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THE ALKYLATION AND BASE-PROMOTED RING-OPENING REACTION OF 3-PHENYLSULFONYL-3-TRIMETHYLSILYLCYCLOBUTANOLS. A NEW METHOD FOR THE PREPARATION OF β-METHYLENE KETONES

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β-Methylene ketones were produced by the alkylation of 1-alkyl-3-phenylsulfonyl-3-trimethylsilylcyclobutanols followed by the treatment with potassium hydride.

The ring-opening reaction of cyclobutanol derivatives which have a leaving group at γ-position is an interesting process for the synthesis of unsaturated ketones, and a few examples have been reported.[1)]

Recently, we showed that 1-alkyl-3-phenylthio-3-trimethylsilylcyclobutanols (1) and their trimethylsilyl ethers were easily prepared by the reaction of α,α-bis(trimethylsilyl)phenylthiomethyllithium with (chloromethyl)oxiranes[2)] and the ring-opening reaction proceeded in the sila-Pummerer rearrangement of sulfoxide derived from 1.[3)] We wish to report here the alkylation of 3-phenylsulfonyl-3-trimethylsilylcyclobutanols (2) which accompanies the rearrangement of trimethylsilyl group and base-promoted ring-opening reaction of the alkylated products (4) (Eq.1).

The oxidation of 1 was carried out by the treatment with m-chloroperbenzoic acid (2.5 equiv.) in CH_2Cl_2 at 0 °C for 1 h and the corresponding sulfones (2) were obtained in high yields (R^1= Et; 94%, Bu; 92%, $Ph(CH_2)_2$; 96%, Ph; 96%). When 2 was treated with butyllithium at 0 °C, the 1,4-silyl group shift from carbon to oxygen was observed.[4)] The resulting carbanion (3) was allowed to react with alkyl halide, and 3-alkylcyclobutanol (4) was obtained in good yield by the acid hydrolysis of the trimethylsilyl ether (Table 1).

Typical experimental procedure was as follows: To a THF (6 ml) solution of 1-phenyl-3-phenylsulfonyl-3-trimethylsilylcyclobutanol (2) (721 mg, 2 mmol) was added a hexane solution of butyllithium (2.2 mmol) at 0 °C and the reaction mixture was stirred until the silyl group shift completed (checked by TLC). Benzyl bromide (684 mg, 4 mmol) in HMPA (0.6 ml) was added to the reaction mixture and it was refluxed for 1 h. After cooling, the reaction mixture was quenched with a phosphate buffer solution (pH 7) and organic layer was extracted with AcOEt. The extract was condensed under reduced pressure. The crude trimethylsilyl ether was dissolved in EtOH (10 ml)-HCl (1 mol dm^{-3}, 1 ml) and stirred for 30 min at r.t. The reaction mixture was diluted with water. The organic layer was extracted with AcOEt and dried over Na_2SO_4. The solvent was removed, the residue was chromatographed on silica gel (AcOEt-hexane), and 3-benzyl-1-phenyl-3-phenyl-

sulfonylcyclobutanol (4) (702 mg) was isolated in 93% yield.

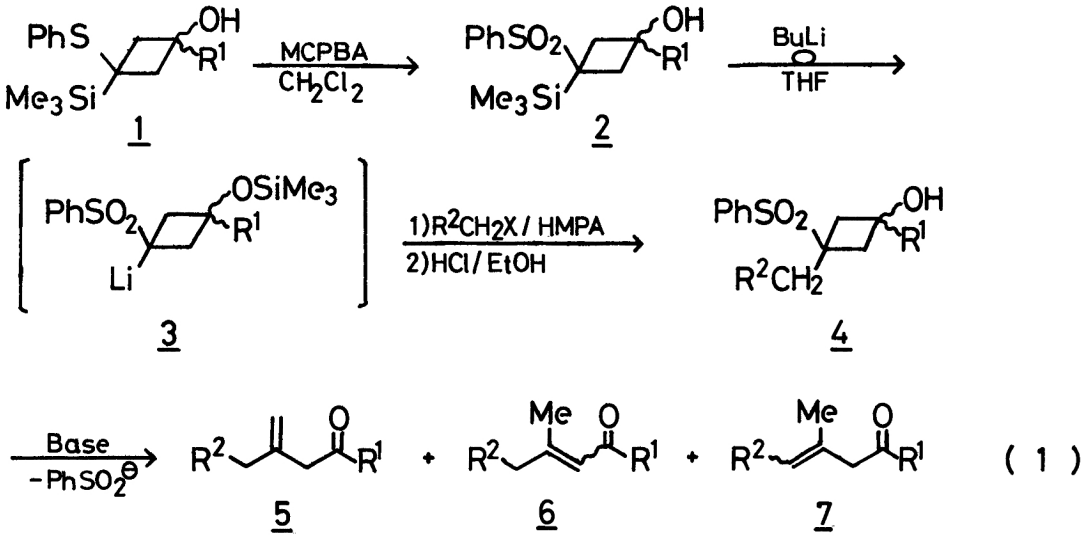

Table 1. Alkylation of 3-Phenylsulfonyl-3-trimethylsilylcyclobutanols (2).

R^1	R^2CH_2X MeOTs	$n\text{-}C_8H_{17}I$	$PhCH_2Br$	Yield of (4)[5] (%) $CH_2=CHCH_2Br$
Et	74	83	81	
Bu	74	87	82	84
$Ph(CH_2)_2$	78		83	
Ph	84	87	93	

The base-promoted conversion of 3-benzylcyclobutanols (4; R^2=Ph) to the unsaturated ketones was examined under various reaction conditions and it was found that potassium hydride was effective for the present ring-opening reaction and β-methylene ketone (5) and β,γ-unsaturated ketone (7) were produced in high yield (run 7). Further, β-methylene ketone (5) was obtained as a major product when the large excess amounts of base was used (run 9) (Table 2).

In a similar manner, various 3-phenylsulfonylcyclobutanols (4) were treated with potassium hydride and the corresponding unsaturated ketones were synthesized (Table 3).

The typical experimental procedure was as follows: To a THF (5 ml) suspension of potassium hydride (4.7 mmol) was added a THF (7 ml) solution of 3-methyl-1-phenylethyl-3-phenylsulfonylcyclobutanol (4) (387 mg, 1.17 mmol) at r.t. over 5 min. After stirring for 5 min, the reaction mixture was cooled to -78 °C and quenched with a phosphate buffer solution (pH 7). The organic layer was extracted with ether and dried over Na_2SO_4. After evaporation of the solvent, the residue was purified by TLC (AcOEt-hexane) and 2-methyl-4-oxo-6-phenyl-1-hexene (5) and 2-methyl-4-oxo-6-phenyl-2-hexene (6) (214 mg) were obtained in 97% yield.

The ratio of the isomers was determined by the NMR spectrum of the mixture.

Many reactions for the preparation of β,γ-unsaturated ketones[6] including the isomerization of α,β-unsaturated ketones[7] have been reported. Some of these ractions were employed for the synthesis of β-metylene ketones.[6b,e,f,j),7b]

Table 2. Effect of the Reaction Conditions in the Ring-opening Reaction of 3-Benzyl-3-phenylsulfonylcyclobutanols (4;R^2=Ph).[a]

Run	R^1	Base (equiv.)	Solvent (3 ml/mmol)	Temp	Time min	Yield %	Ratio of isomers[b] (5)	(7)
1	Et	BuLi (1.1)	THF	reflux	180	0	—	—
2	Et	BuLi (1.1)	THF-HMPA[c]	reflux	90	42	—	100
3	Bu	BuLi (1.1)	THF-HMPA[c]	reflux	40	26	—	100
4	Bu	NaH (2.1)	THF-HMPA[c]	r.t.	60	61	—	100
5	Bu	NaH (3.0)	THF-HMPA[c]	r.t.	150	71	—	100
6	Et	tBuOK (2.2)	THF	r.t.	15	44	—	100
7	Et	KH (2.2)	THF	r.t.	15	92	12	88
8	Et	KH (4.0)	THF	r.t.	10	70	48	52
9	Et	KH (4.0)	THF[d]	r.t.	10	72	57	43

a) The reaction was quenched at r.t.

b) Determined by NMR spectrum. The formation of 6 was not observed.

c) 0.3 ml/mmol of HMPA was used.

d) 10 ml/mmol of THF was used.

Table 3. Ring-opening Reaction of 4.[a]

R^1	R^2CH_2	Reaction Time min	Total yield %	Ratio of isomers[b] (5)[5]	(6)[5]	(7)[5]
Et	$PhCH_2$	10	72[c]	57	—	43
Bu	$PhCH_2$	7	83	48	—	52
Et	Oct	7	90	84	16	—
Bu	Oct	7	97	87	13	—
$Ph(CH_2)_2$	Oct	7	74[d]	87	13	—
$Ph(CH_2)_2$	Me	5	97	87	13	—
Ph	Oct	3	96	31	69	—

a) The reaction was carried out by the treatment of 6 with KH (4 equiv.) in THF (10 ml/mmol) at r.t. and was quenched at -78 °C.

b) Determined by NMR spectrum.

c) The reaction was quenched at r.t.

d) Overall yield from 2.

Though the result listed in Table 3 shows that the partial isomerization of the initially formed β-methylene ketone (5) to 6 or 7 proceeds under the basic conditions, the present reaction provides a general method for the preparation of β-methylene aliphatic ketones.

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