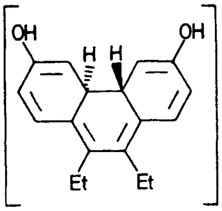
Isolation of a 1,8a-Dihydronaphthalene Derivative in the Photocyclisation of 3,3′-Diphenyl-2,2′-bi-(1-oxoindenyl)

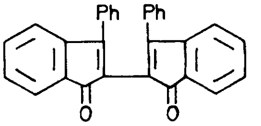
By Fumio Toda* and Yozo Todo

(*Department of Chemistry, Faculty of Engineering, Ehime University, Matsuyama* 790, *Japan*)

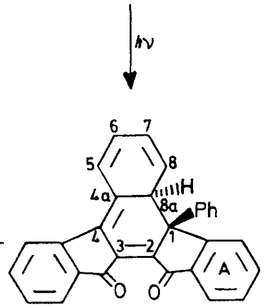
Summary In the photocyclisation of 3,3′-diphenyl-2,2′-bi-(1-oxoindenyl) (**2**), the 1,8a-dihydronaphthalene intermediate (**3**) was isolated.



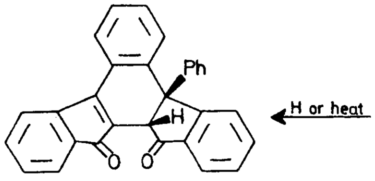
(1)



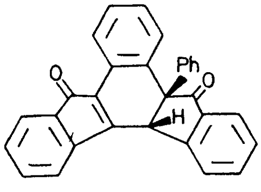
(2)



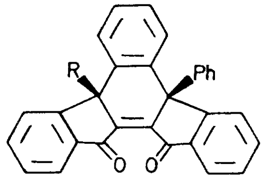
(3)



(4)



(5)



(6)

a; R = Br
b; R = OMe
c; R = Ph

Although the photo-oxidative cyclisation of stilbenes[1] and 2-α-styrylthiophens[2] to phenanthrenes and naphtho[2,1-*b*]thiophens respectively have been proposed to proceed *via* 4a,4b-dihydrophenanthrene and 1,8a-dihydronaphtho-[2,1-*b*]thiophen intermediates, such intermediates have not yet been isolated owing to their extreme instability. Recently, Doyle, *et al.*[3] have isolated the keto-form of the 4a,4b-dihydrophenanthrene intermediate (**1**) in the photocyclisation of 3,4-bis-*p*-hydroxyphenylhex-3-ene. We have now isolated the 1,8a-dihydronaphthalene intermediate (**3**) in the photocyclisation of 3,3′-diphenyl-2,2′-bi-(1-oxoindenyl) (**2**).[4]

Irradiation of (**2**) (2 g) in benzene (400 ml) with a 400-W high pressure mercury lamp under nitrogen at room temperature for 20 h, afforded (**3**)† (1·4 g, 70%) as blue-black prisms, m.p. 194 °C (decomp.) [ν_{max} 1670, 1615, 1590, 1560, and 1520 cm^{-1}; λ_{max} 297 (ϵ, 35,700), 373 (13,800), and 604 nm (2800); τ 1·6—3·0 (m, ArH and CH); *m/e* 410 (M^+)]. 8a-H and the 1-phenyl group are *trans* with respect to each other, because the signal due to 8a-H was at lower field than τ3, and probably overlapped with the aromatic signals. Molecular models show that 8a-H is in the deshielding region of the benzene ring A. The formation of (**3**) can be interpreted in terms of a ($4\pi + 2\pi$) conrotatory photocyclisation[5] of (**2**), in agreement with that of 3,4-bis-*p*-hydroxyphenylhex-3-ene into (**1**)[3] and of bis(benzylidene)-succinic anhydrides into 1,8a-dihydronaphthalene intermediates.[6]

The structure of (**3**) was further characterised by the following reactions. Treatment of (**3**) with HCl in $CHCl_3$ easily gave (**4**) as orange prisms in 90% yield, m.p. 245—247 °C (decomp.) [ν_{max} 1710 and 1695 cm^{-1}; λ_{max} 292 (ϵ, 11,300), 332 sh (4700), and 430 nm (1700); τ 1·5—3·1 (17H, m, ArH) and 5·75 (1H, s, CH); *m/e* 410 (M^+)]. Heating of (**3**) in toluene under reflux for 24 h also gave (**4**) in 60% yield. The phenyl group and the hydrogen atom marked in (**4**) are *cis* to each other because the signal due to this hydrogen atom was at relatively higher magnetic field, and because the spectral data of (**4**) are comparable to those of *cis*-(**5**)[7] [ν_{max} 1710 cm^{-1}; λ_{max} 279 (ϵ, 49,400) and 454 nm (2100); τ 1·4—3·1 (17H, m, ArH) and 5·35 (1H, s, CH)]. Treatment of both (**3**) and (**4**) with Br_2 in $CHCl_3$ gave (**6a**) as yellow prisms in 93% yield [m.p. 209—210 °C; ν_{max} 1740 and 1700 cm^{-1}; λ_{max} 310 nm (ϵ, 15,600); *m/e* 488 and 490 (M^+)]. The spectral data of (**6a**) and its methoxy-derivative (**6b**) prepared by treatment with $AgClO_4$–MeOH in 91% yield [m.p. 258—260 °C; ν_{max} 1710 and 1640 cm^{-1}; λ_{max} 302 nm (ϵ, 17,400)] are comparable to those of (**6c**) which was prepared by the $AlCl_3$-catalysed Friedel–Crafts reaction of (**2**) in benzene in 37% yield [m.p. > 270 °C; ν_{max} 1710 and 1645 cm^{-1}; λ_{max} 298 nm (ϵ, 19,600)].

(*Received*, 16*th July* 1976; *Com.* 811.)

---

† I.r., u.v., and n.m.r. spectra were measured for Nujol mulls and solutions in $CHCl_3$, and $CDCl_3$, respectively. Mass spectra were measured with an ionisation energy of 75 eV. All new compounds gave satisfactory elemental analyses.

[1] F. B. Mallory, C. S. Wood, J. T. Gordon, L. C. Lindquist, and M. L. Savitz, *J. Amer. Chem. Soc.*, 1962, **84**, 4361.

[2] W. Carruthers and H. N. M. Stewart, *Tetrahedron Letters*, 1965, 301.

[3] T. D. Doyle, W. R. Benson, and N. Filipescu, *J. Amer. Chem. Soc.*, 1976, **98**, 3262.

[4] J. C. Eck and C. S. Marvel, *J. Amer. Chem. Soc.*, 1935, **57**, 1898.

[5] R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, 1965, **87**, 395.

[6] H. G. Heller and M. Szewczyk, *J.C.S. Perkin I*, 1974, 1487.

[7] A. L. Bednowitz, R. G. Brown, L. G. Donaruma, W. C. Hamilton, R. A. Kropf, P. L. Southwick, and R. E. Stansfield, *J. Org. Chem.*, 1974, **39**, 3537.