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REACTION OF FURYLLITHIUM WITH ACYLTRIMETHYLSILANES. SPECIFIC GENERATION OF 5-TRIMETHYLSILOXY-3,4-PENTADIENONE ENOLATES

Isao KUWAJIMA,* Kunio ATSUMI, Toshihiko TANAKA, and Tan INOUE
Department of Chemistry, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

5-Trimethylsiloxy-3,4-pentadienone enolates can be generated efficiently by treating furyllithium with acyltrimethylsilanes and can be isolated in good yield as their silyl enol ethers.

It has well been documented as the Brook rearrangement that, under basic conditions, some of 1-trialkylsilyl alcohols undergo a facile conversion into the corresponding trialkylsilyl ethers via transfer of the silyl group from carbon to the neighboring oxygen.[1] In this process, a transient formation of highly reactive carbon nucleophile, $R^1R^2\underline{C}\text{-}OSiR_3$, has been proved. Unfortunately, employment of this kind of species for synthetic purposes has been reported in only limited cases[2] probably because of the structural limitation for such a kind of rearrangement[3] and difficulties to trap them effectively which are formed in only quite a low concentration as the equilibrium mixtures with the corresponding alkoxides, $R^1R^2C(SiR_3)\text{-}O^-$.[4]

We have recently reported that furfuryl carbanion undergoes ring opening reaction to yield some useful synthetic intermediates.[5] In the present paper, we wish to describe examples of Brook type rearrangement which may offer another type of synthetically versatile reagents. Thus, we have examined the reaction of furyllithium with acyltrimethylsilanes[6] in expectation that, with the initially formed adduct 1, the anion stabilizing effect of the furan ring would facilitate the rearrangement to yield the furfuryl carbanion 2, which further undergoes a facile ring opening reaction to generate the corresponding 5-trimethylsiloxy-3,4-pentadienone enolate 3. Indeed, the expected reaction has been found to take place efficiently and the corresponding enolates can be obtained as their silyl enol ethers as shown in the following example.

2-Methylfuran (360 mg, 2.2 mmol) was treated with an equimolar amount of butyllithium in THF (10 ml) at 0°C. To the resulting solution was added a THF (3 ml) solution of 3-phenylpropionyltrimethylsilane (412 mg, 2.0 mmol) at -78°C. It was stirred for 5 hr at 0°C and then treated with chlorotrimethylsilane (3.0 mmol) at room temperature for 1 hr. After removal of the solvent, the residual oil was diluted with hexane (50 ml) and the precipitate was filtered off.[7] The filtrate was concentrated and then distilled in vacuo, giving 2,6-bis(trimethylsiloxy)-8-phenyl-2,4,5-octatriene 4b [648 mg (90%), nmr(CCl_4): δ 0.16 (s, 9H), 0.20 (s, 9H), 1.76 (s, 3H), 2.2∿2.6 (m, 4H), 4.79 (d, J = 11 Hz, 1H), 6.28 (d.t., J = 3 and 11 Hz, 1H), and 7.08 (s, 5H). ir(neat): 1937, 1645, 1257, and 852 cm^{-1}].

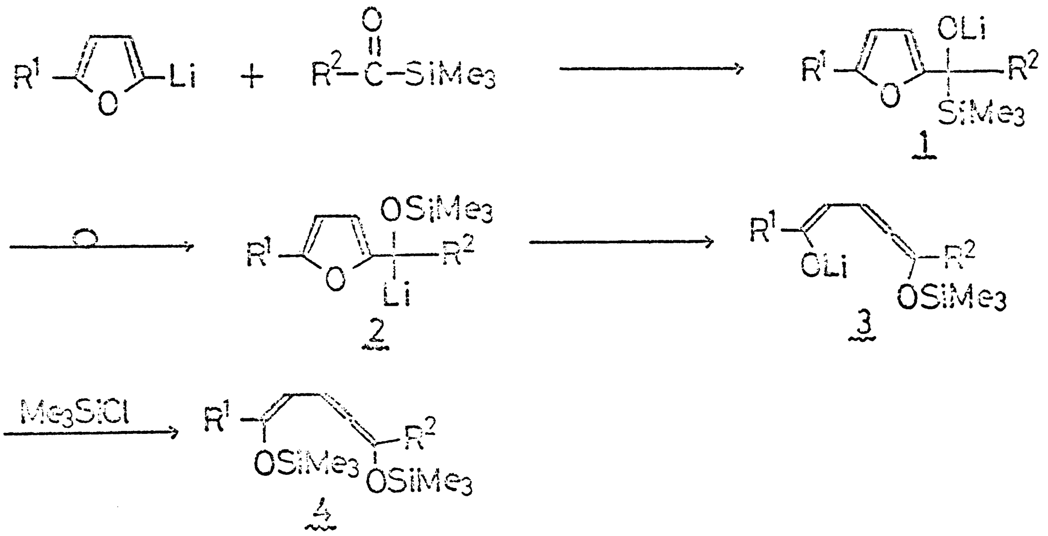

Table. Preparation of Bis-silyl Enol Ethers 4.

	R^1	R^2	Period(hr)	Yield,%	B.p.(°C/Torr.)
a)	CH_3	C_3H_7	5	83	75-8/0.03
b)	CH_3	$C_6H_5CH_2CH_2$	5	90	118-122/0.02
c)	H	C_3H_7	80	72	78-80/0.05
d)	H	$C_6H_5CH_2CH_2$	14	90	105-8/0.02
e)	$(C_2H_5O)_2CHCH_2CH_2$	C_3H_7	5	76	105-8/0.009

As shown in the Table, longer reaction period is usually required with 5-unsubstituted furyllithium, but in every case examined, the corresponding bis-silyl enol ether 4 can be prepared in good yield by this procedure.

References and Notes

1) A. G. Brook, Acc. Chem. Res., 7, 77 (1974).
2) H. J. Reich, J. J. Rusek, and R. E. Olson, J. Am. Chem. Soc., 101, 2225 (1979); I. Kuwajima and M. Kato, J. Chem. Soc., Chem. Commun., in press.
3) Anion stabilizing groups are usually required for such a kind of rearrangement. See, ref 1.
4) Carbon chain homologation by using such a kind of species has been achieved in only limited cases. A. Wright and R. West, J. Am. Chem. Soc., 96, 3214 (1974); I. Kuwajima, M. Arai, and T. Sato, ibid., 99, 4181 (1977).
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7) Because of lability to hydrolysis, aqueous workup of the reaction mixture usually led to complex results.

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