Photorearrangement of Dihydroxytriptycene

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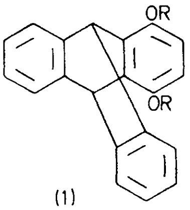
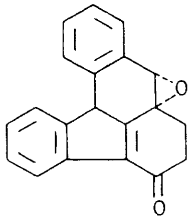
Summary Irradiation of 1,4-dihydroxytriptycene gave mainly 5-hydroxybenz[*a*]aceanthrylene and also the compound from the ketonisation of the initially formed product of a di-π-methane-to-vinylcylopropane rearrangement; the structure of the latter has been determined by *X*-ray crystallography.

IWAMURA and TUKADA[1] reported that irradiation of dihydroxytriptycene (**1a**) in methanol with u.v. light gave mainly (**2**) (m.p. 201—202 °C) and no (**3a**).[2]† We are also investigating the same reaction, but obtain different results. Irradiation of (**1a**) in methanol (under nitrogen, with or without a Pyrex filter) gave a mixture from which (**3a**) (m.p. 203—204 °C) was obtained as the major product (*ca.* 70% yield based on recovered starting material). The structure of (**3a**) was established by m.p. and spectral comparison with an authentic sample prepared from the demethylation of (**3b**).[2,4] We also isolated (in *ca.* 15% yield based on recovered starting material) a second product, m.p. 207—209 °C; *m/e* 286 (58%, M^+) and 202 (100%); the n.m.r. and i.r. spectra agree with those reported for (**2**).[1] The spectroscopic data, especially the strong $M-84$ peak in the mass spectrum, suggested that the structure of this second product is (**4**), resulting from a di-π-methane rearrangement of (**1a**) to (**5a**) followed by ketonisation.

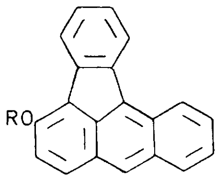
The structure (**4**) has been confirmed by *X*-ray crystallographic analysis. *Crystal data*: $C_{20}H_{14}O_2$, monoclinic, space group $P2_1/c$ (C^5_{2h}, No 14) $a = 5{\cdot}874(1)$, $b = 16{\cdot}517(2)$, $c = 15{\cdot}123(1)$ Å, $\beta = 95{\cdot}54(1)^\circ$; $Z = 4$. A total of 1965 independent reflections having $2\theta < 115^\circ$ were collected with a computer-controlled Syntex $P\bar{1}$ autodiffractometer using full (1° width) ω-scans and graphite-monochromated Cu-K_α radiation. Of these, 1625 reflections having $I > 2\sigma(I)$ were used in the subsequent refinement. The 22 crystallographically independent non-hydrogen atoms of the asymmetric unit were located using direct methods (MULTAN). Unit-weighted full-matrix least-squares refinement employing anisotropic thermal parameters for these 22 atoms has resulted in a conventional *R* index of 0·087.



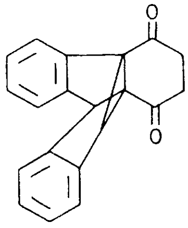
(1)
a; R = H
b; R = Me



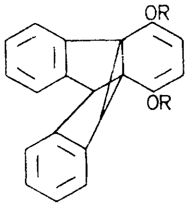
(2)



(3)
a; R = H
b, R = Me



(4)



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

The results of our earlier work indicated that (**5b**) is an intermediate in the rearrangement of (**1b**) to (**3b**).[2] The isolation of (**4**) from the photoreaction of (**1a**) strongly supports an analogous pathway for the rearrangement of (**1a**) to (**3a**). The intermediate (**5a**), in addition to rearranging further to (**3a**), can also ketonise to (**4**). Compound (**5a**) would arise from a di-π-methane rearrangement of (**1a**). Its formation by the addition of a carbene‡ to the 2,3-bond of the hydroquinone ring is unlikely; such an addition would be expected to take place at the 1,2 bond. Our work and Iwamura's[3,5] indicate that the mechanism of the photorearrangements of triptycenes varies with the substituents present in the molecule.

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† Iwamura and Tukada (ref. 3) subsequently reported that (**3a**) is obtained as a minor product when the irradiation of (**1a**) is carried out in the presence of a trace of acid.

‡ Neither we nor Iwamura have isolated from the irradiation of (**1a**) or (**1b**) any products that would result from the reaction of methanol with a carbene (*cf.* refs. 1 and 5).

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[2] R. O. Day, V. W. Day, S. J. Fuerniss, and D. M. S. Wheeler, *J.C.S. Chem. Comm.*, 1975, 296.
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[4] S. J. Fuerniss, Ph.D. Thesis University of Nebraska, 1975.
[5] H. Iwamura and K. Yoshimura, *J. Amer. Chem. Soc.*, 1974, **96**, 2652; H. Iwamura, *Chem. Letters*, 1974, 5.