The Relative Migration Tendencies of *p*-Substituted Phenyl Groups in Carbonium Ion Doubly-degenerate Rearrangements

By V. G. SHUBIN,* D. V. KORCHAGINA, G. I. BORODKIN, B. G. DERENDJAEV, and V. A. KOPTYUG
(*Institute of Organic Chemistry, Siberian Division of the Academy of Sciences, Novosibirsk,* 90, *U.S.S.R.*)

Summary The order of the migration tendencies of *p*-X-phenyl groups in the doubly-degenerate rearrangement of stable 9-*p*-X-phenyl-9,10-dimethylphenanthrenonium ions (Ia—e) is $X = Me > F \sim H > Cl > CF_3$.

WE present some preliminary studies of the 9-*p*-X-phenyl-9,10-dimethylphenanthrenonium ions (Ia—e) formed by protonation of the neutral precursors (IIa—e)† in strongly acid media.

The n.m.r. and absorption spectra of the ions (Ia—e) are listed in Tables 1 and 2, respectively. Some difference between the methyl chemical shifts of the ions (Ia—e) and those of 9,9,10-trimethylphenanthrenonium ion (τ 6·46 for 10-CH_3 and 8·15 for 9-CH_3[1]) is not unexpected and results from the influence of neighbouring *p*-X-phenyl groups.‡

---

† Satisfactory analytical and spectral data were obtained for all new compounds.

‡ π-Aryl bridging, to some extent, may be operative (*cf.* ref. 2).

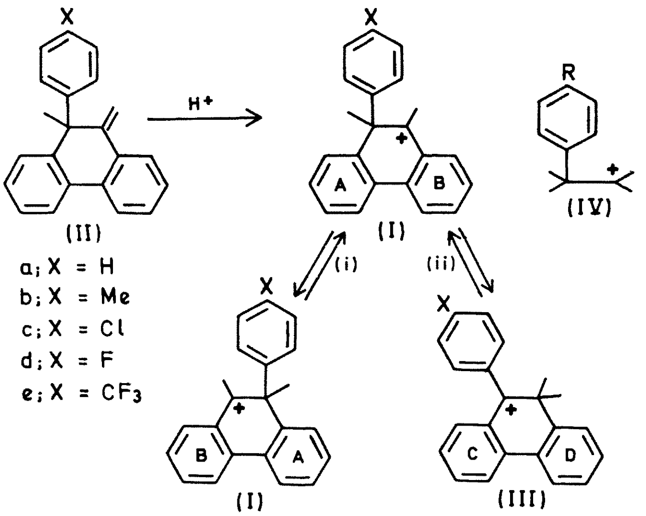
As the temperature is raised the signals of 9- and 10-methyl groups broaden, coalesce, and turn into a sharp singlet for all the ions. These changes are reversible and are apparently due to rapid 1,2-aryl shifts [Pathway (i)]. The observed significant changes of phenanthrene ring pattern are similar to those of 9,9,10-trimethylphenanthrenonium ion and are consistent with the mechanism *via* a 1,2-aryl shift [Pathway (i); equilibrium $A \rightleftarrows B$] but inconsistent with that *via* a 1,2-methyl shift [Pathway (ii)]. Taking into account the lack of signals due to isomeric 9,9-dimethyl-10-(*p*-X-phenyl)-phenanthrenonium ions (IIIa—e) in the n.m.r. spectra it may be concluded that the coalescence of methyl signals owing to reversible 1,2-methyl shift (Pathway ii) should not be accompanied by noticeable changes of the phenanthrene ring pattern [equilibria $A \rightleftarrows C$ and $B \rightleftarrows D$, the lifetime of (III) being very short, *cf.* ref. 3]. An alternative four-step mechanism involving ring-contraction followed by methyl equilibration *via* 9-*p*-X-cumyl-9-fluorenyl cation appears not to be operative because of instability of the intermediary ions (*cf.* ref. 4).

TABLE 1

N.m.r. data for the 9-p-*X-phenyl*-9,10-*dimethylphenanthrenonium ions in* FSO_3H–SO_2ClF (1 : 5)[a]

X	^1H Chemical shifts (−100°)[b]			Collapsed line	^{19}F Chemical
	9-CH_3	10-CH_3	*p*-CH_3	of 9- and 10-CH_3	shifts (−100°)[c]
H	7·87	6·87		7·38 (−70)[d]	
Me	7·93[e]	6·90[e]	7·65 (7·82)[f]	7·41 (−100)	
Cl	7·89	6·87		7·34 (−55)	
F	7·89	6·86		7·33 (−70)	+110·0 (+116·8)[f]
CF_3	7·85	6·87		7·33 (0)	+61·3 (+62·8)[f]

[a] All the ^1H n.m.r. spectra show the deshielded complex multiplets of phenanthrene ring protons (τ *ca.* 1—2·5) and the patterns of *p*-X-phenyl groups (to be considered in detail elsewhere).
[b] Referred to internal CH_2Cl_2 taken as τ 4·67.
[c] In p.p.m. (internal CCl_3F).
[d] Coalescence temperature, °C (100 Mc/sec.).
[e] At −115°.
[f] Numbers in parentheses are the chemical shifts for neutral precursors in CCl_4 at +20°.



The observed order of the migration tendencies[5] of *p*-X-phenyl groups, Me > F ~ H > Cl > CF_3, is in accord with the suggested mechanism [Pathway (i)], the essential feature of which is electrophilic attack of the carbonium centre on the *p*-substituted aromatic ring.

TABLE 2

Absorption spectra of 9-p-*X-phenyl*-9,10-*dimethylphenanthrenonium ions in* 70%-$HClO_4$ *at* 25°

X	λ_{max}, nm and log ϵ (in parentheses)			
H[a]	269(4·50)	335(3·99)	373sh	558(3·79)
Me	269(4·41)	336(3·95)	397(3·50)	558(3·70)
Cl	270(4·46)	335(3·97)	382sh	556(3·75)
F	269(4·50)	336(4·00)	376sh	556(3·81)
CF_3	269(4·49)	339(4·00)		556(3·84)
9,9,10-Trimethyl-phenanthrenonium ion[b]	266(4·28)	338(3·92)		530(3·59)

[a] 268(4·34), 333(3·96), 549(3·78) in $HClO_4$[3]; [b] in 75% H_2SO_4[1]

In the related 1,1,2-trimethyl-2-phenyl propyl cations (IV), the rate of migration even for R = CF_3 is probably too high to be measured by n.m.r. spectroscopy (sharp singlet of methyl protons at −78°).[6]§ The more effective delocalization of positive charge in 9-(*p*-X-phenyl)-9,10-dimethylphenanthrenonium ions results in retardation of the rearrangement and it is thus possible to establish the structure–reactivity correlations.

(*Received, March 25th,* 1970; *Com.* 425.)

---

§ Such ions with R = H, Me, OMe undergo rapid transformation into more stable isomeric species.[6]

[1] V. G. Shubin, D. V. Korchagina, A. I. Rezvukhin, and V. A. Koptyug, *Doklady Akad. Nauk S.S.S.R.*, 1968, **179**, 119.
[2] H. C. Brown and C. J. Kim, *J. Amer. Chem. Soc.*, 1968, **90**, 2082.
[3] R. L. Shriner and L. Geipel, *J. Amer. Chem. Soc.*, 1957, **79**, 227.
[4] V. G. Shubin, D. V. Korchagina, and V. A. Koptyug, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1969, 1201.
[5] M. Stiles and R. P. Mayer, *J. Amer. Chem. Soc.*, 1959, **81**, 1497.
[6] G. A. Olah, M. B. Comisarow, and C. J. Kim, *J. Amer. Chem. Soc.*, 1969, **91**, 1458.