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THE CHEMISTRY OF PHENALENIUM SYSTEM. III.[1)]

1,3-DI-t-BUTYL-5-ETHOXYPENTALENO[4,5,6-cd]PHENALENE.

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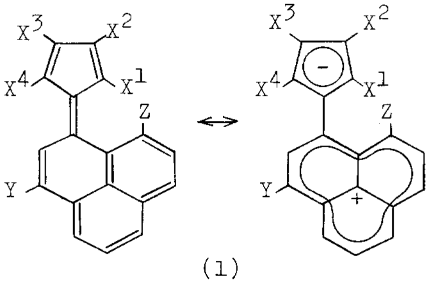
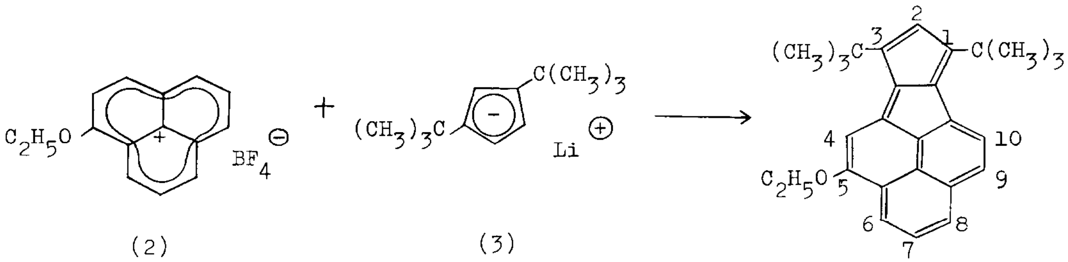
ALTHOUGH the field of cyclic cross-conjugated nonbenzenoid aromatic compounds has been extensively investigated in recent years,[2)] only three examples of a penta-phenafulvalene (cyclopentadienylidene-phenalene) system (1) have been reported.



(1)

(1a) : $X^1 = X^2 = X^3 = X^4 = Cl$
$Y = OC_2H_5$, $Z = H$
(1b) : $X^1 = X^4 = Y = Z = H$
$X^2 = X^3 = CN$
(1c) : $X^2 = X^3 = Cl$, $Y = OCH_3$
$X^4 = H$, X^1 $Z = C_5Cl_4$

The compounds (1a),[1a)] (1b)[3)] and (1c)[1b)] are interest because of a significant contribution of charge-separated resonance form (phenalenium-cyclopentadienide) to the ground-state of these molecules. Since the possibility of isolation of the parent hydrocarbon (1 : X = Y = Z = H) is negligible, it was decided to attempt the synthesis of di-t-butyl substituted derivative in which the two t-butyl groups would sterically retard the polymerization and would minimally perturb the pi-electron system from that of the parent compound. During a study of the reaction of ethoxyphenalenium fluoroborate (2) with lithium 1,3-di-t-butylcyclopentadienide (3), an unexpected product was obtained.



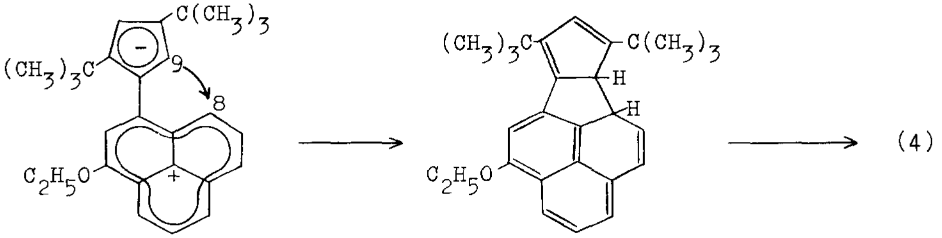
(2) (3) (4)

The reaction of (2)[30 m mol] with (3) [15 m mol] at 5 - 10°C in ether-tetrahydrofuran-acetonitrile under nitrogen lead on repeated alumina chromatography to wine red prisms (4) with mp. 125.5 - 126°C (decomp) in 1.8 % yield. Elemental analyses and molecular weight determination confirmed that (4) had a molecular formula of $C_{28}H_{30}O$. Anal. Found : C, 87.70; H, 7.73 %; mol. wt., 379 (osmometer), 382 (M^+). Calcd. for $C_{28}H_{30}O$: C, 87.91; H, 7.91 %; mol. wt., 382.

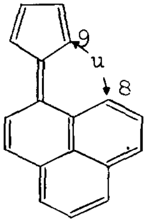
Conclusive evidences for the structure of (4) were obtained *inter alia* from its spectroscopic properties. I. r. spectrum (KBr) contains the strong absorption for aromatic ether linkage at 1235 cm^{-1} and C=C absorptions at 1632 and 1572 cm^{-1}. In the electronic spectrum of (4) the small bathochromic shift, on going from cyclohexane to acetonitrile, was observed. λ_{max} (in cyclohexane) : 209.5 nm (log ε, 4.55), 287 (4.51), 303 (sh, 4.45), 316(sh, 4.37), 360 (sh, 3.94), 468 (sh, 4.06), 497 (4.21), 520 (sh, 4.19), 563 (sh, 3.78); λ_{max} (in acetonitrile) : 212 (4.31), 287 (4.45), 304 (sh, 4.39), 314 (sh, 4.34), 360 (sh, 3.86), 468 (sh, 4.01), 502 (4.19), 520 (sh, 4.16). P. m. r. spectrum consists of two sharp singlets at δ = 0.90 ppm (9H) and 0.98 (9H) due to the two nonequivalent *t*-butyl groups, triplet at 1.40 (3H, J = 7.0 Hz) and quartet at 3.89 (2H, J = 7.0 Hz) for the ethoxyl group, H-2 singlet at 4.03, H-4 singlet at 5.09 [irradiation at the site of methylene protons of ethoxyl group (3.89 ppm) causes this signal to exhibit an about 30 % increase in peak hight],[1b, 5)] AB-quartet of H-9 and H-10 at 6.38 and 6.76 (J = 6.7 Hz) and AMX-type signals of H-6, H-7 and H-8 at 6.20 (d, J = 8.3 Hz), 6.73 (dd, J = 8.3, 7.3 Hz) and 6.45 (d, J = 7.3 Hz). These spectroscopic evidences are accord with the structure, 1,3-di-*t*-butyl-5-ethoxypentaleno[4,5,6-cd]phenalene, proposed for (4).

Even though 2-ethoxy-10,12-di-*t*-butylpentaphenafulvalene (1 : $X^1 = X^3 = Z =$

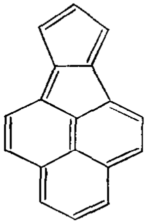
H, $X^2 = X^3 = C(CH_3)_3$, $Y = OC_2H_5$) which would be an initial reaction product was not isolated, the formation of (4) could be explained by the intramolecular nucleophilic attack of C-9 to C-8. This would be feasible both on electronic and stereochemical points of view. The highest and the lowest pi-electron densities are found at C-9 (1.093) and C-8 (0.935) respectively by the VESCF-MO calculation.[1a)]



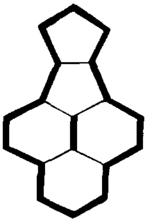
In connection with the ring system of (1), a new pentacyclic peri-condensed pi-electron system, pentaleno[4,5,6-cd]phenalene (6) which has an additional sigma-bond between positions C-8 and C-9 of the pentaphenafulvalene skeleton (5), is of an area of great interest from the following reasons. Application of Craig's rule[6)] to any of the Kekulé structures of (6) gives the result of f + g = 7 that predicts the valence-bond ground-state to be nontotally symmetric and therefore to be pseudo-aromatic. Although the total pi-electron number is 4n + 2 with n = 4, two non-charge-separated resonance forms possess a 16 pi-electron moiety peripheral to the central ethylene fragment (7). If the cross links are regarded to contribute only negligible perturbations, the present hydrocarbon (6) should be antiaromatic.[7)]



(5)



(6)



(7)

The chemical shifts of ring hydrogens, H-4, 6, 7, 8, 9, 10, are about 1.0 - 1.5 ppm upfield than those of naphthalene. We regard this shielding effect as evidence of a induced paramagnetic ring-current[8)] in the peripheral antiaromatic 16 pi-electron system or a polyolefinic character in the periphery of this molecule. Furthermore, significant upfield shift of H-2 singlet (δ = 4.03 ppm) may be attributed not only to the adjacent two <u>t</u>-butyl groups but also to the high electronic charge density on this carbon atom.[9)]

Efforts to isolate 2-ethoxy-10,12-di-<u>t</u>-butylpentaphenafulvalene and its conversion to (4) are currently under investigation.

The authors are indebted to the Research and Development Division, Takeda Chemical Industries for the 100 MHz p.m.r. spectral measurement.

REFERENCES AND FOOTNOTES

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4) P. m. r. spectrum was run in CCl_4 solution on a Varian HA-100 spectrometer using TMS as an internal standard.

5) M. C. Woods, S. Ebine, M. Hoshino, K. Takahashi and I. Miura, <u>Tetrahedron Letters</u>, 2879 (1969) and references cited therein.

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9) Simple Hückel molecular orbital treatment of (6) predicts that the pi-electronic charge density at C-2 is 1.175. More sophisticated calculations using PPP-SCF-MO method are now in progress.