

THE REACTION OF PHENANTHRO[7]CYCLOBUTADIENE

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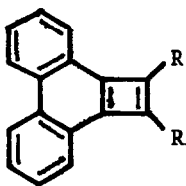
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It has been previously reported by Cava and Mangold¹ that 1,2-diphenylphenanthro[7]cyclobutadiene (I) is generated by the debromination of 1,2-dibromo-1,2-diphenylphenanthro[7]cyclobutene with both zinc dust and nickel tetracarbonyl, but that (I) cannot be trapped in a Diels-Alder reaction by conducting zinc debromination in the presence of 1,3-diphenylisobenzofuran.

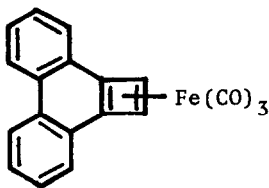
More recently,² we have described the synthesis of phenanthro[7]cyclobutadieneiron tricarbonyl (III) and demonstrated that phenanthro[7]cyclobutadiene (II), generated by the oxidative degradation of the complex (III) with ceric ion, can be readily trapped by cyclopentadiene to give the endo adduct (IV).

This has led us now to investigate the reaction of (II) with 1,3-diphenylisobenzofuran under conditions similar to those employed by them and to report the results indicating that phenanthro[7]cyclobutadiene (II) can be trapped with ease by 1,3-diphenylisobenzofuran as well as by tetracyanoethylene.

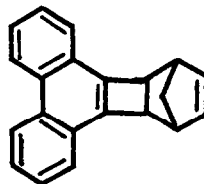


(I) R=Ph

(II) R=H

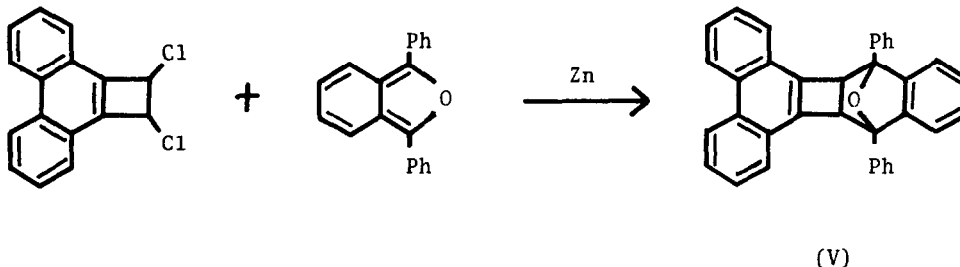


(III)



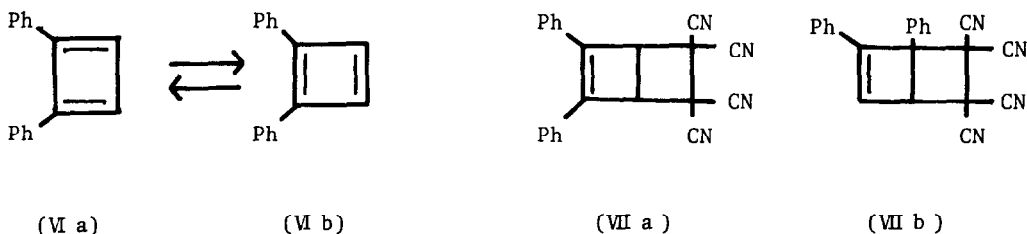
(IV)

The reaction of 1,2-dichlorophenanthro[1]cyclobutene with zinc dust in boiling ethanol in the presence of 1,3-diphenylisobenzofuran for 9 hr afforded the Diels-Alder adduct (V) in 23.4% yield.



[V; mp $>300^\circ$, Found: C, 91.19; H, 5.07%, M^+ 472. Calcd. for $C_{36}H_{24}O$: C, 91.50; H, 5.12%, Mol wt., 472, nmr (in C_6D_6), τ 1.60-1.80 (m, 2H, aromatic), 2.08-2.32 (m, 4H, aromatic), 2.50-3.10 (m, aromatic), δ 5.80 (s, 2H, methine), uv λ_{max} . (in 1,2-dichloroethane), 253 nm ($\log \epsilon$ 4.68), 260 (4.73), 272sh (4.46), 285 (4.23) 298 (4.25), 310 (4.24).]

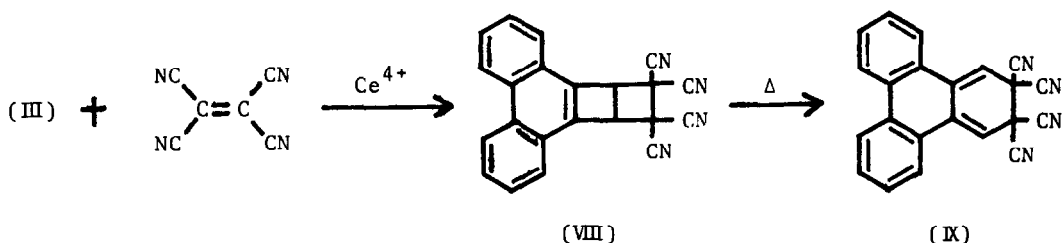
The spectral data given above are in agreement with this structural assignment. While the configuration of the adduct (V) was not completely assigned, (V) would have an endo configuration in analogy with (IV).



Pettit and his co-workers have recently indicated⁴ that *o*-diphenylcyclobutadiene exists as an equilibrium mixture of the two isomers (VI a) and (VI b) and when generated through the oxidative degradation of its iron tricarbonyl complex in the presence of tetracyanoethylene, it yields the two adducts (VII a) and (VII b) in the ratio of 1:7.

In order to examine whether such behavior is seen also in the reaction of (II) with tetracyanoethylene, oxidative degradation of the complex (III) with ceric ion in the presence of tetracyanoethylene at 0° was carried out.

Interestingly, the addition took place exclusively at 1,2-positions of (II) to give the adducts (VIII) and (IX) in 41.2 % combined yield. The adduct (VIII) undergoes the facile thermal isomerization to (IX) upon heating under reflux in 1,2-dichloroethane and, as a result, (IX) would be formed during purification of (VIII).



[IX; mp 285-287°dec. yellow plates from 1,2-dichloroethane, Found: C, 80.14; H, 2.92; N, 16.85%, M^+ 330. Calcd. for $C_{22}H_{10}N_4$: C, 79.99; H, 3.05; N, 16.96%, Mol wt., 330, ir, 2230 cm^{-1} (-CN), nmr (in CD_3COCD_3), τ 0.74 (s, 2H, vinyl), 0.92-1.08 (m, 2H, aromatic), 1.70-1.80 (m, 2H, aromatic), 2.02-2.30 (m, 4H, aromatic), uv λ_{max} . (in 1,2-dichloroethane), 245 nm ($\log \epsilon$ 4.70), 252.5 (4.73), 272.5 (4.35), 367 (3.82).]

No rigorous proof that the adduct (VIII) has been formed through the normal Diels-Alder reaction is available at this time. Because tetracyanoethylene acts as a very reactive dienophile in a Diels-Alder reaction but it also reacts either with a few diene systems incapable of forming Diels-Alder adducts⁵, or with electron rich olefins⁶ to afford cyclobutane derivatives.

Further work on this subject is now under way.

References and Notes

- (1) M. P. Cava and D. Mangold, *Tetrahedron Letters*, 1751 (1964).
- (2) T. Miyamoto, S. Tanaka, and Y. Odaira, *J. Chem. Soc. Perkin I*, in press.
- (3) As nmr spectrum was measured in hexadeuterobenzene (99%), the number of protons could not be accurately determined.
- (4) P. Reeves, T. Devon, and R. Pettit, *J. Amer. Chem. Soc.*, 91, 5890 (1969).
- (5) A. T. Blomquist and Y. C. Meinwald, *ibid.*, 81, 667 (1959); R. Criegee, *Angew. Chem.*, 74, 703 (1962).
- (6) J. K. Williams, D. W. Wiley, and B. C. McKusic, *J. Amer. Chem. Soc.*, 84, 2210 (1962).