CHEMISTRY LETTERS, pp. 1015-1016, 1977. Published by the Chemical Society of Japan

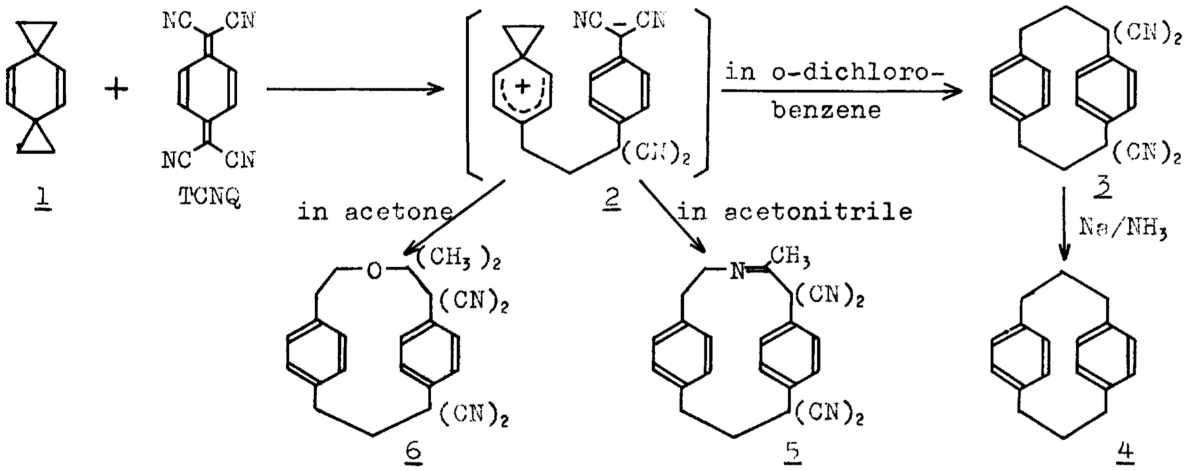
# DONOR-ACCEPTOR TYPE CYCLOADDITION OF DISPIRO[2.2.2.2]DECA-4,9-DIENE WITH TETRACYANOQUINODIMETHANE

Takashi TSUJI, Yutaka HIENUKI, and Shinya NISHIDA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

Dispiro[2.2.2.2]deca-4,9-diene undergoes the cycloaddition with tetracyanoquinodimethane to give [3.3]paracyclophane derivative via a zwitterionic intermediate which can be trapped by polar multiple bonds.

The donor-acceptor cycloaddition reaction is currently a subject of much interest. Since the ionization potential of dispiro[2.2.2.2]deca-4,9-diene 1[1] is unusually low,[2] effective participation of 1 in such a reaction is expected. We now report the cycloaddition of 1 with electron-deficient quinodimethanes, which provides a new and efficient way of preparing [3.3]paracyclophanes.

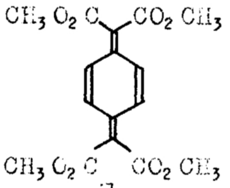
When a 1:1 mixture of 1 and tetracyanoquinodimethane (TCNQ) in o-dichlorobenzene was stirred at 60°C, 1 was consumed in 20 hr and a single cycloaddition product 3 was obtained in a 35% yield. Proof of the structure of 3 was provided by its elemental analysis and spectral properties, and finally by reductive decyanation[3] to the parent compound 4[4] in 79% yield. 3: mp 260-260.5°C; m/e 336 ($M^+$); $\lambda$max($CH_2Cl_2$) 297 nm ($\varepsilon$ 160); $\delta$($CDCl_3$) 2.8-3.2 (AA'BB' m, 8H), 6.7 (s, 4H), and 7.3 (s, 4H). In acetonitrile, the reaction of 1 with TCNQ was completed within 20 hr at room temperature. The sole product isolated from the reaction mixture was a solvent-incorporated cycloadduct, 5 (65%). 5: mp 110°C (decomp); m/e 377 ($M^+$); $\nu$(Nujol) 1680 $cm^{-1}$ (C=N); $\delta$($CDCl_3$) 2.2 (s, 3H), 2.8-3.1 (m, 6H), 3.7-3.9 (t, 2H), 6.6 (s, 4H), and 7.2 (AB quart, 4H). Analogously the reaction in acetone resulted in the formation of 6 (28%). 6: mp 153°C (decomp); $\delta$($CDCl_3$)



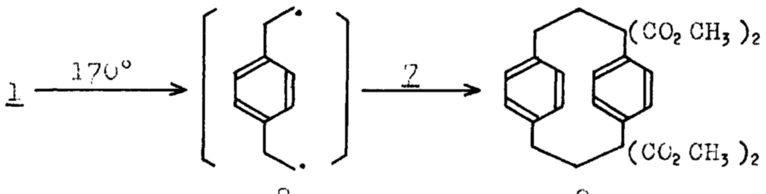
1.58 (s, 6H), 2.80-2.95 (m, 4H), 3.10-3.20(m, 2H), 3.75 (t, 2H), 6.72 (AB quart, 4H), and 7.12 (s, 4H). None of 3 was detected in those reactions.

These results may be rationalized by the initial formation of a zwitter-ion, 2. In o-dichlorobenzene, 2 collapses directly to 3.[5] In acetonitrile and acetone, however, the interception of 2 by the polar multiple bond of solvent molecule would be much faster than the ring closure to 3 and hence the solvent-incorporated cycloadducts would be produced. The formation of 5 and 6 strongly argues against radical mechanism.

Tetramethoxycarbonylquinodimethane 7 which possesses poorer electron-accepting ability as compared to TCNQ[6] did no longer undergo donor-acceptor type cycloaddition with 1 and only its spontaneous polymerization took place when a mixture of 1 and 7 in acetonitrile was stirred at room temperature. [3.3]Paracyclophane derivative 9 was, however, obtained in a 10% yield when the mixture in benzene was heated at 170°C for 5 hr. Previously, we have reported the cycloaddition of 1 with conjugated dienes by way of a biradical intermediate, 8, generated thermally from 1.[7] Although the possibility that the reaction proceeded via a zwitterionic intermediate was not rigorously ruled out, 9 would probably be formed through the addition of 8 to 7. The reaction of 1 with TCNQ in o-dichlorobenzene at 170°C resulted in an increased yield of 3 (60%).



7



8 9

It is noteworthy that the cycloaddition reaction of TCNQ is rare[8] and, to our knowledge, paracyclophane formation in which TCNQ participates is not precedented. The cycloaddition (1 + TCNQ)-decyanation gives [3.3]paracyclophane, which can be prepared only after tedious synthetic procedures,[4] in a 47% overall yield in two steps.

## REFERENCES AND NOTES

1. T. Tsuji, S. Nishida, and H. Tsubomura, Chem. Commun., 1972, 284.
2. Y. Harada, K. Ohno, K. Seki, and H. Inokuchi, Chem. Lett., 1974, 1081; P. Asmus, M. Klessinger, L. Meyer, and A. de Meijere, Tetrahedron Lett., 1975, 381.
3. P. G. Arapakos, M. K. Scott, and F. E. Huber, Jr., J. Am. Chem. Soc., 91, 2059 (1969).
4. D. J. Cram and R. C. Helgeson, J. Am. Chem. Soc., 88, 3515 (1966).
5. At 60°C, the homolysis of the cyclopropane ring in 1 should be very slow[1] and hence the reaction via 8 may be neglected.
6. D. S. Acker and W. R. Hertler, J. Am. Chem. Soc., 84, 3370 (1962).
7. T. Tsuji and S. Nishida, J. Am. Chem. Soc., 96, 3649 (1974).
8. R. Noyori, N. Hayashi, and M. Kato, Tetrahedron Lett., 1973, 2983.

(Received July 6, 1977)