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THE CHEMISTRY OF PHENALENIUM SYSTEM VIII[1)]

GENERATION AND REACTIONS OF PHENALENYLIDENE

Ichiro Murata, Tomoo Nakazawa and Shuichi Yamamoto

Department of Chemistry, Faculty of Science, Osaka University,
Toyonaka, Osaka 560, Japan

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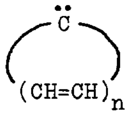
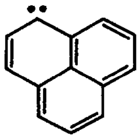
Recently, many attempts have been made to generate carbenes in which unique electronic situation might be anticipated due to the participation of the p-orbital at the carbenic center in a potentially aromatic ring system, such as cyclopropenylidene (1: n=1),[2)] cyclopentadienylidene (1: n=2)[3)] and cycloheptatrienylidene (1: n=3).[4)]



(1)

In connection with our interest in conjugated systems having phenalene ring, we have examined new carbenic species, phenalenylidene (2), which is an intriguing chemical entity due to its three possible electronic configurations (2a, 2b and 2c). Thus, for the singlet carbenes (2a) and (2b), the vacant and the doubly occupied p-orbitals are incorporated into the pi-system to form stable aromatic phenalenium (12-pi) and phenalenide (14-pi), respectively.[5)] On the other hand, however, the triplet ground state (2c) would also be stable because in this case an unpaired electron is localized in the in-plane sp^2-orbital, while another electron is delocalized in the pi-system to produce a stable phenalenyl radical.[5)]



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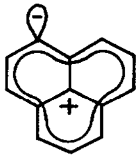
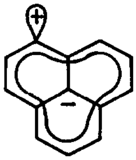
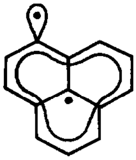


(2a)



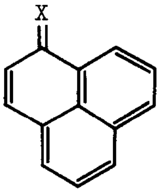
(2b)



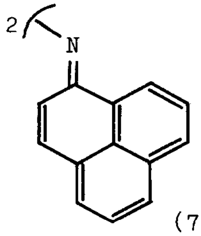
(2c)

We wish to present the results of our attempt to generate a carbene in which the singly occupied p-orbital is an integral part of a phenalenyl radical.

Phenalenone tosylhydrazone (4), mp 188° (d) [lit.[6] 180-182°], 96 % yield, a potential precursor to the carbenic species (2), was easily derived from the ketone (3) and tosylhydrazine in the presence of catalytic amount of hydrochloric acid.[6] The tosylhydrazone was converted to its sodium salt (5) with sodium hydride in tetrahydrofuran. The thermal decomposition of (5) in dimethoxyethane at 60° was carried out in the presence of oxygen, the major reaction product was



(3) : X = O
(4) : X = NNHTs
(5) : X = $\overset{\ominus}{N}$NTs
(6) : X = H_2

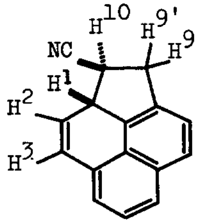


(7)

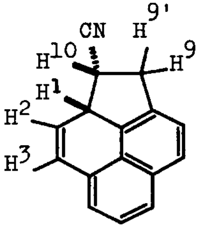
phenalenone (3) [14 % yield], which was hardly found in the decomposition under a nitrogen atmosphere, along with phenalenone azine (7)[6] [3 % yield] as a minor product. Furthermore, the thermal decomposition of (5) in toluene resulted in the formation of hydrogen abstracted product phenalene (6) in 12 % yield[7], with some unidentified products. All these are typical free-radical reactions[8] and are best understood by assuming that the carbenic species produced on decomposition of (5) is the diradical (2c).

An odd electron distribution around the carbon skeleton can be estimated based on the reaction of (2) with acrylonitrile. The decomposition of (5) in acrylonitrile at 82° affords two isomeric adducts [m/e 217 (M^+), 216 (M-1, 100 %), common to both], in 15 % and 11 % yield, respectively. Irradiation of a solution of (5) and acrylonitrile in dimethoxyethane with a 300-w tungsten lamp resulted in the isolation of the same adducts with improved yields. The major product (air sensitive colorless crystals, mp 103-105°, 28.8 % yield, Anal. Found : C, 88.62; H, 5.10; N, 6.47 %) was assigned as (8a) on the basis of its spectral properties. The ir spectrum of (8a) was characterized by band at 2250 cm^{-1} (CN). The uv spectrum was characteristic of phenalene : λ_{max} (ethanol), nm (log ε), 216 (4.46), 230 (4.61), 237 (4.65), 248 (4.21), 258 (4.02), 270 (3.71), 310 (4.00), 323 (4.04) and 341 (3.96). The 100 MHz nmr spectrum (CCl_4) showed signals at δ, 7.0-7.9

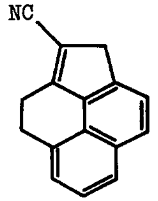
(m, 5H not 6H, aromatic), 6.64 (dd., 1H, H-3, $J_{3,2}$=10.0 and $J_{3,1}$=3.0 Hz), 6.20 (dd., 1H, H-2, $J_{2,3}$=10.0 and $J_{2,1}$=3.0 Hz), 4.15 (broad d., 1H, H-1, $J_{1,10}\simeq10$ Hz) and 2.8-3.5 (m, 3H, H-9, 9' and 10). Stereochemical assignment of (8a) was based on nmr coupling constant datum of H-1 and H-10. The broad splitting of the signal assigned to H-1, ca. 10 Hz, observed for $J_{1,10}$ is consistent with a trans arrangement of these vicinal hydrogens, whence the dihedral angle is about 150°. The identity of the minor product (air sensitive colorless crystals, mp 146.5-147°, 13.4 % yield, Anal. Found: C, 88.07; H, 5.11; N, 6.40 %) was established as



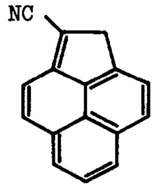
(8a)



(8b)



(9)



(10)

(8b) through its spectral characteristics: ir max (KBr) 2250 cm^{-1} (CN); uv max (ethanol), nm (log ε), 216 (4.32), 237 (4.62), 250 (4.13), 260 (3.85), 315 (3.88), 326 (3.98) and 342 (3.91); nmr (100 MHz, CCl_4), δ, 7.0-7.9 (m, 5H, aromatic), 6.76 (dd., 1H, H-3, $J_{3,2}$=10.0 and $J_{3,1}$=2.5 Hz), 6.16 (dd., 1H, H-2, $J_{2,3}$=10.0 and $J_{2,1}$=3.0 Hz), 4.29(broad s, 1H, H-1), 3.80 (ddd., 1H, H-10, $J_{1,10}$=7.0, $J_{9,10}$ =4.0 and $J_{9,10}$=2.5 Hz) and 3.33 (broad s, 2H, H-9, 9'). These assignments for the spin-spin coupling interactions were tested by double resonance experiments. When the signal assigned to H-9 and 9' was saturated with an external field, the doublet of doublets of doublets at 3.80 assigned to H-10 collapsed to a doublet with the coupling constant of 7.0 Hz which support the cis configuration of H-1 and H-10 $[\theta_{1,10}\simeq20°]$.

Treatment of the both isomeric adducts (8a) and (8b) with alumina or (8a) with acidic and/or basic conditions lead rapidly and almost quantitaitvely to the formation of the same product (9): ir max (KBr) 2200 cm^{-1} (conjugate CN); uv max (ethanol) nm (log ε), 242 (4.33), 355 (s, 4.10), 320 (s, 3.83), 333 (3.94) and 347 (3.82); m/e, 217; nmr (60 MHz, CCl_4), δ, 7.1-8.0 (m, 5H, aromatic), 3.85 (m, 2H) and 3.30 (m, 4H).

Further chemical confirmation of these structures (8a) and (8b) was obtained by treating (8a) and/or (8b) with chloranil in benzene to give the dehydrogenated product in 60 % yield, mp 150-152°. The structure of this product was established unambiguously to be 10-cyano-8,10-methanophenafulvene (10) by its elemental analysis [Found: C, 88.83; H, 4.14; N, 6.49 %] and spectroscopic properties: uv max (ethanol) nm (log ε), 252 (s, 4.29), 259 (4.35), 268 (4.34), 284 (4.04), 296 (3.99), 372 (s, 3.86), and 416 (4.19). (cyclohexane), 251 (s, 4.31), 259 (4.37), 269 (4.37), 285 (4.03), 297 (4.01), 356 (3.64), 370 (3.86), 397 (4.15), 410 (4.22), 415 (4.25), 433 (4.05) and 441 (3.99); ir max (KBr), 2185 cm^{-1} (conjugate CN); nmr (60 MHz, CCl_4), δ, 3.60 (s, 2H) and 7.1-8.0 (m, aromatic 7H); ms, m/e 215 (M^+, 75 %), 214 (M-1, 100 %), 213 (M-2, 100 %).

Although the intervention of spiro adduct in the reaction of (5) with acrylonitrile cannot be ruled out at this stage the observations reported here are best rationalized by the postulate that the triplet species or at least a considerable amount of triplet species (2c) is involved in these reactions.

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