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THE REACTION OF HEXAMETHYL(DEWAR BENZENE) WITH TETRACYANOETHYLENE

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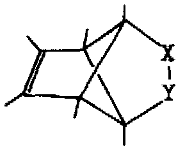
The reaction of Dewar benzenes as a homo-conjugated diene has not been clearly established as opposed to the homo Diels-Alder reactions of norbornadienes and barrelenes. When dienophiles are allowed to react with hexamethyl-(Dewar benzene) (1), the adducts in which the molecular framework of 1 has undergone rearrangement to bicyclo[2.1.1]- (2) and bicyclo[3.1.0]hexane (3) skeletons are often formed.[1)] Since the reactions of electrophilic reagents with 1 lead initially to bicyclic cations 4, which is the subject of recent interest,[2)] the formation of 2 and 3 is considered to take place via ionic paths. In the case of hexafluoro(Dewar benzene), it behaves as a dienophile rather than a diene.[3)] Only two examples of the Diels-Alder type reactions giving products 5 are previously reported. Schafer described the TCNE adduct of 1 as 5a without any detail.[4)] To a transient product of the reaction of 1 with 4-phenyl-1,2,4-triazoline-3,5-dione as observed by nmr was tentatively assigned structure 5b.[1a)]



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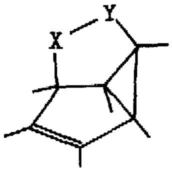

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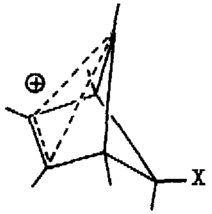

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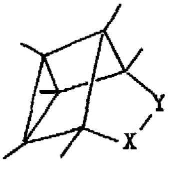

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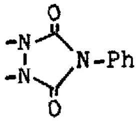
-X-Y-

a: $-C(CN)_2C(CN)_2-$

b:



In this communication we wish to report that the main product of the reaction of 1 with TCNE is indeed 5a, but that the reaction is more complex than a closely concerted and symmetric interaction of the π-electron systems of the reactants as in typical Diels-Alder reactions.

The reaction of 1 with 1.1 molar TCNE in chlorobenzene at 120 °C afforded a 85 % yield of a mixture of two 1:1 adducts in a ratio of 10 to 1.5) The less soluble major component was purified by recrystallization from benzene: mp 247~9 °; ^{1}H nmr (CCl_4) δ 1.62 (s, 2 CH_3), 1.25 (s, 2 CH_3), 1.24 (s, CH_3)6) 1.03 (s, CH_3); ^{13}C nmr ($CDCl_3$) δ 3.7 (CH_3), 4.8 (2 CH_3), 7.1 (CH_3), 13.1 (2 CH_3), 32.5 (2 cyclopropyl C), 40.3 (cyclopropyl C), 49.6 (2 quaternary C), 60.4 (quaternary C), 61.3 (2 quaternary C), 110.6 (C≡N), 111.1 (C≡N). The minor adduct was isolated by chromatography on silica gel: mp 202~3 °; ^{1}H nmr ($CDCl_3$) δ 1.73 (s, 2 CH_3), 1.33 (s, 2 CH_3), 1.20 (s, 2 CH_3); uv (cyclohexane) λ_{max} 223 nm, log ε_{max} 3.70.

Only two structures have a priori possibility by symmetry for the major product which shows the methyl proton signals in a ratio of 2:2:1:1. The confirmation of structure 5a was obtained by single-crystal X-ray analysis.

The colorless crystals of the main adduct grown from benzene are monoclinic, space group $P2_1/n$, with a = 12.620(9), b = 13.296(14), c = 9.685(14) Å and β = 95.87(3) °. The calculated density, based on four molecules of the adduct per unit cell, is 1.193 g/cm^3. The intensity data were collected on a Rigaku automated four-circle diffractometer by employing a ω-2θ scan technique. Of accessible 2345 reflections with $2\theta \leq 120$ °, significant counts ($|F| \geq 3\sigma$) were recorded for 2112 reflections. The structure was solved by the symbolic addition procedure. The full-matrix least-square refinement gave a final R-value of 0.065. Molecular geometry and the atomic numbering of 5a are illustrated in Fig. 1. An alternative structure 6 is thus ruled out.

Structure 2a of the minor adduct is suggested by the uv absorption maximum at 223 nm. The parent tricyclo[3.3.0.0^{2,6}]oct-3-ene has its uv maximum at ca. 215 nm due to mixing of high-lying σ orbitals of a cyclobutane ring with the ethylenic chromophore to effect bathochromic shift.7) When the minor adduct was treated with osmium tetroxide in the presence of pyridine,8) colorless needles

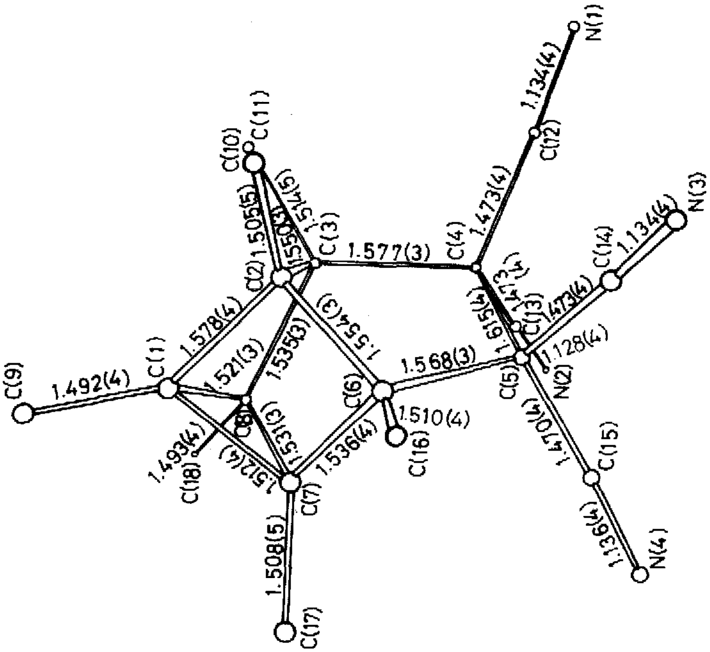
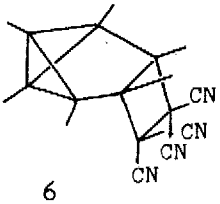


Fig. 1. A perspective drawing of 1,2,3,6,7,8-hexamethyl-4,4,5,5-tetracyanotetracyclo[5.1.0^{2,6}.0^{3,8}]octane (5a). The hydrogen atoms have not been included for clarity.

were obtained in 90 % yields: mp 133 ~ 4 °; ^{1}H nmr (CDCl$_3$) δ 1.30 (s, 2 CH$_3$), 1.50 (s, 2 CH$_3$), 1.55 (s, CH$_3$), 2.00 (s, CH$_3$), 7.49 (m, 2 × 2 H-3 of pyridine), 7.98 (m, 2 H-4 of pyridine), 8.73 (m, 2 × 2 H-2 of pyridine). Of the several candidates which have symmetry to give the nmr lines due to the methyl protons in a 2:2:2 ratio,$^{9)}$ only 2a can afford the osmate-pyridine complex with the methyl proton signals separated in a ratio of 2:2:1:1 as in 7.



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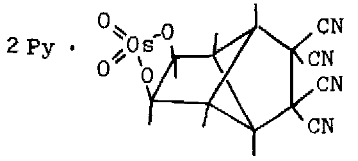

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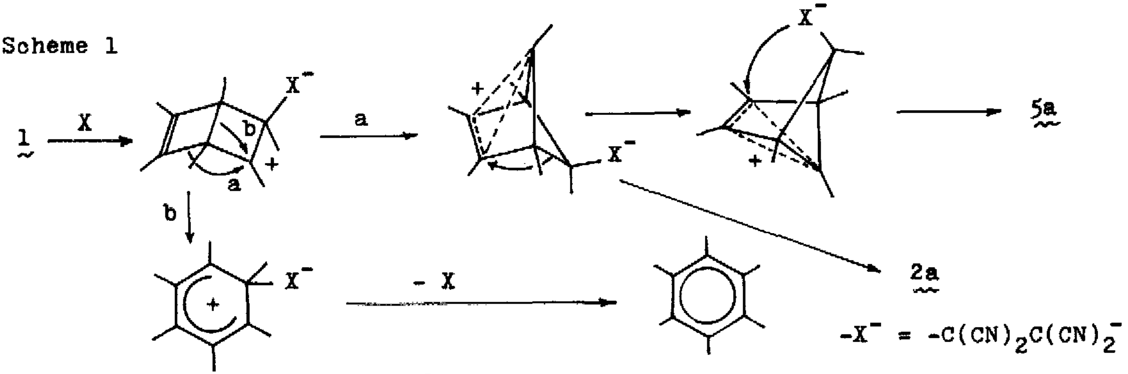
The effect of solvents on the reaction of 1 with TCNE has been examined at 84.0 °. The rates of the reaction were enhanced about 30 times in benzonitrile and 10^2 times in nitrobenzene relative to that in chlorobenzene ($k_2^{obs} = 2.4 \times 10^{-5}$ l. mol^{-1}.sec^{-1}). The yields of 5a and 2a did not depend on the solvent, and the products were always accompanied by a 12～15 % yield of hexamethylbenzene.[10)]

All the results are interpreted in terms of the ionic character of the TCNE addition as proposed in Scheme 1. A larger dihedral angle (124.5°) between two CC=CC planes in **1** appears to be unfavorable for the two-center Diels-Alder reaction electronically as well as geometrically.[11)]

Scheme 1



$-X^- = -C(CN)_2C(CN)_2^-$

References and Notes

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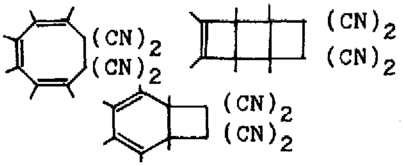
2) H. Hogeveen and P. W. Kwant, Accounts Chem. Res., **8**, 413 (1975).
3) R. N. Haszeldine, M. G. Barlow, and R. Hubbard, J. Chem. Soc., C, 95 (1971).
4) W. Schäfer, Angew. Chem., **78**, 716 (1966).
5) Satisfactory elemental analyses were obtained for $C_{18}H_{18}N_4$.
6) Chemical shifts of these two lines coincide in $CDCl_3$, while their separation is better in aromatic solvents ($\Delta\delta$ = 0.1 ppm in chlorobenzene).
7) J. Meinwald and B. E. Kaplan, J. Amer. Chem. Soc., **89**, 2611 (1967); R. Gleiter and T. Kobayashi, Helv. Chim. Acta, **54**, 1081 (1971).
8) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, p. 759.
9) These include the followings in addition to **2a**.



10) The valence-isomerization of **1** to hexamethylbenzene in the absence of TCNE is negligibly slow at this temperature.[4)]
11) For recent applications of the perturbation MO theory to the Diels-Alder reactivity, see; K. N. Houk, J. Amer. Chem. Soc., **95**, 4092 (1973); Accounts Chem. Res., **8**, 361 (1975).