Preparation, Thermolysis, and Photolysis of 2-Diazo-1,3-dimesityl-2*H*-indene: a Sterically Stabilised 2-Diazoindene

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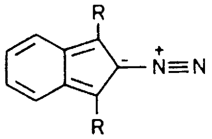
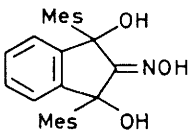
2-Diazo-1,3-dimesityl-2*H*-indene (**2**) is prepared by reaction of 2-amino-1,3-dimesityl-2*H*-indene with sodium nitrite–acetic acid; though isolable (**2**) decomposes either thermally (20 °C) or on exposure to visible light to give the hydrocarbons (**6**), (**7**), and (**8**) derived *via* the carbene (**9**) and the *o*-quinodimethane (**10**).

Diazocyclopentadienes[1a] and 1-diazoindene[1b] are well known aromatic species but 2-diazo-2*H*-indene (**1**) and its derivatives have remained unknown. We describe the isolation and properties of 2-diazo-1,3-dimesityl-2*H*-indene (**2**), a sterically stabilised derivative of (**1**).

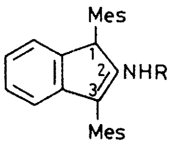
The 2-oxime of indan-1,2,3-trione reacted with mesityl-



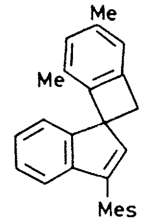
(1) R = H
(2) R = 2,4,6-$Me_3C_6H_2$ = Mes



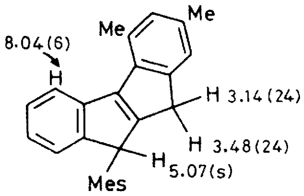
(3)



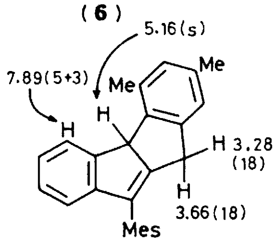
(4) R = H
(5) R = Ac



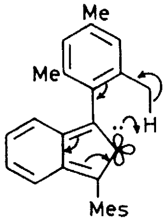
(6)



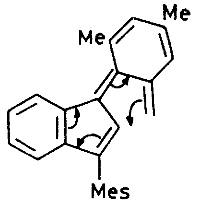
(8)



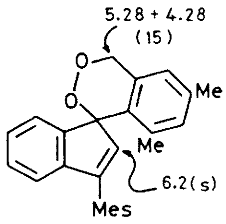
(7)



(9)



(10)



(11)

^1H N.m.r. δ values (J/Hz) are shown for (7) and (8).

lithium in boiling ether to give the dihydroxy-oxime (**3**) which with HI–HOAc (100 °C, 3 h) gave the primary enamine (**4**) (90%), as an air-sensitive but hydrolytically stable meringue. This showed i.r. ν_{max} 1 626, 3 455, and 3 360 cm^{-1}, a singlet proton n.m.r. resonance ($CDCl_3$) at δ 4.95 (1-H) and ^{13}C n.m.r. resonances ($CDCl_3$) at δ 51.3 (C-1) and 112.2 p.p.m. (C-3). With acetic anhydride in pyridine (**4**) gave the crystalline amide (**5**) m.p. 207—210 °C. Dihydroxy-oximes less hindered than (**3**) react with HI–HOAc to give ketones[2] which may also be formed by hydrolysis of the enamines related to (**4**); (**4**) remained largely unchanged after treatment with boiling concentrated hydrochloric acid–dioxan (1 : 1). This remarkable stability is attributed to steric protection of C-3; (**4**) accordingly protonates only at the nitrogen atom and can be regarded as a true vinyl analogue of an aromatic amine. Enols substituted with mesityl groups are also extraordinarily stable.[3] On treatment with $NaNO_2$–HOAc (20 °C, 15 min) (**4**) gave the 2-diazo-2*H*-indene (**2**) isolated in 40% yield by silica chromatography and trituration with acetonitrile.† The deep blue colour of (**2**) [u.v. λ_{max} (EtOH) 560 nm, ε *ca.* 1434], and the strong diazo-band in its i.r. spectrum [ν_{max} (Nujol) 2090 cm^{-1}] strongly support the assigned structure. Moreover the ^{13}C n.m.r. spectrum of (**2**) (C_6D_6, 20 °C) shows the presence of only two kinds of methyl group (δ 20.46 and 21.22 p.p.m.) and a peak for C-2 (δ 79.5 p.p.m.) in the region expected for diazo-carbon atoms. The C-2 resonance appears at lower field than the nitrogen-bearing carbon atoms in 1-diazoindene (δ 67.1 p.p.m.) and diazocyclopentadiene (δ 72.2 p.p.m.) but to higher field than that in tetracyanodiazocyclopentadiene (δ 92.6 p.p.m.) which receives little contribution from fulvenoid canonical forms.[4] The shift for C-2 in (**2**) therefore suggests greater diazonium cyclopentadienylide character here than found in diazocyclopentadiene and 1-diazoindene; Hückel calculations place a positive charge of 0.81 on the nitrogen atoms of (**1**), a positive charge of 0.68 on the nitrogen atoms of diazocyclopentadiene, but a positive charge of only 0.39 on the nitrogen atoms of 1-diazoindene.

Reduced C-2–N double bond character in (**2**) is consistent with the easy loss of nitrogen from this compound. Although diazocyclopentadiene and 1-diazoindene can be distilled (above 50 and 80 °C respectively) even solid (**2**) decomposes at 20 °C. After storing in the dark under argon for 8 days (**2**) is converted into the hydrocarbons (**6**), (**7**), and (**8**) (ratio 8 : 1.75 : 1). The ^1H n.m.r. spectrum of (**6**) [$(CD_3)_2SO$] shows the presence of only five methyl groups while the methylene protons appear as an AB-system (J_{AB} 14 Hz) centred at δ 3.72, and the olefinic proton appears as a singlet at δ 6.49. The structures of (**7**) and (**8**) were assigned as a result of the ^1H n.m.r. data supported by the interconversion of (**7**) and (**8**) with triethylamine in boiling ethanol, and the formation of (**7**) and (**8**) (ratio 1 : 2) upon heating (**6**) in boiling benzene. At 140 °C (**8**) is converted into a mixture of (**7**) and (**8**) (ratio 1 : 2) presumably *via* two 1,5-sigmatropic hydrogen shifts. Unlike solid state decomposition of (**2**) which gives mainly (**6**), decomposition of an acetonitrile solution of (**2**) (20 °C, 8 days, Ar atmosphere) gives only (**6**), (**8**), and 1,3-dimesityl-1*H*-indene. Irradiation of an acetonitrile solution of (**2**) (100 W tungsten lamp) gives (**6**), (**7**), and (**8**).

The decomposition of (**2**) presumably involves initial formation of the singlet carbene (**9**) which by a 1,8-sigmatropic hydrogen shift (shown by arrows) would give the *o*-quinodimethane (**10**). Under the constraints imposed by the solid matrix (**10**) apparently prefers a 4π-electrocyclic closure to (**6**). On the other hand when produced in solution (**10**) prefers an 8π-electrocyclic closure (shown by arrows) to a 2*H*-indene intermediate which by a 1,5-hydrogen shift gives (**8**). Topochemical control of reaction *stereochemistry* is common for photoreactions.[5] The intermediate (**10**) is also implicated in the conversion of (**6**) into (**7**) and (**8**) in boiling benzene.‡ The intervention of (**10**) in the decomposition of (**2**) is supported by isolation of the peroxide (**11**) on photolysis of (**2**) in acetonitrile saturated with oxygen.

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† The sensitivity of (**2**) to both heat and light requires its rapid manipulation below 25 °C with exclusion of light; it can be stored at −25 °C in an argon atmosphere without noticeable deterioration after one week.

‡ Compare the easy rearrangement of the parent spiro-octatriene (R. D. Miller and M. Schneider, *Tetrahedron Lett.*, 1975, 1557).

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