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THE CHEMISTRY OF PHENALENIUM SYSTEM XI[1)]

1,6-ADDITION OF PHENALENYLIDENE ONTO CYCLOHEPTATRIENE

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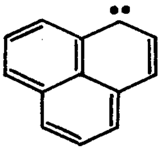
In the recent communication[2)] we have described the generation and the reaction of phenalenylidene (1), a novel carbene species in which the divalent carbon center was incorporated with a phenalenyl conjugated system, and the triplet electronic ground state (2) has been suggested as an intermediate in the thermal and the photochemical decomposition of sodium salt (3) of phenalenone tosylhydrazone. The present paper deals with the reaction between phenalenylidene (1) and cycloheptatriene and provides evidence for the first example of 1,6-addition of carbene species onto cyclic polyene.[3)]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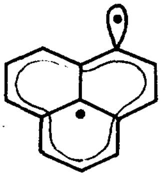
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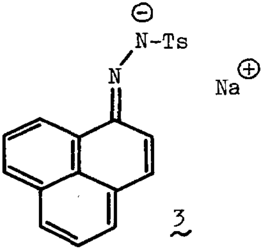

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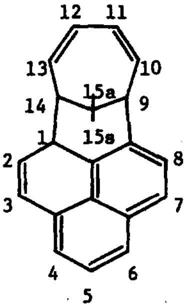
The sodium salt 3, when thermolyzed in the presence of cycloheptatriene at 90-95° for 1 hr under nitrogen atmosphere, afforded, after cautious chromatography on alumina deactivated with 6% water, two adducts (4) and (5) in 23% and 1% yield, respectively,[4)] besides phenalenone (6), 8% yield, and bitropyl (7), 5% yield. The formation of 7 can be explained by a hydrogen atom abstraction from cycloheptatriene by phenalenylidene followed by dimerization of the resulting cycloheptatrienyl radical. This confirms the intermediacy of a radical species 2 of phenalenylidene. On the other hand, irradiation of a solution of 3 and cycloheptatriene in diglyme with a 450-w high pressure Hg-lamp through an aqueous solution filter containing 9% sodium nitrite at 0° resulted in isolation of 4, 5, 6 and phenalenoneazine in 7%, 1%, 5% and 1% yield respectively.

The structure of the major adduct 4 was determined in the following ways. The adduct 4, air sensitive and thermally labile colorless liquid, was found to be a 1:1 adduct of 1 and cycloheptatriene from its elemental analysis and molecular weight determination (m/e 256). Substance 4 shows absorption bands characteristic of the phenalene chromophor, λ_{max} (in cyclohexane) 230 nm (log ε 4.63), 310(3.89), 324(4.01), 338(3.94) and 342(sh, 3.87). The nmr spectrum of 4 was fully assigned with the aid of double resonance experiments. At 100 MHz, the five aliphatic and the five aromatic proton resonance of 4 were well resolved in CCl_4 [see Fig-1].

Assignments of the resonances of the aromatic protons were made as follows: The AMX-type signals at δ 6.94, 7.16 and 7.43 ppm are assigned to H-4, H-5 and H-6 with coupling constants $J_{4,5}=7.0$, $J_{5,6}=8.2$ and $J_{4,6}=1.5$ Hz, and the AB-quartet at δ 7.23 and 7.45 ppm are assigned to H-8 and H-7 in light of their vicinal coupling, $J_{7,8}=8.5$ Hz. The long-range couplings with H-1 observed for H-4, 6 and 7, $J_{1,4}=J_{1,6}=J_{1,7}=1.5$ Hz, imply that H-1 is disposed in C-1 position of the phenalene moiety.$^{5)}$

A pair of doublet of doublets at δ 6.10 and 6.53 ppm are assigned to the vinyl H-2 and H-3 which are coupled each other with coupling constant of 9.5 Hz. Additional splittings for H-2 (3.5 Hz) and for H-3 (2.5 Hz) are due to spin couplings with vicinal and allylic H-1 respectively.



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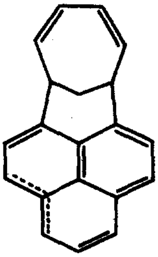

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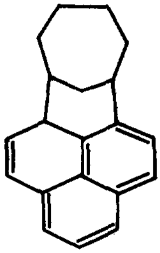

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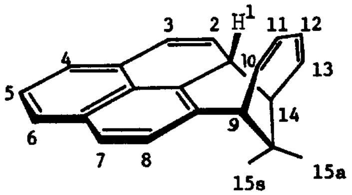
Although most of the olefinic resonances except H-2 and H-3 overlapped at 100 MHz, these resonances were well separated and were identified at 220 MHz [see Fig-2]. The absence of the vinyl proton resonances at δ 5.66, 5.83, 5.93 and 6.79 ppm in tetrahydro-compound (8) which was obtained by catalytic hydrogenation of 4 as a thermally labile colorless liquid, the characteristic vicinal coupling between the protons resonating at δ 5.66 and 5.83 (11.0 Hz), δ 5.83 and 5.93 (7.0 Hz), δ 5.93 and 6.79 (10.0 Hz), as well as the chemical shifts of these protons resulted in the assignment of the resonances to H-10, H-11, H-12 and H-13, respectively. H-10 and H-13 exhibit an additional vicinal coupling with H-9 (5.0 Hz) and with H-14 (8.0 Hz), respectively.

H-15s and H-15a, which appear as the AB-part of an ABXY-system centered at δ 1.53 ppm, are assigned to geminal methylene protons. Irradiation of the H-15 resonance resulted in simplification of both the protons of one-proton multiplet at δ 3.74 and 2.73 ppm revealing the positions of resonance due to H-9 and H-14. No change was observed on the signals due to the any of the olefinic protons upon this irradiation indicating that the vicinal neighbour of the geminal methylene protons, H-15s and H-15a, are not olefinic but the aliphatic H-9 and H-14 protons. Irradiation of the H-9 resonance resulted in simplification of the one proton doublets at δ 5.66 ppm due to H-10. Similarly, decoupling experiments established that H-14 is strongly coupled with H-1, H-13 and H-15s,a.



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Orientation of the methine proton H-1 was determined as cis to the diene segment of the cycloheptatriene moiety (9) by comparison of the chemical shift of H-1 with that of the tetrahydrocompound (8). The nmr spectrum of 8 shows a H-1 proton multiplet at δ 3.65 ppm in addition to the signals of H-9 (3.15, m, 1H), H-2 (6.00, dd, J=10.0 and 3.0 Hz), H-3 (6.57, dd, J=10.0 and 2.0 Hz), aromatic protons (6.8-7.6, m, 5 H) and aliphatic protons (1.0-2.4, m, 11 H). It is apparent that the long-range shielding effect of the C_{12}-C_{13} double bond of the cycloheptatriene moiety is responsible for the shift of H-1 in the original adduct 4 being at such a high field (δ 3.03 ppm). The assignments of all the

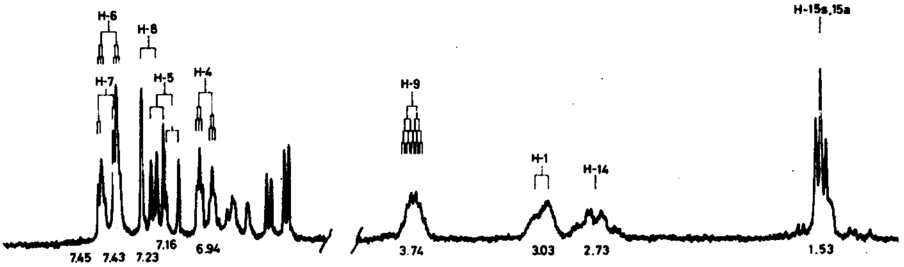


Fig - 1. 100 MHz nmr spectrum of 4 (aliphatic and aromatic regions)

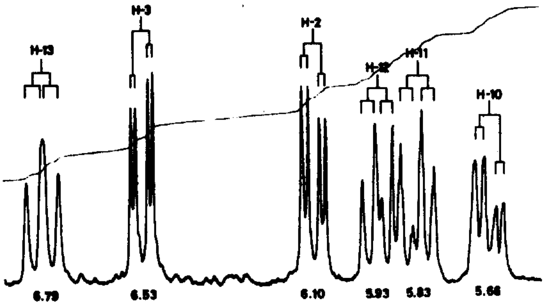
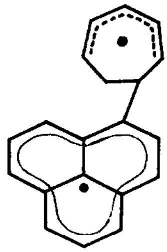


Fig - 2.
220 MHz nmr spectrum of 4
(olefinic region)

resonances and couplings in the nmr spectra resulted in elimination of the all possible isomers arising from any 1,2- and 1,4-addition of **1** to cycloheptatriene.

The structure of the minor adduct,4) air sensitive colorless needles of mp 102-105°, was not fully elucidated to date, its spectral properties, λ_{max} (in ether), 228, 296, 340 and 360 nm; m/e 256 (M^+); nmr, δ 2.0-2.5 (2H, m, aliphatic methylene), 3.4-4.1 (4H, m, allylic and benzylic) and 5.4-7.4 (10 H, m, vinyl and aromatic), suggest that this adduct is an isomeric mixture of **5**. The attempted silica gel chromatography of **4** or heating a solution of **4** in diglyme at 140° for 6 hr afforded an isomeric mixture of **5** in moderate yield. Since many phenalenes undergo ready hydrogen shifts6) it was postulated that an initial addition of phenalenylidene across the termini of the cycloheptatriene to give **4** was followed by a hydrogen shift to give the thermodynamically more stable phenalene **5** as a secondary product.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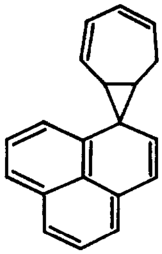
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We tentatively propose an intermediate diradical (**10**) for this addition reaction. Although the spiro-compound (**11**) could not be detected in the low temperature photolysis peviously described, the intervention of **11** was not fully eliminated because the energy required for bond dissociation of **11** should be lower than usual since the radical centers produced possess unusual stability, the one center because it is phenalenyl, the other because it is a pentadienyl radical.

REFERENCES AND FOOTNOTES

1) For part X, see I. Murata, K. Yamamoto and T. Hirotsu, *Tetrahedron Letters*, 3389 (1972).

2) I. Murata, T. Nakazawa and S. Yamamoto, *ibid*., 2749 (1972).

3) Carbenes very rarely add to polyenes in a 1,4-fashion, only two examples have been reported to date : H. Nozaki, M. Yamabe and R. Noyori, *Tetrahedron*, **21**, 1657 (1965);A. G. Anastassiou, R. P. Cellura and E. Ciganek, *Tetrahedron Letters*, 5267 (1970).

4) All new compounds gave satisfactory elemental analyses.

5) H. Prinzbach, V. Freudenberger and U. Scheidegger, *Helv. Chim. Acta*, **50**, 1087 (1967).

6) Cf. D. H. Reid, *Quart. Revs*., **19**, 274 (1965).