

Metalation of Olefinic Positions in Norbornadiene: Enhancement and Attenuation of Kinetic CH-Acidities by a Neighboring Enesilane Moiety**

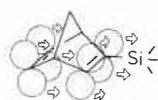
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Abstract: When treated with butyllithium in the presence of sodium or potassium *tert*-butoxide, 2-trimethylsilyl- and 2-triethylsilyl-norbornadiene undergo hydrogen/metal-exchange mainly at the 5-position. The latter position is found to be slightly activated relative to unsubstituted norbornadiene while the two other olefinic positions prove to be quite inert. Two side reactions are observed: the metalation of silicon-attached methyl groups and the replacement of the entire trialkylsilyl group by a metal atom.

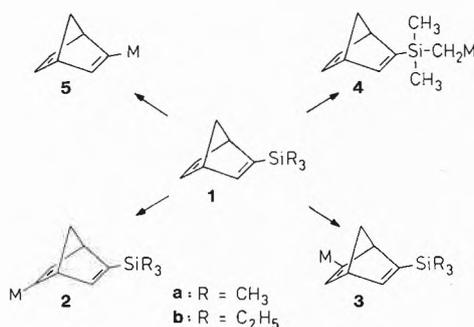
In a previous communication^[1] we have reported the abnormally high reactivity of olefinic sites which undergo transmetalation when activated by additional double bonds located in their vicinity (generally, occupying a homo-conjugated position). This enhancement of kinetic CH-acidity was tentatively attributed to a «polarizing effect» involving a deformation or receding of π -electron clouds^[2]. As bond length increases, as with second-row elements, for example, n - or π -electrons expand more readily, thus possibly amplifying this polarizing effect. To test this hypothesis we now have studied silylated norbornadienes (bicyclo[2.2.1]hepta-2,5-dienes) as substrates in metalation reactions.

1b, 88% and 79%, respectively) have been prepared by metalation^[1, 3] of norbornadiene and subsequent treatment with chlorotrimethylsilane or chlorotriethylsilane. They were found to react with «superbasic»^[4] organometallics in several different, competitive ways (see Table 1):

- hydrogen/metal-exchange at the 5- and 6-position affording new organometallic intermediates **2** and **3**;
- metalation of silicon-attached methyl groups (in **1a**) leading to the α -metalated silane **4**^[5];
- metalloïd/metal-exchange replacing the trialkylsilyl moiety to produce again a 2-norbornadienylmetal compound **5**.



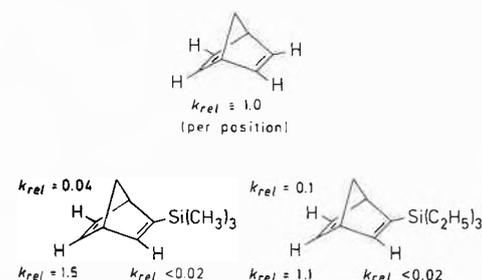
The starting materials, 2-trimethylsilyl- and 2-triethylsilyl-norbornadiene (**1a** and



To our knowledge the latter reaction, the electrophilic abstraction of a trimethylsilyl or triethylsilyl group from an 1-alkenyl position by the action of an organometallic reagent, is without precedent^[6]. Note-

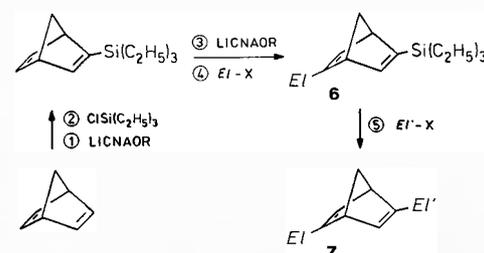
worthy is also the superior performance (see Table 1) of butyllithium in the presence of sodium *tert*-butoxide («LICNAOR»^[1]) when compared with butyllithium in the presence of potassium *tert*-butoxide («LICKOR»). This difference may reflect the greater aptitude of the smaller metal to enter a four-center type transition state^[1, 7] or merely the better chemical stability of the «LICNAOR»-reagent, for example towards hydride elimination.

Competitive experiments between **1a** and **1b** as well as between norbornadiene and **1b** enabled us to determine the relative rates of hydrogen/metal-exchange at various olefinic positions. Trimethylsilyl-norbornadiene **1a** was found to be 1.7 times as reactive towards «LICNAOR» in hexane medium than its triethylsilyl analog **1b** and half as reactive as the unsubstituted bicyclic diene. When the partial rate factors were evaluated, positions 5 of **1a** and **1b** indeed turned out to be activated, although only slightly. In contrast, positions 6 and, of course, 3 were found to be considerably deactivated.



Evidently trialkylsilyl groups do polarize the double bonds of norbornadiene and thus facilitate the hydrogen/metal-exchange at the most distant position. At the same time, however, they exert a stronger reaction-retarding effect on the two other olefinic positions. Its origin remains still to be clarified; steric screening certainly plays a major, but not exclusive role.

The high regioselectivity with which the «LICNAOR»-reagent attacks the 5- rather than the 6-positions of **1a** or **1b** offers a convenient entry to the synthesis of 2,5-disubstituted norbornadienes (**7**). After introduction of the first electrophile (affording intermediate **6**) the trialkylsilyl group can be replaced by a wide variety of other electrophiles^[9].



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Table 1. Metalation of 2-trimethylsilyl- and 2-triethylsilyl-norbornadiene (**1a** and **1b**, respectively) with organometallic «superbases»: product composition ^{a)}.

sub- strate	reagent (2 equiv.) ^{b)}	solvent; temp. c)	recov'd 1	deriv. of 2	deriv. of 3	deriv. of 4	deriv. of 5
1a	LICNAOR	HEX, +25°C	29 %	33 %	0.8 %	1 %	11 %
1a	LICNAOR	THF, -50°C	21 %	24 %	13 %	11 %	16 %
1a	LICKOR	THF, -50°C	9 %	14 %	18 %	6 %	44 %
1b ^{d)}	LICNAOR	HEX, +25°C	18 %	55 %	5 %	-	-
1b	LICNAOR	THF, -50°C	35 %	37 %	16 %	-	-
1b	LICKOR	THF, -50°C	11 %	41 %	14 %	-	8 %

^{a)} In all runs 5 mmol of substrate (**1a** or **1b**), 10 mmol of metalating agent (LICNAOR or LICKOR) and 15 mL of solvent (HEX = hexane fraction of petroleum ether, THF = tetrahydrofuran) were employed. The heterogeneous mixtures obtained in hydrocarbon medium were vigorously stirred during 75 h until precooled THF (10 mL) and chlorotriethylsilane (for reactions with **1a**) or chlorotrimethylsilane (for reactions with **1b**) were consecutively added at -75 °C. The THF solutions were simply kept 40 h in a cryostatic bath before quenching with the respective chlorosilane. Product composition was analyzed on two different gas chromatographic columns (2 m Apiezon-L; 25 m SE-30 [capillary]) using tetradecane as an «internal standard». All new compounds (derivatives of **2**, **3**, **4** and **5**), were isolated by distillation and preparative gas chromatography; they were identified by combustion analysis, NMR spectroscopy, and mass spectrometry: 2-trimethylsilyl- and 2-triethylsilyl-norbornadiene,

2,5- and 2,6-bis(trimethylsilyl)-norbornadiene, 5- and 6-triethylsilyl-2-trimethylsilyl-norbornadiene, 2-[dimethyl(trimethylsilylmethyl)silyl]methyl-norbornadiene and 2-[dimethyl(triethylsilylmethyl)silyl]methyl-norbornadiene.

^{b)} In general, 2.0–3.5 mmol (0.4–0.7 equiv.) of LICNAOR-, but only 0.01–0.02 mmol (0.02–0.04 equiv.) of LICKOR-reagent remained unconsumed at the end of the reactions and were trapped as butyltrimethylsilane or butyltriethylsilane. What happened to the rest is unknown. Fragmentation of the bicyclic ring skeleton in a Diels-Alder retro-fashion^[8] can be ruled out under the chosen reaction conditions. On the other hand, decomposition of the organometallics due to metal hydride elimination appears quite probable. With only 1 equivalent of LICNAOR or LICKOR roughly 60% and 40%, respectively, of the starting material (**1a** or **1b**) was recovered. However the yield did not significantly change if a further excess of metalating reagent (e.g., 4 equiv.) was used.

^{c)} LICKOR reactions which were performed at -75 °C gave quite similar results.

^{d)} When the metalation time was doubled (150 h), only 7% of starting material **1b**, but 62% of product **2b** together with 4.5% of its isomer **3b** were obtained. In either case, however, prolonged exposure time improved neither the yields nor the ratios of products.

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