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RADICAL REACTION OF ACETONYLTRIBUTYLSTANNANE WITH α -(PHENYLSELENO)CARBONYL COMPOUNDS: A NOVEL PROCEDURE FOR PREPARATION OF 1,4-DICARBONYL COMPOUNDS.

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Summary: Radical reaction of acetonyltributylstannane 1 with α -(phenyl-seleno)carbonyl compounds 2 gave 1,4-dicarbonyl compounds in high yield. The $S_{\mu}2'$ mechanism via the stannyl enolate in equilibrium with acetonyl-stannane is postulated.

Allylstannanes are useful reagents for the C-C bond formation and their versatile applications via radical process have been investigated¹ [1]. We have previously shown that the radical reaction of α -(phenylseleno)-carbonyl compounds with various allylic stannanes gives α -monoallylated carbonyl compounds in high yield and high stereoselectivity.² We report here a new synthetic method for 1,4-dicarbonyl compounds by the use of a radical reaction involving a S_H² process of acetonyltributylstannane with α -(phenylseleno)carbonyl compounds³ [2]. Our approach is based upon the assumption that the O-metallated form, which is in equilibrium with thermodynamically more predominant C-metallated form⁴ [3], would react with an alkyl radical via the S_H² process.



The reactions of acetonyltributylstannane⁵ 1 with several alkyl radical precursors 2 were carried out under photolytically or thermally stimulated radical reaction conditions. The results are summarized in Table. Although

either an alkyl selenide or iodide except benzyl iodide was innert on irradiation with 1 (entry 1, 2, and 3), α -(phenylseleno)carbonyl compounds gave the corresponding 1,4-dicarbonyl compounds in moderate to high yields. Thus, the reaction of methyl α -(phenylseleno)acetate with 1 afforded the γ ketoester 3 (R=CH₂CO₂CH₂) in 81% yield (entry 4). The selenide was found to be a better radical precursor than the sulfide (entry 6), the iodide (entry 7), or the bromide (entry 8). This reaction also proceeded under thermal conditions, but the yield was lowered (entry 5). Cyclic α -(phenylseleno)carbonyl compounds (entry 9-11) and α -(phenylseleno)acetophenone (entry 12) gave the acetonylated products in high yields. The reaction did not occur in the dark and was inhibited by the addition of 10 mol% of hvdroguinone. Thus, the present reaction proceeds through the free radical chain S_{H}^{2} process⁶ presumably involving the isomerization of acetonyltributylstannane from the C-metallated form to the O-metallated enolate during the irradiation as shown below.⁷ Indeed 1-[(tributylstannyl)oxy]-



1-cyclohexene which exists as an enolate form³ gave 2-acetonylcyclohexanone in 76% yield on irradiation with α -(phenylseleno)acetone.



The present reaction serves as a convenient method for preparation of 1,4-dicarbonyl compounds. The process is notable for its characteristic mode of reaction via a radical pathway: the regiospecific α -monoacetonylation without formation of 0-acetonylated or polyacetonylated side products. Furthermore, a practical advantage of the present method using α -(phenylseleno)carbonyl compounds as a radical precursor is a clean and easy



Table. Photoinitiated Reaction of Acetonyltributylstannane 1 with RX 2.^{a)}

Entry	RX 2		Reaction time (h)	Product 3	Yield (%)
1	Et02C	∧ _{SePh}	10	No reaction	
2	ме0 ₂ с	\sim_{I}	12	No reaction	-
3	PhCH ₂ I		6		45
4	MeO2CCH2X	X=SePh	1		81
5		X=SePh	2		54 ^{b)}
6		X=SPh	1		65
7	EtO2CCH2X	X=I	1	<u>لا</u> م	74
8		X=Br	1	eto ₂ c / / /	50
9	SePh		3	L'	82
10	SePh		1.5		71
11	of se	≥Ph	1		80
12	Ph Se	≥Ph	2	Ph 0	80

a) General experimental procedure is as follows. A pyrex glass tube containing a 1 M degassed benzene solution of 2 and ca. 5 equiv. of 1 was irradiated by a 400-W high pressure mercury lamp at room temperature. The product was purified directly by silica gel column chromatography [petroleum ether/ethyl ether (8 : 2)] to afford a 1,4-dicarbonyl compound. b) The yield obtained by the thermally initiated reaction in the presence of 10 mol% of azobis(isobutyronitrile). separation of the products from organostannanes produced during the reac tion.

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- Acetonyltributylstannane 1 was prepared from tributyltin methoxide and isopropenyl acetate by transesterification: M. Pereyre, B. Bellegarde, J. Mendelsohn, and J. Valade, J. Organomet. Chem., 1968, 11, 97. Acetonyltributylstannane 1 is moisture- and airsensitive, so it was used without purification after removal of methylacetate and unreacted isopropenylacetate.
- 6. The reaction may be chain-transferred by a tributylstannyl radical generated from 1.
- 7. Unfortunately, we could not observe ¹H NMR signals due to the stannyl enolate possibly produced on irradiation.

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