structures **27** and **28** by 2 + 4 addition, structure **29** by 2 + 6 addition and structure **30** by 2 + 8 addition.



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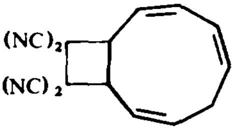

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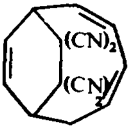

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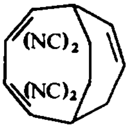

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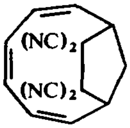

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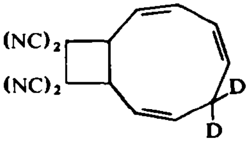
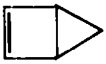
The NMR spectrum of the TCNE adduct is not consistent with structures **28** and **30**, which possess planes of symmetry and should have simpler spectra than that observed. In the NMR spectrum, the signal at τ 7·30 must be assigned to the methylene protons and the signals at τ 5·61 and τ 6·27 to the bridgehead protons. Double irradiation experiments showed that the τ 5·61 and τ 6·27 are coupled together, and the magnitude of the coupling (J = 10 Hz) strongly suggests that the bridgehead protons are joined. The NMR spectrum thus favours structure **25** or **26**. Of these structures **25** would be expected to show a 1,3,5-triene chromophore in the UV spectrum (e.g. **6** has a UV maximum at 247 nm), and the absence of such an absorption suggests that the adduct has the structure **26**. Further support for this assignment was obtained by preparing the adduct from 9,9-dideuteriobicyclo[6.1.0]nonatriene. In the NMR spectrum of the dideuterio adduct the signal at τ 7·30 is absent, the olefinic region is modified, but the bridgehead signals are virtually unaltered, all of which is consistent with the structure **31**.



31

The mass spectral fragmentation pattern of **26** differs from that of the tetracyclic adducts of type **10**. The base peak in the mass spectrum of **26** is at *m/e* 117·0702 (*m/e* 119 in **31**) due to the fragment $C_9H_9^{\oplus}$. By contrast, all of the tetracyclic adducts show a base peak at *m/e* 66 ($C_5H_6^{\oplus}$) presumably resulting from a retro-Diels-Alder reaction in which bicyclo[2.1.0]pent-2-ene (**32**), or its equivalent, is eliminated.



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The NMR spectrum of **26** is both temperature and solvent dependent. In $(CD_3)_2CO$ at −40°, the multiplet at τ 3·88–4·24 has lost much of its fine structure and the band at τ 7·33, formerly an overlapping double doublet, has become a more complex multiplet. At −80°, both the multiplet at τ 3·84–4·24 and the signal at τ 7·34 appears as broad, unresolved bands, while the signal now at τ 5·31 has simplified to a well resolved doublet (J = 10 Hz), and the signal now at τ 6·36 has simplified to a well resolved double doublet (J = 10 Hz). The lowest field broad doublet at τ 3·60 (1H) remains virtually unaffected throughout the temperature range. In $(CCl_3)_2CO$ at 35° the doublet which appeared at τ 5·61 in $(CD_3)_2CO$ now appears at τ 6·06, while the remaining signals are at similar positions in both solvents. The spectrum in $(CCl_3)_2CO$ remains virtually unaltered up to 135°.

These changes are due to the conformational mobility of the system, and are again consistent with the structure **26**, in which the 9-membered ring would be expected to be flexible.

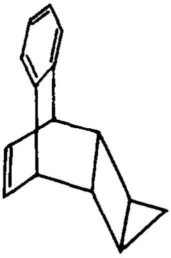
The adduct **26** is formally derived from cyclononatetraene, but the mechanism of the reaction is not known. Cyclooctatrienes open in an orbital symmetry controlled manner.[21] and **6** should therefore ring open to give mono-*trans*-cyclononatetraene. However, since the annulenes[22] and related systems[23] readily rearrange to the most stable configuration, the reaction might have proceeded via all-*cis*-cyclononatetraene.[16] The reaction of TCNE with all-*cis*-cyclononatetraene was therefore examined at −30° and 68°, but only the adduct derived from *cis*-8,9-dihydroindene was formed.

The stereochemistry of the ring junction of **26** is unknown. The magnitude of the bridgehead coupling is unhelpful, since the coupling constants between *syn* and *anti* 3,4-vicinal protons on 1,1,2,2-tetracyanocyclobutanes are variable.[24] A knowledge of this stereochemistry would be valuable in elucidating the pathway of formation of the adduct **26**, and an X-ray crystallographic examination is in progress.

Attempts to confirm the structure of **26** by chemical methods proved unrewarding. For example, catalytic hydrogenation was either ineffective or gave complex mixtures, while oxidation with a variety of reagents gave intractable products. The adduct **26** is sensitive to photoirradiation, and the nature of the products depends on the presence or absence of a sensitiser. However, in both cases the resulting compounds are thermally labile and have not been characterised.

The difficulties encountered in the chemistry of **26** appeared to be due to the presence of the cyanide groups, and an examination of alternative molecules which could give bicyclic adducts with **6** was therefore undertaken. Benzyne has been reported to undergo 2 + 2 additions with cyclooctatetraene[25] and cyclooctene.[26] and the reaction of **6** with benzyne was investigated.

The decomposition of excess benzenediazonium 2-carboxylate in the presence of **6** gave a complex mixture of products from which two 1:1 adducts could be isolated in low yield. One of the adducts was crystalline (mp 59°–60°), and it was assigned the structure **33** on the basis of its spectral properties. The NMR spectrum showed only the expected differences from that of the adduct **10**, while the mass spectrum showed a base peak at *m/e* 128 and a significant peak at *m/e* 66, the two fragments expected from a retro-Diels-Alder cleavage of **33**. The second adduct was obtained as an oil and was assigned the structure **34**. The NMR spectrum showed signals at τ 2·90 (m, 4H, aromatic), 3·90–4·64 (m, 6H, olefinic), 6·08–6·54 (m, 2H, H^A, H^B) and 7·06–7·94 (m, 2H, H^C). This spectrum is similar to that observed for **26**, but the greater complexity suggests that **34** is a mixture of stereomers. The mass spectrum showed the molecular ion at *m/e* 194, with the base peak at *m/e* 179. As expected, the ions which would result from a retro-cycloaddition are *not* prominent in the spectrum.



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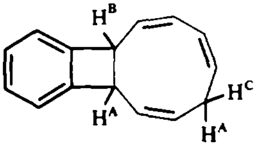
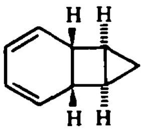


34

The normal mode of reaction of **6** with dienophiles appears to involve the *cis-anti-cis*-tricyclo[4.3.0.$0^{7,9}$]nonadiene (**35**) valence tautomer. Thus **6** resembles cycloheptatriene, cyclooctatetraene and cyclooctatetraene epoxide, all of which react with dienophiles as if in the polycyclic form. The reactions of **6** with TCNE and benzyne to give products formally derived from 2 + 2 addition to cyclononatetraene have analogies with related reactions of these dienophiles.[24, 25, 26] The actual pathway followed by the reactions must await a complete characterisation of the stereochemistry of the adducts.



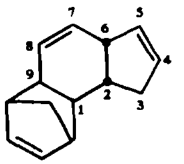
35

Reaction of cis-*bicyclo*[6.1.0]*nonatriene* (**6**) *with dienes*

Since it is known that the reaction of cycloheptatriene with reactive dienes gives adducts resulting from both 4 + 2 and 6 + 4 π-additions,[27] it was of interest to study the reaction of **6** with similar dienes.

cis-Bicyclo[6.1.0]nonatriene (**6**) did not react with cyclopentadiene at temperatures below 100°. However, at 200° a new hydrocarbon, mp 60°–61° was formed in 14% yield. The mass spectrum molecular ion, *m/e* 184, confirmed that this was a 1:1 adduct, and the UV spectrum showed no maximum above 220 nm. Catalytic hydrogenation in MeOH over Pd/C resulted in the uptake of 3 moles of H_2, indicating that the adduct was tetracyclic. A new saturated hydrocarbon (mp 40°–41°) was formed in this reaction. The NMR spectrum of the adduct also indicated that it was tetracyclic and further suggested that it was derived from *cis*-8,9-dihydroindene (*cis*-**7**). This was confirmed by preparation of the same adduct by treatment of *cis*-8,9-dihydroindene under the same conditions.

There are three alternative structures for the adduct, **36**–**38**, assuming that the cyclopentadiene reacts as the diene. The UV spectrum shows the absence of conjugation, and **38** is therefore excluded. The NMR spectrum supports structure **37** rather than **36**, since the proton at position **6** in **36** is doubly allylic, and should appear at lower field (*ca* τ 6·5) than the observed signals for the bridgehead protons in the adduct (τ 7·28, τ 7·64).



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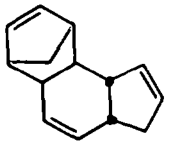

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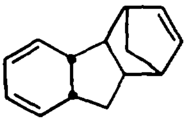

38

Reaction of **6** with 5,5-dimethoxy-1,2,3,4-tetrachlorocyclopentadiene gave a complex mixture of products which were not further examined, and no adduct was formed with tetrachlorocyclopentadienone itself. With tetracyclone in boiling xylene, **6** gave a mixture of three components which rapidly polymerised on subsequent examination, but which are being further investigated. In the reaction of **6** with cyclobutadiene (generated from the cyclobutadiene iron tricarbonyl complex[28]) no adducts were obtained.

The double bonds of *cis*-bicyclo[6.1.0]nonatriene (**6**), in these reactions, appear to be unreactive towards dienes. The thermal conversion of **6** to 8,9-dihydroindene and the subsequent reaction of this molecule appears to be the preferred reaction pathway.

In order to compare the reactivity of **6** towards dienes with that of cyclooctatetraene, the reaction of cyclooctatetraene and cyclopentadiene was investigated.* No reaction occurred below 100°, but at 200° a complex mixture of products was formed. From this mixture one component (mp 163·5°–164·5°) crystallised, which was assigned the structure **39**.

The mass spectrum molecular ion, *m/e* 274, was consistent with a 2:1 adduct of cyclooctatetraene and cyclopentadiene. Hydrogenation over Pd led to the uptake of

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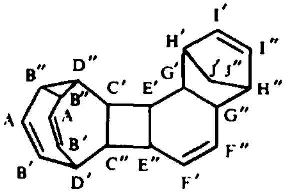
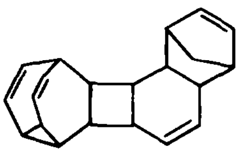
* Cyclooctatetraene is known to react as a dienophile with tetrachlorocyclopentadione ketals, giving 1:2 adducts.[29]



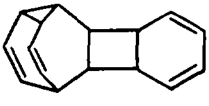
39a



39b

5 moles of hydrogen, giving a new hydrocarbon (mp 65°–66°). The UV spectrum of **39** showed only end absorption, and the NMR spectrum at 30° showed a signal at τ 3·80 (dd, 2H, H^{I}, $H^{I''}$), an AB multiplet centred at 4·06 (1H, $J = 9$ Hz) and 4·30 (1H, $J = 9$ Hz) due to $H^{F'}$, $H^{F''}$, and signals at 4·46 (m, 2H, H^{A}), 6·22 (m, 4H, $H^{B'}$, $H^{B''}$) and 8·30 (m, 12H). The NMR spectrum is similar to that of a number of related systems investigated by Merényi, Oth and Schröder,[30] and it exhibits the expected temperature dependence for a homotropilidene system. Thus on cooling the sample, the signals at τ 6·22 ($H^{B'}$, $H^{B''}$) broaden, lose their fine structure and eventually the band disappears at *ca.* $-50°$, while the signal at τ 4·46 (H^{A}) loses its fine structure. Peak broadening of the highfield bands also occurs on cooling. The spectrum at 30° is due to an equilibrium between structures **39a** and **39b**, which is slowed on cooling.

After this investigation was complete, Daub and Trautz[31] reported the formation of a similar adduct from the reaction of cyclooctatetraene with the dienophile, vinylene carbonate, at high temperature. The spectral properties of their adduct were closely similar to those of **39**. They suggested that their adduct could be derived either by addition of vinylene carbonate to cyclooctatetraene, followed by subsequent reaction of this adduct with another molecule of cyclooctatetraene, or from attack of vinylene carbonate as the cyclooctatetraene dimer **40**.[32] Only the latter reaction pathway appears appropriate to our case.



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EXPERIMENTAL

M. ps are uncorrected. NMR spectra were determined on a Varian HA-100 Spectrometer in $CDCl_3$ soln (unless otherwise stated) with TMS as internal standard. UV spectra were taken in 95% EtOH (unless otherwise stated) on a Unicam SP 800 spectrophotometer. Mass spectra were determined on either an AEI MS12 or MS9 instrument. IR spectra were recorded on a Unicam SP 200 spectrophotometer.

Reaction of cis-*bicyclo*[6,1,0]*nonatriene* (**6**) *with maleic anhydride*

The preparation of 4-*oxapentacyclo*[5.5.2.$0^{2,6}0^{8,12}0^{9,11}$]*tetradeca*-13-*ene*-3.5-*dione* (**10**). A soln of **6** (1·18 g. 10 mmoles) and maleic anhydride (0·98 g, 10 mmoles) in benzene (25 ml) was heated to reflux for 4 hr. The solvent was removed under reduced pressure. and the residue was dissolved in the minimum EtOAc. ligroin added. and the resulting ppt removed by filtration. Recrystallisation (ligroin) gave **10** (colourless needles. 530 mg. 25%. m.p. 149·5–150°) mass spectrum *m/e* 216. 143. 78. 66 (base peak); ν_{max}^{KBr} 1760. 1850 cm^{-1}; NMR spectrum, see discussion. (Found: C. 71·89; H. 5·64. $C_{13}H_{12}O_3$ requires: C. 72·22; H. 5·56%).

The filtrate obtained after precipitation was evaporated under reduced pressure to leave a residue (1·46 g. 65%) consisting of a mixture of **10** and **11**. the latter identified by comparison of the NMR spectra with that of an authentic sample.

Compound **16** was prepared by reaction of 9.9-dideuteriobicyclo[6.1.0]nonatriene under identical conditions; mass spectrum *m/e* 218. 145. 119. 68 (base peak). 67; NMR 3·71 (dd. 2H). 6·8 (m. 2H). 7·05 (m. 2H). 8·10 (m. 2H) and 8·79 (s. 2H).

Hydrogenation of **10**

The preparation of 4-oxatetracyclo$[5.5.2.0^{2,6}0^{8,12}]$*tetradeca-13-ene-3.5-dione* (**12**). A soln of **10** (108 mg) in EtOAc (2 ml) was shaken under a H_2 atm with 10 mg pre-reduced Adams catalyst. The solvent was removed under reduced pressure and the residue was recrystallised (hexane) to give **12** (90 mg. 83%. m.p. 134·5°–135°. lit. 134·5–135°[18]).

Attempted thermal rearrangement of **10**. The adduct **10** (50 mg) was heated at 150° for 4 hr. The NMR spectrum of the sample showed only peaks due to the adduct **10**.

Hydrolysis and methylation of **10**. The adduct **10** (21·6 mg. 1 mmole) was added to 10% Na_2CO_3 aq (5 ml) and the mixture was then heated to reflux for 4 hr. Water (2 ml) was added. the resulting soln acidified with conc HCl. The resulting mixture was extracted with EtOAc (3 × 5 ml). and the organic layer evaporated. The residue was dissolved in anhydrous MeOH (5 ml) and treated with ethereal diazomethane (100 mg/ml) until the yellow colour just persisted. Removal of the solvent under reduced pressure gave an oil which crystallised. Recrystallisation (light petroleum 60°–80°) gave **13** (m.p. 80°–81°); mass spectrum *m/e* 262. 231. 202. 196. 143. 137. 93. 66; ν_{max}^{KBr} 1720 (C=O). 1180. 1150 cm^{-1}; λ_{max} 235 (ε 650); NMR 3·58 (dd. 2H). 6·40 (s. 6H). 7·00 (m. 2H). 7·17 (m. 2H). 8·13 (m. 2H). 9·36 (m. 2H). (Found: C. 68·44; H. 6·92. $C_{15}H_{18}O_4$ requires: C. 68·69; H. 6·92%).

Reaction of **6** *with* N-*phenylmaleimide*

The preparation of 4-phenyl-4a,2a pentacyclo$[5,5,2,0^{2,6}0^{8,12}0^{9,11}]$*tetradeca-13-ene-3,5-dione* (**18**). **6** (1·18 g. 10 mmoles) was added to a soln of N-phenylmaleimide (1·9 g. 10 mmoles) in THF (5 ml). The resulting soln was heated to reflux for 3 hr. and the solvent then removed under reduced pressure to give a yellow residue (2·90g). Four recrystallisations from EtOH gave **18** (130 mg. 4·2%. m.p. 186·5°–187°); mass spectrum *m/e* 291. 226. 144. 143. 119. 117. 91. 78. 66 (base peak); ν_{max} 1745. 1690 cm^{-1}; NMR 2·27–2·89 (m. 5H). 3·67 (dd. 2H). 6·72 (m. 2H). 7·23 (m. 2H). 8·04 (m. 2H). 8·79 (m. 2H). 9·30 (m. 2H). (Found: C. 78·33; H. 5·97; N. 4·87. $C_{19}H_{17}NO_2$ requires: C, 78·34; H. 5·85; N. 4·81%).

The combined mother liquors were evaporated under reduced pressure to give a 3:1 mixture of **18** and **19** (1·36 g. 45%).

Reaction of cis-*8.9-dihydroindene with* N-*phenylmaleimide*

The preparation of 4-phenyl-3-azatetracyclo$[5,5,2,0^{2,6}0^{8,12}]$*tetradeca-9,13-diene-3,5-dione* (**19**). A soln of *cis*-8.9-dihydroindene (120 mg. 1 mmole) and N-phenyl maleimide (190 mg. 1 mmole) in THF (2 ml) was heated under reflux for 3 hr. The solvent was removed under reduced pressure and the residue was recrystallised (EtOH) to give **19** (140 mg. 50%. m.p. 211–212°). mass spectrum *m/e* 291. 226. 143. 119. 117. 114. 91. 93. 66 (base peak); ν_{max}^{KBr} 1745. 1690 cm^{-1}; λ_{max} 215 nm (ε 8300); NMR spectrum 2·27–2·89 (m. 5H). 3·86 (dd. 2H). 4·46 (m. 2H). 7·01 (m. 2H). 6·9–7·6 (m. 6H); (Found: C. 78·24; H. 5·88; N. 4·56. $C_{19}H_{17}NO_2$ requires C, 78·34; H, 5·85; N, 4·81%).

Reaction of **6** *with hexafluoro-2-butyne* (**20a**)

The preparation of 8.9-di(trifluoromethyl)tetracyclo$[5.2.2.0^{2,6}0^{3,5}]$*-undeca-8.10-diene* (**21a**). Compound **6** (1·09 g. 9 mmoles) and hexafluoro-2-butyne (2·70 g. 16 mmoles) were sealed in a glass tube which was then vigorously shaken at room temp until a single liquid phase was formed (*ca* 4 weeks). The tube was cooled. opened. the excess hexafluoro-2-butyne allowed to escape. and the resulting mobile liquid (2·6 g) was examined by GLC. The liquid contained. besides **6**. four other components. and **21a** formed about 65% of the total reaction mixture. Preparative GLC (Apiezon L. 150°). followed by bulb to bulb distillation at low pressure (10^{-4} mm), gave pure **21a**, m.p. 39–40°, ν_{max}^{KBr} 1185, 1145. 1260. 1290 cm^{-1}: λ_{max} 236 nm (ε 370), NMR spectrum 3·57 (dd. 2H). 5·96 (m. 2H). 8·14 (m. 2H). 8·78 (m. 2H). 9·20 (m. 2H). (Found: C. 55·77; H. 3·73; F. 40·77. $C_{13}H_{10}F_6$ requires: C. 55·71; H. 3·60; F. 40·68%).

Reaction of **6** *with dicyanoethylene* (**20b**)

The preparation of tetracyclo[5.2.2.0^{2,6}0^{3,5}]*undeca*-8,10-*diene*-10,11-*dinitrile* (**21b**). A soln of **6** (140 mg, 1·2 mmoles) and dicyanoacetylene (360 mg, 2·4 mmoles) in THF (2 ml) was allowed to stand at room temp for 12 hr. and the resulting dark green soln was then heated to reflux for 1 hr. and the solvent then removed under reduced pressure. The residue was extracted with benzene (3 × 3 ml) and the combined extracts were evaporated under reduced pressure. Preparative TLC gave a crystalline solid, which was recrystallised from ether at −30° to give **21b** (7 mg, 3%) m.p. 139–140°; ν_{max}^{KBr} 2200 (C≡N); λ_{max} 238 (ε 8500); NMR spectra 3·67 (dd 2H), 6·12 (m, 2H), 8·40 (m, 2H), 8·60 (m, 2H), 9·14 (m, 2H); mass spectrum, *m/e* 194, 128, 115, 77, 66 (base peak). (Found: C, 80·24; H, 5·31. $C_{13}H_{10}N_2$ requires: C, 80·39; H, 5·19%).

Reaction of **6** *with TCNE in toluene*

The preparation of tetracyclo[5.2.2.0^{2,6}0^{3,5}]*undeca*-8-*ene*-10,10,11,11-*tetranitrile* (**23**). A soln of **6** (580 mg, 5 mmole) in toluene (10 ml) was added to a soln of TCNE (640 mg, 5 mmoles) in toluene (20 ml), when an intense red soln was formed. This soln was then refluxed for 5 hr, cooled, and the ppt removed by filtration. Recrystallisation (toluene) gave **23** (860 mg, 70%) m.p. 262°–263° (dec); mass spectrum *m/e* 246·0882, 181, 128, 91, 66 (base peak); ν_{max}^{KBr} 2240 (C≡N), 750 cm^{-1} (*cis* C=C); NMR spectrum (acetone-d_6) 3·20 (dd, 2H), 6·07 (m, 2H), 7·57 (m, 2H), 8·66 (d, J = 6 Hz, 2H), 9·20 (m, 2H). (Found: C, 73·40; H, 4·31; N, 23·15. $C_{15}H_{10}N_4$ requires: C, 73·15; H, 4·09; N, 22·75%).

Reaction of **6** *with TCNE in THF*

The preparation of bicyclo[7.2.0]*undeca*-2,4,7-*triene*-10,10,11,11-*tetranitrile* (**26**). A soln of **6** (118 mg, 1 mmole) in THF (0·2 ml) was added to a soln of TCNE (256 mg, 2·0 mmole) in THF (0·8 ml). The soln was heated to reflux for 48 hr. and the solvent then removed under reduced pressure. The resulting dark green solid was extracted with hot CCl_4, and the extracts decolourised with Norit. On cooling a pale yellow solid was precipitated, which was removed by filtration, heated at 80° under *vacuo* to remove any TCNE, and recrystallised (CCl_4) to give white needles of **26** (180 mg, 75%), m.p. 141·5–142° (lit. 141·5–142°[11]); mass spectrum *m/e* 246, 219, 187, 155, 117 (base peak), 115, 91 ν_{max}^{KBr} 2270 (C≡N), 775 cm^{-1} (*cis* C=C); λ_{max} 230 sh (log ε 3·41); NMR spectrum (220 MHz, 35° $(CD_3)_2CO$) 3·63 (dd, 1H), 4·0 (m, 2·8H), 4·24 (m, 2·3H), 5·61 (d, 1H), 6·26 (dd, 1H), 7·33 (dd, 2H).

Reaction of cis^4*-cyclononatetraene with TCNE*

A soln of *cis*^{4}-cyclononatetraene (200 mg, 1·7 mmoles) in THF (1 ml), prepared according to the method of Boche *et al.*,[16] was added to a soln of TCNE (246 mg, 2·0 mmoles) in THF (5 ml) and at −30°, when a pale red colouration formed. After 7 days at −30°, the crystalline ppt was removed by filtration, and identified as **24** (110 mg, 26%). The mother liquors gave a second crop of **24** (60 mg, 14%), and the filtrate was shown to be a mixture of **24** and TCNE.

A similar experiment in which *cis*^{4}-cyclononatetraene was added to TCNE in refluxing THF also gave **24** as the only observed adduct.

Reaction of **6** *with benzyne*

The preparation of 10,11-*benzotetracyclo*[5.2.2.0^{3,5}0^{2,6}]*undeca*-8,10-*diene* (33) *and* 10,11-*benzobicyclo* [7,2,0]*undeca*-2,4,7-*triene* (**34**). Diazotised anthranilic acid (2·20 g anthranilic acid) was added to **6** (472 mg, 4 mmoles) dissolved in ethylene dichloride (5 ml) and the volume of suspension was made up to 10 ml. The mixture was stirred until the solid disappeared (3 days). Three such solns were added to vigorously stirred light petroleum (200 ml, 30°–40°), the soln filtered, and the filtrate evaporated under reduced pressure. The resulting oil was re-extracted with light petroleum (2 × 100 ml, 30°–40°), the extracts evaporated under reduced pressure and chromatographed (silica gel). Elution gave first **34** (colourless oil, 30 mg, 4%); mass spectrum, *m/e* 194, 179 (base peak), 178, 152, 165, 115, 91; ν_{max}^{liquid} 1480, 730, 710, 670 cm^{-1}; λ_{max} 230 (sh) (ε 4000); 237 (3600), 247 (3400), 258 (1600), 264 (2000); 270 nm (1700); NMR 2·90 (m, 4H), 3·90–4·64 (m, 6H), 6·08–6·54 (m, 2H), 7·06–7·94 (m, 2H) and then **33** (20 mg, 3%, m.p. 59°–60°); mass spectrum *m/e* 194, 178, 128, 66 (base peak); ν_{max}^{KBr} 1460, 800, 760, 735, 700 cm^{-1}; λ_{max} 257, (ε 240), 263 (300), 270 nm (300); NMR (CCl_4) 3·07 (m, 4H), 3·53 (dd, 2H), 6·15 (m, 2H), 8·19 (m, 2H), 8·63 (m, 2H), 9·24 (m, 2H). (Found: C, 92·75; H, 7·62. $C_{15}H_{14}$ requires: C, 92·74; H, 7·26%).

Reaction of **6** *with cyclopentadiene*

The preparation of tetracyclo[9.2.1.0^{2,10}0^{3,7}]*tetradeca*-4,8,12-*triene* (**37**). Bicyclo[6.1.0]nonatriene

(590 mg, 5 mmole) and freshly distilled cyclopentadiene (550 mg, 14·5 mmole) were mixed in a thick wall tube which was sealed under *vacuo* and plunged into a bath at 160°. The temp was maintained for 5 hr, the tube cooled, opened and the contents diluted with pentane. Chromatography (silica gel), eluting with pentane gave dicyclopentadiene, 8,9-dihydroindene and then **37** as colourless plates (150 mg, 14%, m.p. 60–61°); mass spectrum *m/e* 184; ν_{max}^{KBr} 2800, 720, 710 cm^{-1}; NMR (CCl_4) 4·16 (dd, 2H), 4·66 (m, 4H), 7·26 (m, 2H), 7·30–7·90 (m, 6H), 9·06–9·28 (m, 2H). (Found: C, 91·13; H, 8·60. $C_{14}H_{16}$ requires: C, 91·25; H, 8·75%).

A similar reaction of 8,9-dihydroindene with cyclopentadiene gave **37** (14%), identical in all respects with sample prepared as described above.

Hydrogenation of **37**

The preparation of tetracyclo[9.2.1.0^{2,7}0^{3,10}]*tetradecane.* A soln of **37** (31·5 mg, 0·15 mmole) in MeOH (5 ml) was hydrogenated over Pd/C (5%, 10 mg) catalyst, 3 molar equivts (12·3 ml) of H_2 were absorbed, and removal of the solvent and catalyst gave tetracyclo[9,2,1,0^{2,7}0^{3,10}]tetradecane (28 mg, 0·14 mmole, 90%, m.p. 40–41°); mass spectrum *m/e* 190, 121, 67; ν_{max}^{KBr} 2900, 2800 cm^{-1}; NMR 7·80–8·30 (m). (Found: C, 88·74; H, 11·48, $C_{14}H_{22}$ requires: C, 88·35; H, 11·65%).

Reaction of cyclooctatetraene with cyclopentadiene

The preparation of (**39**). A mixture of cyclooctatetraene (318 mg, 3 mmole) and cyclopentadiene (198 mg, 3 mmole) was sealed under *vacuo* and plunged into a bath at 190° for 5 hr. The contents were cooled, diluted with pentane, and the crystalline solid which precipitated was removed by filtration and recrystallised (hexane, cyclohexane) to give **39** (80 mg, 15% m.p. 163·5°–164°); mass spectrum *m/e* 274; ν_{max}^{KBr} 2850, 760, 740, 700 cm^{-1}; λ_{max} 226 nm; NMR temp 3·80 (dd, 2H), 4·19 (m, 2H), 4·46 (m, 2H), 6·22 (m, 4H), 7·20–8·38 (m, 12H). (Found: C, 90·96; H, 8·21. $C_{21}H_{22}$ requires: C, 91·22; H, 8·08%).

Hydrogenation of **39**. A soln of **39** (25 mg, 0·9 mmole) in EtOH (3 ml) was stirred under H_2 with a Pd/C (10%, 20 mg) catalyst. Five moles of H_2 were absorbed, and removal of the solvent and catalyst gave **40** (15 mg, 80%, m.p. 65·5°–66°); mass spectrum *m/e* 284; ν_{max} 2370 cm^{-1}; NMR (CCl_4) 7·08–9·00 (m). (Found: C, 88·56; H, 11·31. $C_{21}H_{32}$ requires: C, 88·66; H, 11·34%).

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