ipso-Attack in the Cyclisation of 4-(α-Naphthyl)butan-1-ol to 1,2,3,4-Tetrahydrophenanthrene

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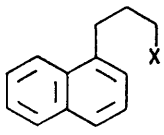
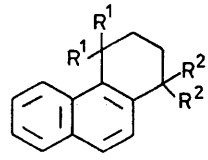
Summary Whereas electrophilic substitution of 4-(β-naphthyl)butanol takes place with BF_3–ether exclusively at the α-naphthyl position, cyclisation of 4-(α-naphthyl)-butanol, under identical conditions, occurs *via* two pathways, the major one (81%) corresponding to direct attack at the β-naphthyl position whilst the minor one (19%) involves prior *ipso*-attack at the α-naphthyl position.

IN many of its reactions with electrophilic reagents naphthalene shows a preference for α-substitution, although the β-substituted products may also be formed depending on the reagents and reaction conditions. This preference for electrophilic substitution at the 1-position (or 4-position in the case of naphthalenes with electron releasing substituents already present in the 1-position) may be accounted for by considerations of stability of the Wheland intermediates involved.[1] However, little is known of the

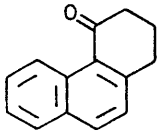
mechanisms where the formation of 1,2-disubstituted naphthalenes is dictated by steric constraints as in many syntheses of the phenanthrene nucleus from suitable 1- or 2-substituted naphthalenes.



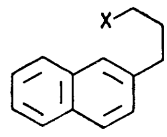
(1) X = CO_2H
(2) X = CD_2OH



(3) R^1 = H, R^2 = D
(4) R^1 = D, R^2 = H
(5) R^1 = R^2 = H

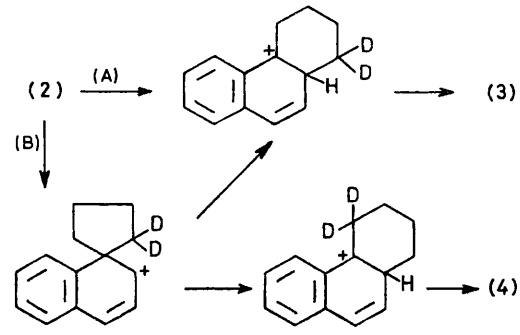


(6)



(7) X = CO_2H
(8) X = CD_2OH

Following similar studies in the indole series[2] (where initial 3-substitution is the rule for indole and its simple alkyl derivatives) we reduced 4-(α-naphthyl)butanoic acid[3] (**1**) to 4-(α-naphthyl)[1,1-$^2H_2$]butanol[4] (**2**) (using $LiAlD_4$) and cyclised the latter to the tetrahydrophenanthrenes (**3**) and (**4**) (total yield 86%) with boiling boron trifluoride–ether under nitrogen for 4 h. This mixture of deuteriated tetrahydrophenanthrenes was converted into the picrates, m.p. 109–110 °C [lit.[5] 110 °C for (**5**)], and the proportions of the two isomers were estimated from the 220 MHz n.m.r. spectrum; assignments of the 1- and 4-methylene proton resonances (τ 7·00 and 7·14 respectively) were made from the ^1H n.m.r. spectrum of the dideuteriotetrahydrophenanthrene (**4**) prepared by reduction of the ketone (**6**)[3,5] with deuteriodiborane. If allowance is made for a small secondary isotope effect (assumed to be the same as that observed[2c] in the indole series studied earlier) the alcohol (**2**) cyclises by the two pathways (A) and (B) in the proportions 81 : 19 (see Scheme).



SCHEME

In a similar series of experiments we reduced the acid[3] (**7**) to the dideuterio-alcohol (**8**),[6] m.p. 36–38 °C. The latter, on cyclisation in boiling boron trifluoride–ether, afforded only the dideuteriotetrahydrophenanthrene (**4**) (as shown by the 220 MHz n.m.r. spectrum). This result also indicated that equilibration of the two isomers (**3**) and (**4**) did not occur under the cyclisation conditions, and this was confirmed by a further series of experiments which will be described elsewhere.

The results show that under identical kinetically controlled conditions the 4-(α-naphthyl)butan-1-ol (**2**) undergoes intramolecular electrophilic cyclisation by two pathways, the minor route involving *ipso*-attack at the 1-position, whereas the 2-isomer (**8**) cyclises exclusively by substitution at the 1-position. The relatively small proportion of *ipso*-attack in the cyclisation of (**2**) contrasts with the larger effect observed in the corresponding free radical substitution.[7] Sulphonation[8] or acylation of naphthalene itself at the 2-position may also occur by two mechanisms, *i.e.* by initial attack at the 1-position followed by rearrangement to the 2-position, as well as by direct attack at the 2-position.

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