

Synthesis of Trimethylsilyloxy and Hydroxy Compounds from Carbanions and Bis(trimethylsilyl)peroxide.

Lucia Camici^a, Pasquale Dembech^b, Alfredo Ricci^{a*}, Giancarlo Seconi^b and Maurizio Taddei^a

^aCentro CNR Composti Eterociclici, Dipartimento di Chimica Organica "U.Schiff", Via G.Capponi 9, I-50121 Firenze, Italy and ^bIstituto CNR Composti Carbonio Contenenti Eteroatomi, Ozzano Emilia (Bologna), Italy.

(Received in UK 24 November 1987)

Summary : The reactions of bis(trimethylsilyl)peroxide with alkyl, vinyl, alkynyl, aromatic and heteroaromatic anions are described. Depending on the reaction conditions, the trimethylsilyloxy derivatives can be obtained alone or together with the corresponding trimethylsilyl derivatives, which is sometimes the major product. Enolates, generated using magnesium diisopropylamide give the corresponding hydroxy-carbonyl compounds in good yields. An attempt to rationalise the above results is given, emphasising the wide use of bis(trimethylsilyl)peroxide in organic synthesis as an electrophilic hydroxylation reagent.

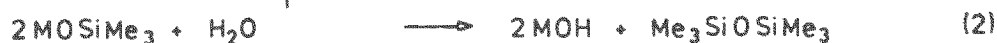
The use of carbanions is nowadays very popular in organic chemistry and various methods are available for their preparation.¹ At the same time, interest in developing new electrophilic reagents which can be used in reactions with carbanions is growing rapidly², keeping up with new methods for coupling the carbanion and the electrophile.³

Whereas the formation of a new C-C bond is often the major aim, the introduction of new functionalities into a carbon skeleton, with the formation for example of a new C-N or C-O bond, is an additional interesting and less explored field of carbanion-based chemistry.

In previous papers, it was shown by us^{4,5} and others⁶, that bis(trimethylsilyl)peroxide **1** can be successfully employed to prepare ketones from vinyl anions⁶, phenols from lithium aryls⁴ and heterocyclic silyl enol ethers from the corresponding heterocyclic anions.⁷ These observations, suggesting that **1** might have potential as a reagent for electrophilic hydroxylation, prompted us to continue our investigation on a larger series of carbanionic systems: in this paper we report the results of a comprehensive study on the reaction between **1** and alkyl, alkenyl, alkynyl, aryl and heteroaryl carbanions, which demonstrates the potential of this synthetically attractive reagent and the possible limitations due to a competitive silylation reaction occurring at the carbanionic centre, together with an attempt to explain this dichotomy.

Results and discussion.

The reaction under study is described by the equations in Scheme 1. The formation of the silyloxy derivative by electrophilic oxy-silylation is usually followed by a hydrolytic step, in which the strong base MOSiMe_3 , is destroyed to give $\text{Me}_3\text{SiOSiMe}_3$. The silyloxy derivative ROSiMe_3 , can be isolated as such or transformed into the corresponding alcohol in acidic medium.



Scheme 1

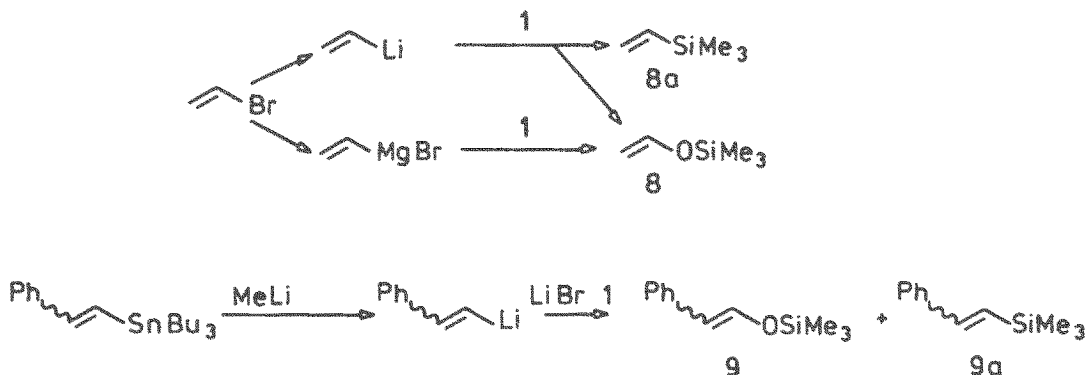
The results of reactions with different carbanions are collected in Table I.

a) Reaction between 1 and alkyl anions. Sources of alkyl carbanions were predominantly lithium alkyls and Grignard reagents. All these carbanions exhibit good reactivity with 1, affording the corresponding silyloxy derivatives (entries 1-5 in Tab. I) in high yields (70-90%).

In the reaction with Grignard reagents we never detected (glc/mass analysis) the silyl derivatives RSiMe_3 , which, on the other hand, were present when the reaction was performed with lithium alkyls.

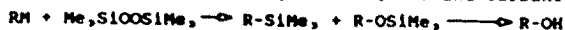
Different results were obtained for alkyl carbanions α -substituted with heteroatoms: with the lithium salt of the dithiane (entry 6 in Tab. I), the silyl derivative was obtained almost exclusively with only traces (5% ca.) of the expected oxysilylation product.


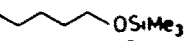


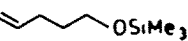
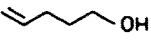

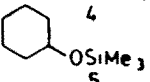


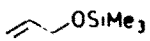

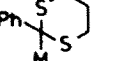
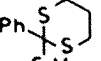

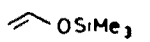

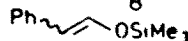

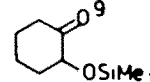
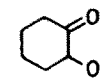

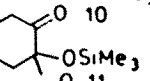
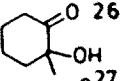
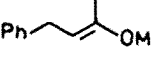
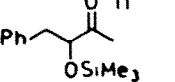
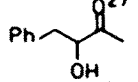

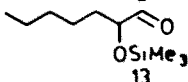
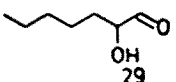

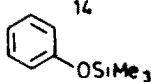

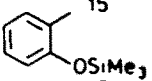

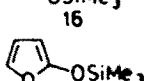

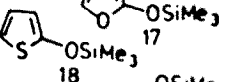

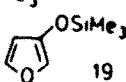

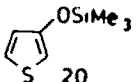
b) Reaction between 1 and vinyl anions. Reaction of 1 with vinyl carbanions, led to isolation of the expected silyl enol ethers if the hydrolytic workup was avoided. The ratio of oxysilylation to silylation, as well as the overall yields, varied on changing the method by which the carbanions were formed: thus, with vinyl lithium prepared from vinyl bromide by Br-Li exchange, an inseparable mixture of the silyl enol ether 8 and vinylsilane 8a in a 20/80 ratio was obtained in a 45% isolated yield. On the other hand, when the lithium derivative was generated from a vinylstannane and MeLi, 9 and 9a were formed in a 55/45 ratio in the absence of LiBr and a 75/25 ratio in presence of LiBr (Scheme 2).



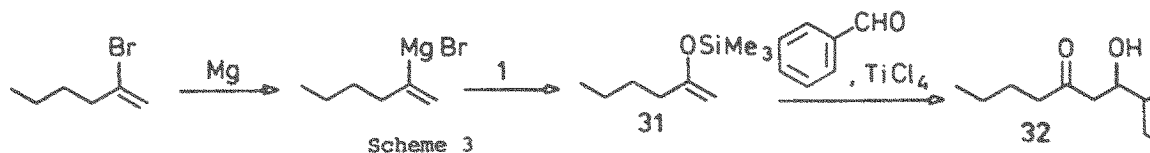
Scheme 2

Starting from vinylmagnesium bromide, the silyloxy derivative was the only product isolated, in yields ranging from 40 to 60%. This method, therefore, allows the regio-controlled preparation of silyl enol ethers, the generation of which from carbonyl compounds can sometimes be complicated by the formation of regioisomers. An example of the application of such a procedure is shown in Scheme 3.

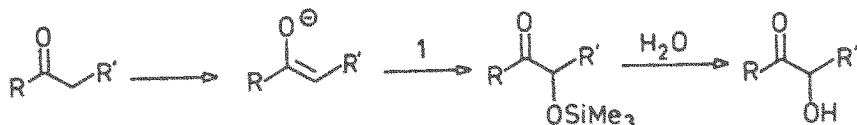
Table 1. Reaction between $\text{Me}_3\text{SiOOSiMe}_3$ (1) and carbanions.


Entry	Starting material	M=Li ⁻		M=Li/LiBr ^o		M=MgBr ^o		Isolated products	(Yields) ^a	
		-SiMe ₃	-OSiMe ₃	-SiMe ₃	-OSiMe ₃	-SiMe ₃	-OSiMe ₃			
1	BuM	-	-	2	98	-	-	BuOSiMe ₃ 2	BuOH 21	(89%)
2		-	-	-	-	0	100			(70%)
3		-	-	-	-	0	100			(85%)
4		-	-	-	-	0	100			(78%)
5		-	-	-	-	0	100			(74%)
6		95	5	95	5	no reaction				(56%) ^c
7		80	20	-	-	0	100			(53%)
8		55	45	25	75	-	-			(65%) ^d
9		100	0	50	50	0	100			(61%)
10		-	-	-	-	0	100			(40%)
11		-	-	-	-	0	100			(42%)
12		-	-	-	-	0	100			(46%) ^e
13	Ph-C≡C-M	100	0	94	6	100	0	Ph-C≡C-SiMe ₃ 14		(40%) ^f
14		7	93	2	98	0	100			(84%)
15		10	90	-	-	0	100			(82%)
16		10	90	-	-	-	-			(57%)
17		40	60	35	65	-	-			(53%)
18		20	80	-	-	0	100			(60%)
19		8	92 ^g	5	95	-	-			(52%)

a) Ratio determined by glc analysis. b) Yields of isolated and fully characterized products. c) Glc yields. d) Isolated yields of a mixture of 9 and 9a. e) Glc yields calculated on the crude. f) Data relative to the lithium derivative from 3-bromothiophene. g) Data relative to the lithium derivative from 3-tributylstannylthiophene.

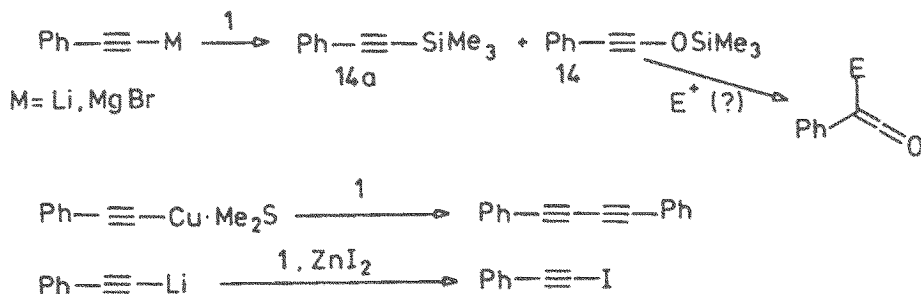


c) Reaction between 1 and enolates. Bis(trimethylsilyl)peroxide 1 reacts with lithium enolates, generated from carbonyl compounds and LDA, to give, as the major product, the silyl derivative i.e. the silyl enol ether. However the presence of salts turned out to affect considerably the features of this reaction: with LiBr the amount of the α -silyloxycarbonyl compound was increased substantially (entry 9 in Tab.I). When magnesium diisopropylamide, which is known to generate predominantly kinetic enolates, was used, the β -siloxy derivatives were again obtained in reasonable yields (Scheme 4). The hydroxy compounds, in this case, could be obtained directly after hydrolytic work up, depending on the structure of the substrates. A common by-product of these reactions was diisopropyltrimethylsilylamine.



d) Reaction between 1 and alkynyl anions. Both lithium phenylacetylene or the corresponding Grignard reagent gave predominantly the silyl derivative 14a in the reaction with 1.

This result was quite disappointing because of the high potential interest of the expected silyloxy compound, as a precursor of ketenes (Scheme 5).



Neither the presence of LiBr nor the use of other salts led to any improvement of the oxysilylation reaction: whereas in the first case 14 was detected by glc/mass analysis in very small amounts not exceeding 2-6%, with cuprates we got dimerisation and with ZnI_2 iodoacetylene was isolated as the major product (Scheme 5).

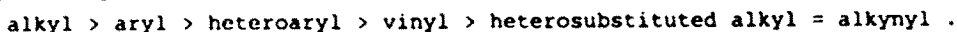
e) Reaction between 1 and aromatic anions. Aromatic lithium or Grignard derivatives both behave as good substrates for the electrophilic hydroxylation with 1. Although, generally speaking, lithium derivatives gave higher yields, their reaction led to 7-10% of the silyl derivative; Grignards, on the other hand, gave lower conversions yields (60-70%), but no trace of the silyl derivative were detectable in the reaction mixture.

f) Reaction between 1 and heteroaromatic anions. 2-Lithiumfuran and -thiophene, treated with 1, gave predominantly 2-trimethylsilyloxyfuran 17 and -thiophene 19 with ca. 10% of the silyl derivative, whereas 1-methyl-2-lithiumpyrrole appeared to

be completely unreactive. 3-Lithiumfuran and -thiophene, obtained by Br-Li exchange from the corresponding bromo heterocycles, afforded the silyloxyderivatives 18 and 20, whether LiBr was present or not.

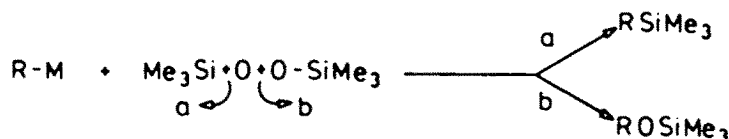
The results collected in Table I provide convincing evidence for the wide applicability of 1 in the electrophilic hydroxylation of carbanions. The dichotomy in the reaction, which in several cases leads silylation to be the major process, requires an interaction of the negatively charged species with either of two potential electrophilic centres in 1, viz. the silicon and the peroxidic oxygen (Scheme 6). Since the efficiency of 1 as an hydroxy cation equivalent is related to the possibility of favouring a high yielding oxysilylation process, it seemed of importance to identify the factors affecting which of the two pathways is followed.

Among the carbanion sources, the Grignard reagents gave the best results in the oxysilylation process, and the efficiency of the reaction follows the sequence:



Moreover good results were also achieved with magnesium enolates for the preparation of α -hydroxycarbonyl compounds.

We tried then to give a rational explanation for the competing oxysilylation vs. silylation process. In bis(trimethylsilyl)peroxide 1 the bonds to be broken are the O-O to give the -OSiMe₃ and the O-Si to give the -SiMe₃, the first possibly through a homolytic, the latter through a heterolytic pathway (Scheme 6).



Scheme 6

The predominant formation of the -OSiMe₃ derivative observed with Mg organometallics and which occurs through O-O cleavage might then be related to their higher radical character⁷ in respect to that of the lithium compounds³⁰. The improvement of yields of the silyloxy derivative due to the presence of lithium bromide can be ascribed to the same cause⁸.

With the type of metal kept constant, the differences of reactivity on the substrates described in this paper can be rationalized in terms of the HSAB principle. If we consider 1 as having two "acidic" centres, the silicon hard and the oxygen soft, harder carbanions will react preferentially at silicon whereas softer carbanions will react at oxygen, leading to the oxysilylation products. This explanation fits well with the results in Table I, since the sequence of increasing hardness⁸ (alkyl > aryl > heterovinyl > vinyl > alkynyl) parallels well the increasing ability of these carbanions to undergo oxysilylation (see above).

According to the above results, 1 can be considered an excellent reagent for the electrophilic oxysilylation of carbanions with soft character, that is a good reagent to transform a Grignard reagent into an alcohol or into a phenol, and an enolate into the corresponding hydroxycarbonyl compound.

Experimental section.

WARNING Use of bis(trimethylsilyl)peroxide (prepared following ref.4) never gave us any trouble from explosions or any other kind of uncontrolled reaction in the presence of metal surfaces or on warming up. Nevertheless, in presence of the peroxide all the reactions were carried out in a fume cupboard with safety-glass windows.

Reaction between bis(trimethylsilyl)peroxide 1 and alkyl lithium derivatives. 1-Butanol (21), general procedure.

To a solution of n-butyllithium (3.12 ml of a solution 1.6 M in hexane, 5 mmol) in diethyl ether (5 ml) at 0°C, bis(trimethylsilyl)peroxide* (1) (890 mg, 5 mmol) is added slowly with a syringe. The mixture is warmed to room temperature, then methanol (1 ml) is added together with a drop of a solution of hydrochloric acid ca 10 M. The solvent is evaporated under vacuum and the residue purified by distillation to give butanol 21 330 mg (89% yield).

B.p. 116°C Lit.¹⁰ 117.7°.

1-Hexanol (22). Yields 70% B.p. 154 °C Lit.¹¹ 156.5 °C.

Reaction between 1 and alkyl magnesium bromides. Cyclohexanol (24), general procedure.

To magnesium (200 mg, 8.23 mmol) in diethyl ether (1 ml) a solution of 1-bromocyclohexane (1 g, 6.14 mmol) in THF (2.5 ml) is added under nitrogen.

The mixture is then refluxed for 1.5 h, then cooled to 0°C and 1 (1.09 g, 6.14 mmol) is added. The reaction mixture is warmed to room temperature, then methanol (2 ml) and a catalytic amount of a solution of hydrochloric acid 10 M is added. The solvent is evaporated under vacuum and the residue purified by distillation to give cyclohexanol, 480 mg (78% yield). B.p. 159-160°C Lit.¹⁵ 160-161°C.

1-Hexanol (22). Yield 74% .

5-Hexen-1-ol.(23). Yield 85%. B.p. 70-73°C/20 mmHg Lit.¹⁶ 78-80°C/25 mmHg.

Allyl alcohol (25). Yield 88%. B.p. 96-97°C Lit.¹⁷ 96-97°C.

Reaction between 1 and vinyl lithium derivatives. 1-Phenyl-2-trimethylsiloxyethylene (23), general procedure.

To a solution of 1-phenyl-2-tributylstannylethylene 23 (1 g, 2.5 mmol) in THF (2.5 ml) at -78°C, methyllithium (1.59 ml of a solution 1.6 M in diethyl ether, 2.5 mmol) is added slowly with a syringe. The reaction mixture is warmed to room temperature then cooled again at 0°C and 1 (445 mg, 2.5 mmol) is added, and the solution warmed to room temperature. After evaporation of the solvent the composition of the mixture is monitored by glc-mass analysis, showing the presence of 1-phenyl-2-trimethylsiloxyethylene (9) and 1-phenyl-2-trimethylsilylethylene (9a) in a ratio of 55 to 45 . When the reaction is carried out performing the Sn-Li exchange in the presence of LiBr (430 mg, 5 mmol), 9 and 9a are present in a ratio of 74 to 26. In both cases pentane (10 ml) is added and the mixture centrifuged. The liquid phase is dried on anhydrous sodium sulphate, the solvent evaporated and the residue distilled to give a mixture of 9 and 9a in an overall yield of ca. 65% .

9 MS (m/e) : 192 (M⁺), 177 (M⁺-15), 75, 73 (base).

9a MS (m/e) : 176 (M⁺), 161 (M⁺-15), 73 (base).

Trimethylsiloxyethylene(8). The mixture of silyl- and siloxy derivatives is isolated by distillation (b.p. 71-75°C, Lit. value for pure 8 ¹⁸ is 73-75°C) and analyzed by glc-mass analyses: 8 MS (m/e) : 116 (M⁺), 101 (M⁺-15), 75 (base), 73. Trimethylsilylethylene (8a) MS (m/e) : 100 (M⁺), 73 (base).

Reaction between 1 and vinyl magnesium bromides. Trimethylsilyloxyethylene (8).

To a solution of vinyl magnesium bromide (5 ml of a 1 M solution in THF, 5 mmol), 1 (860 mg, 5 mmol) in diethyl ether (8 ml) is added at 0°C with a syringe. The mixture is allowed to warm to room temperature and pentane (15 ml) is added. After centrifugation of the solution and evaporation of the solvent through a short path Vigreux column, product 8 is isolated by fractional distillation. 310 mg, (53% yield). B.p. 74-75°C. The product is gas chromatographically pure.

2-Trimethylsilyloxy-1-hexene(31). A suspension of magnesium turnings (1.0 g, 41.0 mmol) in dry THF (15 ml) is heated under gentle reflux. 2-Bromo-1-hexene (4.07 g, 25 mmol) and 1,2-dibromoethane (1.7 ml, 20 mmol) are dissolved in dry THF (45 ml) and 10 ml of this solution is added to the magnesium. A vigorous reaction initiates and the remaining solution of the halide and 1,2-dibromoethane is then added dropwise under refluxing conditions. After 6 h of further reflux, the mixture is cooled to 0°C and 1 (3.5 g, 20 mmol) in diethyl ether (50 ml) is added dropwise. After 1 h of stirring at room temperature, pentane (300 ml) is added and the mixture passed through a small column filled with neutral alumina. After evaporation of the solvent 31 is isolated by fractional distillation, 2 g, 61% yield. B.p. 53-56°C/10 mmHg. ¹H NMR (CDCl₃) δ 0.3 (s, 9H, Me₃Si), 0.9 (m, 3H, Me), 1.2 (m, 4H, CH₂), 1.3 (m, 2H, CH₂-C=), 4.01 and 4.22 (AB system, 2H, J=10 Hz, CH₂=). MS (m/e) : 172 (M⁺), 157 (M⁺-15), 73 (base). The product is gas chromatographically pure.

1-Phenyl-1-hydroxy-3-heptanone (32). To benzaldehyde (530 mg, 5 mmol) in dry CH₂Cl₂ (5 ml) titanium tetrachloride (950 mg, 5 mmol) is added with a syringe at 0°C. The yellow solution is stirred for 5 min. then it is added to a solution of 31 (860 mg, 5 mmol) in dry CH₂Cl₂ (3 ml) cooled to -78°C. The mixture is raised to 0°C and a buffer solution at pH 7 (2 ml) is added followed by diethyl ether (15 ml). The ethereal layer is separated, washed with water and dried on anhydrous sodium sulphate. Evaporation of the solvent and column chromatography on silica gel (eluant: hexane - ethyl acetate, 3 - 1) gave 32, 525 mg (51% yield). IR _{max} (neat): 3120 (OH), 1760 (CO) cm⁻¹. ¹H NMR (CDCl₃) δ 0.9 (m, 3H, Me), 1.1 (m, 4H, CH₂), 1.9 (m, 3H, CH₂CO and OH), 2.1 (m, 2H, CH₂CO), 4.11 (t, 1H, J=6 Hz, CH), 7.3 (m, 5H, Arom). MS (m/e) : 206 (M⁺), 188 (M⁺-18), 77 (base).
Anal. Calc. C 75.69, H 8.80 ; Found C 74.98 H 8.71.

Reaction between 1 and lithium enolates. 1-Hydroxy-2-cyclohexanone (24).

To a suspension of LiBr (445 mg, 5.1 mmol) and diisopropylamine (515 mg, 5.1 mmol) in dry diethyl ether (5 ml), n-butyllithium (3.2 ml of a 1.6 M solution in hexane) is added at 0°C and the mixture stirred at this temperature for 15 min. Cyclohexanone (500 mg, 5.1 mmol) is added and the mixture is warmed to room temperature, then cooled again and treated with 1 (910 mg, 5.1 mmol). The resulting mixture is stirred at room temperature for 12 h, washed with a saturated solution of ammonium chloride and the ethereal layer separated and dried on anhydrous sodium sulphate. The solvent is evaporated under vacuum and the residue purified by fractional distillation to give 24, 314 mg (54% yield).
B.p. 63-65°C/6.5 mmHg Lit¹² 71°C/7mmHg.

Reaction between 1 and magnesium enolates. 1-Hydroxy-1-methyl-2-cyclohexanone(28), general procedure.

Methyl magnesium bromide (1.8 ml of a 2.8 M solution in diethyl ether, 5.1 mmol), is added to a solution of diisopropylamine (515 mg, 5.1 mmol) in dry diethyl ether (5 ml) at 0°C. After 15 min at this temperature, 2-methyl-1-cyclohexanone (570 mg, 5.1 mmol) is added and the resulting mixture is stirred at 0°C for 12 h. After cooling to -78°C, 1 (910 mg, 5.1 mmol) is added and the mixture raised to room temperature,

stirred for 2 h, treated with a saturated solution of ammonium chloride and the ethereal layer separated and dried on anhydrous sodium sulphate. The solvent is evaporated under vacuum and the product purified by column chromatography on silica gel (eluant: hexane - ethyl acetate 4 - 1), 226 mg (40% yield). The product is identified through its semicarbazone : m.p. 203°C Lit.¹⁸ 203-203.5°C.

1-Hydroxy-2-cyclohexanone (24). Yield 61%. Product identified by glc comparison with the product of the above mentioned reaction.

1-Phenyl-2-hydroxy-3-butanone (28). Yield 42%. B.p. 95-96°C/1 mmHg Lit.²⁰ 135-137°C/10 mmHg. The product is identified through its semicarbazone : m.p. 174-175°C Lit.²⁰ 176-178°C.

2-Hydroxy-1-heptanal (29). Crude yield 46%. B.p. 100°C/4 mmHg Lit.²¹ 103-105°C/4 mmHg. (Yields after distillation were dramatically reduced by the strong tendency of 30 to oligomerise).

Reaction between 1 and lithium aryls. Trimethylsilyloxybenzene(15), general procedure.

To a solution of phenyllithium, prepared from bromobenzene (1 g, 6.4 mmol) and *n*-butyllithium (8 ml of a 1.6 M solution in hexane, 12.8 mmol), in dry diethyl ether (15 ml) at -78°C, 1 (1.1 g, 6.4 mmol) is added with a syringe. The mixture is warmed to room temperature and stirred for a further 3 h. Pentane (15 ml) is added and the fine solid so formed separated by centrifugation. After evaporation of the solvent under vacuum (200 mmHg), 15 is purified by fractional distillation, 893 mg, (84% yield). B.p. 85-86°C/20 mmHg Lit.¹³ 182°C. The product was identified by comparison with an authentic sample.

Trimethylsilyloxytoluene (16). Yield 82%. B.p. 194°C Lit.¹⁴ 194-195°C.

Reaction between 1 and aromatic Grignards. Trimethylsilyloxybenzene(15), general procedure.

To phenyl magnesium bromide, prepared in situ from bromobenzene (1 g, 6.4 mmol) and magnesium (200 mg, 8.23 mmol) in dry diethyl ether (5 ml), 1 (1.18 g, 6.6 mmol) is added at 0°C. After 2 h of stirring at room temperature, pentane is added, the solid filtered away, the solvent evaporated and the residue distilled to give 15, 763 mg, (69 % yield). The product was identified by comparison with an authentic sample.

Trimethylsilyloxytoluene (16). Yield 62%.

Reaction between 1 and lithium heteroaromatic derivatives. 3-Trimethylsilyloxyfuran (18), general procedure.

To a solution of 3-bromofuran (2 g, 13.6 mmol) in dry diethyl ether (15 ml), *n*-butyllithium (8.5 ml of a 1.6 M solution in hexane, 13.6 mmol) is added at -78°C. After 2 h of stirring at this temperature, 1 (2.42 g, 13.6 mmol) is added slowly, and the mixture warmed to 10°C. Pentane (25 ml) is added and the fine solid formed is separated by centrifugation. The dark red solution is concentrated under vacuum (200 mmHg), and 18 is isolated by Kugelrohr distillation, 1.1 g, (53% yield). B.p. 105-110°C/15 mmHg.

¹H NMR (CDCl₃) δ 0.24 (s, 9H, Me₃Si), 6.1 (m, 1H, H_a), 7.14(d, 1H, J=1.5 Hz, H₂), 7.2 (m, 1H, H_b). M/S (m/e) 156 (M⁺), 141 (base), 73.

3-Trimethylsilyloxythiophene (20) from 3-trimethylstannylthiophene.

Yield 52%. B.p. 125-130°C/0.5 mmHg. ¹H NMR (CDCl₃) δ 0.37 (s, 9H, Me₃Si), 6.2 (m, 1H, H_a), 6.60 (d, 1H, J=4.5 Hz, H₂), 7.0 (m, 1H, H_b). M/S (m/e): 172 (M⁺), 157 (base), 73.

3-Trimethylsilyloxythiophene (18) from 3-bromothiophene. Yield 60%.

2-Trimethylsilyloxyfuran (17). Yield 57%. B.p. 92-94°C/70 mmHg. ¹H NMR (CDCl₃) δ 0.45 (s, 9H, Me₃Si), 5.2 (m, 1H), 6.3 (m, 1H), 6.9 (m, 1H). M/S (M/E) 156 (M⁺), 73 (base).

2-Trimethylsilyloxythiophene (19). Yield 61%. B.p. 55-57°C/0.7 mmHg Lit²² 50-52°C/0.75 mmHg.

Reaction between 1 and heteroaromatic Grignard reagents. 2-Trimethylsilyloxythiophene (19).

To a suspension of magnesium (200 mg, 8.23 mmol) in diethyl ether (2 ml), 2-bromothiophene (1 g, 6.1 mmol) is added and the mixture refluxed 30 min, cooled to 0° and 1 (1.09 g, 6.1 mmol) added slowly. After warming to room temperature, the usual work up gave 19, 520 mg, (51% yield).

Reaction between 1 and lithium phenylacetylene.

To a suspension of lithium bromide (170 mg, 1.96 mmol) at -78°C in diethyl ether (5 ml), phenylacetylene (200 mg, 1.96 mmol) is added followed by n-butyllithium (1.22 ml of a 1.6 M solution in hexane, 1.96 mmol). The mixture is warmed to room temperature, then, after cooling to -78°C, 1 (850 mg, 1.96 mmol) is added. The glc-mass analysis of the mixture shows the following composition: Phenylacetylene 57%, 1-phenyl-2-trimethylsilylacetylene 40% (M/S (m/e) 174 (M⁺), 159 (base), 129.), 1-phenyl-2-trimethylsilyloxyacetylene (14) 3% (M/S (m/e) 190 (M⁺), 175 (M⁺-15, base), 145 (PhC=COSi), 75.

The same procedure in the presence of CuBr.Me₂S gave predominantly 1,4-diphenyl-1,3-butadiyne.

Working in the presence of ZnI₂ (626 mg, 1.96 mmol) in the same reaction conditions described above, 1-phenyl-2-iodoacetylene is obtained (M/S (m/e) 228 (M⁺), 127 (I), 101 (M⁺-I).

Reaction between 1 and dithiane anion.

To a solution of 2-phenyl-1,3-dithiane (330 mg, 1.68 mmol) in the minimum amount of dry diethyl ether, n-butyllithium (1.16 ml of a 1.6 M solution in hexane) is added at -40°C. After 1 h at this temperature the reaction mixture is cooled to -78°C and 1 (300 mg, 1.68 mmol) is added. The glc-mass analysis of the reaction mixture showed the following composition:

2-Phenyl-1,3-dithiane 40%, 2-phenyl-2-trimethylsilyl-1,3-dithiane 56% (M/S (m/e): 268 (M⁺), 195 (M⁺-73), 163, 135, 121 (base), 73.), 2-phenyl-2-trimethylsilyloxy-1,3-dithiane (7) 4% (M/S (m/e) 284 (M⁺), 211 (M⁺-73), 163, 77, 73 (base).

Acknowledgments. This project is supported by the Consiglio Nazionale delle Ricerche (CNR, Roma), Progetto Finalizzato "Chimica Fine - Nuove Sintesi".

References and Notes

- 1) Brandsma L.; Verkruijesse H.D. Preparative Polar Organometallic Chemistry; Springer Verlag: Berlin, 1987; pp.3-213. Lai Y.H. Synthesis 1981, 585-604. Reuman M.; Meyers A.Y. Tetrahedron 1985, 41, 837-860. Wilhelm D.; Clark T.; Von Rague Schleyer P.; Courtneige J.L.; Davies A.G. J.Am.Chem.Soc. 1984, 106, 361-367. Schlosser M.; Strunk S.; Tetrahedron Lett. 1984, 25, 783-784. Schlosser M.; Mordini M.; Chimia 1986, 40, 309-310.
- 2) See for example: Trost B.M.; Pearson W.H. J.Am.Chem.Soc. 1981, 103, 2483-2485. Djuric S.W. J.Org.Chem 1984, 49, 1311-1312. Morimoto T.; Takahashi T.; Sekiya M. J.Chem.Soc.Chem.Comm. 1984, 794-795.
- 3) Kumar Das V.G.; Chu C.K. The chemistry of the Metal Carbon Bond; F.R.Hartley and S.Patai Ed., J.Wiley and Sons: New York, 1985; 2-97. Johnson C.R.; Marren T.S. Tetrahedron Lett. 1987, 28, 27-30. Reetz M.T. Topics Cur.Chem. 1984, 106, 1-54.
- 4) Taddei M.; Ricci A.; Synthesis 1985, 633-635.

- 5) Camici L.; Ricci A.; Taddei M. Tetrahedron Lett. 1986, 27, 5155-5158.
- 6) Neumann H.; Seebach D. Chem. Ber. 1978, 111, 2785-2812.
- 7) Maruyama K.; Katagiri T. J. Am. Chem. Soc. 1986, 108, 6263-6270.
- 8) Wakefield B.J.; The Chemistry of Organolithium Compounds Pergamon Press, Oxford, 1974, 1-18.
- 9) Ho T.L.; Tetrahedron 1985, 41, 1-86.
- 10) Beilstein Handbuch der Organischen Chemie, 1, 367.
- 11) Beilstein Handbuch der Organischen Chemie, 1, 407.
- 12) Beilstein Handbuch der Organischen Chemie, 8, E III, 4.
- 13) Langer S.H.; Connel S.; Wender I. J. Org. Chem. 1958, 23, 50-58.
- 14) Langer S.H.; Pantages P.; Wender I. Chem. Ind. (London) 1958, 1664-1665.
- 15) Beilstein Handbuch der Organischen Chemie, 6, 5.
- 16) Beilstein Handbuch der Organischen Chemie, 1, E IV, 2137.
- 17) Beilstein Handbuch der Organischen Chemie, 1, 436.
- 18) Nguyen D.H.; Fainberg V.S.; Baukov Y.I.; Lutscenko I.F. Zh. Obshch. Kim. 1968, 38, 191-192.
- 19) Beilstein Handbuch der Organischen Chemie, 8, E III, 13.
- 20) Beilstein Handbuch der Organischen Chemie, 8, E III, 456.
- 21) Beilstein Handbuch der Organischen Chemie, 1, E III, 3240.
- 22) Fiorenza M.; Reginato G.; Ricci A.; Taddei M. J. Org. Chem. 1984, 49, 551-552.