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THE CHEMISTRY OF PHENALENIUM SYSTEM IX[1)]
REACTION OF LITHIUM PHENALENIDE WITH 1,2-DISUBSTITUTED 3,3-DICHLOROCYCLOPROPENES

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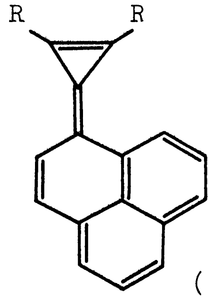
Reaction of lithium phenalenide (2) with 1,2-di-n-propyl-3,3-dichlorocyclopropene (3: R=n-C_3H_7), and with 1,2-diphenyl-3,3-dichlorocyclopropene (3: R=C_6H_5) in ether under nitrogen gives rearranged products, 1,3-di-n-propylpyrene (4) and 10-phenyl-10-phenylethynylphenafulvene (5), respectively.

Hitherto unknown triaphenafulvalene (1: R=H)$^{2)}$ is an interesting mixed fulvalene, since the contribution of the dipolar character — the positive and the negative poles are located in the three membered and the phenalene rings, respectively — may be anticipated from theoretical consideration to its ground state.



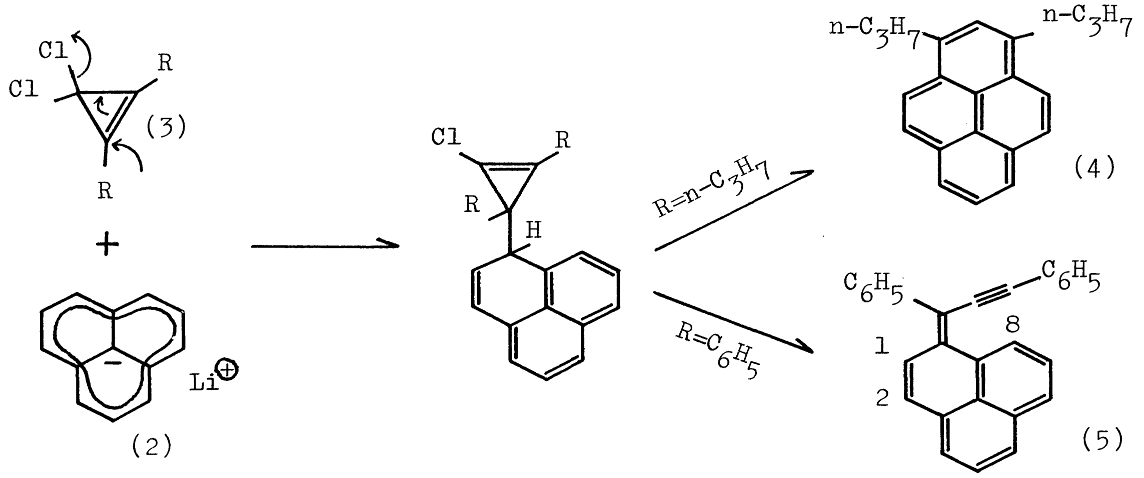
(1)

During attempts to prepare triaphenafulvalene system from lithium phenalenide (2) by the use of 1,2-disubstituted 3,3-dichlorocyclopropenes (3), the anomalous formation of isomeric hydrocarbons of (1) derived from unexpected attack of (2) on the double bond of (3) was observed.

Addition at 0°C during 30 min of a solution of 1,2-di-n-propyl-3,3-dichlorocyclopropene (3: R=n-C_3H_7) (3 mmol) in dichloromethane (5 ml) to a stirred suspension of lithium phenalenide (2) (3 mmol) in ether (5 ml) under nitrogen followed by stirring of the mixture at 0°C for 1 hr afforded a colorless crystalline hydrocarbon (4)$^{3)}$, mp 76.5-77.2°C (4% yield) along with the 50% recovery of phenalene on pouring the mixture into water and subsequent separation by column chromatography on alumina.

The structure of (4) was proved to be 1,3-di-n-propylpyrene by elemental analysis and spectroscopic data. The uv spectrum displays the characteristic absorption pattern of pyrene with a slight bathochromic shift caused by alkyl substitution: λ_{max} (ethanol), 235(log ε, 4.64), 244(4.82), 257(4.09), 267(4.46), 278(4.75), 317(4.12), 332(4.50) and 348 nm (4.66). The pmr spectrum indicates the presence of signals responsible for the two equivalent n-propyl groups and symmetrically substituted aromatic hydrogens: δ (CCl_4, 60 MHz), 1.16(t, 6H), 1.92(sext, 4H), 3.32 (t, 4H), 7.75(s, 1H), 8.03 and 8.30(AB-q, 4H, J=8.5 Hz) and 8.10 ppm (s, 3H). The mass spectrum exhibits the molecular peak at m/e 286.

On the other hand, however, 1,2-di-phenyl-3,3-dichlorocyclopropene (3: R=C_6H_5) reacts with (2) to yield yellow oily product (11% yield)$^{3)}$, $C_{28}H_{18}$ (M^+, m/e 354), which is assigned to the 10-phenyl-10-phenylethynylphenafulvene (5) on the basis of its spectroscopic characteristics. The uv spectrum shows similar absorption with 10-phenyl-$^{4)}$ and 10,10-diphenylphenafulvene$^{5)}$: λ_{max} (methanol), 270(log ε, 4.35), 342 (3.69) and 460 nm (4.24). ir : ν_{max} (CCl_4), 2150 cm^{-1} (w, C≡C); pmr, δ(CCl_4, 60 MHz): 8.08(dd, J=7.0, 3.0 Hz, 1H, H-8), 6.71 and 6.93 (AB-q, J=10.0 Hz, 2H, H-1 and H-2) and 6.8-7.8 ppm (m, 15H, aromatic). Although the exact geometrical configuration of the two substituents at 10-position is obscure, we felt that a phenylethynyl group would be oriented syn to the phenalene residue (because of the low field chemical shift of H-8 due to the anisotropy effect of the acetylenic triple bond).



In these reactions, the first step involves probably attack of (2) on the carbon-carbon double bond of (3) with expulsion of chloride ion and is similar to that of the reaction of (3: R=C_6H_5) with diphenylmethyl lithium leading to the formation of tetraphenylbutenyne reported by Melloni and Ciabattoni.$^{6)}$

Unfortunately, we are not able to offer a satisfactory explanation of how the substituents (phenyl and n-propyl) control the mode of reaction at this moment.

We are now investigating the reaction of (2) with 1,2-di-t-butyl-3,3-dichlorocyclopropene (3: R=t-C_4H_9) in which nucleophilic attack of (2) on the double bond is hindered by the bulky t-butyl group.

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