Photorearrangement of Dimethoxytriptycene to Methoxybenz[*a*]aceanthrylene

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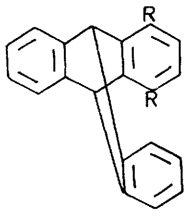
Summary Irradiation of 1,4-dimethoxytriptycene in methanol or benzene with u.v. light gave 5-methoxybenz[*a*]aceanthrylene; the result with methanol shows that a carbene is not an intermediate in the rearrangement.

Iwamura and Yoshimura[1] found that irradiation of triptycene (**1a**) in methanol with u.v. light gave the methoxy compound (**2a**). They concluded that the photorearrangement of (**1a**) to (**3a**) in nonhydroxylic solvents involved the carbene (**4a**) and did not proceed by a di-π-methanevinylcyclopropane rearrangement to (**5a**) followed by a Cope rearrangement to (**3a**) as had been originally suggested.[2]

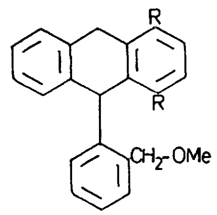
We[3] now report that irradiation with u.v. light of the dimethoxytriptycene (**1b**) in benzene or methanol gives in over 60% yield [based on recovered (**1b**)] 5-methoxybenz[*a*]aceanthrylene (**6**), m.p. 209—10°; [λ_{max} (MeOH) 448 (ϵ 7900), 375 (13500), 353 (6750), 268 (80000) and 232 nm (34400); ^{1}H n.m.r. ($CDCl_3$) δ 4·17 (3H, s, –OMe) and 7·34—8·91 (11H, m, aromatic-H)].† No trace of (**2b**) was detected when the irradiation was done in methanol.

The structure of (**6**) has been confirmed by *X*-ray crystallographic analysis. *Crystal data:* $C_{21}H_{14}O$, monoclinic, space group $p2_1/c$–C^5_{2h} (No. 14) with eight molecules per unit cell, $a = 19{\cdot}775(3)$, $b = 12{\cdot}631(3)$, $c = 11{\cdot}470(2)$ Å and $\beta = 95{\cdot}18(1)°$. A total of 6543 independent reflections having 2θ (Mo-K_α) $< 55°$ (the equivalent of 1·0 limiting Cu-K_α sphere) were collected with a computer-controlled Syntex P$\bar{1}$ autodiffractometer using full (1·0° width) ω-scans and graphite monochromated Mo-K_α radiation. The 44 crystallographically independent non-hydrogen atoms of the totally general-position asymmetric unit were located using direct methods (MULTAN). Unit-weighted full-matrix least-squares refinement employing anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms has resulted in a conventional unweighted residual, $R = 0{\cdot}044$ for those 3110 independent reflections having 2θ(Mo-K_α) $< 55°$ and $I > 3\sigma(I)$. The two molecules of the asymmetric unit are related by a non-crystallographic pseudo-inversion centre located at: *x ca.* 0·25, *y ca.* 0·60, *z ca.* 0·37. Examination of the correlation matrix, however, reveals no unusually high correlation coefficients.

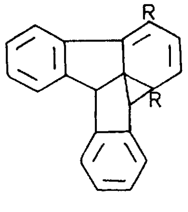
The isolation of (**6**) rather than (**2b**) when irradiation is in methanol shows that the carbene (**4b**) is not an intermediate in the rearrangement of (**1b**); that the reaction follows the pathway to (**3b**) originally suggested[2] for (**1a**) followed by loss of methanol to (**6**); and that the carbene mechanism found[1] for (**1a**) is not a general one. To reconcile our results and those of Iwamura on the basis that (**4a**) is formed from (**3a**)[4] would require that (**2a**) be formed from (**3a**) by irradiation in methanol and neither we nor Iwamura[1] have been able to observe that reaction. In addition to its mechanistic implications our work provides a simple route for obtaining 2,3-benzofluoroanthrenes, which up to now have not been readily obtainable.[5]



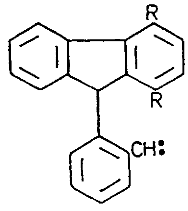
(1a); R = H
(1b); R = OMe



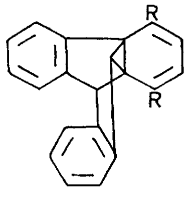
(2a); R = H
(2b); R = OMe



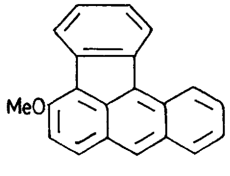
(3a); R = H
(3b); R = OMe



(4a); R = H
(4b); R = OMe



(5a); R = H
(5b); R = OMe



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† The ^{13}C n.m.r. spectrum confirms the presence of aromatic carbons and only 1 methoxy carbon in (**6**), and a satisfactory analysis was obtained.

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[3] *Cf.* M. G. Waite, G. A. Sim, C. R. Olander, R. J. Warnet, and D. M. S. Wheeler, *J. Amer. Chem. Soc.*, 1969, **91**, 7763; Z. J. Barneis, R. J. Warnet, D. M. S. Wheeler, M. G. Waite, and G. A. Sim, *Tetrahedron*, 1972, **28**, 4683; C. R. Olander, Ph.D. Thesis, University of Nebraska, 1971; S. J. Fuerniss unpublished work.

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[5] H. W. D. Stubbs and S. H. Tucker, *J. Chem. Soc.*, 1951, 2939; N. Campbell and A. Marks, *ibid.*, p. 2941.