Novel Photorearrangement of 2,5-Dihydroxytriptycene and Ionic Rearrangement of the Photoproduct

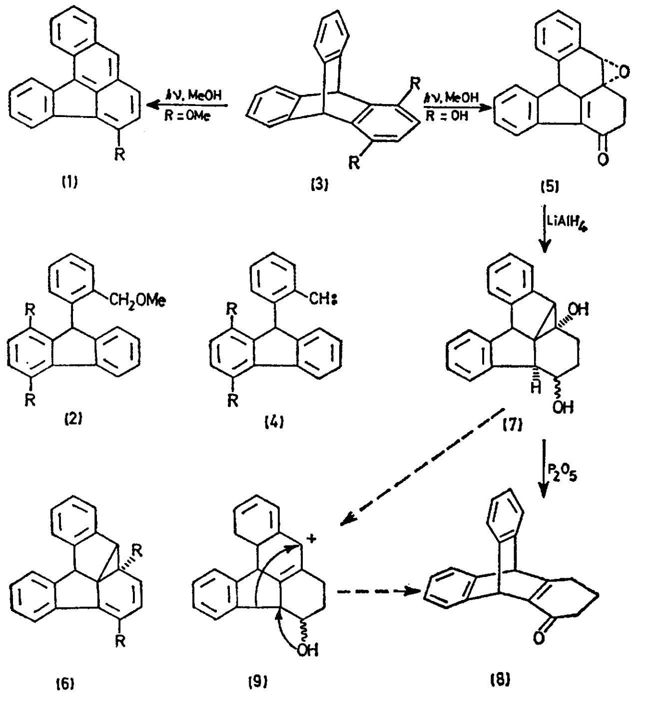
By HIIZU IWAMURA* and HIDEYUKI TUKADA

(*Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo* 113, *Japan*)

Summary Irradiation of 2,5-dihydroxytriptycene in methanol with Pyrex-filtered u.v. light gave an epoxyketone which rearranged back to a triptycene-like ketone by reduction with $LiAlH_4$ followed by dehydration over P_2O_5.

THE formation of (**1a**) instead of the expected (**2a**) on photolysis of (**3a**) in methanol was recently presented as evidence against the carbene mechanism [(**4**) as an intermediate] for the rearrangement of (**3a**).[1]

We now report that Pyrex-filtered irradiation of (**3b**) in methanol gives (**5**), m.p. 201—202 °C [λ_{max} (cyclohexane) 225, (log ϵ 4·54), 243 (4·30), 315 nm (2·34); i.r. (KBr disc) 1682, 1650 (sh), 1595, 1255, 1160, 950, 760, 740 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 2·3—3·3 (4H, m, CH_2CH_2), 4·51 (1H, s, ArCHO-), 5·09 (1H, s, ArCHAr), 6·9—7·4 (7H, m, aromatic), 7·8—8·1 (1H, m, aromatic)]. The product yield of (**5**) is *ca.* 80% based on recovered (**3b**) after 1 h irradiation. No trace of (**1b**), (**2b**) or (**6**) was detected in the crude photolysis mixture.



a, R = OMe; b, R = OH; c, R = H

While the spectral data are fully in accord with structure (**5**), the attempted chemical transformation to (**1c**) led to an unexpected result. On treatment of (**5**) with $LiAlH_4$ in ether an epimeric mixture of the diol (**7**), m.p. 84—86 °C is obtained [^{1}H n.m.r. ($CDCl_3$) δ 1·3—2·0 (6H, m, CH_2CH_2, 2OH), 3·19 (0·4H, s, cyclopropyl), 3·33 (0·6H, s, cyclopropyl), 4·25—4·6 (1H, m, >CH–), 4·48 (0·4H, s, bridgehead), 4·69 (0·6H, s, bridgehead), 4·65–4·95 (1H, m, >CHO-), 6·8—7·4 (8H, m, aromatic)].† Dehydration of (**7**) over P_2O_5 in CCl_4 gives the ketone (**8**) m.p. 264—265 °C [i.r. (KBr disc), 1658, 1620 cm^{-1}; ^{1}H n.m.r. ($CDCl_3$) δ 1·60—2·45 (4H, m, CH_2CH_2), 2·62 (2H, t, CH_2CO), 4·98 (1H, s, bridgehead), 5·75 (1H, s, bridgehead), 6·85—7·10 (4H, m, aromatic), 7·20—7·46 (4H, m, aromatic)]. The skeletal structure of the rearranged ketone (**8**) was confirmed by converting it into triptycene after reduction with $NaBH_4$ to give the corresponding alcohol, m.p. 203—205 °C [^{1}H n.m.r. ($CDCl_3$) δ 1·65—2·25 (7H, m, $CH_2CH_2CH_2$, OH), 4·34 (1H, m, >CHO–), 4·78 (1H, s, bridgehead), 5·18 (1H, s, bridgehead), 6·8—7·4 (8H, m, aromatic)] followed by dehydration and dehydrogenation. The formation of (**8**) is rationalized by a 1,4 sigmatropic shift of the phenyl group in the allylic cation (**9**) and a pinacolinic rearrangement.

Our photochemical result on (**3b**) can be interpreted, as in other triptycene photochemistry,[2] in terms of the carbene mechanism. Intermediate (**4b**) can be trapped internally either by the aromatic C=C bond activated by the hydroxyl group to give (**6**) followed by epoxide ring formation or by the carbonyl group of the photo-ketonized hydroquinone chromophore. The latter may be considered as a reverse reaction of the well-documented photo ring opening of the epoxide ring.

The Wheeler product (**1a**) is also not incompatible with the carbene mechanism. The aromatic C=C bond on the 1,4-dimethoxyfluorene ring is so much activated by the methoxyl substitution[3] that the intramolecular addition reaction to afford (**6a**) may not be intercepted by an external trap, *e.g.*, methanol.[4]

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† The ^{13}C n.m.r. spectrum confirms the presence of a cyclopropyl carbon at δ ($CDCl_3$) 17·5 among other unassigned signals. All new compounds have satisfactory analytical data.

[1] R. O. Day, V. W. Day, S. J. Fuerniss, and D. M. S. Wheeler, *J.C.S. Chem. Comm.*, 1975, 296.

[2] H. Iwamura, *Chem. Letters*, 1974, **5**, 1205; H. Iwamura and K. Yoshimura, *J. Amer. Chem. Soc.*, 1974, **96**, 2652.

[3] W. Kirmse, 'Carbene Chemistry,' 2nd edn., Academic Press, New York, 1971, p. 392.

[4] A logical precedent may be found in the decomposition of *o*-methoxy-α-diazoacetophenone in which there is competition between the external trapping of the intermediate carbene by solvent methanol to give *o*,α-dimethoxyacetophenone and intramolecular attack on the methoxy group to give chromanones. The former reaction is favoured by the higher concentration of methanol (T. Ibata, K. Ueda, and M. Takebayashi, *Bull. Chem. Soc. Japan*, 1973, **46**, 2897).