Rearrangement of *r*-5-methyl-*c*-2-(trimethylsilyl)cyclohexan-*t*-yl 2,4-dinitrobenzoate in Chloroform

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Isomerisation of the title compound **3** to the ester **4** in deuteriochloroform is believed to occur *via* rearrangement of an intermediate β -trimethylsilyl substituted carbocation, with subsequent capture by the 2,4-dinitrobenzoate anion.

We recently investigated the conformational equilibria of a range of conformationally mobile β -trimethylsilyl esters 1 using the coupling-constant method.¹ These esters were shown to have a strong preference for the diaxial conformation 1a, in contrast to predictions from molecular mechanics which suggested that the diequatorial conformation 1b should be more stable. This was interpreted as being the result of stabilising σ_{C-Si} - σ^*_{C-O} interactions which are maximised in the diaxial conformation.

We noticed that the esters derived from moderately strong carboxylic acids ($pK_a RCO_2 H < 3.5, e.g. R = CHCl_2, CCl_3$, CF₃, 3,4-dinitrophenyl, 2,4-dinitrophenyl) slowly decomposed over several hours in deuteriochloroform solution to give a mixture of 4-methylcyclohexene as the major product along with varying amounts of an isomeric β-trimethylsilyl substituted ester 2 (10-30%). For example a solution of the 2,4-dinitrobenzoate ester 3 in CDCl₃ rearranged within 24 hours at room temperature to give a mixture of 4-methylcyclohexene (90%) and the isomeric 2,4-dinitrobenzoate ester 4 (10%) as the only products along with trimethylsilyl 2,4-dinitrobenzoate, the proportion of cyclohexene to the isomeric ester remained constant throughout the rearrangement. The structure of 4 was tentatively assigned on the basis of the ¹H NMR, in which 1-H appeared as a triplet (10 Hz) of doublets (3.8 Hz) (total coupling 27.6 Hz) consistent with two diaxial vicinal couplings and one axial-equatorial coupling; these couplings contrasted to those observed for 3 in which 1-H appeared as a narrow multiplet (total coupling = 11.2Hz), consistent with the assigned diaxial conformation 1a.1 The structure of 4 was subsequently confirmed by a single crystal X-ray analysis (Fig. 1).†

A plausible mechanism for this rearrangement is outlined in Scheme 1. Heterolysis of the C-O bond of 3 in the reactive diaxial conformation occurs with assistance from the trimethylsilyl substituent² (there is good structural evidence that C-O bonds which are disposed anti to a trimethylsilyl substituent are lengthened and hence weakened relative to C-O bonds which are disposed gauche to a trimethylsilyl substituent),³ giving an intermediate cationic species stabilised by the silicon substituent. The structure of the initially formed cation is likely to be the classical open cation $a^{4,5}$ which is stabilised by hyperconjugation with the C–Si σ bond, this cation can rearrange to the classical open cation c by a 1,2 silicon migration through the intermediate silacyclopropylium cation **b** which is expected to have higher energy.⁵ The open cation c must exist in either a boat or twist boat conformation with the trimethylsilyl substituent in a pseudo axial position to



benefit from overlap between the C-Si bond and the carbocation p orbital. Reaction of these intermediate cations with the 2,4-dinitrobenzoate counterion can conceivably follow two pathways: either attack of the counterion at the silicon which leads to the major, elimination, product 4-methylcyclohexene and trimethylsilyl 2,4-dinitrobenzoate (evidence from laser flash photolysis studies suggest that elimination of silicon from $\hat{\beta}$ -silyl carbocations occurs with nucleophilic assistance)^{6,7} or attack at carbon. Attack at carbon on cation a is likely to occur from the face opposite to the bulky trimethylsilyl substituent for steric reason and because this approach would allow effective overlap to occur between the C-Si σ orbital and the σ^* orbital of the developing C-O bond, and this path would result in return to the starting ester 3. Attack at carbon on the silacyclopropylium cation b can result in return to 3 (path i) or formation of the isomeric dinitrobenzoate ester 4 (path ii). Attack on the cation c is expected to occur from the face opposite to the trimethylsilyl substituent to give the isomeric ester 4 (for the same reasons discussed above for capture of cation a). The isomeric ester 4 is significantly more stable than the reactive ester 3² and does not undergo return to the cation under these conditions, a process which would ultimately result in complete conversion to a mixture of 4-methylcyclohexene and trimethylsilyl 2,4dinitrobenzoate.

This is the first reported example of the isomerisation of a β -trimethylsilyl ester, and we believe this to be the result of rearrangement of the intermediate β -trimethylsilyl substituted carbocation from the initially formed open cation **a**, to the open cation **c**, *via* the silacyclopropylium cation **b**. It is not possible to conclude whether the isomeric ester **4** arises from capture of cation **b** or cation **c** by the dinitrobenzoate anion or whether both pathways are involved, however calculations on simple secondary systems⁵ and kinetic studies⁴ on closely



Scheme 1 Proposed mechanism for rearrangement of 2,4-dinitrobenzoate ester 3 to a mixture of 4-methylcyclohexene and the isomeric ester 4



Scheme 2 Reaction of deuterium labelled 2-trimethylsilylethanol with phosphorus tribromide

related systems, suggest that the cation **b** is likely to be less stable than the open cations a and c. This would suggest that ester 4 most likely arises from capture of the open cation c by the 2,4-dinitrobenzoate counterion. This is not the first example of an implied facile rearrangement of a β -silyl carbocation, indeed such a result is suggested in the conversion of the deuterium labelled alcohol 5 to a mixture of the deuterium scrambled bromides 6 and 78 (Scheme 2) upon treatment with phosphorus tribromide. However, in contrast to predictions that the open cation is the most stable structure of the secondary cations above,⁵ the opposite is observed for the primary system 8 where the bridged cation 8b is predicted to be slightly more stable.9 Therefore the bromides 6 and 7 most likely arise from Br- attack on the bridged cation 8b, rather than 8a or 8c, in contrast to the isomerisation of the ester 3 to 4, which we believe arises from nucleophilic attack on the open cation **c**.



Fig. 1 Thermal ellipsoid plot of the isomeric ester 4 at 130 K, ellipsoids are drawn at 50% probability level

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Footnote

⁺ Crystal data for 4: C₁₇H₂₄N₂O₆Si, M = 380.47, triclinic $P\overline{1}$, a = 7.719(1), b = 8.677(3), c = 16.941(7) Å, $\alpha = 78.63(2)^{\circ}$, $\beta = 79.70(2)^{\circ}$, $\gamma = 65.32(2)^{\circ}$, U = 1004.8(6) Å³, Z = 2, $D_c = 1.27$ g/cm³, μ (Mo-Kα) = 1.5 cm⁻¹, R = 0.069 for 2304 observed data [$I \ge 2.0 \sigma$ (I)]. Enraf-Nonius CAD-4Machs single crystal diffractometer (graphite crystal monochrometer, $\lambda = 0.71069$ Å) at 130 K (using an Oxford Cryostream cooling device) in the ω-2θ scan mode, $2\theta_{max} = 55^{\circ}$. Solution by direct methods (SHELXS 86¹⁰) and refinement using SHELXL-93¹¹. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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