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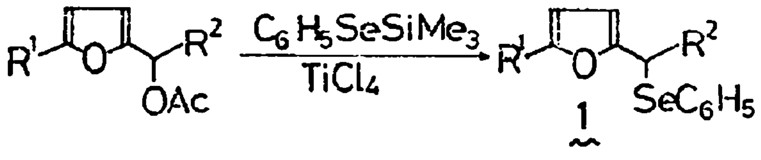
A FACILE RING OPENING REACTION OF FURFURYL SELENIDES. HIGHLY EFFICIENT METHOD FOR DIENONES

Isao Kuwajima,* Showay Hoshino, Toshihiko Tanaka, and Makoto Shimizu
Department of Chemistry, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152

Summary: Treatment of furfuryl phenyl selenides with butyllithium or metallic lithium induces the facile ring opening reaction of their furan ring and the corresponding dienones are obtained in high yields.

In the previous papers, we reported that, on treatment with butyllithium, furan derivatives possessing some anion-stabilizing groups undergo a facile ring opening reaction to afford the corresponding unsaturated carbonyl compounds.[1,2] In such a transformation, it is required to generate the furfuryllithium, and the procedure has not been applicable to the general synthesis of such compounds, starting from furans having no anion-stabilizing groups.

In the present paper, we wish to describe a general method for generating the furfuryllithium, which enables to prepare various conjugate dienones, accompanied with four carbon chain elongation, starting from aldehydes. It has been reported that carbon-selenium bond undergoes a facile cleavage under the influence of alkyllithium.[3] Based on this characteristic feature of organoselenium compounds, we have examined the reaction of furfuryl phenyl selenides 1 with butyllithium with the expectation that lithium selenium exchange would take place to generate the corresponding furfuryllithiums which yield the enolates of allenic ketones. The starting materials 1, furfuryl phenyl selenides, could be prepared easily by treating the corresponding furfuryl acetates with trimethylsilyl phenyl selenide (1.2 equiv) in the presence of Lewis acid. For conversion of some alkyl acetates into the alkyl phenyl selenides, zinc iodide has been reported to be a good catalyst by



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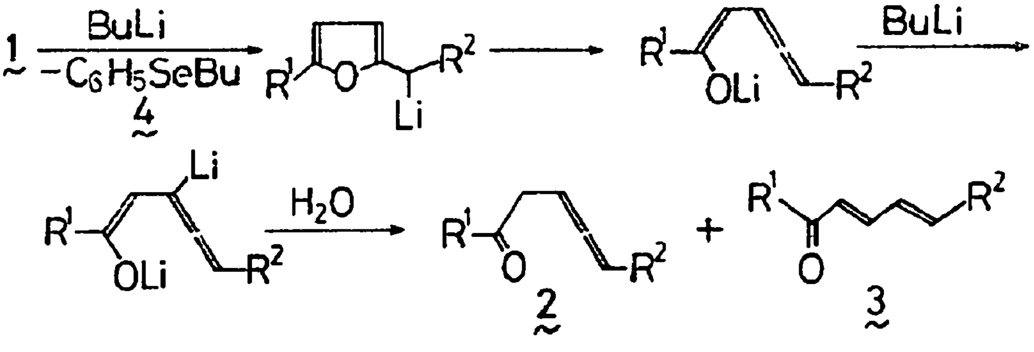
Sonoda et al,[4] but in this case titanium tetrachloride appears to be preferable and the corresponding furfuryl phenyl selenides 1 were usually obtained in ca. 80% isolated yield.[5]

The reaction of 1 with butyllithium proceeded, as expectedly, in THF at -78°C within 3 hr and, as shown in Scheme 1, the corresponding ring opening products 2 and 3 were obtained along with butyl phenyl selenide 4. For completion of this ring opening reaction 2 equiv of butyllithium were usually required probably because of highly acidic character of the resulting allenic hydrogen.[6] The initial product, allenic ketone 2, underwent an isomerization into 3 readily during treatment with p-toluenesulfonic acid, and the product was usually isolated in high yield as the conjugate dienone 3.

Metallic lithium can also be employed for cleavage of carbon-selenium bond of 1 to induce a similar ring opening reaction. For example, treatment of 5-methyl-2-(1-phenylselenoheptyl)furan 1 ($R^1 = CH_3$, $R^2 = C_6H_{13}$) with metallic lithium (10 equiv) in THF at 0°C afforded the corresponding 2 ($R^1 = CH_3$, $R^2 = C_6H_{13}$, 65%) and 3 ($R^1 = CH_3$, $R^2 = C_6H_{13}$, 15%) accompanied with the recovered starting material 1 (18%).

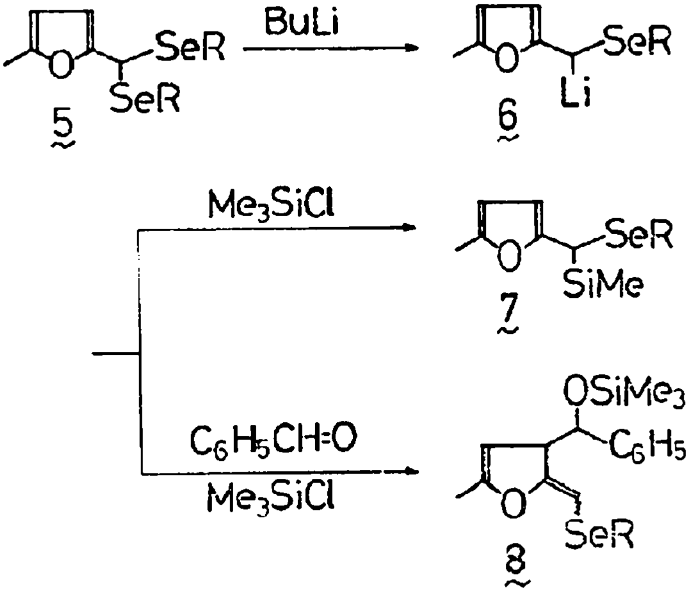
Considering that the initial starting material can be prepared easily by the reaction of an aldehyde with the furyllithium followed by acetylation, this procedure appears to offer a useful method for conjugate poly-enone type of compounds.

Scheme 1

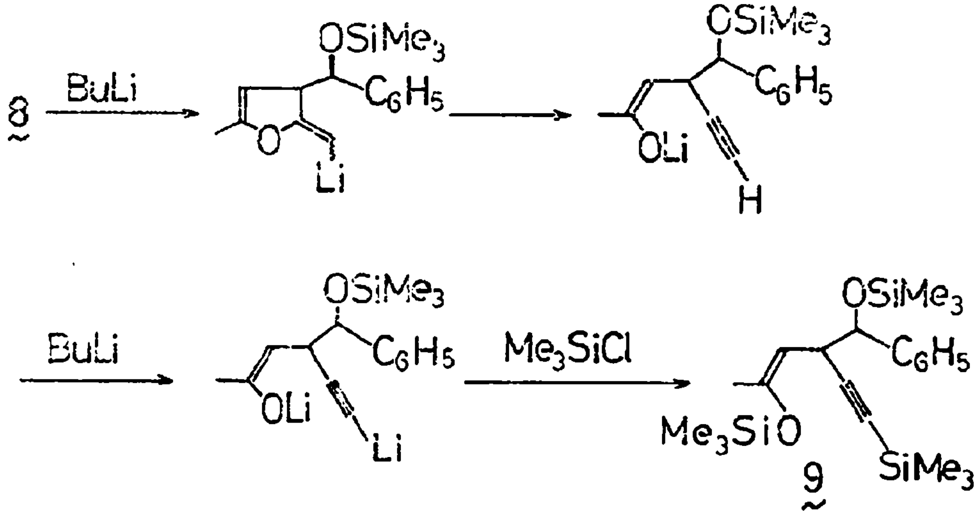


R^1	R^2	Yield(%) of 3
CH_3	C_4H_9	75
CH_3	C_6H_{13}	95
CH_3	C_8H_{17}	86
CH_3	$C_{10}H_{21}$	88

Similar reactions have also been examined with furfural diselenoacetals 5.[7] When treated 5 (R = CH_3 or C_6H_5) with butyllithium (2 equiv) at 0°C, it resulted in the formation of complex mixtures. This may be attributable to the direct formation of a carbonyl compound through the removal of lithium phenylselenelate from the enolate formed via a similar ring opening reaction.[8] Further examinations have revealed that the lithiated intermediate 6 can be generated even at -78°C and is quite stable at that temperature. For example, α-silylated furan 7 was obtained in 75% yield by treating with chlorotrimethylsilane. On the contrary, on treating the intermediate 6 with benzaldehyde,



Scheme 2



the addition reaction took place on furan ring and the corresponding adduct 8[9] was isolated in 45% yield as its silylated derivative after treating the reaction mixture with the chlorosilane. Ring opening reaction of 8 (R = CH_3) could also be effected by treating with 2 equiv of butyllithium at 0°C for 1 hr and the corresponding product 9[10] was isolated in 83% yield as the silyl enol ether as shown in Scheme 2.

References and Notes

1) K. Atsumi and I. Kuwajima, J. Am. Chem. Soc., 101, 2208 (1979).

2) I. Kuwajima, K. Atsumi, T. Tanaka, and T. Inoue, Chemistry Lett., 1239 (1979).

3) D. Seebach and N. Peleties, Chem. Ber., 105, 511 (1972); W. Dumont, P. Bayer, and A. Krief, Angew. Chem., 86, 857 (1974); D. Seebach and A. K. Beck, ibid., 86, 859 (1974); W. Dumont and A. Krief, ibid., 87, 347 (1975); D. Van Ende, W. Dumont, and A. Krief, ibid., 87, 709 (1975).

4) N. Miyoshi, H. Ishii, S. Murai, and N. Sonoda, Chemistry Lett., 873 (1979).

5) The reaction was carried out in toluene at room temperature for 1.5 hr in the presence of 0.1 equiv of $TiCl_4$.

6) On treating the reaction mixture of 1 (R^1 = CH_3, R^2 = C_6H_{13}) with chlorotrimethylsilane, bis-silylated product, $CH_3C(OSiMe_3)=CH-C(SiMe_3)=C=CH-C_6H_{13}$, was obtained. For a similar lithiation of allenic hydrogen, see ref 1.

7) W. Dumont and A. Krief, Angew. Chem. Int. Ed. Engl., 16, 540 (1977); D. L. J. Clive and S. M. Menchen, J. Chem. Soc., Chem. Commun., 356 (1978).

8) The following elimination reaction may be conceivable:
$R-C(OLi)=CH-CH=C=CH-SeC_6H_5 \longrightarrow R-CO-CH=CH-C{\equiv}CH + C_6H_5SeLi$

9) The following spectral data was obtained for this compound. ir(neat): 2975, 2908, 1670, 1623, 1560, 1245, and 845 cm^{-1}. nmr(CCl_4, dichloromethane as an internal standard): δ 0.10 (s, 9H), 1.64 (t, J = 1 Hz, 3H), 2.08 (s, 3H), 3.40∿4.03 (m, 1H), 4.57∿4.73 (m, 1H), 4.69 (d, J = 6 Hz, 1H), 5.57∿5.70 (m, 1H), and 7.07∿7.27 (m, 5H).

10) The following spectral data was obtained for this compound. ir(neat): 2160, 1665, 1250, and 950 cm^{-1}. nmr(CCl_4, dichloromethane as an internal standard): δ 0.02 (s, 9H), 0.11 (s, 9H), 0.14 (s, 9H), 1.67 (s, 3H), 3.46 (d.d., J = 5 and 9 Hz, 1H), 4.27 (d, J = 9 Hz, 1H), 4.47 (d, J = 5 Hz, 1H), and 7.13 (s, 5H).

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