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1,4,5,8,9-PENTAMETHYLANTHRACENE. SYNTHESIS AND PROTONATION

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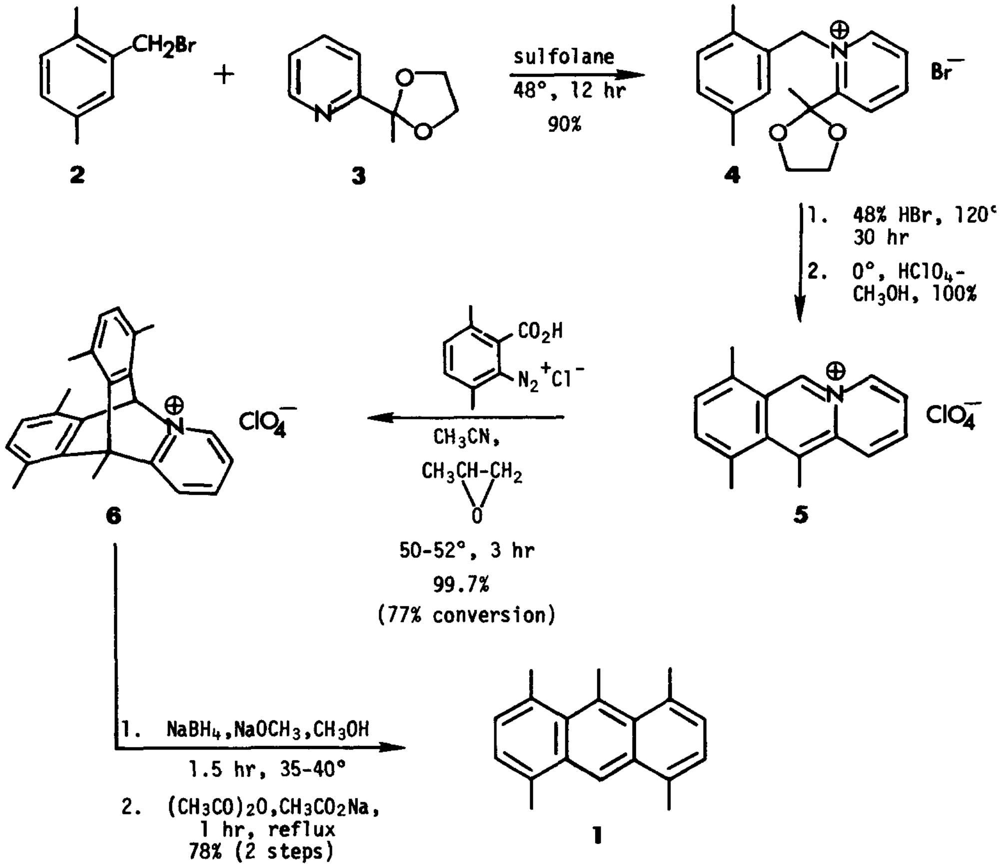
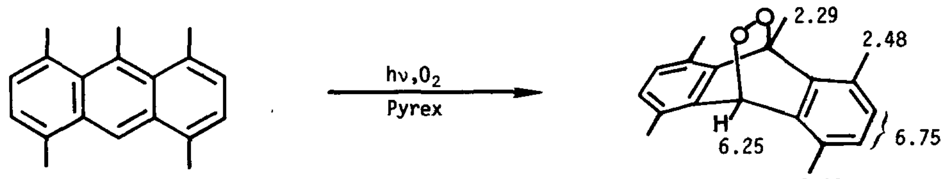
A recent report[1] on the synthesis of the title compound 1 prompts us to report our own efforts along these lines.[2] Whereas previous workers[1] had some difficulty with purification and were unable to obtain an analytically pure sample of 1 due to its facile oxidation, we encountered no problems in this regard. We report here (a) our synthetic scheme, (b) the structure of the easily formed endoperoxide of 1 and (c) the unusual protonation of 1 which is illustrative of its considerable steric strain.

Our synthesis follows the general scheme devised by Fields.[3] The salt 4 deposited when 3 [4] was heated with 2 [5] in tetramethylenesulfone.[6] Cleavage of the dioxolane ring and cyclization was accomplished with HBr and the resulting salt was converted to the perchlorate 5 (since a non-nucleophilic anion was desired for the next step).[7] Addition of 3,6-dimethylbenzyne afforded 6 in essentially quantitative yield.[8] Reduction to the dihydropyridine and aromatization[9] gave the desired 1 which was readily obtained analytically pure as light yellow needles, mp 158-159° (lit.[1] 154-157°).

Solutions of 1 in organic solvents fluoresce strongly. As expected, 1 showed absorption maxima at considerably longer wavelengths than anthracene, extending into the visible region [$\lambda_{max}^{CH_3CN}$ 407 nm(ε3600), 386(4200), 368(3500), 267(62,000) and 224 (16,000)].



We confirm that 1 reacts readily with oxygen.[1] Exposure of cyclohexane solutions of 1 to laboratory fluorescent lights for 1 week, or irradiation of undegassed cyclohexane solutions of 1 with a Hanovia lamp (450W) through Pyrex for 3 hr gave a quantitative yield of the endoperoxide 7, mp 210-212° (methanol).[10] The pmr spectrum (shown in δ on the structure) confirms that addition occurred across the 9,10-positions. Irradiation of 1 in scrupulously degassed solutions affords a different product whose structure is being determined.



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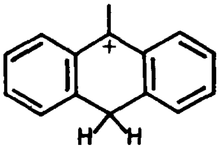
It is well known that 9-methylanthracene is protonated at C10 to give the tertiary carbocation 8.[11] In sharp contrast, we find that 1 is protonated in trifluoracetic acid exclusively at C9 to give the secondary carbocation 9. The pmr spectrum (shown on the



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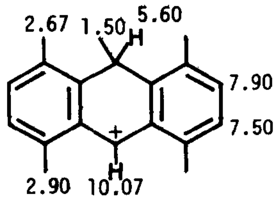

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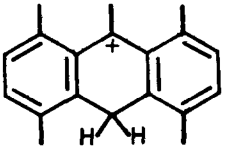

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structure; the peaks at δ1.50 and 5.60 were a mutually coupled doublet and quartet, respectively, J = 7 Hz, and those at δ7.90 and 7.50 were doublets, J = 7 Hz) conclusively eliminates the tertiary structure 10 or any structure resulting from protonation of an 'end' ring. Undoubtedly the secondary ion 9 is more stable than the tertiary ion 10 due to relief of the severe double-peri interactions. Indeed, we find that 1 is very much more basic than 1,4,5,8-tetramethylanthracene (although the resulting ions have nearly identical stabilities).

These studies are being extended to other reactions of 1 and to the synthesis of more highly substituted anthracenes.[12]

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References and Notes

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2. Our interest developed from our previous work on octamethylnaphthalene and other strained, methylated aromatic compounds; A. Oku, T. Kakihana and H. Hart, J. Am. Chem. Soc., **89**, 4554 (1967); H. Hart and J.F. Janssen, J. Org. Chem., **35**, 3637 (1970); H. Hart and A. Oku, Chem. Commun., 254 (1972); H. Hart and A. Oku, J. Org. Chem., **37**, 4269,4274 (1972).

3. D.L. Fields, J. Org. Chem., **36**, 3002 (1971).

4. C.K. Bradsher and J.C. Parham, J. Org. Chem., **28**, 83 (1963).

5. Prepared in 90% yield from p-xylene, paraformaldehyde, anhydrous HBr in acetic acid.

6. A mixture of **2** (44.0 g, 0.22 mole) and **3** (41.7 g, 0.25 mole) in tetramethylenesulfone (45 ml) was heated at 48° for 12 hr, during which time **4** deposited as a white solid. The mixture was cooled to 0°, diluted with ethyl acetate (100 ml) and filtered to give **4** (72.6 g, 90%) which was purified by washing with ethyl acetate.

7. A solution of **4** (37.0 g, 0.1 mole) in 48% HBr (160 ml) was heated at 120° for 30 hr, cooled to 0°, and methanolic perchloric acid (100 ml of 70% $HClO_4$ + 100 ml of CH_3OH) was added. The yellow solid **5** was filtered and washed with petroleum ether-ether (2:1) to give **5** (30.6 g, 100%), mp >265°. An analytical sample was obtained by recrystallization from acetonitrile. Calcd for $C_{16}H_{16}NClO_4$: C, 59.72; H, 5.01. Found: C, 59.69, H, 5.00.

8. A suspension of **5** (12.82 g, 0.045 mole) in acetonitrile (600 ml) was refluxed until solution was complete, cooled to room temperature, and propylene oxide (12 ml) and 3,6-dimethylbenzenediazonium carboxylate hydrochloride[2] (5.0 g, 0.025 mole) were added. After being heated at 50-52° for 20 min, the mixture was cooled, another portion (4.9 g) of benzyne precursor was added, and the mixture was heated at 50-52° (1.5 hr), then refluxed (1.5 hr). Cooling in ice and filtration gave **6** as a cream-colored solid (13.5 g). The mother liquor was concentrated to 100 ml, and a mixture of ether-petroleum ether (2:1, 200 ml) was added to precipitate 2.9 g of recovered **5**.

9. Perchlorate **6** (2.6 g, 6.67 mmole) was added to a solution of sodium methoxide (0.9 g) and sodium borohydride (0.6 g) in methanol (40 ml). The mixture was stirred at 25° for 20 min, then 35-40° for 1.5 hr. Dilution with cold water (200 ml), extraction with ether and drying (Na_2SO_4) gave the dehydro compound as a light orange-colored solid (2.1 g). This solid was refluxed (1 hr) in acetic anhydride (50 ml) containing sodium acetate (1.25 g). After removing most of the solvent under vacuum, the mixture was diluted with water, extracted with chloroform. Chloroform extracts were washed with water, $NaHCO_3$ solution, dried (Na_2SO_4) and the solid obtained after solvent removal was recrystallized from chloroform-methanol (1:4) to give 1.30 g of pure **1**, mp 158-159°. Calcd for $C_{19}H_{20}$: C, 91.88; H, 8.12. Found: C, 91.83; H, 8.15. The pmr and cmr spectra we obtained are in approximate agreement with those reported.[1]

10. Calcd for $C_{19}H_{20}O_2$: C, 81.39; H, 7.19. Found: C, 81.64; H, 7.34. Mass spectrum (70eV) m/e (rel intensity): 280(1), 265(14), 264(14), 250(20), 249(50), 248(100), 247(22), 233(50).

11. J.P. Colpa, C. MacLean and E.L. Mackor, Tetrahedron, **19**, Suppl. 2, 65 (1963).

12. Analyses were performed by Spang Microanalytical Laboratories, Ann Arbor, Michigan and by Clark Microanalytical Laboratories, Urbana, Illinois.