Cycloaddition of Sterically Hindered 1,2-Dicyclopropylethylenes with Tetracyanoquinodimethane; One-step Formation of [10]Paracyclophadienes

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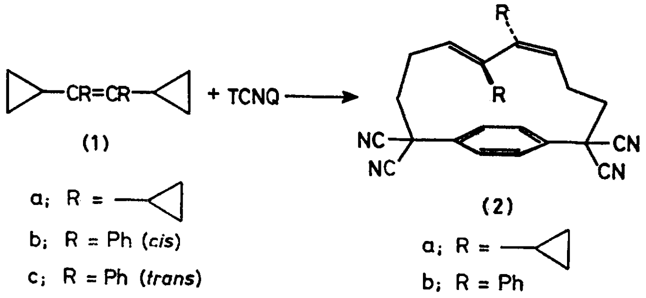
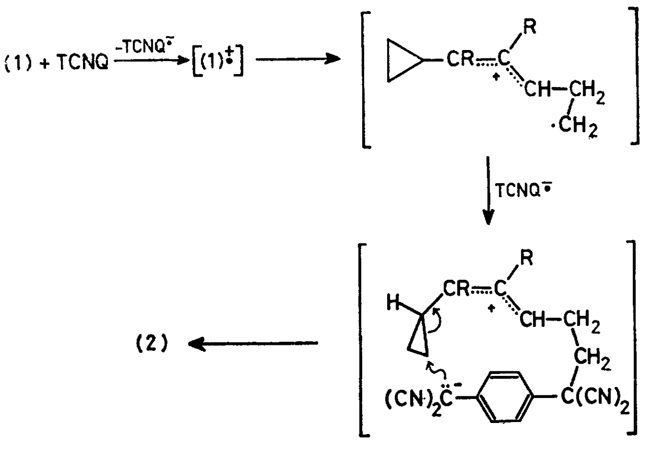
Summary [10]Paracyclopha-4,6-dienes were produced in the reaction of sterically hindered 1,2-dicyclopropylethylenes with tetracyanoquinodimethane in a $\pi 6 + \sigma 2 + \pi 2 + \sigma 2$ cycloaddition.

In a donor–acceptor type of cycloaddition, tetracyanoethylene (TCNE) reacts with the π bond of cyclopropylethylene in a $\pi 2 + \pi 2$ manner.[1] When the double bond is sterically hindered, however, the cycloaddition takes place with a σ bond of the cyclopropane to give a vinylcyclopentane derivative; formally a $\pi 2 + \sigma 2$ cycloaddition.[2] We now report that the reaction of sterically hindered 1,2-dicyclopropylethylenes with 3,6-bis(dicyanomethylene)cyclohexa-1,4-diene (tetracyanoquinodimethane; TCNQ) occurs in a similar sense with incorporation of two cyclopropane σ bonds. The reaction may be termed as a $\pi 6 + \sigma 2 + \pi 2 + \sigma 2$ cycloaddition and [10]paracyclopha-4,6-diene is produced in a single step.



A solution of tetracyclopropylethylene[3] (**1a**; 0·80 mmol) and TCNQ (0·90 mmol) in acetonitrile (15 ml) was heated at 85—90 °C for 15 days. Unchanged (**1a**) (0·28 mmol) and the 1:1 adduct (**2a**), m.p. 157·5—158·5 °C [70% yield based on (**1a**) consumed] were isolated. The same adduct was also produced in 1,2-dichloroethane (53%). The adduct (**2a**) gave satisfactory elemental analyses and was characterized by its spectral data: i.r. (KBr disc) 2250, 1650, 1620, and 1020 cm^{-1}; n.m.r. (δ in CDCl$_3$) 0·05—0·28 (m, 4H), 0·28–0·7 (m, 4H), 0·9—1·4 (m, 2H), 1·64 (d of t, J 9 and 7·5 Hz, 2H), 2·0—2·3 (m, 2H), 2·3—2·5 (m, 2H), 2·5—2·8 (m, 2H), 3·78 (t, J 5 Hz, 1H), 4·94 (t, J 7·5 Hz, 1H), 7·61 (d, J 9 Hz, 2H), and 7·70 (d, J 9 Hz, 2H); *m/e* 392 (M^+). The n.m.r. spectrum suggests a lack of symmetry in the structure, indicating a *cis–trans* configuration of the diene unit.

The stereoisomeric *cis*- and *trans*-1,2-dicyclopropylstilbenes (**1b**) and (**1c**)[4] reacted similarly, and it is interesting that they both yielded the same adduct (**2b**),† m.p. 222—222·5 °C, in 53—56% and 50—52% yield, respectively (85—90 °C; 15 days). N.m.r. examination again showed that (**2b**) had the *cis–trans*-configuration. Although mutual isomerization of (**1b**) and (**1c**) occurred slowly under the reaction conditions,‡ it was too slow to account for the production of (**2b**) from both isomers. In contrast to (**1a**)—(**1c**), tricyclopropylethylene failed to give a cycloadduct analogous to (**2**). The presence of a sterically hindered double bond may be required to effect the cycloaddition.



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The formation of (**2**) may be explained as follows (Scheme). The radical cation derived from (**1**) would open its cyclopropane ring in such a way as to give a rearranged radical cation having a *transoid* allylic unit. This would then couple with the TCNQ anion radical to produce the zwitterionic intermediate (**3**),§ the cyclization of which would be accomplished by intramolecular attack of the carbanion on C-2 of the second cyclopropyl group with generation of a *cis*-olefinic linkage. The *trans*-configuration of the allylic unit would be maintained in these transformations. This mechanism thus accommodates the *cis-trans*-configuration of (**2**) and the fact that the same adduct (**2b**) was obtained from both (**1b**) and (**1c**).

If a suitable decyanation method could be found, this cycloaddition would provide a simple route to a wide range of previously inaccessible paracyclophanes.

We acknowledge the financial support of the Ministry of Education of Japan.

(*Received*, *22nd May* 1978; *Com.* 546.)

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† Satisfactory elemental analyses and spectroscopic data were obtained.

‡ Although (**1b**) and (**1c**) were thermally stable at 85—90 °C, they isomerized slowly in the presence of TCNQ. For example, in the reactions of (**1c**), the recovered stilbene was contaminated by a small amount of (**1b**) (2% in acetonitrile and 12% in 1,2-dichloroethane).

§ Alternatively, TCNQ$^{-\cdot}$ may directly attack (**1**)$^{+\cdot}$ to produce (**3**).

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