Double *peri*-Interactions: Reactions of 1,4,5,8,9-Pentamethylanthracene

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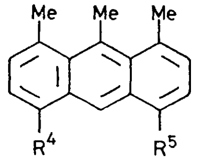
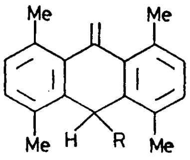
Summary Double *peri* interactions of the C-9 methyl group in 1,4,5,8,9-pentamethylanthracene lead to a variety of reactions under mild conditions, all of which result in destruction of aromaticity in the central ring; this loss is more than compensated for by strain relief.

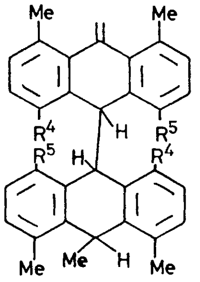
Recent reports[1,2] on the exceptionally ready loss of aromaticity in the central ring of strained anthracenes prompt us to communicate results which augment, and in one instance are at slight variance with, those reports. We found recently[3] that 1,4,5,8,9-pentamethylanthracene (**1**)[3,4] is protonated by trifluoroacetic acid at C-9 (to give a secondary carbocation) in preference to C-10 (to give a tertiary carbocation) because the double *peri* interaction at C-9 can be relieved in this way. However, treatment of (**1**) with acid (conditions unspecified) gave a 1 : 1 mixture of (**1**) and (**3**),[2] presumably as a consequence of protonation at C-10 and proton loss from the C-9 methyl group.



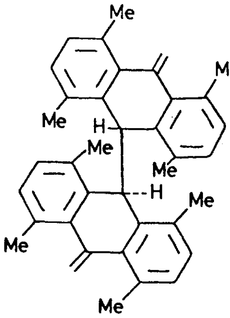
(1) $R^4 = R^5 = Me$
(2) $R^4 = H$ or Me, $R^5 = H$



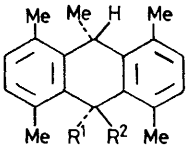
(3) R = H
(4) R = OH
(5) R = CH_2OAc



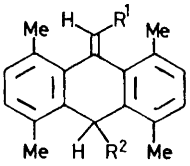
(6) $R^4 = H$ or Me, $R^5 = H$
(7) $R^4 = R^5 = Me$



(8)



(9a) $R^1 = OH, R^2 = H$
(9b) $R^1 = H, R^2 = OH$



(10) $R^1 = CH_2OAc, R^2 = CH_2Cl$
(11) $R^1 = R^2 = Me$

We find that this tautomerization can also be accomplished with base. Treatment of (**1**) with Bu^tOK in Me_2SO (55 °C, 2 h) followed by quenching with water and chromatography (alumina, benzene) gave (**3**), m.p. 150—152 °C (EtOH), in 48% yield, together with 33% of the oxidation product (**4**),† m.p. 139—141 °C (benzene–light petroleum). In the n.m.r. spectrum ($CDCl_3$, room temperature) of (**3**) the vinyl protons gave a sharp singlet at δ 5·47 but the aliphatic methylene protons appeared as an exceptionally broad peak centred at δ 3·70; this peak sharpened on heating and separated to an AB quartet on cooling (−50 °C), δ 4·10 and 3·28, *J* 18 Hz. Consequently the central ring in (**3**) is in a boat conformation with a significant barrier to 'flipping' (*ca.* 14·7 kcal mol^{-1}).[5] When (**3**) was heated (80 °C, $CDCl_3$, 1—2 h) it was converted in part (*ca.* 15%) into (**1**).

Analogues of (**1**) such as (**2**) experienced relief from double *peri* strain in a different manner; with *p*-MeC_6H_4-SO_3H they dimerized to (**6**) in which the crowded C-9 became tetrahedral in one half of the molecule. It was claimed[2] that (**1**) does not dimerise in this way owing to the steric hindrance in (**7**; $R^4 = R^5 = Me$). However in an attempt to chlorinate (**1**) we obtained a product with just this type of steric hindrance. Treatment of (**1**) with sulphuryl chloride and silica gel in hexane[6] and hydrolytic work-up gave the 'dimer' (**8**)† in 43% yield (m.p. > 310 °C) together with the alcohol (**9a**) (34%, m.p. 135—137 °C).† The two sets of aromatic methyl groups in (**8**) appeared as singlets at δ 1·60 and 2·49, one set obviously shielded by the adjacent aryl ring (methine protons at δ 4·88, vinyl protons at δ 5·73). The failure of (**7**) to be formed on treatment of (**1**) with acid[2] must therefore be due to a delicate balance of a variety of factors, steric hindrance being only one of these.

The hydration product (**9a**) was also obtained (75% yield) when (**1**) was treated with acetic acid saturated with hydrogen chloride (50—60 °C, 5 h) followed by hydrolytic work-up and chromatography (silica gel, benzene). However treatment of (**1**) under the same conditions but in the presence of 1 equiv. of formaldehyde (in an attempt to effect chloromethylation) gave an epimeric alcohol (**9b**),† m.p. 128—130 °C (light petroleum), in 47% yield, together with the acetate (**5**)† in 23% yield. The stereochemical assignments of (**9a**) and (**9b**) are based on chemicals shifts‡ and must be regarded as tentative, but each of these hydration products of (**1**) was formed stereospecifically under the conditions described. Vacuum sublimation of (**9b**) at 90 °C afforded (**9a**) whereas sublimation of either alcohol at 140—150 °C caused dehydration to (**1**).

Finally, subjection of (**1**) to the same chloromethylation conditions but with a large excess (20 equiv.) of formaldehyde gave (**10**).† Treatment of (**10**) with an excess of lithium aluminum hydride reduced the chloromethyl group and converted the ester function into the allylic alcohol.† This was converted into its tosylate and reduced to give (**11**),† m.p. 119—121 °C. All attempts to aromatize the central ring in (**11**) failed. It is clear that the unusual reactions of (**1**) which we have described are a consequence of the severe strain caused by double *peri* interactions.

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† All new compounds were thoroughly characterized by their spectra, and most by elemental analysis.

‡ The O*H*, -C*H*(OH)-, -CH(*Me*)-, and -C*H* (Me)- signals appear at δ 1·67, 6·04, 1·44, and 4·28 in (**9a**), and at δ 1·28, 5·87, 1·38, and 4·15 in (**9b**); these shifts are most consistent with boat conformations with the large (methyl) group in axial positions; see P. P. Fu, R. G. Harvey, J. W. Paschal, and P. W. Rabideau, *J. Amer. Chem. Soc.*, 1975, **97**, 1145.

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