

On the Reaction of Silylperoxides with Carbanions.

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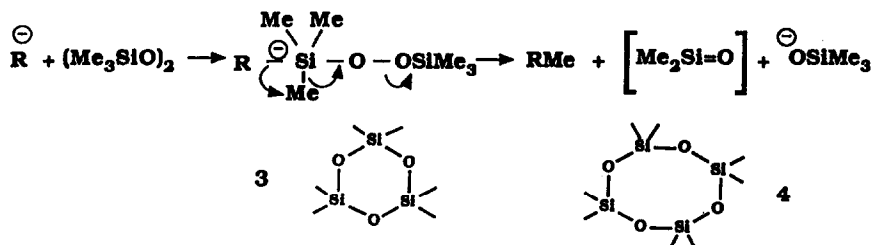
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Abstract: Silylperoxides **1a-f** react with organolithiums **2,5,9** and **11** giving alkylation products, silylethers or silanes depending upon substitution on the silicon. A hypervalent silicon intermediate is proposed.

We have recently shown¹ that bistrimethylsilylperoxide **1a**, when treated with certain stabilized carbanions, may act as a methylating agent other than as a synthetic equivalent of Me_3SiO^+ and OH^+ .² This intriguing and unprecedented demethylation reaction of **1a** drove us to study it in more details and to extend the investigation to other silylperoxides.

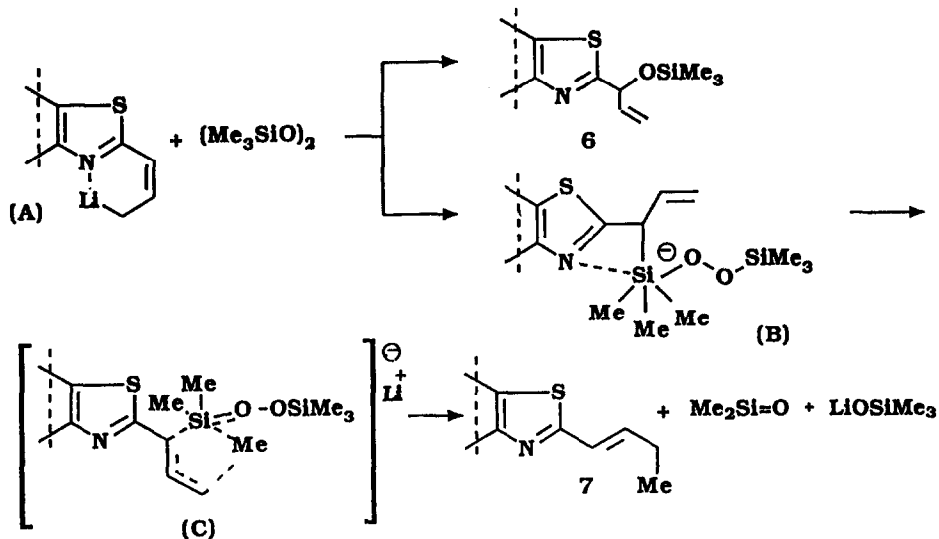
First of all, the possibility that the methylation of the abovementioned carbanions by MeOSiMe_3 or $\text{MeOMe}_2\text{SiOSiMe}_3$, eventually formed from **1a**, could definitively be ruled out as no reaction occurred when 2-benzothiazolymethylithium (BTCH_2Li) **2** was treated with MeOSiMe_3 , prepared from Me_3SiCl and NaOMe , or with $\text{MeOMe}_2\text{SiOSiMe}_3$, prepared by treating $\text{MeOMe}_2\text{SiCl}$ with NaOSiMe_3 . We may tentatively rule out also the involvement of a radical process in the demethylation of **1a** as in the reaction with **2** we did not observe the formation of $\text{BTCH}_2\text{CH}_2\text{BT}$ that would derive from the coupling of two BTCH_2 radicals.

The demethylation of **1a** might be envisaged as due to the nucleophilic attack of the carbanion to one of the methyl groups linked to silicon thus promoting an elimination reaction that would produce the dimethyl silanone upon removal of the trimethylsilylanolate.¹ This sounds unusual as the occurrence of a methyl transfer involving C-Si bond cleavage in a silicon compound as a consequence of nucleophilic attack at the methyl group has been mentioned hitherto only rarely.³ A likely explanation for the demethylation of **1a** by **2** takes into consideration the nucleophilic attack of the carbanion on the silicon leading to a hypervalent silicon



intermediate that could then produce the methylation product through migration of the newly entered R group from silicon to one of the methyl groups with subsequent displacement of dimethyl silanone and silanolate.

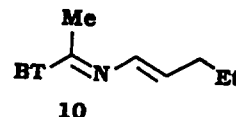
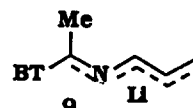
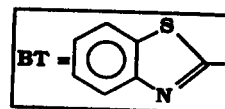
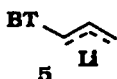
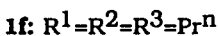
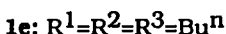
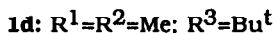
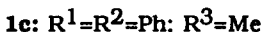
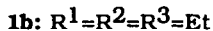
The possibilities shown above for the demethylation of **1a** need to be substantiated first of all by the detection or the trapping of the dimethyl silanone. Indeed, we have been able to trap it as the trimer **3** and the tetramer **4** in the reaction of **1a** with **2**.⁴ Moreover, we have found that the reaction of **1a** with an ambident anion such as 2-benzothiazolylallyllithium **5**⁵ proceeds in a regioselective and stereoselective manner leading to the silyloxylation product **6** and the methylation product **7** (trans).



To rationalize the outcome of this reaction we suggest that form (A) of **5**, stabilized by intramolecular chelation,⁵ reacts with **1a** with allylic rearrangement through the a carbon of the allylic chain attacking the peroxidic oxygen, to give the silyl ether **6** upon displacement of the trimethylsilanolate, and the silicon to produce the pentavalent silicon intermediate (B) that then goes to the alkene **7** via migration of the benzothiazolylalkenyl group yet with allylic rearrangement from silicon to one of the methyl groups, passing through a five-membered cyclic transition state (C) in which the geometry of the double bond of **7** is already fixed in a trans arrangement. It is worth pointing out that the heterogroup which provides stabilization to the carbanion must be playing an important role as we have found that the abovementioned demethylation of **1a** does not take place with aryl, alkyl and vinyl carbanions.⁶ We may suppose that the heterogroup provides coordinative assistance to the silicon in the hypervalent silicon intermediate.

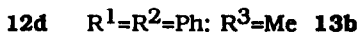
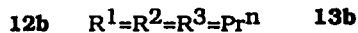
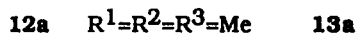
In order to get more informations on the demethylation of **1a** we have also prepared some other silylperoxides and studied their reactions with some carbanions. All the new peroxides were prepared according to the procedure

described for **1a**⁷ and characterized by NMR and GC-MS.⁸ We have found that **2** reacts with bistriethylsilylperoxide **1b** giving almost exclusively 2-n-propyl-BT **8c**. Moreover, the 2-azapentadienyllithium **9** underwent regio and stereoselective ethylation to give **10** upon treatment with **1b**. In contrast, **2**, upon treatment with bisdiphenylmethylsilylperoxide **1c**, under the usual experimental conditions, afforded a mixture of the silane **8d** and the silyl ether **8e** (Table). Similarly, the reaction of **2** with **1d** gave a mixture of the silane **8f** and silyl ether **8g**, while the reaction with **1e** gave mainly silyl ether **8i**. In none of the last three peroxides was observed dealkylation. These results may tentatively be rationalized in terms of steric hindrance that from one hand impedes the nucleophilic attack of the carbanion on the silicon and from the other makes difficult the migration of the benzothiazolymethyl group in the eventually formed hypervalent silicon intermediate. In accordance with these considerations were the results obtained in the reaction of phenylethynyllithium **11** with some silylperoxides. Indeed, the reaction of **11** with **1a** afforded almost exclusively silane **12a**, while the reactions with sterically hindered silylperoxides afforded mixtures of silanes **12** and silyl



11

1a-f



ethers **13** (Table).⁹ A plausible explanation for these results might be given in terms of the increasing steric hindrance on the silicon of the silylperoxide that would make the nucleophilic attack of the carbanion on the peroxidic oxygen easier. This sounds very interesting from the synthetic viewpoint as ethynyl silyl ethers, that are potential useful precursors of substituted ketenes, could be obtained this way.

In conclusion, the results in our hands indicate that in the reactions with carbanions silylperoxides undergo nucleophilic attack at the silicon or/and at oxygen depending upon the steric hindrance at the silicon centre. Moreover, the pentavalent silicon intermediate may evolve to the silanes or to the alkylated products depending upon the alkyl groups linked to silicon.

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Table. Reactions of organolithiums RLi with silylperoxides in THF at -78°C under Nitrogen

RLi	$(\text{R}_1\text{R}_2\text{R}_3\text{SiO})_2$	Reaction Products (% Yield) ^a			overall yield
2	1a	8a (40) ^{1a}	8b (60)	-	90
5	1a	6 (40) ^{1b}	7 (60)	-	79
2	1b	8c (100)	-	-	10
9	1b	10 ^{1b}	-	-	40
2	1c	-	8e (70)	8d (30)	35 ^b
2	1d	-	8g (75)	8f (25)	59
2	1e	-	8i (50)	8h (10)	69
11	1a	-	-	12a (100)	86 ^c
11	1c	-	13d (40)	12d (60)	67
11	1e	-	13c (40)	12c (60)	90
11	1f	-	13b (<10) ^d	12b (>90)	48

a) Yields calculated on isolated, purified products. b) Yields calculated by GC-MS. c) Reaction carried out in the presence of HMPA. d) Not isolated, identified by GC-MS.

References

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4. The trimer **3** and the tetramer **4** (2 to 1 ratio) have not been isolated but only detected by GC-MS and compared with authentic specimen.
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7. P.G.Cookson, A.G.Davies and N.Fazal, *J.Organomet.Chem.*, **1975**, 99, C31.
8. All the new silylperoxides showed consistent IR, ^1H NMR, ^{13}C NMR and MS data.
9. The reactions between carbanions and silylperoxides were all carried out as described in Ref. 1