Tetrahedron Letters No. 50, pp 4799 - 4802, 1971. Pergamon Press. Printed in Great Britain.

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

SOME DERIVATIVES OF PYRANYLIDENEPHENALENE.

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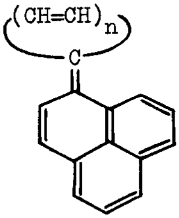
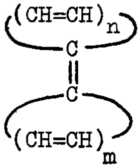
(Received in Japan 2 November 1971; received in UK for publication 11 November 1971)

The fulvalenes containing a phenalene fragment such as (1) are of interest because of their electronic characteristics distinct from the normal mixed fulvalenes (2).



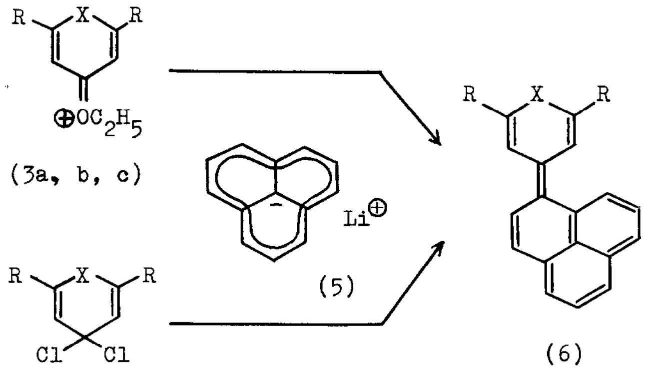
(1)



(2)

It may be expected that the pentaphenafulvalene (1: n=2) will be polarized in such a way that the positive end of the dipole is localized in phenalene ring and the negative pole in the five-membered ring, whereas the triaphenafulvalene (1: n=1) and the heptaphenafulvalene (1: n=3) will bepolarized in the reverse direction. This is because of the special property of the phenalenium system, unlike that of the odd-membered conjugated monocyclic systems, that the pi-electron energies of both the phenalenium ion (12-pi) and the phenalenide ion (14-pi) are same magnitude (17.568 β) as predicted by HMO calculations.[2)] Consequently, the situation of the polarization in (1) is dependent solely on the electronic characteristics of the conjugated monocyclic moiety.

The only phenafulvalenes known are derivatives of pentaphenafulvalene (1: n=2).[3,4,5)] In the present paper, we report the syntheses and properties of a series of some hetero-analogs which are iso-pi-electronic[6)] with heptaphenafulvalene (1: n=3) and secure evidence showing that these compounds have dipolar ground state electronic structures directed from pyranylidene ring to phenalene ring, as predicted.



(3a, b, c)

(5)

(6)

(4d, e, f, g)

	X	R
6a	O	CH_3
6b	S	CH_3
6c	O	C_6H_5
6d	O	p-$C_6H_4CH_3$
6e	S	p-$C_6H_4CH_3$
6f	NCH_3	p-$C_6H_4CH_3$
6g	O	$COOCH_3$

The preparation of pyranylidenephenalenes (6a - 6g) can be illustrated generally as in the above scheme. (6d) formed rather unstable violet amorphous solids with mp. 151-153°C. MS, m/e 424(M^+); λ_{max}(cyclohexane), 264 nm (log ε, 4.50), 278(4.53), 312(sh, 4.43), 516(4.58); λ_{max}(ethanol), 280(4.48), 310(sh, 4.36), 518(4.53); nmr (CCl_4, 60 MHz, TMS as an internal standard), δ 2.39 ppm (s, 6H), 6.6 - 7.9 (m, 10H), 7.15 and 7.57 (broad AB-quartet, 8H, J=8.5 Hz).

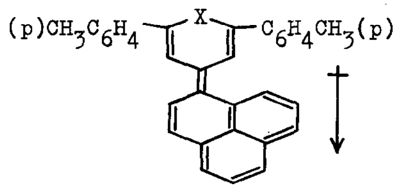
(6e) : fairly stable dark violet needles, mp. 173-174°C (from ether and pet. ether). MS, m/e 440(M^+); λ_{max}(cyclohexane), 242 nm (log ε, 4.48), 286 (4.42), 534 (4.57); λ_{max}(ethanol), 244 (4.42), 282 (4.37), 532 (4.52); nmr (CCl_4), δ 2.44 ppm (s, 6H), 6.7 - 8.2 (m, 10H), 7.27 and 7.55 (broad AB-quartet, 8H, J=8.0 Hz).

(6g) : violet needles, mp. 147.5-148.5°C (from benzene and pet. ether). MS, m/e 360(M^+); λ_{max}(cyclohexane), 284 (4.28), 302 (sh, 4.16), 492 (4.60); λ_{max} (ethanol), 284 (4.22), 302 (sh, 4.09), 490 (4.60); nmr ($CDCl_3$), δ 3.84 (s, 3H), 3.87 (s, 3H), 6.83 and 7.03 (broad AB-quartet, 8H, J=10.0 Hz), 7.2~7.9 (m, 8H).

Unfortunately, the application of this method to the syntheses of parent pyranylidenephenalene and the simple derivatives such as (6a, 6b, and 6c) are fraught with experimental difficulties. Addition of the ethoxy cations (3a, b, c) to lithium phenalenide (5) in ether at 0° gave deeply colored solutions showing the absorption maxima at 470, 497, 507 nm (in pet. ether), respectively, which might be taken to indicate formation of the desired fulvalenes (6a, b, c). On allowing the reaction mixtures to stand in the atmosphere these absorption peaks decayed slowly, and work-up of the reaction mixtures by column chromatography with alumina and/or silica-gel gave no evidence for the fulvalene components.

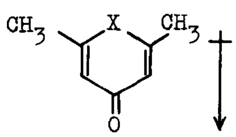
In the case of the reaction of (4f) with (5), we obtained the blue violet ether solution with the absorption maximum at 570 nm also indicating the formation of (6f). The solution, however, is extremely air-sensitive and decolorized within few minutes when allowed to stand in contact with the atmosphere.

The observed dipole moments of (6d) and (6e) in benzene solution at 25°C are 2.95 D and 1.85 D, respectively.[7] The direction of dipole moment can be determined from the comparison of the moments of 2,6-diphenyl-4H-pyran-4-one (4.74 D)[8] and 2,6-diphenyl-4H-thiopyran-4-one (4.41 D)[8] and of 2,6-dimethyl-4H-pyran-4-one (4.58 D)[9] and 2,6-dimethyl-4H-thiopyran-4-one (4.30 D);[9] and the knowledge of the direction of the moments of 4H-pyran-4-one and 4H-thiopyran-4-one.[10] The increase of the dipole moments going from 2,6-diphenyl-4H-thiopyran-4-one to 2,6-diphenyl-4H-pyran-4-one qualitatively parallels those found in our compounds (6e) and (6d). It may therefore be concluded that the negative pole of the dipoles of (6d) and (6e) are located in the phenalene ring.



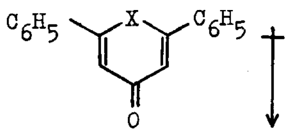
(6d), X=O : μ=2.95 D

(6e), X=S : μ=1.85 D



X=O : μ=4.58 D

X=S : μ=4.30 D

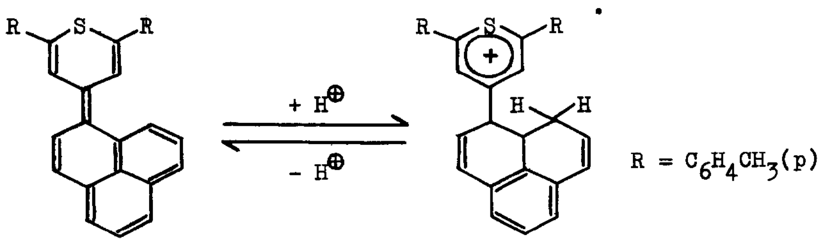


X=O : μ=4.74 D

X=S : μ=4.41 D

These polarization is also reflected in the behavior of (6e) to strong acids. (6e) dissolves reversibly in trifluoroacetic acid and sulfuric acid. In trifluoroacetic acid, the electronic spectrum of (6e) changes; the maximum at 534 nm disappears and two new maxima at 434 and 576 nm are observed. The NMR spectrum of

(6e) in trifluoroacetic acid exhibit a 2H broad singlet at δ 3.91 indicating that the protonation of (6e) could not lead to a compound of phenalenium ion, but to one in which the thiopyrylium ion is conjugated with a naphthalene moiety of the phenalene skeleton such as (7). The exact site of protonation is still remain unexplored.[11]



(6e) (7)

The authors are grateful to Dr. K. Kuriyama of the Shionogi Research Laboratory, Shionogi and Co., for the dipole moment measurements. Technical assistance for the preparation of the phenalene by the Hashimoto Chem. Ind. Co. is gratefully acknowledged.

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