SHORT PAPER

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An efficient method for the synthesis of β-dicarbonyl enones using polymer-supported *N, N*-diethylbenzeneselenenamide†

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A novel polystyrene-supported N, N-diethylbenzeneselenenamide reagent has been prepared. Reaction of the resin with β-formylcycloanones and subsequent oxidative deselenation afforded β-dicarbonyl enones in good yields and high purities.

Keywords: solid-phase organic synthesis, polystyrene-supported N, N-diethylbenzeneselenen-amide, α-formylcycloanones, β-dicarbonyl enone.

During the last few years, solid-phase methodology has been widely applied to the preparation of small organic molecules. Polymer-supported reagents have attracted growing interest because they can provide attractive and practical methods for combinatorial chemistry and solid-phase synthesis.[1] 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. In general, these compounds have been prepared by DDQ oxidation of the corresponding saturated β-dicarbonyl compounds,[2] but the yields obtained from this procedure are only modest. Liotta *et al.*[3] previous reported a synthetic method for the title compounds in good yields by the 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 were difficult. Furthermore, organic selenium reagents always have a foul smell and are quite toxic, which is often problematic in organic synthesis. With the successful synthesis of carbonyl compounds [4] and allylic esters or ethers [5] from resin-bound selenium reagents, we here wish to report the very simple preparation of a novel polystyrene-supported N, N-diethylbenzeneselenenamide and its application as a powerful reagent for α-selenenylation of α-formylcycloanones and a deselenenylation reaction by oxidation-elimination. The method is illustrated in Scheme 1, using α-formyl-cyclohexanone. A useful advantage of this new polymer-supported selenium reagent is the convenience of handling and totally odourless nature as compared to the non-bound reagents.

Simply stirring polystyrene-supported selenium bromide **1**[6] with diethylamine in CH_2Cl_2 at room temperature resulted in a rapid decolourisation of the resin (<5 min) to produce a yellow N, N-diethylbenzeneselenenamide resin **2** in nearly quantitative yield by elemental analysis of nitrogen. Treatment of the resin **2** with α-formylcyclohexanone gave the corresponding α-seleno-β-dicarbonyl compound resin **3.** This was shown by the IR spectrum showing strong carbonyl absorption at 1705-1725 cm^{-1} and an aldehydic CH stretching absorption at 2700 cm^{-1}. Resin **2** and **3** are quite stable under the reaction conditions and can be stored in the air at room temperature for several months without diminution of their capacity or the liberation of disagreeable odours. Oxidation-elimination of resin **3** was very rapid and efficient with excess of 30% H_2O_2 at room temperature to form the corresponding product in good yield and high purity as shown in Table 1. The residual resin, phenylseleninic acid, was obtained as a by-product, whose infrared data was identical to the previously reported data [7] and showed no residual carbonyl absorption, indicating the oxidation-elimination was complete.

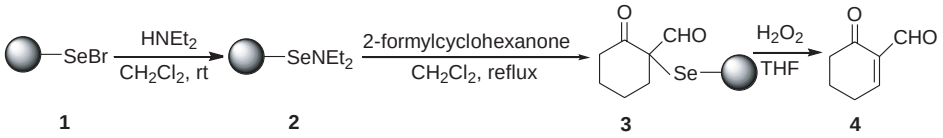
In summary, we have prepared a novel polystyrene-supported N, N-diethylbenzeneselenenamide, which is an efficient reagent for the synthesis of β-dicarbonyl enones. Simple workup procedure replaces the time-consuming isolation and purification steps in the solution phase synthesis.

Experimental

Melting points were uncorrected; ^1H NMR spectra were recorded on Bruker Avance 400 MHz spectrometer using $CDCl_3$ as the solvent and with TMS as internal standard; IR spectra were determined on a Bruker Vector 22 spectrophotometer. α-Formylcycloanones were prepared according to the procedure described in the literature [8-9].

Preparation of polystyrene-supported N, N-diethylbenzene-selenenamide **2**: Polystyrene-supported selenium bromide (1.0 g, 1.18 mmol Br/g), prepared from 1% cross-linked polystyrene beads, [6] was swelled in CH_2Cl_2 (10 ml) for 30 min, and diethylamine (2.50 mmol) was added. The mixture was stirred at room temperature for 20 min and filtered. After washing successively with H_2O, CH_3OH, CH_2Cl_2 (2×3 ml of each) and then drying in vacuum. The resin **2** containing 1.19 mmol N /g was obtained as a yellow beads. IR (KBr): 3056, 3022, 2920, 2848, 1600, 1583, 1490, 1449, 1274, 1108, 1065, 902, 755, 695 cm^{-1}; Anal calcd: N, 1.67%. Found: N, 1.63%.

General procedure for preparation of β*-dicarbonyl enones:* Resin **2** (1.0 g, 1.19 mmol) was preswollen with CH_2Cl_2 (10 ml), α-formylcycloanone (1.30 mmol) was added. The suspension was refluxed for 5 h, then cooled, filtered and washed successively with THF, CH_3OH, CH_2Cl_2 (3×3 ml of each) to afford the corresponding



1 **2** **3** **4**

Scheme 1

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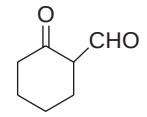
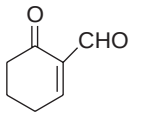
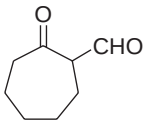
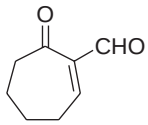
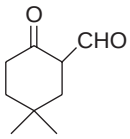
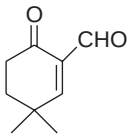
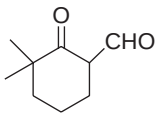
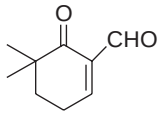
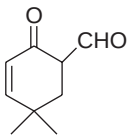
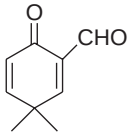
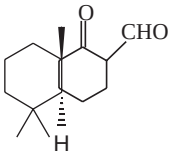
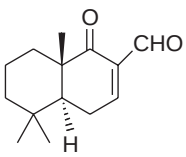
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Yields and purities of β-dicarbonyl enones

Entry	Substrate	Product	Yield /%[a]	Purity /%[b]
1			86	>95
2			85	>95
3			90	>95
4			88	>95
5			90	>95
6			91	>95

[a]Overall yield based on polymer-bound N, N-diethylbenzeneselenenamide (1.19 mmol N/g).
[b]Purity determined by ^{1}H NMR (400 MHz) of crude cleavage product.

polystyrene-supported α-seleno-β-dicarbonyl compound**.** This resin was then suspended in THF and treated with 1 ml (11.6 mmol) of 30 % H_2O_2. The mixture was stirred for 30 min at room temperature, and then the residual resin was collected by filtration and washed with THF. The filtrate was transferred to a separating funnel and was extracted with Et_2O, washed successively with saturated $NaHCO_3$, water. After being dried over magnesium sulfate, the solution is filtered and the solvent evaporated *in vacuo* to give product.

2-Formylcyclohex-2-en-1-one[3]: oil, ^{1}H NMR δ 10.10 (d, *J* = 7.4 Hz 1H), 7.26 (dt, *J* = 7.4, 3.1 Hz, 1H), 1.98 (t, *J* = 7.0 Hz, 2H), 1.66–2.01 (m, 2H), 1.30-1.55 (m, 2H); IR (film) 3030, 2928, 2720, 1694, 1668, 1602 cm^{-1}.

2-Formylcyclohept-2-en-1-one [10]: oil, ^{1}H NMR δ 10.08 (d, *J* = 7.5 Hz 1H), 7.28 (dt, *J* = 7.5, 3.1 Hz, 1H), 1.95 (t, *J* = 7.1 Hz, 2H), 1.64–2.00 (m, 2H), 1.35–1.55 (m, 4H); IR (film) 3032, 2925, 2725, 1698, 1665, 1605 cm^{-1}.

2-Formyl-4,4-dimethylcyclohex-2-en-1-one [3]: oil, ^{1}H NMR δ 10.03 (d, *J* = 7.4 Hz 1H), 7.41 (d, *J* = 7.4 Hz 1H), 2.59 (t, *J* = 7.9 Hz, 2H), 1.85 (t, *J* = 7.9 Hz, 2H), 1.30 (s, 6H); IR (film) 3030, 2929, 2722, 1680, 1610, 1378 cm^{-1}.

2-Formyl-6,6-dimethylcyclohex-2-en-1-one [3]: oil, ^{1}H NMR δ 10.07 (d, *J* = 7.6 Hz 1H), 7.56 (dt, *J* = 7.6, 4.1 Hz, 1H), 2.59 (dt, *J* = 4.1, 7.1 Hz, 2H), 1.82 (t, *J* = 7.1 Hz, 2H), 1.15 (s, 6H); IR (film) 3035, 2925, 2725, 1680, 1608, 1377 cm^{-1}.

2-Formyl-4,4-dimethylcyclohexa-2,5-dien-1-one[3]: m.p. 61–62 °C (lit.[3] 60–61°C); ^{1}H NMR δ 10.25 (d, *J* = 7.0 Hz, 1H), 7.58 (d, *J* = 7.0 Hz, 1H), 6.93 (d, *J* = 10.0 Hz, 1H), 6.22 (d, *J* = 10.0 Hz, 1H), 1.45 (s, 6H); IR (film) 3035, 2926, 2722, 1702, 1665, 1600, 1376 cm^{-1}.

5,5,9-Trimethyl-2-formyl-Δ^2*-trans-1-octalone*[11]: m.p. 74–75 °C (lit.[4] 74–76°C); ^{1}H NMR δ 10.0 (d, *J* = 7.4 Hz 1H), 7.60 (dt, *J* = 7.4, 4.1 Hz, 1H), 2.44–2.64 (m, 2H), 1.19–2.02 (m, 7H), 1.15 (s, 6H), 1.00 (s, 3H); IR (film) 3030, 2928, 2720, 1685, 1655, 1604, 1372 cm^{-1}.

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