Reaction of Chloromethylcarbene with Trimethylsilyl Enol Ethers; Preparation of α-Methylene Ketones and α-Methyl-α,β-unsaturated Ketones and Aldehydes

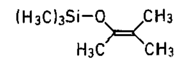
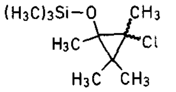
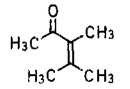
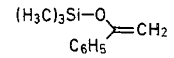
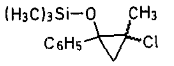
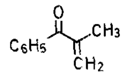
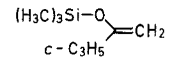
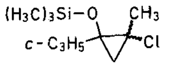
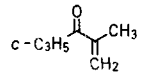
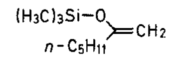
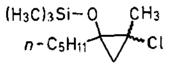
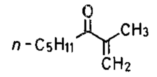
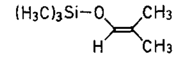
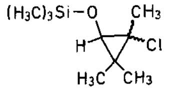
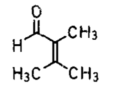
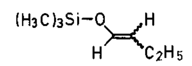
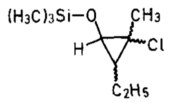
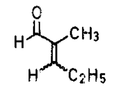
Luis Blanco, Philippe Amice, Jean-Marie Conia

Laboratoire des Carbocycles, Université de Paris-Sud, Bâtiment 420, F-91405 Orsay, France

In the preceding communication, we showed that the cycloaddition of chloromethylcarbene to trimethylsilyl enol ethers of cycloalkanones, followed by elimination of chlorotrimethylsilane with opening of the cyclopropane ring, leads to higher ring α-methylcycloalkenones[1]. In the present paper, we report that

0039-7881/81/0432-0291 $ 03.00

Table 1. α-Methyl-α,β-unsaturated Carbonyl Compounds 3 from Enol Silyl Ethers 1 via Cyclopropanes 2

Entry	Silyl Enol Ether 1[a]	Chlorosilyloxycyclopropane 2[b]	(*E*/*Z*) ratio	b.p. [°C]/torr	Reaction conditions solvent/reflux time	Product 3	Yield [%][c]
a			85/15		toluene/1 day methanol/$(C_2H_5)_3N$/1.5 days[d]		79 84
b			43/57	43–46°/0.03	xylene/5 h methanol/$(C_2H_5)_3N$/8 h[d]		80 76
c			50/50	—	toluene/3 days methanol/$(C_2H_5)_3N$/1 day[d]		61 76
d			60/40	39–42°/0.03	toluene/1 day methanol/$(C_2H_5)_3N$/1 day[d]		82 89
e			60/40	—	toluene/4.5 h methanol/$(C_2H_5)_3N$/2 h[d]		57 46
f (*Z*/*E*)= 60/40			60/40	—	toluene/4 days methanol/$(C_2H_5)_3N$/1 day[d]		72 (*cis*/*trans* = 5/95) 78

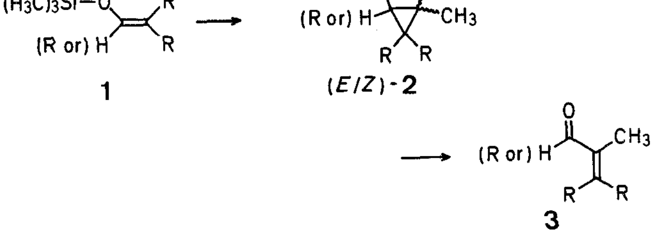
[a] Prepared from the corresponding aldehydes or ketones according to Ref.[3].

[b] Purities by ¹H-N.M.R. spectrometry: 2b, 95%; 2d, 90%; yields in the range 85–95%.

[c] Carbonyl compounds 3 have been isolated by chromatography on silica gel and yields are based on trimethylsilyl enol ethers 1. The yield of enal 3e determined by means of 2,4-dinitrophenylhydrazones was 82% after rearrangement by reflux in toluene and 75% when the mixture methanol/triethylamine was used. The purity of carbonyl compounds 3 checked by G.L.C. on Carbowax 20M and SE30 were higher than 95%.

[d] In the mixture methanol/triethylamine, the amine functions as a scavenger of the by-product hydrogen chloride and avoids the formation of methoxylated products.

such a facile sequence, applied to various open-chain ketones and aldehydes is a good method for the preparation of carbonyl compounds such as the so far not readily available α-methylene ketones (for recent papers concerning their preparation see Ref.[2]) and α-methyl-α,β-unsaturated ketones and aldehydes (Table 1).



The reaction of trimethylsilyl enol ethers 1 with chloromethylcarbene yields an (*E*/*Z*)-mixture (isolable in some cases by distillation under high vacuum) of the chloro-siloxy-methylcyclopropanes 2 in >90% yield. The crude mixture of 2, obtained after evaporation of solvents, is heated, either in toluene (or xylene) or in methanol/triethylamine, under reflux to give the final product 3 which is isolated by chromatography on silica gel (Table 1).

In the reaction of the enol ether (1f) of *n*-butanal with chloromethylcarbene, the mixture of both (*Z*)- and (*E*)-isomers was used, leading to a mixture of four chloro-siloxy-methylcyclopropanes 2f. On heating this mixture, 2f essentially gave the (*E*)-isomer, 2-methyl-pent-2-enal (3f), although both (*E*)- and (*Z*)-isomers were formed. The formation of (*E*)- and (*Z*)-isomers, and the (*Z*)→(*E*) isomerisation can be easily followed by N.M.R. or T.L.C. techniques. In the near future, we will report on synthetic and stereospecific applications of the reaction.

Chlorotrimethylsilyloxycyclopropanes 2:

Compounds 2 are prepared on a 0.01 molar scale by producing chloromethylcarbene from 1,1-dichloroethane (4 g, 0.04 mol) and *n*-butyllithium (0.03 mol) according to Ref.[4] in the presence of the enol ether 1 (0.01 mol) in anhydrous ether at a temperature of −30 to −40 °C (*n*-butyllithium is added slowly during 1.5 h); yield: 85–95% (determined by ¹H-N.M.R. spectrometry; some by-products also present).

The thermally stable compounds 2 can be roughly purified by rapid distillation under high vacuum when the boiling points are less than about 30 °C/0.03 torr although this purification is not necessary.

The (*E*/*Z*) ratio was determined from the ¹H-N.M.R. spectra, characteristic signals being assigned to each isomer using the known rules[5]. The stereochemistry of (*E*)- and (*Z*)-2d was assigned on the basis of the ¹H-N.M.R. and I.R. data of the corresponding cyclopropanols. The four isomers of 2f were easily detectable and their stereochemistry determined from the ¹H-N.M.R. spectrum in 2:1 CCl_4/C_6D_6 using the four doublets for the H—C—OSi proton at $\delta=2.64$ ($J=4$ Hz); 2.92 ($J=7.5$ Hz); 3.14 ($J=4$ Hz); and 3.50 ppm ($J=7.5$ Hz) which are respectively attributed to the (*Z*)-*trans*-2f, (*Z*)-*cis*-2f, (*E*)-*trans*-2f, and (*E*)-*cis*-2f isomers.

3,4-Dimethyl-3-pentene-2-one (3a):

3-Methyl-2-trimethylsiloxy-2-butene (1a): To a solution of chlorotrimethylsilane (32.5 g, 0.3 mol) and triethylamine (60.6 g, 0.6 mol) in dimethylformamide (100 ml) is added methyl isopropyl ketone (17.2 g, 0.2 mol) according to the general procedure[3], and the mixture is refluxed for 18 h under nitrogen. After the usual work-up[3], the crude mixture of 1a and 3-methyl-2-trimethylsiloxy-1-butene [1a′ (1a/1a′ ~ 60/40)] is obtained. (If the mixture is refluxed for 64 h, the ratio 1a/1a′ reaches 87/13). To the crude mixture of 1a/1a′ (60/40) dissolved in pentane (400 ml) is added iodine (0.5 g, 0.002 mol). After 12 h at room temperature, copper powder (1.9 g, 0.03 mol) is added and stirring is continued for 2 h. The mixture is filtered and the pale yellow solution is concentrated under moderate vacuum (200 torr). A flash distillation under vacuum (12 torr) leads to a crude mixture of silyl enol ethers 1a and 1a′ with a ratio 1a/1a′ ~ 94/6[11]; yield: 27 g. A careful distillation through a spinning band column allows isolation of the pure enol ether 1a; yield: 20 g (63%); b.p. 80 °C/220 torr.

A New, Convenient Synthesis of *N,N*-Bis[trimethylsilyl]arenesulfonamides

V. D. Romanenko, V. I. Tovstenko, T. V. Pidvarko,
L. N. Markovski*

Institute of Organic Chemistry Academy of Sciences of the Ukrainian SSR, 252660 Kiev, U.S.S.R.

The application of *N,N*-bis[trimethylsilyl]arenesulfonamides 3 in organic synthesis is a subject of current interest[1-4]. However, a convenient method for their preparation has hitherto not been reported. Although *N,N*-bis[trimethylsilyl]benzenesulfonamide

0039-7881/81/0432-0293 $ 03.00