Efficient conversion of 9-Isopropenylphenanthrene to 4,6,6-trimethyl-6*H*-benz[*de*]anthracene in FSO_3H; 5,6-dihydro-4*H*-benzanthracen-4-ium ion and its charge delocalization mode

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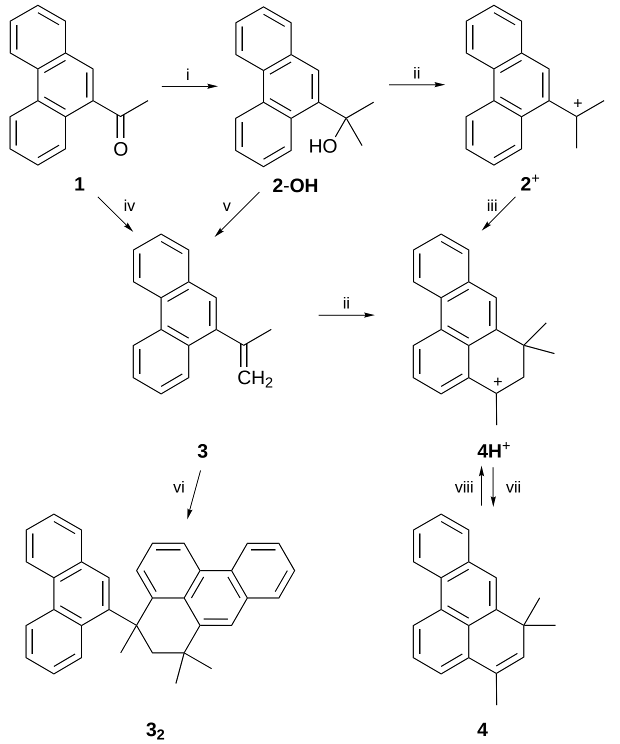
Low temperature protonation of 9-isopropenylphenanthrene in FSO_3H–SO_2ClF (or FSO_3H–CH_2Cl_2) leads to direct observation of 5,6-dihydrobenzanthracenium cation $4H^+$ from which the corresponding benz[*de*]anthracene is obtained in 92% yield upon quenching.

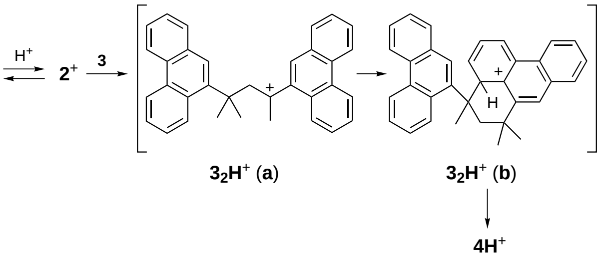
In the course of our work on charge delocalization mapping in arenium ions of polycyclic aromatic hydrocarbons (PAHs) and on various classes of PAH–C^+R_2 carbocations as models of epoxide ring opening,[1] we had prepared several regioisomeric phenanthrylpropane-2-carbenium ions including 2^+ which was stable up to room temperature. Attempted conversion of **2-OH** to the chloro derivative (**2-Cl**) led only to elimination to give the isopropenyl derivative **3**,[2] which was also independently synthesized by a Wittig type reaction[3] from **1** (Scheme 1).

Surprisingly, the expected quantitative conversion to 2^+ did not occur by low temperature protonation with FSO_3H–SO_2ClF; a mixture of the benzanthracene cation $4H^+$ and 2-(9-phenanthryl)propane-2-carbenium ion 2^+ were formed, even if highly diluted PAH solutions were added to a large excess of the superacid. Raising the temperature led to increased formation of $4H^+$ at the expense of 2^+ (NMR) and complete conversion to $4H^+$ occurred at room temp. Quenching of the superacid solution furnished the benzanthracene **4** in 92% yield.†



Scheme 1 *Reagents and conditions*: i, MeLi, Et_2O, 92%; iii, FSO_3H, SO_2ClF or CH_2Cl_2, −78 °C–room temp.; iii, cat. phenanthrene; iv, $MePr(Ph)_3Br$, $NaNH_2$–THF, 94%; v, $SOCl_2$, CH_2Cl_2; vi, $TiCl_4$, CH_2Cl_2 (ref. 5); vii, NaOH–H_2O, 92%; viii, FSO_3H, SO_2ClF or CH_2Cl_2

The mechanistic scheme outlined in Scheme 2 is suggested, with intermediate formation of the dimer cation 3_2H^+**(a)** and the cycloalkylation product 3_2H^+**(b)**, converting rapidly to $4H^+$. The proposed pathway requires the formation of a stoichiometric amount of phenanthrene. However, no protonated



Scheme 2

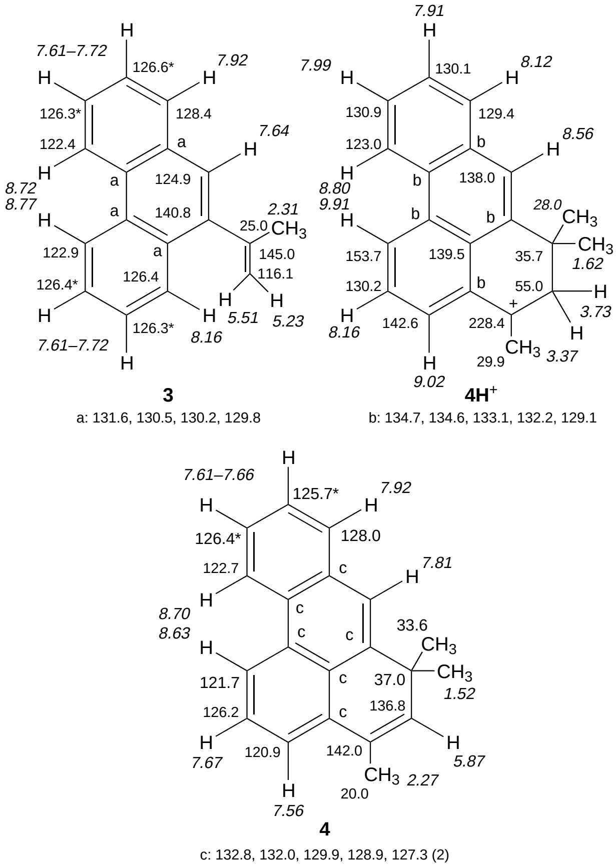


Fig. 1 ^1H NMR (300 MHz, *italic*) and ^{13}C NMR (75 MHz) chemical shifts, referenced to internal $CHCl_3$ (7.26 ppm, 77.0 ppm, **3** and **4**) or CH_2Cl_2 (5.32 ppm, 53.8 ppm, $4H^+$) *assignment may be interchangeable

phenanthrene was observed in the superacid solution and no phenanthrene could be isolated on work-up. This can be rationalized since in line with previous studies, the parent phenanthrenium ion is elusive;[4] furthermore control experiments confirm that once phenanthrene is reacted with FSO_3H, no intact phenanthrene can be isolated on work-up (→polymer). An important question that remained was why **2**$^+$ generated from the propan-2-ol would not undergo dimerization and cyclization. Addition of catalytic amounts of phenanthrene to a solution of **2**$^+$ (generated *via* **2-OH**) gave **4H**$^+$, demonstrating that either phenanthrene or its polymer induces *in situ* deprotonation forming **2** in equilibrium, which can then react with **3**$^+$, cyclize and eliminate (→**4H**$^+$).

The $TiCl_4$-mediated dimerization of **3** to give an isolable dimer **3**$_2$[5] and similar dimerization of other isopropenyl-PAHs[6*a–c*] have been reported where depending on the regio-isomer, isopropenyl-PAHs would either undergo polymerization or dimerization. The observed facile dimerization, cyclization and cleavage in the superacid, offers synthetic potential for preparation of various benzophenalenes in simple one-pot reactions. Another noteworthy feature of this chemistry is facile access to 1-phenanthryl-substituted carbocations which are otherwise not available due to difficulties associated with synthesis of 1-substituted phenanthrene derivatives by electrophilic chemistry.

In the ^{13}C NMR, the C^+ centre in **4H**$^+$ is at 228.4 ppm which is slightly shielded if compared to the C^+ of **2**$^+$ (230.1 ppm),[1*c*] indicating a similar degree of charge delocalization into the phenanthrene moiety and therefore comparable C^+–C(*ipso*) double bond character (Fig. 1). Charge delocalization mapping in **4H**$^+$ as deduced from $\Delta\delta^{13}C$ values shows arene π-participation primarily *via* a naphthalenium ion (AB ring of phenanthrene moiety) and is in qualitative agreement with the overall mode of charge delocalization deduced based on the AM1-calculated[7] carbon charges.[1]

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Footnotes and References

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† *Experimental procedure for the synthesis of* **4**: 9-isopropenylphenanthrene (170 mg, 0.78 mmol) was dissolved in 5 ml of CH_2Cl_2 under argon and cooled to −78 °C. Fluorosulfonic acid (*ca.* 1 ml) was slowly added to the stirred solution; the colour suddenly turned deep red. After 5 min, the solution was warmed to room temp. (blue colour), stirred for additional 20 min, and poured into ice-cold aqueous 5% NaOH. Extraction with CH_2Cl_2 and column chromatography (hexane) gave 93 mg (92%) of a white solid (mp 80–81 °C; for NMR spectral data see Fig 1; *m/z* 258 (M^+).

‡ AM1 semi-empirical calculations[7] were carried out using the HYPERCHEM package (HYPERCUBE 1995).

1 (*a*) K. K. Laali, *Chem. Rev.*, 1996, **96**, 1873; (*b*) K. K. Laali and P. E. Hansen, *J. Org. Chem.*, 1997, **62**, 5804; (*c*) K. K. Laali and S. Hollenstein, unpublished work.

2 E. Bergmann and F. Bergmann, *J. Am. Chem. Soc.*, 1937, **59**, 1443; D. F. Church and G. J. Gleicher, *J. Org. Chem.*, 1976, **46**, 2327.

3 R. M. Pike, D. W. Mayo, S. S. Butcher, D. J. Butcher and J. Hinkle, *J. Chem. Educ.*, 1986, **63**, 917.

4 K. Laali and H. Cerfontain, *J. Org. Chem.*, 1983, **48**, 1092.

5 J. Coudane, M. Brigodiot and E. Marechal, *Polym. Bull.*, 1979, **1**, 475.

6 (*a*) C. Bunel, M. Brigodiot and E. Marechal, *J. Macromol. Sci. Chem.*, 1978, **A12**, 1283; (*b*) J. Coudane, M. Brigodiot and E. Marechal, *Polym. Bull.*, 1979, **1**, 465; (*c*) J. Coudane, M. Brigodiot and E. Marechal, *Polym. Bull.*, 1979, **1**, 469.

7 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

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