Degenerate rearrangement of 9,10-dimethyl-9-(*cis*-1-methylprop-1-enyl)phenanthrenium cation. First example for the 1,2-vinyl shift in the persistent carbocation

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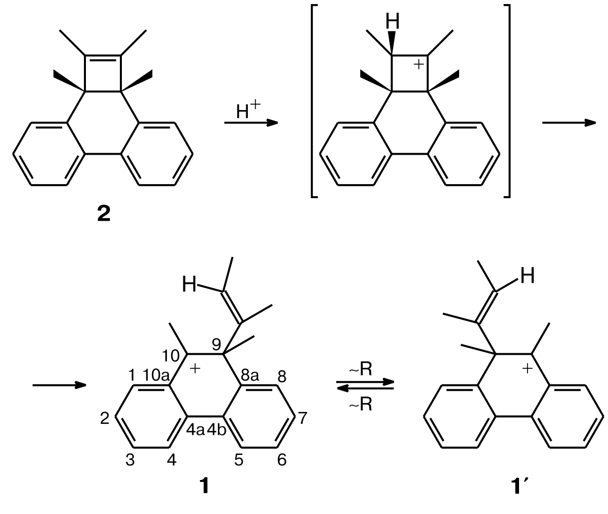
The problem of 1,2-vinyl shift in carbocations has attracted attention since the 1960s.[1] Some examples for acid-catalyzed skeletal rearrangements with migration of a vinyl fragment in assumed undetectable carbocationic intermediates have been reported.[1—4] However, as far as we know, data on 1,2-vinyl shifts in carbocations observed by physical methods under "long-lived" conditions are lacking (*cf.* Refs 5—7).

Using ^{1}H and ^{13}C NMR spectroscopy, we found a degenerate rearrangement of a 9,10-dimethyl-9-(*cis*-1-methylprop-1-enyl)phenanthrenium cation (**1**), which is the first example for 1,2-vinyl migration in persistent carbocations (Scheme 1).

Scheme 1



R = —C(Me)=CHMe

We succeeded to generate cation **1** quite cleanly by the protonation of hydrocarbon **2** [8] in an acidic system $HSO_3F—SO_2ClF$ at −130 °C. A comparison of the ^{1}H and ^{13}C NMR spectra of the resulting solution recorded at temperatures from −120 to −109 °C with the corresponding spectra of 9-R-9,10-dimethylphenanthrenium ions (R = Alk, Ar),[9] which undergo degenerate rearrangements *via* the 1,2-shift of groups R, suggests fast 1,2-shifts of the dimethylvinyl group in ion **1** (see Scheme 1). The spectra of all these species exhibit averaged signals of the 9- and 10-Me groups and symmetric H (^{1}H NMR) and C atoms (^{13}C NMR spectrum) of the aromatic rings. We failed to observe the averaged signal of the C(9) and C(10) atoms, evidently, because of the great difference in chemical shifts of signals of the C^+ and quaternary C atoms (*cf.* Refs 10 and 11).

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 instrument (^{1}H, 400.13 MHz; ^{13}C, 100.61 MHz).

^{1}H NMR (−109 °C), δ: 1.06 (s, 3 H, Me(1) of butenyl); 1.95 (d, 3 H, Me(2) of butenyl, *J* = 7 Hz); 2.54 (br.s, 6 H, C(9)Me, C(10)Me); 6.42 (q, 1 H, =CH of butenyl, *J* = 7 Hz); 7.88, 8.20 (both t, 2 H each, H(2), H(7) and H(3), H(6), *J* = 8 Hz); 8.26, 8.71 (both d, 2 H each, H(4), H(5) and H(1), H(8), *J* = 8 Hz). ^{13}C NMR (−109 °C), δ: 13.0, 15.3 (both Me of butenyl); 25.9 (C(9)Me, C(10)Me); 126.3 (C(2), C(7)); 127.1, 130.8 (both =C of butenyl); 132.4 (C(4), C(5)); 132.6 (C(1), C(8)); 137.8 (C(8a), C(10a)); 141.0 (C(4a), C(4b)); 141.4 (C(3), C(6)).

Alternative mechanisms of degenerate rearrangement of ion **1** (Scheme 2), *i.e.*, reversible 1,2-shifts of the Me groups (route *a*) or more sophisticated transformations (routes *b* and *c*) (*cf.* Refs 11 and 12), do not occur in our case: route *a* cannot provide the observed pairwise averaging of states of atoms of the aromatic rings, and route *b* does not lead to the averaging of states of the 9- and 10-Me groups. States of the C(9) and C(10) atoms of cation **1** cannot be averaged *via* route *c*.

It remains unclear whether the 1,2-vinyl shift is a one-step or two-step process. In the second case, cation **4** should be formed as an intermediate (route *d*). According to the NMR spectra, if cation **4** does form, its content in an equilibrium mixture with ion **1** is negligible. Therefore, the reaction mixture obtained by the neutralization of an acidic solution contains no products of cation **4** quenching,[8] and the quantum-chemical calculation by the DFT

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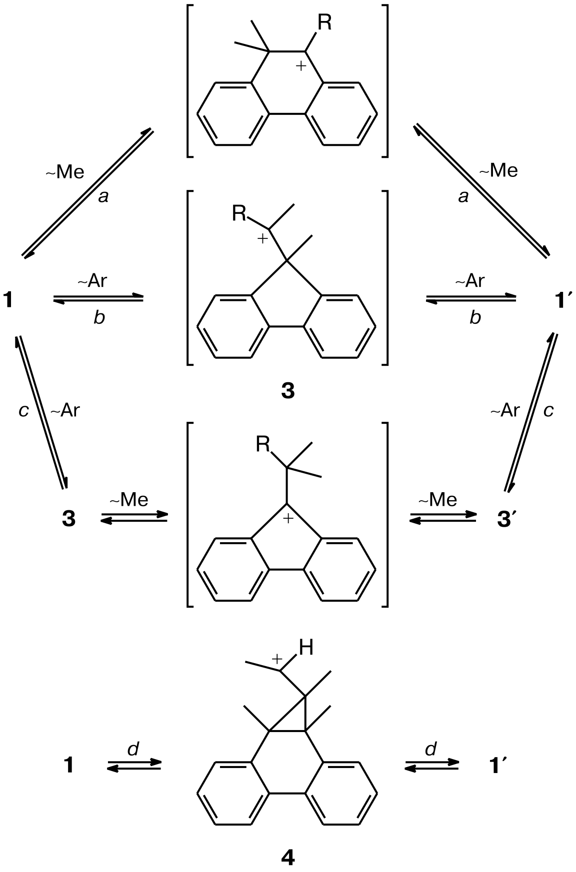
method reveals no minima on the potential energy surface of the 1,2-shift of the dimethylvinyl group.

Scheme 2



The rate of degenerate rearrangement of ion **1** was estimated by the dynamic ^{13}C NMR method from signals of the C atoms of the aromatic rings. Chemical shifts in the absence of exchange, which are necessary in determination of constants, were accepted equal to the corresponding values for the 9,10-dimethyl-9-phenylphenanthrenium cation[**10**] (close analog of cation **1**). The following values were obtained: at −120 °C $k = 1 \cdot 10^5$ s^{-1}, $\Delta G^{\#} = 22.0$ kJ mol^{-1}; at −109 °C $k = 5 \cdot 10^5$ s^{-1}, $\Delta G^{\#} = 21.5$ kJ mol^{-1}.

These data show that the 1,2-dimethylvinyl group is considerably superior over other hydrocarbon migrants (Me, Et, All, $PhCH_2$, and Ph),[**13**] which is evidently due to the efficient participation of the double bond in positive charge delocalization when the transition state of the 1,2-vinyl shift is achieved.

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References

1. N. S. Zefirov, A. F. Davydova, and Yu. K. Yur′ev, *Zh. Obshch. Khim.*, 1966, **36**, 1217 [*J. Gen. Chem. USSR*, 1966, **36** (Engl. Transl.)].
2. A. F. Thomas, *J. Chem. Soc. D*, 1970, 1054.
3. R. S. Bly and R. T. Swindell, *J. Org. Chem.*, 1965, **30**, 10.
4. J. A. Miller and G. M. Ullah, *J. Chem. Soc., Chem. Commun.*, 1982, 874.
5. H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, 1973, **95**, 4096.
6. H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, 1975, **97**, 2459.
7. G. A. Nisnevich, A. I. Vyalkov, G. T. Kamshii, V. I. Mamatyuk, and V. A. Barkhash, *Zh. Org. Khim.*, 1983, **19**, 2081 [*J. Org. Chem. USSR*, 1983, **19**, 1805 (Engl. Transl.)].
8. V. A. Bushmelev, A. M. Genaev, S. A. Osadchii, M. M. Shakirov, and V. G. Shubin, *Zh. Org. Khim.*, 2003, **39**, 1374 [*Russ. J. Org. Chem.*, 2003, **39** (Engl. Transl.)]; T. V. Rybalova, Yu. V. Gatilov, N. V. Kochubei, S. A. Osadchii, and V. G. Shubin, *Zh. Strukt. Khim.*, 1997, **38**, 1140 [*J. Struct. Chem. (Russia)*, 1997, **38**, 954 (Engl. Transl.)].
9. V. A. Koptyug, *Arenonievye iony. Stroenie i reaktsionnaya sposobnost′* [*Arenonium Ions. Structure and Reactivity*], Nauka, Novosibirsk, 1983, p. 45, 97, 98, 182, 183 (in Russian).
10. A. I. Rezvukhin, D. V. Korchagina, and V. G. Shubin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 1253 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, **25** (Engl. Transl.)].
11. V. A. Bushmelev, M. M. Shakirov, B. G. Derendyaev, and V. A. Koptyug, *Zh. Org. Khim.*, 1979, **15**, 1934 [*J. Org. Chem. USSR*, 1979, **15** (Engl. Transl.)].
12. D. V. Korchagina, B. G. Derendyaev, V. G. Shubin, and V. A. Koptyug, *Zh. Org. Khim.*, 1971, **7**, 2582 [*J. Org. Chem. USSR*, 1971, **7** (Engl. Transl.)].
13. G. I. Borodkin and V. G. Shubin, *Chemistry Rev.*, 1999, **24**, Part 2, 1; G. I. Borodkin and V. G. Shubin, *Usp. Khim.*, 1995, **64**, 672 [*Russ. Chem. Rev.*, 1995, **64**, 627 (Engl. Transl.)].

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