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PHENYLTHIOMETHYLSTANNYLATION OF SILYL ENOL ETHERS AND SILYL DIENOL ETHERS

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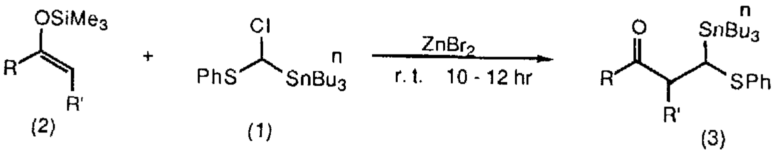
Summary: Silyl enol ethers (2) react with tributyl [(phenylthio) chloromethyl] stannane (1) in the presence of Zinc bromide to give β-phenylthiomethylstannyl ketones (3) in good yields. Silyl dienol ethers (4) mainly give products (5) due to γ-attack, under these conditions.

β-Stannyl Carbonyl compounds have found widespread[1] use in organic synthesis owing to their ability to act as masked homoenolate anion equivalent. The utility of Carbon-tin bond in carbon-carbon bond formation has been exploited with remarkable success by transmetallation[2] with organo lithium reagents or by their activation[3] with Lewis acids like $TiCl_4$. Recently a new dimension has been added to this area of research where a carbon-tin bond can be induced to undergo a carbon-carbon bond formation promoted by free-radical initiators[4] or transition metal catalysts[5]. β-Stannyl carbonyl compounds are accessible[6] by the addition of Stannyl anion to α,β-unsaturated carbonyl compounds. We, now present a different approach to β-stannylated ketones by a Lewis acid catalyzed[7] reaction of silyl enol ethers with tributyl [(phenylthio)chloromethyl] stannane[8] (1) and a preliminary account of this finding is given below.

Phenylthiomethylstannylation of Silyl Enol Ethers



a	R = Ph, R' = H	(3a)	73%
b	R = C_2H_5, R''= H	(3b)	78%
c	R = Ph, R' = Me	(3c)	76%
d	R = C_2H_5, R' = Me	(3d)	69%
e	R = R' = - $(CH_2)_4$-	(3e)	74%

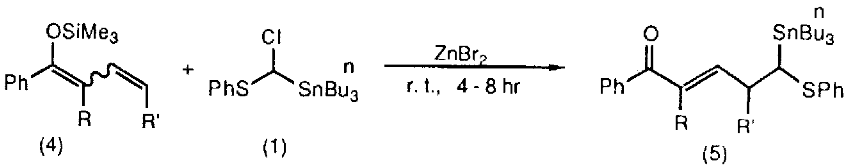
Scheme 1

Typically, anhydrous Zinc bromide (catalytic ≃ 30 mg) is added to a solution of silyl enol ether (2a) (10 mmol) in dry dichloromethane (40 ml) and compound (1) (11 mmol) and the resulting mixture is stirred under nitrogen at ambient temperature for 10-12 hours.

The progress of the reaction is monitored by TLC and after completion of the reaction a saturated solution of sodium bicarbonate (10 ml) is added to it and the resulting mixture is stirred for five minutes. The organic layer is successively washed with saturated brine (2 x 10 ml) and water (3 x 10 ml). Drying (Na_2SO_4) and evaporation of the organic layer yielded a gum, which on a flash column chromatography (SiO_2) gave compound (3a) is good yields (Scheme 1). The reaction mixtures were carefully monitored by TLC and ^{1}H-NMR to check the presence of any destannylated products but in no case could we detect them. This clearly indicates that a carbon-tin bond is quite stable under these experimental conditions. Compounds (3) have an added advantage over the β-stannylated ketones for they have phenylthio group attached to the carbon bearing the tributyltin group, where sulphur group can be manipulated oxidatively to useful vinyl tin[1a] intermediates. We are currently looking into this useful transformation.

Silyl dienol ethers (4a-d) also react with (1) in the presence of $ZnBr_2$ to yield only product (5a-d) which results due to γ-attack (Scheme 2). In none of these reactions, product due to attack at α-position was observed. This observation is supported by the

Phenylthiomethylstannylation of Silyl Dienol Ethers



a	R = H, R' = H	(5a)	71%
b	R = Me, R' = H	(5b)	69%
c	R = H, R' = Me	(5c)	63%
d	R = R' = Me	(5d)	55%

Scheme 2

^{1}H-NMR spectrum of the crude reaction mixture, indicating that no gross errors had been introduced during the purification. Electrophile (1) is highly γ-selective as even a methyl group at the γ-position did not encourage any α-attack (Scheme 2, 5c). One of us[9c] has shown earlier that phenylthiomethyl chloride is the least γ-selective electrophile and hence electrophile (1) seems to possess complimentary electrophilicity with respect to it. Thus, enhancement in γ-selectivity (as compared to phenylthiomethyl chloride) due to the presence of tributyl tin group in (1) may turn out to be a good solution to the long standing problem of getting d^4 reactivity[9] from silyl dienol ethers. In summary, electrophile (1) shows the promise of becoming a useful reagent in organic synthesis. We are currently pursuing its application to other reactions.

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8. a) Compound (1) is prepared by chlorination (NCS, CCl_4, 30°C) of tributyl [(phenylthio) methyl] stannane[8b] for 8 hours: (1) was used without purification as any

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10. All the new compounds had the following ^{1}H-NMR (δ,CCl$_4$) data: (1): 7.76 - 7.08 (5H, m), 4.96 (1H, s), 1.85 - 0.89 (27H, m); (2a); 7.35 - 7.12 (10H, m), 3.46 (1H, t J7Hz), 2.59 (2H, d, 7Hz), 1.89 - 0.82 (27H, m); (2b): 7.32 - 7.1 (5H, m), 3.4 (1H, t, 7Hz), 2.05 - 2.29 (4H, m), 1.9 - 0.82 (30H, m); (2c): 7.89 - 7.12 (10H, m), 3.47 (1H, d, 7Hz), 2.59 (1H, m), 1.91 - 0.86 (30H, m); (2d): 7.32 - 7.08 (5H, m), 3.52 (1H, d, 7Hz), 2.06 - 2.4 (3H, m), 1.96) - 0.81 (33H, m); (2e): 7.5 - 7.22 (5H, m), 3.43 (1H, d, 7Hz), 2.12 - 0.82 (36H, m); (5a): 8.06 - 6.9 (10H, m), 5.62 (2H, m), 3.38 (1H, t, 7Hz), 2.6 (2H, m), 1.89 - 0.9 (27H, m); (5b): 7.96 - 7.07 (10H, m), 6.31 (1H, m), 3.51 (1H, t 7Hz), 2.61 (2H, m), 1.9 - 0.89 (30H, m); (5c): 8.07 - 6.92 (10H, m), 5.63 (2H, m), 3.52 (1H d, 7Hz), 2.49 (1H, m), 1.92 - 0.8 (30H, m); (5d): 8.1 - 7.09 (10H, m), 6.23 (1H, m), 3.46 (1H, d 7Hz), 2.32 (1H, M), 2.1 - 0.92 (33H, m).

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