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THE SILA-PUMMERER REARRANGEMENT OF 1-ALKYL-3-PHENYLSULFINYL-3-TRIMETHYLSILYLCYCLOBUTANOLS. A NEW METHOD FOR THE PREPARATION OF 3-ALKYL-2-CYCLOBUTENONES

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3-Alkyl-2-cyclobutenones were produced by the sila-Pummerer rearrangement of 1-acetoxy-1-alkyl-3-phenylsulfinyl-3-trimethylsilylcyclobutanes followed by hydrolysis. β-Phenylthio-α,β- and β,γ-unsaturated ketones were major products when the corresponding cyclobutanols were employed.

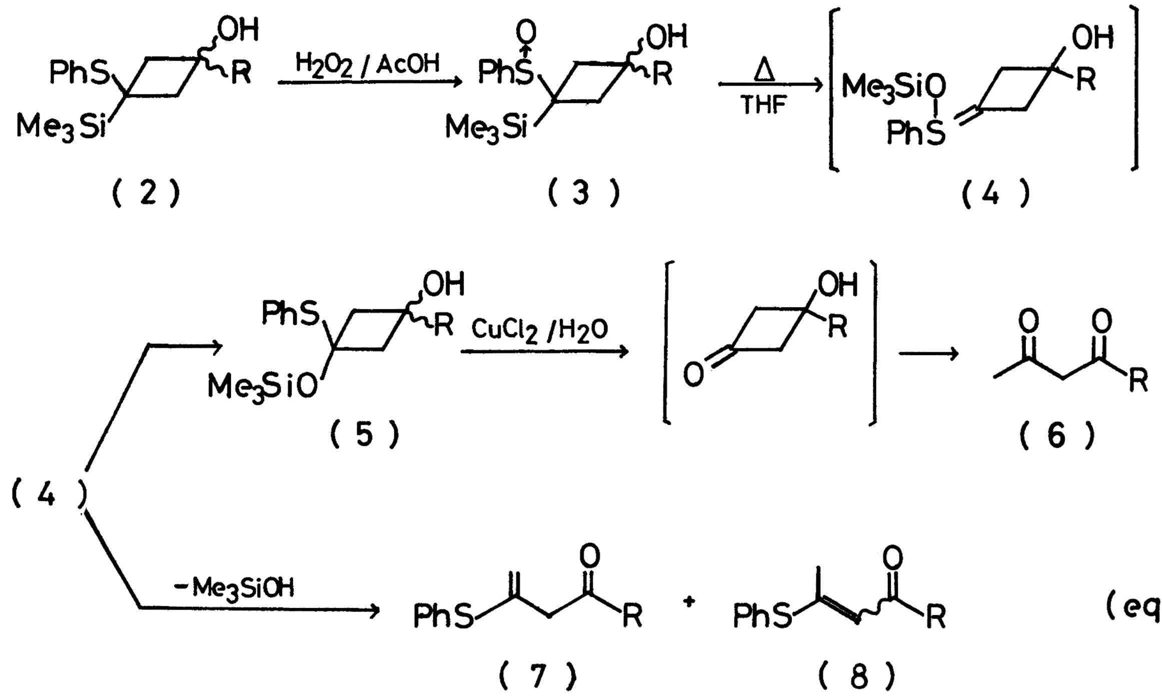
Sila - Pummerer rearrangement has been extensively studied and was applied for the mild conversion of sulfoxide to various carbonyl compounds.$^{1)}$

Recently, we showed that 1-alkyl-3-phenylthio-3-trimethylsilyl-1-trimethylsiloxycyclobutanes (1) were easily prepared by the reaction of α,α-bis(trimethylsilyl)phenylthiomethyllithium with (chloromethyl)oxiranes in good yields.$^{2)}$ The cyclobutane (1) can be regarded as a precursor of cyclobutanone derivatives which are generally prepared by the reaction of ketene or its equivalent with alkene or alkyne. We wish to report here the result of the sila-Pummerer rearrangement of 1-alkyl-3-phenylsulfinyl-3-trimethylsilylcyclobutanols (2) prepared from 1 and a procedure for the conversion of 2 to 3-alkyl-2-cyclobutenones (11), which were previously synthesized by the reaction of 1,1-dichloro-2,2-difluoroethylene with phenylacetylene followed by the chemical conversions,$^{3)}$ the oxidation and elimination of sulfinic acid of 3-alkyl-3-(phenylsulfonyl)cyclobutanols,$^{4)}$ or the reaction of 3-ethoxy-2-cyclobutenone with Grignard reagents.$^{5)}$

1-Phenyl-3-phenylthio-3-trimethylsilylcyclobutanol (2d)$^{6)}$ was treated with hydrogen peroxide in acetic acid to give the corresponding sulfoxide (3d). When the THF solution of 3d was refluxed for 15 min, the formation of two products was observed. After hydrolysis of the crude material, it was found that only a trace amount of benzoylacetone (6d) which is a normal product of the present sila-Pummerer rearrangement was obtained and β-methylene-β-phenylthio ketone (7d) and its isomer (8d) were isolated as major products (58%, 7d/8d=0.21). This result shows that the rate of ring-opening reaction of betaine intermediate (4) was much faster than that of the formation of S,O-acetal (5) by the nucleophilic attack of trimethylsiloxy anion (eq-1).

Since 7 and 8 were the interesting synthetic intermediates as selectively protected 1,3-diketones, we examined the preparation of them under the similar reaction conditions and the various β-phenylthio unsaturated ketones were obtained.

The ratio of isomers varied with the alkyl substituent of 3 and reaction time (Table-1).



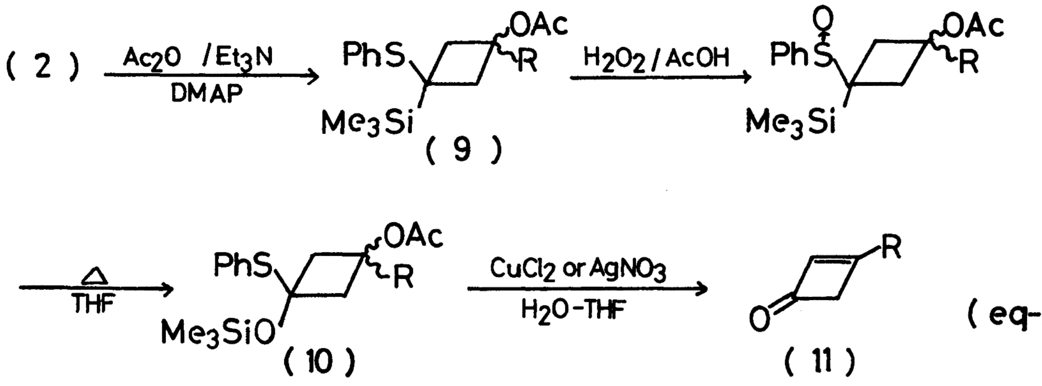
(eq-1)

The typical experimental procedure was as follows; to a AcOH (5 ml) solution of 1-(2-phenylethyl)-3-phenylthio-3-trimethylsilylcyclobutanol (2c) (357 mg, 1 mmol) was added 35% hydrogen peroxide (1.1 mmol) and stirred for 5 h. The reaction mixture was quenched with water and organic layer was extracted with CH_2Cl_2, washed with 5% $NaHCO_3$ aqueous solution and water successively and dried over Na_2SO_4. The extract was condensed under reduced pressure at r.t. The crude sulfoxide (3c) was dissolved in THF (8 ml) and refluxed for 15 min. After cooling, the solvent was removed and the residue was purified by TLC (AcOEt-hexane) to give 4-oxo-6-phenyl-2-phenylthio-1-hexene (7c) and its isomer (8c) (191 mg, 68%). The ratio of the isomers was determined by nmr spectrum of the mixture.

Based on the above result, 2 was acetylated in order to prepare the cyclobutenone (11). The acetylation was carried out by the treatment with acetic anhydride and triethylamine in the presence of a catalytic amount of 4-dimethylaminopyridine (DMAP) in good yields. The oxidation and rearrangement of acetate (9) were carried out in a similar manner applied for the cyclobutanol (2). The S,O-acetal (10) was hydrolized in the presence of $AgNO_3$ or $CuCl_2$ to produce 3-alkyl-2-cyclobutenone (11) in moderate yield (eq-2, Table-2).

The following experimental procedure is representative; to a triethylamine (2 ml) solution of 1-phenyl-3-phenylthio-3-trimethylsilylcyclobutanol (2d) (329 mg, 1 mmol) were added acetic anhydride (2 ml) and DMAP (5 mg, 0.04 mmol) at r.t. After stirring overnight, the reaction mixture was quenched with a phosphate buffer solution (pH 7), extracted with AcOEt and dried over Na_2SO_4. The extract was condensed under reduced pressure and the residue was chromatographed on silica gel (AcOEt-hexane) and the acetate (9d) (355 mg) was isolated in 96% yield. Silver nitrate (170 mg, 1 mmol) and water (8 ml) were added to the THF (8 ml) solution of the crude

S,O-acetal (10d) prepared by the oxidation and thermal rearrangement of 1-acetoxy-1-phenyl-3-phenylthio-3-trimethylsilylcyclobutane (9d) (371 mg, 1 mmol) and the solution was stirred overnight. After addition of water, the reaction mixture was filtered and the filtrate was extracted with ether. The extract was dried over Na_2SO_4 and condensed. The residue was purified by TLC (AcOEt-hexane) and 3-phenyl-2-cyclobutenone (11d) (104 mg, 72%) was obtained.



(eq-2)

Table-1

Entry	R	Time[a] (min)	Yield[b),7)] (%)	7/8
a	Et	15	58	0.81
b	Bu	13	64	3.4
c	Ph(CH$_2$)$_2$	15	68	12
	Ph(CH$_2$)$_2$	120	66	1.9
d[c]	Ph	47	59	0.83

a) Reflux time of the thermal reaction of 3. b) Overall yield from 2. c) Ether was used as a solvent.

Table-2

	Yield(%)		
R	9[7,8]	Catalyst for hydrolysis	11[a),7)]
Et	99		
Bu	93	CuCl$_2$	43[9]
Ph(CH$_2$)$_2$	94	CuCl$_2$	63
Ph	96	AgNO$_3$	72

a) Overall yield from 9.

Further investgation on the reaction of 1 is now in progress.

References

1) E. W. Colvin, "Silicon in Organic Synthesis," Butterworths, London (1981), P. 33; D. J. Ager, Tetrahedron Lett., 21, 4759 (1980); 22, 587 (1981); I. Cutting and P. J. Parsons, ibid., 22, 2021 (1981); D. J. Ager, ibid., 22, 2803 (1981).

2) T. Takeda, S. Naito, K. Ando, and T. Fujiwara, Bull. Chem. Soc. Jpn., in press. The yield of 1 increased by the modification of reaction procedure. When α,α-bis(trimethylsilyl)phenylthiomethyllithium was prepared by the method reported by Gröbel and Seebach and the reaction with (chloromethyl)oxirane was carried out at -78°C to r.t. overnight, 1a and 1d were obtained in 82% and 49% yields, respectively; B-T. Gröbel and D. Seebach, Chem. Ber., 110, 852 (1977).

3) S. L. Manatt, M. Vogel, D. Knutson, and J. D. Roberts, J. Am. Chem. Soc., 86, 2645 (1964).

4) B. Corbel, J. M. Decesare, and T. Durst, Can. J. Chem., 56, 505 (1978).

5) H. H. Wasserman, J. U. Piper, and E. V. Dehmlow, J. Org. Chem., 38, 1451 (1973).

6) The hydrolysis of 1 was carried out in EtOH (5 ml/mmol)-1N HCl (0.5 ml/mmol) at r.t. for 1 h and the yields of 2 were as follows; 2a 95%, 2b 96%, 2c 96%, 2d 98%.

7) All products were identified by ir and nmr spectra.

8) The nmr spectrum of 1 suggested that 1 was a mixture of stereoisomers. While the isomers of 1 could not be separated each other by TLC, the two isomers (9 and 9') were isolated after acetylation. The ratio and nmr data of 9 and 9' are as follows; 9a:9a'=89:11, ^{1}H-nmr(CCl$_4$) 9a δ=0.07 (s,9H), 0.53 (t, J=7.5 Hz, 3H),1.12-1.60 (m, 2H),1.90 (s, 3H),2.31 (br d, J=14 Hz, 2H),2.66 (br d, J=14 Hz, 2H),7.22-7.65 (m, 5H). 9a' δ=0.14 (s, 9H),0.65 (t, J=7.5 Hz, 3H),1.53 (s, 3H), 1.81 (q, J=7.5 Hz, 2H), 2.54 (s, 4H), 7.28-7.70 (m, 5H). 9b:9b'=89:11, ^{1}H-nmr (CCl$_4$) 9b δ=0.06 (s, 9H),0.56-1.51 (m, 9H),1.88 (s, 3H),2.15-2.86 (m, 4H),7.11-7.73 (m, 5H). 9b' δ=0.14 (s, 9H),0.65-1.38 (m, 7H),1.49 (s, 3H),1.63-2.05 (m, 2H), 2.44-2.71 (m, 4H),7.20-7.78 (m, 5H). 9c:9c'=79:21, ^{1}H-nmr(CCl$_4$) 9c δ=0.11 (s, 9H),1.41-1.78 (m, 2H),1.84 (s, 3H),2.14-2.93 (m, 6H),6.85-7.70 (m, 10H). 9c' δ= 0.13 (s, 9H),1.43 (s, 3H),1.93-2.48 (m, 4H),2.48-2.86 (m, 4H),6.84-7.77 (m, 10H). 9d:9d'=97:3, ^{1}H-nmr(CCl$_4$) 9d δ=0.27 (s, 9H),1.87 (s, 3H),2.96 (s, 4H),6.92-7.48 (m, 10H). 9d' δ=-0.14 (s, 9H),1.37 (s, 3H),2.62-3.35 (m, 4H),6.95-7.78 (m, 10H).

9) The cyclobutenone (11b) obtained in 56% yield by the usual work-up was contaminated by a trace amount of 3-acetoxy-3-butylcyclobutanone. The treatment of the crude product with triethylamine in THF at r.t. afforded the pure product in 43% yield.

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