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(19) Combustion analyses were obtained for the two major isomers and high-resolution mass spectra for the two minor isomers.

(20) For a review of the conformational analysis of cyclohexenes, see H. Günther and G. Jikeli, *Chem. Rev.*, **77**, 599 (1977).

(21) Typical values of coupling constants (in hertz) to be expected for pure conformers are the following: $J_{5a,6e'} = 5-6$;[22] $J_{5a,6a'} = 10-12$;[22,23] $J_{4a,5a} = 12-13.2$;[11a,22,23,26b] $J_{4e,5a} = J_{4a,5e} = 2.5-4.0$;[11a,20,23] $J_{4e,5e} = 4.7-4.9$ [These values are derived by substituting 12 and 13.2,[24a] respectively, for $J_{a,a}$ in the expression[20] $(J_{a,a} + J_{e,e})/2 = 8.94$, which was determined for $J_{4,5\ trans}$ of 1,2,3,3,6,6-hexadeuteriocyclohexene.]. Equatorial, axial, quasiequatorial, and quasiaxial are designated by e, a, e′, and a′, respectively.

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# Scope of the Homo-Diels-Alder Reaction

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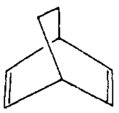
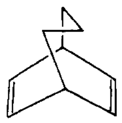
The reactivity of bicyclo[2.2.2]octa-2,5-diene, bicyclo[3.2.2]nona-6,8-diene, and 3,3-dimethyl-1,4-pentadiene in the homo-Diels-Alder reaction has been investigated to aid in an assessment of the scope of this reaction. The scope is seen to be rather limited, with the efficiency of the diene in the reaction generally being related to the distance between the double bonds.

The 1,5-addition of dienophiles to 1,4-dienes (the homo-Diels-Alder reaction) is a useful synthetic reaction for the preparation of certain tetracyclic compounds (Scheme I). Most studies of this reaction have involved norbornadiene with a variety of dienophiles.[1] Recent studies with norbornadiene have been concerned with the stereochemistry of the reaction,[2] a competing ionic reaction,[3] and the effects of Ni(0) catalyst on the reaction.[4] Other diene systems studied include the Dewar benzene,[5] barrelene,[6] and 1,4-cyclohexadiene systems.[7]

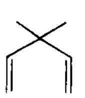
We were interested in the scope of the homo-Diels-Alder reaction with regard to the diene to see what the limitations are on the ring systems that can be synthesized by this reaction. Since the ease of the reaction must depend critically on the alignment and distance between the double bonds, we have investigated the behavior in this reaction of several dienes in which the double bonds are at increasingly greater distances than in norbornadiene. The dienes studied were bicyclo[2.2.2]octa-2,5-diene (**1**), bicyclo[3.2.2]nona-6,8-diene (**2**), and 3,3-dimethyl-1,4-pentadiene (**3**). The results of these studies along with previous information in the literature can be used to assess the scope of the homo-Diels-Alder reaction.



1

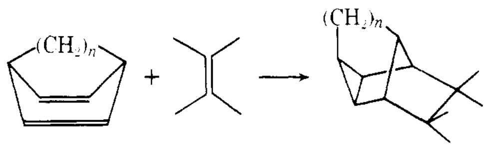


2



3

Scheme I

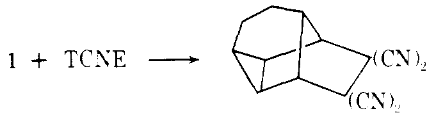


## Discussion

Bicyclo[2.2.2]octa-2,5-diene (**1**) was prepared by the method of Grob et al.,[8,9] which ultimately involves a Cope elimination from the *N*-oxide of 5-(dimethylamino)bicyclo[2.2.2]oct-2-ene. In order to avoid contamination of the diene with tricyclo[3.2.1.0$^{2,7}$]oct-3-ene, which apparently results from elimination from the exo amine oxide,[10] an attempt was made to prepare the starting material for the synthesis, *endo*-5-carbethoxybicyclo[2.2.2]oct-2-ene, with a high degree of configurational purity. It was found that the procedure of Inukai et al. for the aluminum chloride catalyzed Diels-Alder reaction[11] gave this ester in yields comparable to the uncatalyzed reaction[12] but the bicyclic ester was 98% endo isomer compared to 76% for the uncatalyzed reaction.

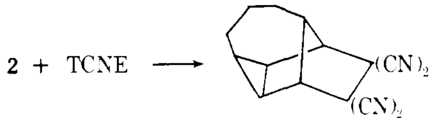
The same procedure was used to prepare bicyclo[3.2.2]nona-6,8-diene (**2**).[13] In this case, the aluminum chloride catalyzed reaction of ethyl acrylate with 1,3-cycloheptadiene gave the bicyclic ester in 54% yield. Analysis showed that it was 98.5% exo isomer (this relates to the endo isomer in the bicyclooctyl case). 3,3-Dimethyl-1,4-pentadiene (**3**) was prepared by a modification of the procedure of Ciola and Burwell.[14]

The homo-Diels–Alder reaction of bicyclooctadiene **1** was first tried with the highly reactive dienophile tetracyanoethylene (TCNE). A solution of these two in benzene produces an orange-amber color, presumably due to the formation of a charge-transfer complex. Refluxing for 30 h gives a crystalline product in yields as high as 85%. Spectral and elemental analyses of the compound were consistent with the expected 1:1 adduct 9,9,10,10-tetracyanotetracyclo[5.3.0.0$^{2,4}$.0$^{3,8}$]decane (**4**). Attempts to shorten the reaction time by carrying the reaction out at a higher temperature (100 °C, 11 h, benzene solvent) led to a lower yield of product (53%); this is apparently due to a competing retro-Diels–Alder reaction of the diene to benzene and ethylene.[8] The reaction of **1** with a less reactive dienophile, dimethyl acetylenedicarboxylate, was also attempted. In this case, no adduct was obtained after heating the reactants at reflux in benzene for 4 days (some polymer is formed). Heating at 100 °C for 36 h still did not produce the desired product, but led instead to thermal decomposition of the diene. Attempts to catalyze the reaction with aluminum chloride also failed (polymeric material is formed). In contrast, reaction of this dienophile with norbornadiene produces the adduct in 50% yield when a mixture of the two is heated at reflux for 12 h.[1i]



**4**

Bicyclononadiene **2** was found to be considerably less reactive than the bicyclooctadiene in the homo-Diels–Alder reaction, but because of its greater thermal stability and lesser tendency to polymerize than **1** (no change after heating at 150 °C for 24 h) more forcing conditions can be used. Addition of **2** to a benzene solution of TCNE again produced an orange-amber color, but no reaction was observed when the mixture was heated at reflux. However, heating the benzene solution to 145 °C for 15 h gave the desired product in yields to 24%. At this temperature the TCNE undergoes considerable decomposition to give a black carbon-like residue. The crystalline adduct was assigned the structure 10,10,11,11-tetracyanotetracyclo[6.3.0.0$^{2,4}$.0$^{3,9}$]undecane (**5**) on the basis of its IR and NMR spectra. As with the octadiene **1**, none of the tetracyclic adduct was observed for the reaction of **2** and dimethyl acetylenedicarboxylate (150 °C, 24 h).

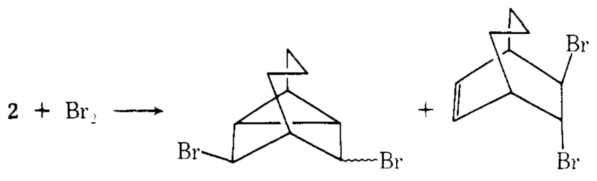


**5**

The reactivity of 3,3-dimethyl-1,4-pentadiene (**3**) in the homo-Diels–Alder reaction was examined with a variety of dienophiles. Although the addition of TCNE to a benzene solution of **3** produces a light amber color, heating of this solution, even at 145 °C for 52 h, does not lead to any detectable reaction. Attempted reaction also with dimethyl acetylenedicarboxylate, maleic anhydride, and *N*-phenylmaleimide (the latter two reactions at elevated temperatures) failed to produce the 1,5-adduct.

The above results, taken with others reported in the literature, indicate that the scope of the homo-Diels–Alder reaction is indeed rather limited. The reaction works well with norbornadiene, giving a quantitative yield of adduct with TCNE after 30 min at reflux in benzene,[1b] and with numerous other less reactive dienophiles.[1] Hexamethyl Dewar benzene has been reported to give an 85% yield of mono adduct when refluxed with TCNE in chlorobenzene. The product is 90% homo-Diels–Alder adduct and 10% rearranged product. In this case, the reaction is considered to be an ionic one.[5] Barrelene also gives a good yield of the homo-Diels–Alder product (95% with dicyanoacetylene at room temperature[6b]). In the present study bicyclooctadiene **1** was found to give an 85% yield of adduct with TCNE after 30 h at reflux in benzene, but it did not react with the less reactive dienophile dimethyl acetylenedicarboxylate.

The efficiency of the reaction decreases markedly with bicyclo[3.2.2]nona-6,8-diene (**2**); a 25% yield of adduct was obtained on heating with TCNE at 145 °C for 15 h. This decreased reactivity parallels a decreased tendency for homoconjugate addition of bromine to this diene compared to some of the compounds mentioned above. We find that the addition of bromine to **2** gives only 11% of the tricyclic dibromide **6** and 89% of the bicyclic dibromide **7**. The tricyclic dibromide appears to be a mixture of epimers. In contrast, norbornadiene gives 80% of tricyclic dibromide,[15] barrelene 83%,[16] and bicyclooctadiene **1** about 30%.[17] Both 1,4-cyclohexadiene and 3,3,6,6-tetramethyl-1,4-cyclohexadiene fail to undergo the homo-Diels–Alder reaction at all.[7] This parallels their failure to undergo homoconjugate addition with, for example, bromine or the Prevost reagents (iodine and silver benzoate).



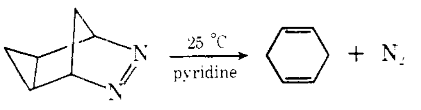
**6**, 11% **7**, 89%

Only 1,2-addition products are formed in these reactions. The more flexible but less hindered 3,3-dimethyl-1,4-pentadiene (**3**) also gives no homo-Diels–Alder product, and it gives an inseparable mass of tarry products in the Prevost reaction.

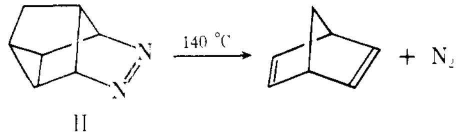
It is apparent in considering the series of dienes mentioned above that there is a good correlation between the ease of homo-Diels–Alder reaction and the distance between the double bonds in the diene. These distances as determined from Dreiding models are as follows: norbornadiene, 2.40 Å (a more flexible Framework Molecular Model, Prentice Hall, Inc., was used for this diene); barrelene, 2.46 Å; bicyclooctadiene **1**, 2.47 Å; bicyclononadiene **2**, 2.51 Å; 3,3,6,6-tetramethyl-1,4-cyclohexadiene, 2.54 Å; and 3,3-dimethyl-1,4-pentadiene (**3**), 2.51 Å (for the more flexible systems, the distance is for the conformation giving the closest approach and parallel orientation of the double bonds).

The ease of the reaction can in turn be correlated with other effects dependent upon the distance between double bonds, for example, electronic interaction of the double bonds. The homo-Diels–Alder reaction is considered to be a concerted [$2_\pi + 2_\pi + 2_\pi$] cycloaddition reaction since it leads to the stereospecific formation of products,[2] although, as mentioned, the reaction of hexamethyl Dewar benzene with TCNE is apparently an ionic reaction[5] and a competing ionic reaction has been found in the case of norbornadiene and chlorocyanoacetylene.[3] Interaction of the double bonds in nonconjugated dienes can be classified into two types: through-space and through-bond interaction.[18] It is the through-space interaction which is thought to be important for the homo-Diels–Alder reaction.[2b] Norbornadiene is considered to be a model compound for through-space interaction, while 1,4-cyclohexadiene is a good model for through-bond interaction.[18] The interaction energy of the double bonds in these two systems has been measured by photoelectron spectroscopy.[19] This technique shows that through-space interaction is also important for barrelene[20] and bicyclooctadiene **1**,[19] while bicyclononadiene **2** has a near cancellation of through-space and through-bond interactions and seems to be the transition point for dienes with regard to the relative importance of these two types of interactions.[13b] It is clear that there is a good correlation between the ease of homo-Diels–Alder reaction and the amount of through-space interaction in these dienes.

The relative reactivities of the dienes can also be correlated with the ease of approach to the transition state for formation of the homo-Diels–Alder product. Generally speaking, the closer together the double bonds are the closer the diene would be to the transition state for the reaction. The superiority of norbornadiene to the other dienes from this point of view can be seen by looking at the ease of the reverse reaction, the retro homo-Diels–Alder reaction, of the azo compounds I[21] and II.[1e] As can be seen, I is much more reactive than II due to the greater relief of strain associated with the formation of 1,4-cyclohexadiene than the formation of norbornadiene. Apparently, the strain associated with formation of the three-membered ring as well as a lack of through-space interaction of the double bonds is sufficient to limit the homo-Diels–Alder reaction to dienes with double bonds no farther apart than they are in the bicyclononadiene **2**. For acyclic dienes such as **3**, entropy effects would also be important.

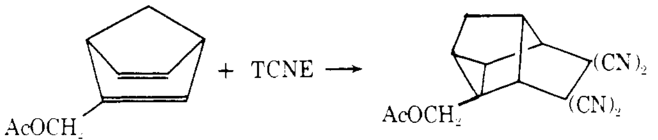


I



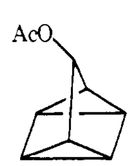
II

In an attempt to look at the effects of substituents in the diene on the homo-Diels–Alder reaction, the reaction of TCNE with 2-(acetoxymethyl)norbornadiene (**8**) was investigated. Mixing of the two in benzene produces an orange-red solution, and heating to reflux causes the formation of a 1:1 adduct in yields to 41%. The adduct was assigned structure **9** on the basis of its NMR spectrum, which showed a broad singlet at $\delta$ 1.80 (4 H), assigned to the two cyclopropyl hydrogens and the hydrogens of the methylene bridge, a broad multiplet at $\delta$ 2.55 (1 H), assigned to the bridgehead hydrogen facing the cyano groups, a broad singlet at $\delta$ 3.41 (2 H), assigned to the two remaining bridgehead hydrogens, and a quartet at $\delta$ 4.42 (2 H), assigned to the methylene adjacent to the acetate group. The acetate methyl appears as a sharp singlet at $\delta$ 2.05. The methylene adjacent to the acetate group is also adjacent to an asymmetric center, which causes it to appear as an AB quartet ($J_{AB}$ = 12.5 Hz and $\Delta\nu_{AB}$ = 43 Hz). Compound **8** is apparently less reactive in the homo-Diels–Alder reaction than norbornadiene itself since we were unable to isolate any adduct from **8** and dimethyl acetylenedicarboxylate after heating the two for 24 h at 120 °C in benzene.

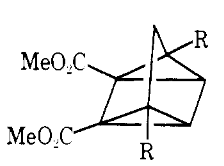


**8** **9**

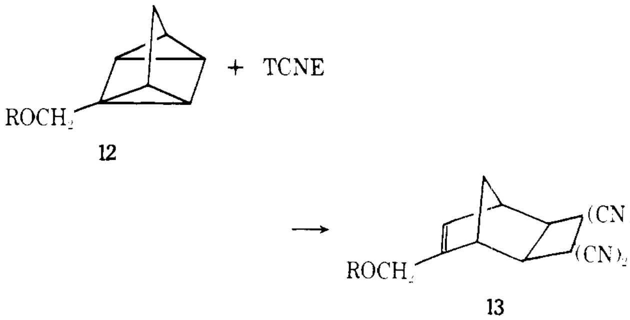
The product from **8** is formed by addition of the dienophile at the least hindered side of the diene. This regiospecificity may be explained by both steric and electronic factors. It is interesting to note that the same regiospecificity is seen in 1,2-cycloaddition reactions of quadricyclanes. The quadricyclanes **10** and **11** have both been reported to give the 1,2-addition product resulting from reaction at the side away from the substituent.[22,23] We have found analogous results with 1-(hydroxymethyl)quadricyclane (**12a**) and 1-(acetoxymethyl)quadricyclane (**12b**). These quadricyclanes with TCNE produce **13** as shown by NMR analysis. Thus, it appears that the substituent effect may be general for both of these 1,2- and 1,5-cycloaddition reactions and steric in origin.



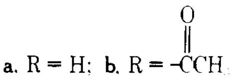
**10**



**11**, R = H or $C_6H_5$



**12** **13**



**a**, R = H; **b**, R = $-\overset{O}{\overset{\|}{C}}CH_3$

## Experimental Section[24]

**Bicyclo[2.2.2]octa-2,5-diene (1).** 5-Carbethoxybicyclo[2.2.2]oct-2-ene was prepared by a procedure similar to that reported for aluminum chloride catalyzed Diels–Alder reactions.[11] A benzene solution of 1,3-cyclohexadiene[8] was added dropwise to a stirred solution of a 5:1 mixture of ethyl acrylate and aluminum chloride in benzene at 50–55 °C over a 3-h period. The reaction mixture was stirred for an additional 8 h after the addition was complete. Workup and fractional distillation gave the ester in 80% yield, bp 106 °C (15 mm) [lit.[8] bp 98–100 °C (12 mm)]. GC analysis showed the ester to be 98% endo isomer. The ester was converted to **1** using the method of Grob et al.,[8] along with some modifications of Wilcox et al.,[25] mp 58–60 °C (after sublimation at 50 °C (10 mm); lit.[8] mp 57 °C).

**Bicyclo[3.2.2]nona-6,8-diene (2)** was prepared in the same manner as **1**. The procedure of Grob et al.[8] for the preparation of 1,3-cyclohexadiene was used to prepare 1,3-cycloheptadiene from 3-chlorocycloheptene (bp 88 °C (45 mm); 68% yield from cycloheptene) in 62% yield, bp 112–114 °C (650 mm) [lit.[26] bp 120–121.5 °C (758 mm)]. 8-Carbethoxybicyclo[3.2.2]non-6-ene was obtained in 53% yield using the aluminum chloride catalyzed Diels–Alder reaction described above and stirring the reaction for 62 h, bp 110–113 °C (6 mm). GC showed that the ester was 98.5% exo isomer.

Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.17; H, 9.34. Found: C, 74.57; H, 9.32.

The bicyclic ester was converted to **2** using the same seven-step procedure used to prepare **1**. The hydrazide was obtained as a white solid [mp 90–91 °C (from benzene)]. The carbamate was obtained as a thick oil and was reduced without purification to the monomethylamine, bp 77–78 °C (14 mm). The dimethylamine, a colorless oil, bp 80 °C (4.5 mm), was converted to the *N*-oxide, a white waxy solid. The *N*-oxide was decomposed to the diene, without purification or drying, at 90–115 °C in 74% yield. **2** was obtained as a white waxy solid that sublimed readily at 75 °C (20 mm), mp 89–91 °C (st) (lit. mp 83–84[13a] and 84 °C[13b]). The NMR spectrum was in agreement with that reported for **2**.[13b] **2** showed UV absorption (ethanol) at 205 nm ($\epsilon$ 4040) and 245 (41).

**Bromine Addition to 2.** A solution of 320 mg (2.0 mmole) of freshly distilled bromine in 10 mL of carbon tetrachloride was added dropwise to an ice-cold solution of 240 mg (2.0 mmol) of **2** in 10 mL of carbon tetrachloride, and the reaction mixture was stirred for an additional 24 h after addition was complete. Removal of solvent on a rotary evaporator left 560 mg (100%) of dibromide as a light orange oil. TLC indicated the presence of two components. The mixture was separated on a slurry-packed Florisil column using hexane as the eluting solvent. The major component (89% by NMR) was a colorless oil, and it was assigned the structure of the 1,2-addition product, *trans*-8,9-dibromobicyclo[3.2.2]non-6-ene (**7**), by analogy to the reaction of bromine with **1**[10,17] and on the basis of the following spectral data: IR (neat) 3055 (m, vinyl hydrogens), 1640 (m, double bond), 710 (s, cis disubstituted double bond) cm$^{-1}$; NMR ($CCl_4$) $\delta$ 1.15–1.95 (m, 5 H, propyl bridge), 2.42 (m, 2 H, bridgehead), 2.72 (m, 1 H, hydrogen of the propyl bridge over the endo bromine), 4.47 (poorly resolved quintet, 1 H, exo CHBr), 5.25 (broad d, 1 H, endo CHBr), 5.35–5.74 (m, 1 H, vinyl), 6.09 (q, 1 H, vinyl hydrogen across from exo bromine).

Anal. Calcd for $C_9H_{12}Br_2$: C, 38.61; H, 4.32. Found: C, 38.44; H, 4.31.

The minor component (11% by NMR) appeared to be pure by TLC, but NMR spectroscopy indicated it to be a mixture of *syn*- and *anti*-6,9-dibromotricyclo[3.2.2.0$^{7,8}$]nonane (**6**), although the exact ratio of the two isomers could not be determined. The structural assignment was based on the following spectral data: IR (neat) 3030 cm$^{-1}$ (w, cyclopropyl hydrogens), no double-bond absorption; the NMR spectrum ($CCl_4$) was weak but indicated absorptions at $\delta$ 1.25 (m, cyclopropyl), 1.59 (m, propyl bridge), 2.42 (m, bridgehead), 2.82 (m, hydrogen over endo bromine) 4.30 (m, CHBr of syn isomer), 4.42 and 5.21 (m, CHBr of anti isomer). Due to the small amount of tricyclic dibromide isolated, no elemental analysis was obtained.

**3,3-Dimethyl-1,4-pentadiene (3)** was prepared by the method of Ciola and Burwell,[14] bp 65–66 °C (650 mm) [lit.[14] bp 70.2 °C (750.5 mm)].

**2-(Acetoxymethyl)norbornadiene (8).** 2-(Hydroxymethyl)norbornadiene was prepared according to the procedure of Graham et al.,[27] bp 96–97 °C (8 mm) [lit.[27] bp 100–103 °C (9–11 mm)], and acetylated using acetic anhydride and sodium acetate,[28] bp 103–105 °C (25 mm) [lit.[27] bp 80–82 °C (4 mm)].

**1-(Hydroxymethyl)quadricyclane (12a) and 1-(acetoxymethyl)quadricyclane (12b)** were obtained by irradiating a 2% ether solution of 2-(hydroxymethyl)- or 2-(acetoxymethyl)norbornadiene (**8**) for 20 h in a Rayonet photochemical reactor.[29] IR and NMR spectroscopy showed the loss of double bond and the appearance of cyclopropyl hydrogens. GC analysis showed the alcohol to be 90% pure and the acetate 95% pure. Due to the instability of these quadricyclanes, no elemental analyses were obtained; the ether solutions from photolysis were used directly for the cycloaddition reactions.

**Cycloaddition Reactions with TCNE.[30] A. 9,9,10,10-Tetracyanotetracyclo[5.3.0.0$^{2,4}$.0$^{3,8}$]decane (4).** To a yellow solution of 0.35 g (2.7 mmol) of TCNE in 3 mL of benzene was added 0.50 g (4.7 mmol) of bicyclo[2.2.2]octa-2,5-diene (**1**). The resulting orange-amber colored solution was refluxed with stirring for 30 h (after 6 h, the solution had become noticeably darker and a precipitate had formed) and then cooled in an ice bath. The crystals were suction filtered to give 0.48 g (75%) of a grayish-brown amorphous solid, which gave white needles on recrystallization from benzene, mp 244–245 °C. The overall yield of adduct was about 85% based on workup of material from the mother liquors. Assignment of structure **4** to the adduct was based on the following spectral data: NMR $\delta$ 1.25 (broad m, 1 H, cyclopropyl), 1.45 (broad s, 2 H, cyclopropyl), 1.70 (broad s, 4 H, ethano bridge), 2.05 (m, 1 H, bridgehead), 3.50 (broad s, 2 H, bridgehead); IR (KBr) 3040 (w, cyclopropyl hydrogens), 2250 (w, unconjugated nitrile) cm$^{-1}$, no double-bond absorption.

Anal. Calcd for $C_{14}H_{10}N_4$: C, 71.79; H, 4.30. Found: C, 71.53; H, 4.22.

**B. 10,10,11,11-Tetracyanotetracyclo[6.3.0.0$^{2,4}$.0$^{3,9}$]undecane (5).** To a heavy-walled tube containing 200 mg (1.6 mmol) of TCNE and a few crystals of hydroquinone was added a solution of 100 mg (0.84 mmol) of bicyclo[3.2.2]nona-6,8-diene (**2**) in 0.7 mL of benzene. The tube was flushed with nitrogen, cooled, sealed, and heated in an oil bath at 140–145 °C for 15 h. After cooling, the tube was opened and the dark contents were dissolved in excess benzene and filtered hot to remove the insoluble residue. After concentration and cooling, the benzene solution yielded 50 mg (24%) of light brown platelets. Decolorization with activated carbon and two recrystallizations from benzene gave 10 mg of white platelets, mp 235–236 °C. Structure **5** was assigned to the adduct on the basis of the following spectral data: NMR $\delta$ 1.00 (m, 1 H, cyclopropyl), 1.48 (broad s, 2 H, cyclopropyl), 1.75 (m, overlapped with cyclopropyl hydrogens, 6 H, propyl bridge), 2.10 (m, 1 H, bridgehead), 3.71 (broad s, 2 H, bridgehead); IR (KBr) 3025 (w, cyclopropyl hydrogens), 2250 (w, unconjugated nitrile) cm$^{-1}$, no double-bond absorption.

Anal. Calcd for $C_{15}H_{12}N_4$: C, 72.56; H, 4.87. Found: C, 72.57; H, 5.01.

**C. 2-Acetoxymethyl-8,8,9,9-tetracyanotetracyclo-[4.3.0$^{2,4}$.0$^{3,7}$]nonane (9).** To a solution of 130 mg (1.0 mmol) of TCNE in 3 mL of benzene was added 170 mg (1.0 mmol) of 2-(acetoxymethyl)norbornadiene (**8**) and a few crystals of hydroquinone. No apparent reaction had taken place on standing for 2 days at room temperature. Refluxing for 1 h caused the initial red color to fade to an orange-amber color. Evaporation of solvent left an orange crystalline mass which was recrystallized from 3 mL of benzene to give 120 mg (41%) of tan platelets. After decolorization with activated carbon and two recrystallizations from benzene, the product was obtained as white platelets: mp 147.5–148.5 °C; IR (KBr) 3070 (w, cyclopropyl hydrogens), 2250 (w, unconjugated nitrile) cm$^{-1}$, no double-bond absorption; NMR data is given in the text.

Anal. Calcd for $C_{16}H_{12}N_4O_2$: C, 65.74; H, 4.15; N, 19.17. Found: C: 65.55; H, 4.23; N, 19.60.

**D. 8-Hydroxymethyl-3,3,4,4-tetracyanotricyclo[4.2.1.0$^{2,5}$]non-7-ene (13a).** A solution of 800 mg (6.5 mmol) of 1-(hydroxymethyl)quadricyclane (**12a**) in 10 mL of benzene was added all at once to a yellow solution of 210 mg (1.6 mmol) of TCNE in 10 mL of benzene. The yellow color disappeared instantaneously, and after a few minutes a colorless precipitate began to form. The solution was cooled and filtered to give 410 mg (100%) of a white powder, mp 171.5–173.5 °C dec. After two recrystallizations from ethylene dichloride and decolorization with activated carbon (material turned pink on heating), the product was a white powder, mp 175–176 °C. Repeated recrystallizations from ethylene dichloride failed to raise the melting point, but the elemental analysis remained slightly off for the compound named. The IR, NMR and mass spectra, however, were all consistent with the assigned structure **13a**: IR (KBr) 3540 (s, hydroxyl), 3020 (w, vinyl hydrogens), 2250 (w, unconjugated nitrile), 1620 (w, double bond), 1030 (s, C–O bond) cm$^{-1}$; NMR $\delta$ 1.82 (q, 2 H, methylene bridge), 3.05 (s, 2 H, cyclobutyl), 3.22 (broad s, 2 H, bridgehead), 3.75 (s, 1 H, OH), 4.02 (d, 2 H, $CH_2OH$), 5.88 (m, 1 H, vinyl); mass spectrum (70 eV), *m/e* (relative intensity) 250 (3, M$^+$), 232 (36, M$^+$ − $H_2O$).

Anal. Calcd for $C_{14}H_{10}N_4O$: C, 67.19; H, 4.03; N, 22.40. Found: C, 66.52; H, 4.31; N, 22.01.

**E. 8-Acetoxymethyl-3,3,4,4-tetracyanotricyclo[4.2.1.0$^{2,5}$]non-7-ene (13b).** To a solution of 82 mg (0.64 mmol) of TCNE in 25 mL of ether was added all at once a solution of 100 mg (0.61 mmol) of 1-(acetoxymethyl)quadricyclane (**12b**) in 10 mL of ether. The light orange color of the TCNE-ether complex disappeared in about 10 s, and after about 30 s a white precipitate began to form. The solution was allowed to stand at room temperature for 2 h and then was cooled and filtered with suction to give 150 mg (79%) of a white powder, mp 163–165 °C. The product was recrystallized twice from a 1:1 mixture of ethylene dichloride–hexane (benzene was not suitable for recrystallization since it seemed to complex with the product) to give white needles, mp 167–168 °C. Structure **13b** was assigned to the product on the basis of its spectral data: IR (KBr) 3005 (w, vinyl hydrogens), 2250 (w, unconjugated nitrile), 1720 (s, acetate carbonyl), 1640 (w, double bond), 1035 (m, C–O bond) cm$^{-1}$; NMR $\delta$ 1.84 (q, 2 H, methylene bridge), 2.07 (s, 3 H, acetate methyl), 3.07 (poorly resolved d, 2 H, cyclobutyl), 3.25 (broad s, 2 H, bridgehead), 4.62 (broad s, 2 H, $CH_2$ adjacent to acetate), 6.02 (m, 1 H, vinyl).

Anal. Calcd for $C_{16}H_{12}N_4O_2$: C, 65.74; H, 4.14; N, 19.18. Found: C, 65.55; H, 4.33; N, 19.41.

**Attempted Cycloaddition Reactions. A. Bicyclo[2.2.2]octa-2,5-diene (1) with Dimethyl Acetylenedicarboxylate.** To a solution of 670 mg (4.7 mmol) of dimethyl acetylenedicarboxylate in 3 mL of benzene was added 500 mg (4.7 mmol) of **1**. After stirring at reflux for 4 days, a small amount of waxy precipitate was observed. Solvent and unreacted starting materials were removed on a rotary evaporator to leave about 50 mg of an orange waxy material. Attempts to isolate the adduct from this material by chromatography on alumina were unsuccessful. The same reaction was carried out in a heavy-walled tube (sealed under nitrogen) at 100 °C for 36 h. Distillation of the contents of the tube yielded only benzene and dienophile.

Catalysis of the reaction with aluminum chloride was attempted. To a stirred solution of 125 mg (0.94 mol) of aluminum chloride in 4 mL of benzene heated at 50 °C was added dropwise 670 mg (4.7 mmol) of dimethyl acetylenedicarboxylate in 2.0 mL of benzene. After addition was complete, a solution of 500 mg (4.7 mmol) of **1** in 2.0 mL of benzene was added slowly over a 30-min period while the reaction mixture was maintained at 50–55 °C. The mixture was stirred at 50–55 °C for an additional 8 h and then cooled in an ice bath while 2 mL of 5% hydrochloric acid was added. The layers were separated, and the benzene layer was washed once with water and dried over sodium sulfate. Chromatography on alumina gave only starting material and a trace of yellow amorphous material. The experiment was repeated using a 2:1 molar excess of aluminum chloride to dienophile and the reaction mixture was stirred at 50–55 °C for 25 h after addition of the diene. Workup and removal of solvent left 1 g of a viscous orange oil which yielded no adduct on chromatography on alumina.

**B. Bicyclo[3.2.2]nona-6,8-diene (2) with Dimethyl Acetylenedicarboxylate.** To a solution of 120 mg (1 mmol) of **2** in 1 mL of benzene was added 142 mg (1 mmol) of dimethyl acetylenedicarboxylate and a few crystals of hydroquinone. The mixture was sealed in a heavy-walled tube under nitrogen and heated at 150 °C for 24 h. Removal of solvent left a red tarry residue. Attempts to purify this residue by chromatography on silica gel failed to yield any cycloaddition product.

**C. Reactions of 3,3-Dimethyl-1,4-pentadiene (3). With TCNE.** To a solution of 2.5 g (0.026 mol) of **3** in 20 mL of benzene was added 2.0 g (0.016 mol) of TCNE, and the resulting light amber solution was refluxed for 9 h. Workup gave only recovered TCNE. Heating the solution in a sealed tube at 140–145 °C for up to 52 h also produced no adduct.

**With Dimethyl Acetylenedicarboxylate.** A solution of 3.0 g (0.031 mol) of **3**, 3.0 g (0.021 mol) of dimethyl acetylenedicarboxylate, and a few crystals of hydroquinone was refluxed for 6 h. Distillation of unreacted diene and dienophile from the reaction mixture left a trace of a viscous oil in which none of the adduct could be detected.

**With Maleic Anhydride and *N*-Phenylmaleimide.** A mixture of 0.5 g (5.2 mmol) of **3**, 1 mmol of maleic anhydride or *N*-phenylmaleimide, and 0.25 mL of chloroform was heated at 50 °C for 1 week. NMR analysis showed that no reaction had occurred. The experiments were repeated at a higher temperature by heating 0.7 g (7.3 mmol) of **3**, 5 mmol of maleic anhydride or *N*-phenylmaleimide, and 1 mL of dry diglyme at 125–130 °C for 2 days in a tube sealed under nitrogen. Workup gave no detectable amounts of cycloadduct. The experiment was repeated at 190 °C for 3 days in the absence of solvent. No reaction occurred with the *N*-phenylmaleimide, but some brown oil was produced in the maleic anhydride case. Attempts to purify this material by column chromatography failed. Although the IR spectrum of the material showed some aliphatic absorption, the NMR spectrum was very complex and no definite structure could be assigned.

**Registry No.**—**1**, 500-23-2; **2**, 7164-08-1; **3**, 1112-35-2; **4**, 61822-60-4; **5**, 67271-14-1; **6** (isomer 1), 67271-15-2; **6** (isomer 2), 67335-53-9; **7**, 67271-16-3; **8**, 56682-74-7; **9**, 67271-17-4; **12a**, 56682-76-9; **12b**, 56682-75-8; **13a**, 67271-18-5; **13b**, 67271-19-6; *endo*-5-carbethoxybicyclo[2.2.2]oct-2-ene, 67335-54-0; *exo*-8-carbethoxybicyclo[3.2.2]non-6-ene, 23217-51-8; *exo*-8-carbethoxybicyclo[3.2.2]non-6-ene hydrazide, 23217-54-1; 8-(methylamino)bicyclo[3.2.2]non-6-ene, 67271-20-9; 8-(dimethylamino)bicyclo[3.2.2]non-6-ene, 67271-21-0; 8-(dimethylamino)bicyclo[3.2.2]non-6-ene *N*-oxide, 67271-22-1; 1,3-cyclohexadiene, 592-57-4; ethyl acrylate, 140-88-5; 1,3-cycloheptadiene, 4054-38-0; 3-chlorocycloheptene, 35021-99-9; bromine, 7726-95-6; TCNE, 670-54-2; dimethyl acetylenedicarboxylate, 762-42-5; maleic anhydride, 108-31-6; *N*-phenylmaleimide, 941-69-5.

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