

Solid-phase Synthesis of Unsaturated β -Dicarbonyl Compounds from Polymer-supported 4-(Phenylseleno)morpholine

Xiao Ling LIU¹, Xing Cong WANG¹, Shou Ri SHENG^{1*}, Xian HUANG²

¹ Department of Chemistry, Jiangxi Normal University, Nanchang 330027

² Department of Chemistry, Zhejiang University (Xixi Campus), Hangzhou 310028

Abstract: The solid-phase synthesis of unsaturated β -dicarbonyl compounds has been reported.

Keywords: Solid phase organic synthesis, 4-(phenylseleno)morpholine, α -formylcycloanone, unsaturated β -dicarbonyl compound.

Polymer-supported organic reagents have been rapidly applied to the preparation of small organic molecules¹. Recently, polymer-bound selenium reagents are increasingly used in organic synthesis with their convenience of handling and totally odorless nature comparing to the non-bound reagents. Among them polymer-supported 4-(phenylseleno)morpholine could be used as an efficient α -selenenylating agent for aldehydes².

Unsaturated β -dicarbonyl compounds are useful substrates for a number of important chemical reactions, including inter alia the Michael reaction and the Diels-Alder reaction. Liotta *et al.*³ previously reported a synthetic method for the title compounds by reaction of phenylselenenyl chloride/pyridine complex with β -dicarbonyl compounds and subsequent oxidative deselenation. However, separation of the products from the phenylselenenyl oxide by-product and any excess of substrate was difficult. Furthermore, organic selenium reagents always have a foul smell and are quite toxic, which is often problematic in organic synthesis. Here we report a novel traceless cleavage strategy to prepare unsaturated β -dicarbonyl compounds on solid-phase with outstanding advantages of easy operations and environmental benign characteristics. The method is illustrated in **Scheme 1**, using α -formylcyclohexanone.

Treatment of resin **1** (1.12 mmol N/g) with α -formylcycloanones (1.30 mmol) gave the corresponding β -dicarbonyl selenides resins, which were indicated by FT-IR spectra showing strong carbonyl absorption at 1705-1725 cm^{-1} and an aldehydic CH stretching absorption at 2700-2710 cm^{-1} . Subsequent oxidation-elimination with 30% H_2O_2 (11.6 mmol) at room temperature efficiently yielded the corresponding products in good yields (85-90 %) and with high purities of crude materials in all cases (>95 % by ¹H NMR

* E-mail: shengsr@163.com

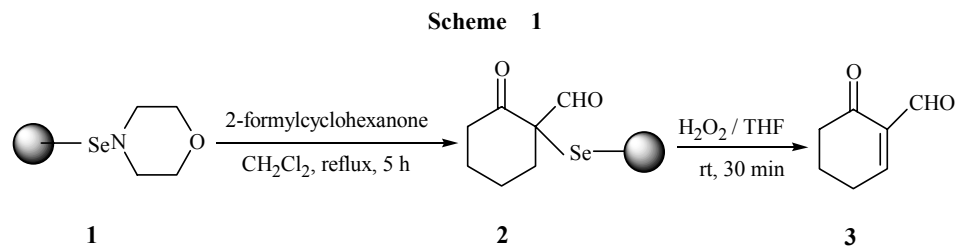










Table 1 Yields and purities of unsaturated β -dicarbonyl compounds

Entry	Substrate	Product	Yield (%) ^a	Purity (%) ^b
1			85	>95
2			86	>95
3			90	>95
4			90	>95

a) Overall yields based on the loading of resin **1**. b) Determined by ^1H NMR (400 MHz).

analysis) as shown in **Table 1**. The residual resin with no residual carbonyl absorption in FT-IR indicated the oxidation-elimination was complete.

References

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