Electrophilic Aromatic Reactivity. Part 24.[1] Protiodetritiation of Pentahelicene (Dibenzo[c,g]phenanthrene)

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All seven tritium-labelled dibenzo[c,g]phenanthrenes have been prepared and their rates of detritiation by anhydrous trifluoroacetic acid at 70 °C measured; these lead to the partial rate factors (positions in parentheses) : 3 500 (1), 2 405 (2), 930 (3), 6 560 (4), 18 400 (5), 6 930 (6), and 10 200 (7) and corresponding σ^+-values: -0.40, -0.385, -0.34, -0.435, -0.49, -0.44, and -0.46. The positional reactivity order in this, the first study of electrophilic substitution in pentahelicene, is: $5 > 7 > 6 > 4 > 1 > 2 > 3$ in good agreement with that predicted by localisation energies calculated by the Hückel method viz.: $5 > 4 > 6 > 7 > 1 > 2 > 3$. Each position is more reactive than the corresponding position in benzo[c]phenanthrene (tetrahelicene) by a factor of 2—3, a similar amount to that by which the positions in the latter exceeded the reactivities of the corresponding positions in phenanthrene. By contrast the localisation energies predict that the corresponding positions in all three molecules should be of closely similar reactivity. The data therefore indicate that loss of conjugation in penta- and tetrahelicene through non-planarity of the rings destabilises the ground state and produces enhanced reactivity. Position 7 in pentahelicene and position 6 in tetrahelicene show the most significant exaltation in reactivity. The reason for this is not yet clear, but the implication is that maximum distortion of the π-framework occurs at these, the central positions in each molecule.

The reactivity of the 1-position exceeds that of the 1-position in tetrahelicene, by an amount which is similar to the differences between the reactivities of the other pairs of corresponding positions. This indicates that exchange at the 1-position is unaffected by steric hindrance and this is consistent with X-ray studies which show that the hydrogens on the terminal rings are the same distance apart as the corresponding hydrogens in tetrahelicene; in the latter, exchange at the 1-position is virtually unhindered.

Two series of aromatic hydrocarbons provide unique series in which the effect of annelation can be investigated. Starting with naphthalene, regular annelation of the b bond leads in turn to anthracene, benzo[a]anthracene, etc., whilst annelation at the a bond leads in turn to phenanthrene, benzo[c]phenanthrene, dibenzo[c,g]phenanthrene, etc. This latter series, termed helicenes (phenanthrene may be regarded as the first member, trihelicene) is of particular interest because the annelation produces severe distortion of the aromatic ring, and the effect of distortion on aromatic reactivity has not been rigorously investigated. In addition, interactions at the terminal rings (which cause the distortion) may affect the reactivity through steric hindrance, or (with the higher homologues—which might be appropriately termed 'annelogues') through transannular stabilisation. The advantages of hydrogen exchange over all other electrophilic aromatic substitutions are now well known, and the reactivity towards exchange of phenanthrene,[2] and benzo[c]phenanthrene[3] have been reported. For the latter we found that the reactivity of each of the 1—4-positions was greater than that of the corresponding position in phenanthrene by a closely similar factor of ca. 2.5.[3] The lowest factor (1.95) was obtained for the 1-position and since this was only slightly less than the average we reasoned that exchange at the 1-position was not affected to any great extent by steric hindrance, and thus is reasonable since distortion in the molecule places the 1- and 12-carbon atoms 3 Å apart.

For dibenzo[c]phenanthrene no studies of its reactivity in electrophilic substitution have been reported, which is perhaps not too surprising because with seven positions for substitution, analysis of the product data would be formidable. With molecules of this size, even the advantages of hydrogen exchange become tempered somewhat by the synthetic difficulties attendant upon specifically labelling each position in the molecule. However we have devised routes to the preparation of each isomer and now report their rates of acid-catalysed detritiation.

RESULTS AND DISCUSSION

Rate coefficients $(10^7 \ k/s^{-1})$ for detritiation in anhydrous trifluoroacetic acid at 70 °C are as follows (positions in parentheses): 332(1), 228(2), 88.5(3),
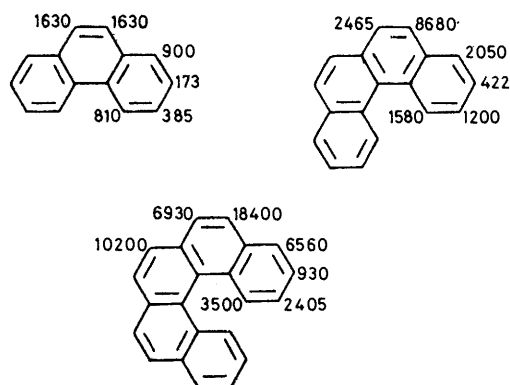
SCHEME 1

623(4), 1 750(5), 658(6), and 970(7). The rate coefficients for the 1- and 3-positions were obtained from measurements on the doubly labelled compound, the reactivity of the 1-position being confirmed by measurements on the isomer specifically labelled at the 1-position. From the rate coefficient for exchange of benzene under the same conditions (0.095),[4] the partial rate factors given in Scheme 1 may be derived. In Scheme 1 also

are shown the partial rate factors for detritiation of phenanthrene,[2] and benzo[c]phenanthrene.[3]

The main features of these results are as follows. (i) All positions are more reactive than the corresponding positions in benzo[c]phenanthrene by factors of 2.00—3.20 (average 2.41) and thus identical to the increment in reactivity of the positions in benzo[c]phenanthrene over those in phenanthrene, i.e. 1.95—3.12, average 2.49.* The increment in reactivity for the 1-position (2.20) is not abnormally small indicating that exchange at this position is unhindered. X-Ray studies [5] (which though they relate to the solid are probably relevant to the structure in solution) indicate that the distance between C-1 and C-18 is 3.0 Å and thus the same as in tetrahelicene, i.e. the rings pucker more in order to maintain this minimum distance. However there is a difference between the molecules in that substitution at the 1-position of pentahelicene involves interaction in the transition state between one of the hydrogens at the tetrahedral 1-carbon atom, and the hydrogen on C-18, but the corresponding interaction in tetrahelicene is indicated by models to be trivial. Thus we would expect greater hindrance for 1-exchange in pentahelicene, but none is evident.

(ii) The positional reactivity order is $5 > 7 > 6 > 4 > 1 > 2 > 3$ which is in good agreement with the order predicted from localisation energies (Table 1) calculated by the Hückel method viz.: $5 > 4 > 6 > 7 > 1 > 2 > 3$. Although the order for the 4-, 6-, and 7-positions appears to be incorrect, only the value for the 7-position is significantly anomalous, because the partial rate factors and the localization energies for the 4- and 6-positions are very similar. Interestingly, it is the position nearest to the centre of the molecule, the 7-position, which has too high a reactivity and the same was noted with tetrahelicene where the reactivity of the 6-position was too high. Whether this has any fundamental significance cannot be stated at this time, though we note that the C(7)–C(8) bond distance [or C(9)–C(10) bond distance if bridgehead carbons are numbered] is the longest in pentahelicene.[5] This may lead to extra localisation of electrons at these carbons with consequent higher reactivity.

The good agreement between observed and calculated reactivity orders show that the order is not appreciably affected by the severe deformation of pentahelicene (which is such that the angles between the planes of the terminal rings is ca. 45°). This is because the deformation is more or less uniformly spread amongst all of the carbon atoms.

(iii) The uniform spread of the deformation results in a (calculated) loss of resonance energy of 18 kcal mol⁻¹.[6] This leads however to the expectation that pentahelicene will be relatively more reactive than tetrahelicene than calculations predict. This is observed and, for example,

the calculations in Table 1 show that the 1- and 3-positions in pentahelicene ought to be less reactive than the corresponding positions in tetrahelicene, whereas they are 2—3 times more reactive. The same discrepancy is evident in the corresponding data for phenanthrene and tetrahelicene [3] and likewise points to increased reactivity arising from deformation of the aromatic rings. This can be demonstrated also by comparing the average localisation energy per position within the molecules, with the average partial rate factors (Table 2). This Table (which incidentally shows

TABLE 1

Hückel localisation energies $L_r^+/\text{-}\beta$

Position	Pentahelicene	Tetrahelicene
1	2.3973	2.3318
2	2.4538	2.4605
3	2.4834	2.4767
4	2.3107	2.3118
5	2.2830	2.2972
6	2.3144	2.3204
7	2.3198	(2.3204)

TABLE 2

Average localisation energy vs. average partial rate factor (per position)

Molecule	No. of positions, n	$(\Sigma L_r^+/ -\beta)/n$	$\Sigma f_x/n$
Naphthalene	8	2.390	660
Phenanthrene	10	2.387	780
Tetrahelicene	12	2.366	2 700
Pentahelicene	14	2.366	7 000

that the average localization energy remains virtually constant) predicts that there should be only a very slight increase in average positional reactivity whereas there is clearly a marked increase on going from phenanthrene to tetrahelicene and from tetrahelicene to pentahelicene; these increments we may attribute to the loss of resonance energy as a result of deformation. Previously we concluded that puckering of the rings in tetrahelicene did not produce any effect on reactivity since the observed and predicted positional reactivity orders were the same. However this view needs modification, for if we can assume that the calculations are meaningful, then the reactivity per position is increased 2—3-fold in tetrahelicene, and 6—9-fold in pentahelicene as a result of the ring distortion.

(iv) σ^+-Values may be derived as follows (positions in parentheses): $-0.40(1)$, $-0.385(2)$, $-0.34(3)$, $-0.435(4)$, $-0.49(5)$, $-0.44(6)$, and $-0.46(7)$. Since the reactivities of all the positions are rather similar it follows that in reactions of low selectivity, substitution will produce fairly equal amounts of all isomers. Since other electrophilic substitutions will be more hindered than hydrogen exchange we can expect that there will be relatively more of the 2- and 3-isomers and substantially less of the 1-isomer than the σ^+-values predict.

(v) The activating effect of a 2,3-benzo-substituent is consistently greater than that of a 3,4-benzo-substituent, though the magnitude of the effect varies from one

* The 7-position of pentahelicene may be considered to be derived from either the 5- or the 6-position of tetrahelicene (depending upon the direction of annelation). The average partial rate factor for these latter is 5 070, so the average rate enhancement on going to the 7-position of pentahelicene is just under 2.0.

system to another. The relevant data are given in Table 3. The large difference in the effect between benzene and naphthalene and the other pairs of positions derives of course from the fact that substitution in benzene involves total loss of resonance energy on going to the transition state, whereas this is not the case for naphthalene. For the other pairs of compounds the loss of resonance energy will be comparable; throughout all the pairs of compounds the *difference* in the benzo-

rate coefficient was confirmed by kinetic studies on the pentahelicene specifically labelled at the 1-position.

The general routes for preparation of the labelled compounds are shown in Schemes 2—6, and involved specific labelling of a precursor, followed by photocyclisation.

[1-³H]*Dibenzo*[c,g]*phenanthrene*.—This was prepared by the route shown in Scheme 2. *p*-Bromotoluene was converted *via* *p*-allyltoluene, 1,1,1,3-tetrachloro-4-(*p*-tolyl)-butane, and 1-chloro-7-methylnaphthalene into 7-methyl-[1-³H]naphthalene according to the literature method.[9]

TABLE 3

Activating effects of the benzo-substituent

Initial molecule	Position	Annelated molecule	Position	Benzo substituent effect	
				2 : 3-	3 : 4-
Benzene	1	Naphthalene	2		151
	1		1	1 165	
Naphthalene	1	Phenanthrene	9		1.4
	2		10	11	
Phenanthrene	1	Tetrahelicene	6		2.74
	2		5	50	
Tetrahelicene	4	Pentahelicene	6		3.4
	3		5	44	

substituent effects is, in fact, fairly constant, ranging from 8- to 18-fold.

EXPERIMENTAL

The general method for carrying out the kinetic studies has been described previously [7] and was modified [8] in order to take account of the very low solubility of pentahelicene; approximately 2 mg of this was used in each kinetic run in which *ca.* 15 ml of trifluoroacetic acid was used. Each compound gave good first-order kinetics linear to beyond 95% of reaction, except the 1,3-ditritiated compound. This showed the presence of a radioactive impurity, unreactive towards exchange. Subtraction of the activity of this from each sample gave a curve of log activity *vs.* time, and this analysed into two excellent first-order plots of rate co-efficients 332×10^{-7} and 88.5×10^{-7} s^{-1}, attributed to exchange at the 1- and 3-positions respectively; the former
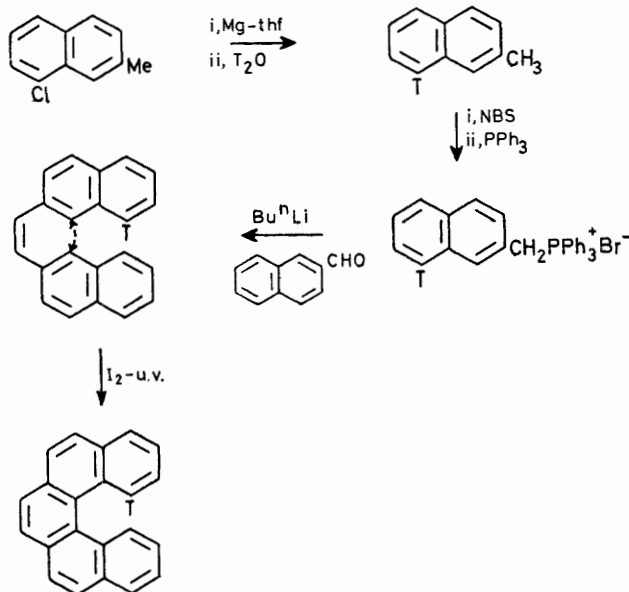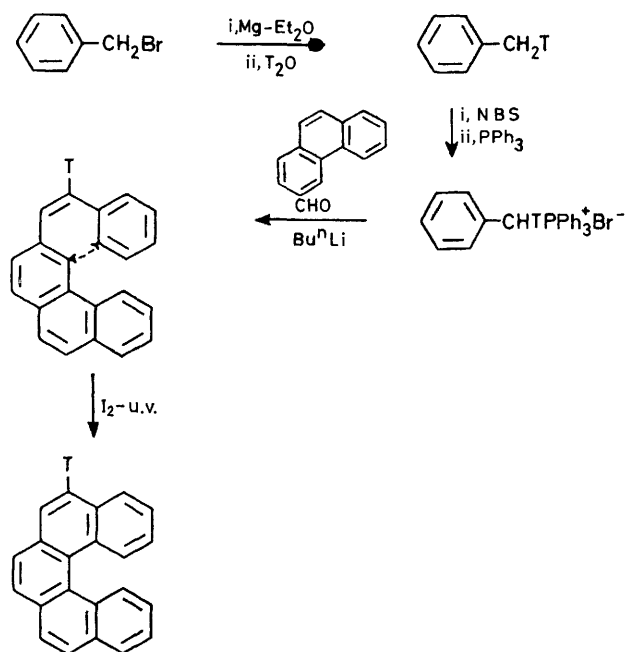
SCHEME 2

7-[1-³H]*Naphthylmethyl(triphenyl)phosphonium Bromide*.—7-Bromomethyl[1-³H]naphthalene, m.p. 54 °C, was prepared in 95% yield by bromination of 7-methyl[1-³H]-naphthalene with *N*-bromosuccinimide (NBS).[10] Reaction
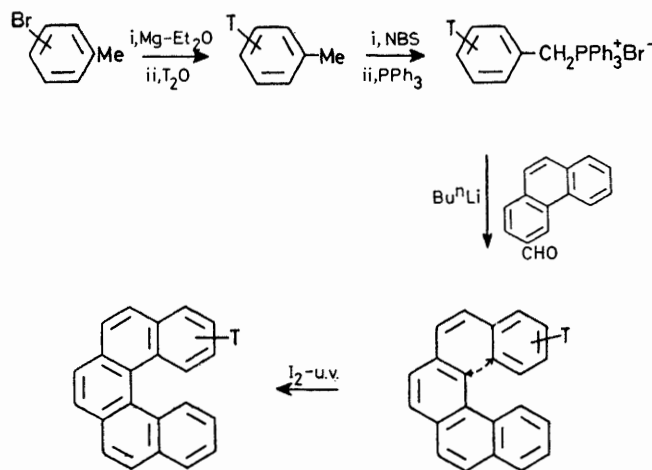
SCHEME 3

of this compound (55.5 g, 0.25 mol) with triphenylphosphine (65.5 g, 0.25 mol) in boiling xylene during 3 h gave after filtration and vacuum drying, a quantitative yield of 7-[1-³H]naphthylmethyl(triphenyl)phosphonium bromide.

1-(7-[1-³H]*Naphthyl)ethylene*.—The above phosphonium salt was converted into the corresponding ylide, using n-butyl-lithium as a base.[3] The ylide was treated with naphthalene-2-carbaldehyde to give 1-(7-[1-³H]naphthyl)-2-(2-naphthyl)ethylene. This was produced as a *cis*- and *trans*-mixture, the latter being almost insoluble in ether and therefore removed by filtration. It was washed several times with a 3 : 1 (by volume) mixture of methanol and water, air dried, sublimed and recrystallized from benzene–ethanol, to give the pure *trans*-alkene, m.p. 257—258 °C (lit.,[11] 257—258 °C). The ethereal solution (which contained mainly *cis*-alkene) was evaporated to dryness and then sublimed and recrystallized a number of times from benzene–ethanol to give the pure *cis*-alkene, m.p. 180 °C.

SCHEME 4

The total yield of alkenes was 50% with a *cis* : *trans* ratio of 3 : 2.

Attempts to cyclize the *cis*-alkene using a medium-pressure 125 W u.v. lamp gave mainly dibenzo[*g,h,i*]-perylene, whilst irradiation by a 125 W high-pressure lamp (glass envelope) gave only a trace of the desired penta-
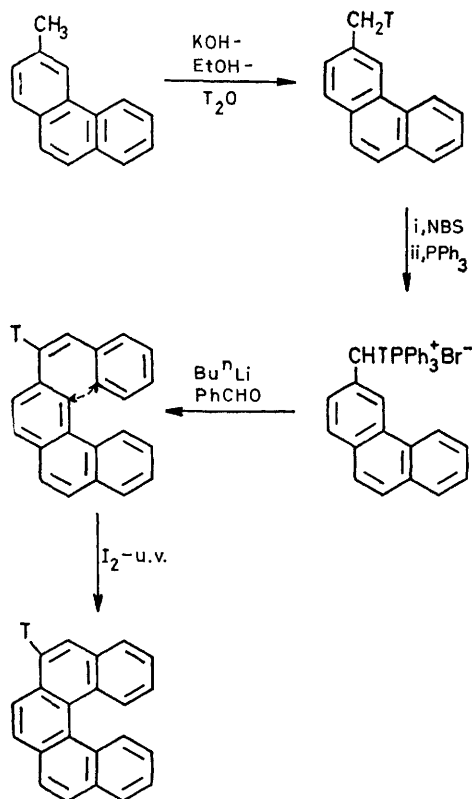
SCHEME 5

helicene together with another unidentified product. However, irradiation of the *trans*-alkene (in benzene with a trace of iodine as catalyst) gave a 50% yield of [1-³H]dibenzo-[*c,g*]phenanthrene, m.p. 182 °C (lit.,[12] 178 °C) after column chromatography on neutral alumina (activity grade III) using light petroleum (b.p. 60—80 °C) as eluant, followed by recrystallisation from ethanol.

[2-³H, 4-³H-, and 1,3-³H₂]*Dibenzo*[*c,g*]*phenanthrene.*— These were prepared according to the route shown in Scheme 3. Phenanthrene-3-carbaldehyde was prepared from phenanthrene *via* 3-acetylphenanthrene, phenanthrene-3-carboxylic acid, and phenanthrene-3-carbonyl chloride;[13] the product had m.p. 80 °C (lit.,[13] m.p. 78—80 °C). 2-, 3-, and 4-bromotoluenes were converted into the corresponding [2-, 3-, or 4-³H]toluenes *via* hydrolysis of the Grignard reagents with tritiated water, and these were converted into the corresponding benzyl bromides *via* bromination with NBS. Each benzyl bromide was converted by reaction with triphenylphosphine as above, into the corresponding [2-, 3-, or 4-³H]benzyltriphenyl phosphonium bromide, m.p. 300 °C. Each was converted into the ylide
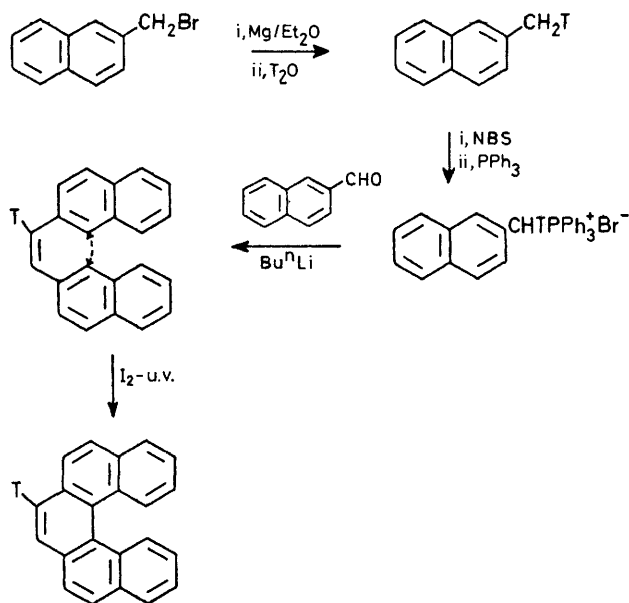
SCHEME 6

as above and treated with phenanthrene-3-carbaldehyde to give a *cis*- and *trans*-mixture of 1-([2-, 3-, *or* 4-³H]*phenyl*)-2-(*3-phenanthryl*)*ethylene*. This was resolved into the pure *cis*- (m.p. 115 °C) and *trans*- (m.p. 154, lit.,[14] 154 °C) components (*ca.* 40 : 60 ratio) as above, the overall yield being 40%. Cyclization was carried out on a mixture of the alkenes dissolved in benzene with iodine as catalyst, using a 125 W medium-pressure u.v. lamp, followed by work-up as above to give [2-³H-, 4-³H-, and 1,3-³H₂]dibenzo[*c,g*]-phenanthrenes, m.p. 182 °C in each case.

[5-³H]*Dibenzo*[*c,g*]*phenanthrene.*—This was prepared by the route shown in Scheme 4. Benzyl bromide was converted *via* hydrolysis of the Grignard reagent with tritiated water into [α-³H]toluene. This was rebrominated in the side chain using NBS, and the [α-³H]benzyl bromide converted as for the [2-, 3-, and 4-³H] isomers (above) *via* 1-[³H]-1-phenyl-2-(3-phenanthryl)ethylene into [5-³H]di-benzo[*c,g*]phenanthrene, m.p. 182 °C

[6-³H]*Dibenzo*[c,g]*phenanthrene*.—This was prepared according to Scheme 5

3-*Methylphenanthrene*.—The reaction between the ylide prepared from benzyltriphenylphosphonium bromide in the presence of n-butyl-lithium was treated with *p*-tolualdehyde, to give, after work-up and several recrystallisations from light petroleum (b.p. 60—80 °C), a 59% yield of a mixture of *cis*- and *trans*-4-methylstilbene, m.p. 117 °C (lit.,[15] 117 °C). Cyclization of this as above gave a 50% yield of 3-methylphenanthrene, m.p. 62 °C (lit.,[15] 62 °C), after several recrystallizations from methanol.

3-*Methyl*[α-³H]*phenanthrene*.—A mixture of 3-methylphenanthrene (1.95, 0.01 mol), potassium hydroxide (4 g), ethanol (20 ml), and 0.01 ml of tritiated water (500 mCi ml⁻¹ activity) was heated under reflux during 24 h. Extraction and work-up gave an almost quantitative recovery of [α-³H]-3-methylphenanthrene. [α-³H]-3-Methylphenanthrene was brominated in the side chain by using NBS to give 3-bromomethyl[α-³H]phenanthrene, m.p. 114 °C (lit.,[16] 114 °C) after recrystallisation from light petroleum (b.p. 60—80 °C). This was converted into 3-bromomethyl-[α-³H]phenanthrenetriphenylphosphonium bromide (m.p. 273—276 °C), the ylide of which was treated with benzaldehyde to give after work-up as above, 1-*phenyl*-2-(3-*phenanthryl*)*ethylene* as a *cis,trans*-mixture, m.p. 135 °C. Cyclization as above gave [6-³H]*dibenzo*[c,g]*phenanthrene*, m.p. 182 °C.

[7-³H]*Dibenzo*[c,g]*phenanthrene*.—Bromination of 2-methylnaphthalene with NBS gave 2-bromomethylnaphthalene, m.p. 54 °C (lit.,[10] 54 °C) which was converted *via* hydrolysis of the Grignard reagent with tritiated water into 2-methyl[α-³H]naphthalene. Reaction with triphenylphosphine gave the phosphonium salt, m.p. 250 °C (lit.,[11] 248—250 °C). The Wittig reaction was carried out as above using this salt and naphthalene-2-carbaldehyde to give a *cis*- and *trans*-mixture of 1-(2-*naphthyl*)-2-(2-[2-³H]*naphthyl*)-*ethylene* which was separated into the two isomers, the *trans*-compound being cyclized only, as described above.

This yielded a 50% yield (based on the alkene) of [7-³H]-*dibenzo*[c,g]*phenanthrene*, m.p. 182 °C.

The nature of each alkene intermediate and of the dibenzo[*c,g*]phenanthrene products were confirmed by mass spectrometry and C and H analyses which were satisfactory in each case. The cyclizations to give the [2-, 4-, 5-, 6-³H, and 1,3-³H₂]dibenzo[*c,g*]phenanthrenes were accompanied by the formation of the correspondingly labelled dibenzo[*a,h*]anthracenes which were separated from the corresponding dibenzo[*c,g*]phenanthrenes prior to chromatography of the latter, the anthracenes being insoluble in light petroleum. It is hoped to report on the rates of exchange of some of these isomers along with data for related compounds in a future publication.

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