Imino Diels–Alder Reaction of 2-t-Butyldimethylsilyloxycyclohexadiene: Isolation of an Azabicyclo[2.2.2]octene Silyl Enol Ether Adduct

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The imino Diels–Alder reaction of (**1**) with 2-t-butyldimethylsilyloxycyclohexadiene (**2**) gave after acidic work-up mainly the bicyclic enol ethers (**5a**) (for which a novel *X*-ray crystal structure determination is reported) and (**5b**) together with small amounts of bicyclic ketones (**3a,b**) and cyclohexenones (**4a,b**).

In the previous paper we reported the addition of trimethylsilyloxycyclohexadiene to the imine (**1**) to give, after acidic work-up, either azabicyclo-octanones or cyclohexenone derivatives according to the conditions.[1] The corresponding reaction with 2-t-butyldimethylsilyloxycyclohexadiene (**2**)[2] showed a similar dependence upon conditions, but also yielded substantial quantities of bicyclic silyl enol ether adducts. Thus the reaction in benzene (6 °C, 3 h) gave in 69% overall yield (**3a**), (**3b**), (**4a**), (**4b**), (**5a**),† and (**5b**)† in the relative ratio 4 : 3 : 28 : 2 : 61 : 3.‡

Crystalline silyl enol ethers are relatively rare. The *exo*-ester enol ether (**5a**) was obtained as crystals (colourless cubes, m.p. 98—99 °C, from dichloromethane–hexane) suitable for *X*-ray diffraction.¶ The structure is shown in Figure 1. The bond lengths and angles compare well in general with the only other reported crystal structure of a t-butyldimethylsilyl enol ether,[3] with the exception of the torsion angle Si(1)–O(3)–C(5)–C(6) which is 155° in (**5a**) and 101° in the previously determined structure. This suggests that in (**5a**) the σ(Si-O)-π(C=C) overlap is reduced, and the n(O)-σ*(C=C) is increased,[4] although packing factors cannot be ruled out as an alternative explanation. The nitrogen atom is planar, similar to the structure discussed in the preceding paper.[1] The equivalent torsion angle S(1)–N(1)–C(3)–C(4) is 160.6°.

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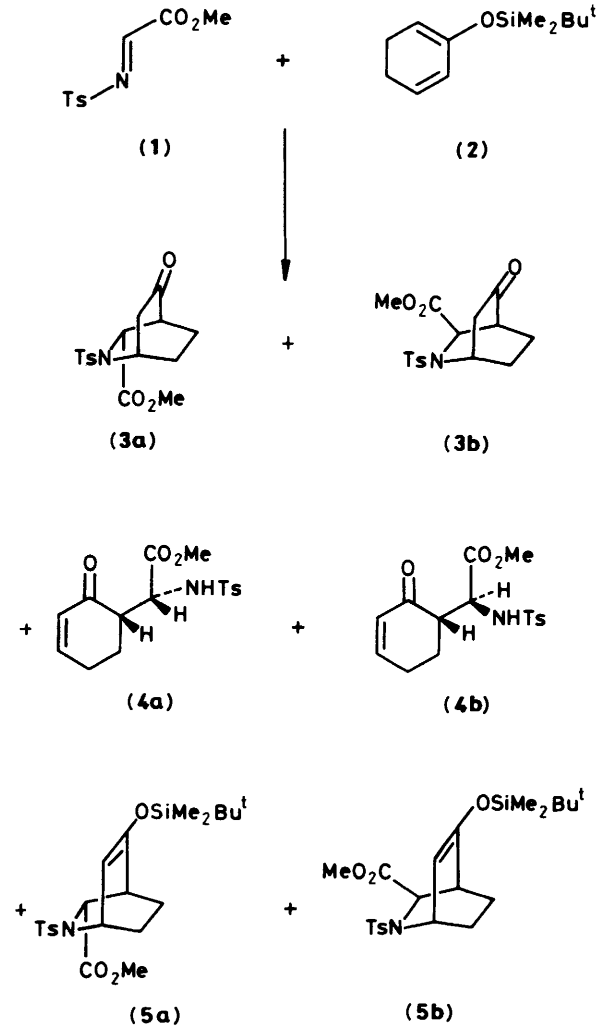
† All new compounds exhibited spectroscopic data in accordance with the assigned structure. ^{1}H N.m.r. data (CDCl$_3$, 250 MHz) for (**5a**): δ −0.13 (3H, s), −0.03 (3H, s), 0.82 (9H, s), 1.0—2.2 (4H, m), 2.41 (3H, s), 2.70 (1H, m), 3.80 (3H, s), 3.93 (1H, dd, *J* 2.6, 1.1 Hz), 4.35 (1H, m), 4.79 (1H, dd, *J* 6.2, 2.1 Hz), 7.3 and 7.7 (4H, AA'BB', *J* 10 Hz).

‡ The formation of the ketones (**3a,b**) was unexpected as the acid work-up (20% solution of 0.005 M HCl in tetrahydrofuran) conditions were sufficiently mild not to have hydrolysed the silyl enol ether.

¶ *Crystal data* for (**5a**): $C_{22}H_{33}NO_5SSi$, M = 451.64, monoclinic, space group $P2_1/a$ (alternative setting of $P2_1/c$, no. 14), a = 12.208(6), b = 17.768(5), c = 12.375(4) Å, β = 114.58(3)°, U = 2447 Å^3, D_c = 1.226 g cm^{-3}, Z = 4, μ = 18.76 cm^{-1}, $F(000)$ = 968. 3966 reflections measured ($5 \leqslant 2\theta \leqslant 120°$) on a Nicolet R3mμ diffractometer, averaged to give 2631 unique observed reflections with $F \geqslant 4\sigma(F)$. Structure solved by direct methods, and refined by blocked-cascade least squares, with all non-hydrogen atoms anisotropic, to R and R_w values of 0.087 and 0.085. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



Ts = p-$MeC_6H_4SO_2$

The results of a systematic variation of solvent, temperature, and Lewis acid on the outcome of the reaction of (**1**) with (**2**) resemble the pattern reported for the trimethylsilyl analogue of (**2**), but with several important differences. Firstly, the *exo*/*endo* ratio of bicyclic adducts derived from (**2**) is greater than that for the trimethylsilyl analogue, and secondly, there is a corresponding greater preference for (**4a**) over (**4b**). Under certain low temperature conditions only cyclohexenone products (**4a,b**) and no bicyclic products were obtained. Hydrolysis of the hindered bicyclic silyl enol ether (**5a**) under relatively forcing conditions (AcOH–THF, 50 °C) barely produced any retro-Michael product (**4b**). These observations are consistent with (**3a**) and (**5a**) being derived from a [2 + 4] transition state in which the unfavourable steric interaction between the *N*-tosyl and t-butyldimethylsilyl groups is minimised,[5] while (**4a**) is derived from an open transition state in which the bulky silyl substituent avoids the steric clash with the ester group of the imine (**1**). Thus the proposed mechanism (c) in the previous paper,[1] involving a dual pathway explanation[6] for the origin of bicyclic and monocyclic products, seems to be supported in the present study.

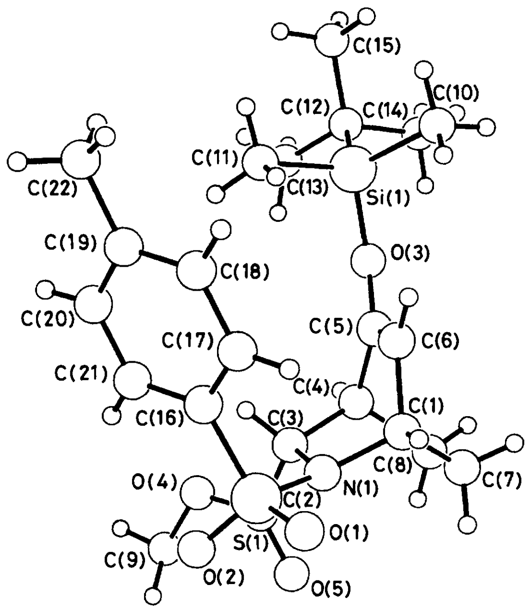


Figure 1. The structure of the *exo* silyl enol ether (**5a**).

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