mixture, are particularly convenient from a preparative viewpoint as an asymmetrically dialkylsubstituted PAN derivative can be obtained in good yields and practically free from the symmetrically substituted ones, especially if care is taken in the first step of alkylation to maximize the PAN conversion with a minimum extent of symmetric dialkylation. This can be selectively performed by using a relatively small excess of alkylating agent and therefore longer reaction times.

The in situ formation of the quaternary ammonium salt is not the only factor controlling the catalytic activity of amines in the dialkylation and monoalkylation of PAN, at least in the reported conditions. In fact, the extent of quaternization (determined kinetically) of tri-*n*-butylamine reaches only a 30% value after 400 min and therefore does not suffice to explain the kinetic feature of PAN mono- and dialkylation.

## Experimental Section

Starting and final product were characterized by a Varian T60 NMR spectrophotometer with $Me_4Si$ as internal standard.

Gas-chromatographic analyses were done on a Perkin-Elmer F 30 gas chromatograph equipped with a 6 ft × ⅛ in. 2% silicon gum rubber SE 30 on high performance Chromosorb W (AW-DMCS) 80–100 mesh columns.

Viscometric measurements were carried out in methanol at 25 °C by using a Desreux-Bishoff dilution viscometer.

**Reagents.** Commercial grade phenylacetonitrile (PAN), bromoethane, 1-bromobutane, and tri-*n*-butylamine were purified by distillation.

**Poly(4-vinylpyridine)** was prepared by polymerization of 4-vinylpyridine in bulk at 40 °C in the presence of AIBN. The polymeric product was purified by dissolution in methanol and reprecipitation in diethyl ether (conversion >90%). The average molecular weight ($\overline{M}_v$) as determined by viscometric measurements was $3.15 \times 10^5$.[6]

**Tetra-*n*-butylammonium Bromide.**[7] A mixture of 4.62 g (25 mmol) of tri-*n*-butylamine and 17.1 g (125 mmol) of 1-bromobutane was heated at 70 °C in a sealed vial. After 70 h the reaction product was precipitated into diethyl ether and recrystallized from absolute ethanol–pentane (2:3) as white crystals.

**Dialkylation Reactions.** The reactions were carried out under nitrogen in a 100-mL two-necked flask equipped with a condenser and a serum cap. To a mixture of PAN (15 mmol) and alkyl bromide (75 mmol) heated at 70 °C (temperature of the heating oil bath) were added under magnetic stirring 2.5 mmol of catalyst (amine or quaternary ammonium salt) immediately followed by 45 mL of aqueous 50% NaOH preheated at 70 °C. At intervals small samples of the organic layer were withdrawn directly from the mixture through the serum cap by a hypodermic syringe and analyzed by gas chromatography.

In the case of asymmetric dialkylation the same procedure was used as far as the amount of reagents and other operative conditions are concerned. When PAN conversion was higher than 98% the reaction mixture was cooled to room temperature and after removal of the unreacted excess alkyl bromide under vacuum 75 mmol of the more reactive alkyl bromide was added and the mixture was heated again at 70 °C until there was complete dialkylation.

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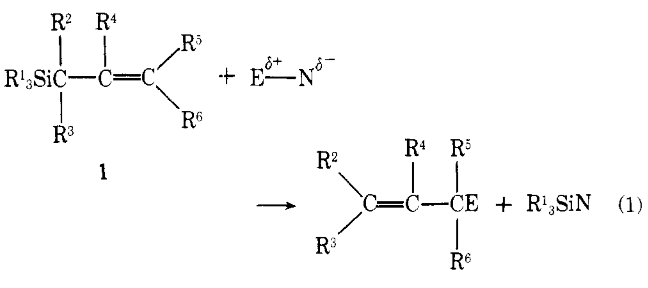
# *Communications*

## α-Siloxyallylsilanes as Homoenolate Anion Equivalents. A Novel Synthesis of γ-Keto Aldehydes[1,2]

*Summary:* This paper reports a versatile method of formation of γ-keto aldehydes by the reaction of α-siloxyallysilanes with acid chlorides, which takes place under mild conditions to give products in high yields.

*Sir:* In earlier papers,[3] we have described new synthetic reactions using allylsilanes (**1**), in which allyl transfer accompanied by transposition of the allyl group took place very smoothly from **1** to electrophilic carbons of carbonyl compounds or acetals activated by a Lewis acid such as $TiCl_4$ in the direction shown in eq 1.


**1**

**2**

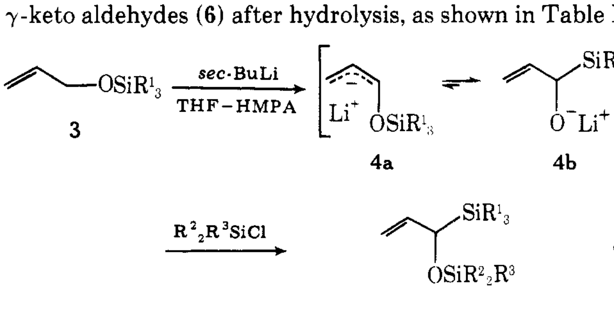
(1)

Introduction of a functionality in the allyl group of **1** will expand the scope of the reaction. For example, introduction of a silyloxy group at the α carbon of 1 ($R^2$ = silyloxy) could result in the formation of a silyl enol ether which should give a carbonyl compound on hydrolysis. In this paper, we report the synthesis of γ-keto aldehydes,[4] which can serve as valuable precursors for the synthesis of natural cylopentanoids, furans, and pyrroles.

For this strategy of synthesis, we have prepared a variety of α-siloxyallylsilanes, the requisite precursors, by silylation of allyloxy carbanions.[5,6]

Still and Macdonald[6] have suggested that while allyloxy carbanions (**4a**) were in rapid equilibrium with the corresponding silyl alkoxide (**4b**), alkylation of 4 resulted in the formation of only C-alkylated products. We have found, however, that silylation of 4 with chlorosilane occurred exclusively at oxygen to give **5**.[7] Several examples of **5** are shown in Table I.[8]

The reaction of **5** with a variety of acid chlorides in the presence of titanium tetrachloride gave the corresponding γ-keto aldehydes (**6**) after hydrolysis, as shown in Table II.



**3** **4a** **4b**

(2)

**5a**, $R^1 = R^2 = R^3 = Me$
**b**, $R^1 = Me$; $R^2 = R^3 = Et$
**c**, $R^1 = R^2 = Me$; $R^3 = t\text{-}Bu$
**d**, $R^1 = Et$; $R^2 = R^3 = Me$
**e**, $R^1 = R^2 = R^3 = Et$

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**Table I. Reactions of Metalated Allyl Silyl Ethers with Chlorosilanes**

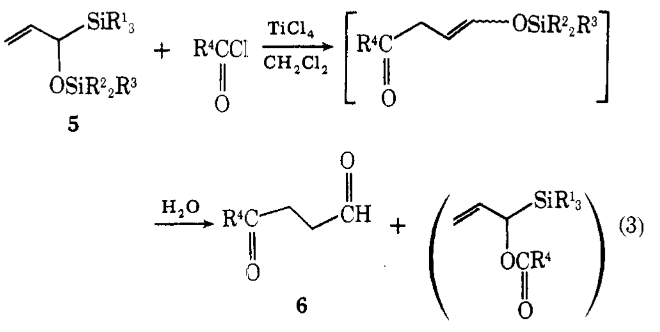
| Run | Allyl silyl ether | Chlorosilane | Product[a] (% yield) | Bp, °C (mmHg) | $n^{20}_D$ |
|---|---|---|---|---|---|
| 1 | $\mathrm{CH_2{=}CHCH_2OSiMe_3}$ | $\mathrm{Me_3SiCl}$ | **5a** (80) | 62 (35) | 1.4228 |
| 2 | $\mathrm{CH_2{=}CHCH_2OSiMe_3}$ | $\mathrm{Et_3SiCl}$ | **5b** (72) | 97 (15) | 1.4440 |
| 3 | $\mathrm{CH_2{=}CHCH_2OSiMe_3}$ | *t*-$\mathrm{BuMe_2SiCl}$ | **5c** (76) | 91 (17) | 1.4389 |
| 4 | $\mathrm{CH_2{=}CHCH_2OSiEt_3}$ | $\mathrm{Me_3SiCl}$ | **5d** (60) | 85 (9) | 1.4431 |
| 5 | $\mathrm{CH_2{=}CHCH_2OSiEt_3}$ | $\mathrm{Et_3SiCl}$ | **5e** (71) | 111 (4) | 1.4580 |

[a] Products have been isolated and fully characterized.

**Table II. Reactions of α-Siloxyallylsilanes with Acid Chlorides in the Presence of Titanium Tetrachloride[a]**

| Run | α-Siloxyallylsilane | Acid chloride | Product | % yield[b] |
|---|---|---|---|---|
| 1 | **5a** | $\mathrm{(CH_3)_2CHCOCl}$ | $\mathrm{(CH_3)_2CHCOCH_2CH_2CHO}$ | 20[c,d] |
| 2 | **5b** | $\mathrm{(CH_3)_2CHCOCl}$ | $\mathrm{(CH_3)_2CHCOCH_2CH_2CHO}$ | 43[c,e] |
| 3 | **5c** | $\mathrm{(CH_3)_2CHCOCl}$ | $\mathrm{(CH_3)_2CHCOCH_2CH_2CHO}$ | 70[c,f] (80)[i] |
| 4 | **5c** | $\mathrm{CH_3(CH_2)_3COCl}$ | $\mathrm{CH_3(CH_2)_3COCH_2CH_2CHO}$ | 45 |
| 5 | **5c** | $\mathrm{(CH_3)_2CHCH_2COCl}$ | $\mathrm{(CH_3)_2CHCH_2COCH_2CH_2CHO}$ | 53 (63)[i] |
| 6 | **5c** | $\mathrm{CH_3CH_2CH(CH_3)COCl}$ | $\mathrm{CH_3CH_2CH(CH_3)COCH_2CH_2CHO}$ | 67 |
| 7 | **5b** | $\mathrm{(CH_3)_3CCOCl}$ | $\mathrm{(CH_3)_3CCOCH_2CH_2CHO}$ | 79 |
| 8 | **5c** | $\mathrm{(CH_3)_3CCOCl}$ | $\mathrm{(CH_3)_3CCOCH_2CH_2CHO}$ | 75[c] |
| 9[g] | **5c** | $\mathrm{(CH_3)_3CCOCl}$ | $\mathrm{(CH_3)_3CCOCH_2CH_2CHO}$ | 43 |
| 10[h] | **5c** | $\mathrm{CH_3(CH_2)_5COCl}$ | $\mathrm{CH_3(CH_2)_5COCH_2CH_2CHO}$[j)] | 68 |
| 11[h] | **5c** | c-$\mathrm{C_6H_{11}COCl}$ | c-$\mathrm{C_6H_{11}COCH_2CH_2CHO}$ | 65 |
| 12[h] | **5c** | $\mathrm{(CH_3)_2C{=}CHCOCl}$ | $\mathrm{(CH_3)_2C{=}CHCOCH_2CH_2CHO}$ | 58 |

[a] All reactions were carried out at −78 °C for 3 h unless otherwise noted. [b] Yields after isolation by TLC unless otherwise noted. [c] Determined by NMR relative to an internal standard. [d] The ester (**7**) was obtained in 30% yield. [e] The ester was obtained in 17% yield. [f] No ester was observed at all. [g] Aluminium chloride was used as a Lewis acid. [h] The reaction was carried out at −78 °C for 4 h. [i] Yields after isolation as a 2,4-dinitrophenylhydrazone. [j] This compound is known as an intermediate for the synthesis of dihydrojasmone; K. Oshima, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **95**, 4446 (1973).



**5** **6** **7** (3)

In some cases, O-acylation of the alkoxy group of **5** affording esters (**7**) can compete with the regiospecific carbon–carbon bond formation at γ carbon of the allylsilane under these reaction conditions. Cleavage of alkoxysilanes with acid chlorides is one of the well-documented reactions in the organosilicon chemistry.[9] However the formation of esters can be efficiently excluded by means of increasing the steric bulkiness of the siloxy groups in **5**. Thus γ-keto aldehydes were obtained effectively by the introduction of *tert*-butyldimethylsiloxy group in place of trimethylsiloxy group into the α position of the allylsilane.

This work demonstrates that α-siloxyallylsilanes (**5**) can be viewed as one of the "homoenolate anion equivalents".[10] The synthetic utility of the present reaction was mostly displayed by complete regiospecificity of the acylation, ready accessibility of starting materials, and simple manipulation of the conversion.

As a general procedure, to a solution of 1 mmol of an acid chloride in 2 mL of dry dichloromethane at −78 °C, titanium tetrachloride (1.1 mmol) was added dropwise with stirring under a nitrogen atmosphere. When addition was completed, 1 mmol of an α-siloxyallylsilane (**5**) in 2 mL of dichloromethane was added slowly and the mixture was stirred continuously for an additional 3 h. The solution was allowed to warm up to 0 °C slowly and a mixture of water and ether was then added. The organic layer was washed with aqueous sodium bicarbonate and water and dried over anhydrous sodium sulfate. Evaporation of the solvent yields crude product which is purified by preparative thin-layer chromatography.

Related works are in progress.

**Acknowledgment.** We thank Toshiba Silicone Co., Ltd., for a gift of chlorosilanes.

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