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A CONVENIENT METHOD FOR THE SYNTHESIS OF α-PHENYLSELENENYL CARBONYL COMPOUNDS

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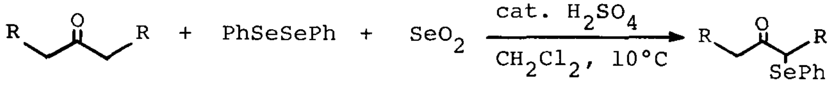
Summary: Treatment of ketones or aldehydes with selenium dioxide and diphenyl diselenide in the presence of acid catalyst afforded the corresponding α-phenylselenenyl carbonyl compounds in good yields.

In recent years, α-phenylselenenylation of carbonyl compounds has been recognized as a powerful tool in organic synthesis, particularly for the introduction of unsaturated function.[1,2] Preparation of α-phenylselenenyl carbonyl compounds has been done by the reaction of enol acetates, enol ethers, enol silyl ethers or ketone enolates with benzeneselenenyl halides, and also by the reaction of ketone enolates with diphenyl diselenide.[2] The direct phenylselenenylation of ketones seems to be limited to the reaction of ketones with benzeneselenenyl chloride reported by Sharpless.[3] Recently Tsuji[4] and Kuwajima[5] have reported preparation of α-phenylselenenyl carbonyl compounds from olefins.

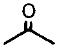
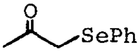
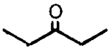
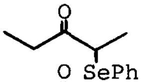
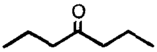
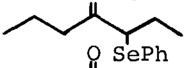
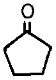
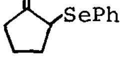
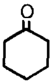
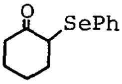
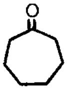
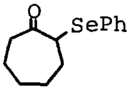
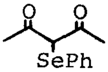
We report here a new and convenient method for α-phenylselenenylation of carbonyl compounds, i.e., the reaction of ketones, aldehydes, or β-dicarbonyl compounds with diphenyl diselenide and selenium dioxide in the presence of a catalytic amount of sulfuric acid(eq. 1). The results are given in Tables 1, 2, and 3. While the yields are moderate to high, the simple experimental procedures make the new method to be that of choice especially for phenylselenenylation of readily available carbonyl compounds.



[eq. 1]

A typical example is as follows. To a suspension of selenium dioxide(3 mmol) in 5 ml of dichloromethane containing diphenyl diselenide(3 mmol) and a catalytic

Table 1. α-Phenylselenenylation of Dialkyl Ketones[a)]

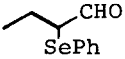
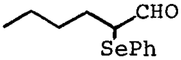
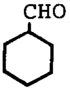
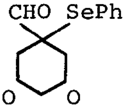
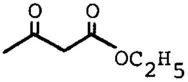
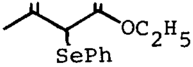
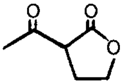
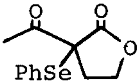
Substrate	Product	Yield %[b)]
		53[c)] (53)
		62[d)] (85)
		38
		60[c)]
		84
		60
		60[d)]

a) Carried out using diphenyl diselenide(3 mmol), SeO_2(3 mmol), a ketone (5 mmol) and sulfuric acid(0.6 mmol) in dichloromethane(10 ml) at 10°C for 10 h, unless otherwise noted. b) Isolated yields based on ketones. Yields indicated in parentheses are for the reactions carried out using the ketones themselves as the solvent(reaction time 15 h) and based on diphenyl diselenide. c) Reaction time: 20 h. d) Diphenyl diselenide (6 mmol) was used.

amount of sulfuric acid(0.6 mmol) was added a solution of cyclohexanone(5 mmol) in 5 ml of dichloromethane at 10°C. The mixture was stirred for 10 h at 10°C until the color changed from yellow to reddish brown with precipitation of amorphous selenium. The reaction mixture was poured into 100 ml of ether and washed with saturated aqueous sodium hydrogen carbonate(20 ml × 2). The organic layer was dried($MgSO_4$) and evaporated to give a reddish oil, which was purified by silica gel column chromatography to afford α-phenylselenenyl cyclohexanone (4.2 mmol: 84% yield) and unreacted diphenyl diselenide(0.6 mmol).

In the absence of sulfuric acid, the reaction did not take place. It may be worth mentioning that α-phenylselenenylation of simple ketones such as acetone and diethyl ketone proceeded smoothly even when the ketones themseleves were used as the solvent(Table 1). As shown in Table 2, α-phenylselenenylation of aldehydes and β-ketoesters also proceeded under similar conditions. When the present method was applied to alkyl aryl ketones, the yields of the corresponding α-phenylselenenyl carbonyl compounds were not satisfactory. However, the yields have been improved by modifying the reaction conditions as footnoted in Table 3.

Table 2. α-Phenylselenenylation of Aldehydes and β-Ketoesters[a)]

Substrate	Product	Yield %
		60
		50
		76[b)]
		75
		66

a) Carried out using diphenyl diselenide(6 mmol), substrate(5 mmol), selenium dioxide(3 mmol), and sulfuric acid(0.6 mmol) in dichloromethane(10 ml) at 10°C for 15 h. b) Using 3 mmol of diphenyl diselenide.

We suggest the mechanism as depicted in Scheme 1. The type of the products and the required acidic reaction conditions may suggest that electrophilic attack of phenylselenenyl cation, $PhSe^+$, to an enol form of a ketone is important in the product determining step.[6)] This step may resemble mechanistically to the well known acid catalyzed bromination of ketones[7)] with bromine and closely related to α-phenylselenenylation of cyclohexanone with benzeneselenenyl chloride.[3)] Generation of the phenylselenenyl cation by the oxidation of diphenyl diselenide may begin with the activation of selenium dioxide with proton.[8)] Then, oxidative cleavage of diphenyl diselenide would follow with concomitant change in oxidation state of selenium from Se(IV) of selenium dioxide to Se(II). The latter may undergo disproportionation to Se(IV) and Se(0). This is suggested by the observation that the reaction of cyclohexanone(5 mmol) with 3 mmol of diphenyl

Scheme 1.

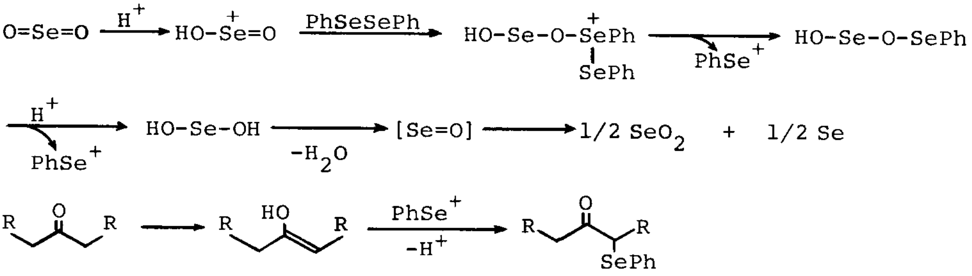
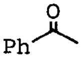
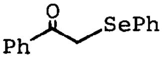
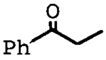
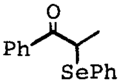
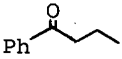
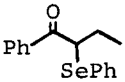
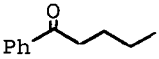
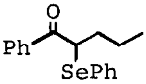
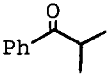
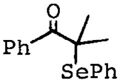


Table 3. α-Phenylselenenylation of Alkyl Aryl Ketones[a)]

Substrate	Product	Yield %
		58
		82
		87
		86
		49

a) Carried out using diphenyl diselenide(6 mmol), a ketone(5 mmol), selenium dioxide(3 mmol), and sulfuric acid(0.6 mmol) in ethanol (10 ml) under refluxing for 20 h.

diselenide and 1.5 mmol of selenium dioxide gave 3.7 mmol of α-phenylselenenyl cyclohexanone the amount of which is greater than 3 mmol calculated assuming selenium dioxide to be a two-electron oxidizing species.

References

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6. Recently Kuwajima described briefly the reaction of styrene with diphenyl diselenide and selenium dioxide in dioxane to give 1-phenyl-2-(phenyseleno) ethanol(see footnote 11 of ref. 4b). Relation between the mechanism of this reaction and that of ours is not clear.
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