CHEMISTRY LETTERS, pp.609-610, 1978. Published by the Chemical Society of Japan

SYNTHESIS OF SILYL ENOL ETHER. REACTION OF SILYLENE WITH CARBONYL COMPOUNDS

Wataru ANDO* and Masayuki IKENO
Department of Chemistry, The University of Tsukuba,
Niiharigun, Ibaraki 300-31

Under neutral and mild conditions, silyl enol ethers are synthesized in good yields by the reactions of ketones or aldehydes with dimethylsilylene, which generated by the photolysis of dodecamethylcyclohexasilane.

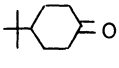
Recently, the silylation of organic compounds has become important parts of organic chemistry and biochemistry, because of protection for the functional groups, and of increasing volatility and solubility of intractable materials toward distillation or glc analysis such as amino acids[1),2)] and steroids.[3),4)] Generally, silylations of organic compounds are well known with chlorosilanes and a tertiary amine,[5)] silyl-proton exchange reactions using silylamines[6)] and silylamides.[7),8)] However, these approaches which require the basic conditions, have some problems involving formation of large amount of amine salts.

We now wish to report a new type of silylation using the reaction of dimethylsilylene with ketones and aldehydes. Under mild and neutral conditions, this method provides the most direct synthesis of silyl enol ethers which have an active hydrogen at silicon center.

$$\underset{\text{I}}{(Me_2Si)_6} + \underset{\text{II}}{R\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_2R'} \xrightarrow[EtOEt]{h\nu} \underset{\text{III}}{R\text{-}\overset{OSiMe_2H}{\overset{|}{C}}\text{=}CHR'}$$

Typically, an ether solution of dodecamethylcyclohexasilane(I)[9)] (0.4 mmol) and carbonyl compounds(II)(0.6 mmol) in quartz tube was irradiated with a low pressure mercury lamp for 6 hr. The reaction mixture was distilled to give silyl enol ethers. The structure of silyl enol ethers (III) was confirmed by mass, IR, and NMR spectra.[10)] The results are summarized in Table I.

Table I. Silylation of ketones and aldehydes.

RCOR' (II-1~10)	Conversion of (II) %[a]	Silyl enol ether (III-1~10) %[a]	bp, °C[c]	ν(Si-H), (C=C) cm^{-1}		M^+ m/e
1 MeCOMe	100	93 (61)[b]	74-75	2120	1660	116
2 EtCOEt	100	100 (80)[b]	115-116	2125	1675	144
3 	100	96 (80)[b]	143	2140	1645	142
4 	100	100 (90)[b]	160-161	2120	1670	156
5 	100	100		2120	1680	212

(Table continued)

Table I (continued)

RCOR' (II-1~10)	Conversion of (II) %[a]	Silyl enol ether (III-1~10) %[a]	bp, °C[c]	ν(Si-H), (C=C) cm^{-1}		M^+ m/e
6 $Me(CH_2)_2CHO$	100	50		2120	1660	130
7 $Me(CH_2)_3CHO$	100	52		2120	1665	144
8 $Me(CH_2)_4CHO$	100	66		2120	1665	158
9 $Me(CH_2)_6CHO$	100	63		2120	1665	186
10 $Me(CH_2)_7CHO$	100	83		2120	1670	200

a; Yields were obtained by GLPC analyses relative to the area of known amount of internal standards. b; Yields after distillation. c; The boiling points are uncorrected.

References and Notes

1) L.Birkofer and A.Ritter, Chem. Ber., 93, 424 (1960).
2) K.Rühlmann, Chem. Ber., 94, 1876 (1961).
3) J.F.Klebe, H.Finkbeiner and D.M.White, J. Am. Chem. Soc., 80, 3390 (1966).
4) H.Vorbruggen, P.Strehlke, Chem. Ber., 106, 3039 (1973).
5) H.O.House, L.J.Czuba, M.Gall and H.D.Olmstead, J. Org. Chem., 34, 2324 (1969).
6) R.Fessenden and D.F.Crowe, J. Org. Chem., 26, 4638 (1961).
7) L.Birkofer, A.Ritter and R.Bentz, Chem. Ber., 97, 2196 (1964).
8) L.Birkofer, A.Ritter and W.Gieddler, Angew. Chem., 75, 93 (1963).
9) M.Ishikawa and M.Kumada, J. Organomet. Chem., 42, 325 (1972).
10) III-1; nmr(CCl_4) (δ) [0.26(Me_2Si, d, 6H), 1.75(Me-C, s, 3H), 3.96(CH_2=C, s, 2H), 4.56-4.90(Si-H, m, 1H)]. III-2; nmr(CCl_4) (δ) [0.23(Me_2Si, d, 6H), 0.91(Me-CH_2, t, 3H), 1.50(Me-CH=, d, 3H), 2.06(CH_2-C=, q, 2H), 4.50(CH=C, q, 1H), 4.56-4.86(Si-H, m, 1H)]. III-3; nmr(CCl_4) (δ) [0.25 (Me_2Si, d, 6H), 1.56-2.43(ring protons, m, 6H), 4.48(vinylic proton, broad s, 1H), 4.56-4.80 (Si-H, m, 1H)]. III-4; nmr(CCl_4) (δ) [0.23(Me_2Si, d, 6H), 1.26-2.16(ring protons, m, 8H), 4.50-4.87(vinylic proton and Si-H, m, 2H)]. III-5; nmr(CCl_4) (δ) [0.25(Me_2Si, d, 6H), 0.87 (Me_3C, s, 9H), 1.33-2.16(ring protons, m, 7H), 4.53-4.80(vinylic proton and Si-H, m, 2H)]. III-6; nmr(CCl_4) (δ) [0.25(Me_2Si, d, 6H), 0.95(Me-C, t, 3H), 1.53-2.23(CH_2-C=, m, 2H), 4.50-4.83 (Si-H, m, 1H), 4.98(CH=C, t, 1H), 6.09(C=CH-O, d, 1H)]. III-7; nmr(CCl_4) (δ) [0.25(Me_2Si, d, 6H), 0.86(Me-C, t, 3H), 1.06-1.60(CH_2-C, m, 2H), 1.60-2.10(CH_2-C=, m, 2H), 4.56-4.81(Si-H, m, 1H), 4.96(CH=C, t, 1H), 6.10(C=CH-O, d, 1H)]. III-8; nmr(CCl_4) (δ) [0.25(Me_2Si, d, 6H), 0.73-1.10(Me-C, m, 3H), 1.10-1.56(-$(CH_2)_2$-, m, 4H), 1.56-2.13(CH_2-C=, m, 2H), 4.53-4.86(Si-H, m, 1H), 4.96(CH=C, t, 1H), 6.13(C=CH-O, d, 1H)]. III-9; nmr(CCl_4) (δ) [0.25(Me_2Si, d, 6H), 0.70-1.10(Me-C, m, 3H), 1.10-1.50(-$(CH_2)_4$-, m, 8H), 1.50-2.10(CH_2-C=, m, 2H), 4.60-4.83(Si-H, m, 1H), 4.96(CH=C, t, 1H), 6.13(C=CH-O, d, 1H)]. III-10; nmr(CCl_4) (δ) [0.25(Me_2Si, d, 6H), 0.66-1.06(Me-C, m, 3H), 1.06-1.56(-$(CH_2)_5$-, m, 10H), 1.56-2.06(CH_2-C=, m, 2H), 4.60-4.80(Si-H, m, 1H), 4.95(CH=C, t, 1H), 6.10(C=CH-O, d, 1H)].

(Received April 5, 1978)