

affected by the use of these reagents.

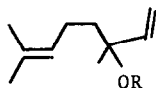
The reagents react very rapidly with water, so normal precautions in their preparation and handling must be taken. Thus, reagent 1a was prepared as follows: 27.4 g (1.15 equiv.) of freshly distilled trimethylchlorosilane was added to a mixture of 15.162 g of imidazole in 125 mL of dry THF under an argon atmosphere in a rigorously dried two-necked reaction flask fitted with a reflux condenser and a rubber septum. A jelly-like precipitate formed. Distilled 2,4-pentanedione (22 g; 22 mmoles) was injected through the septum and the septum was then replaced by a teflon-lined glass stopper. The reaction mixture was magnetically stirred under gentle reflux overnight. The end of the reaction was indicated by the replacement of the gel by crystalline imidazole hydrochloride. Cooling, followed by filtration through a sintered glass funnel filled with anhydrous Na_2SO_4 and then evaporation under reduced pressure (dry argon back flush) gave 48 g of a very mobile yellowish liquid. Fractional distillation using a 20 cm Vigreux column gave 32.7 g (86% yield) of pure 1a (b.p. 63 C/3 Torr (Lit. 66-8 C/4 Torr⁹ and 61-3 C/3 Torr¹⁰) which consists of the cis and trans isomers in a 3:1 ratio.¹¹ A very convenient and high yield preparation of 1a from HMDZ was also recently described by Chu and Huckin.¹⁰ 1b was obtained in the same manner and in similar yields: b.p. 73-5 C/8 Torr.

These reagents were tested with a representative primary (2-phenylethanol), secondary (trans-2-methylcyclopentanol), and a tertiary (linalool (2a)) alcohol as well as with a base-sensitive glycol (terrein (3a)). The reactions were monitored by GLC, however, all the products were isolated and characterized. Both reagents reacted quantitatively in several minutes at room temperature without catalytic assistance with all the substrates, even the notoriously difficult linalool,^{7,12} providing the useful trimethyl ethers (see table). The absence of extraneous by-products makes the resulting ethers extremely easy to isolate and analyze. Besides its volatility, the considerable water solubility of 2,4-pentanedione is, also, of significant advantage in this respect. When the alcohol is in excess, the reagent is consumed rapidly to give the silylated products at room temperature with or without solvent. Since the silylation reactions are basically equilibrium reactions,^{3c,11} the polarity of the solvent was expected to exert some effect on the reaction. Indeed, reactions with these reagents are facilitated by more polar solvents (DMF>acetonitrile>THF>dichloromethane). In DMF, even linalool (a tertiary allylic alcohol) was quantitatively silylated in 5-6 minutes with stoichiometric amounts of 1a. When the silyl reagent is present in sufficient excess, the alcohol is silylated quantitatively and even more rapidly. In the extreme case represented by neat linalool, an 80% excess of 1a was required to give quantitative reaction in 10-15 minutes. Reagent 1a is more reactive than 1b. Both 1a and 1b, though stable for months, react rapidly with water, and therefore excess reagent is destroyed easily when necessary.

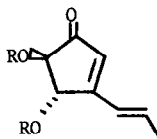
The following examples demonstrate the typical procedure used: 1. A slight molar excess of reagent 1a (182 mg) was added to a solution of terrein (77 mg; 0.5 mmole) in dry DMF (1.5 ml) in a 4 ml vial with a teflon septum. The solution was shaken for 20 mins. and the volatile compounds were removed under reduced pressure to give 163 mg of a liquid which was dissolved in 3 ml CCl_4 , filtered through a sintered glass funnel and concentrated to give 143 mg (96%) of glc and analytically pure oily terrein ditrimethylsilyl ether (3b): nmr (CCl_4) τ 9.80 (s, 18H), 8.10 (d, J=6 Hz, 3H), 5.93 (d, J=3 Hz, 1H), 4.20 (s, 1H), and 3.30-3.77 (m, 2H); ir (CCl_4) 2980, 1720, 1642, 1590, 1442, 1360, 1335, 1245, 1170, 1134, 1100, 1040, 955, 895, 870, and 830 cm^{-1} ; eims (m/e) 298, 293, 193, 179,

Alcohol	Reagent	Conditions for Quantitative Conversion to Product as Judged by GLC ¹²	Isolated Yield
2-phenylethanol	1a	5-6 mins., neat, r.t. 3-5 mins., DMF, r.t.	84% ¹⁴
	1b	5-6 mins., neat, r.t. 3-5 mins., DMF, r.t.	
<u>trans</u> -2-methylcyclopentanol	1a	8-10 mins., neat, r.t. 5-6 mins., DMF, r.t.	80% ¹⁴
	1b	8-10 mins., neat, r.t. 5-6 mins., DMF, r.t.	
linalool (<u>2a</u>)	1a	8-10 mins., DMF, r.t.	75-85% ¹⁴
terrein (<u>3a</u>)	1a	20 mins., DMF, r.t.	96%

147(base), 75 and 59; found: C, 56.05; H, 8.60. 2. 1a (3.490 g; 20.2 mmole) was added to distilled linalool (3.01 g; 20 mmole) in 20 ml dry DMF. After shaking 10 mins. the solution was extracted with ligroin (5 x 10 ml), the combined extracts were cooled and then washed with cold water (4 x 10 ml), dried (Na_2SO_4), and concentrated. The resulting product was distilled to give 3.758 g of 2b: b.p. 134 C/98 Torr; nmr (CCl_4) τ 9.90 (s, 9H), 8.56 (s, 3H), 8.46 (s, 3H), 8.35 (s, 3H), 4.8-5.23 (2H), and 3.95-4.43 (2H); ir (CCl_4) 2950, 2925, 2885, 1450, 1410, 1370, 1250, 1175, 1115, 1045, 990, 860, and 830 cm^{-1} ; eims (m/e) 226, 211, 183(base), 121, 93, 80, 75, and 73; found: C, 68.80; H, 11.60.



2a, R=H
2b, R=(CH_3)₃Si



3a, R=H
3b, R=(CH_3)₃Si

The ease of preparation of these reagents, their high reactivity and the ease with which pure products can be obtained persuade us that these new silylating agents will find substantial use. Our present efforts in this area involve a survey of the reactivity of other functional groups toward these and analogous reagents.

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References:

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 13. The reactions were monitored and purity was established in all cases using a Varian Model 3700 Gas Chromatograph; flame ionization detector; He; a 3% Se-30 on Chromasorb W 80/100 column and column temps. of 70-210 C.
 14. The actual yields are considerably higher, loss in isolated yields incurred because of small quantities distilled.

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