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A NOVEL ROUTE FROM TRIPTYCENES TO A DIBENZO(HAFNER'S HYDROCARBON), BENZ[a]INDENO[1,2,3-cd]AZULENE

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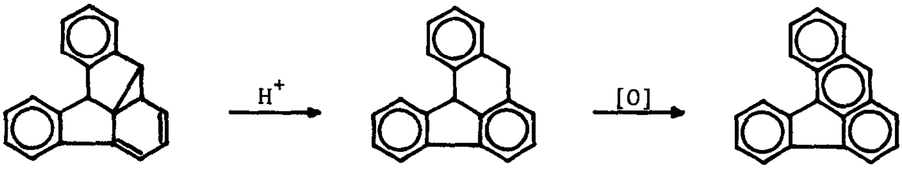
Summary: Triptycenes carrying a leaving group at one of the bridgehead carbons afforded the title compound in good to moderate yields when irradiated with a low-pressure Hg lamp. The tropylium ion and the strong CT-complexes of the hydrocarbon were prepared.

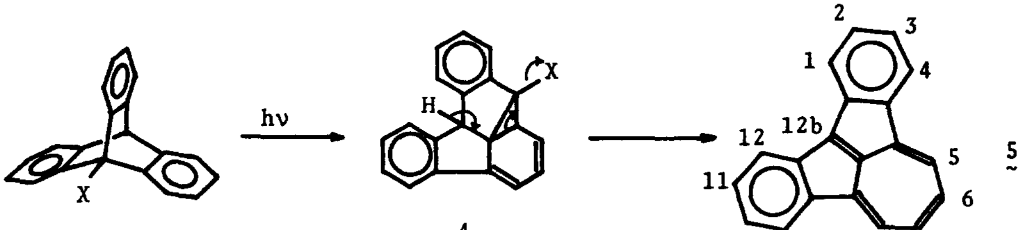
Photoisomer 1 of triptycene undergoes thermal isomerization in protic solvents to give via dihydro derivative 2 benz[a]aceanthrylene 3.[1] A unique norcaradiene structure in 1 suggests that, when it is suitably substituted with a good leaving group as in 4, it would lead to a novel condensed aromatic ring.

The idea was born out by irradiation of 1-benzoyloxy-, 1-methylthio-, and 1-phenoxytriptycenes 6.[2] When a 2 mM solution of 6a in cyclohexane was irradiated under nitrogen with a low pressure mercury lamp (Original Hanau TNN 15/32, 15 W) in an immersion apparatus, 90 % of the starting material was consumed in 2 h. The green solution thus obtained was subjected to chromatography on the Lobar column to give 5: yellow-brown needles with metallic luster, mp 200–201 °C, decomp., in 70 % yield. Photolysis of 6b gave 5 in 28 % yield together with 3 (15 %) and 7b (7.5 %). Hydrocarbon 5 was also obtained in a similar yield from irradiation of 6c.

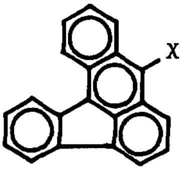
The structure of 5 was confirmed by elemental analyses[3] and by its NMR spectra showing high symmetry of the molecule. ^{1}H NMR($CDCl_3$) δ 7.41(t of d, 2 benzo H), 7.70(t of d, 2, benzo H), 7.94(d of d, 2, olefinic H), 8.07(d of q, 2 benzo H), 8.35(d of q, 2, benzo H) and 8.50(d of d, 2, olefinic H). ^{13}C NMR ($CDCl_3$) δ 120.0(2, tert C), 122.8(2, tert C), 123.2(2, tert C), 123.6(2, tert C), 129.4(1, quart C), 130.3(2, tert C), 131.0(2, tert C), 138.1(1, quart C), 138.4 (2, quart C), 139.8(2, quart C) and 141.0(2, quart C).



1 2 3



6 4 5



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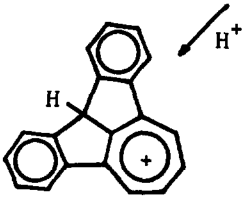
	X
a	OCOPh
b	SCH_3
c	OPh



8

Benzo H
J_{ortho} = 7.5 Hz
J_{meta} = 1.2 Hz
J_{para} = 0.8 Hz
Olefinic H
$J_{5,6}$ = 5.7 Hz
$J_{5,7}$ = 3.3 Hz

When dissolved in trifluoromethanesulfonic acid, 5 gave a green solution. Formation of tropylium ion 8 by protonation at position 12b was indicated by the appearance of the one-proton singlet at δ 5.66 and by the downfield shift of the olefinic H to δ 8.55(m, 2) and 8.80(m, 2). A chloroform solution of TCNQ and a slight excess of 5 deposited red-brown needles of $C_{20}H_{12}\cdot TCNQ$:[3] mp 150 °C, decomp.; CT-absorption max. at 1015 nm. Similarly obtained were dark green needles of $C_{20}H_{12}\cdot TCNE$:[3] mp 184 °C, decomp.; CT-absorption max. at 896 nm.

The present results have two facets of chemical interest. Firstly, 5 constitutes a dibenzo derivative of less aromatic one of the Hafner's hydrocarbons.[4] The bonds with highest double bond character are now condensed with the benzo rings to make the hydrocarbon very stable, and yet its donor character is still considerable. Secondly, we point out that the electrophilic reactivity towards the aromatic ring of the ambivalent carbenes which was lost in the corresponding alkoxycarbenes[5] has revived in the benzoyloxy-, methylthio-, and phenoxycarbenes to give internal adducts 4. These two points will be elaborated in a full paper.

1) T. D. Walsh, J. Am. Chem. Soc., **91**, 515 (1969); N. J. Turro, M. Tobin, L. Friedman, and J. B. Hamilton, ibid., **91**, 516 (1969); H. Iwamura and K. Yoshimura, ibid., **96**, 2652 (1974).
2) 6a and 6c were obtained from the corresponding anthracenes. The reaction of 1-triptycyllithium with dimethyldisulfide gave 6b: mp 235—237 °C.[3]
3) Satisfactory elemental analyses were obtained for all new compounds.
4) K. Hafner, Pure Appl. Chem., **28**, 153 (1971); K. Hafner, K.-P. Meinhardt, and W. Richarz, Angew. Chem. internat. Edit., **13**, 204 (1974).
5) H. Iwamura and H. Tukada, Tetrahedron Lett., 3451 (1978).

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