

Retention of Configuration at the Tetragonal Migrating Carbon Atom for 1,2-Shift Processes in Long-lived Carbonium Ions

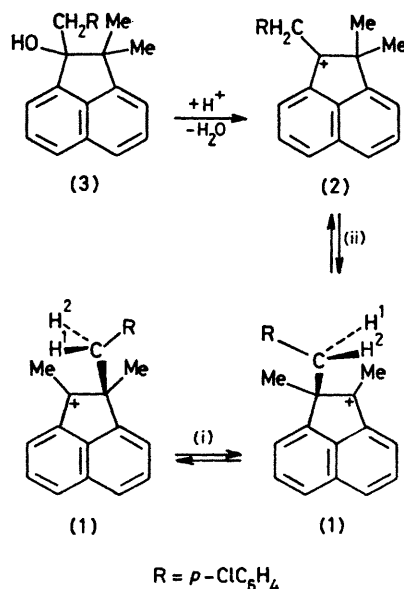
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Summary From a study of the degenerate 1,2-shift of the *p*-chlorobenzyl group in 2-(*p*-chlorobenzyl)-1,2-dimethyl-1-acenaphthenium ion (1) it follows that the configuration at the tetragonal migrating carbon atom is retained.

ONE aspect which is of particular importance in theories of carbonium ion sigmatropic rearrangements proceeding by a 1,2-shift is the stereochemistry at the migrating centre. It has been shown that in the pinacol¹ and related rearrangements² the migrating group retains its configuration (*cf.* ref. 3). However, these investigations concern reactions in which the 1,2-shift and the loss of anion are probably concerted or the anion is associated with an intermediate. For these reasons the stereochemical result of such reactions may prove to be distorted (*cf.* ref. 4).

We have studied the stereochemistry at the migrating tetragonal carbon atom during degenerate 1,2-shifts in 'long-lived' carbonium ions. Our studies were based on the diastereotopy of the methylene protons in the migrating group CH_2R attached to a chiral carbon atom of the rearranging carbonium ion.

2-(*p*-Chlorobenzyl)-1,2-dimethyl-1-acenaphthenium ion (1) was taken as a model for the study and was generated in FSO_3H at -20°C through the rearrangement of the acenaphthenium ion (2), which in turn was prepared from



the acenaphthenol† (3) at -70°C . The ^1H n.m.r. spectral data of the ions (1) and (2) are listed in the Table. Some differences between the chemical shifts for the ions (1) and

† Satisfactory analytical and spectral data were obtained for this compound.

TABLE. ^1H N.m.r. data for the ions (1), (2), and (4) in FSO_3H^a

Ion	Temperature/ $^\circ\text{C}$	2-Me	1-Me	CH_2	$p\text{-ClC}_6\text{H}_4$	3-H—8-H
(1)	-15	8.07	6.49	6.53 6.23 ^c (J 13.3 Hz)	3.23, 2.99 ^c (J 8.2 Hz)	1.6—2.1 (m, 3-H—5-H, 7-H) 1.06 (d, J 8.0 Hz, 8-H or 6-H), 0.78 (d, J 7.6 Hz, 6-H or 8-H)
(2)	-40	8.11	—	5.03	2.57, 2.48 ^c (J 8 Hz)	1.5—2.2 (m, 3-H—5-H, 7-H, 8-H or 6-H), 0.73 (br d, 6-H or 8-H)
(4) ^b	30	8.07	6.53	—	—	1.5—2.1 (m, 3-H—5-H, 7-H) 0.93 (d, J 8.0 Hz, 8-H or 6-H), 0.69 (d, J 7.7 Hz, 6-H or 8-H)

^a Referred to internal CH_2Cl_2 taken as τ 4.67. ^b From ref. 6 ^c AB-Type system.

(2) and those for 1,2,2-trimethyl-1-acenaphthium ion (4)^{5,6} are not unexpected and result from the influence of the p -chlorophenyl group.

It is reasonable to expect the ion (1) to undergo degenerate rearrangement by a 1,2-shift of the p -chlorobenzyl group (cf. refs. 6,7). Indeed, as the temperature is raised to 0°C ,[†] reversible broadening of the signals of the Me groups and of

the acenaphthene ring protons is observed (Figure). The signals of the two methylene protons also undergo a similar change, the rate constants obtained from the line-shape analysis of these signals and of the singlets of the Me groups being essentially equal [$k(\text{CH}_3; 0^\circ\text{C}) = 10.2 \text{ s}^{-1}$, $k(\text{CH}_2; 0^\circ\text{C}) = 10.4 \text{ s}^{-1}$].[§] These data strongly support retention of configuration at the methylene carbon atom in the migrating p -chlorobenzyl group during the rearrangement [pathway (i)] and are in accordance with the orbital symmetry predictions.^{8¶}

An intermolecular exchange of the p -chlorobenzyl group could be an alternative process. However, such an exchange process appears not to occur as 4-fold dilution of the solution does not alter the temperature-dependent ^1H n.m.r. spectra. Another alternative mechanism involving an intramolecular 1,2-methyl shift [pathway (ii)] is not significant since the free activation energy for the transformation of the ion (2) to (1), determined from the ^1H n.m.r. spectra [$\Delta G^\ddagger (-28^\circ\text{C}) = 72.7 \pm 0.1 \text{ kJ mol}^{-1}$] greatly exceeds that for p -chlorobenzyl migration [pathway (i), $\Delta G^\ddagger (0^\circ\text{C}) = 61.4 \pm 0.4 \text{ kJ mol}^{-1}$]. The high value of the migration tendency of the p -chlorobenzyl group relative to that of the methyl group⁶ [$k(p\text{-ClC}_6\text{H}_4\text{CH}_2)/k(\text{Me}) = \text{ca. } 10^3$ at 0°C] is interesting. It may result from the smaller bond dissociation energy of $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{-C}$ in the ion (1) as compared with that of $\text{CH}_3\text{-C}$ in the ion (4) (cf. ref. 9) and also from the additional stabilization of the transition state of the p -chlorobenzyl shift due to charge delocalization on the p -chlorophenyl group (cf. ref. 10).

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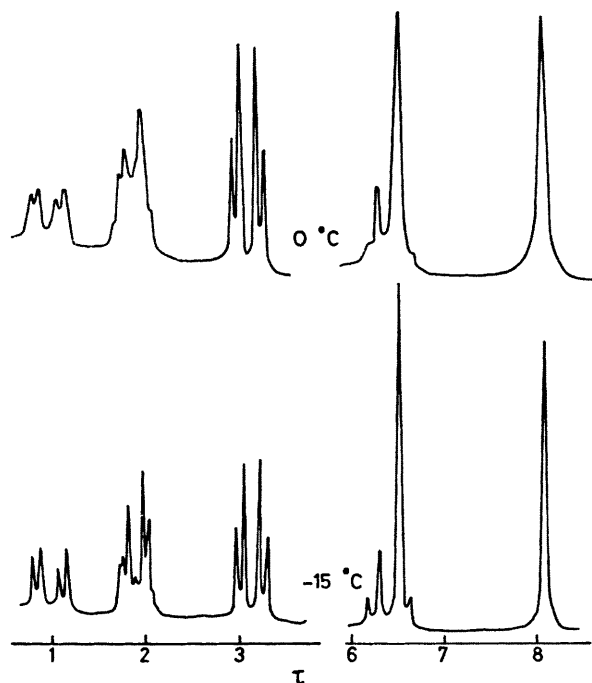


FIGURE. ^1H N.m.r. spectra (100 MHz) of the ion (1).

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[†] At higher temperatures the ion is unstable.

[§] The average deviations of these rate constants were within $\pm 11\%$.

[¶] Similar conclusions were drawn from data obtained in $\text{CF}_3\text{SO}_3\text{H-SO}_2\text{FCl}$.

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