

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

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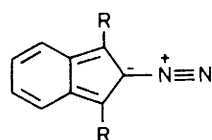
2-Diazo-1,3-dimesityl-2*H*-indene (**2**) is prepared by reaction of 2-amino-1,3-dimesityl-2*H*-indene with sodium nitrite–acetic acid; though isolable (**2**) decomposes either thermally (20 °C) or on exposure to visible light to give the hydrocarbons (**6**), (**7**), and (**8**) derived *via* the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

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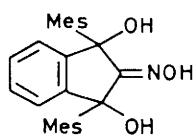
Diazocyclopentadienes<sup>1a</sup> and 1-diazoindene<sup>1b</sup> are well known aromatic species but 2-diazo-2*H*-indene (**1**) and its derivatives have remained unknown. We describe the isolation and

properties of 2-diazo-1,3-dimesityl-2*H*-indene (**2**), a sterically stabilised derivative of (**1**).

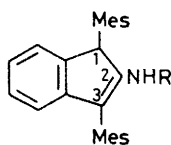
The 2-oxime of indan-1,2,3-trione reacted with mesityl-



(1) R = H

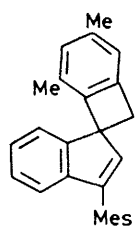
(2) R = 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub> = Mes

(3)

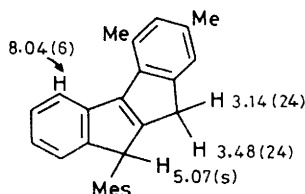


(4) R = H

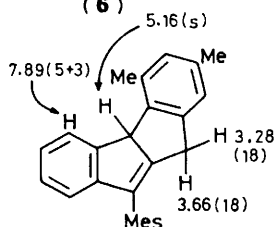
(5) R = Ac



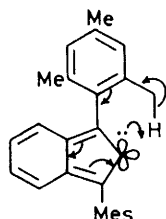
(6)



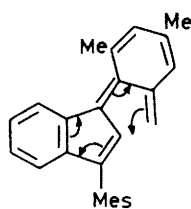
(8)



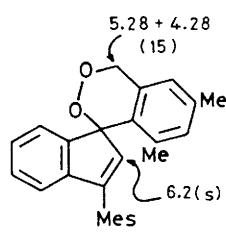
(7)



(9)



(10)



(11)

<sup>1</sup>H N.m.r.  $\delta$  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.  $\nu_{\text{max}}$  1 626, 3 455, and 3 360 cm<sup>-1</sup>, a singlet proton n.m.r. resonance (CDCl<sub>3</sub>) at  $\delta$  4.95 (1-H) and <sup>13</sup>C n.m.r. resonances (CDCl<sub>3</sub>) at  $\delta$  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<sup>2</sup> 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 extra-

ordinarily stable.<sup>3</sup> On treatment with NaNO<sub>2</sub>-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.  $\lambda_{\text{max}}$  (EtOH) 560 nm,  $\epsilon$  ca. 1434], and the strong diazo-band in its i.r. spectrum [ $\nu_{\text{max}}$  (Nujol) 2090 cm<sup>-1</sup>] strongly support the assigned structure. Moreover the <sup>13</sup>C n.m.r. spectrum of (2) (C<sub>6</sub>D<sub>6</sub>, 20 °C) shows the presence of only two kinds of methyl group ( $\delta$  20.46 and 21.22 p.p.m.) and a peak for C-2 ( $\delta$  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 ( $\delta$  67.1 p.p.m.) and diazocyclopentadiene ( $\delta$  72.2 p.p.m.) but to higher field than that in tetracyanodiazocyclopentadiene ( $\delta$  92.6 p.p.m.) which receives little contribution from fulvenoid canonical forms.<sup>4</sup> The shift for C-2 in (2) therefore suggests greater diazonium cyclopentadienylidene 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 <sup>1</sup>H n.m.r. spectrum of (6) [(CD<sub>3</sub>)<sub>2</sub>SO] shows the presence of only five methyl groups while the methylene protons appear as an AB-system ( $J_{\text{AB}}$  14 Hz) centred at  $\delta$  3.72, and the olefinic proton appears as a singlet at  $\delta$  6.49. The structures of (7) and (8) were assigned as a result of the <sup>1</sup>H 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 4 $\pi$ -electrocyclic closure to (6). On the other hand when produced in solution (10) prefers an 8 $\pi$ -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.<sup>5</sup> 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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