Electrophilic Aromatic Substitution. Part 36.[1] Protiodetritiation of Some Annelated *meta*-Cyclophanes: Effect of Ring-buckling on Reactivity, and the First Example of Electrophilic Substitution through a Hole

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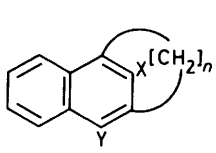
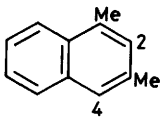
A series of 1,3-bridged naphthalenes in which the alkyl bridge contains ten, eight, or seven methylene groups have been prepared with tritium located at either the 2- or the 4-position. Their rates of detritiation in anhydrous trifluoroacetic acid at 70 °C have been measured. The partial rate factors for exchange at the 4-position increase as the size of the bridge decreases *viz.* 1.28×10^7 ($[CH_2]_{10}$) 2.71×10^7 ($[CH_2]_8$), 2.97×10^7 ($[CH_2]_7$); *cf.* 1.15×10^7 for 1,3-dimethylnaphthalene, the corresponding σ^+ values being −0.812, −0.849, −0.854, and −0.807. This is consistent with increased loss of ground-state aromaticity as the aromatic ring becomes more buckled. At the 2-positions the partial rate factors are 2.37×10^5 ($[CH_2]_{10}$), 2.92×10^5 ($[CH_2]_8$), and 1.50×10^5 ($[CH_2]_7$); *cf.* 2.82×10^5 for 1,3-dimethylnaphthalene, the corresponding σ^+ values being −0.614, −0.625, −0.592, and −0.623. The results here reflect the opposing effects of increased reactivity due to loss of ground-state aromaticity, and steric hindrance to exchange as the bridge is made smaller. Because of the symmetry of the reaction pathway for hydrogen exchange, reaction at the 2-positions involves attack of the electrophile at one face of the loop formed between the alkyl chain and the aromatic ring, and departure of the leaving group (triton) from the opposite face, *i.e.* substitution occurs through a 'hole'. This is the first example of electrophilic substitution at an enclosed site. The fact that steric effects in both reagent and product in hydrogen exchange are almost identical is postulated as a primary reason for the extremely low steric hindrance generally observed in the reaction. The effect of fusing a bicyclic substituent onto an aromatic ring has been determined for the first time. For hexahydrophenanthrylene and hexahydroaceanthrylene (naphthalenes with bicyclic substituents attached to the 1-, 2-, and 3-positions) the average partial rate factor for detritiation of the '4'-positions is 5.7×10^7, and σ^+ is −0.886. This is greater than calculated on the basis of additivity of the alkyl group substituent effects and is attributed to steric facilitation of hyperconjugation. The recent suggestion (based on structure counts) that the exalted reactivities of helicenes (and by implication of other aromatic systems containing bent benzene rings) is not due to loss of ground-state stability is shown to be invalid.

Despite the century and more of detailed studies of electrophilic aromatic substitution, there has not been, as far as we are aware, any observation or study of electrophilic substitution at a totally surrounded site. We were interested to see if such a reaction could be achieved, and what would be the effect of such an enclosure upon the reaction rate. Because hydrogen exchange is the least hindered of all electrophilic substitutions (and indeed is unhindered at all but a very few extremely crowded sites) it is a reaction most suitable for such an investigation. An additional advantage of detritiation over many other electrophilic substitutions, and one particularly valuable here, is the specificity of the reaction site achieved through labelling.

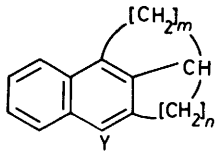
For synthetic convenience we chose the cyclophanes (**1**), since the preparation of the parent hydrocarbons had already been described.[2] In these the site X, comparable to the 2-position of 1,3-dimethylnaphthalene (**2**), is enclosed by the alkyl chain and is therefore effectively activated by two *ortho*-alkyl groups. Site Y, analogous to the 4-position of 1,3-dimethylnaphthalene, is unenclosed and is activated by an *ortho*- and a *para*-alkyl group. The electronic effects of the alkyl chain at the two sites will therefore be fairly similar, though somewhat lower at position X because of the effect the low 2,3-bond order in naphthalene has on substituent effects.[3] In (**1**), the aromatic ring containing the alkyl chain becomes increasingly non-planar as the chain is made smaller.[2] Previously one of us showed that the reactivity of aromatic systems increases with twisting from planarity.[4,5]



(**1**) n = 10, 8, or 7; X or Y = T



(**2**)



(**3**) **a**; m = 3, n = 2
b; m = 2, n = 3

Thus any steric effect observable from exchange at X could be complicated by reactivity changes arising from the non-planarity effects. Our strategy was therefore also to measure the exchange rates at position Y in order to obtain a measure of the effects of non-planarity. Comparison of the exchange rates at X with those at Y should then reveal information regarding possible steric effects at X.

We had hoped to prepare also specifically labelled [6]-(1,3)naphthalenophanes (**1**; n = 6). We did not pursue our unsuccessful initial attempts (using the chloro precursor) because kinetic studies with the higher homologues indicated that acid-catalysed ring opening or rearrangement would probably occur at such a rate as to render inaccurate any exchange data that were subsequently obtained. We did, however, and as a result of a new reaction (see Discussion section), succeed in preparing the isomeric hexahydrophenanthrylene (**3a**) and hexahydroaceanthrylene (**3b**), and rate data

Table 1. Rate data for detritiation of cyclophanes (**1**) and (**2**) under standard conditions (trifluoroacetic acid at 70 °C)

Compound	Position	$10^7\ k/s^{-1}$	Medium[a]	$10^7\ k/s^{-1}$ (corr.)[b]	f	σ^+
(**1**; n = 10)	X	66	A	2.25×10^4	2.37×10^5	−0.614
	Y	3 565	A	1.22×10^6	1.28×10^7	−0.812
(**1**; n = 8)	X	16 800	C	2.77×10^4	2.92×10^5	−0.625
	Y	7 530	A	2.57×10^6	2.71×10^7	−0.849
(**1**; n = 7)	X	8 650	C	1.43×10^4	1.50×10^5	−0.592
	Y	8 280	A	2.82×10^5	2.97×10^7	−0.854
Hexahydrophenanthrylene + hexahydroanthanthrylene (**3a** and **b**)	Y	14 900	B	5.42×10^6	5.7×10^7	−0.886

[a] A and B, 50:50 vol. % TFA in HOAc. Rate reduction relative to TFA determined as 341-fold (batch A) or 364-fold (batch B); C, 91:9 vol. % TFA in $CHCl_3$. Rate reduction relative to TFA determined as 1.65-fold. [b] Rate coefficients under standard conditions.

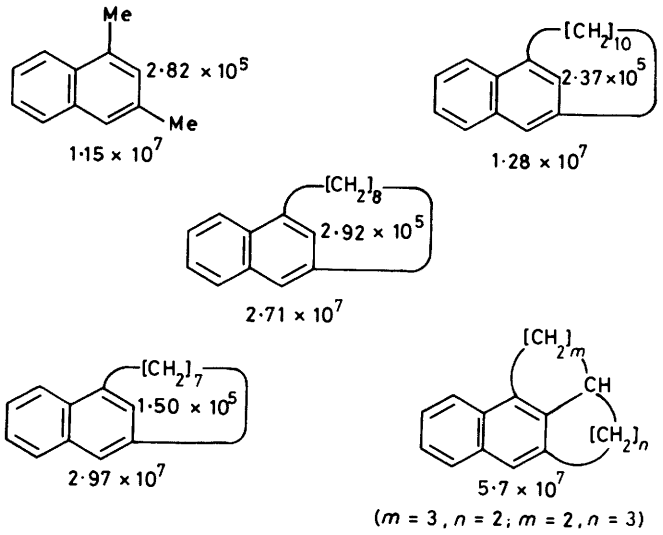
for exchange at the positions Y of these planar molecules were obtained.

Results and Discussion

Tritium was incorporated into the enclosed positions of the cyclophanes (**1**) by preparing the bromo precursors and then replacing bromine by tritium through the use of n-butyl-lithium and tritiated water. Tritium was incorporated into positions Y by direct acid-catalysed exchange, these positions being much more reactive than any others. Rate coefficients for detritiation under standard conditions [anhydrous trifluoroacetic acid (TFA) at 70 °C] are given in Table 1 along with the partial rate factors (relative to a position in benzene for which $10^7\ k/s^{-1}$ = 0.095)[6] and derived σ^+ values. The partial rate factors are shown in Scheme 1 together with those determined previously for 1,3-dimethylnaphthalene.[1] The main features of these results are as follows.

(i) *Effect of Cyclophane Distortion on Reactivity.*—For the cyclophanes with tritium at the position equivalent to the 4-position in 1,3-dimethylnaphthalene, the partial rate factors are all greater than that for the latter, and increase regularly as the ring is made smaller. This is consistent with the loss of ground-state aromaticity due to buckling of the aromatic ring containing the alkyl chain, as the chain is made smaller. Increases in exchange rate due to bending of aromatic rings has previously been noted in detritiation of helicenes and polymethylphenanthrenes.[4,5] The effect obtained was fairly small (2—3 fold), and comparable results are obtained here. The [6]naphthalenophane (**1**; n = 6) is much more severely distorted,[2] and the resultant loss of aromaticity is such that addition reactions, *e.g.* with bromine or potassium permanganate, occur readily.[2] Addition does not take place in the higher homologues.[2] (The suggestion that the exalted reactivity of bent aromatic systems is not due to loss of ground-state stability, but rather is predicted by calculations,[7] does not stand up to rigorous inspection; see later).

(ii) *Steric Hindrance at the Enclosed Sites.*—For the cyclophanes with tritium at the sites analogous to the 2-position in 1,3-dimethylnaphthalene, a different pattern emerges. For the [10]naphthalenophane the reactivity at position X is very slightly less than in the 2-position of 1,3-dimethylnaphthalene, indicating the possibility of a very small amount of steric hindrance. However, for the [8]naphthalenophane any hindrance appears to be outweighed by the increase in reactivity arising from loss of ground-state aromaticity, and the partial rate factor increases slightly. For the [7]naphthalenophane the effect of steric hindrance is now substantial and the reactivity of position X is reduced *ca.* 2-fold. The ratios of the

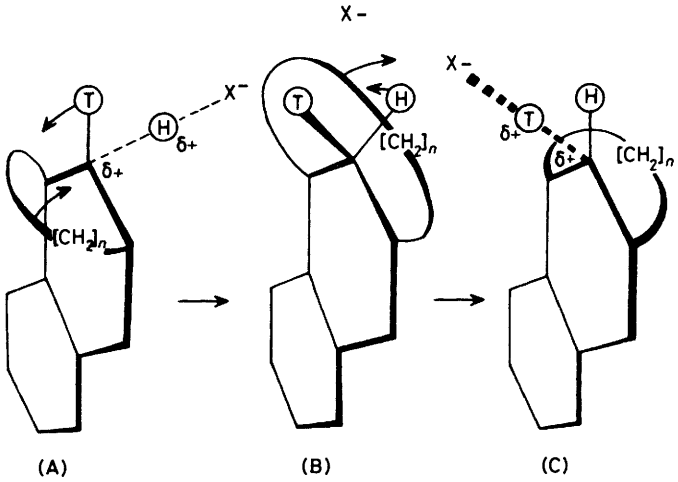


Scheme 1. Partial rate factors for detritiation in TFA at 70 °C

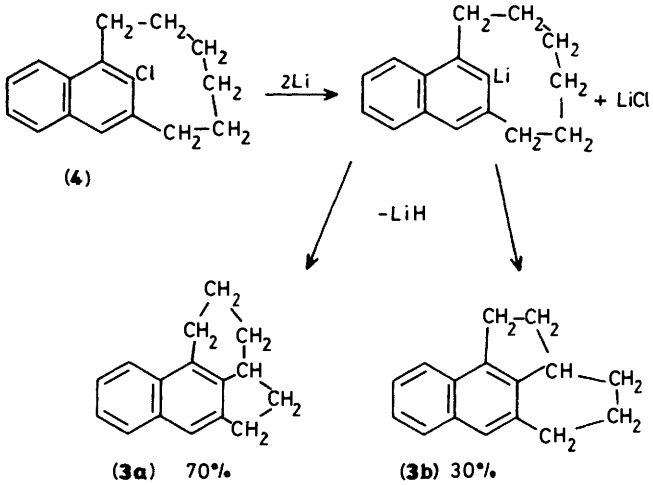
reactivities at the enclosed relative to those of the unenclosed sites (effectively *ortho* : *para* ratios) are shown in Table 2. Differences in electronic effects are here cancelled out and the steric effects show up very clearly.

(iii) *Mechanism of Substitution at the Enclosed Site.*—Because electrophilic substitution proceeds *via* an sp^3-hybridised Wheland intermediate, the entering group must approach the plane of the aromatic ring on the side opposite to that from which the leaving group departs. This is shown in detail in Scheme 2. In the ground state the alkyl chain will oscillate on either side of the enclosed tritium. It is logical to assume that from a given side of the molecule the attacking proton may closely approach the reaction site only when the alkyl chain is displaced on the opposite side [as in (A) in Scheme 2]. The Wheland intermediate, which must be symmetrical (B), is then achieved, and loss of tritium follows (C). This substitution effectively involves passage through a completely surrounded site, *i.e.* a 'hole', as shown in Scheme 2.

(iv) *Origin of the Low Steric Hindrance to Hydrogen Exchange.*—The present results constitute the third example only of steric hindrance to hydrogen exchange, the others being exchange at the 2-positions of 1,3,5-triphenylbenzene[8] and tetraphenylmethane.[9] These sites are so hindered that substitution of them by most other electrophiles is negligible, yet by contrast hindrance to hydrogen exchange at these positions is



Scheme 2. Passage of the electrophile and leaving group through the alkyl side chain



Scheme 3. Reaction of 16-chloro[6](1,3)naphthalenophane with lithium

Table 2. Relative rates of hydrogen exchange at sites X and Y

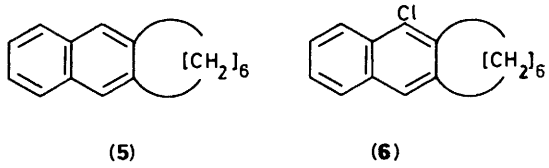
Compound	$10f_X/f_Y$
1,3-Dimethylnaphthalene	0.245
(**1**; n = 10)	0.185
(**1**; n = 8)	0.108
(**1**; n = 7)	0.051

relatively trivial. Models indicate that access to the enclosed sites of the cyclophanes, especially that of [7]naphthalenophane, is severely restricted, yet the data show only a *ca.* 2-fold rate reduction.

It would be reasonable to assume that the low hindrance to hydrogen exchange is a direct consequence only of the small size of the proton electrophile. However, since the proton must be quite closely associated with the counterion and also solvated, its effective size may be appreciable. The overall steric effect in an electrophilic substitution is a balance between steric hindrance to the incoming electrophile, and steric acceleration arising from the size of the leaving group. Usually only one of these effects is present, but when both operate, as for example in bromodesilylation, they do in fact cancel each other out.[10] This cancellation will be almost exact in hydrogen exchange because of the near identity of reagent and product; this should be reflected by trivial changes. We suggest that this is a major if not the primary reason for the apparent virtual absence of observed hindrance to hydrogen exchange.

(v) *Reactivity of Hexahydrophenanthrylene* (**3a**) *and Hexahydroaceanthrylene* (**3b**).—We attempted to prepare [16-^{3}H]-[6](1,3)naphthalenophane* by reaction of the 16-chloro precursor (**4**) with lithium metal followed by tritiated water. Instead of the desired product we obtained at 70:30 mixture of hexahydrophenanthrylene (**3a**) and hexahydroaceanthrylene (**3b**), evidently as a result of elimination of lithium hydride from the lithiated intermediate. Alternatively the side chain could become lithiated at the mid-positions, the carbanion then carrying out nucleophilic aromatic substitution, though here the first step seems much less probable.

This new reaction gives exactly the same proportions of (**3a**) and (**3b**) which Parham *et al.* obtained from the photochemical



elimination of hydrogen chloride from (**4**),[2] so the proportions would seem to reflect the relative stabilities.

Tritium was incorporated into positions Y of (**3a**) and (**3b**) *via* direct exchange, this site being much more reactive than any other. The rate coefficient for detritiation of the isomer mixture was 5.2×10^{-7} s^{-1}, giving $f = 5.5 \times 10^7$. The reaction showed excellent first-order kinetic behaviour, indicating that, as expected, the exchange rates for the two compounds were not significantly different. The partial rate factor is 4.8-times that of the 4-position of 1,3-dimethylnaphthalene, *i.e.* approximately double the factor by which a 3-methyl group activates the 1-position of naphthalene.[3] This enhanced reactivity over that predicted is not unexpected despite both (**3a**) and (**3b**) having flat aromatic rings. The C–H bonds of both methylene groups adjacent to the naphthalene ring, as well as that at the bridgehead carbon atom, are constrained almost or entirely parallel to the *p*-orbitals of the ring. In addition, strain in the five-membered side chain will facilitate C–C hyperconjugation. The enhanced reactivity is thus due to a combination of steric facilitation of C–H and C–C hyperconjugation, factors which have been shown previously to account for the high reactivity of acenaphthene as compared with 1,8-dimethylnaphthalene,[11] for the relative activation order of cycloalkyl substituents,[12] and for the greater activation by the bicyclo[2.2.2]octyl substituent than by the adamantyl substituent.[13]

Further attempts were made to prepare the [6]naphthalenophane. Reaction of (**4**) with n-butyl-lithium gave a trace of what appeared to be the 16-butyl derivative, but there was insufficient material for a full characterisation. Attempts to form the Grignard reagent also failed, rearrangement to the [6](1,2)-naphthalenophane (**5**) with loss of halogen occurring instead. The ease of this rearrangement suggested that a comparable reaction of the parent hydrocarbon would be rapid under the conditions required for the kinetic studies, and indeed Parham *et al.* found that (**4**) rearranged to (**6**) on treatment with toluene-*p*-sulphonic acid in trifluoroacetic acid.[2] Since kinetic studies with the higher homologues also showed evidence of a small amount of either ring opening or rearrangment, further attempts to prepare the labelled [6](1,3)naphthalenophane were abandoned.

* Note that throughout this paper different nomenclature and numbering are used from that given in ref. 2.

Table 3. Correlation of partial rate factors for detritiation against localisation energies or structure count parameters

	Tetrahelicene			Chrysene		
Position[a]	*f*	L_r^+	ln s.c.	*f*	L_r^+	ln s.c.
1	1 580	2.332	1.012	696	2.349	0.965
2	1 200	2.461	0.916	307	2.448	0.965
3	422	2.477	0.916	186	2.492	0.865
4	2 050	2.312	1.012	975	2.302	1.056
Σ	5 252	9.582	3.855	2 164	9.591	3.851
	Hexahelicene			**Benzo[*a*]naphth[1,2-*h*]anthracene**		
Position[a]	*f*	L_r^+	ln s.c.	*f*	L_r^+	ln s.c.
1	10 250	2.338	1.066	3 810[b]	2.367	1.063
3	905	2.479	0.981	268[b]	2.487	1.007
4	8 770	2.311	1.083	1 190	2.313	1.081
5	25 000	2.288	1.218	11 100	2.259	1.229
Σ	44 925	9.416	4.348	16 368	9.426	4.380

[a] Numbering as in tetrahelicene; positions in chrysene are these corresponding. [b] Numbering of these positions was transposed in ref. 5.

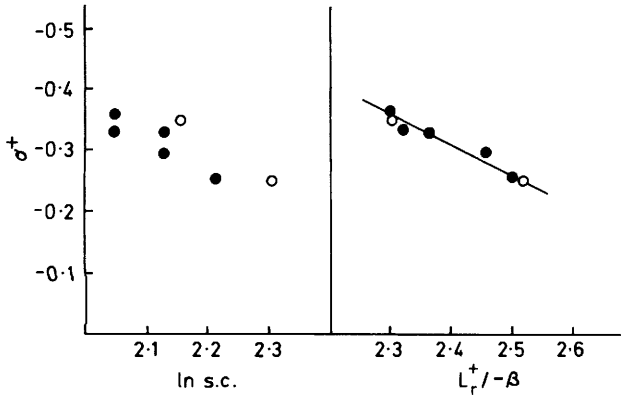
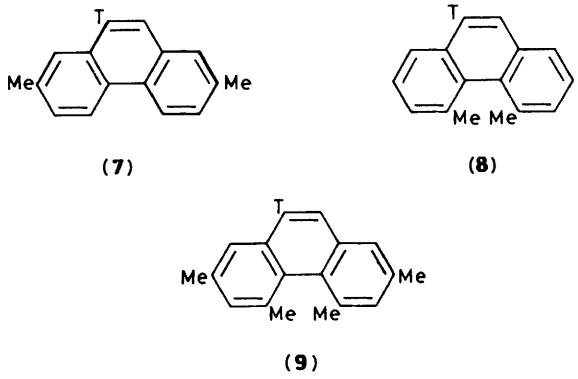


Figure. Correlation of positional reactivities for detritiation of naphthalene and phenanthrene with structure counts and with localisation energies: (●) positions in phenanthrene; (○) positions in naphthalene



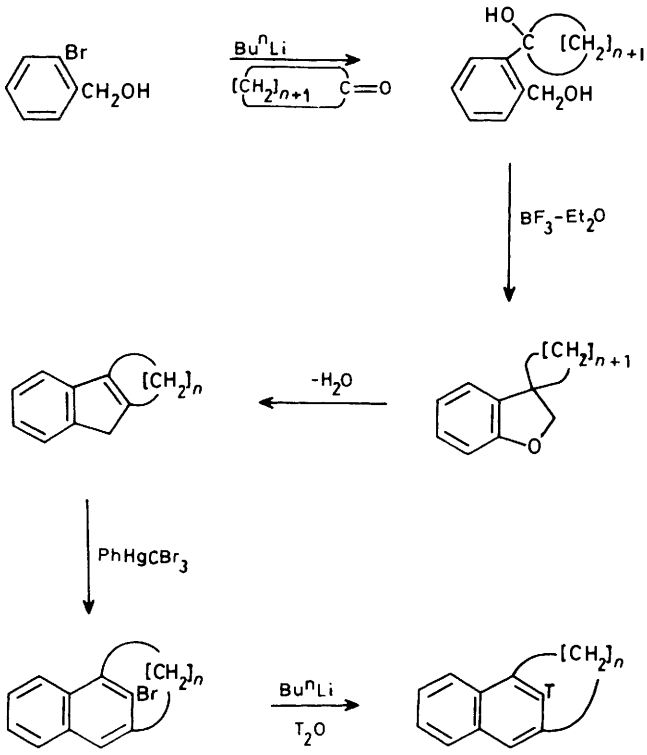
(vi) *The Invalidity of using Structure Counts to Correlate the Exalted Reactivities of Bent Aromatic Systems.*—It was suggested recently[7] that the exalted reactivities of helicenes, in which the benzene rings are bent out of plane, is not due to loss of ground-state aromaticity. This conclusion was based solely on the fact that the 'Structure Count' method *appears* to give a better correlation of the rate data[5] for detritiations of helicenes than do Hückel calculations. This conclusion is incorrect for the following reasons:

(*a*) The *apparently* higher quality of the structure count correlations is an illusion. It is inherent in the method that it predicts ever higher reactivities the greater the number of benzene rings in a molecule. Along the series of increasingly bent helicenes it therefore fortuitously predicts (in contrast to the Hückel method) the increasing reactivity which we believe arises from increasing loss of ground-state stability.

(*b*) Compelling evidence for our conclusion is provided in the Figure. This shows the reactivity data (σ^+ values) for naphthalene and phenanthrene, *both of which are planar*, plotted against both localisation energies and structure count parameters (ln s.c.). In these unambiguous examples (they are the first two members of the helicene series, but the only planar ones) the better correlation with the former parameters is self-evident. The structure count method fails here because it predicts that a given position in phenanthrene will be substantially more reactive than the corresponding position in naphthalene, which is incorrect. Were phenanthrene bent to the extent that it gave exalted reactivities, the structure count method would then *appear* to have correctly predicted the observed result. It may also be noted that localisation energies predict the correct reactivity of all five positions in phenanthrene whereas the structure count method predicts the correct order for only three of them.

(*c*) Our previous conclusions concerning the effect of ring bending upon reactivity were not based solely upon correlations of rate data with localisation energies, but used in addition comparisons of reactivity at like positions in planar and bent isomers; this appears to have been overlooked.[7] As an example, consider the partial rate factors for detritiation in the terminal rings of tetrahelicene (benzo[*c*]phenanthrene) and chrysene[14] (Table 3). The data are summed in the last row for ease of assimilation. Positions in the distorted helicene are on average 2.5-times as reactive as the corresponding positions in chrysene. By contrast both localisation energies *and* structure counts predict the same reactivity. Structure counts also predict, as do localisation energies. that the reactivities of the 1-, 3-, 4-, and 5-positions of hexahelicene and benzo[*a*]naphth[1,2-*h*]anthracene should be the same (Table 3). (These positions in benzo[*a*]naphth[1,2-*h*]anthracene are at the planar end of the molecule.) Yet the sum of the partial rate factors for the bent molecule is 2.75-times greater than that of the planar one.

(*d*) Unambiguous evidence that bending of aromatic rings produces exalted reactivity was provided by detritiation of dimethylphenanthrenes (**7**) and (**8**).[15] The former is planar; the



Scheme 4. Preparation of tritiated metacyclophanes

latter is bent. The reactivity of the latter, based upon the additive effects of the methyl substituents [which is *exact* for planar (**7**)] was 3.37-times greater than predicted. A similarly exalted rate was obtained for (**9**), which is also bent.

Experimental

Kinetic Studies.—The general kinetic method has been described previously. Compounds with tritium incorporated at positions Y in (**1**) were labelled by direct exchange and hence some tritium entered less reactive sites. Plots of log activity *vs.* time therefore showed the expected departure from linearity. Runs were followed until the secondary slope (due to exchange at the secondary site or sites) became linear. Back extrapolation of the secondary plots and correction of the initial activities in the usual manner gave very good first-order plots for exchange at the most reactive sites Y. These sites and those in (**3a**) and (**3b**) were too reactive for their exchange rates to be determined directly in TFA at 70 °C. Mixtures (50:50 vol %) of TFA and Aristar acetic acid were therefore used, the rates under standard conditions being obtained by multiplying, by either 341 and 364, the rate differences between two batches of this medium and anhydrous trifluoroacetic acid (determined from rates of exchange of mesitylene).

Compounds with tritium specifically labelled at the enclosed sites X were in some cases measured in trifluoroacetic acid containing a little chloroform to increase solubility and hence accuracy, through raising the count per extracted sample. The rate reduction of 1.65-fold relative to exchange in anhydrous trifluoroacetic acid was determined from measurements on [9-^{3}H]phenanthrene. The kinetic behaviour of these compounds also showed some departure from first-order form, this deviation becoming greater the smaller the alkyl chain. This is thought to be due to acid-catalysed rearrangement arising from protonation at the α-alkyl-substituted position in the naphthalene ring, followed by migration of the alkyl group to the β-position and the β-tritium to the α-position. A similar migration of the alkyl group had previously been observed under more acidic conditions for the [6]naphthalenophane. The extent of the secondary detritiation was however small and did not significantly affect the accuracy of the rates for the primary reaction, determined by the back-extrapolation technique already described.

Preparation of Compounds.—Compounds with tritium specifically located at the enclosed sites were obtained from the corresponding bromo compounds as shown in Scheme 4. The preparation of the bromo precursers has been described previously in detail for $n = 10$ and 8; for $n = 7$ the compound was also said to have been prepared but no details were given. We therefore describe this preparation fully below.

For compounds with tritium specifically located at positions Y in (**1**), the bromo compounds were converted into the inactive parent cyclophane, which was then heated under reflux with trifluoroacetic acid and tritiated water for such a time as to incorporate the label largely into the desired (and much the most reactive) site.

[15- *and* 17-^{3}H][7](1,3)*Naphthalenophane.*—1-(o-*Hydroxymethylphenyl*)*cyclononanol.* n-Butyl-lithium in hexane (19.7 ml, 0.0315 mol) was slowly added to *o*-bromobenzyl alcohol (2.54 g, 0.0137 mol) in dry THF (13.3 ml) and hexane (3.3 ml) at −15 °C under nitrogen. A thick white precipitate formed and the mixture was stirred during an additional 2 h. Cyclononanone (2.0 g, 0.0143 mol) in hexane (8 ml) was added during 30 min at −15 °C, and the mixture was stirred during an additional 2 h. Hydrolysis, normal work-up, and removal of the solvent gave the crude diol as a yellow oil, which was partially purified by distillation through a short-path column to give product (1 g).

6,7,8,9,10,11,12-*Heptahydro*-5H-*cyclonon*[a]*indene.* Distilled boron trifluoride–ether (0.57 g, 0.004 mol) was added to the semi-pure diol (1 g, 0.004 mol) in benzene (40 ml) and the mixture was heated under reflux during 6 h. The indene is unstable and this length of reflux time was found to give the maximum yield. Hydrolysis with water (the solution changed from red to yellow) and normal work-up gave an orange oil. Column chromatography gave a yellow oil, n_D^{20} 1.5763, indicated by g.l.c. to be 95% pure; δ($CDCl_3$) 1.2—2.1 (10 H, m, CH_2), 2.45—2.73 (3.8 H, m, CH_2), 3.2 (2.1 H, s, CH_2), and 6.95—7.4 (3.9 H, m, ArH).

17-*Bromo*[7](1,3)*naphthalenophane.* 6,7,8,9,10,11,12-Heptahydro-5*H*-cyclonona[*a*]indene (0.75 g, 0.0035 mol) and phenyl(tribromomethyl)mercury (2.71 g, 0.007 mol; recrystallised from 3:1 hexane–chloroform) in anhydrous benzene (50 ml) were heated with stirring under nitrogen during 67 h, to give a white precipitate of phenylmercury(II) bromide. The cooled mixture was filtered, washed with sodium hydrogencarbonate, and dried, and unreacted phenyl(tribromomethyl)mercury was removed by trituration with hexane. Solvent removal left a crude oil, which was purified by column chromatography (light petroleum as eluant) to give 17-bromo[7](1,3)naphthalenophane (0.5 g, 48%) as a white solid, *m/z* 304, 302, and 223.

n-Butyl-lithium in hexane (0.001 mol) was added to a stirred solution of the bromo derivative (0.1 g, 0.000 33 mol) in dry THF (3 ml) under nitrogen. The solution rapidly turned black. Hydrolysis with tritiated water (0.030 ml of 500 mCi ml^{-1} activity) followed by an excess of ordinary water, and normal work-up, gave the crude product. This was purified first by column chromatography and then by thin-layer chromatography (25 nm thickness; Kieselgel, Schleicher and Schull; hexane as eluant) to give [17-^{3}H][7](1,3)*naphthalenophane* (0.0057 g, 0.000 25 mol, 77%), *m/z* 224; δ($CDCl_3$) 0.78—1.82 (12 H, m, CH_2), 2.78—3.72 (2 H, m, CH_2), 7.427 (3 H, m, β-ArH),

7.612 (1 H, d, 11 ArH), 7.790 (1 H, m, α-ArH), and 8.038 (1 H, m, α-ArH).

The inactive material was prepared in a similar way. [7]-(1,3)naphthalenophane (0.05 g, 0.000 23 mol), trifluoroacetic acid (1 ml, 0.00 135 mol), and tritiated water (0.02 ml of 500 mCi ml^{-1} activity) were heated under reflux during 24 h. Neutralisation and work-up as before gave [15-^{3}H][7](1,3)-*naphthalenophane* (99%).

Attempted Preparation of [6](1,3)*Naphthalenophane*.—The 16-chloro precursor was prepared as described in the literature.[2] Treatment of this with n-butyl-lithium during 4 h in the usual way produced only a trace (21%) of a compound, *m/z* 266, which suggests that butyl had entered the 14-position, the alkyl chain rearranging to give 8-butyl[6](1,2)naphthalenophane.

Reaction with lithium was therefore attempted. Lithium chips (3.3 mg, 0.0047 mol) were added to 16-chloro[6](1,3)naphthalenophane in dry THF under argon at 0 °C with ultrasonic agitation. G.l.c. analysis indicated the presence (80%) of a major component (or components). The crude product was purified by column chromatography to give a clear oil, which was crystallised from ethanol yielding white crystals (20 mg, 47%), m.p. 36.0—37.0 °C, *m/z* 208. This corresponds exactly to the results obtained by Parham *et al.*[2] for a 70:30 mixture of hexahydrophenanthrylene (**3a**) and hexahydroaceanthrylene (**3b**) produced by photochemical elimination of hydrogen chloride from 16-chloro[6](1,3)naphthalenophane. They reported δ($CDCl_3$) 7.87—7.14 (5 H, ArH) and we find (360 MHz) aromatic peaks in the region δ 7.87—7.33 *viz.* 7.85 (d), 7.74 (d), 7.48 (s), and 7.43—7.33 (overlapping triplets); there is additional fine structure evident in this high-field spectrum.

An attempt to produce the desired compound through reaction of 16-chloro[6](1,3)naphthalenophane with magnesium in THF with entrainment using 1,2-dibromoethane, followed by hydrolysis (aq. acid) and normal work-up (including column chromatography), gave a clear oil, *m/z* 210; δ($CDCl_3$) 7.71 (q, 1 H, α-ArH), 7.55 (s, 1 H, α-ArH), 7.34 (q, 1 H, β-ArH), and 1.72—0.83 (m, 12 H, CH_2). This clearly corresponds to [6](1,2)naphthalenophane (**5**) and the ease of the rearrangement indicates that kinetic studies could not be carried out satisfactorily on the (1,3)cyclophane even if it could be prepared, so further work was abandoned.

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