

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.

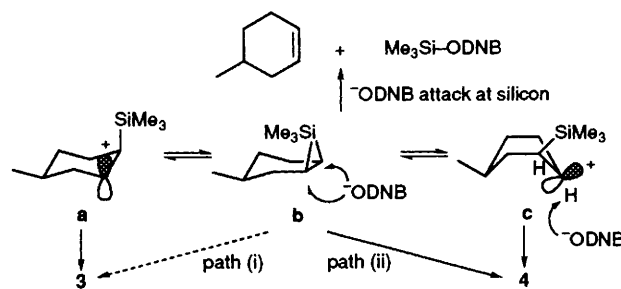
We recently investigated the conformational equilibria of a range of conformationally mobile β -trimethylsilyl esters **1** using the coupling-constant method.¹ These esters were shown to have a strong preference for the diaxial conformation **1a**, in contrast to predictions from molecular mechanics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

We noticed that the esters derived from moderately strong carboxylic acids (pK_a $RCO_2H < 3.5$, *e.g.* $R = CHCl_2, CCl_3, CF_3, 3,4$ -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 $CDCl_3$ 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 = 11.2 Hz), consistent with the assigned diaxial conformation **1a**.¹ The structure of **4** was subsequently confirmed by a single crystal X-ray analysis (Fig. 1).[†]

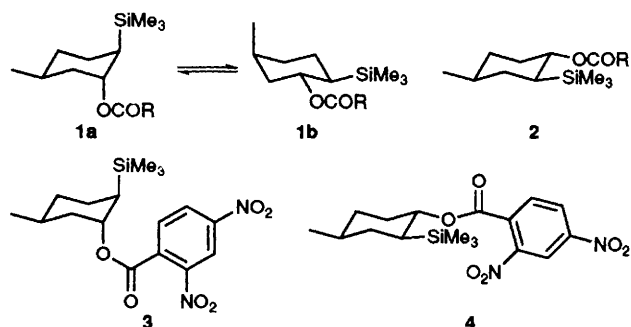
A plausible mechanism for this rearrangement is outlined in Scheme 1. Heterolysis of the C–O bond of **3** in the reactive diaxial conformation occurs with assistance from the trimethylsilyl substituent² (there is good structural evidence that C–O bonds which are disposed *anti* to a trimethylsilyl substituent 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 silacyclopropyl 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 β -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 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 silacyclopropyl 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 **3**² 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 2,4-dinitrobenzoate.

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 silacyclopropyl 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 **7**⁸ (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**.

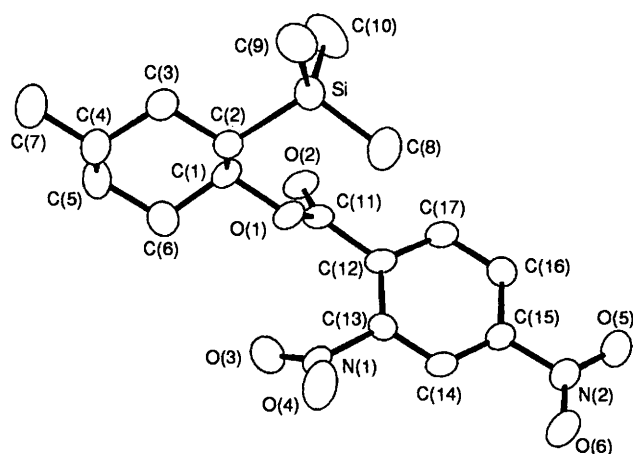


Fig. 1 Thermal ellipsoid plot of the isomeric ester **4** at 130 K, ellipsoids are drawn at 50% probability level

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Footnote

† Crystal data for **4**: C₁₇H₂₄N₂O₆Si, *M* = 380.47, triclinic *P* $\bar{1}$, *a* = 7.719(1), *b* = 8.677(3), *c* = 16.941(7) Å, α = 78.63(2)°, β = 79.70(2)°, γ = 65.32(2)°, *U* = 1004.8(6) Å³, *Z* = 2, *D_c* = 1.27 g/cm³, μ (Mo-K α) = 1.5 cm⁻¹, *R* = 0.069 for 2304 observed data [*I* \geq 2.0 σ (*I*)]. Enraf-Nonius CAD-4Machs single crystal diffractometer (graphite crystal monochromator, λ = 0.71069 Å) at 130 K (using an Oxford Cryostream cooling device) in the ω -2 θ scan mode, 2 θ_{\max} = 55°. 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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