Electrophilic Aromatic Substitution. Part XV.[1] Protiodetritiation of the Helicene, Benzo[*c*]phenanthrene

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All six tritium-labelled benzo[*c*]phenanthrenes have been prepared and their rates of detritiation by anhydrous trifluoroacetic acid at 70° measured; these lead to the following partial rate factors (positions in parentheses): 1580 (1), 1200 (2), 422 (3), 2050 (4), 8680 (5), and 2465 (6). The order of positional reactivities is in very good agreement with that predicted from localization energies calculated by the Hückel method and the exchange data correctly predict that the 5-isomer should be principally obtained in preparative substitutions. Each position in benzo[*c*]phenanthrene is more reactive than the corresponding position in phenanthrene, and by a closely similar amount. There is no evidence with this ' helicene ' that puckering of the rings has any effect upon the positional reactivities nor is there any indication of steric hindrance to exchange of the hydrogen atom at the 1-position, this being the position where interactions cause the rings to pucker.

WHILST prediction of rates of chemical reactions in solution by theoretical means is not yet a practical proposition, prediction of relative rates is more advanced and electrophilic aromatic substitutions probably provide the most valuable test reactions towards this end, since it is possible to alter reaction rates without altering structure at the reaction site. Unfortunately steric hindrance prevents most analyses from being meaningful or complete. Hydrogen exchange is the electrophilic substitution of least steric requirement and indeed only in 1,3,5-triphenylbenzene,[2] tetraphenylmethane,[3] and some isoalkylbenzenes[4] has hindrance been detected and even then it is very slight. Consequently the re-

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[1] Part XIV, H. V. Ansell, J. Le Guen, and R. Taylor, *Tetrahedron Letters*, 1973, 13.

[2] H. V. Ansell, R. B. Clegg, and R. Taylor, *J.C.S. Perkin II*, 1972, 766.

[3] H. V. Ansell and R. Taylor, *J.C.S. Chem. Comm.*, 1973, 936.

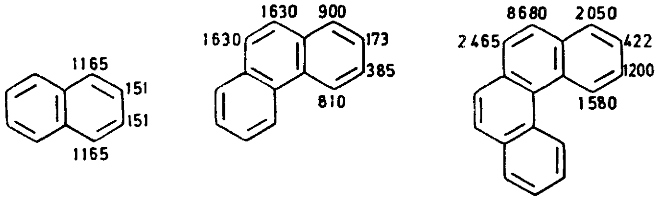
[4] J. Le Guen and R. Taylor, unpublished work.

action is particularly suitable for testing theoretical predictions. Thus hydrogen exchange of phenanthrene gives the reactivity order of the positions as 9 > 1 > 4 > 3 > 2 [5] which is predicted by Hückel localization energies,[6] and other workers have found aromatic hydrogen exchange rates to correlate well with these parameters.[7] The Hückel localization energies appear then to be very satisfactory indices of true reactivity (and certainly so in terms of cost effectiveness compared to all-electron calculations [8]) and it seemed that this might be true for benzo[*c*]phenanthrene.

Whereas the electrophilic reactivity of most simple polycyclic molecules have been determined in at least semi-quantitative terms, for the helicenes no data exist as far as we are aware. We considered it would be useful to fill this gap not only to evaluate the effect of the deformation of the aromatic rings but also because the 'helicene' series, *viz.* naphthalene, phenanthrene, benzo[*c*]phenanthrene, dibenzo[*c,f*]phenanthrene, hexahelicene, might be a useful series in which to evaluate theoretical predictions of reactivity. In this paper we report the preparation of all the tritium-labelled benzo[*c*]phenanthrenes and their rates of protiodetritiation.

RESULTS AND DISCUSSION

Rate coefficients, 10^7k/s^{-1}, for detritiation in anhydrous trifluoroacetic acid at 70° are as follows (positions in parentheses): 150 (1), 114 (2), 40·0 (3), 195 (4), 825 (5), and 234 (6). These rates, taken along with the rate coefficient for exchange in benzene (0·095) [9] give the partial rate factors shown in Scheme 1 along with those for naphthalene,[10] and phenanthrene.[5] Certain features are noteworthy. (i) The ratios of the reactivities of the 1-, 2-, 3-, and 4-positions in benzo[*c*]phenanthrene over their counterparts in phenanthrene are 1·95, 3·12, 2·44, and 2·43 respectively. The similarity in the values could be expected in view of the remote annulation and indeed they are predicted to be so (see below). This gives good support to the belief that exchange at the 1-position of benzo[*c*]phenanthrene is not hindered. For the 5- and 6-positions the increase in reactivity factors are 5·55 and 1·52 respectively. They are dissimilar because of course the symmetry of the 9- and 10-positions in phenanthrene is lost in the corresponding positions in benzo[*c*]phenanthrene, but even so the average increase in reactivity is close to that for the other four positions. (ii) Hückel localization energies for electrophilic substitution in benzo[*c*]phenanthrene are shown in the Table together with the literature values for phenanthrene and naphthalene.[6] The predicted positional reactivity order for benzo[*c*]phenanthrene is therefore 5 > 4 > 6 > 1 > 2 > 3 which is in very good agreement with the observed order of 5 > 6 > 4 > 1 > 2 > 3. Since the 4- and 6-positions are predicted to be very close in reactivity (as indeed they are) the discrepancy in the relative order is trivial. Furthermore the reactivities of the 1-, 2-, 3-, and 4-positions in benzo[*c*]phenanthrene are predicted to have similar reactivities to the corresponding positions in phenanthrene and this is also observed. We feel we are therefore justified in concluding that puckering of the aromatic ring is insufficient to produce any noticeable effect on reactivity in benzo[*c*]phenanthrene. This observation is in keeping with the conclusion of a recent paper in which it was claimed that aromatic rings normally considered to be flat, may flex as much as 20°,[11] and this does not produce any noticeable effect on reactivity. Benzo[*c*]phenanthrene is deformed to the extent that C-1 and -12 are 3·0 Å apart, from which it may be calculated that C-1 is 30° above the plane of the opposite aromatic ring, the elevation being calculated from the position of C-12. However this deformation is spread over four rings and Herbstein and Schmidt showed from an *X*-ray study that the rings at the extremities of the molecule are deformed 10°, and the inner rings 14°.[12] This is within the limits described above and accounts for the lack of abnormality in the reactivity. Herbstein and Schmidt believed that reaction would most readily occur at the positions where the sp^2 hybridized carbon atoms were most strained towards the sp^3 state, *i.e.* the 5- and 3-positions. Our results show this explanation is unsound, their prediction of the 5-position as the most reactive being fortuitously correct.



SCHEME 1

Hückel localization energies L_r^+

Position in benzo[*c*]-phenanthrene	Energy	Value for corresponding position in phenanthrene	Value for corresponding position in naphthalene
1	2·3318	2·366	2·299
2	2·4605	2·454	2·480
3	2·4767	2·498	2·480
4	2·3118	2·318	2·299
5	2·2972	2·299	
6	2·3204	2·299	

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[6] A. Streitwieser, 'Molecular Orbital Theory for Organic Chemists,' Wiley, New York, 1961, p. 336.

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[8] J. N. Murrell, W. Schmidt, and R. Taylor, *J.C.S. Perkin II*, 1973, 179.

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[10] C. Eaborn, P. Golborn, R. E. Spillett, and R. Taylor, *J. Chem. Soc. (B)*, 1968, 1112.

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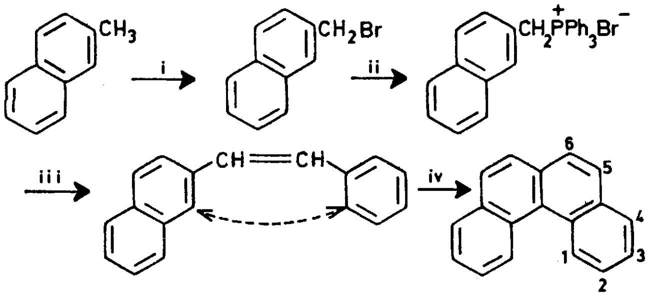
[12] F. H. Herbstein and G. M. J. Schmidt, *J. Chem. Soc.*, 1954, 3302.

It follows from our positional reactivity order in hydrogen exchange that this would be the order of yields of isomers obtained in other electrophilic substitutions (in the absence of steric hindrance), and indeed the 5-isomer is the main product in nitration, bromination, and acetylation.[13] However nothing is yet known about the isomer distribution of the minor products in these reactions. We can predict that in view of the close similarities of the positional reactivities, in a highly hindered reaction like acetylation, the order might well become $5 > 2 > 3 \gg 6 > 4 \gg 1$.

EXPERIMENTAL

The general method of carrying out the kinetic studies has been described previously,[14] but this work employed a modification [15] for dealing with aromatic compounds which have poor solubility in trifluoroacetic acid; this modification will be described in the next paper in this series. Excellent first-order kinetics (to beyond 95% reaction) were obtained for all compounds except the benzo[*c*]phenanthrene which was doubly labelled (in the 1- and 3-positions). Dissection of the composite rate gave two good first-order rates for reaction at the 1- and 3-position of 147×10^{-7} and 36×10^{-7} s^{-1}, and these rates were confirmed by studies on the independently prepared compounds, which gave values of 150×10^{-7} and 44×10^{-7} s^{-1} respectively. Rates were measured at 70°.

The general route for preparation of labelled compounds is shown in Scheme 2 and has previously been used to prepare 2-methylbenzo[*c*]phenanthrene.[16] All products and intermediates were indicated as being pure by g.l.c. analysis and all benzo[*c*]phenanthrenes melted at 68°. By using benzaldehyde labelled in the nucleus and in the side chain, and methylnaphthalene labelled in the methyl group it was possible to prepare [2-, 4-, 5-, and 6-^{3}H]benzo[*c*]phenanthrenes and [1,3-^{3}H$_2$]benzo[*c*]phenanthrene.



SCHEME 2

Reagents: i, *N*-bromosuccinimide; ii, PPh$_3$; iii, Bu^{n}Li–PhCHO; iv, I$_2$–*h*ν

[2-, 4-, *and* 5-^{3}H]*Benzo*[c]*phenanthrenes*.—[2-, 4-, *and* α-^{3}H]*Benzaldehydes*. [2-, 4-, and α-^{3}H]Toluenes were prepared by the routes described previously.[17] These were converted into the corresponding benzaldehydes by dibromination in the side chain under u.v. irradiation, followed by reaction with calcium carbonate.[18]

2-*Naphthylmethyl*(*triphenyl*)*phosphonium bromide*. 2-Bromomethylnaphthalene, m.p. 54° was prepared in 95% yield by bromination of 2-methylnaphthalene with *N*-bromosuccinimide.[19] Reaction of triphenylphosphine (131 g, 0·5 mol) with 2-bromomethylnaphthalene (111 g, 0·5 mol) in boiling xylene during 3 h gave after filtration and vacuum drying an approximately quantitative yield of 2-naphthylmethyl(triphenyl)phosphonium bromide, m.p. 248—251° (decomp.) [lit.,[20] 248—251° (decomp.)].

1-(2-*Naphthyl*)-2-[2- *and* 4-^{3}H]*phenylethylene and* 1-(2-*naphthyl*)-2-*phenyl*[2-^{3}H]*ethylene*. The above phosphonium salt was converted into the corresponding ylide $Ph_3P{=}CH{-}\beta{-}C_{10}H_7$ using n-butyl-lithium as a base (*cf.* ref. 20). The ylide was treated with the appropriate benzaldehyde to give the corresponding tritium-labelled 1-(2-naphthyl)-2-phenylethylene, m.p. 149·5—150° (lit.,[20] 149·5—150°).

The appropriately labelled 1-(2-naphthyl)-2-phenylethylenes prepared as above, were dissolved in benzene containing iodine and irradiated with u.v. light (125 W) as described by Martin *et al.*[16] to give after work-up [2-, 4-, and 5-^{3}H]-benzo[*c*]phenanthrenes. The yield varied from 35 to 50% and this is considerably higher than the report in the literature [16] which employed a 450 W lamp, though there was some indication that the quantity of iodine used may also affect the result; prior conversion into the appropriate stereoisomer of the substituted ethylene was also omitted since the required isomerization probably occurs under the reaction conditions anyway.

[6-^{3}H]*Benzo*[c]*phenanthrene*.— [α-^{3}H]-2-*Methylnaphthalene*. The Grignard reagent from 2-bromomethylnaphthalene was hydrolysed with tritiated water to give after work-up [α-^{3}H]-2-methylnaphthalene.

[α-^{3}H]-2-*Bromomethylnaphthalene*. [α-^{3}H]-2-Methylnaphthalene was brominated with *N*-bromosuccinimide as described above to give [α-^{3}H]-2-*bromomethylnaphthalene*.

[α-^{3}H]-2-*Naphthylmethyl*(*triphenyl*)*phosphonium bromide*. This was prepared from [α-^{3}H]-2-bromomethylnaphthalene and triphenylphosphine as described above.

1-([1-^{3}H]-2-*Naphthyl*)-2-*phenylethylene*. This was prepared from the preceding compound by the method described above, and cyclization as also described above gave [6-^{3}H]benzo[*c*]phenanthrene.

[1- *and* 3-^{3}H]*Benzo*[c]*phenanthrenes*.—A mixture of these labelled compounds was prepared by the route used for the 2-, 4-, and 5-^{3}H-isomers, by employing [3-^{3}H]benzaldehyde (made from the appropriate toluene) as starting material. Cyclization causes the tritium label to end up in either the 1- or the 3-position.

[1-^{3}H]*Benzo*[c]*phenanthrene*.—The standard Grignard procedure employing 1-bromobenzo[*c*]phenanthrene (kindly donated by Professor M. S. Newman) gave after work-up [1-^{3}H]benzo[*c*]phenanthrene.

[3-^{3}H]*Benzo*[c]*phenanthrene*.— 1-(3-*Bromophenyl*)-2-(2-*naphthyl*)*ethylene*. 3-Bromobenzaldehyde (1·85 g, 0·01 mol) was treated with 2-naphthylmethyl(triphenyl)phosphonium bromide (4·85 g, 0·01 mol) as described above to yield the *ethylene* (1·29 g, 40%), m.p. 124° (Found: C, 69·65; H, 4·4. $C_{18}H_{13}Br$ requires C, 69·9; H, 4·25%).

3-*Bromobenzo*[c]*phenanthrene*. Cyclization of the above

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ethylene (0·5 g, 0·0016 mol) by the usual method gave, after column chromatography (elution with light petroleum) and recrystallization from hexane, 3-*bromobenzo*[c]*phenanthrene* (0·21 g, 42%), m.p. 129—130° (Found: C, 70·65; H, 3·9. $C_{18}H_{11}Br$ requires C, 70·35; H, 3·6%). Cross-metallation of this compound with n-butyl-lithium followed by hydrolysis with tritiated water and work up yielded [3-^{3}H]-benzo[*c*]phenanthrene.

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