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# CARBONIUM ION REARRANGEMENT OF THE 2-PHENYLBORNYL SKELETON

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The application of $^{13}C$ n.m.r. techniques in the study of carbocations generated in super-acid media at low temperature is well established[1]. Carbon-13 chemical shifts have been used in attempts to assess the degree of σ-participation in substituted norbornyl cations. In the 2-phenylnorbornyl case it has been suggested[2] that substantial charge delocalisation on to the neighbouring phenyl group stabilises this cation, while in the analogous 1,2-diphenyl species unfavourable non-bonded interaction between the phenyl rings reduces π-p orbital overlap and results in rapid interconversion, by 1,2-Wagner-Meerwein shifts, of the degenerate classical ions. The 1,2-dimethylnorbornyl cation is considered to parallel the diphenyl analogue while in the 2-methylnorbornyl cation σ-participation is significant.

We have examined[3] the carbocations generated from 2-endo-phenylborneol and 2-phenylborn-2-ene[4] in order to determine the effect of the 1-methyl substituent on π-p and σ-overlap. A common ion[5] was formed from these substrates below -40° which slowly rearranged to a second ion at -10°. The off-resonance $^{13}C$ spectrum of the ion formed below -40° is inconsistent with the structure of the expected ion **1** or the simple W-M rearrangement product **2**. The spectrum (see Table I) exhibits 3 methyl, 2 methylene, 3 methine, 1 quaternary, 1 cation carbon and 6 phenyl carbons, consistent with the structures **3** or **4**. The structure **4**, proposed earlier by Deno and Houser[6] as that of the ion formed from treatment of

TABLE I Carbon-13 Chemical Shifts and Assignments

| Ion 3[b] | | | | | | Ion 4 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $\delta^{13}$C ppm[a] | C-Type | Assignment | $\delta^{13}$C ppm[a] | C-Type | Assignment | $\delta^{13}$C ppm[a] | C-Type | Assignment | $\delta^{13}$C ppm[a] | C-Type | Assignment |
| $262.3_8$ | q-C$^{\oplus}$ | C-2 | $50.6_4$ | C-H | (C-4) | $225.5_4$ | q-C$^{\oplus}$ | (C-1) | $43.2_0$ | C-H | (C-3') |
| $153.0_8$ | C-H | *m*-C | $49.0_2$ | CH$_2$ | C-3 | $210.1_1$ | q-C$^{\oplus}$ | (C-3) | $34.7_9$ | C-H | (C-6) |
| $141.6_5$ | C-H | *o*-C | $41.3_6$ | CH$_2$ | C-7 | $144.1_9$ | C-H | C-2 | $30.0_9$ | CH$_2$ | (C-4)* |
| $140.6_2$ | C-H | *o*-C | $37.5_8$ | q-C | C-5 | $135.4_0$ | q-C | α-C-ϕ | $27.4_4$ | CH$_2$ | (C-5)* |
| $139.9_6$ | q-C | α-C-ϕ | $29.8_7$ | CH$_3$ | *exo*-CH$_3$<br>C-5' | $134.5_4$ | C-H | *o*-C | $21.2_2$ | CH$_3$ | C-6' |
| $132.1_0$ | C-H | *p*-C | $21.2_9$ | CH$_3$ | *endo*-CH$_3$<br>C-5' | $131.4_6$ | C-H | *m*-C | $20.5_2$ | CH$_3$ | C-3" |
| $68.2_3$ | C-H | C-1 | $14.2_3$ | CH$_3$ | C-6' | $129.4_1$ | C-H | *p*-C | $20.3_3$ | CH$_3$ | C-3" |
| $57.2_8$ | C-H | (C-6) | | | | | | | | | |

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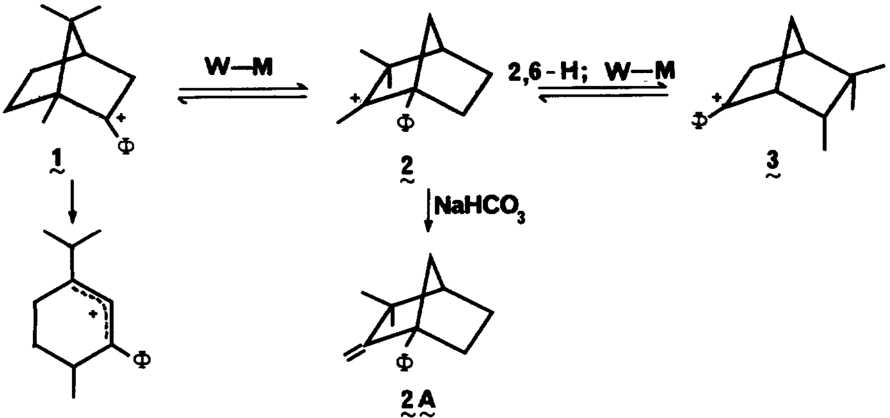
a. Given relative to TMS. Determined relative to internal CCl$_4$ 96.34 ppm downfield from TMS

b. Minor component exhibited a resonance at $261.3_8$ (q-C$^{\oplus}$). All other minor component resonances are unassigned.

Parentheses etc. indicate uncertainties in assignment between given pairs of lines.

TABLE II P.m.r. Data[3] for Ion 3

| Group | Shift δ (p.p.m.)[a] | Coupling Constants (Hz) | |
|---|---|---|---|
| C(2)phenyl | 8.47 ($W_{\frac{h}{2}}$ 24Hz) | | |
| | 7.98 ($W_{\frac{h}{2}}$ 18Hz) | | |
| C(1)H | 4.62 | $J_{1,6exo}$ | 4 |
| C(3)*exo*-H | 4.09 | $J_{3exo,3endo}$ | 22 |
| | | $J_{3exo,4}$ | 5.5 |
| C(3)*endo*-H | 3.95 | $J_{3endo,3exo}$ | 22 |
| C(6)*exo*-H | 3.04 | $J_{CH_3,6}$ | 7 |
| | | $J_{6,1}$ | 4 |
| C(4)H | 2.5 | $J_{4,3exo}$ | 5.5 |
| C(7)H$_2$ | 1.83 ($W_{\frac{h}{2}}$ 5Hz) | | |
| C(5)*exo*-CH$_3$ | 1.23 | | |
| C(5)*endo*-CH$_3$ | 0.76 | | |
| C(6)CH$_3$ | 0.64 | $J_{6,CH_3}$ | 7 |



Scheme 1

2-phenyl-borneol with $H_2SO_4$ at room temperature, can be eliminated. Indeed the proton and $^{13}C$ spectra of the ion obtained at -10°, in the present work, are identical to those obtained for the Deno and Houser ion 4.

The structure 3 is, therefore, proposed for the ion generated from 2-endo-phenylborneol and 2-phenylborn-2-ene at -70° - -40°. The identity of this ion follows further from the p.m.r. spectrum (Table II); C(1)H, deshielded by the C(2)-carbocation, is coupled (J 4Hz) to C(6)exo-H which is coupled (J 7Hz) to methyl - $C(3)H_2$ appears as an AB quartet with the downfield proton (exo) further coupled to C(4)H. Quenching of the ion at -70° using dilute sodium bicarbonate in $SO_2ClF$ results in the formation of the olefin 2A[4]. It is noteworthy that the ion 3 can also be independently generated from an authentic sample of 2A[4] on treatment with $HSO_3F$ at -70°.

Formation of ion 3 from 2-endo-phenylborneol in $HSO_3F$ - $SO_2ClF$ at -70° arises by a W-M shift to ion 2, followed by a 2,6-hydride and W-M shift as shown in scheme 1. The stability of ion 3 at this temperature reflects the tertiary benzylic nature of this ion and the absence of non-bonded interaction between phenyl and C(1)-methyl. This latter interaction, present in ion 1, will result in twisting of the phenyl group with consequent reduction in p-π orbital overlap and accounts for the failure to observe this ion. The reversible equilibrium between ions 2 and 3 is established by quenching of ion 3 at -70° to give olefin 2A and by formation of ion 3 from this olefin. The irreversible formation of ion 4 at -10° probably arises *via* ion 1[7].

At this temperature the system has sufficient energy to overcome the energy barrier to form this thermodynamically stable ion.

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3. $^1H$ and $^{13}C$ spectra were determined on a Bruker HFX90 spectrometer in the Fourier mode for solutions in $HSO_3F$, $SO_2ClF$ using $CDCl_3$ or $CD_2Cl_2$ lock and $CCl_4$ as internal reference.
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5. A minor component (ca. 10%) is observed in the decoupled $^{13}C$ spectrum. The paucity of data precludes identification of this species, though the shift of the carbonium ion carbon (261.4 ppm) suggests a phenyl (**1**) rather than methyl (**2**) stabilized species. See ref. 2 and G.A. Olah and G. Liang, J.Amer.Chem.Soc., 96, 189 (1974).
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