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AZULENES AND RELATED SUBSTANCES—XV[a,b]

AZULENO[2,1-a]AZULENE (Part 1): REACTION OF 3,6,7,8-TETRAHYDRODIBENZOPENTALENE WITH DIAZOMETHANE; SYNTHESIS OF 11H-INDENO[2,1-a]AZULENE[c]

R. S. D. Mittal, S. C. Sethi and Sukh Dev*
National Chemical Laboratory, Poona, India

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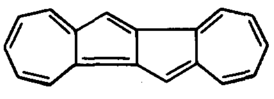
Abstract—In an attempt to synthesise azuleno[2,1-a]azulene (1), Cu^+ ion-catalysed reaction of diazomethane with 3,6,7,8-tetrahydrodibenzopentalene (4) has been investigated. Addition occurred to only one of the aromatic rings to give chiefly 1,2-benzo-4,5-cycloheptatrieno-3,6,7,8-tetrahydropentalene (13/14). Dehydrogenation of 13/14 to 11H-indeno[2.1-a]azulene has been carried out.

Azuleno[2,1-a]azulene (1), an unknown nonalternant hydrocarbon,[d] has several interesting features and its synthesis deserves to be explored. The system bears the same relationship to naphthacene as azulene has to naphthalene; it has 18π-electrons and hence according to generalised Hückel's $4n+2\pi$-electron rule,[1] should possess aromatic stability. The system (1) may also be visualised as consisting of heptafulvene[2] and azulene components (2) or, as [18]annulene[3] (3) with three additional intramolecular single linkages. [18]Annulene[3] has been synthesised and is known to possess delocalization energy. The linkage between C atoms 18 and 9 has a nonvanishing bond order as the two C atoms are of unlike parity; while those between 1 and 7 as also 10 and 16 have each a π-bond order of zero.[4a] The change in π-energy due to the new bond between 18 and 9 is readily calculated.[4] Such calculations show an increase in resonance energy of $\sim 0{\cdot}25\beta$[e] where β is the resonance integral between C atoms 18 and 9. The compound azuleno[2,1-a]azulene should therefore be expected to be a little more aromatic than [18]annulene.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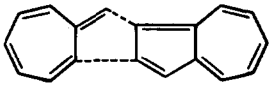
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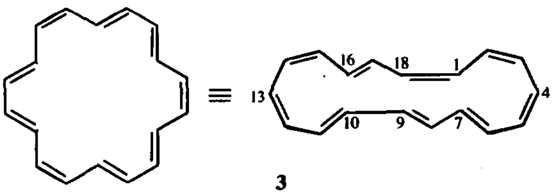

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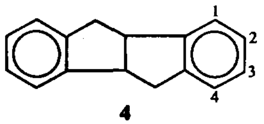
As a first attempt to synthesise 1, ring-expansion of 3,6,7,8-tetrahydrodibenzopentalene (4) by methylene, generated thermally from diazomethane in presence of Cu_2Cl_2[5] has been studied. The starting hydrocarbon (4) was prepared by a known method[6] with some modifications (Experimental), which resulted in much improved overall yields. The compound 4 can have a *cis* or *trans* alicyclic ring junction. However, considering the reaction conditions (conc H_2SO_4, 100°) employed for the cyclization of α,α'-diphenyl succinic acid to the 3,6,7,8-tetrahydro-3,6-diketo-dibenzopentalene (5) it is anticipated that equilibration would have occurred to give the more stable *cis*-fused diketone, as *cis*-bicyclo[3,3,0]octane system is known[7] to be much more favoured energetically over its *trans*-isomer. Thus, both 4 and 5 are considered to have *cis*-geometry.

For the ring-expansion of 3,6,7,8-tetrahydrodibenzopentalene (4), the following procedure was finally adopted. The hydrocarbon (4) in dry



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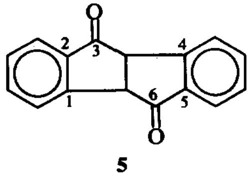

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[a] Part XIV: *Tetrahedron* **28**, 1083 (1972).

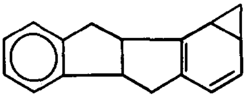
[b] Communication No. 1648, National Chemical Laboratory, Poona 8, India.

[c] Abstracted from the Ph.D thesis (University of Rajasthan, 1970), of R. S. D. Mittal.

[d] It may be pointed out that in all twelve azulenoazulenes are possible and none appears to have been synthesised so far.

[e] The authors are grateful to Dr. M. N. S. Murthy for this treatment.

decalin was maintained at 95–100° while diazomethane diluted with dry N_2 was slowly bubbled through (5–6 hr) in presence of Cu_2Cl_2. The resulting mixture, besides containing ~ 50% starting hydrocarbon, showed (TLC, GLC) the presence of only one major product (~ 35%), which could be isolated by inverted-dry-column-chromatography[8] (IDCC) over $AgNO_3$-SiO_2 gel; all attempts to obtain any of the other five minor products pure, proved futile. The product analyses for $C_{17}H_{16}$ (M^+, *m/e* = 220) and since its PMR spectrum does not show any signal for a Me group, the product has clearly arisen from an addition reaction and an insertion reaction* is ruled out. Neglecting the positional isomers, three structural types are possible for this product. These are: (i) 1,2-addition product (e.g. 6), (ii) 1,4-addition product (e.g. 7) and, (iii) ring-enlarged product (e.g. **8**). Precedents for each of these reactions are available in the literature.[5] Norcaradienes (e.g. **9**)[5] show in their PMR spectra one of the cyclopropane methylene protons (*endo*-proton) at a field-strength close to or higher than that of TMS signal and since, the PMR spectrum of the product from **4** shows no such signal, structures of type **6** are ruled out. A distinction between the types 7 and 8 could be achieved on the basis of hydrogenation studies. Thus, this compound on catalytic hydrogenation (PtO_2/AcOH) furnished two products separable on $AgNO_3$-SiO_2 gel. One of these shows M^+ at *m/e* 226, thus clearly indicating the uptake of three moles of H_2 during catalytic hydrogenation and hence, must be formulated as **10**. The second product from hydrogenation reaction shows M^+ at *m/e* 224, shows no olefinic proton signal (PMR) but, reacts with perbenzoic acid to give an oxirane (M^+ at *m/e* 240) and hence, is considered to be **11**. These results clearly indicate that the product of carbene addition from **4** must be a cycloheptatriene derivative (type **8**). This is clearly supported by its UV absorption (Fig 1) which compares well with the summation of indane[10] and cycloheptatriene[11] absorptions (Fig 1).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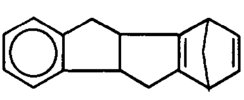
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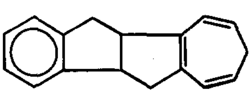
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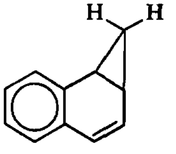

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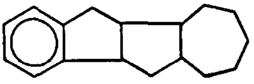
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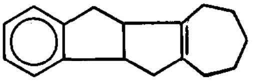
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Based on the gross skeleton **8**, seven cycloheptatriene structures are possible. The PMR spectrum of the product helps in eliminating some of these. Thus, the total olefinic proton (4·8–6·5 ppm) count is ~ 4·1 and the absorption in the region 4·8–5·33 ppm, the area recognised by Berson *et al.*[12] as characteristic of α-protons of a cycloheptatriene (**12**), accounts for ~ 2 protons. The compound reacts with maleic anhydride to give a low yield of an adduct, which was characterised as the corresponding crystalline dimethyl ester. The PMR spectrum of this ester shows the presence of a cyclopropane methylene (2H, complex multiplet located between −0·12 to −1·15 ppm), two cyclopropane methines (2H, complex multiplet located between 0·35–0·85 ppm) and one olefinic proton (1H, broadened doublet centred at 5·61 ppm, *J* = 6 Hz) signals, besides other expected absorptions. These findings suggest structure **15** or **16** for the adduct† and in turn structure **13/14** for the initial carbene addition product.

The addition product (**13/14**) was dehydrogenated in the vapour phase[16] at 425–430° over 10% Pd-C supported on asbestos, using *p*-cymene as a diluent, to furnish 11H-indeno[2,1-a]azulene (**17**) as blue lustrous flakes, m.p. 239–240°. The product was characterised by its UV, visible, IR and mass spectra (Experimental). As expected, the UV absorption is quite similar to that of 2-phenyl-azulene.[17] Its mass spectrum shows strong M^+ peak (*m/e* 216, 72%), while the base peak at *m/e* 215 (M-1) arises due to loss of H resulting in the formation of the ion **18** which is stabilised by both phenyl and azulenyl systems. The spectrum has several doubly charged species e.g. *m/e* 107·5 (14%) assignable to the species resulting from **18** by a further electron loss.

Autoxidation of cycloheptatriene 13/14

During the course of this work it was observed that the cycloheptatriene **13/14** on long usual storage at room temp (~ 25°) slowly deposits a solid, which was identified (m.p., mixed m.p., TLC, IR) as the 5,6,7,8-tetrahydrodibenzo-

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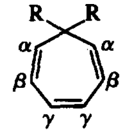
*This is as expected since copper-catalysed diazomethane decomposition generates carbene-copper complexes which do not undergo the C—H insertion reaction.[9]

†Cycloheptatrienes are known to react with maleic anhydride to give products in low yields.[13, 14] The structure of these products have been investigated in some cases[13] and at least in the case of cycloheptatriene[13] itself it has been demonstrated that the adduct has the nor-caradiene structure arising from the valence-bond isomer.[15]



R = H/alkyl

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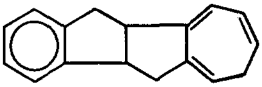

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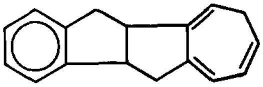

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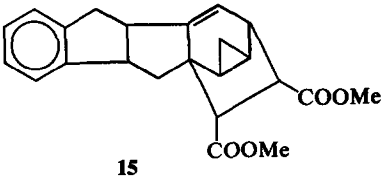

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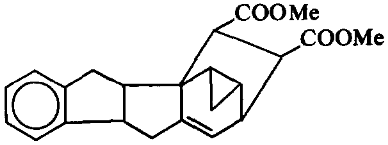

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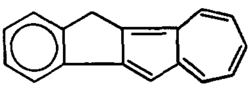

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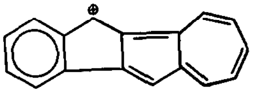

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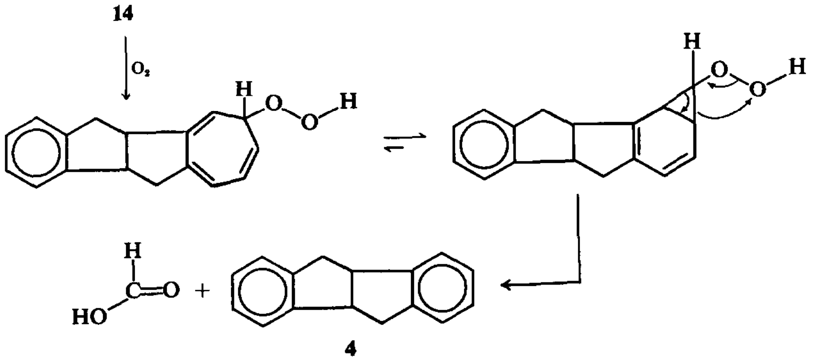
pentalene (4). By conducting suitable control experiments and starting with 100% (GLC) pure **13/14**, it could be demonstrated that audoxidation is involved in this reaction. A plausible gross pathway is indicated below:



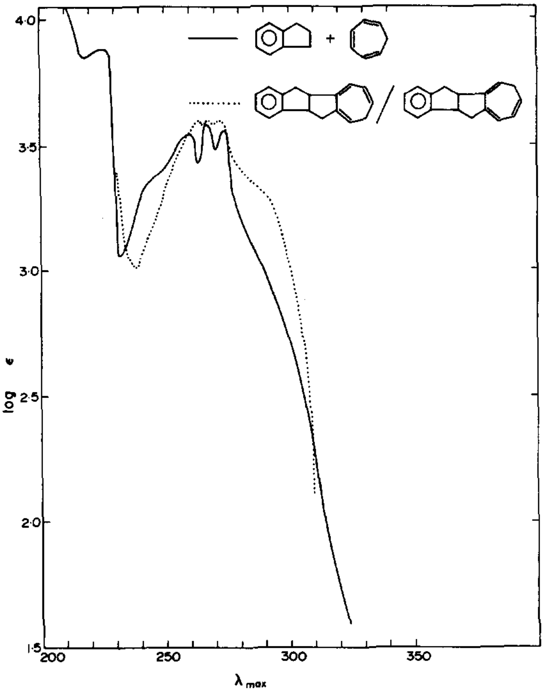


Fig 1. UV absorption of 1,2-benzo-4,5-cycloheptatrieno-3,6,7,8-tetrahydropentalene (**13/14**) and summation curve of cycloheptatriene and indane absorptions.

EXPERIMENTAL

All m.ps are taken on a Kofler hot stage and are uncorrected. Light petroleum refers to the fraction b.p. 40–60°. All solvent extracts were finally washed with brine, before drying (Na_2SO_4).

$AgNO_3$-SiO_2 gel was prepared according to the procedure of Gupta and Dev.[18]

GLC was carried out on 'Aerograph' A-350-B on 150 cm × 5 cm columns packed with 20% diethyleneglycol polysuccinate or 20% cyclized tung oil on Chromosorb W (60–80 mesh) using H_2 as the carrier gas.

Following instruments were used for spectral data: Perkin-Elmer spectrophotometer, model 350 (UV-visible); Perkin-Elmer Infrared, model 137E (I); Varian

Associates A-60 spectrometer (PMR, TMS as internal standard); CEC mass spectrometer, model 21-110B (Mass, 70 eV). While citing PMR data, the following abbreviations have been used: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and b (broad); the chemical shift position given is the centre of the signal.

α,α'-Diphenylsuccinic acid

A suspension of *α,α'*-diphenylsuccinonitrile[19] (100 g) in conc H_2SO_4 (300 ml), H_2O (300 ml) and gl AcOH (150 ml) was refluxed (17 hr), cooled, diluted with H_2O and then separated and collected by filtration. The product was next purified through its K-salt[20] to furnish the succinic acid as a white powder m.p. 228–229°, yield ~ 100% (Lit.,[20] m.p. 220°, yield 85·7%). This was used as such in the next step.

3,6,7,8-*Tetrahydro*-3,6-*diketo-dibenzopentalene* (**5**)

The above acid (20 g) was finely powdered and added gradually to conc H_2SO_4 (280 g) with swirling at room temp. The mixture was next heated on a steam-bath for 2 hr, the resulting light brown soln cooled and poured onto ice (600 g). The separated solid was collected, washed (H_2O) free of H_2SO_4 and dried, m.p. 206–207°, yield (~ 53%), (Lit.:[21a] m.p. 202°, yield 34·6%); IR (Nujol): C=O 1700 cm^{-1}; PMR ($CDCl_3$): two benzylic hydrogens (2H, s, 4·4 ppm), aromatic protons (m, 7·7 ppm). Mass: important peaks at *m/e* (relative intensity) 234 (M^+, 42%), 206 (11%), 178 (100%), 177 (14%), 176 (29%), 152 (19%), 151 (20%) and 76 (23%).

3,6,7,8-*Tetrahydrodibenzopentalene* (**4**)

By following the lit.[6] procedure only low yields (~ 23%); lit yield not specified) could be obtained. The following procedure gave much improved yields.

To amalgamated Zn (prepared[22] from 240 g of Zn wool), covered with HCl aq (400 ml, *d* 1·16), and toluene (200 ml), the above diketone (18·5 g) was added and the mixture refluxed for 10 hr. After cooling, the toluene layer was separated, the aq phase extracted with ether (100 ml × 3). The combined toluene, ether extracts were washed with water, Na_2CO_3 aq (10%, 50 ml) and dried and, freed of solvent to give a solid (14·67 g). This product was dissolved in ether, silica gel/IIA[23] (50 g) added and the whole freed of solvent under suction from a water-bath. This material was loaded on the top of a chromatographic column (silica gel/IIA, 40 cm × 4·0 cm), which was eluted with light petroleum (250 ml × 5). The combined eluates were freed of solvent and the residue (11·45 g, 70%; m.p. 100–102°) recrystallised from EtOH with little loss, m.p. 102–103° (Lit.[6], m.p. 101°). UV (95% EtOH): λ_{max} 275 (log ϵ 3·41), 268 (log ϵ 3·39) and 262 nm (log ϵ 3·24); IR (Nujol): 1480, 1450, 1370, 1305, 1022, 932, 762, 755, 739, 728, 716 cm^{-1}; PMR (CCl_4): benzylic CH and CH_2 (complex multiplet located between 2·85–4·1 ppm), aromatic protons (m, 7·05 ppm). Mass: important peaks at *m/e* (relative intensity) 206 (M^+, 100%), 205 (48%), 191 (11%), 115 (10%) and 91 (15%).

Reaction of 3,6,7,8-*tetrahydrodibenzopentalene with diazomethane*

Nitrosomethylurea (30 g, 0·4 mole) in ~ 1 g lots was added every 10 min to KOH aq (50%, 100 ml) covered with decalin (25 ml; commercial decalin was repeatedly shaken with conc H_2SO_4, then washed with water, dried and distilled), while a small stream of N_2 (~ 80 ml/min) was being bubbled through. The stream of N_2-diluted diazomethane, thus obtained, was dried (KOH pellets) and led into a soln of 3,6,7,8-tetrahydrodibenzopentalene (4·12 g, 0·02 mole) in decalin (20 ml) containing CH_2Cl_2 (300 mg) and which was being stirred (magnetically) and maintained at 95–100°. After completion of the addition (5–6 hr), stirring and heating was continued for another 0·5 hr after which the mixture was diluted with ether (25 ml) and filtered to remove a greenish-yellow inorganic material. Ether was then distilled off from a water-bath and decalin distilled under suction to give a light yellow liquid (4·4 g). GLC (tung oil, 200°, 90 ml H_2/min) of this material showed at least 5 components with RRT of 1·0 (47%), 1·3 (35%), 1·6 (5%), 1·9 (10%) and 2·4 (3%); of these the component with RRT = 1·0 represents unchanged starting material. This product was subjected to IDCC on $AgNO_3$-silica gel (25 cm × 6·6 cm) using 1% EtOAc in C_6H_6 as the solvent; the various cuts were monitored by GLC:

Frac. 1–3	0·861 g	0·5–2·0 cm from origin,
Frac. 4, 5	1·275 g	2–4·5 cm from origin,
Frac. 6–12	1·491 g	4·5–16·5 cm from origin,
Frac. 13	0·211 g	16·5–19 cm from origin.

Only fractions 4, 5 and 13 were GLC pure, the last one representing GLC component with RRT = 1 (starting material). Fractions 4 and 5 corresponded to GLC component with RRT = 1·3 and, were mixed and distilled to give a light yellow liquid (**13/14**), b.p. 100–110° (bath)/0·1 mm; IR (liquid): 1600, 1550, 1480, 1435, 1295, 1025, 822, 745 cm^{-1}; PMR (CCl_4): benzylic and allylic protons (~ 8H, three sets of complex multiplets located between 1·90–4·00 ppm), olefinic protons (~ 4H, two sets of complex multiplets located between 4·80–6·50 ppm), benzene ring protons (4H, essentially a singlet, 7·05 ppm). Mass: important peaks at *m/e* (relative intensity) 220 (M^+, 53%), 205 (27%), 129 (43%), 128 (29%), 115 (57%), 105 (70%), 104 (100%), 91 (37%), 77 (24%), 63 (26%). (Found: C, 92·58; H, 7·50. $C_{17}H_{16}$ requires: C, 92·68; H, 7·32%).

Hydrogenation of **13/14**

The above product (**13/14**, 470 mg) in AcOH (10 ml) was hydrogenated at room temp (25°) and pressure in presence of pre-reduced Adam's PtO_2 catalyst (57 mg) till no more H_2 was absorbed (~ 360 ml). The product was worked up in the usual manner and distilled to give a liquid (370 mg), b.p. 130° (bath)/0·3 mm. On $AgNO_3$-SiO_2 gel TLC (solvent: benzene) it showed two components, which could be readily separated by column chromatography on $AgNO_3$-SiO_2 gel (29 cm × 1·2 cm): (i) light petroleum 50 ml × 4, 12 mg, impure; (ii) light petroleum, 50 ml × 8, 73 mg, pure **10**; (iii) 5% C_6H_6 in light petroleum, 50 ml × 6, 8 mg, mixture of **10** and **11**; (iv) 10% C_6H_6 in light petroleum, 50 ml × 4, 157 mg, pure **11**.

Fraction (ii) on distillation yielded **10**, b.p. 128° (bath)/0·3 mm, UV (95% EtOH): λ_{max} 274 (log ϵ 3·22), 267 (log ϵ 3·16) and 260 nm (log ϵ 2·98); IR (liquid): 755, 745 cm^{-1}; PMR (CCl_4): aromatic protons (4H, s, 6·95 ppm), benzylic CH (1H, m, 3·36 ppm), benzylic CH_2 (2H, d, 2·85 ppm, $J = 2·5$ Hz). Mass: important peaks at *m/e* (relative intensity) 226 (M^+, 75%), 155 (22%), 129 (40%), 128 (37%), 116 (100%), 115 (53%), 67 (22%). (Found: C, 89·62; H, 10·06. $C_{17}H_{22}$ requires: C, 90·20; H, 9·80%).

Fraction (iv) was distilled to give **11**, b.p. 122° (bath)/0·3 mm, UV (95% EtOH): λ_{max} 272 (log ϵ 3·23), 266 (log ϵ 3·20) and 259 nm (log ϵ 3·06); IR (liquid): 748 cm^{-1}; PMR (CCl_4): aromatic protons (4H, s, 7·01 ppm), benzylic and allylic CH, CH_2 (9H, overlapping signals located between 1·8–3·7 ppm), Mass: important peaks at *m/e* (relative intensity) 224 (M^+, 100%), 181 (15%), 167 (18%), 128 (21%), 116 (27%), 115 (23%). (Found: C, 90·80; H, 9·18. $C_{17}H_{20}$ requires: C, 91·01; H, 8·99%). This compound (**11**, 100 mg) in C_6H_6 readily reacted with perbenzoic acid in C_6H_6 to give a product showing the following important peaks in its mass spectrum: *m/e* (relative intensity) 240 (M^+, 32%), 125 (55%), 122 (30%), 116 (100%), 105 (39%), 77 (39%).

Reaction of maleic anhydride with **13/14**

A mixture of **13/14** (464 mg), maleic anhydride (221 mg) and benzene (10 ml) was refluxed for 3 hr, cooled and treated with Na_2CO_3 aq (10%, 10 ml). The mixture was heated (1 hr) on a steam bath and then worked up in the usual manner to give unreacted **13/14** (324 mg) (neutral fraction) and an acid 203 mg; from aq alkaline part, after acidification with HCl aq and extraction with ether). The crude acid was esterified (CH_2N_2) and the product crystallised from MeOH to yield crystals m.p. 155–157°; IR (Nujol): C=O 1730, 1705 cm^{-1}; mass: important peaks at *m/e* (relative intensity) 220 (M^+ 100%), 219 (28%), 205 (22%), 129 (29%), 113 (22%), 105 (32%), 104 (40%). (Found: C, 75·73; H, 6·75. $C_{23}H_{24}O_4$ requires: C, 75·80; H, 6·64%).

11H-*Indeno*[2,1-a]*azulene* (**17**)

The cycloheptatriene **13/14** (400 mg) in dry *p*-cymene (1 ml) was dehydrogenated over 10% Pd-C (1·0 g, supported on 2 g of freshly ignited asbestos) in a stream of N_2 during 15 min at 425–430°, using the method and apparatus described elsewhere.[16] The blue condensate was diluted with light petroleum and extracted with 85% H_3PO_4 aq (1 ml × 6). The acid extract was cooled (0°), covered with ether (10 ml) and diluted with ice-water. The blue ether layer was separated, washed with water (10 ml) and dried. Solvent was flashed off to get a blue solid, which was purified by chromatography over basic Al_2O_3/II (25 cm × 2 cm): (i) light petroleum, 100 ml × 8, 2 mg, rejected; (ii) pet. ether, 100 ml × 10, 85 mg, blue crystalline solid, m.p. 229–230°. This was recrystallised from hexane to furnish blue, lustrous flakes, m.p. 239–240°; UV (cyclohexane): λ_{max} (log ϵ) 236 (4·02), 300 (4·65), 312 (4·77), 326 (4·34), 340 (3·51), 358 (3·70), 373 (4·04) and 395 nm (4·27). Visible absorption (cyclohexane): λ_{max} 576, 630 and 690 nm. IR (Nujol): 1460, 1372, 1160, 1015, 940, 796, 765, 730 cm^{-1}; mass: important peaks at *m/e* (relative intensity) 216 (M^+, 72%), 215 (100%), 213 (18%), 189 (10%), 108 (11%), 107·5 (14%), 106·5 (8%), 94·5 (10%). (Found: C, 94·46; H, 5·50. $C_{17}H_{12}$ requires: C, 94·41; H, 5·59%).

Autoxidation of the cycloheptatriene **13/14**

A sample of GLC pure **13/14** after usual storage at room temp for 7 days slowly deposited a solid, which was separated and identified (m.p., mixed m.p.) as 3,6,7,8-tetrahydrodibenzopentalene (**4**); GLC of the total material showed formation of **4** to the extent of ~ 17%. On the other hand, a sample of pure **13/14** remained unchanged (GLC) at 8–10° under N_2 during 6 months.

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