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REACTION OF BISTRIMETHYLSILYLPEROXIDE WITH 2-BENZOTHIAZOLYLALKYLLITHIUMS: AN UNPRECEDENTED DEMETHYLATION

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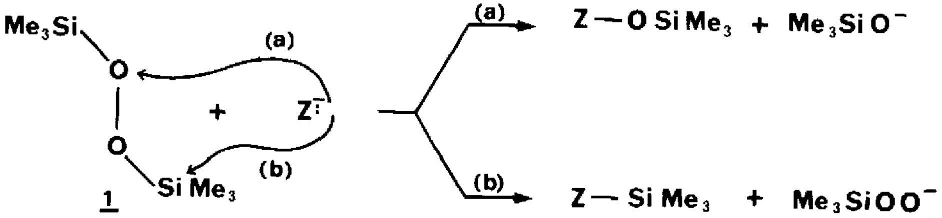
Abstract. Bistrimethylsilylperoxide 1 reacts with 2-benzothiazolylalkyllithiums 3 leading to alkylbenzothiazoles 2, and to benzothiazolylalkyl silyl ethers 4. The reaction of 1 with 3 leading to 2 represents the first example of demethylation of 1. The reaction of 2-benzothiazolyllithium 2g with 1 leads mainly to 2-hydroxybenzothiazole 2h.

Readily accessible bistrimethylsilylperoxide 1,[1] a masked form of 100% hydrogen peroxide, is widely employed as an oxidizing agent in synthetic organic chemistry. Its reasonable thermal stability as well as its high solubility in ordinary aprotic organic solvents make it a useful and clean reagent for the oxidation of several classes of organic substrates.[2] Moreover, it has been recently reported that peroxide 1 has been used as the synthetic equivalent of Me_3SiO^+ and OH^+ in the reaction with C-nucleophiles.[3] The accepted reaction pathway for the abovementioned oxidations and hydroxylations involves nucleophilic displacement of Me_3SiO^- from 1. In some cases nucleophilic attack at silicon may compete with that at oxygen with displacement of Me_3SiOO^-.



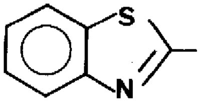
In no case, to the best of our knowledge, demethylation of 1, possibly due to a nucleophilic attack of $Z^{\overline{\cdot}}$ at the methyl groups, has ever been observed.

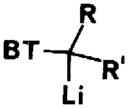
Here we report on an unprecedented demethylation of 1 by certain C-nucleophiles. Following our interest in the coupling of heterocyclic stabilised alkyl metals with electrophiles[4] we have studied the reaction of a number of benzothiazolylalkyllithiums 3 with peroxide 1.

BT—R

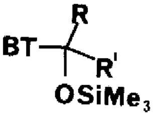
2a : R = CH_3
2b : R = CH_2CH_3
2c : R = $CH(CH_3)_2$
2d : R = $CH(CH_3)CH_2CH_3$
2e : R = $C(CH_3)_3$
2f : R = $CH(CH_3)Ph$
2g : R = Li
2h : R = OH
2i : R = $Si(CH_3)_3$
2l : R = CH(OH)Ph
2m : R = CH_2OH

BT =





3a : R = R' = H
3b : R = H ; R' = CH_3
3c : R = H ; R' = CH_2CH_3
3d : R = R' = CH_3
3e : R = H ; R' = Ph



4a : R = R' = H
4b : R = H ; R' = CH_3
4c : R = H ; R' = CH_2CH_3
4d : R = R' = CH_3
4e : R = H ; R' = Ph

Treatment of 3a, prepared as reported,[3] with 1 in THF at -78°C and subsequent quenching with aqueous sat NH_4Cl led to a mixture of 2-ethylbenzothiazole 2b and 2-benzothiazolylmethyl silyl ether 4a, which were easily separated by flash chromatography and fully characterised by IR, NMR and GC-MS spectroscopy.[5]

Similarly, organolithiums 3b-e reacted with 1 giving mixtures of alkylbenzothiazoles 2c-f and silyl ethers 4b-e (see table).

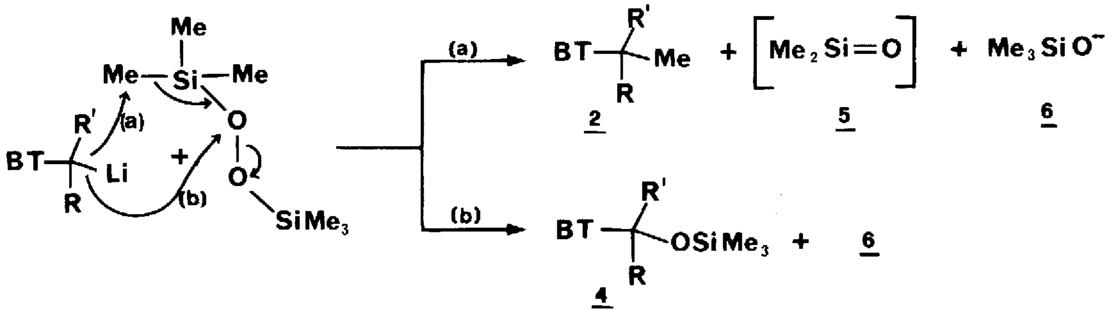
Table. Reaction of 3 with 1.

Organolithium	Reaction products (% yield)[a]	2/4 Ratio
3a	2b (36) 4a (54)	0.66
3b	2c (34) 4b (40)	0.85
3c	2d (47) 4c (34)	1.38
3d	2e (25) 4d (25)	1.0
3e	2f (5) 4e (40) 2l (30)	0.12

a) Yields are not optimised

It was interesting to note that steric hindrance at the reactive site of the organolithiums 3 seems to favour the demethylation reaction of 1. In the reaction with benzothiazolylbenzyllithium 3e peroxide 1 underwent little demethylation, giving mainly silylether 4e and alcohol 2l. 2-Lithiobenzothiazole 2g, reported to give 2-trimethylsilylbenzothiazole 2i upon treatment with 1, under our experimental conditions furnished mainly 2-hydroxybenzothiazole 2b.[6]

Thus, in the reaction of lithiated alkylbenzothiazoles 3 with silylperoxide 1 the formation of methylated products 2 always does compete with the formation of silyl ethers 4. The demethylation of 1 can tentatively be conceived as being derived from the nucleophilic attack of 3 at the methyl groups of 1 with displacement of silanone 5[7] and silanolate 6, while silyl ethers 4 would form by nucleophilic attack of 3 at the oxygen of 1. At present, however, other mechanisms cannot be ruled out.



The demethylation of 1 by 3 actually sounds surprising as it is well known that silylperoxides, when treated with C-nucleophiles, undergo displacement of Me_3SiOO^- to give silanes and Me_3SiO^- to give silyl ethers.[8] More work is in progress in order to understand how the abovementioned demethylation of 1 by 3 takes place and results will be reported in due course. Whatever the mechanism, however, the reaction of 1 with 3 is of potential synthetic value as it allows the preparation of particular 2-alkylbenzothiazoles 2 and 2-benzothiazolylalkyl trimethylsilyl ethers 4 which have not been reported sofar and cannot be obtained by silylation of the corresponding alcohols.[9]

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5) A typical experimental procedure is described for the reaction of 1 with 2-methyllithiobenzothiazole 3a: to a solution of 2a (0.3 g, 2.0 mmol) in 10 ml of dry THF a 2.1 molar hexane solution of n-BuLi (1.15 ml, 2.4 mmol) was added dropwise at -78°C under N_2. Then, after 15 min, bistrimethylsilylperoxide 1 was added dropwise. The mixture was kept at -78°C for 2h and at room temperature overnight. Quenching with aqueous sat NH_4Cl, extraction with ether (3x25 ml) and solvent evaporation left a residue that was a mixture of 2-methylbenzothiazole 2a, 2-ethylbenzothiazole 2b, and benzothiazolylmethyl trimethylsilyl ether 4a, which were separated by flash chromatography (petroleum ether/ether : 9/1) and characterized by IR, ^{1}NMR and GC-MS. Known compounds were compared with authentic specimen. Yields are reported in the Table. New compounds have the following data.

4a: oil; ^{1}H-NMR ($CDCl_3$) δ: 0.15 (s, 9H), 5.15 (s, 2H), 7.30-8.20 (m, 4H); Ms m/e (rel. int.): 237 (22), 222 (100), 192 (8), 148 (24), 73 (11), 45 (12), 43 (3).

4b: oil; ^{1}H-NMR ($CDCl_3$) δ: 0.15 (s,9H), 1.40 (d, 3H, J=7Hz), 5.20 (q, 1H, J=7Hz), 7.1-8.2 (m, 4H); Ms m/e (rel. int.): 251 (13), 136 (100), 192 (15), 162 (22), 110 (19), 75 (23), 73 (60), 45 (19), 43 (10).

4c: oil; ^{1}H-NMR ($CDCl_3$) δ: 0.15 (s, 9H), 1.0 (t, 3H, J=7Hz), 1.95 (q, 2H, J=7Hz), 5.65 (t, 1H, J=7Hz); Ms m/e (rel. int): 265 (9), 250 (60), 236 (67), 221 (24), 192 (11), 176 (12), 75 (14), 73 (14), 73 (100), 45 (22).

4d: oil; ^{1}H-NMR ($CDCl_3$) δ: 0.15 (s, 9H), 1.72 (s, 6H), 7.30- 8.20 (m, 4H); Ms m/e (rel. int.): 265 (6), 250 (100), 235 (13), 234 (20), 192 (20), 176 (22), 75 (34), 73 (88), 45 (30).

4e: oil; ^{1}H-NMR ($CDCl_3$) δ: 0.15 (s, 9H), 6.13 (s, 1H), 7.25-8.10 (m, 9H); Ms m/e (rel. int.): 313 (28), 299 (15), 298 (64), 224 (38), 223 (37), 192 (37), 192 (18), 179 (43), 148 (17), 77 (17), 73 (100).

6) We carried out the reaction in THF, while authors in Ref. 3 used diethyl ether as solvent.

7) The intermediacy of silanone 5 has some precedents: M.C.Golino, R.D. Bush, D. N. Roark, L. H. Sommer, J. Organomet. Chem., 66, 29 (1974); T. J. Barton, J. A. Kilgour, J. Am. Chem. Soc., 98, 7231 (1976).

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9) Indeed, direct treatment of the alcohol 2m with Me_3SiCl in ether failed to give 4a.

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