7-Methoxycyclopenta[*a*]phenalene

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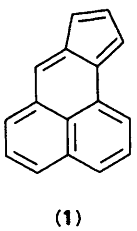
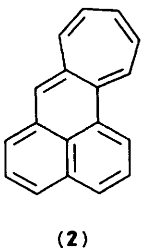
7-Methoxycyclopenta[*a*]phenalene, which shows azulene-like dipolar character in its ground-state, is synthesized from phenalene in nine steps.

Both cyclopenta[*a*]phenalene (**1**) and cyclohepta[*a*]phenalene (**2**) are molecules of theoretical interest.[1] Since the phenalenyl radical readily donates and accepts one electron to form a stable phenalenyl cation and anion, respectively,[2] the presence of the fused cyclopentadiene in (**1**) and cycloheptatriene in (**2**) will bestow azulene-like properties on these novel hydrocarbons.[1a] Three decades ago, Aitken and Reid reported the first synthesis of the former ring system as a benzo-annelated form.[3] Several reports describing the accidental formation of benzo-[4] and naphtho-annelated derivatives[5] followed. However, neither the parent hydrocarbon nor simple derivatives have been found until now. Here we disclose our approach to a simple derivative of (**1**), 7-methoxycyclopenta[*a*]phenalene (**3**).



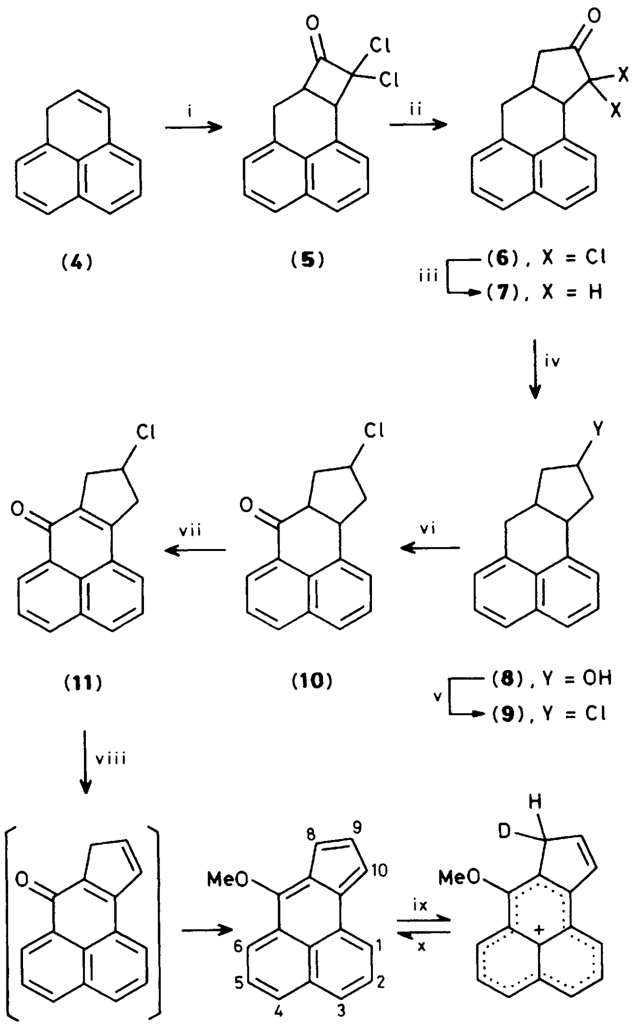
(**1**)



(**2**)

The synthetic sequence leading to (**3**) from the readily available phenalene (**4**) is depicted in Scheme 1.[†] The tetracyclic five-membered ring ketone (**7**), which consists of the required carbon skeleton of (**3**), was prepared by the reported three carbon annelation method.[6] Thus, the dichlorocyclobutanone (**5**) [colourless crystals, m.p. 185 °C (decomp.)], obtained by the cycloaddition of phenalene (**4**) with dichloroketene, was subjected to ring enlargement by diazomethane to afford dichlorocyclopentanone (**6**) (colourless needles, m.p. 120.5—121.5 °C) which was dechlorinated with zinc to give (**7**) (colourless prisms, m.p. 93—94 °C). On reduction with $NaBH_4$ in methanol, (**7**) afforded the alcohol (**8**) (a colourless oil). This was converted into the chloride (**9**) (a colourless oil) with Ph_3P in CCl_4.[7] To obtain the precursor (**12**) of our target molecule (**3**), (**9**) was oxidized first with $Na_2Cr_2O_7$ and $Ce(OAc)_3$[8] in acetic acid to the benzylic ketone (**10**) (colourless needles, m.p. 92—93 °C) followed by dehydrogenation with SeO_2 to generate the phenalenone (**11**) [yellow needles, m.p. 120 °C (decomp.)]. Final dehydrochlorination of (**11**) into (**12**) and its enol fixation were performed in one-pot through treatment of (**11**) with KOBu^t (2 equiv.) in hexamethylphosphoramide then quenched with $MeOSO_2F$ to give (**3**) as dark brown needles, m.p. 140—141 °C.

Spectroscopic evidence[‡] supports the structure of (**3**). It is



Scheme 1. *Reagents and conditions:* i, Cl_3CCOCl, Zn–Cu, $POCl_3$, Et_2O, reflux; ii, CH_2N_2, Et_2O, 0 °C, 76%; iii, Zn, HOAc, 80 °C, 1 h, 82%; iv, $NaBH_4$, MeOH, room temp., 2 h, 97%; v, Ph_3P, CCl_4, reflux, 18—20 h, 70%; vi, $Na_2Cr_2O_7$, $Ce(OAc)_3$, HOAc, room temp., overnight, 38%; vii, SeO_2, abs. dioxane, 90 °C, 4 h, 53%; viii, 2 equiv. KOBu^t, hexamethylphosphoramide, 0 °C, 1 h, then $MeOSO_2F$, 0 °C 30 min → room temp. 20 min, 55% from (**11**); ix, CF_3CO_2D; x, H_2O.

[†] All new compounds were fully characterized by i.r., mass, and ^1H n.m.r. spectral data together with the correct combustion analyses for crystalline compounds. The stereochemistry of (**8**), (**9**), and (**10**) has not been determined.

[‡] Compound (**3**): ^1H n.m.r. (CD_2Cl_2, 100 MHz): δ 8.36 (1H, dd, *J* 7.7, *J* 1.2 Hz, 4-H), 8.15 (1H, dd, *J* 7.2, *J* 1.2 Hz, 6-H), 7.96 (1H, dd, *J* 8.3, *J* 1.1 Hz, 1-H), 7.72 (1H, dd, *J* 8.1, *J* 1.1 Hz, 3-H), 7.61 (1H, dd, *J* 7.7, *J* 7.2 Hz, 5-H), 7.57 (1H, dd, *J* 8.3, *J* 8.1 Hz, 2-H), 7.08 (1H, dd, *J* 2.6, *J* 1.0 Hz, 10-H), 7.02 (1H, dd, *J* 5.0, *J* 1.0 Hz, 8-H), 6.86 (1H, dd, *J* 5.0, *J* 2.6 Hz, 9-H), 4.46 (3H, s, OCH_3); (CF_3COOD, 100 MHz): δ 9.39 (1H, d, *J* 7.3 Hz, 6-H), 9.15 (1H, d, *J* 7.3 Hz, 4-H), 8.87 (2H, d, *J* 7.3 Hz, 1-H, 3-H), 8.27 (2H, t, *J* 7.3 Hz, 2-H, 5-H), 8.13 (2H, br. s, 9-H, 10-H), 4.94 (3H, s, OCH_3), 4.57 (1H, br. s, 8-H); ^{13}C n.m.r. (22.5 MHz, $CDCl_3$): δ 60.4, 117.6, 119.7, 122.9, 124.8, 125.9, 126.7, 126.9, 127.8, 128.5, 129.7, 129.8, 132.4, 132.5, 132.6, 132.9, 157.8; u.v.–vis. (CH_3CN): $\lambda_{max.}$/nm (log ε): 259 (4.21, sh), 265 (4.22), 278 (4.15, sh), 294 (4.06, sh), 305 (4.03, sh), 352 (3.57, sh), 369 (3.63, sh), 402 (3.80), 425 (3.86), 451 (3.72), 519 (3.46), long tailing up to 740 nm; *m*/*z*: 232 (M^+, 43%), 202 (44), 189 (100).

worth noting that in the ^{1}H n.m.r. spectrum of (**3**) the five-membered ring protons appear at lower magnetic field ($\Delta\delta$ 0.5—1.0 p.p.m.) than those of fulvenes.[9] This finding is consonant with the resonance energy calculated using the ω-technique by Aihara[1c] in which fulvene and cyclopenta[*a*]phenalene (**1**) have been shown to be olefinic and semibenzenoid hydrocarbons, respectively. Furthermore, both the dipole moment ($\mu = 1.23$ D in benzene at 25 °C) of (**3**) and its ready susceptibility to protonation at C-8§ in trifluoroacetic acid to form (**3a**) strongly suggest the contribution of a dipolar structure to the ground-state of (**3**). Measurement of the redox potentials of (**3**) by cyclic voltammetry¶ showed $E^{ox} = +0.11$ V and $E^{red} = -1.27$ V, $E^{sum} = 1.38$ V. Interestingly, the oxidation and reduction potentials of (**3**) are more negative and more positive than those of azulene ($E^{ox} = +0.71$ V,[10] $E^{red} = -1.63$ V,[11] $E^{sum} = 2.33$ V) indicating that (**3**) possesses higher electron donating and accepting abilities than azulene.

We are grateful to Professor T. Machiguchi of Saitama University for the dipole moment measurement. Partial support for this work by a Grant-in-Aid for Special Project Research from the Ministry of Education, Science and Culture, Japan is gratefully acknowledged.

Received, 6th May 1986; Com. 594

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§ Although the protonation of (**3**) gave a single cationic species, the exact site of the protonation is obscure. We tentatively assigned C-8 for the protonation site because the calculated charge density by HMO at C-8 ($q_\pi = 1.135$) is higher than that of C-10 (1.123) and the resulting conjugate acid (**3a**) is considered to be more stable than the alternative.

¶ The c.v. was measured on a Yanaco polarographic analyser P-1100 with a Watanabe WX-1000 XY recorder in acetonitrile containing (**3**) and Bu$^n_4$NClO$_4$ (0.1 M) at −60 °C under nitrogen using a standard calomel electrode as a reference electrode and a Pt electrode as a working electrode. Sweep rate was 100 mV s^{-1}.