benzene under a nitrogen atmosphere there was added dropwise with stirring a solution of 274 mg of sodium sulfide nonahydrate in 50 mL of a 1:1 mixture of ethanol and benzene. When the addition was complete, the solution was stirred overnight at room temperature. The mixture was then poured into 100 mL of a 10% aqueous solution of sodium bicarbonate and extracted with 200 mL of ether. The organic layer was washed with water, dried, and concentrated to give 170 mg (92%) of white crystals. Recrystallization of a sample from ethanol gave white crystals; mp 131.5–133.0 °C; ^{1}H NMR δ 6.63 (2 H, s, ArH), 3.50 (4 H, s, CH_2S), 3.30 (16 H, s, CH_2); mass spectrum, *m/e* 319, 318, 303, 289, 176, 175, 174, 173, 144, 143, 142, 141. Anal. ($C_{22}H_{22}S$) C, H.

Acknowledgment. We thank the National Science Foundation for their support of this investigation. P. F. T. Schirch thanks the Conselho Nacional de Desenvolvimento Cientifico e Tecnologico do Brasil (CNP_q) for a graduate fellowship.

Formation of [9]- and [10]Paracyclophane Derivatives in Cycloaddition Reactions[1]

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Abstract: Reactions of tetracyclopropylethylene (**1a**) and *cis*-1,2-dicyclopropylstilbene (**1b**) and its trans isomer (**1c**) with TCNQ gave 5,6-disubstituted [10]paracyclophane-4,6-dienes (**2**) in 50–70% yields. In a similar manner, 1-alkyl- or 1-phenyl-substituted 1-cyclopropyl-1,3-butadiene (**3a–g**) reacted with TCNQ to produce 5-substituted [9]paracyclophane-3,5-diene derivatives (**4**) in 15–89% yields. Reductive decyanation of **2** yielded hydrocarbons **5** and **6**, whereas the same reaction of **4** resulted in the cleavage of the cyclophane ring. All the products possessed a cis,trans configuration at the diene portion irrespective of the stereochemistry of the starting olefin **1** and **3**. The cycloaddition will, therefore, be most neatly rationalized by an assumption that it is a stepwise process involving a zwitterion possessing a transoid allylic cation portion. An intramolecular attack of the dicyano-bearing carbanion at the methylene carbon of the cyclopropyl group, which is activated by the allylic cation moiety, will produce **2** and **4** with the generation of the cis double bond. In contrast to **3a–g**, parent 1-cyclopropyl-1,3-butadiene (**3h**) failed to give a paracyclophanediene, but produced Diels–Alder adducts **9** and **10** in 34 and 28% yields, respectively. **10** is a cycloadduct of **3h** with methylenemalononitrile, which may be generated in situ by the fragmentation of **12**, a presumed [2 + 2] cycloadduct of **3h** with TCNQ. Supporting evidence was provided by the usage of **3h**-d_2 as the substrate.

Since a vinylcyclopropane moiety can be considered as a homo-1,3-diene unit, considerable efforts have been devoted to incorporate such a unit in the cycloaddition reactions.[2-4] We also studied sometime ago the reactions of several cyclopropyl-substituted ethylenes with a variety of reagents.[5] Although the reaction involving such a unit in the transformation has been realized in some cases, somewhat unusual reactions, in which merely the cyclopropane σ bond is involved, have also been uncovered by us. For example, the reaction of tetracyclopropylethylene (**1a**)[6] and related olefins with ethenetetracarbonitrile (TCNE) does not produce a homo-Diels–Alder adduct, but gives a vinylcyclopentane.[5a,b,k] The reaction of dispiro[2.2.2.2]deca-4,9-diene has revealed another case.[5h] The dispiro compound reacts with a number of 1,3-dienes at 160 °C in a stepwise diradical fashion to afford an [8]paracyclophanene derivative, but it reacts smoothly with 3,6-bis(dicyanomethylene)-1,4-cyclohexadiene (TCNQ) at a much lower temperature (60 °C), and a [3.3]paracyclophane is produced.[5h] Since the homolysis of the σ bond in the dispiro compound occurs very slowly at 60 °C, the cycloaddition should proceed in a process different from the diradical pathway in the [3.3]paracyclophane formation. Since smooth reactions are realized particularly in a donor–acceptor pairing of the two reactants, a plausible candidate of the reactive species, in which the prior rupture of the cyclopropane σ bond should occur, will be a cation radical[7] produced in an electron transfer from a cyclopropylethylene to a strongly electron-demanding TCNE or TCNQ. The fact that heavily substituted cyclopropylethylenes as well as the dispiro compound possess a

(1) Preliminary accounts of the present paper: Kataoka, F.; Nishida, S. *J. Chem. Soc., Chem. Commun.* **1978**, 864; *Chem. Lett.* **1978**, 1053. The present work was supported by a Grant-in-Aid for Scientific Research (No. 547017) provided by the Ministry of Education, Science and Culture of Japan.

(2) Sarel, S.; Breuer, E. *J. Am. Chem. Soc.* **1959**, *81*, 6522. Pasto, D. J.; Chen, A. F.-T. *Tetrahedron Lett.* **1973**, 713. Sarel, S.; Felzenstein, A.; Yovell, J. *J. Chem. Soc., Chem. Commun.* **1973**, 859; **1974**, 753; *Tetrahedron Lett.* **1976**, 451. Sarel, S.; Langbeheim, M. *J. Chem. Soc., Chem. Commun.* **1977**, 593. Langbeheim, M.; Sarel, S. *Tetrahedron Lett.* **1978**, 1219; **1978**, 2613.

(3) For fused vinylcyclopropanes, see: Löffler, H. P.; Martini, T.; Musso, H.; Schröder, G. *Chem. Ber.* **1970**, 2111. Paquette, L. A.; Kirschner, S.; Malpass, J. R. *J. Am. Chem. Soc.* **1970**, *92*, 4330. Toong, Y. C.; Borden, W. T.; Gold, A. *Tetrahedron Lett.* **1975**, 1549. Subrahmanyam, G. *Indian J. Chem., Sect. B* **1976**, *14B*, 365. Cernuschi, P.; DeMicheli, C.; Gandolfi, R. *Tetrahedron Lett.* **1977**, 3667. Scott, L. T.; Brunsvold, W. R. *J. Chem. Soc., Chem. Commun.* **1978**, 633.

(4) Unsuccessful homo-Diels–Alder reactions have also been reported: Van Volkenburgh, R.; Greenlee, K. W.; Derfer, J. M.; Boord, C. E. *J. Am. Chem. Soc.* **1949**, *71*, 3595. Smith, L. I.; Rogier, E. R. *Ibid.* **1951**, *73*, 3840.

(5) (a) Nishida, S.; Moritani, I.; Teraji, T. *J. Chem. Soc., Chem. Commun.* **1971**, 36. (b) Nishida, S. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 328. (c) Nishida, S.; Moritani, I.; Teraji, T. *J. Org. Chem.* **1973**, *38*, 1878. (d) Shimizu, N.; Nishida, S. *J. Am. Chem. Soc.* **1974**, *96*, 6451. (e) Shimizu, N.; Ishikawa, M.; Ishikura, K.; Nishida, S. *Ibid.* **1974**, *96*, 6456. (f) Shibata, T.; Tsuji, T.; Nishida, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2039. (g) Shimizu, N.; Fujioka, T.; Ishizuka, S.; Tsuji, T.; Nishida, S. *J. Am. Chem. Soc.* **1977**, *99*, 5972. (h) Tsuji, T.; Shibata, T.; Hienuki, Y.; Nishida, S. *Ibid.* **1978**, *100*, 1806. (i) Kataoka, F.; Shimizu, N.; Nishida, S. *Ibid.* **1980**, *102*, 711. (j) Shibata, T.; Tsuji, T.; Nishida, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 709. (k) Kataoka, F.; Nishida, S. *Chem. Lett.* **1980**, 1115. (l) Hienuki, Y.; Tsuji, T.; Nishida, S. *Tetrahedron Lett.* **1981**, 863.

(6) Nishida, S.; Moritani, I.; Tsuda, E.; Teraji, T. *J. Chem. Soc., Chem. Commun.* **1969**, 781. Nierth, A.; Ensslin, H. M.; Hanack, M. *Liebigs Ann. Chem.* **1970**, *733*, 187. Teraji, T.; Moritani, I.; Tsuda, E.; Nishida, S. *J. Chem. Soc. C* **1971**, 3252.

(7) It has been recently demonstrated that the cleavage of a cyclopropane σ bond occurs in a cation radical generated in the sensitized photoreaction of 1,1,2,2-tetraphenylcyclopropane (Arnold, D. R.; Humphreys, R. W. R. *J. Am. Chem. Soc.* **1979**, *101*, 2743). The authors have suggested that the electron transfer will be equally feasible in the thermal reaction to result in the cleavage of a strained σ bond (see also: Mukai, T.; Sato, K.; Yamashita, Y. *J. Am. Chem. Soc.* **1981**, *103*, 670).

0002-7863/81/1503-6878$01.25/0

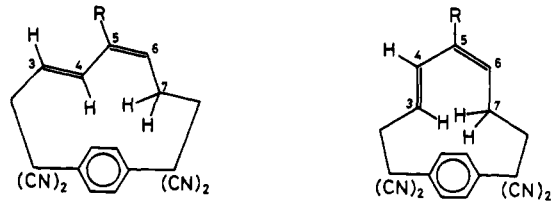
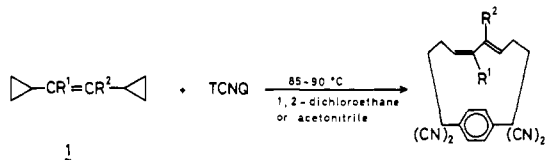


Figure 1. Two plausible conformers, s-trans and s-cis of 5-substituted *trans,cis*-[9]parapcyclophane-3,5-diene-1,1,9,9-tetracarbonitrile.

significantly low ionization potential has been previously uncovered.[5k,8] Accordingly, it is of interest to investigate further the reaction of **1a** and related olefins (**1b–f**) with TCNQ in place of TCNE. In fact, the reaction produced a [10]paracyclophane derivative (**2**) in a one-step operation. The reaction of 1-cyclopropyl-1,3-butadienes (**3**) with TCNQ proceeded in a similar manner, and [9]paracyclophanediene (**4**) was obtained in fair to good yields.

Results

[10]Paracyclophanediene Formation. Heating of a 1:1 mixture of **1a**[6] and TCNQ in acetonitrile at 85–90 °C for 15 days resulted in the formation of a 1:1 adduct in a 70% yield (based on the



1

a: $R^1=R^2=$cyclo-C_3H_5
b: $R^1=R^2=C_6H_5$-(cis)
c: $R^1=R^2=C_6H_5$-(trans)
d: $R^1=$cyclo-C_3H_5, $R^2=CH_3$
e: $R^1=$cyclo-C_3H_5, $R^2=H$
f: $R^1=R^2=H$

2

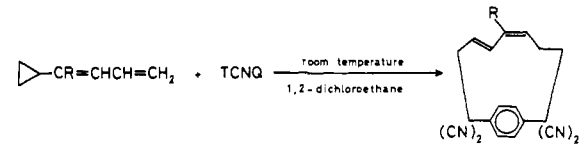
a: $R^1=R^2=$cyclo-C_3H_5
b: $R^1=R^2=C_6H_5$
c: $R^1=$cyclo-C_3H_5, $R^2=CH_3$

consumed amount, 76%, of **1a**). The same adduct was also obtained in 1,2-dichloroethane (85–90 °C, 15 days, 53% yield, 68% consumption). The ^1H NMR spectral examination indicated that the adduct held only two cyclopropyl groups and a benzene ring. Thus, the structure of the adduct was deduced as 5,6-dicyclopropyl[10]paracyclophane-4,6-diene-1,1,10,10-tetracarbonitrile (**2a**). All other data fit the proposed structure as well. Since **2a** showed two vinylic triplets in the ^1H NMR at different chemical shifts (δ 3.78, J = 5 Hz, and δ 4.94, J = 7.5 Hz),[9] the cis,trans configuration was assigned to the conjugated diene portion in **2a**. If the assigned configuration is accepted, the vinylic proton at the trans double bond will be located above the benzene ring, and hence it should resonate at a high magnetic field. This was indeed observed.

Similarly, *cis*-1,2-dicyclopropylstilbene (**1b**)[10] and its trans isomer (**1c**)[10] reacted with TCNQ to give **2b** in 50–56% yields. The cis,trans configuration was again suggested by the ^1H NMR spectral study of **2b**. A remarkable result noted was that both **1b** and **1c** yielded the same adduct **2b**. Although the mutual isomerization of **1b** and **1c** seemed to take place slowly under the reaction conditions, it was too slow to account for the formation of **2b** in the reactions of the two isomeric reactants.

Although the yield was relatively low, 1,1,2-tricyclopropylpropene (**1d**)[6] also gave *cis,trans*-5-cyclopropyl-6-methyl[10]-paracyclophane-4,6-diene-1,1,10,10-tetracarbonitrile (**2c**, 21% yield). A long-range coupling (J = 1.3 Hz) between the methyl proton and a trans-vinylic proton at the C-7 provides support for the assigned structure. In contrast to **1a–1d**, tricyclopropylethylene (**1e**)[6] and 1,2-dicyclopropylethylenes (**1f**)[6] failed to produce any isolable product; only a tarry residue was obtained.

[9]Paracyclophanediene Formation. In dichloromethane, the reaction of 1-cyclopropyl-1,3-butadienes (**3**) with TCNQ proceeded smoothly at room temperature. In order to avoid a



3

a: R = CH_3
b: R = C_2H_5
c: R = $CH(CH_3)_2$
d: R = $C(CH_3)_3$
e: R = cyclo-C_3H_5
f: R = C_6H_5-(Z)
g: R = C_6H_5-(E)

4

a: R = CH_3
b: R = C_2H_5
c: R = $CH(CH_3)_2$
d: R = $C(CH_3)_3$
e: R = cyclo-C_3H_5
f: R = C_6H_5

complication due to an extensive polymerization of **3**, a trace amount of *p*-hydroquinone was added to the starting mixture.[11] The dienes, **3a–g**, substituted by a group at the C-1, produced 5-substituted [9]paracyclophane-3,5-diene-1,1,9,9-tetracarbonitrile (**4**) in fair to good yields. The highest yield (89%) of the [9]-paracyclophanediene formation was achieved in the reaction of **3d**,[12] whereas **4e** was isolated in the poorest yield (15%).

In the reaction of a 1:1 mixture of **3f** and **3g**, **4f** was isolated in a 78% yield. Since only one isomer was obtained in a relatively high yield, the isomeric dienes might produce the same adduct. Indeed, the reaction of **3f** (97% pure) and **3g** (93% pure) with TCNQ in separate flasks gave the same **4f** in 67 and 61% yields, respectively. It is concluded, therefore, that the stereochemical integrity of the starting diene has been lost in the [9]paracyclophanediene formation. Accordingly, a mixture of geometrically isomeric dienes was used in subsequent experiments. Thus, the isolated yields of the adduct were **4a**, 42%; **4b**, 37%; and **4c**, 62%.

In all the adducts, the vicinal coupling constant between the two vinylic protons at C-3 and C-4 was ca. 16 Hz, suggesting a trans configuration at the C-3 double bond. For the configurational assignment of the C-5 double bond, the ordinary ^1H NMR data were no longer helpful. However, examinations of the molecular models suggest that the configuration may be deduced by the nuclear Overhauser effect (NOE).[13] In the trans,trans isomer of [9]paracyclophane-3,5-diene, none of the protons will come closer together in plausibly preferred conformations. In the trans,cis isomer, on the other hand, one of the allylic protons at the C-7 will be in close proximity to a vinylic proton either at C-3 or at C-4 depending upon the conformation of the side chain, s-cis or s-trans (Figure 1). The NOE experiments, carried out for **4a** and **4c** by irradiating the allylic protons at C-7 (δ 1.80 and 1.77, respectively), resulted in the enhancement of the signal intensity of the proton at C-4 (δ 4.76 and 4.79, respectively): **4a** (16.0 ± 1.0)% and **4c** (13.2 ± 1.7)%. The results thus allowed us to conclude that **4** is the trans,cis isomer, once again. As to the preferred conformation of the side chain, the NOE experiments indicates that the s-trans conformer predominates, except for **4d**. The irradiation of the *tert*-butyl protons of **4d** resulted in the increase in the signal intensity of the vinyl proton at C-4 [(15.0 ± 0.5)%], suggesting that this particular adduct takes the s-cis conformation due to the steric effect of the *tert*-butyl group.

Although the present cycloaddition proceeded smoothly in 1,2-dichloroethane, the reactions in a polar solvent were less promising. None of **4a** was obtained in the reaction of **3a** with

(8) (a) Nishida, S.; Moritani, I.; Teraji, T. *J. Chem. Soc., Chem. Commun.* **1972**, 1114. (b) Harada, Y.; Ohno, K.; Seki, K.; Inokuchi, H. *Chem. Lett.* **1974**, 1081. (c) Asmus, P.; Klessinger, M.; Meyer, L.-U.; de Meijere, A. *Tetrahedron Lett.* **1975**, 381.

(9) The fact that different coupling constants were observed for the two vinylic protons in **2a** also supports the cis,trans configuration of the chain.

(10) Nishida, S.; Kataoka, F. *J. Org. Chem.* **1978**, *43*, 1612.

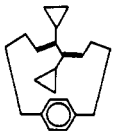
(11) It was indeed observed that the yield of the adduct was low in the absence of *p*-hydroquinone.

(12) A mixture of *E* and *Z* isomers in 95:5 ratio.

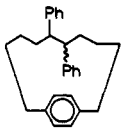
(13) Noggle, J. H.; Schirmer, R. E. "The Nuclear Overhauser Effect"; Academic Press: New York, 1971.

TCNQ in acetonitrile, and **4f** was isolated only in a 9% yield in the same solvent. The yield of **4e** was not improved by utilizing acetonitrile (10% yield) or nitromethane (13% yield) as the solvent. The reaction of 1,3,5-hexatriene with TCNQ under various conditions, including the reaction conditions similar to those for **3d** in 1,2-dichloroethane, gave no isolable product; only a tarry residue was produced.

Reductive Decyanation. On the treatment of **2a** with metallic sodium in liquid ammonia,[14] 5,6-dicyclopropyl[10]paracyclophane-4,6-diene (**5**) was produced in 78% yield. The diene



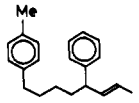
5



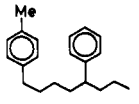
6

portion was not reduced. This may be because the two ethylenic linkages will be twisted by the two groups at C-5 and C-6 in such a way that no significant interaction takes place between them.[15] On the other hand, the reduction of **2b** gave 5,6-diphenyl[10]-paracyclophane (**6**) in 81% yield. In **2b**, the two double bonds are individually conjugated with the benzene ring and hence they were reduced.[15] The configuration of the two carbons bearing the phenyl group has not been clarified as yet.

In contrast to **2a** and **2b**, **4** gave the cyclophane-cleaved products under the reductive decyanation conditions. Thus, the treatment of **4f** with metallic sodium in liquid ammonia resulted in the formation of **7** and **8** in 5 and 11% yields, respectively. The



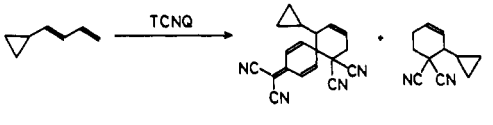
7



8

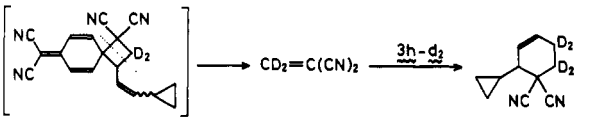
cleavage of the C-1–C-2 bond in **4** will produce an intermediate possessing benzylic and allylic structure for the two sites and hence a fission takes place under the reaction conditions.[16]

Reaction of 3h with TCNQ. In contrast to **3a–g**, parent 1-cyclopropyl-1,3-butadiene (**3h**)[5i] did not produce the corresponding [9]paracyclophanediene. In the reaction of *trans*-**3h** (88% pure), 7,7-dicyano-3-(dicyanomethylene)-11-cyclopropylspiro[5.5]-undeca-1,4,8-triene (**9**) and 2-cyclopropyl-3-cyclohexene-1,1-dicarbonitrile (**10**) were obtained in 34 and 28% yields, respectively. The reaction of *cis*-**3h** (>99% pure) gave no characterizable product. Although the formation of **9** is reasonable, **10** is an unexpected product. **10** might be prodced in the Diels–Alder



trans-**3h** **9** **10**

reaction of **3h** with methylenemalononitrile (**11**).[17] A possible source of **11** will be a [2 + 2] cycloadduct **12** of **3h** and TCNQ, which may split into **11** and a *p*-xylylene derivative. Such a fragmentation is similar to those observed in the thermolysis of 3-alkenylcyclobutane-1,1,2,2-tetracarbonitrile.[5i,18] The *p*-xylylene fragment may be too unstable to be isolated in the reaction.[19] In order to obtain a support for this possibility, 4,4-dideuterated substrate **3h**-d_2 (a mixture of trans and cis isomers in 80:20 ratio) was allowed to react with TCNQ. Besides 8,8-dideuterio **9** (23%),



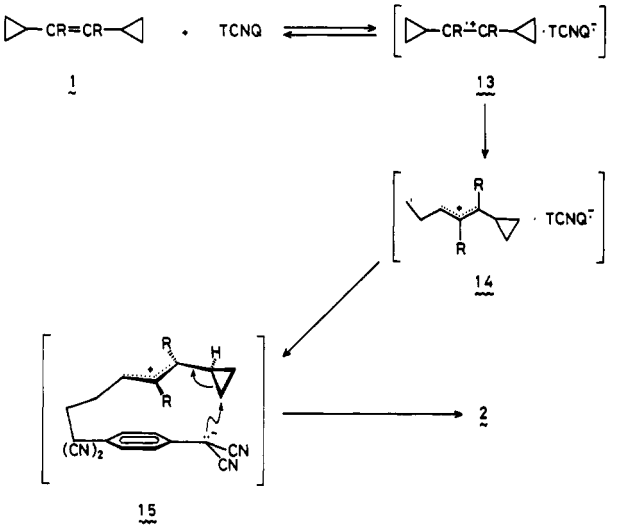
12-d_2 **11**-d_2 **10**-d_4

5,5,6,6-tetradeuterated **10**-d_4 was isolated in a 24% yield. Thus, **11** was most probably derived from **12**.

Discussion

Since **1a–g** were absolutely stable at 85–90 °C, the reaction should not be initiated by a thermal cleavage of the cyclopropane of **1**. Now, the [10]paracyclophanediene formation was most successfully achieved in the reaction of heavily substituted 1,2-dicyclopropylethylenes (**1a–c**) with TCNQ. In the reaction of **1d** the yield of **2c** was low (21%), and no [10]paracyclophanediene was isolated in the reactions of **1e** and **1f**. It reminded us that there have been two distinct reaction courses in the reaction of a variety of cyclopropylethylenes with TCNE.[5a–c,k] Namely, when the steric hindrance at the carbon–carbon double bond is not significant, TCNE attacks the π bond to afford a [$_\pi$2 + $_\pi$2] cycloadduct (type I reaction), whereas if the double bond is severely blocked, the reaction takes place with the cyclopropane σ bond to produce a vinylcyclopentane derivative, a [$_\pi$2 + $_\sigma$2] cycloadduct (type II reaction).[5k] In the analogy of these observations, the failure to obtain the [10]paracyclophanediene in the reaction of **1e** and **1f** will be rationalized by asserting that TCNQ will attack the olefinic carbon preferentially. The intermediate species thus produced will have no way to yield the isolable products. The cyclization similar to those giving [10]- and [9]paracyclophanediene should inevitably lead to the formation of a highly strained [7]paracyclophane derivative.[20]

The first step of the formation of **2** will be an electron transfer from **1** to TCNQ, as proposed in the previous reaction of **1** with TCNE.[5a,k,21] The radical cation **13** will then open its cyclopropane



1 **13** **14** **15**

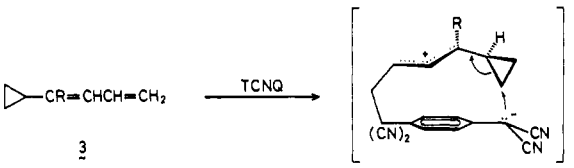
ring slowly to give the rearranged radical cation **14**.[7,22] A combination of **14** with a nearby TCNQ anion radical will give a zwitterion **15**. The cyclization may be accomplished by an in-

(14) Arapakos, P. G.; Scott, M. K.; Huber, F. E. *J. Am. Chem. Soc.* **1969**, *91*, 2059.
(15) (a) Birch, A. J.; Smith, H. *Q. Rev., Chem. Soc.* **1958**, *12*, 17. (b) Birch, A. J.; Subba Rao, G. *Adv. Org. Chem.* **1972**, *8*, 1.
(16) Reference 15b, p 30.
(17) The authentic sample of **10** was prepared in this manner.
(18) See also: Felzenstein, A.; Sarel, S.; Yovell, J. *J. Chem. Soc., Chem. Commun.* **1975**, 918.
(19) Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1968**, *90*, 2342.
(20) Allinger, N. L.; Walter, T. J. *J. Am. Chem. Soc.* **1972**, *94*, 9267. Wolf, A. D.; Kane, V. K.; Levin, R. H.; Jones, M., Jr. *Ibid.* **1973**, *95*, 1680.
(21) The charge-transfer complex may be involved prior to the electron-transfer step. We, however, could not prove the intermediacy of such a complex in the present reaction, and hence the charge-transfer complex formation is not shown in the scheme (Cf.: Bartlett, P. D. *Q. Rev., Chem. Soc.* **1973**, *24*, 473).
(22) The electron-transfer step will be reversible and the first cyclopropane cleavage will be a difficult step. The fact that the mutual isomerization of **1b** and **1c** under the reaction conditions took place very slowly might imply the practical nonreversibility of **14** back to **13**.

tramolecular attack of the cyano-bearing carbanion at the methylene carbon of the second cyclopropyl group, as shown in the scheme. Attack of a nucleophile at the cyclopropyl methylene carbon accompanied by the ring opening is known to occur when the cyclopropyl group is activated by electron-withdrawing substituents.[23] In the present case, the allylic cation portion will be playing a role in activating the cyclopropyl group.

The fact that both **1b** and **1c** produced the same adduct **2b** will be an outcome of easy isomerization at the intermediate stages. The configurational isomerization of the allyl cation is known to occur readily when the cation is substituted by suitable group(s) at the terminal carbon atom.[24] Now, the most interesting result obtained in the [10]paracyclophanediene formation is the specific production of the cis,trans isomer. This may be rationalized in the following manner. According to Danishefsky,[23b] the spiro mode of attack is strongly preferred in the intramolecular nuclephilic ring openings of doubly activated cyclopropanes, such as a carbanion derived from 2-[ω,ω-bis(alkoxycarbonyl)alkyl]cyclopropane-1,1-dicarboxylates. In order to account for the results, Danishefsky et al.[23c] have suggested that the preference may lie in a greater facility for backside attack via the spiro mode. If we assume similarly facile backside attacks in the present reaction, the structure shown in **15**, namely, with the allyl cation in a transoid,transoid configuration and the cyclopropyl group in a s-cis bisected conformation (*ttc* structure), will be the best one to suffer the backside attack, as indicated by the examinations of molecular models. The cycloaddition would then result in the formation of a *trans,cis*-[10]paracyclophane-4,6-diene. There will be two more structures for the zwitterion to be considered, namely, one with a transoid,transoid allylic portion with a s-trans cyclopropane (*ttt* structure) and the other with a cisoid,transoid allyl cation and a s-trans cyclopropane (*ctt* structure). The examinations of the molecular models indicate, however, that the carbanion in the *ttt* zwitterion cannot take the proper position to attack the cyclopropane in the manner described above, provided that favorable conformations are considered for the remaining part of the chain. In the *ctt* structure, the backside attack similar to that considered in the *ttc* intermediate will be feasible, but the steric strain at the cisoid portion will make the *ctt* structure unstable.

A similar reaction scheme could be drawn for the [9]paracyclophanediene formation, except for the first step. In the reaction of **3**, TCNQ may attack the terminal carbon of the diene to form

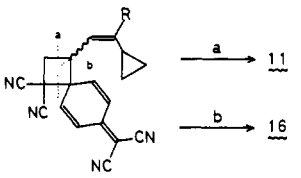


3 16

4

a zwitterion **16**. Since the first step requires no prior cyclopropane cleavage, the reaction proceeds smoothly at room temperature. In this reaction, the adduct with the trans,cis configuration at the diene portion was again produced. Since the side chain in **16** is one carbon atom shorter than that in **15**, the intramolecular nucleophilic attack in the same manner as discussed in the reaction of **15** will be possible either in **16** (*ttc* structure) or in a zwitterion with the *ttt* structure. The experimental results indicate that the cyclization is achieved from the *ttc*-**16**.[25] This may be due to the steric destabilization of the *ttt* zwitterion; e.g., the steric interaction between the substituent R and the cyclopropane methylene groups will make the s-trans conformer less stable.

Now, in the reaction of parent 1-cyclopropyl-1,3-butadiene, only the trans isomer produced **9** and **10**. This is because *trans*-**3h** can take the s-cis conformation requisite to accomplishing the Diels–Alder reaction,[5i,26] whereas *cis*-**3h** can hardly take such a conformation. The cis isomer will react with TCNQ to produce **12**, from which **11** should be generated, but **11** cannot react successfully with *cis*-**3h**, and hence it will be consumed in the polymer formation.[27] In the reactions of **3a–g**, a [2 + 2] cycloadduct **12** (R $\neq$ H) may also be produced, but a favorable route for such a cycloadduct will be a reverse transformation, giving back **16**.[5i] The reaction will thus ultimately produce **4** if **12** were produced. Only in **12** (R = H) does the fragmentation become feasible, which may be in accord with the previous results.[5i] In the present reaction, **12** was not isolated. This may be due to the



12

structural features of the spiro compound **12**, since the cleavage of the cyclobutane ring, either in a homolytic fashion or in a heterolytic manner, results in the formation of a stable dicyanobenzylic system.

The cyclopropane cleavage at the final stage of the cyclization seems to be essential. In an attempted reaction, 1,3,5-hexatriene was allowed to react with TCNQ under similar conditions, but the reaction failed to give any isolable product. The terminal carbon atom in the resultant pentadienyl cation may be very reactive to attack another triene, and hence the intermediate zwitterion would not last long enough to suffer an intramolecular attack, which should be by no means a favorable process judging from the probability factor. As to the effect of solvent polarity on the yield of **4**, it may be argued that **16** will be in an extended shape in a polar solvent, to an extent greater than that in a less polar solvent, which is not a good conformation to achieve the intramolecular cyclization. Accordingly, the intermediate will have more chance to react with the second molecule of **3** to result in a lowering of the yield of **4**. In the [10]paracyclophanediene formation, on the other hand, the reaction in acetonitrile gave a result comparable to that obtained in 1,2-dichloroethane. This is because the π bond in **1a–c** is not sufficiently reactive to suffer an attack by **15**, hence the cyclization will take place effectively in the polar solvent as well. The reason for the fact that the reaction in 1,2-dichloroethane proceeds as fast as that in acetonitrile is not fully understood as yet, but it can be pointed out that the type II reaction of **1a** with TCNE[5k] also exhibits even greater reaction rates in halogen-containing solvents than those observed either in acetonitrile or in nitromethane.[28]

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(25) The cyclization of **16** requires an approach of the two reacting centers in a manner similar to that forming a strained [8]paracyclophane ring system. However, we previously observed that the [8]paracyclophan-4-ene formation was accomplished with high efficiency in the reaction of dispiro[2.2.2.2]-deca-4,9-diene with 1,3-dienes.[5h] Accordingly, **16** may cyclize without severe difficulty.

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(28) Relative rates at 50 °C in various solvents were acetonitrile 1.0, nitromethane 2.3, nitroethane 1.4, nitropropane 1.0, dichloromethane 5.2, 1,1,2-trichloroethane 7.6, and 1,1,2,2-tetrachloroethane 21. A possibility that the heavy-atom effect operates to change the spin state of **13** in such a way that the dissociation of **13** back to **1** and TCNQ is depressed may account for the results.

Experimental Section

IR spectra were recorded on a Hitachi 215 grating infrared spectrophotometer. UV spectra were taken on a Cary Model 17 spectrophotometer. NMR spectra were measured with tetramethylsilane as an internal standard by using a JEOL PS-100 spectrometer. Mass spectra were recorded on a Hitachi Model RMU-6E spectrometer; ions of each spectrum were normalized to the most intense ion set equal to 100, and the relative intensity is given in parentheses. Gas chromatography was carried out by using a Hitachi 063 gas chromatograph. Microanalyses were performed by the Center for Instrumental Analysis of Hokkaido University. Melting points and boiling points are uncorrected.

Preparations of **1a**,[6] **1b**, **1c**,[10] **1d**, **1e**, **1f**,[6] **3a**, **3e**, and **3h**[5i] have been described previously. TCNQ, mp 293–295 °C, was prepared as described in the literature and recrystallized several times from acetonitrile (lit.[29] mp 293.5–296 °C). Dienes **3b**, **3c**, **3d**, **3f**, **3g**, and **3h**-d_2 were synthesized by the dehydrobromination of the corresponding 1-alkyl-4-bromo-1-cyclopropyl-1-butene,[30] which in turn was obtained in the reaction of 1-alkyl-1,1-dicyclopropylmethanol with hydrobromic acid.[30]

1-Alkyl-1,1-dicyclopropylmethanols. The reaction of dicyclopropyl ketone with alkylmagnesium halide gave 1,1-dicyclopropyl-1-propanol (80%), bp 74–77 °C (19 mmHg) (lit. bp 75–78 °C (16.5 mmHg),[31] bp 67.5–69 °C (10 mmHg)[32]), 1,1-dicyclopropyl-2-methyl-1-propanol (80%), bp 65–66 °C (4 mmHg) (lit.[33] bp 81 °C (10 mmHg)), and 1,1-dicyclopropyl-2,2-dimethyl-1-propanol (37%), bp 70–74 °C (6 mmHg); IR (thin film) 3600, 3095, 1020 cm^{-1}; NMR (CCl_4) δ 0.1–0.5 (m, 8 H), 0.5 (br s, 1 H), 0.7–1.1 (m, 2 H), 1.03 (s, 9 H). Anal. ($C_{11}H_{20}O$) C, H.

1-Bromo-4-cyclopropyl-3-hexene. In a 500-mL three-necked flask fitted with a mechanical stirrer and a dropping funnel, 28 g (0.20 mol) of 1,1-dicyclopropyl-1-propanol was introduced. Under ice cooling, 103 g (0.60 mol) of 47% hydrobromic acid was added dropwise, and the resultant mixture was stirred for 20 min. The organic material was extracted with three 50-mL portions of hexane. The combined hexane solution was washed with brine followed by saturated aqueous solution of sodium hydrogen carbonate. The hexane solution was then dried over anhydrous magnesium sulfate and concentrated. Vacuum distillation of the resultant oil gave 29 g (71%) of a fraction boiled at 104–105 °C (17 mmHg), which was a 1:1 mixture of *cis*- and *trans*-6-bromo-3-cyclopropyl-3-hexene. Since the separation and purification of the geometrical isomers were troublesome, the mixture was used in the following experiments. IR (thin film) 1655, 1025, 820 cm^{-1}; NMR (CCl_4) δ 0.2–0.8 (m, 4 H), 0.99 (t, 1.5 H, J = 7.5 Hz), 1.04 (t, 1.5 H, J = 7.5 Hz), 1.1–1.6 (m, 1 H), 1.73 (q, 1 H, J = 7.5 Hz), 2.02 (q, 1 H, J = 7.5 Hz), 2.53 (d of t, 1 H, J = 7 and 7 Hz), 3.24 (t, 1 H, J = 7 Hz), 3.31 (t, 1 H, J = 7 Hz), 4.97 (t, 0.5 H, J = 7 Hz), 5.15 (t, 0.5 H, J = 7 Hz). Anal. ($C_9H_{15}Br$) C, H, Br.

1-Bromo-4-cyclopropyl-5-methyl-3-hexene. The treatment of 1,1-dicyclopropyl-2-methyl-1-propanol (29 g, 0.19 mol) with 47% hydrobromic acid (90 g, 0.57 mol) gave a fraction (36 g, 88%) boiling at 82–85 °C (8 mmHg), which was a 4:6 mixture of *cis*- and *trans*-1-bromo-4-cyclopropyl-5-methyl-3-hexenes: IR (thin film) 1650, 1025, 820 cm^{-1}; NMR (CCl_4) δ 0.2–0.8 (m, 4 H), 1.00 (d, 2.4 H, J = 7 Hz), 1.08 (d, 3.6 H, J = 7 Hz), 1.2–1.6 (m, 1 H), 1.6–2.0 (m, 1 H), 2.4–3.0 (m, 2 H), 3.24 (t, 1.2 H, J = 8 Hz), 3.30 (t, 0.8 H, H = 8 Hz), 4.81 (t, 0.4 H, J = 7 Hz), 5.18 (t, 0.6 H, J = 7 Hz). Anal. ($C_{10}H_{17}Br$) C, H, Br.

1-Bromo-4-cyclopropyl-5,5-dimethyl-3-hexene. The reaction of 1,1-dicyclopropyl-2,2-dimethyl-1-propanol (18 g, 0.11 mol) with 47% hydrobromic acid (55 g, 0.22 mol) gave a 5:95 mixture of *cis*- and *trans*-1-bromo-4-cyclopropyl-5,5-dimethyl-3-hexene (18 g, 73%), bp 80–83 °C (3 mmHg). The spectral bands for the trans isomer were assigned as follows: IR (thin film) 1640, 1035, 825 cm^{-1}; NMR (CCl_4) δ 0.4–0.6 (m, 2 H), 0.6–0.9 (m, 2 H), 1.1 (s, 9 H), 1.1–1.3 (m, 1 H), 2.76 (d of t, 2 H, J = 7 and 7 Hz), 3.30 (t, 2 H, J = 7 Hz), 5.27 (d of t, 1 H, J = 1.5 and 7 Hz). Anal. ($C_{11}H_{19}Br$) C, H, Br.

4-Cyclopropyl-1,3-hexadiene (3b), 4-Cyclopropyl-5-methyl-1,3-hexadiene (3c), 4-Cyclopropyl-5,5-dimethyl-1,3-hexadiene (3d), and 1-Cyclopropyl-1-phenyl-1,3-butadiene (3f and 3g). 1-Bromo-4-cyclopropyl-5-methyl-3-hexene (36 g, 0.166 mol) was treated with potassium *tert*-butyl alkoxide in *tert*-butyl alcohol (prepared from 8.5 g, 0.22 mol, of potassium and 170 mL of dry *tert*-butyl alcohol). After 20-min reflux, the reaction mixture was poured onto an ice–water mixture (500 mL). The organic material was extracted with 150 mL of hexane. The hexane solution was washed with two portions of water and dried over anhydrous calcium chloride. The solvent was then evaporated, and the residue was distilled. A fraction boiling at 67–70 °C (22 mmHg, 17.1 g, 71%) was a 4:6 mixture of *cis*-**3c** and *trans*-**3c**. The separation and purification of the geometrical isomers were unsuccessful. IR (thin film) 1640, 1600, 1025 cm^{-1}; UV (hexane) 240 (18,000) nm; NMR (CCl_4) δ 0.3–0.8 (m, 4 H), 1.04 (d, 3.6 H, J = 6.5 Hz), 1.12 (d, 2.4 H, J = 6.5 Hz), 1.0–1.7 (m, 1 H), 2.01 (heptet, 0.6 H, J = 6.5 Hz), 3.06 (heptet, 0.4 H, J = 6.5 Hz), 4.8–5.15 (m, 2 H), 5.48 (d, 0.4 H, J = 10.5 Hz), 5.82 (d, 0.6 H, J = 10.5 Hz), 6.52 (d of d of d, 0.4 H, J = 10.5, 10.5, and 16.5 Hz), 6.77 (d of d of d, 0.6 H, J = 10.5, 10.5, and 16 Hz). Anal. ($C_{10}H_{16}$) C, H.

In a similar manner, a 4:6 mixture of *cis*-**3b** and *trans*-**3b**, bp 57–58 °C (21 mmHg, 73%), a 5:95 mixture of *cis*-**3d** and *trans*-**3d**, bp 70–72 °C (18 mmHg, 78%), and a 1:1 mixture of **3f** and **3g**, bp 110–114 °C (12 mmHg, 72%), were obtained. The geometrical isomers were separated by means of preparative gas chromatography (Silicon XF 1150 on Uniport B, 10%, 2.5 m, 140 °C). The elemental analyses were carried out with the mixture. **3b**: Anal. (C_9H_{14}) C, H. **3d**: Anal. ($C_{11}H_8$) C, H. **3f, 3g**: Anal. ($C_{13}H_{14}$) C, H. The spectral data of each isomer were as follows.

trans-**3b**: IR (thin film) 1635, 1600, 1020 cm^{-1}; UV (95% ethanol) 241 (ϵ 21 400) nm; NMR (CCl_4) δ 0.3–0.8 (m, 4 H), 1.5–1.9 (m, 1 H), 1.01 (t, 3 H, J = 8 Hz), 1.80 (q, 2 H, J = 8 Hz), 4.88 (d of d, 1 H, J = 2 and 10.5 Hz), 4.99 (d of d, 1 H, J = 2 and 16.5 Hz), 5.80 (d, 1 H, J = 10.5 Hz), 6.74 (d of t, 1 H, J = 10.5 and 16.5 Hz).

cis-**3b**: IR (thin film) 1640, 1605, 1015 cm^{-1}; UV (95% ethanol) 243 (ϵ 24 000) nm; NMR (CCl_4) δ 0.3–0.75 (m, 4 H), 1.05 (t, 3 H, J = 8 Hz), 1.15–1.5 (m, 1 H), 2.12 (q, 2 H, J = 8 Hz), 4.93 (d of d, 1 H, J = 2 and 10.5 Hz), 5.01 (d of d, 1 H, J = 2 and 17 Hz), 5.64 (d, 1 H, J = 10.5 Hz), 6.44 (d of t, 1 H, J = 17 and 10.5 Hz).

trans-**3d**: IR (thin film) 1635, 1595, 1025 cm^{-1}; UV (hexane) 239 (ϵ 13 000) nm; NMR (CCl_4) δ 0.4–0.65 (m, 2 H), 0.65–0.9 (m, 2 H), 1.1–1.3 (m, 1 H), 1.15 (s, 9 H), 4.94 (d of d, 1 H, J = 2 and 10.5 Hz), 4.96 (d of d, 1 H, J = 2 and 16 Hz), 5.90 (d of d, 1 H, J = 1 and 10.5 Hz), 6.85 (d of d of d, 1 H, J = 10.5, 10.5, and 16 Hz).

3f (Z:E = 97:3): IR (thin film) 3095, 3070, 3020, 1635, 1610, 1025, 900, 770, 705 cm^{-1}; UV (hexane) 247 (ϵ 18 600) nm; NMR (CCl_4) δ 0.3–0.9 (m, 4 H), 1.4–1.8 (m, 1 H), 4.85 (d of d, 1 H, J = 2 and 9.5 Hz), 5.07 (d of d, 1 H, J = 2 and 15.5 Hz), 6.14 (d of d of d, 1 H, J = 9.5, 11, and 15.5 Hz), 5.98 (d of d, 1 H, J = 0.5 and 11 Hz), 7.0–7.5 (m, 5 H).

3g (Z:E = 7:93): IR (thin film) 3095, 3070, 3015, 1625, 1605, 1035, 905, 765, 700 cm^{-1}; UV (hexane) 274 (ϵ 21 300) nm; NMR (CCl_4) δ 0.2–0.5 (m, 2 H), 0.7–1.0 (m, 2 H), 1.5–2.0 (m, 1 H), 5.16 (d of d, 1 H, J = 2 and 9.5 Hz), 5.25 (d of d, 1 H, J = 2 and 17 Hz), 6.30 (d of d, 1 H, J = 1.5 and 11 Hz), 7.01 (d of d of d, 1 H, J = 9.5, 11, and 17 Hz), 7.0–7.5 (m, 5 H).

Methyl 4-Cyclopropyl-3-butenoate. Under mechanical stirring, the Jones reagent (prepared from 54 g, 0.54 mol, of chromium trioxide, 47 mL of concentrated sulfuric acid, and 100 mL of water) was added dropwise at or below 20 °C to a solution of 4-cyclopropyl-3-buten-1-ol (30 g, 0.27 mol) in acetone (600 mL). After the mixture was allowed to stand overnight at room temperature, the acetone layer was separated and concentrated. Ether (100 mL) was added to the residue to resolve the organic material. The flask and solid residue were rinsed with two additional 100-mL portions of ether. The combined ether solution was shaken with three 100-mL portions of saturated aqueous solution of sodium hydrogen carbonate. The alkaline extracts were combined, cooled, and acidified by the addition of concentrated sulfuric acid. The separated organic material was extracted with three 100-mL portions of ether. After being dried over anhydrous magnesium sulfate, the ether solution was concentrated and the residue (12.6 g) was dissolved in 150 mL of methanol containing 0.5 g of concentrated sulfuric acid. The methanolic solution was then refluxed for 3 h. Addition of water to the resultant mixture gave an oily product which was extracted with three 100-mL portions of ether. The combined ether solution was dried over anhydrous magnesium sulfate and concentrated. Chromatographic purification (100 g of silica gel, a 1:1 hexane–benzene mixture as the eluant) followed by vacuum distillation gave methyl 4-cyclopropyl-3-butenoate (5.2 g, 15%), bp 88–90 °C (21 mmHg); IR (thin film) 1745, 1030 cm^{-1}; NMR (CCl_4) δ 0.2–0.4 (m, 2 H), 0.5–0.8 (m, 2 H), 1.2–1.6 (m, 1 H), 2.92 (d of d, 2 H, J = 1 and 7 Hz), 3.61 (s, 3 H), 5.04 (d of d of t, 1 H, J = 8, 15, and 1 Hz), 5.53 (d of d, 1 H, J = 7 and 15 Hz). Anal. ($C_8H_{12}O_2$) C, H.

4-Cyclopropyl-1,1-dideuterio-3-buten-1-ol. Reduction of methyl 4-cyclopropyl-3-butenoate (3.2 g, 23 mmol) with lithium aluminum deuteride (0.62 g, 15 mmol) in dry ether (40 mL) gave 4-cyclopropyl-1,1-dideuterio-3-buten-1-ol (2.4 g, 94%): bp 84–86 °C (19 mmHg); IR (thin film) 3330, 2200, 2100, 1670, 1020 cm^{-1}; NMR (CCl_4) δ 0.0–0.4 (m, 2 H), 0.4–0.8 (m, 2 H), 1.1–1.5 (m, 1 H), 1.6–2.0 (m, 1 H), 2.16 (d, 2 H,

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J = 7 Hz), 5.01 (d of d, 1 H, J = 8 and 15 Hz), 5.41 (d of t, 1 H, J = 7 and 15 Hz); mass (70 eV), m/e 114 (M^+ 16). Anal. ($C_7H_{12}O$) C, H. Since a CHN-Analyser was used for the elemental analysis, no differentiation of D_2O and H_2O could be possible. The figure for C was calculated on the basis that the NMR and mass spectral data indicated that the deuterium content was more than 99%.

4-Bromo-1-cyclopropyl-4,4-dideuterio-1-butene. Bromination of 4-cyclopropyl-1,1-dideuterio-3-buten-1-ol (3.3 g, 29 mmol) was carried out with phosphorus tribromide (3.0 g, 11 mmol) at −78 °C in dry ether. The bromide was isolated by vacuum distillation (1.7 g, 33%): bp 67–68 °C (10 mmHg); IR (thin film) 3095, 3020, 2160, 1670 cm^{-1}.

1-Cyclopropyl-4,4-dideuterio-1,3-butadiene (3h-d_2). Dehydrobromination of 4-bromo-1-cyclopropyl-4,4-dideuterio-1-butene (1.38 g, 7.8 mmol) with potassium *tert*-butyl alkoxide in *tert*-butyl alcohol yielded **3h-d_2** (0.49 g, 55%) as a 2:8 mixture of cis and trans isomers, bp 95–96 °C; IR (thin film) 3095, 3010, 1650, 1030, 980, 960 cm^{-1}; NMR (CCl_4) δ 0.1–0.5 (m, 2 H), 0.6–0.9 (m, 2 H), 1.2–1.6 (m, 1 H), 5.18 (d of d, 1 H, J = 8.5 and 14.5 Hz), 6.08 (d of d, 1 H, J = 10 and 14.5 Hz), 6.24 (d, 1 H, J = 10 Hz); mass (70 eV), m/e 96 (M^+ 63). The NMR examination indicated that the percentage of deuterons present at the C-4 in a purified sample was ca. 90%.

Reaction of Tetracyclopropylethylene (1a) with TCNQ. (a) In Acetonitrile. A mixture of **1a** (150 mg, 0.8 mmol) and TCNQ (184 mg, 0.9 mmol, in suspension) in acetonitrile (15 mL) was sealed in a glass ampule and heated at 85–90 °C for 15 days. After evaporation of the solvent, the residue was placed on the top of a silica gel column (20 g), and the elution was carried out with chloroform. From the early few fractions, **1a** (35 mg, corresponding to 76% consumption of **1a**) was recovered. From later fractions, crystalline product (167 mg, 70%, based on the consumed amount of **1a**), mp 157.5–158.5 °C, which was assigned as **2a**, was obtained: IR (KBr) 3080, 2250, 1650, 1620, 1505, 1020, 825 cm^{-1}; NMR ($CDCl_3$) δ 0.05–0.28 (m, 4 H), 0.28–0.72 (m, 4 H), 0.90–1.38 (m, 2 H), 1.64 (d of t, 2 H, J = 7.5 and 9 Hz), 1.96–2.30 (m, 2 H), 2.3–2.5 (m, 2 H), 2.5–2.8 (m, 2 H), 3.78 (t, 1 H, J = 5 Hz), 4.94 (t, 1 H, J = 7.5 Hz), 7.61 (d, 2 H, J = 9 Hz), 7.70 (d, 2 H, J = 9 Hz); mass (70 eV), m/e 392 (M^+ 10); UV (95% ethanol) 273 (shoulder, ϵ 420) nm. Anal. ($C_{26}H_{24}N_4$) C, H, N.

(b) In 1,2-Dichloroethane. The reaction of **1a** (100 mg, 0.53 mmol) with TCNQ (122 mg, 0.60 mmol, in suspension) in 1,2-dichloroethane (10 mL) at 85–90 °C for 15 days resulted in a recovery of **1a** (4 mg) and TCNQ (49 mg, corresponding to 68% consumption) and the formation of **2a** (111 mg, 79% based on the consumed amount of TCNQ, 56% based on **1a**), mp 157.5–158.5 °C. The isolation of **2a** was accomplished in this experiment by preparative thin-layer chromatography (Merk Kieselgel GF_{254}, 25 g on a 20 cm × 20 cm plate, chloroform as the eluant).

Reaction of *cis*-1,2-Dicyclopropylstilbene (1b) with TCNQ. (a) In Acetonitrile. Heating of a mixture of **1b** (130 mg, 0.50 mmol) and TCNQ (120 mg, 0.59 mmol, in suspension) in acetonitrile (5 mL) at 85–90 °C for 1 week resulted in a total consumption of TCNQ, but a substantial amount of **1b** was left in the mixture. Therefore, an additional amount of TCNQ (100 mg, 0.49 mmol) was added to the resultant mixture, and heating was continued for another week. The workup of the reaction mixture as above gave **1b** (31 mg, 76% consumption) and **2b** (93 mg, 53% based on the consumed amount of **1b**): mp 222–222.5 °C; IR (KBr) 3080, 2260, 1620, 1605, 1515, 1495, 840, 800, 770, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.7–2.1 (m, 2 H), 2.3–2.8 (m, 6 H), 4.32 (t, 1 H, J = 5.5 Hz), 5.58 (t, 1 H, J = 7.5 Hz), 6.8–7.0 (m, 2 H), 7.17 (s, 5 H), 7.05–7.4 (m, 3 H), 7.73 (d, 2 H, J = 9 Hz), 7.78 (d, 2 H, J = 9 Hz); mass (80 eV), m/e 464 (M^+ 100). Anal. ($C_{32}H_{24}N_4$) C, H, N.

(b) In 1,2-Dichloroethane. After 3 weeks at 85–90 °C, the reaction of **1b** (130 mg, 0.50 mmol) with TCNQ (120 mg, 0.59 mmol) in 1,2-dichloroethane (10 mL) resulted in a recovery of **1b** (29 mg, 78% consumption) and the formation of **2b** (101 mg, 56% based on the consumed amount of **1b**), mp 221.5–222.5 °C. The recovered stilbene was not contaminated by **1c** in a detectable amount.

Reaction of *trans*-1,2-Dicyclopropylstilbene (1c) with TCNQ. (a) In Acetonitrile. The reaction of **1c** (130 mg, 0.50 mmol) and TCNQ (120 mg, 0.59 mmol) in acetonitrile (5 mL) was carried out in a similar manner as above. An additional TCNQ (100 mg, 0.49 mmol) was added after 1 week of heating at 85–90 °C. After 2 weeks, **1c** (16 mg, 88% consumption) and **2b** (105 mg, 52% based on the consumed amount of **1c**), mp 222–222.5 °C, were obtained. The recovered stilbene was contaminated by **1b** in ca. 2%.

(b) In 1,2-Dichloroethane. After 2 weeks at 85–90 °C, there were obtained **1c** (16 mg, 88% consumption) and **2b** (102 mg, 50% based on the consumed amount of **1c**), mp 221.5–222.5 °C, in the reaction of **1c** (130 mg, 0.50 mmol) with TCNQ (120 mg, 0.59 mmol). The recovered stilbene was found to be a mixture of **1b** and **1c** in a 12:88 ratio. In control experiments, it was observed that both **1b** and **1c** were stable in acetonitrile at 100 °C, if TCNQ was absent, but the mutual isomerization took place to considerable extents in 1,2-dichloroethane.

Reaction of 1,1,2-Tricyclopropylpropene (1d) with TCNQ. (a) In Acetonitrile. Heating of a mixture of **1d** (162 mg, 1.0 mmol) and TCNQ (245 mg, 1.2 mmol) in acetonitrile (10 mL) at 100 °C for 7 days resulted in the consumption of **1d** to an extent of 83% (GC with decane as an internal standard). The workup and purification similar as above gave **2c** (55 mg, 17%): mp 160–160.5 °C; IR (KBr) 3100, 2255, 1650, 1630, 1510, 1020, 830, 810, 800 cm^{-1}; NMR ($CDCl_3$) δ 0.0–0.3 (m, 2 H), 0.3–0.6 (m, 2 H), 1.9–2.2 (m, 4 H), 2.3–2.6 (m, 2 H), 3.66 (d of t, 1 H, J = 1.3 and 5.5 Hz), 4.89 (t, 1 H, J = 7.5 Hz), 7.62 (d, 2 H, J = 8.5 Hz), 7.69 (d, 2 H, J = 8.5 Hz); mass (70 eV), m/e 366 (M^+ 60). Anal. ($C_{24}H_{22}N_4$) C, H, N.

(b) In 1,2-Dichloroethane. A similar mixture as above in 1,2-dichloroethane resulted in 89% consumption of **1d** after 8 days at 100 °C. From the reaction mixture **2c** (63 mg, 21%), mp 160–160.5 °C, was isolated and characterized.

In attempts to react tricyclopropylethylene (**1e**) with TCNQ in a similar manner, a mixture of **1e** (100 mg, 0.63 mmol) and TCNQ (200 mg, 0.98 mmol) in either acetonitrile (5 mL) or 1,2-dichloroethane (5 mL) was heated at 90–95 °C for 90 h. The GLPC analyses indicated that **1d** was completely consumed. A similar workup as above, however, gave none of the isolable products. The TLC analysis of the reaction mixture revealed no spot corresponding to the formation of the cycloadduct. Similar results were obtained in the reaction of **1f** with TCNQ.

Reaction of 1-Alkyl-1-cyclopropyl-1,3-butadiene (3a–g) with TCNQ. A mixture of **3** (1.0 mmol), TCNQ (224 mg, 1.1 mmol, in suspension), and hydroquinone (10 mg) in dry dichloromethane (10 mL) was stirred at room temperature until the solution turned from reddish-brown to yellow. After evaporation of the solvent, the residue was placed on the top of a silica gel column (30 g), and the elution was carried out with chloroform. From the middle fractions, a crystalline 1:1 adduct was obtained. The reaction time, yield, physical properties, spectroscopic data, and microanalytical results were as follows.

4a: 3 h, 42%, mp 194.5–195.5 °C; IR (KBr) 2255, 1920, 1795, 1640, 1610, 825, 730 cm^{-1}; UV (95% ethanol) 248 (ϵ 10600), 218, (13700) nm; NMR ($CDCl_3$) δ 1.64 (d, 3 H, J = 1.2 Hz), 1.80 (d of t, 2 H, J = 6 and 8 Hz), 2.48 (t, 2 H, J = 6 Hz), 2.88 (d, 2 H, J = 7.5 Hz), 4.76 (d, 1 H, J = 16 Hz), 5.15 (d of t, 1 H, J = 1.2 and 8 Hz), 5.32 (d of t, 1 H, J = 16 and 7.5 Hz), 7.53 (d, 2 H, J = 8.5 Hz), 7.67 (d, 2 H, J = 8.5 Hz); mass (70 eV), m/e 312 (M^+ 99). Anal. ($C_{20}H_{16}N_4$) C, H, N.

4b: 7 h, 37%, mp 191–192 °C; IR (KBr) 2250, 1920, 1800, 1640, 1610, 825, 730 cm^{-1}; UV (95% ethanol) 248 (ϵ 7600), 218 (11600) nm; NMR ($CDCl_3$) δ 0.91 (t, 3 H, J = 7.5 Hz), 1.89 (d of t, 2 H, J = 8.5 and 6 Hz), 2.01 (q, 2 H, J = 7.5 Hz), 2.47 (t, 2 H, J = 6 Hz), 2.95 (d, 2 H, J = 7.5 Hz), 4.72 (d, 1 H, J = 16 Hz), 5.15 (t, 1 H, J = 8.5 Hz), 5.36 (d of t, 1 H, J = 16 and 7.5 Hz), 7.54 (d, 2 H, J = 8.5 Hz), 7.68 (d, 2 H, J = 8.5 Hz); mass (70 eV), m/e 326 (M^+ 100). Anal. ($C_{21}H_{18}N_4$) C, H, N.

4c: 24 h, 62%, mp 190–191 °C; IR (KBr) 2260, 1915, 1795, 1645, 1615, 820, 735 cm^{-1}; UV (95% ethanol) 250 (ϵ 10000), 218 (13600) nm; NMR ($CDCl_3$) δ 0.92 (d, 6 H, J = 7 Hz), 1.77 (d of t, 2 H), J = 8.5 and 6 Hz), 2.39 (heptet, 1 H, J = 7 Hz), 2.44 (t, 2 H, J = 6 Hz), 2.93 (d, 2 H, J = 7.5 Hz), 4.79 (d, 1 H, J = 16 Hz), 5.12 (t, 1 H, J = 8.5 Hz), 5.34 (d of t, 1 H, J = 8.5 Hz); mass (70 eV), m/e 340 (M^+ 80). Anal. ($C_{22}H_{20}N_4$) C, H, N.

4d: 40 h, 89%, mp 218.5–219.5 °C; IR (KBr) 2260, 1920, 1805, 1640, 1615, 830, 740 cm^{-1}; UV (95% ethanol) 248 (ϵ 7000), 218 (13000) nm; NMR ($CDCl_3$) δ 0.99 (s, 9 H), 1.53 (d of d of d, 2 H, J = 6, 8, and 8 Hz), 2.29 (d of d, 2 H, J = 6 and 8 Hz), 2.96 (d, 2 H, J = 6 Hz), 5.08 (d, 1 H, J = 16 Hz), 5.15 (d of t, 1 H, J = 16 and 6 Hz), 5.20 (t, 1 H, J = 8 Hz), 7.58 (d, 2 H, J = 9 Hz), 7.68 (d, 2 H, J = 9 Hz); mass (70 eV), m/e 354 (M^+ 11). Anal. ($C_{23}H_{22}N_4$) C, H, N.

4e: 2 h, 15%, mp 187–188 °C; IR (KBr) 2260, 1915, 1790, 1645, 1615, 1020, 820, 730 cm^{-1}; UV (95% ethanol) 251 (ϵ 9500), 218 (13000) nm; NMR ($CDCl_3$) δ 0.1–0.3 (m, 2 H), 0.5–0.7 (m, 2 H), 1.1–1.4 (m, 1 H), 1.80 (d of t, 2 H, J = 8.5 and 6 Hz), 2.45 (t, 2 H, J = 6 Hz), 3.98 (d, 2 H, J = 7.5 Hz), 4.80 (d, 1 H, J = 15.5 Hz), 5.11 (t, 1 H, J = 8.5 Hz), 5.70 (d of t, 1 H, J = 15.5 and 7.5 Hz), 7.54 (d, 2 H, J = 8.5 Hz), 7.64 (d, 2 H, J = 8.5 Hz); mass (70 eV), m/e 338 (M^+ 85). Anal. ($C_{22}H_{18}N_4$) C, H, N.

The reaction of **3** with TCNQ in the solvent other than dichloromethane produced the same adduct, but the yield was significantly low: for **4a**, none in acetonitrile, for **4e**, 10% in acetonitrile and 13% in nitromethane, and for **4f**, 9% in acetonitrile. In the absence of hydroquinone, the reaction seemed to proceed faster, but the yield of the adduct was low: for **4f**, only 36%. The reactions under more dilute conditions resulted in rather decreased yields of the adduct.

In attempts to obtain a similar cycloadduct, 1,3,5-hexatriene was allowed to react with TCNQ under various conditions. However, no

characterizable product was obtained; only a polymeric residue was produced in all cases.

For stereochemistry assignments at the diene portion in **4**, the NOE experiments were carried out for **4a**, **4c**, and **4d**. The chloroform-*d* solution (0.5–0.8 mL) of **4** (20–50 mg) was placed in an NMR tube, and the solution was degassed by freeze–thaw cycles. The tube was then sealed and placed in a cavity of a JEOL-PS 100 spectrometer, and the NOE experiments were carried out. The results are described in the text.

Reaction of 1-Cyclopropyl-1-phenyl-1,3-butadienes (3f and 3g) with TCNQ. The reaction of a 1:1 mixture of **3f** and **3g** under the similar conditions as above (50-h reaction time) produced **4f**, mp 218–224 °C dec, in 78% yield: IR (KBr) 2270, 1925, 1810, 1640, 825, 780, 735, 715, 705 cm^{-1}; UV (95% ethanol) 250 (ϵ 13 500) nm; NMR ($CDCl_3$) δ 1.90 (d of t, 2 H, J = 8.5 and 6 Hz), 2.55 (t, 2 H, J = 6 Hz), 2.90 (m, 2 H), 5.05 (s, 1 H), 5.00–5.15 (m, 1 H), 5.26 (t, 1 H, J = 8.5 Hz), 6.9–7.1 (m, 2 H), 7.2–7.4 (m, 3 H), 7.48 (d, 2 H, J = 8.5 Hz), 7.68 (d, 2 H, J = 8.5 Hz); mass (70 eV), m/e 374 (M^+ 77). Anal. ($C_{25}H_{18}N_4$) C, H, N.

The reaction of **3f** (97% pure, 92 mg, 0.54 mmol) with TCNQ (121 mg, 0.60 mmol) in dichloromethane (5.4 mL) in the presence of *p*-hydroquinone (5.4 mg) gave **4f** (123 mg, 67%). The same adduct **4f** was isolated in 61% yield in the reaction of **3g** (93% pure) with TCNQ.

Reaction of 1-Cyclopropyl-1,3-butadiene (3h) with TCNQ. On the addition of *trans*-**3h** (88% pure, 113 mg, 1.2 mmol) to a mixture of TCNQ (204 mg, 1.0 mmol, in suspension) and *p*-hydroquinone (20 mg, 0.18 mmol) in dichloromethane (10 mL), a reddish brown solution was obtained. After 50 h at room temperature the color of the solution turned to yellow. The solution was then concentrated, and the resultant residue was placed on the top of a silica gel column (30 g). The elution was carried out with chloroform, and nine fractions (30 mL each) were collected. Fractions 3 and 4 contained 2-cyclopropyl-3-cyclohexene-1,1-dicarbonitrile (**10**, 48 mg, 28%), mp 52.0–52.5 °C, which was identical in all respects with an authentic sample prepared from *trans*-**3h** and methylenemalononitrile in 85% yield: IR (KBr) 2250, 1650, 1030 cm^{-1}; NMR (CCl_4) δ 0.1–0.5 (m, 1 H), 0.5–1.4 (m, 4 H), 1.90 (br d of t, 1 H, J = 10 and 2 Hz), 2.0–2.8 (m, 4 H) 5.58 (br d of d, 1 H, J = 2 and 10 Hz), 5.81 (br d of d, 1 H, J = 2 and 10 Hz); mass (70 eV), m/e 172 (M^+ 14). Anal. ($C_{11}H_{12}N_2$) C, H, N.

From the fractions 6–8 there was obtained 11,11-dicyano-3-(dicyanomethylene)-7-cyclopropylspiro[5.5]undeca-1,4,8-triene (**9**, 101 mg, 34%): mp 175–176 °C; IR (KBr) 2255, 2230, 1650, 1595, 1030 cm^{-1}; UV (CH_2Cl_2) 318 (ϵ 17 600) nm; NMR ($CDCl_3$) δ 0.0–0.7 (m, 5 H), 1.8–2.2 (m, 1 H), 2.80 (br d, 1 H, J = 20 Hz), 3.00 (br d, 1 H, J = 20 Hz), 5.83 (br d, 1 H, J = 11 Hz), 5.95 (d, 1 H, J = 11 Hz), 6.58 (br d, 1 H, J = 10 Hz), 6.69 (br d, 1 H, J = 10 Hz), 7.26 (br d, 2 H, J = 10 Hz); mass (70 eV), m/e 298 (M^+ 1.2). Anal. ($C_{19}H_{14}N_4$) C, H, N. The reaction of *cis*-**3h** (>99% pure) gave none of these products; only untractable residues were obtained in the column chromatography.

The reaction of **3h**-d_2 (trans:cis = 80:20, 115 mg, 1.2 mmol) with TCNQ (204 mg, 1.0 mmol) in the presence of *p*-hydroquinone (20 mg) was carried out in dichloromethane (10 mL) in a manner similar as above. There were obtained 11,11-dicyano-3-(dicyanomethylene)-7-cyclopropyl-10,10-dideuteriospiro[5.5]undeca-1,4,8-triene (**9**-d_2, 69 mg, 23%) and 2-cyclopropyl-5,5,6,6-tetradeuterio-3-cyclohexene-1,1-dicarbonitrile (**10**-d_4, 43 mg, 24%). The NMR examinations indicated that 91% of the hydrogens at C-11 in **9**-d_2 and 89% of the methylene hydrogens at C-5 and C-6 in **10**-d_4 were deuterated. **9**-d_2: mp 173.5–175 °C; NMR ($CDCl_3$) δ 0.0–0.7 (m, 5 H), 1.8–2.2 (m, 1 H), 5.83 (br d, 1 H, J = 11 Hz), 5.95 (d, 1 H, J = 11 Hz), 6.58 (br d, 1 H, J = 10 Hz), 6.69 (br d, 1 H, J = 10 Hz), 7.26 (br d, 2 H, J = 10 Hz); mass (70 eV), m/e 300 (M^+ 1.4). **10**-d_4: mp 51–52 °C; NMR (CCl_4) δ 0.1–0.5 (m, 1 H), 0.5–1.4 (m, 4 H), 1.90 (br d of t, 1 H, J = 10 and 2 Hz), 5.58 (br d of t, 1 H, J = 10 and 2 Hz), 5.82 (br d of d, 1 H, J = 2 and 10 Hz); mass (70 eV), m/e 176 (M^+ 24).

Reductive Decyanation. Under a nitrogen atmosphere, metallic sodium (580 mg, 25.2 mmol) was added to liquid ammonia (50 mL). To the resultant dark blue solution, pulverized **2a** (330 mg, 0.84 mmol) was added in several portions in a period of 15 min. After the mixture was stirred for 30 min, it was transferred into ice-cooled ether (100 mL). Small pieces of ice were then added carefully until the blue color of the ether–ammonia solution dissipated. The solution was kept standing at room temperature to evaporate off the ammonia. The ether layer was then separated from the water layer, which was subsequently extracted with two portions of ether. The combined ether solution was dried over anhydrous magnesium sulfate. The residue obtained after evaporation of the solvent was placed on the top of a silica gel column (10 g). Elution of the column with benzene gave 191 mg (78%) of a liquid, bp 140–150 °C (bath temperature, 0.01 mmHg), which was assigned as *cis,trans*-5,6-dicyclopropyl[10]paracyclophane-4,6-diene (**5**); IR (thin film) 3100, 1640, 1520, 1030, 820 cm^{-1}; UV (hexane) 268 (650), 277 (490) nm; NMR (CCl_4) δ 0.0–0.6 (m, 8 H), 0.8–1.3 (m, 2 H), 1.3–1.6 (m, 4 H), 1.7–2.0 (m, 2 H), 2.0–2.3 (m, 2 H), 2.49 (t, 2 H, J = 6 Hz), 2.67 (t, 2 H, J = 6 Hz), 3.89 (t, 1 H, J = 5.5 Hz), 4.91 (t, 1 H, J = 6.5 Hz), 6.89 (d, 2 H, J = 8 Hz), 6.99 (d, 2 H, J = 8 Hz); mass (70 eV), m/e 292 (M^+ 100). Anal. ($C_{22}H_{28}$) C, H.

Similar treatments of **2b** (232 mg, 0.50 mmol) gave 5,6-diphenyl[10]paracyclophane (**6**, 150 mg, 81%), mp 109–111 °C; IR (KBr) 3070, 1605, 1515, 1500, 870, 840, 795, 770, 735 cm^{-1}; UV (hexane) 243 (290), 250 (400), 254 (540), 260 (690), 262 (670), 266 (650), 269 (630), 277 (350) nm; NMR ($CDCl_3$) δ 0.5–1.6 (m, 10 H), 1.7–2.1 (m, 2 H), 2.2–2.4 (m, 2 H), 2.4–2.7 (m, 2 H), 2.7–3.0 (m, 2 H), 6.4–6.8 (m, 4 H), 6.8–7.1 (m, 6 H), 7.14 (d, 2 H, J = 1 Hz), 7.28 (d, 2 H, J = 1 Hz); mass (70 eV), m/e 368 (M^+ 69). Anal. ($C_{28}H_{32}$) C, H.

The reductive decyanation of **4** did not produce the expected hydrocarbon, but some cyclophane ring cleaved products were obtained in relatively low yields. Thus, **4f** (374 mg, 1.0 mmol) gave a hydrocarbon fraction (56 mg) which consisted of two components in a 1:4 ratio. They were separated and purified by means of preparative GC. The spectroscopic examination suggested that the minor component was 4-phenyl-8-*p*-tolyl-2-octene (**7**, 5%), whereas the major component was its saturated analogue, 5-phenyl-1-*p*-tolyloctane (**8**, 16%). A prolonged treatment of **4f** with metal–ammonia solution reduced the amount of **7** in the product mixture. **7**: IR (thin film) 3020, 2920, 2850, 1740, 1600, 1515, 1490, 1450, 1375, 1110, 1070, 1030, 965, 800, 850, 695 cm^{-1}; UV (hexane) 248 (480), 255 (470), 260 (480), 266 (450), 268 (430), 275 (380) nm; NMR (CCl_4) δ 1.0–1.5 (m, 6 H), 1.62 (d, 3 H, J = 5 Hz), 2.29 (s, 3 H), 2.50 (t, 2 H, J = 7.5 Hz), 3.11 (d of t, 1 H, 6 and 6 Hz), 5.30 (d of q, 1 H, J = 15 and 5 Hz), 5.53 (d of d, 1 H, J = 6 and 15 Hz), 6.91 (s, 4 H), 6.8–7.3 (m, 5 H). **8**: IR (thin film) 3030, 2960, 2940, 2860, 1605, 1495, 1465, 1455, 1380, 1120, 1060, 1030, 805, 760, 700 cm^{-1}; UV (hexane) 248 (470), 255 (528), 260 (620), 266 (630), 268 (640), 275 (570) nm; NMR (CCl_4) δ 0.83 (t, 3 H, J = 6 Hz), 1.0–1.4 (m, 4 H), 1.4–1.8 (m, 6 H), 2.17 (s, 3 H), 2.3–2.6 (m, 1 H), 2.45 (t, 2 H, J = 7.5 Hz), 6.90 (s, 4 H), 6.8–7.4 (m, 5 H). Anal. ($C_{21}H_{28}$) C, H.