CHEMISTRY LETTERS, pp. 1219-1222, 1977. Published by the Chemical Society of Japan

TWO TYPES OF INDIRECT CYCLODIMERIZATION OF BIACETYL *VIA* ITS ENOL SILYL ETHERS1)

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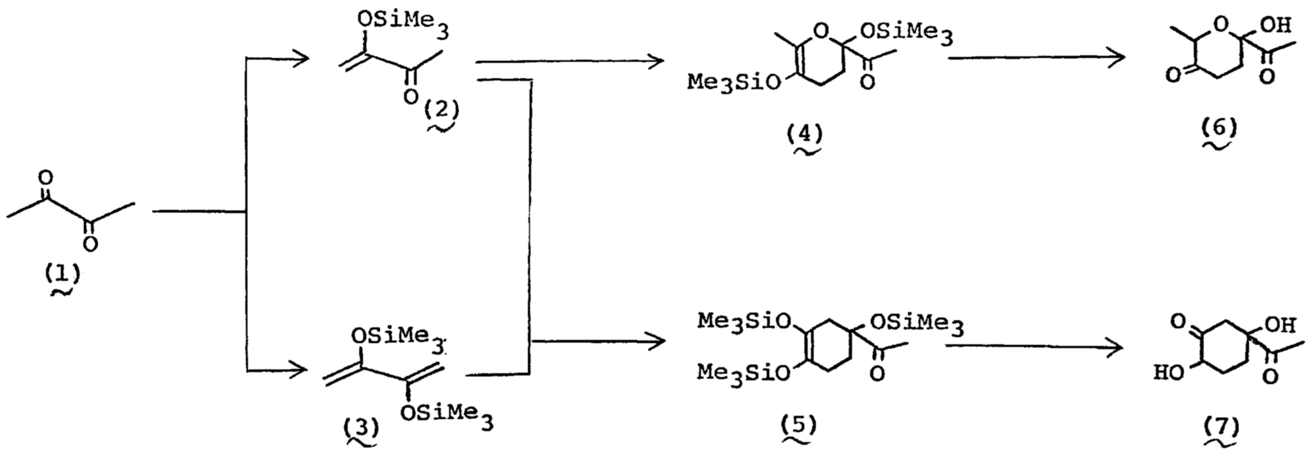
Silyl ethers of biacetyl enols, an enone 2 and a diene 3, were prepared. Cyclodimerization of 2 gave a dihydropyran 4, while reaction of 3 with 2, maleic anhydride, and ethyl acrylate gave Diels-Alder adduct 5, 8, and 9, respectively. The compounds 4 and 5 were desilylated to afford 6 and a mixture of 7 and 7', respectively.

Of late years, synthetic utility of cycloaddition of enol silyl ethers has been shown2) and we have already reported [2+1] and [2+2] cycloaddition reactions of enol silyl ethers.3) These reactions are important from the viewpoint that cycloaddition of parent enols is usually difficult to bring about because the enols normally exist only in low concentrations as the tautomers of the corresponding ketones. In principle, any kind of enol derivatives such as enol alkyl ethers or enol esters can be employed in these cycloaddition. However enol silyl ethers are those of choice because of convenience in preparation and desilylation2) before and after cycloaddition, respectively. In this paper, we describe two types of indirect cyclodimerization of biacetyl *via* its enol silyl ethers. The results are shown in Scheme I.

The selective synthesis of mono- and bis-trimethylsilyl derivatives of biacetyl

$$\mathbf{1} \;\text{—}\begin{cases} \xrightarrow[\text{pentane, 25°C, 6 hr}]{\text{Me}_3\text{SiCl(1.0 equiv.), Et}_3\text{N(1.0 equiv.)}} \mathbf{2}\ (60\%) \\[2ex] \xrightarrow[\text{DMF, reflux, 5 hr}]{\text{Me}_3\text{SiCl(2.3 equiv.), Et}_3\text{N(2.7 equiv.)}} \mathbf{3}\ (60\%) \end{cases} \qquad (1)$$

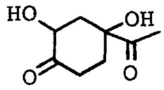


Scheme I. Cyclodimerization of biacetyl *via* enol silyl ethers.

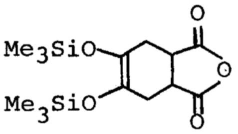
enols, **2** and **3**, was carried out as shown in eq. 1. The preparation of **2**[4] was performed in a manner similar to the silylation of acetyl acetone,[5] while House's method was used for the preparation of **3**.[6,7] Although two other methods for the synthesis of **3** have been published,[8] the present straightforward method is far more convenient and practical.

The α,β-unsaturated ketone **2** underwent [4+2] cyclodimerization to give a dimer **4**[9] on prolonged standing at room temperature. Preparatively, **4** was obtained by heating **2** (2.0 g) with a small amount of hydroquinone(10 mg) at 100°C for 4 hr. Distillation of the reaction mixture gave pure **4** in 59% yield, b.p. 86-87°C(0.4 mmHg). The Diels-Alder reaction of **2**(4.7 g, 0.03 mol) with the diene **3**(6.9 g, 0.03 mol) was carried out at 160°C(reflux) for 48 hr in the presence of hydroquinone(10 mg). The [4+2] adduct **5**[10] was isolated by fractional distillation in a yield of 57%, b.p. 101-102°C(0.2 mmHg). When the reaction of **2** with **3** was carried out at lower temperature, for example at 120°C, the Diels-Alder adduct **5** was obtained only in a poor yield and the cyclodimer **4** was formed as main product instead.

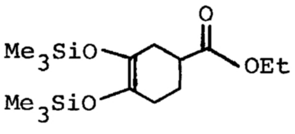
Desilylation of **4** and **5** was performed in a following way. A sample of **4**(0.89 g) was dissolved in a mixture of THF(30 ml) and 1N aq. HCl(1.5 ml). The solution was heated under reflux for 1 hr, neutralized with $CaCO_3$(2 g), filtered to remove the calcium salts, dried($MgSO_4$), and then distilled to give desilylated products **6**[11] (0.40 g, 82%) boiling at 89-95°C(0.6 mmHg). The NMR spectrum of **6** exhibited two singlets(CH_3CO-, δ 2.29 and 2.31) of nearly equal peak area indicating that **6** was a 1:1 mixture of two stereoisomers. A rather complex situation might be foreseen for the hydrolysis of **5**, since hydrolysis of the ene-diol disilyl ether unit of **5** would be expected to take place in non-regioselective manner. Desilylation of **5** in the same way as described for **4** gave a mixture$^{12,13)}$ of the two regioisomers, **7** and **7'**, in 82% yield, b.p. 107-120°C(0.9 mmHg).



(**7'**)



(**8**)



(**9**)

The overall transformation described above can be considered that cyclodimerization of biacetyl enols are performed indirectly.

Typical dienophiles also react with 2,3-bis(trimethylsiloxy)butadiene **3**. The reaction of maleic anhydride with **3** (in benzene, 80°C, 6 hr) gave an adduct **8**$^{14)}$ in 73% yield (b.p. 167-169°C(5 mmHg)) and that of ethyl acrylate (without solvent, reflux, 18 hr) afforded **9**$^{15)}$ in a yield of 73% (b.p. 110-115°C(1.5 mmHg)).

REFERENCES AND NOTES

1) Synthesis <u>via</u> Silyl Alkenyl Ethers, Part XI. Part X: I. Ryu, S. Murai, S. Otani, and N. Sonoda, Tetrahedron Lett., 1995(1977).
2) For a recent review, see J. K. Rasmussen, Synthesis, 91(1977). See also M. E. Jung and C. A. McComs, Tetrahedron Lett., 2935(1976) and refs. cited therein.
3) For [2+1] see S. Murai, T. Aya, and N. Sonoda, J. Org. Chem., **38**, 4354(1973). See also Part X$^{1)}$ and refs. cited therein. For [2+2] see K. Mizuno, H. Okamoto, C. Pac, H. Sakurai, S. Murai, and N. Sonoda, Chem. Lett., 237(1975).
4) To a mixture of biacetyl(0.5 mol) and Me_3SiCl(0.5 mol) in pentane(200 ml) was added Et_3N(0.5 mol) at 20°C over a period of 30 min and the mixture was stirred at 20°C, 6 hr. After filtration and concentration, the remaining $Et_3N.HCl$ was further removed by a short column(Al_2O_3). Distillation of the elute gave **2** in 60% yield, b.p. 64-65°C(25 mmHg); IR(neat) 1730 and 1640 cm^{-1}; NMR(CCl_4) δ 0.22 (s, 9H), 2.33(s, 3H), 4.88(d, 1H), and 5.33(d, 1H).
5) R. West, J. Amer. Chem. Soc., **80**, 3246(1958).
6) H. O. House, L. J. C. Czuba, M. Gall, and H. D. Olmstead, J. Org. Chem., **34**, 2324 (1969).
7) To a mixture of Me_3SiCl(0.7 mol) and Et_3N(0.8 mol) in DMF(175 ml) was added bi-

acetyl(0.3 mol) in DMF(25 ml) at 25°C over a period of 30 min. Then the mixture was stirred under reflux for 5 hr. Work-up with pentane[6] afforded **3** in 60% yield, b.p. 125-130°C(80 mmHg); IR(neat) 1595 cm^{-1}; NMR(CCl_4) δ 0.22(s, 18H), 4.20(s, 2H), 4.69(s, 2H).

8) J. M. Denis and J. M. Conia, Tetrahedron Lett., 4593(1972); G. Simchen and W. Kober, Synthesis, 259(1976).

9) Compound **4**; IR(neat) 1740 cm^{-1}; NMR(CCl_4) δ 0.04(s, 18H), 1.17(s, 3H), 2.10(s, 3H), 1.40-2.40(m, 4H); MS m/e P^+ 316, P^+-(CH_3CO) 273. Anal. Calcd for $C_{14}H_{28}O_4Si_2$: C, 53,12; H, 8.92. Found: C, 52.87; H, 9.08.

10) Compound **5**; IR(neat) 1733 cm^{-1}; NMR(CCl_4) δ 0.11(s, 9H), 0.13(s, 9H), 0.15(s, 9H), 2.14(s, 3H), 1.57-2.77(m, 6H); MS m/e P^+ 388, P^+-(CH_3CO) 245. Anal. Calcd for $C_{17}H_{36}O_4Si_3$: C, 52.53; H, 9.33. Found: C, 52.34; H, 9.40.

11) Compound **6**; IR(neat) 3450, 1755, 1725 cm^{-1}; NMR(CCl_4) δ 1.12 and 1.25(equal area, total 3H), 1.35-1.37(2H), 2.29-2.31(two singlets, equal area, total 3H), 2.42-2.69(2H), 3.12-3.36(1H), 3.52-4.32(1H, disappeared with D_2O); MS m/e P^+ 172, P-(H_2O) 154. Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 55.61; H, 6.74.

12) *For simplicity,* ***7'*** *is not shown in Scheme I.*

13) Analytical data of a mixture of **7** and **7'**; IR(neat) 3450, 1720 cm^{-1}; NMR($CDCl_3$) δ 1.12-3.14(m, 10H)[four closely spaced singlets(ca. δ 2.30, 3H) overlaps in methylene and methin protons(7H)], 3.86(s, 2H, disappeared with D_2O); MS m/e P^+ 172, P-(H_2O) 154. Anal. Calcd for $C_8H_{12}O_4$: C, 55.80; H, 7.03. Found: C, 56.08; H, 6.94. No effort was made to seperate each isomer.

14) Compound **8**; IR(neat) 1854, 1789, 1691 cm^{-1}; NMR(CCl_4) δ 0.14(s, 18H), 2.48(m, 4H), 3.35(m, 2H). Anal. Calcd for $C_{14}H_{24}O_5Si_2$: C, 50.90; H, 7.27. Found: C, 51.18; H, 7.36.

15) Compound **9**; IR(neat) 1750, 1699 cm^{-1}; NMR(CCl_4) δ 0.12(s, 9H), 0.15(s, 9H), 1.26(t, 3H), 1.60-2.50(m, 7H), 4.07(q, 2H). Anal. Calcd for $C_{15}H_{30}O_4Si_2$: C, 54.38; H, 9.42. Found: C, 54.50; H, 9.15.

(Received July 25, 1977)