2-Diazo-1,3-dimesityl-2*H*-indene and 1,3-Dimesitylisoindenylidene

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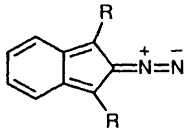
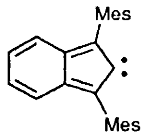
Reduction of 1,3-dihydroxy-1,3-dimesitylindan-2-one oxime **5** with HI–HOAc gives the primary enamine, 2-amino-1,3-dimesitylindene **7**. This resists hydrolysis to 1,3-dimesitylindan-2-one **6** even with boiling concentrated HCl–dioxane (1 : 1); steric protection of C-3 by the mesityl group and an overwhelming preference for the enamine tautomer may account for the unusual stability of **7**. With $NaNO_2$–HOAc **7** gives 2-diazo-1,3-dimesityl-2*H*-indene **2**, the only known 2-diazoindene. The ^{13}C and ^{15}N NMR shifts of C-2 and the terminal nitrogen in **2** suggest somewhat greater diazonium indenylide character than for 1-diazoindene. Though isolable, **2** decomposes slowly at 20 °C or upon exposure to visible light to give the hydrocarbons **14**, **15** and **16**, which probably arise *via* 1,3-dimesitylisoindenylidene **3** and the *o*-quinodimethanes **18** and **19**. The decomposition of **2** in the presence of oxygen, 4-phenyltriazoline-3,5-dione, and *N*-phenylmaleimide are described.

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** as well as the behaviour of the related carbene, 1,3-dimesitylisoindenylidene **3**. Preliminary publication of our own work on **3**[2a] coincided with Tolbert and Siddiqui's work on 1,3-diphenylisoindenylidene.[2b]



1 R = H
2 R = 2,4,6 – $Me_3C_6H_2$ = Mes



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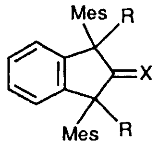
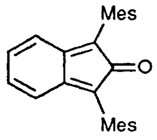


5 R = OH, X = NOH
6 R = H, X = O
31 R = OH, X = O



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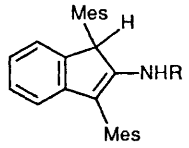
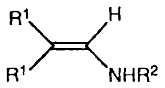


7 R = H
8 R = Ac



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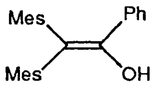

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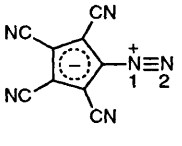
Results and Discussion

In an attempt to obtain possible precursors of the unknown and perhaps isolable sterically stabilised inden-2-one **4** we reacted mesityllithium with the 2-oxime of indan-1,2,3-trione to give the dihydroxyoxime **5** as a mixture of stereoisomers. Our objective was to react **5** with HI-HOAc to produce the ketone **6**, a reaction that works well for closely related but less hindered compounds.[3] However with HI–HOAc (100 °C, 3 h), **5** gave the primary enamine **7** (90%) as an air sensitive but hydrolitically stable meringue. This showed ν_{max}/cm^{-1} 1626, 3455 and 3360, a singlet ^1H NMR resonance at δ 4.95 (1-H) and ^{13}C NMR resonances at δ 51.3 (C-1) and 112.2 (C-3). With Ac_2O–pyridine, **7** gave the crystalline amide **8**. The ability of **7** to withstand treatment with boiling concentrated hydrochloric acid–dioxane (1 : 1) is very unusual. Although simple secondary enamines like **9** ($R^1 = R^2$ = Me) are less stable than their imine tautomers[4a] the presence of phenyl groups as in 2,2-diphenylvinylamine **9** (R^1 = Ph, R^2 = H) renders the enamine tautomer more stable.[4b] Enols substituted with mesityl groups, *e.g.* **10**, are also very stable in comparison with the related ketones. This effect was uncovered by Fuson and his collaborators many years ago[4c] and more recent investigations suggest that steric effects preferentially destabilise the keto tautomers.[4d] The remarkable stability of **7** is associated with an overwhelming preference for the enamine tautomer in which protonation at C-3 is inhibited by the attached mesityl group. Accordingly, **7** protonates only at the nitrogen atom and can be regarded as a true vinylogue of an aromatic amine. Indeed, upon reaction with an excess of bromine, the enamine groups in **7** remains unchanged and three bromine atoms are substituted into the aromatic rings.

The enamine **7** was treated with nitrous acid ($NaNO_2$–HOAc) in the hope that the intermediate diazonium cation would provide **6**, its enol, or a derivative thereof. However, the diazonium cation preferred deprotonation to give instead the 2-diazoindene **2** isolated in 40% yield by silica chromatography and trituration with acetonitrile. The sensitivity of **2** to both heat and light requires its rapid handling below 25 °C with exclusion of light. It can be stored at −25 °C in an argon atmosphere without noticeable deterioration after two weeks. The deep-blue colour of **2** [UV λ_{max}(EtOH) 560 nm, ε *ca.* 1434], and the diazo band in its IR spectrum [ν_{max}(Nujol) = 2090 cm^{-1}] strongly support the assigned structure. Moreover, the ^{13}C NMR spectrum of **2** (C_6D_6, 20 °C) showed the presence of only two kinds of methyl group (δ 20.46 and 21.22) and a peak for C-2 (δ 79.5) 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) and diazocyclopentadiene (δ 72.2) but to higher field than in tetracyanodiazocyclopentadiene **11** $\longleftrightarrow$ **12** (δ 92.6) for which the dipolar canonical form **11** is much more important than the fulvenoid structure **12**.[5] The shift of C-2 in **2** therefore suggests greater diazonium cyclopentadienylide character **13** than in diazocyclopentadiene and 1-diazoindene. The shift of the remote nitrogen (^{15}N-2) in **11** $\longleftrightarrow$ **12** (δ 332.4) is smaller than that in diazocyclopentadiene itself (δ 382.8) and closer to that of the terminal nitrogen atom in *p*-hydroxybenzenediazonium chloride (δ 316.88).[6] The shift of N-2 in **2** (δ 373) therefore also indicates a modest increase in diazonium character **13** compared to diazocyclopentadiene.



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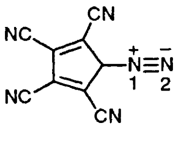

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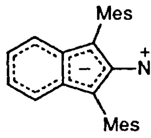

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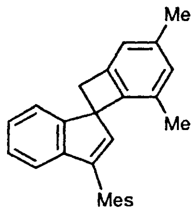
Reduced C-2–N double bond character in **2** is consistent with the easy loss of nitrogen from this compound. Although diazocyclopentadiene and 1-diazoindene can be distilled (above 50 and 80 °C, respectively), even solid **2** decomposes at 20 °C. After being stored in the dark at 20 °C under argon for 10 d, **2** is converted into the hydrocarbons **14**, **15** and **16**. The ^{1}H NMR spectrum of **14** [(CD$_3$)$_2$SO] 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 **15** and **16** were assigned as a result of the ^{1}H NMR data (Experimental section). These structures are distinguished by the larger geminal coupling in **16** (24 Hz) than in **15** (J_{gem} 18 Hz); **16** has an arrangement of the double bonds more like that in fluorene for which J_{gem} is 22.3 Hz.[7] In addition, **16** appears to be more highly conjugated than **15** as judged by UV spectra (Experimental section) and with triethylamine in boiling ethanol **15** and **16** are interconverted. The decomposition of **2** presumably involves initial formation of the singlet carbene **3** ≡ **17** which by a 1,8-sigmatropic hydrogen shift (**17**; arrows) would give the *o*-quinodimethane **18**. 4π-Electrocyclic ring-closure of the *o*-quinodimethane **18** would give the benzocyclobutene **14**. Alternatively, 8π-electrocyclic ring-closure of **18** would lead to the isoindene **19** which would give **15** and **16** by the alternative 1,5-hydrogen shifts indicated. Several points can be noted in conjunction with this rationalisation. The triplet and singlet states of electron deficient carbenes like fluorenylidene may be in rapid equilibrium[8] and triplet isoindenylidene **17** could be responsible for the hydrogen shift. Indeed, atom transfer reactions within aromatic carbenes are used to generate biradicals.[9] The tendency of **17** to abstract hydrogen intramolecularly agrees with the pronounced reactivity of 1,3-diphenylisoindenylidene in intermolecular hydrogen abstraction.[2b] Whilst 4π-electrocyclic closure of **18** to give **14** is favoured for crystalline **2** (ratio **14**–**15**–**16** = 8:1.75:1), decomposition of **2** in acetonitrile solution (20 °C, 8 d) gives similar quantities of **14** and **16** and 1,3-dimesityl-1*H*-indene. Irradiation of an acetonitrile solution of **2** with a 100 W tungsten lamp gives **14**, **15** and **16** in a ratio of 1.3:1:2.3. These variations in the relative quantities of **14**, **15** and **16** may reflect topochemical control[10] in the electrocyclic ring closures of **18** and the 1,5-hydrogen shifts of **19**. The intervention of **18** in the formation of **15** and **16** is supported by independent generation of **18** by electrocyclic ring-opening of **14** by heating in boiling benzene. This produced **15** and **16**; the related cyclobutene ring-opening (**20**; arrows) is known to be particuarly easy.[11] Isolation of the peroxide **21** after photolysis of **2** in acetonitrile saturated with oxygen also supports the intermediacy of the *o*-quinodimethane **18**. Other trapping experiments are more equivocal. Thus in the presence of a large excess of *N*-phenylmaleimide the decomposing diazoindene **2** gives the adduct **22** which could have arisen *via* the carbene adduct **23** by a 1,7-shift (**23**; arrows) or a two step equivalent. Alternatively, **22** could be formed from the diazoindene **2** and the dienophile *via* the zwitterion **24**, as indicated (**24**; arrows). The formation of a similar adduct from 1,3-diphenylisoindenylidene generated from a different carbene precursor supports the carbene route *via* **23**. Trapping intermediates in the spontaneous decomposition of **2** with the potent dienophile 4-phenyltriazoline-3,5-dione **25** was not possible as **25** induced rapid decomposition of **2** at 20 °C. The products were a mixture of **26** and **27**. Since **25**



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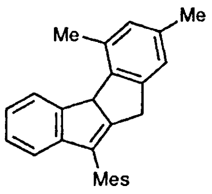

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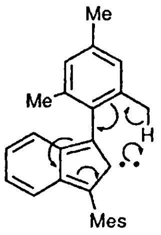

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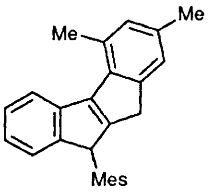

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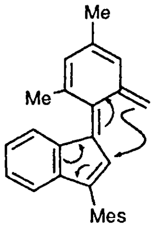

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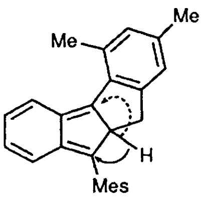

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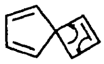

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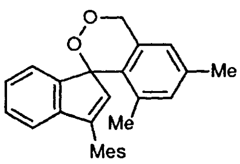

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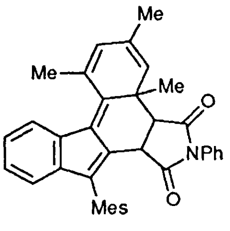

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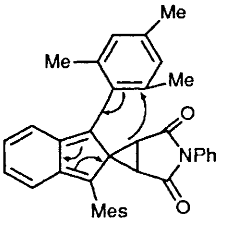

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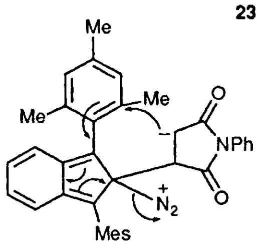

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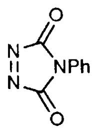

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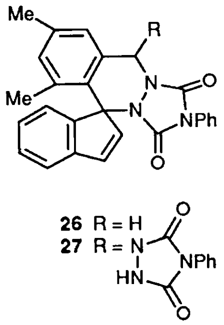
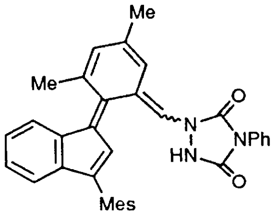


26 R = H
27 R =



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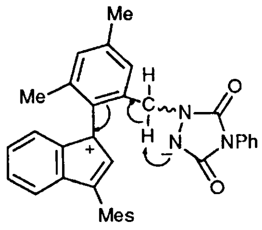

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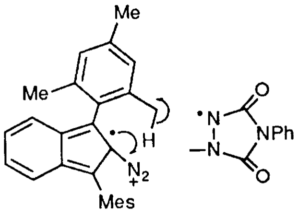

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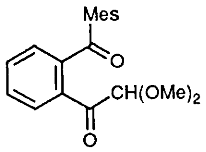

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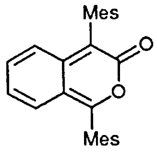

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and **26** failed to produce **27** at 20 °C a common intermediate to **26** and **27** is indicated. This could be the zwitterion **28** which could collapse to **26** or tautomerise (**28**; arrows) to the new *o*-quinodimethane **29**. Addition of **25** to **29** would give **27**. Several routes to **28** are possible. One which accounts for *induced* decomposition of **2** by **25** as well as the failure of **25** to end up bonded to the less hindered C-2 of the diazoindene, involves electron transfer between the reactants to give the radical cation–radical anion pair **30**. Hydrogen atom transfer (**30**; arrows), radical combination and nitrogen loss would give **28**. In support of the postulated electron-transfer, diphenyldiazomethane is readily converted into its radical cation [12a] and Diels–Alder additions proceeding *via* radical cation–radical anion pairs are known.[12b] The Experimental section details two failed attempts to prepare the dihydroxyketone **31** which with HI–HOAc would be expected to give the ketone **6** or its enol. Attempted addition of mesityllithium to 2,2-dimethoxyindan-1,3-dione gave instead the product **32** derived by a reverse aldol reaction. Treatment of **5** with nitrous acid, a useful way of 'hydrolysing' sterically hindered oximes,[13] gave a variety of products including the pyrone **33**.[14]

Experimental

For general details see ref. 15. All *J* values are in Hz. Ether refers to diethyl ether, light petroleum to the fraction boiling 60–80 °C.

1,3-Dihydroxy-1,3-dimesitylindan-2-one Oxime.—Indan-1,2,3-trione 2-oxime[16] (6 g) was added in small portions over *ca.* 30 min to mesityllithium [from lithium (containing 1% Na) (3.6 g) and mesityl bromide (48 g) in ether (120 ml) in the usual way but with completion of reaction by boiling under reflux (1 h)]. After completion of the addition the mixture was boiled under reflux (1.5 h). The product was filtered through glass wool to remove excess Li shot and the filtrate washed with saturated ammonium chloride solution, washed with water, dried ($MgSO_4$), and evaporated, the excess mesityl bromide being removed in a high vacuum at 100 °C. The product crystallised from methanol with the aid of a seed to give one stereoisomer of the *title compound* **5** (3.47 g) m.p. 235–237 °C after being washed with methanol and dried 70 °C (18 h). Chromatography of the evaporated mother liquor on silica in benzene–ether (95:5) gave an additional quantity (1.67 g) of this product (Found: C, 77.8; H, 7.15; N, 3.35. $C_{27}H_{29}NO_3$ requires C, 78.0; H, 7.0; N, 3.4%), ν_{max}(Nujol)/cm^{-1} 3140–3620 and 1610, δ(60 MHz; $CDCl_3$) 2.2 (12 H, s), 2.45 (6 H, s), 2.65 (1 H, s, exch. D_2O), 3.71 (1 H, s, exch. D_2O), 6.75 (4 H, m), 7.28 (4 H, s) and 7.43 (1 H, s, exch. D_2O). Continued elution of the column gave a *second stereoisomer of the title compound* **5** that recrystallised benzene–light petroleum to give 200 mg of product m.p. 198–200 °C (total yield of dihydroxy oximes 63%). The analytical sample was recrystallised from methanol and dried at 70 °C (2.5 d) (Found: C, 77.75; H, 7.2; N, 3.45%); δ(60 MHz; $CDCl_3$) 2.25 (18 H, ill-resolved), 3.3 (1 H, br s), 3.76 (1 H, br s), 6.85 (4 H, br s) and 7.3 (5 H, m, aromatic and oxime OH).

An attempt to add mesityllithium to ninhydrin dimethyl acetal (1.0 g) in the manner described above and work-up with water gave after recrystallisation from a small volume of methanol *2-mesitoyl-ω,ω-dimethoxyacetophenone* **32** (0.54 g) m.p. 89–90 °C (Found: C, 73.6, H, 6.9. $C_{20}H_{22}O_4$ requires C, 73.6; H, 6.8%); ν_{max}(Nujol)/cm^{-1} 1665 and 1708; δ(60 MHz; $CDCl_3$) 2.1 (6 H, s), 2.31 (3 H, s), 3.43 (6 H, s), 5.1 (1 H, s), 6.89 (2 H, br s) and 7.4 (4 H, m).

Reaction of 1,3-Dihydroxy-1,3-dimesitylindan-2-one Oxime with Nitrous Acid.—The title compound (100 mg), acetic anhydride (1 ml) and acetic acid (1 ml) were stirred at 20 °C and sodium nitrite (3 × 20 mg) was added over *ca.* 2 h. The mixture was stirred for a further hour and the product was poured into water and isolated in CH_2Cl_2 in the usual way. Chromatography on silica in benzene–ether (95:5) eluted an orange band (25 mg). Recrystallisation from dichloromethane–light petroleum gave *1,4-dimesityl-2-benzopyran-3-one* **33**, m.p. 273–275 °C (Found: C, 85.05; H, 6.75. $C_{27}H_{26}O_2$ requires C, 84.8; H, 6.8%); ν_{max}(Nujol)/cm^{-1} 1700; δ(90 MHz; $CDCl_3$) 2.06 (6 H, s), 2.1 (6 H, s), 2.31 (3 H, s), 2.33 (3 H, s) and 6.5–7.1 (8 H, m); *m/z* 382.193 (M^+), 354 (M − CO), 262, 206, 192, 147, 119, 91 (100, 45.4, 22.5, 38.3, 21.4, 98.3, 34.2, 8.6%).

Preparation of 2-Amino-1,3-dimesitylindene **7**.—A solution of 1,3-dihydroxy-1,3-dimesitylindan-2-one 2-oxime **5** (300 mg, 0.723 mmol), hydriodic acid (2 ml; freshly distilled from red phosphorus), glacial acetic acid (8 ml) and red phosphorus (50 mg) were stirred at 100 °C under argon (3 h). The cooled mixture was diluted with methylene chloride and rapidly washed with sodium metabisulphite solution and water and dried ($MgSO_4$). Evaporation of the solvent gave the unstable *2-amino-1,3-dimesitylindene* **7** (240 mg, 90.5%) as a meringue (Found: M, 367.2296. $C_{27}H_{29}N$ requires M, 367.2299); ν_{max}/cm^{-1} 3460, 3360, 1625 and 1598, δ_H(90 MHz) 7.40–6.60 (8 H, m, aromatic), 5.05 (1 H, s, methine), 3.35 (2 H, br s, NH_2, exchange D_2O), 2.56 (3 H, s), 2.31 (3 H, s), 2.27 (3 H, s), 2.17 (6 H, s) and 1.77 (3 H, s); δ_C 19.34, 20.42, 20.86, 21.34, 21.56, 22.10 (methyl carbons), 51.30 (quaternary carbon C-1), 121.89, 122.36, 127.15, 128.99, 129.53, 130.13, 130.78, 131.92, 137.12, 138.79, 138.96, 140.66, 146.54 and 150.39; *m/z* 367 (M, 100%), 248 (5.1) and 232 (49).

Reaction of 2-*Amino*-1,3-*dimesitylindene* **7** *with:*

(*a*) *Acetic anhydride at* 25 °C. A mixture of 2-amino-1,3-dimesitylindene **7** (65 mg, 0.177 mmol), acetic anhydride (0.5 ml) and pyridine (1 ml) were stirred for 22 h. Evaporation of the solvent at 100 °C under high vacuum and chromatography of the residue on silica using benzene–ether (19:1) gave 2-*acetamido*-1,3-*dimesitylindene* **8** (40 mg, 55.2%), m.p. 207–210 °C from benzene–light petroleum (Found: C, 85.1; H, 7.9; N, 3.1; M(osmometer) 392. $C_{29}H_{31}NO$ requires C, 85.1; H, 7.6; N, 3.4%; M, 409); ν_{max}/cm^{-1} 3210, 1650 and 1625, δ(90 MHz) 7.60–6.50 (8 H, m, aromatic), 6.75 (1 H, br, amide, exchange D_2O), 5.40 (1 H, s, methine), 2.75 (3 H, s), 2.37 (3 H, s), 2.25 (3 H, s), 2.18 (3 H, s), 2.10 (3 H, s), 1.81 (3 H, s) and 1.72 (3 H, s); *m/z* 409 (M, 67.2%), 367 (100) and 232 (20.9) (Found: M, 409.241. $C_{29}H_{31}NO$ requires M, 409.241).

(*b*) *Bromine at* 20 °C. A mixture of 2-amino-1,3-dimesitylindene **7** (95 mg, 0.259 mmol), bromine (150 mg, 0.938 mmol) and dry carbon tetrachloride (3 ml) were stirred for 15 min. Evaporation of the solvent and chromatography of the residue on silica using benzene–light petroleum (1:1) gave a *tribromide* (60 mg, 38.5%), m.p. 214–222 °C, from benzene–light petroleum (Found: C, 53.75; H, 4.5; N, 2.2. $C_{27}H_{26}Br_3N$ requires C, 53.6; H, 4.3; N, 2.3%); ν_{max}/cm^{-1} 3350, 1630 and 1570, δ(90 MHz) 7.10–6.60 (5 H, m, aromatic), 4.95 (1 H, s, methine), 3.58 (2 H, br s, amino, exchange D_2O), 2.58 (3 H, s), 2.30 (3 H, s), 2.24 (3 H, s), 2.11 (6 H, s) and 1.71 (3 H, s), (Found: M, 602.958. $C_{27}H_{26}N^{79}Br_2{}^{81}Br$ requires M, 602.960).

(*c*) *Sodium nitrite and glacial acetic acid at* 25 °C. A mixture of 2-amino-1,3-dimesitylindene **7** (240 mg, 0.64 mmol), glacial acetic acid (30 ml) and sodium nitrite (50 mg, 0.685 mmol) were stirred in the dark for 15 min. The mixture was poured into aqueous sodium hydrogen carbonate, extracted with ether, and the ether layer washed with brine and dried ($MgSO_4$). Evaporation of the solvent at 25 °C under vacuum, and chromatography of the residue on silica using light petroleum–benzene (9:1) gave the purple 2-*diazo*-1,3-*dimesitylindene* **2** (100 mg, 40.5%), ν_{max}/cm^{-1} 2090, δ_H(90 MHz) 7.10–6.85 (4 H, s, aromatic), 6.86–6.50 (4 H, m, aromatic), 2.31 (6 H, s) and 2.10 (12 H, s); δ_C 20.20, 21.07, 121.73, 123.25, 128.28, 129.31, 137.33 and 138.31, $\delta_C(C_6D_6)$ 20.46, 21.22, 79.51, 121.17, 122.15, 124.21, 126.92, 128.00, 128.81, 129.08, 129.73, 130.11, 137.53 and 138.40. Compound **2** enriched at its terminal nitrogen with ^{15}N was prepared using ^{15}N enriched $NaNO_2$. The shift of the ^{15}N in **2** was measured in $CDCl_3$ relative to external $(NH_4)_2SO_4$ taken as 21 relative to liquid NH_3 at 25 °C.

Reaction of 2-*Diazo*-1,3-*dimesitylindene* **2** *with:*

(*a*) 4-*Phenyl*-1,2,4-*triazoline*-3,5-*dione*. To a solution of 2-diazo-1,3-dimesitylindene **2** (45 mg, 0.119 mmol) in benzene (2 ml), 4-phenyl-1,2,4-triazoline-3,5-dione (30 mg, 0.171 mmol) was added and the mixture stirred at 25 °C in the dark for 16 h. After this time, 4-phenyl-1,2,4-triazoline-3,4-dione (10 mg, 0.057 mmol) was added and the mixture stirred for a further 5 min. Evaporation of the solvent and chromatography of the residue on silica in benzene–ether (9:1) gave the 1:1 *adduct* **26** (17 mg, 27.2%) m.p. 195–199 °C, from chloroform–light petroleum (Found: C, 80.1; H, 6.0; N, 8.05; M(osmometer) 516. $C_{35}H_{31}N_3O_2$ requires C, 80.0; H, 5.9; N, 8.0%; M, 525); ν_{max}/cm^{-1} 1780 and 1725; δ(90 MHz) 7.50–7.10 (9 H, m, aromatic), 7.10–6.75 (4 H, m, aromatic), 6.26 (1 H, s, olefinic), 5.10 (1 H, d, *J* 15), 4.75 (1 H, d, *J* 15), 2.33 (3 H, s), 2.31 (3 H, s), 2.20 (3 H, s), 2.10 (3 H, s) and 1.68 (3 H, s); *m/z* 525 (M, 70.7), 350 (100%) and 348 (13.8). Further elution of the column with benzene–ether (4:1) gave the 2:1 *adduct* **27** (15.5 mg, 18.6%) m.p. 208–212 °C, from benzene–light petroleum (Found: C, 73.35; H, 5.15; N, 12.3; M(osmometer), 706. $C_{43}H_{36}N_6O_4$ requires C, 73.7; H, 5.1; N, 12.0%; M, 700); ν_{max}/cm^{-1} 1765, 1730 and 1700, δ(90 MHz) 8.15 (1 H, br s, amide, exchange D_2O), 7.57–6.75 (18 H, m, aromatic, 1 H, methine), 6.20 (1 H, s, olefinic), 2.34 (3 H, s), 2.30 (3 H, s), 2.19 (3 H, s), 2.08 (3 H, s), 1.68 (3 H, s).

(*b*) *Perchloric acid.* A mixture of 2-diazo-1,3-dimesitylindene **2**, (140 mg, 0.37 mmol), dioxane (15 ml), water (5 ml) and 69–71% perchloric acid (5 ml) were heated under reflux for 15 min. The cooled mixture was poured into sodium hydrogen carbonate solution, extracted with ether, and the ether layer washed with water and dried ($MgSO_4$). Evaporation of the solvent and chromatography of the residue on silica in light petroleum gave 1,3-*dimesitylindene* (79.6 mg, 61.2%) m.p. 126–128 °C from chloroform–ethanol (Found: C, 92.3; H, 7.9; M, 352.219. $C_{27}H_{28}$ requires C, 92.05; H, 7.95%; M, 352.219), δ(90 MHz) 7.35–6.80 (7 H, m, aromatic), 6.72 (1 H, br s, aromatic), 6.35 (1 H, d, *J* 1.8), 5.15 (1 H, br s, methine), 2.62 (3 H, s), 2.33 (3 H, s), 2.26 (3 H, s), 2.18 (3 H, s), 2.10 (3 H, s) and 1.62 (3 H, s); *m/z* 352 (M, 100%), 337 (M − CH_3, 15.8), 232 (149) and 217 (13.3).

(*c*) *Oxygen.* A steady stream of oxygen was passed through a solution of 2-diazo-1,3-dimesitylindene **2** (100 mg, 0.265 mmol) in acetonitrile (20 ml) for 20 min to saturate the solution. Oxygen was passed through the solution for a further 2 h while the solution was irradiated (240 V, 100 W tungsten bulb). Evaporation of the solvent and chromatography of the residue on silica in benzene–light petroleum (1:1) gave a mixed hydrocarbon fraction (22 mg) identified by ^1H NMR comparison with authentic spectra of **14**, **15** and **16**. Continued elution gave the *dioxygen adduct* **21** (20 mg, 19.8%) m.p. 113–117 °C , from methylene chloride–methanol (Found: C, 84.85; H, 6.85; M, 382.193. $C_{27}H_{26}O_2$ requires C, 84.8; H, 6.8%; M, 382.193); δ(90 MHz) 7.50–6.70 (8 H, m, aromatic), 6.20 (1 H, s, olefinic), 5.48 (1 H, d, *J* 15), 5.28 (1 H, d, *J* 15), 2.35 (6 H, s), 2.23 (6 H, s) and 1.88 (3 H, s); *m/z* 382 (M, 100%), 366 (15.1), 365 (17.5), 339 (16.0), 246 (36.2) and 206 (70.3).

Thermal Decomposition of 2-*Diazo*-1,3-*dimesitylindene*.—Freshly prepared 2-diazoindene **2** (290 mg) was allowed to decompose in the dark at *ca.* 20 °C over 10 d in a flask flushed with argon. Chromatography of the product on silica in benzene–light petroleum (10:90) gave first the *spirobenzocyclobutene* **14** (86 mg) m.p. 109–111 °C (From $CHCl_3$–MeOH) (Found: C, 92.45; H, 7.35; M, 350.204. $C_{27}H_{26}$ requires C, 92.6; H, 7.4%; M, 350.203); δ(90 MHz) 7.40–6.75 (8 H, m), 6.34 (1 H, s, olefinic), 3.60 (2 H, s, CH_2), 2.38 (3 H, s), 2.35 (3 H, s), 2.18 (6 H, s), 1.76 (3 H, s); in $(CD_3)_2SO$ the singlet at δ 6.34 becomes a clear AB-system δ_A 3.61, δ_B 3.75, J_{AB} 14; δ_C 15.55 (CH_3), 20.26 (CH_3), 20.37 (CH_3), 21.07 (CH_3), 22.10 (CH_3), 38.3 (CH_2), 60.78 (CH_2), 120.10 (CH), 120.92 (CH), 121.67 (CH), 125.47 (CH), 126.82 (CH), 128.12 (CH), 129.26 (CH), 132.13 (C), 132.29 (C), 136.68 (C), 137.87 (CH), 138.14 (C), 141.83 (C), 142.59 (C), 143.02 (C), 143.99 (C) and 147.90 (C); *m/z* 350 (M, 100%), 335 (34.7), 231 (9.3), 215 (7.6) and 206 (7.1). Continued elution of the column gave a mixture of **14**, **15** and **16** (44 mg) and finally the oxygen adduct **21** (43 mg) described earlier. Careful rechromatography of the mixture of **14**, **15** and **16** on Kieselgel G Merck[17] (44 g) in benzene–light petroleum (10:90) using 60 cmHg pressure to achieve a rapid elution of the column gave first **14** (10 mg) followed by the *hydrocarbon* **15** (21 mg) as a gum (Found: M, 350.2036. $C_{27}H_{26}$ requires M, 350.2034) δ(90 MHz; $CDCl_3$) 1.79 (3 H, s), 2.22 (3 H, s), 2.27 (3 H, s), 2.35 (3 H, s), 2.70 (3 H, s), 3.28 (1 H, d, *J* 18), 3.66 (1 H, d, *J* 18), 5.16 (1 H, br s), 6.70–7.30 (7 H, m), 7.89 (1 H, m); λ_{max}(EtOH)/nm 272 (ε 9625) and 280sh (ε 7000); *m/z* 350 (100%), 335 (52.3), 320 (7.0), 303 (5.7), 231 (16.7), 206) (14.1), 175 (7.7), 152 (8.3) and 119 (18.4). Continued elution gave the *hydrocarbon* **16** (12 mg) m.p. 158–160 °C (from ethyl acetate–methanol) (Found: C, 92.65; H, 7.4. $C_{27}H_{26}$ requires C, 92.6; H, 7.4%); δ(90 MHz) 1.32 (3 H, s), 2.29 (3 H, s), 2.39 (3 H, s), 2.63 (3 H, s), 2.91 (3 H, s), 3.35 (2 H, apparent s), 5.11 (1 H, s), 6.67 (1 H, br s), 6.9–7.5 (6 H, s) and 8.04 (1 H, d, *J* 6); in $(CD_3)_2SO$ containing a little CF_3CO_2 H the apparent singlet at δ 3.35 becomes an easily recognised AB-system centred at δ 3.35 with J_{AB} 24; λ_{max}(EtOH)/nm 239 (ε 16 722), 244 (16 528), 252 (13 999), 262 (7972), 270 (7583), 297 (3889) and 322 (1167); *m*/*z* 350 (100%), 335 (27.8), 279 (9.0), 231 (8.7), 167 (9.6) and 149 (43.4) (Found: M^+, 350.2034). When a solution of 2-diazo-1,3-dimesitylindene in deoxygenated acetonitrile (10 ml) was set aside for 8 d at 20 °C, similar quantities of **14**, **16** and 1,3-dimesitylindene were formed as judged by 90 MHz ^{1}H NMR spectroscopy of the evaporated residue.

Photochemical Decomposition of 2-*Diazo*-1,3-*dimesitylindene*.—A solution of the title compound **2** (96 mg) in deoxygenated acetonitrile (8 ml) was irradiated (100 W tungsten lamp) for 1 h. Evaporation of the solvent and chromatography as described above gave 1,3-dimesitylindene (4.8 mg), compound **14** (11 mg), compound **15** (8.6 mg) and compound **16** (20 mg); all of which were identified by 90 MHz ^{1}H NMR spectra.

Thermolysis of the Hydrocarbon **14**.—The hydrocarbon **14** (9 mg, 0.0257 mmol) was heated under reflux in deoxygenated xylene (2 ml) (90 min). Evaporation of the solvent at 100 °C under vacuum and examination of the residue by ^{1}H NMR (JEOL) showed a mixture of the two isomeric hydrocarbons **15** and **16**. No signal was observed at δ 6.34 for the olefinic hydrogen of the starting hydrocarbon **14** but signals were observed at δ 5.11 and 5.16 for the methine protons in the hydrocarbons **16** and **15**, respectively.

Isomerisation of Hydrocarbon **16** *with Triethylamine and Ethanol*.—The hydrocarbon **16** (7.2 mg, 0.0206 mmol) was added to a deoxygenated solution of absolute ethanol (1.5 ml) and triethylamine (0.5 ml) and heated under reflux for 60 min. Evaporation of the solvent and examination of the residue by ^{1}H NMR (JEOL) spectroscopy showed a mixture of the isomeric hydrocarbons **15** and **16**.

Attempted Trapping of 1,3-*Dimesitylisoindenylidene with* N-*Phenylmaleimide*.—The diazoindene **2** (175 mg) and *N*-phenylmaleimide (500 mg) were heated in deoxygenated benzene (5 ml) in an argon atmosphere (30 min). The deep-blue colour of the solution was replaced by an orange colour after 10 min reflux. The product was chromatographed on silica in benzene–ether (95:5) to give first a mixture of hydrocarbons in which **16** and **15** predominate. Continued elution gave an orange band that gave *adduct* **22** (*ca.* 40 mg) m.p. 187–190 °C (from ethanol) (Found: M^+, 523.2509. $C_{37}H_{33}NO_2$ requires M, 523.2511); δ(90 MHz), 1.29 (3 H, s), 1.96 (3 H, s), 1.98 (3 H, s), 2.14 (3 H, s), 2.33 (3 H, s), 2.39 (3 H, s), 3.24 (1 H, d, *J* 9), 4.10 (1 H, d, *J* 9), 5.99 (1 H, br s), 6.26 (1 H, br s), 6.7–7.4 (10 H, m), 7.6 (1 H, m); ν_{max}(Nujol)/cm^{-1} 1728 and 1790; λ_{max}(EtOH)/nm 435; *m*/*z* 523 (54.9%), 428 (60.6), 350 (100), 349 (98.5), 175 (29.1), 173 (23.9) and 119 (11.9).

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