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2,7,15,16-TETRAMETHYL-*TRANS*-15,16-DIHYDROPYRENE[1]

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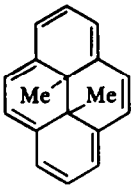
Abstract—The synthesis of 2,7,15,16-tetramethyl-*trans*-15,16-dihydropyrene has been accomplished by two different routes. The compound is of interest in providing a better understanding of the ESR spectra of 15,16-dihydropyrenes.

The ESR spectral properties of *trans*-15,16-dihydropyrene (**1**) are anomalous in that both its radical cation and radical anion show the unpaired electron occupying a symmetric orbital with high spin density at the 2- and 7-positions.[2] To explain this behavior an interpretation was proposed suggesting that the central "butane" unit of **1** acts as an electron releasing group in the radical cation and as an electron accepting group in the radical anion, invoking a type of hyperconjugative interaction.



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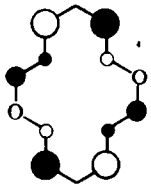
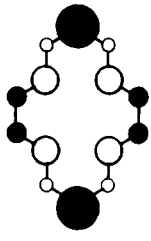
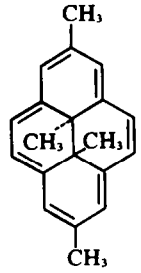


$\psi_{A\text{-}R}A$



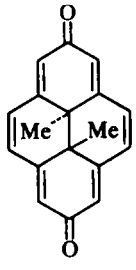
$\psi_{A\text{-}R}S$

The antisymmetric ($\psi_{A\text{-}R}A$) and symmetric ($\psi_{A\text{-}R}S$) antibonding orbitals available to the unpaired electron of the radical anion of **1** are illustrated above in the usual way. Though the two orbitals are doubly degenerate in the pure perimeter model the presence of the central butane unit alters this and causes the symmetric orbital to be of lower energy. Since it is well known that the presence of a methyl group has a destabilizing effect for orbitals requiring spin density on the carbon bearing the methyl group,[3] it was of interest to see what the ESR spectrum of 2,7,15,16-tetramethyl-*trans*-15,16-dihydropyrene (**2**) would be. The presence of Me groups at the 2- and 7-positions should raise the energy of the symmetric orbital ($\psi_{A\text{-}R}S$) while having little or no effect on the antisymmetric orbital ($\psi_{A\text{-}R}A$). Thus one might expect that the ESR spectrum of the radical anion of **2** would either show a hyperfine structure indicative of occupancy of the antisymmetric orbital by the unpaired electron or, in the event of a delicate balance of energies, a complicated pattern might result indicating spin density population of both the symmetric and antisymmetric orbitals. In fact, the ESR spectrum of the radical anion of **2** is quite complicated and is interpreted to be in accord with this latter possibility.* The present paper describes two synthetic routes developed for the preparation of **2** for these ESR studies.



2

From the work of Corey and Chaykovsky, it is known that dimethylsulfonium methylide reacts with α,β-unsaturated ketones to give exclusively oxirane derivatives.[4] In an attempt to introduce carbon at the 2- and 7-positions of the dihydropyrene skeleton, *trans*-15,16-dimethyldihydropyrene-2,7-quinone (**3**) was treated with dimethylsulfonium dimethylide. Surprisingly, none of the expected bisoxirane **6** was observed but, instead, there was isolated *trans*-15,16-dimethyldihydropyrene-2,7-dialdehyde (**4**) in 18 per cent yield and 7-hydroxymethyl-*trans*-15,16-dimethyldihydropyrene-2-aldehyde (**5**) in 47 per cent yield.



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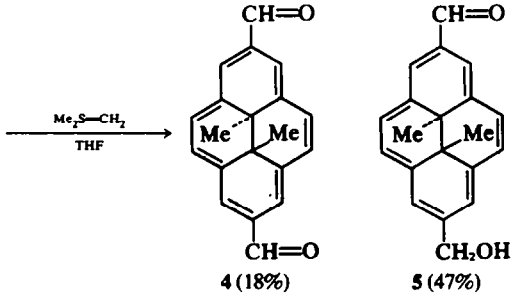
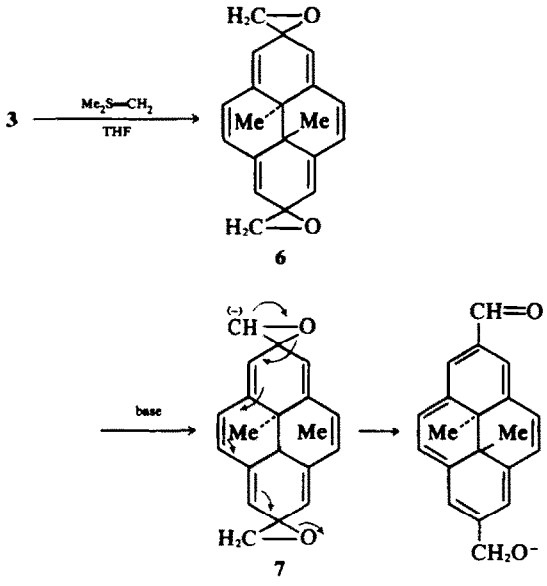


4 (18%) **5** (47%)

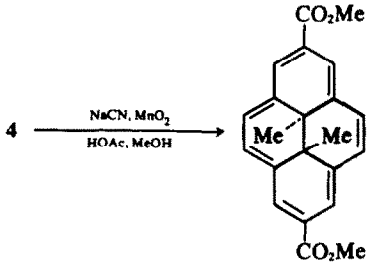
Presumably the bisoxirane **6** is first formed but, on reaction with base, gives the anion **7**, which can undergo valence tautomerization to the anion of **5**. The formation

*The ESR spectrum of the radical anion of **2** has been measured by Professor C. E. Klopfenstein and his colleagues and their computer analysis of it will be reported elsewhere.

of **4** could be simply the result of a crossed-Cannizzaro reaction of **5** under the basic conditions.

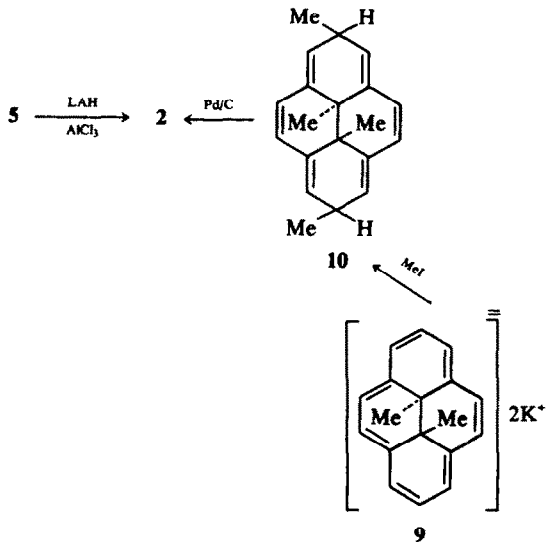


The interrelationship of **4** and **5** was established by oxidation of **5** with activated manganese dioxide following the procedure of Attenburrow *et al.*[5] This gave a sample of dialdehyde **6**, identical in all respects to that isolated directly from the reaction mixture. As additional structure proof, the dialdehyde **6** was converted to the corresponding dicarbomethoxy derivative **8** in 81 per cent yield following the oxidative cyanide procedure of Corey, Gilman and Ganem.[6] The sample of diester **8** thus prepared was identical in all respects to a sample of **8** described previously.[7]



To complete the synthesis of **2** reduction of **5** was carried out with a lithium aluminium hydride-aluminium chloride mixture, giving **2** in 58 per cent yield.

Meanwhile, it had been shown that *trans*-15,16-dimethyldihydropyrene (**1**) reacts with potassium in tetrahydrofuran to form the dianion **9**, which can be protonated to give *trans*-15,16-dimethyl-2,7,15,16-tetrahydropyrene[8] or acylated to give the corresponding 2,7-diacyltetrahydropyrene.[7] It was of interest, therefore, to explore the direct methylation of **9** as an alternative synthetic approach to **2**. In fact methylation of the dianion **9** with methyl iodide gave the desired bistriene **10**, as a mixture of isomers, in 45% yield. Dehydrogenation of **10** over a 30% Pd–C catalyst then gave **2**, identical in all respects to the earlier preparation, in 70% yield.



EXPERIMENTAL

Reaction of trans-15,16-*dimethyldihydropyrene*-2,7-*quinone* (**3**) *with dimethylsulfonium methylide.* A soln of dimethylsulfonium methylide was prepared as described,[5] using 425 mg of sodium hydride (59% dispersion in mineral oil), and 1·85 g of trimethylsulfonium iodide in 10 ml DMSO. This was added with stirring under N_2 to a soln of 240 mg of **3** in 40 ml dry THF held at −78°. The mixture, which immediately became a deep violet, was slowly allowed to warm to room temp. and was then poured onto ice. The organic layer was extracted with methylene chloride, washed with water, dried, and concentrated. The residual solid was taken up in benzene and chromatographed over silica gel. The first two bands off the column, which were bright yellow and violet, respectively, and small in amount, were not identified. The third band was a deep violet and from its spectral data has been identified as trans-15,16-*dimethyldihydropyrene*-2,7-*dialdehyde* (**4**). The material from this third band, after recrystallization from MeOH, gave 47 mg (18%) of violet crystals; m.p. 187–190°; NMR ($CDCl_3$), a singlet at τ −0·68 (2H, –CHO), a singlet at 0·97 (4H, ArH), a singlet at 1·17 (4H, ArH), and a singlet at 13·60 (6H, $-CH_3$); mass spectrum (70 eV), *m/e* (rel intensity), 288 (14), 273 (35) and 258 (100). (Found: C, 82·99; H, 5·58. Calc. for $C_{20}H_{16}O_2$: C, 83·31; H, 5·59%).

The fourth band from the above chromatography was eluted with a 9:1 benzene–ether mixture. The product, identified from its spectral data as 2-*formyl*-7-*hydroxymethyl*-trans-15,16-*dimethyldihydropyrene* (**5**), was recrystallized from CCl_4 to give 123 mg (47%) of purple-black needles; m.p. 198–200°; NMR ($CDCl_3$), a singlet at τ −0·62 (1H, –CHO), a multiplet at 0·8–1·6 (9H, ArH and –OH), a singlet at 4·58 (2H, $-CH_2OH$), and a singlet at 13·80 (6H, $-CH_3$); mass spectrum (70 eV) *m/e* (rel intensity), 290 (16), 275 (40), 260 (100), 245 (65) and 230 (75). (Found: C, 82·79; H, 6·39. Calc. for $C_{20}H_{18}O_2$: C, 82·73; H, 6·25%).

Oxidation of 20 mg of 2-*formyl*-7-*hydroxymethyl*-trans-15,16-*dimethyldihydropyrene* (**5**) in 8 ml of methylene chloride with 120 mg of activated MnO_2, following the procedure of Attenburrow *et al.*,[5] gave 16 mg (82%) of violet crystals, m.p. 187–190°, identical in all respects to the sample of dialdehyde **4** described previously.

2,7-*Dicarbomethoxy*-trans-15,16-*dimethyldihydropyrene* (**8**). A mixture of 35 mg of *trans*-**4**, 59 mg of NaCN, and 209 mg of activated MnO_2 in 30 ml MeOH containing 3 ml ether and 8 mg AcOH was stirred at room temp. for 3 min, following the procedure of Corey *et al.*[7] The mixture was then filtered to remove the ppt and the filtrate was concentrated. The residual solid was chromatographed over silica gel using benzene for elution. The main eluate fraction yielded 34 mg (81%) of deep purple crystals; m.p. 237–239° dec.; NMR ($CDCl_3$), a singlet at τ 0·77 (4H, ArH), a singlet at 1·23 (4H, ArH), a singlet at 5·85 (6H, $-OCH_3$), and a

singlet at 13·92 (6H, $-CH_3$). (Found: C, 75·84; H, 6·03. Calc. for $C_{22}H_{20}O_4$: C, 75·84; H, 5·79%).

2,7,15,16-*Tetramethyl*-trans-15,16-*dihydropyrene*, **2**

(a) *By reduction of* 2-*formyl*-7-*hydroxymethyl*-trans-15,16-*dimethyldihydropyrene* (**5**). A soln of **5** (109 mg) in 50 ml ether was added dropwise with stirring to a suspension of LAH (440 mg) and $AlCl_3$ (1·52 g) in 100 ml ether. After the addition was complete, the mixture was stirred an additional 3 hr before carefully decomposing it with ice water. The ether layer was removed, washed with water, dried, and concentrated. Chromatography of the residual solid over silica gel using pentane for elution gave dark green crystals. These, after low-temp. recrystallization from MeOH, yielded 57 mg (58%) of deep green crystals; m.p. 194–195° dec; UV (cyclohexane), 340 nm (ϵ, 95,000), 377·5 (35,500), 470 (8630), 534·5 (214), 600 (214), 635 (805) and 648 (1500); NMR ($CDCl_3$), a singlet at τ 1·51 (4H, ArH), a singlet at 1·61 (4H, ArH), a singlet at 6·97 (6H, $-CH_3$), and a singlet at 14·09 (6H, $-CH_3$); mass spectrum (70 eV), *m/e* (rel intensity), 260 (10), 245 (38) and 230 (100). (Found: C, 91·90; H, 8·14. Calc. for $C_{20}H_{20}$: C, 92·26; H, 7·74%).

(b) *By methylation of the dianion of* trans-15,16-*dimethyldihydropyrene* (**9**). This experiment was carried out using a vacuum train. In separate reservoirs attached to the train via stopcocks were placed (1) 5 ml of MeI, (2) 12 ml THF and (3) a cube of K. Also, attached to the train was a reaction vessel containing a cube of K and bearing a side-arm tube on a swivel which, by rotation, would introduce 100 mg of *trans*-15,16-dimethyldihydropyrene into the reaction vessel. First, the samples of K in the separate tube and the reaction vessel were heated to form bright mirrors. Then the sample of THF was transferred to the tube bearing the K-mirror to insure its dryness and purity. After the THF had stood over the K-mirror overnight, it was transferred by distillation to the reaction vessel and the sample of *trans*-15,16-dimethyldihydropyrene was added with magnetic stirring. This stirring was maintained at −30° for 60 hr to insure complete conversion to the dark red dianion. At this point the mixture was frozen and the MeI was introduced by distillation. The mixture was warmed rapidly to −80°, and then slowly warmed to room temp. (4 hr) with stirring. After gaseous N_2 was allowed to fill the reaction vessel, it was removed from the train and a mixture of benzene and EtOH was added cautiously, to decompose the excess K. The mixture was then acidified with dilute aqueous acid and extracted with benzene. The benzene extract was washed with water, dried, and concentrated. Chromatography of the residual solid over silica gel using light petroleum for elution gave 46 mg (45%) of a mixture of diastereoisomets of the bistriene **10**; m.p. 150–165°; UV (cyclohexane), 251 nm (ϵ, 58500) and 260 (78200); NMR ($CDCl_3$), a singlet at τ 4·05 (4H, $=CH-$), a doublet at 4·36 (4H, J = 4·5 Hz, $=CH-CH(CH_3)-$), a multiplet at 6·8–7·2 (2H, $-CH(CH_3)-$), a doublet at 8·82 (6H, J = 7·2 Hz, $-CH(CH_3)-$), and a singlet at 9·00 (6H, $-CH_3$); mass spectrum (70 eV), *m/e* (rel intensity), 262 (95), 261 (35) and 247 (100). Without further purification, 40 mg of the bistriene **10** was dissolved in 50 ml cyclohexane containing 30 mg of a 30% Pd–C catalyst and boiled under reflux for 5 hr. After removal of the catalyst and solvent, the residual solid was chromatographed over silica gel using light petroleum for elution to give 29 mg (70%) of green crystals. These were recrystallized from cold MeOH to yield 22 mg of deep green crystals, m.p. 194–195°, identical in all respects to the crystals described under (a).

REFERENCES

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[2]F. Gerson, E. Heilbronner and V. Boekelheide, *Helv. Chim. Acta* **47**, 1123 (1964).

[3]D. Lazdins and M. Karplus, *J. Am. Chem. Soc.* **87**, 920 (1965).

[4]E. J. Corey and M. Chaykovsky, *Ibid.* **87**, 1353 (1965).

[5]J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hemsa, A. B. A. Jansen and T. Walker, *J. Chem. Soc.* 1094 (1952).

[6]E. J. Corey, N. W. Gilman and B. E. Ganem, *J. Am. Chem. Soc.* **90**, 5616 (1968).

[7]R. H. Mitchell and V. Boekelheide, *Chem. Commun.* 1557 (1970).

[8]R. H. Mitchell, C. E: Klopfenstein and V. Boekelheide, *J. Am. Chem. Soc.* **91**, 4931 (1969).