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ONE-STEP FORMATION OF [9]PARACYCLOPHA-3,5-DIENES BY A CYCLOADDITION REACTION

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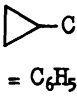
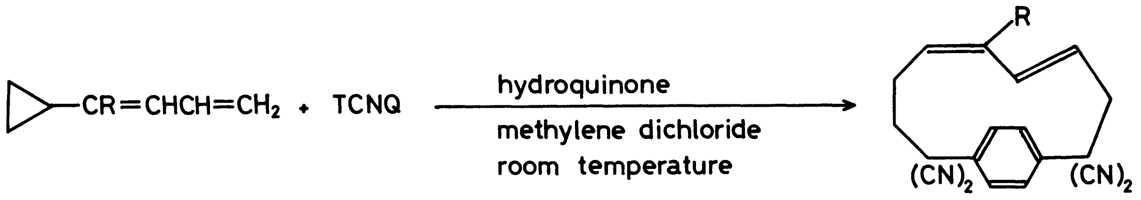
The reaction of certain 1-substituted 1-cyclopropyl-1,3-butadiene (1 : —CR=CHCH=CH$_2$, a: R = (CH$_3$)$_3$C–, b: R = (CH$_3$)$_2$CH–, c: R = cyclo-C$_3$H$_5$–, d: R = C$_6$H$_5$) with TCNQ yielded a [9]paracyclopha-3,5-diene (2). Formation of the same adduct 2d from both _E_-1d and _Z_-1d suggests a stepwise mechanism probably involving a dipolar intermediate.

Synthesis of a medium or a large membered carbocyclic compound has been of long standing interest in organic chemistry.[1] We recently found that [10]paracyclopha-4,6-diene is produced in good yield in the reaction of certain 1,2-dicyclopropylethylene with 3,6-bis(dicyanomethylene)-1,4-cyclohexadiene (TCNQ).[2] Although the product is rigid in part, and hence the rigid group principle[1] may be operating, it should be noted that the formation of a 14 membered ring is achieved successfully by the donor-acceptor type cycloaddition.[3] In the present letter, we wish to report that the reaction of 1-substituted 1-cyclopropyl-1,3-butadiene (1)[4] with TCNQ proceeds even with a greater ease to afford 13 membered [9]paracyclopha-3,5-diene (2). In particular, such dienes as those substituted by a bulky group at C-1 gave good results.

To a suspension of TCNQ (224 mg, 1.1 mmol) and hydroquinone (10 mg) in dry methylene dichloride (10 ml), 4-cyclopropyl-5,5-dimethyl-1,3-hexadiene (1a) (150 mg, 1.0 mmol) was added and the resulting reddish-brown colored mixture was stirred at room temperature. After 40 h, the solution became yellow and all TCNQ went into the solution. The solvent was then evaporated and the residue was subjected to column chromatography (silica gel 30 g, chloroform as the eluant). From the middle fractions, a crystalline 1 : 1 adduct (m.p. 218.5-219.5°C, 317 mg, 89%) was obtained. This was assigned as *trans*,*cis*-5-*t*-butyl-1,1,9,9-tetracyano[9]paracyclopha-3,5-diene (2a): i.r. (KBr) 2260, 1640, 1615, and 980 cm^{-1} ; n.m.r. ($CDCl_3$) δ 0.99 (s, 9H), 1.53 (d of d of d, J = 8, 8, and 6 Hz, 2H), 2.29 (d of d, J = 8 and 6 Hz, 2H), 2.96 (d, J = 6 Hz, 2H), 5.08 (d, J = 16 Hz, 1H), 5.15 (d of t, J = 16 and 6 Hz, 1H), 5.20 (t, J = 8 Hz, 1H), 7.58 (d, J = 9 Hz, 2H), and 7.68 (d, J = 9 Hz, 2H); m/e 354 (M^+); Anal. Calcd for $C_{23}H_{22}N_4$: C, 77.9; H, 6.3; N, 15.8. Found: C, 78.1; H, 6.1; N, 15.7. The trans configuration at the C-3 double bond is deduced from the n.m.r. coupling constant (J = 16 Hz) whereas the cis configuration at the C-5 double bond may be assumed both from steric reasons and from an analogy to the formation of *trans*,*cis*-[10]paracyclopha-4,6-diene in the reaction of 1,2-dicyclopropylethylene with TCNQ.[2]



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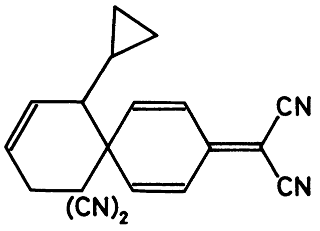
a : R = $(CH_3)_3C$
b : R = $(CH_3)_2CH$
c : R = ▷
d : R = C_6H_5

e : R = C_2H_5
f : R = CH_3
g : R = H

Similarly, 1b gave 2b[5,6] (m.p. 190-191°C, 62%) and 1c yielded 2c[5] (m.p. 187-188°C, 15%). In the last reaction, TCNQ was consumed more rapidly than 1c suggesting a side reaction which could possibly be responsible for the low yield of 2c. Utilization of isomeric 1-cyclopropyl-1-phenyl-1,3-butadiene (1d)[7] allowed us to examine the stereochemical characteristics of the reaction. Thus, the reaction of *E*-1d proceeded smoothly to give an adduct 2d[5] (m.p. 218-224°C(dec.), 61%). Interestingly, *Z*-1d also yielded *the same adduct 2d* (67%). Apparently, the stereochemical individuality of the starting diene was lost in the course of the reaction. Accordingly, it could well be a stepwise reaction, and most probably involves a dipolar intermediate similar to that included in the reaction of 1,2-dicyclopropylethylene.[2] The reactions of 1e and 1f were less promising. The yields of the adduct were low (37-41%) and the adducts were somewhat unstable by the present purification procedure.

In contrast to 1a-1f, the parent 1g failed to produce any [9]paracyclophadiene but gave a 4 + 2 cycloadduct 3 (m.p. 175-176°C, 34%) and 4,4-dicyano-3-cyclopropylcyclohexene (4) (m.p. 52.0-52.5°C, 28%). Since the reaction of 4,4-dideuterated 1g yielded 5,5,6,6-tetradeuteriocyclohexene (4-d$_4$), 4 is a Diels-Alder adduct of 1g with methylenemalononitrile, which might be the fragmentation product of a 2 + 2 cycloadduct 5 of 1g and TCNQ.[8] The reaction of 1,3,5-hexatriene with TCNQ under similar conditions did not produce any characterizable product but gave only a tarry residue.



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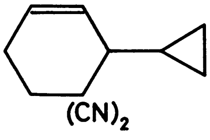

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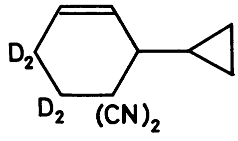
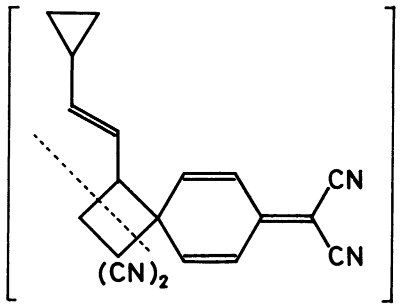


4-d$_4$



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References and Notes

1) K. Ziegler, in "Houben Weyl's Methoden der Organischen Chemie," Band 4/2, Georg Thieme Verlag, Stuttgart, 1955, p. 729.

2) F. Kataoka and S. Nishida, J. Chem. Commun., 0000 (1978).

3) TCNE is known to react with a variety of electron rich olefins in a 2 + 2 manner by, in most cases, a stepwise dipolar mechanism (see, for example: P. D. Bartlett, Quart. Rev., 24, 473 (1970); R. Huisgen, R. Schug, and G. Steiner, Angew. Chem., Int. Ed., 13, 80, 81 (1974); I. Karle, J. Flippen, R. Huisgen, and R. Schug, J. Am. Chem. Soc., 97, 5285 (1975)). The reaction of vinylcyclopropane with TCNE is also shown to be an example of such reactions (S. Nishida, I. Moritani, and T. Teraji, J. Org. Chem., 38, 1878 (1973); F. Effenberger and O. Gerlach, Chem. Ber., 107, 278 (1974); N. Shimizu, T. Fujioka, S. Ishizuka, T. Tsuji, and S. Nishida, J. Am. Chem. Soc., 99, 5972 (1977)), and hence the reaction of 1,2-dicyclopropylethylene with TCNQ[2] and the present cycloaddition will be of the same type.

4) Olefins 1a–1g were prepared by the standard procedures. Separation of the stereoisomers was carried out only for 1d whereas the other olefins were used as a mixture of *E* and *Z* isomer. This is because the isomeric 1d gave the same adduct 2d.

5) Appropriate microanalytical and spectral (i.r., n.m.r., and mass) data were obtained. The configuration at the diene moiety has not been established for 2b, 2c, and 2d. However, they may have the same configuration as that of 2a.

6) The reaction in acetonitrile (in the presence of hydroquinone at room temperature) gave 2b only in a 9% yield. Methylene dichloride was indeed found to be the best solvent to perform the present cyclization.

7) Separation of isomeric 1d was achieved by preparative g.l.c. Olefins possessing isomeric purity of 97 : 3 for *E*-1d and 93 : 7 for *Z*-1d were used in the reaction. In a separate experiment using a larger quantity of a mixture of *E*- and *Z*-1d, the yield of 2d was as high as 78%.

8) Since the other half possesses a *p*-quinodimethane structure, it may be unstable under the present conditions.

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