Electrophilic Aromatic Substitution. Part 22.[1] The Effect of Methyl Substituents on Detritiation of the 9-Position of Phenanthrene; Tritium Migration During Exchange

By **Herbert V. Ansell, P. Julian Sheppard, Colin F. Simpson, Mark A. Stroud,** and **Roger Taylor,*** School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, Sussex

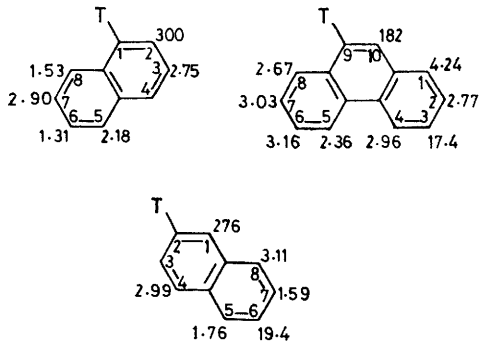
Rates of protiodetritiation in trifluoroacetic acid at 70 °C have been measured for 9-tritiated phenanthrenes containing a methyl substituent in each of the positions 1—8. The activating effects of these substituents are as follows (positions in parentheses): 4.24(1); 2.77(2); 17.4(3); 2.96(4); 2.37(5); 3.16(6); 3.05(7); 2.67(8). The methyl substituent effects (with the exception of 6-methyl) closely parallel those obtained for the corresponding interactions in naphthalene, such differences as do exist being predicted by empirical calculations which simply consider the change in bond orders on going from ground state to transition state; calculations of the effect of a CH_2^- substituent on localization energies are also satisfactory models. The reactivity of the 6-methyl compound is anomalously high and is believed to be due to migration of tritium across the 9,10-bond accompanying the exchange, thereby giving a small amount of the more reactive 3-methyl[9-^{3}H]phenanthrene. Likewise, detritiation of 3-methyl[9-^{3}H]phenanthrene gave a curved kinetic plot indicating the presence of an isomer, less reactive towards exchange, *i.e.* from tritium migration to give 6-methyl[9-^{3}H]phenanthrene. This, the first example of a 1,2-migration of hydrogen in non-super acid media is calculated to occur to the extent of 6—10% during the time of the kinetic runs. σ^+-Constants for all but the 3-methyl compound are closely similar and in the range −(0.415—0.44); the high reactivity of the 3-methyl compound for which σ^+ is −0.51 derives from the strong conjugative interaction leading to a *p*-quinonoid-like transition state.

ALTHOUGH the effects of substituents have been studied intensively during the past century, with regard to orientation and reactivity in electrophilic substitution of benzene, studies of their effects in polycyclic systems have been very few. This is because there are a great number of positions for further substitution to the extent that accurate determination of the isomer distribution is difficult, even with modern analytical techniques such as g.l.c. The nature of this problem is exemplified by studies of the nitration of methyl- and methoxynaphthalenes.[2] The problems can be overcome however, by specifically labelling a given position in a substituted polycyclic and measuring the rate at which the label is removed. The simplest label is a hydrogen isotope, and hydrogen exchange has the added advantage that there is virtually no steric hindrance in the reaction. The problem is then reduced to one of synthesis of the labelled compound (though this is by no means an easy solution in many cases). This technique was used to determine the reactivity of a wide range of substituted naphthalenes towards hydrogen exchange, in what is the most complete study to data, of the reactivity of a substituted polycyclic.[3] The effects of methyl substituents in this study are shown in Scheme 1.

For phenanthrene, the only previous study concerned the effects of substituents across the 9,10-bond,[4] and the effect obtained for the methyl substituent is also shown in Scheme 1. The advent of the photocyclization method for the formation of phenanthrenes from the corresponding stilbenes [5] has facilitated the ease with which a more detailed study of substituent effects in phenanthrenes may be undertaken. Accordingly we have synthesized [9-^{3}H]phenanthrenes with methyl substituents in each of the positions 1—8 and have measured their rates of protiodetritiation in trifluoroacetic acid at 70 °C.

RESULTS AND DISCUSSION

The rate coefficients ($10^7k/s^{-1}$) for exchange were as follows (positions of the methyl substituents in parentheses): 664(1), 433(2), 2 720(3), 480(4), 370(5), 495(6), 474(7), and 408(8). All the isomers gave good first-order kinetics except for the 3-methyl compound the derived rate coefficient for which decreased with time during a kinetic run. This is attributed to tritium

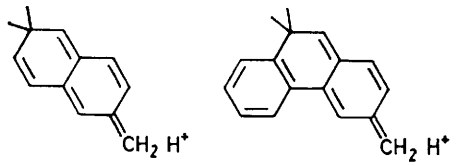


SCHEME 1

Activating effects at the positions shown, of a methyl substituent on the rate of detritiation of naphthalene and phenanthrene

migration across the 9,10-bond (see below) and the above rate coefficient was obtained from the initial part of the kinetic run. Since the rate coefficient for exchange at the 9-position of phenanthrene is 156.5×10^{-7} s^{-1}, these data yield the activation effects of a methyl substituent upon exchange at the 9-position, as shown in Scheme 1 where the numbers refer to the effect for a methyl substituent at that position. For comparison the corresponding activation effects in naphthalene [3] are given in Scheme 1.

Notable features of our results are: (i) With the exception of 3-methyl, all the methyl substituents produce a closely similar activation of the 9-position. The corresponding positions in naphthalene show the same effect, and the strong 2,6-interaction has been attributed to the stability of structure (I) which is

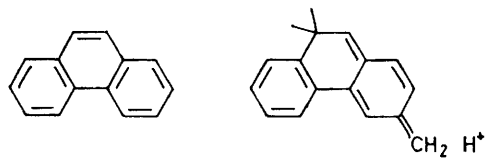


(I) (II)

p-quinonoid.[6] The same will be true of the corresponding structure (II) for phenanthrene and indeed we can expect that this structure will be even more favourable than (I) because (II) is also benzenoid. The only reason that the activation of the 9-position by the 2-methyl substituent (17.4-fold) is less than the comparable 2,6-interaction in naphthalene (19.4-fold) is because the positive charge in the transition state is delocalized over a greater number of carbons. (The same factor accounts for the lower 9,10-activation in phenanthrene relative to the 1,2- or 2,1-activation in naphthalene, even though the 9,10-bond order in phenanthrene is higher than the 1,2-bond order in naphthalene.[4])

(ii) The order of activation by the methyl groups in phenanthrene closely parallels the order for the corresponding positions in naphthalene, *e.g.* the activation orders 3 > 1 > 4 > 2(phenanthrene) *vs.* 6 > 8 > 5 > 7(2-position of naphthalene) and 7 > 5(phenanthrene) *vs.* 7 > 5(1-position of naphthalene). However, the order 8 > 6 for activation of the 1-position of naphthalene becomes reversed in phenanthrene, and it appears that the reactivity of 6-methyl[9-^{3}H]phenanthrene is anomalous because the methyl group activates more than when it is in the adjacent 5- and 7-positions which are conjugated with the 9-position. Further indications that the reactivity of this compound is anomalous comes from the ratios of activation effects for the phenanthrenes with methyls in non-conjugated positions, compared to their naphthalene counterparts *viz.* 1.74(2), 1.68(4), 2.41(6), and 1.74(8). The reason for this anomaly is described below.

(iii) The reactivities of the various methylphenanthrenes both relative to one another and to their naphthalene counterparts can be accounted for by theoretical calculations. One method is to calculate the effect of a CH_2^- substituent at the appropriate position on the localization energy for substitution at the 9-position (and at the corresponding positions in naphthalene[7]). The results of these calculations are given in the Table. A somewhat related approach which has the advantage of being not only very simple, but also demonstrates the fundamental reason for the differences in the substituent effects, takes account of the changes in bond localization between the preferred ground state structure and the transition state (approximated to the Wheland intermediate), coupled with the fraction of charge likely to be delocalized to the conjugated positions in each molecule. An example suffices. Consider the most stable canonical form (III) for the ground state of phenanthrene, and the structure of the intermediate approximately to the transition state for 9-substitution of 3-methylphenanthrene (IV). Count up the number of C–C linkages in (IV) which are in the same position relative to that in (III). There are 11 such linkages. Divide this number by the product of the total number of C–C linkages (16) and the number of positions over which the transition state charge can be delocalized (7), *i.e.* 112. (For benzene, naphthalene,



(III) (IV)

and benz[*a*]anthracene, the corresponding products are 18, 55, and 189.) The quotient is then the *substituent activation factor* A_f, and the larger this is, the larger will be the substituent effect. For the above example, $10^2A_f = 9.8$, and other values are shown in the Table.

Effects of methyl substituents on reactivity of aromatics towards detritiation at 70°, compared to calculated reactivity indices

Aromatic	Inter-action	10^2A_f	Effect of CH_2^- on localization energy/β	Activation by methyl
Benzene	1, 2	16.7 [a]	−0.80	220
	1, 4	16.7 [a]	−0.71	450
Naphthalene	1, 2;	18.2	−0.85;	270;
	2, 1	18.2	−0.80	300
	1, 4	14.5	−0.66	83
	1, 5	3.2	−0.33	2.18
	1, 7;	7.3	−0.38;	2.90;
	2, 8	7.3	−0.40	3.11
	2, 3	10.9	−0.58	3.60
	2, 6	10.9	−0.43	19.4
Phenanthrene	9, 10	13.4	−0.66	182
	9, 1	8.0	−0.415	4.24
	9, 3	9.8	−0.425	17.4
	9, 5	6.25	−0.22	2.37
	9, 7	8.0	−0.25	3.05
Benz[*a*]anthracene	5, 7	9.0	−0.44	5.79
	7, 12	9.5	−0.56	24.0

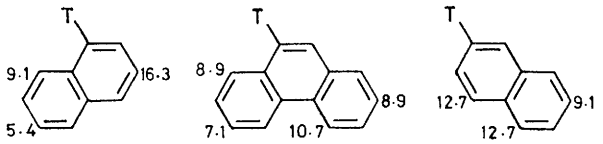
[a] Because there is no bond fixation in benzene, these values are the averages, calculated for the two Kekulé forms for the ground state.

The A_f-factor method is extraordinarily successful, and so too is the localization energy method. Both correctly predict the following. (*a*) That *para*-activation by methyl should decrease along the series: benzene(1,4) > naphthalene(1,4) > benz[*a*]anthracene-(7,12). (*b*) That *ortho*-activation by methyl should decrease along the series: benzene(1,2) > naphthalene(1,2 or 2,1) > phenanthrene(9,10). (*c*) That the comparable methyl activation should decrease along the series: benz[*a*]anthracene(5,7) > phenanthrene-

(9,1) > naphthalene(1,7 or 2,8). (*d*) That the 9,3-interaction in phenanthrene should be less than the comparable 2,6-interaction in naphthalene, whereas the 9,1-interaction in phenanthrene should be greater than the 2,8-(or 1,7-)interaction in naphthalene.

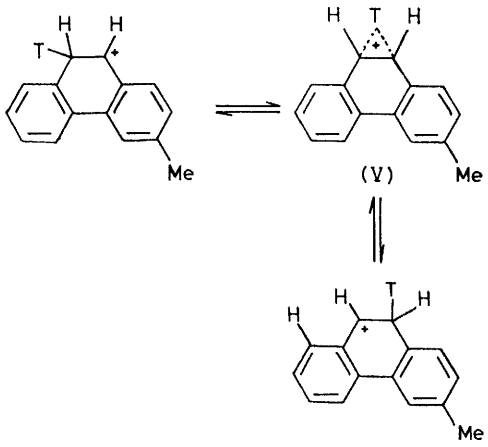
The A_f factor correctly predicts the relative interactions in naphthalene except for the 2,6- *vs.* 2,3-interactions which are predicted to be equal. The localization energy method is less successful in this respect since it predicts the wrong order of these two interactions. On the other hand the latter method is more successful in phenanthrene and predicts precisely the observed order; the A_f factor is slightly less successful in that it predicts the 9,1- and 9,7-interaction to be equal. The A_f factor method is also more successful than the localization energy method in predicting the *ortho vs. para* methyl activating effects in benzene.

For non-conjugated positions, the localization energy method is unsatisfactory since it predicts deactivation from all positions. The A_f factor method can, however, be empirically adapted to give A_f' factors which are the average A_f values for the adjacent positions. (This adaption is based upon the assumption that electronic effects at non-conjugated positions are derived substantially from secondary relay from adjacent conjugated positions.) The A_f' factors (which are not quantitatively comparable with the A_f factors) are shown in Scheme 2; they correctly predict the following. (*a*) That activation of the 1-position of naphthalene by methyl substituents should decrease along the series: 3-Me > 8-Me > 6-Me; for detritiation of the 2-position, the order 5-Me > 7-Me is correctly predicted, but 4-Me is predicted to be equal to 5-Me whereas it is somewhat more activating. (*b*) That the 1,8- and 2,7-interactions in naphthalene should be equal. (*c*) That activation of the 9-position of phenanthrene by methyl substituents should follow the order: 4-Me > 2-Me = 8-Me. However the 6-methyl substituent is predicted to be less activating than any of these whereas it is more activating. This effect is clearly anomalous and contradicts the comparable effects in naphthalene. We have carefully checked this result and there appears to be no possibility that it arises from experimental error. The reason for this anomaly is described below.



SCHEME 2 Substituent interaction factors A_f' for non-conjugating positions

1,2-*Hydrogen Shifts across the* 9,10-*Bond*.—The high rate of exchange of the 6-methyl isomer, coupled with the curved kinetic plot for exchange of the 3-methyl isomer indicates that in the transition state, a 1,2-tritium shift takes place across the 9,10-bond. Such a process will be aided by the near symmetry of the intermediate (V), and the retention through the shift, of the benzenoid character of the two terminal rings. This is the first example of a hydrogen shift detected during kinetic studies of hydrogen exchange, and the only previous examples relate to *o*-difluorobenzene, *o*-xylene, and other alkylbenzenes in superacids;[8] in the former, the



activation energy for the shift from the 4- to the 5-position was half that for the shift from the 3- to the 4-position, again pointing to the importance of symmetry. Migration of alkyl and aryl groups across the 9,10-bond in the phenanthrenonium ion has also been detected in superacids.[9]

As a result of this shift the 3- and 6-methyl isomers become in effect, partially interconverted. Since the former exchanges *ca.* 5 times faster than the latter, any conversion of the 6- to the 3-methyl isomer results in relatively rapid subsequent exchange which will not affect the overall kinetic form, but will give an anomalously high exchange rate. By contrast the reverse conversion produces an isomer which is relatively unreactive and the rate coefficient will decrease with time. Both these phenomena are observed.

From the kinetic plot for exchange of the 3-methyl compound we estimate, from the residual activity after the primary exchange is largely complete, that *ca.* 10% of the tritium migrates during the time for a kinetic run. Migration will not be equally fast in each direction, and if we make the reasonable assumption that the methyl substituent effect in phenanthrene relative to that of the comparable effect in naphthalene will be constant (a factor of *ca.* 1.7) then we calculate [according to equation (1), where x is the true rate of exchange of the 6-methyl isomer] that 6.5% of the exchange observed takes place *via* migration. Solution of equation (1) gives $x =$

$$\left[\frac{93.5x}{100} + \frac{6.5}{100} \times 2720 = 495\right] \times 10^{-7}\ \text{s}^{-1} \quad (1)$$

340×10^{-7} s^{-1} and $f_6^{Me} = 2.17$. Since the exchange rates of the 1- and 8-methyl isomers also differ somewhat (the former being the most reactive) the exchange rate for the latter is also likely to be slightly in error and correction of this *via* equation (2) where y is the true rate of exchange of the 8-methyl isomer gives $y = 401 \times 10^{-7}$ s^{-1}

$$\left[\frac{93.5y}{100} + \frac{6.5}{100} \times 664 = 408\right] \times 10^{-7}\ s^{-1} \quad (2)$$

and $f_8^{Me} = 2.56$. The activating effects of the 6- and 8-methyl substituents now exceed those for the corresponding positions in naphthalene by factors of 1.66 and 1.67 respectively. Moreover the activating effect of 6-methyl is now less than that of 8-methyl as predicted and also less than that of the adjacent 5- and 7-methyl substituents which are conjugated with the 9-position.

Since the activating effects of the 5- *vs.* 4- and 7- *vs.* 2-methyl substituents are so similar, tritium migration will not produce any significant errors in the observed activation factors.

σ-*Constants*.—Elsewhere the suitability of hydrogen exchange in trifluoroacetic acid at 70 °C as a model reaction for determining σ^+-constants, has been described.[10] The present data give values as follows (methyl positions in parentheses): −0.44(1), −0.42(2), −0.51(3), −0.42(4), −0.41(5), −0.405(6), −0.42(7), and −0.415(8). These are obtained using the corrected rate coefficients for exchange of the 6- and 8-methyl compounds. In using these values the possibility of migration of an electrophile across the 9,10-bond must be taken into account.

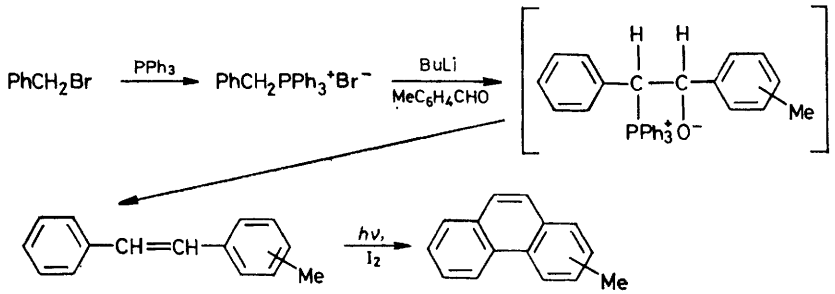
EXPERIMENTAL

All preparations involved the Wittig reaction in which the ylide from benzyltriphenylphosphonium bromide was treated in the presence of n-butyl-lithium with the appropriate tolualdehyde to give the corresponding methylstilbene which was photocyclized by the method of Mallory *et al.*,[11] and using a 125 W, medium-pressure lamp, with an irradiation time of *ca.* 8 h. The methylphenanthrenes were purified by column chromatography (type H alumina) with light petroleum, then carbon tetrachloride, as eluants; uncyclized methylstilbenes were eluted first followed by the methylphenanthrenes.

1-, 2-, 3-, and 4-*Methyl*[9-^{3}H]*phenanthrenes*. [α-^{3}H]-*Benzyltriphenylphosphonium bromide*. This compound was required for synthesis of each of the title compounds and was obtained by treating the Grignard reagent from benzyl bromide with tritiated water, rebrominating in the side chain, and treating the resultant [α-^{3}H]benzyl bromide with triphenylphosphine in the usual way.

Reaction of the phosphonium salt with *o*-tolualdehyde as in Scheme 3, gave 1-*methyl*[9-^{3}H]*phenanthrene*, m.p. 123 °C (lit.,[12] 123 °C), and likewise with *p*-tolualdehyde gave 3-*methyl*[9-^{3}H]*phenanthrene*, m.p. 62 °C (lit.,[12] 62 °C).

Reaction of the phosphonium salt with *m*-tolualdehyde gave a mixture of the 2- and 4-methyl compounds; one isomer formed in a slightly larger amount was assumed to be the 2-methyl compound since less steric hindrance would be involved in the cyclization leading to its formation. G.l.c. using a 5 ft column packed with 5% Carbowax adsorbed on 100—120 mesh Chromosorb G operated at 200 °C gave a partial resolution of the isomers, the isomer considered to be the 2-methyl compound being eluted first. They were partially resolved by preparative g.l.c. using a 7 ft column packed with 20% Carbowax adsorbed



SCHEME 3 General method for formation of the methylphenanthrenes

on 80—100 mesh Chromosorb P, and operated at 250 °C. Final separation was achieved by employing a 7 ft column packed with 5% Bentone 34—10% SE 30 adsorbed onto 60—80 mesh BSS silanized Chromosorb P, operated at 190 °C to give 2-*methyl*[9-^{3}H]*phenanthrene* and 4-*methyl*-[9-^{3}H]*phenanthrene*. The isomers were identified by the difference in the ^1L_a band in the u.v. spectrum, and this appeared at 2 955 ± 5 Å for the 2-methyl compound and 2 975 ± 5 Å for the 4-methyl compound; this difference is confirmed in the literature [13] and is also theoretically predicted.[14]

5-, 6-, 7-, *and* 8-*Methyl*[9-^{3}H]*phenanthrenes*. Each of these compounds was made by treating benzyltriphenylphosphonium bromide with tolualdehydes labelled in the aldehyde group. The labelling was achieved in the manner of the following example.

p-Tolualdehyde (6.0 g, 0.05 mol) was dissolved in THF (150 ml) in a three-necked flask (250 ml) fitted with an inlet for dry nitrogen, and a reflux condenser. Sodium [^{3}H]-borohydride (1 mg; 8 mCi) was added and the mixture heated under reflux during 15 min. Inactive sodium borohydride (0.95 g, 0.025 mol) was added to the cooled mixture which was then heated under reflux during a further 2 h. The product was extracted with water, and the dried ethereal layer concentrated to yield the crude [α-^{3}H]benzyl alcohol.

Potassium permanganate (160 g) was dissolved in deionized water (2 l) and the solution boiled. Activated carbon (50 g, Nuchar C-190-N) was added in small amounts with stirring. The mixture was heated during a further 5 min and then allowed to cool. The precipitate was filtered off, washed with deionized water (4 × 500 ml), and dried (120 °C) during 2 days. The dried powder (66 g) and dried benzene (150 ml) were added to the crude benzyl alcohol in a flask fitted with a stirrer, nitrogen inlet, and a Dean–Stark apparatus and the mixture heated under reflux during 4 h. The carbon was filtered off and dry benzene was added to it; the mixture was then stirred and filtered; this process was repeated four times. The combined benzene extracts were washed with water (3 × 100 ml) and then with 10%

sodium chloride solution (100 ml). The benzene was removed from the dried solution using a rotary evaporator, to give the aldehyde, the i.r. spectrum of which indicated the absence of any alcohol; the aldehydes were obtained in *ca.* 80% yields.

Each aldehyde was then treated with benzyltriphenylphosphonium bromide to give, after work-up as above, 5-, 6-, 7-, and 8-*methyl*[9-^{3}H]*phenanthrenes*.

Kinetic Studies.—These were carried out in the manner previously described.[15]

We thank N.A.T.O. for a research grant in partial support of this work.

[8/1040 *Received*, 5*th June*, 1978]

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