Photorearrangement of a Benzoquinoxalinobicyclo[2,2,2]octatriene

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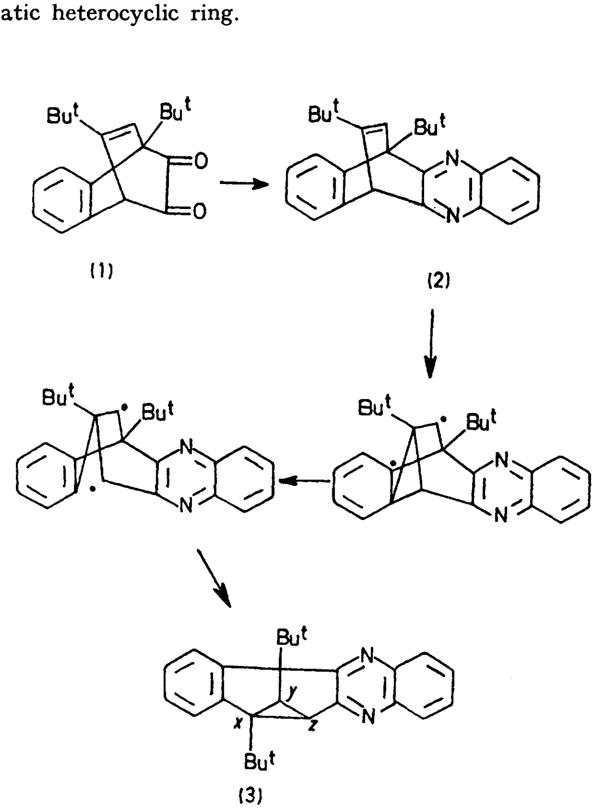
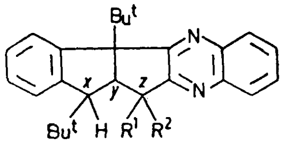
Summary Transformation of the benzoquinoxalinobicyclo-[2,2,2]octatriene (**2**) into the benzoquinoxalinotricyclo-[3,3,0,$0^{2,8}$]octadiene (**3**) was brought about by direct photolysis and attributed to a highly specific di-π-methane rearrangement.

IRRADIATION of a di-t-butylbenzoquinoxalinobarrelene (**2**) yielded one (**3**) of four di-t-butylbenzo-2,3-quinoxalinosemibullvalenes available by di-π-methane rearrangements initiated by arene–vinyl bonding. The isomerization (**2**) $\rightarrow$ (**3**) is the first example of a di-π-methane rearrangement of a barrelene with one ethylenic linkage in an aromatic heterocyclic ring.

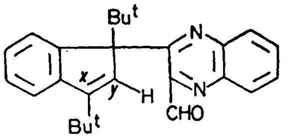


The preference for intermediate benzo–vinyl bonding rather than quinoxalino–vinyl bonding is impressive since there was equal participation between benzo- and β-naphtho–vinyl bonding in the similar reaction of benzo-2,3-naphthobarrelene.[1] One of the two possible paths for benzo–vinyl bonding in (**2**) does not occur apparently because it leads to a product with an unfavourable bonding between two tetra-substituted carbon atoms with a t-butyl group as one substituent at each.

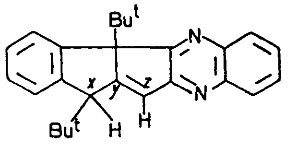
Condensation of the diketone (**1**)[2] with *o*-phenylenediamine gave the quinoxaline (**2**)[3] as yellow prisms, m.p. 231—232° (70%), δ 5·22 (1H, d, CH) and 6·48 (1H, d, C=CH).† Irradiation in furan (254 nm; 22 h; 16 low pressure lamps in a Rayonet photochemical unit) isomerized (**2**) into the tricyclo-octadiene (**3**), m.p. 134—135° (62%), δ (CCl$_4$) 3·33 and 3·45 (2H 2d, 2, cyclopropyl H, J 7 Hz). The presence of the cyclopropane ring in (**3**) was confirmed by three transformations. Hydrogenation (10% Pd–C; 3 h; 25°)[4] gave the bicyclo-octadiene (**4**) (94%) m.p. 144—145°, δ (CCl$_4$) 2·56—3·70 (4H, m, CH$_2$ at z and 2CH at x and y), λ (EtOH) 332 (ϵ 13,500) and 242 nm (ϵ 30,800);‡ oxidation (CrOCl$_2$ 0°)[5] gave the aldehyde (**8**) (61·4%), m.p. 179—180°. ν_{max} (CCl$_4$) 1695 cm^{-1} (CHO), λ_{max} (hexane) 355 nm (ϵ 21,570), δ (CCl$_4$) 10·96 (1H, s, CHO); and ring cleavage (HBr in AcOH)[1] gave the bromide (**5**) (78%), m.p. 179—180°, δ (CCl$_4$) 2·71 (1H, d, CH at y, J 8 Hz), 3·48 (1H, d, CH at z, J 8 Hz) and 5·16 (1H, s, CH at z). Hydrolysis (80% aqueous acetone, a few drops of pyridine)[1] transformed (**5**) into the alcohol (**6**) (82%), m.p. 182—183°, ν_{max} (CHCl$_3$) 3597 cm^{-1} (OH), δ (CDCl$_3$) 2·63 (1H, d, CH at y, J 8 Hz), 3·15 (1H, d, CH at x, J 8 Hz), and 5·06 (1H, s, CH at z). The latter was oxidized (CrO$_3$)[1] into the ketone (**7**) (94%), m.p. 192—193°, ν_{max} (CHCl$_3$) 1704 cm^{-1} (>C=O), λ_{max} (hexane) 327 (ϵ 20,100), δ (CDCl$_3$) 2·87 (1H, d, CH at y, J 8 Hz), and 3·57 (1H, d, CH at x, J 8 Hz).



(4) R^1 = R^2 = H
(5) R^1 = H, R^2 = Br
(6) R^1 = H, R^2 = OH
(7) R^1 R^2 = O



(8)



(9)

Treatment with *N*-bromosuccinimide transformed (**4**) into an olefin (**9**) (53%), m.p. 81—82° (decomp.), δ (CCl$_4$) 3·80 (1H, s CH at x) and 6·40 (1H, s, CH at z), λ_{max} (EtOH) 335 nm (ϵ 21,700). Hydrogenation (10% Pd–C; 3 atm.; 1 h) 25°) reconverted (**9**) into (**4**) (60%).

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† For (**2**) and the new compounds (**3**)—(**9**) satisfactory elemental analyses, molecular weights by mass spectroscopy, and n.m.r. data for t-butyl and aromatic protons have been obtained.

‡ Selected u.v. absorptions for compounds (**5**), (**8**), and (**9**) show a bathochromic shift [compared with 332 nm for (**4**)] as the quinoxaline azomethine bond becomes conjugated with aldehyde (**5**), keto (**8**), and ethylenic (**9**) groups. Complete data will be reported elsewhere.

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