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Degenerate rearrangements of long-lived 9,10-dimethyl-9-(1-methyl-1-vinyl)-phenanthrenium and 9,10-dimethyl-9-(*trans*-1-methyl-1-propenyl)phenanthrenium ions: unexpected strong retardation of vinyl migrations

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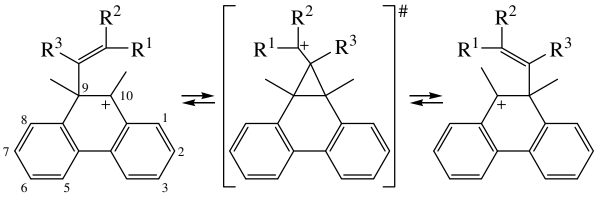
As found by dynamic NMR, the rates of degenerate rearrangements of long-lived 9,10-dimethyl-9-(1-methyl-1-vinyl)phenanthrenium and 9,10-dimethyl-9-(*trans*-1-methyl-1-propenyl)phenanthrenium ions proceeding by 1,2-vinyl shifts are unexpectedly much lower than those of the 9,10-dimethyl-9-vinylphenanthrenium and 9,10-dimethyl-9-(*cis*-1-methyl-1-propenyl)phenanthrenium ions.

Long-lived 9-vinyl-substituted 9,10-dimethylphenanthrenium cations capable of degenerate rearrangement by 1,2-vinyl shifts (Scheme 1) are suitable for determining the migration ability of vinyl and substituted vinyl groups.[1,2] The migration ability of unsubstituted vinyl and *cis*-1-methyl-1-propenyl groups (ions **1a**,**c**) is the highest among hydrocarbon migrants, *cf*. refs. 3, 4.

We studied the kinetics of degenerate rearrangements of 9,10-dimethyl-9-(1-methyl-1-vinyl)- and 9,10-dimethyl-9-(*trans*-1-methyl-1-propenyl)phenanthrenium ions (**1b** and **1d**, respectively) proceeding by 1,2-shifts of vinyl groups by dynamic NMR. Cations **1b** and **1d** were generated under long-life conditions by the ionization of carbinols **2b**,**d**[†] in $FSO_3H–SO_2ClF–CD_2Cl_2$ at –130 °C (Scheme 2). Their structures were confirmed by ^1H and ^{13}C NMR spectroscopy.[‡]

[†] Satisfactory NMR, IR and MS data were obtained for compounds **2b**,**d** prepared from 10,10-dimethyl-9-oxo-9,10-dihydrophenanthrene[5] and CH(R)=C(Me)MgBr (R = H, Me) in THF.



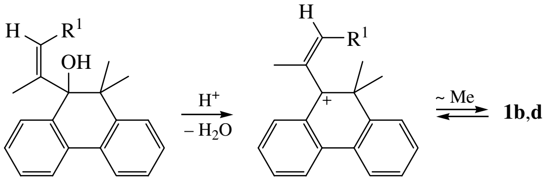
1a–d **1′a–d**

a $R^1 = R^2 = R^3 = H$
b $R^1 = R^2 = H$, $R^3 = Me$
c $R^1 = H$, $R^2 = R^3 = Me$
d $R^1 = R^3 = Me$, $R^2 = H$

Scheme 1

As the temperature increased, reversible changes in the ^{1}H NMR spectra of cations **1b** and **1d** typical of degenerate rearrangements of the carbocations of such a type by 1,2-vinyl shifts were observed. The alternative mechanisms of similar degenerate rearrangements were thoroughly analysed and firmly rejected previously.[1,2] The rates of the degenerate rearrangements of cations **1b** and **1d** by 1,2-shift of vinyl groups (Table 1) were determined by dynamic ^{1}H NMR. Comparison of these data with those obtained earlier for cations **1a**[2] and **1c**[1] shows unexpected very strong retardation of 1,2-shifts of 1-methyl-1-vinyl and *trans*-1-methyl-1-propenyl groups. For example, in passing from cation **1c** having *cis*-1-methyl-1-propenyl group to **1d** having *trans*-1-methyl-1-propenyl group, the rate of rearrangement decreased by a factor of 10^5. Note that the rate of migration of the *trans*-1-methyl-1-propenyl group is close to that of the 1-methyl-1-vinyl group in spite of the presence of a methyl group in the β-position of the former.

The reasons of the retarding effects observed are yet unknown. Now we try to solve this problem by quantum chemistry calculations.



2b,d

Scheme 2

Table 1 Rates of 1,2-shifts of vinyl groups in cations **1a**–**d**.

Ion	k^a/s^{-1}	T/°C	$\Delta G^{\#}$/kJ mol^{-1}	k^b/s^{-1}
1a[2]	1.1×10^5	–103	24	1×10^5
1b	12±2	–102±2	37.5±0.5	10±4
1c[1]	1.0×10^5	–120	22	6×10^5
1d	40±10	–88±2	38.9±0.6	4±2

[a] Experimental values. [b] At –103 °C, calculated from the Eyring equation.

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‡ For **1b** (–107 °C): ^{1}H NMR, δ: 8.87–8.52 (m, 4H), 8.05–7.64 (m, 4H), 5.89 (s, 1H), 5.77 (s, 1H), 3.42 (s, 3H), 1.77 (s, 3H), 1.22 (s, 3H). ^{13}C NMR, δ: 231.6 (s), 149.4 (s), 147.8 (s), 142.4 (s), 133.7 (s), 127.2 (s), 154.4 (d), 137.5 (d), 134.6 (d), 131.1 (d), 129.5 (d), 128.1 (d), 127.3 (d), 126.1 (d), 118.2 (t), 63.9 (s), 28.5 (q), 24.6 (q), 21.0 (q).

For **1d** (–114 °C). ^{1}H NMR, δ: 9.0–8.4 (m, 4H), 8.2–7.7 (m, 4H), 5.70 (q, 1H, *J* 6 Hz), 3.40 (s, 3H), 2.50 (s, 3H), 1.72 (s, 3H), 0.57 (d, 3H, *J* 6 Hz). ^{13}C NMR, δ: 233.4 (s), 151.9 (s), 147.0 (s), 134.3 (s), 131.9 (s), 126.1 (s), 152.5 (d), 136.8 (d), 134.2 (d), 131.0 (d), 129.1 (d), 128.3 (d), 127.6 (d), 127.1 (d), 125.9 (d), 62.4 (s), 31.4 (q), 25.7 (q), 24.1 (q), 14.4 (q) (Bruker AM-400 spectrometer; CD_2Cl_2 as an internal standard, δ 5.33 for ^{1}H and 53.6 for ^{13}C).