SHORT PAPER

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Synthesis of allylic esters and ethers using polymer-supported selenium bromide†

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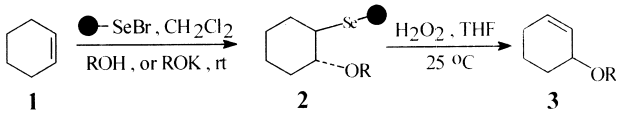
The treatment of adducts from polymer-supported selenium bromide on olefins with anhydrous carboxylate or alcohol and oxidation of the resulting products afford allylic esters and ethers in good yield and purity.

Keywords: allylic esters, allylic ethers, polymer-supported selenium bromide

The utilisation of polymer-bound reagents in organic synthesis has gained popularity in recent years.[1] Among the several advantages offered by these reagents,[2] the one most frequently utilised is the convenience of handling, which often consists of a simple filtration. This feature is of more importance especially when the non-bound reagents are toxic or noxious and when they are unstable to lengthy and tedious work-ups. We have developed a convenient method for the synthesis of allylic esters and ethers in good yield and purity using polymer-bound selenium bromide.[3] Polymer-supported selenium bromide has been recently used in the solid-phase combinatorial synthesis of natural products,[4] substituted indolines[5] and δ-lactones.[6] An early report of the solution-phase synthesis of the allylic acetates and ethers by Sharpless and Lauer[7] used PhSeBr. However, separation of the products from the phenylselenenyl oxide by-product and any excess of phenylselenenyl bromide is difficult. Herein we report the synthesis of allylic esters and ethers using polymer-supported selenium bromide. For example, polymer-supported selenium bromide undergoes *trans*-1, 2-addition to cyclohexene to yield resin 2, which is treated with H_2O_2 to afford the corresponding compound as shown in Scheme 1.



Scheme 1

Treatment of a suspension of polymer-supported selenium bromide and olefin with carboxylate or alcohol in CH_2Cl_2 at room temperature resulted in a rapid decolourisation of the resin (< 10min). These newly loaded resins as evidenced by ester or ether group absorption in the IR spectrum (1734 cm^{-1} and 1103 cm^{-1}, respectively) were then treated with H_2O_2 in THF to form the corresponding products in good yield and purity as shown in Table 1. The phenylseleninic acid is obtained as a by-product, which is separated by filtration and can be used as oxidant.[8]

However, the reaction is not highly regioselective for unsymmetrical olefins. For example, polymer-supported selenium bromide adds to 2-methyl-2-hexene to give nearly equal amounts of the two possible adducts followed by oxidation to form a mixture of the four final products.

In conclusion, the use of polymer-supported selenium bromide exhibits a very effective procedure for the synthesis of allylic esters and ethers. Simple workup procedure replaces the time-consuming isolation and purification steps in the solution phase synthesis.

Table 1 Synthesis of allylic esters and ethers using polymer-supported selenium bromide

Entry	Olefin	Product	Yield/ %[a]	Purity/ %[b]
1	Cyclohexene	2-hexenyl acetate	76	90
2	cyclohexene	2-hexenyl benzoate	75	91
3	cyclohexene	3-methoxyhexence	85	93
4	Cyclopentene	2-cyclopentenyl acetate	80	88
5	cyclopentene	2-cyclopentenyl benzoate	82	90
6	(*E*)-4-octene	(*E*)-5-acetoxy-3-octene	78	87
7	(*E*)-4-octene	(*E*)-1-propyl-2-pentenyl benzoate	77	88
8	(*E*)-4-octene	(*E*)-5-methoxy-3-octene	80	91

[a]Overall yields based on polymer-supported selenium bromide (1.18mmol/g).

[b]Purity determined by ^{1}HNMR of crude cleavage product.

Experimental

^{1}HNMR spectra were recorded on Bruker Avance 400 MHz spectrometer using $CDC1_3$ as the solvent and with TMS as internal standard; IR spectra were determined on a Bruker Vector 22 spectrophoto-meter.

General procedure for the synthesis of allylic esters and ethers: The polymer-supported selenium bromide (1.0 g, 1.18 mmol/g) was swelled in CH_2Cl_2 for 2–4h at room temperature, olefin (3.0 mmol) was added followed by anhydrous carboxylate (3.0 mmol) or alcohol (3.0 mmol). The mixture was stirred at room temperature for 6h, filtered and washed successively with H_2O, THF and Et_2O (10.0 ml of each) to afford the corresponding resin. The resin was then suspension in THF and treated with 1 ml (11.6 mmol) of 30% H_2O_2. The mixture was stirred for 1–2h at room temperature, the resin was collected by filtration. The filtrate was transferred to a separating funnel and was extracted with Et_2O, and the aqueous layer was extracted with Et_2O. The combined extracts were washed with water, dried over magnesium sulfate and evaporated to give products.

2-cyclohexenyl acetate[9]: oil, ^{1}HNMR δ 5.99–5.90 (m, 1H), 5.73–5.60 (m, 1H), 5.24–5.21 (m, 1H), 2.05 (s, 3H), 2.10–1.45 (m, 6H); IR (film) 3321, 2961, 2938, 1732, 1662, 1461, 1374, 1015, 960, 940, 821 cm^{-1}.

2-cyclohexenyl benzoate[10]: oil, ^{1}HNMR δ 8.04 (d, *J*=7.5Hz, 2H), 7.53 (t, *J*=7.5Hz, 1H), 7.41 (t, *J*=7.5Hz, 2H), 6.02–5.98 (m, 1H), 5.84–5.80 (m, 1H), 5.51–5.48 (m, 1H), 2.20–1.75 (m, 6H); IR (film) 3028, 2938, 1712, 1651, 1600, 1582, 1490, 1451, 1315, 1271, 1175, 1110, 1065, 1025, 1012, 965, 712 cm^{-1}.

3-methoxycyclohexence[11]: oil, ^{1}HNMR δ 5.66–5.60 (m, 1H), 5.55–5.41 (m, 1H), 4.20–4.01 (m, 1H), 3.29 (s, 3H), 2.41–1.14 (m, 6H); IR (film) 3320, 2932, 2883, 1665, 1469, 1376, 1122, 1070, 1025, 990 cm^{-1}.

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2-cyclopenenyl acetate[10]: oil, ^{1}HMNR δ 5.98–5.82 (m, 1H), 5.80–5.74 (m, 1H), 5.42–5.25 (m, 1H), 1.99 (s, 3H), 1.88–1.52 (m, 4H); IR (film) 3048, 2940, 2845, 1723, 1472, 1428, 1356, 1240, 1158, 1108, 1025, 961, 912, 725 cm^{-1}.

2-cyclopentenyl benzoate[10]: oil, ^{1}HNMR δ 8.04 (d, *J*=7.4, 2H), 7.52 (t, *J*=7.51, 1H), 7.40 (t, *J*=7.41, 2H), 6.02–5.98 (m, 1H), 5.85–5.81 (m, 1H), 5.53–5.50 (m, 1H), 2.13–1.73 (m, 4H); IR (film) 3030, 2935, 1710, 1650, 1601, 1581, 1485, 1450, 1310, 1265, 1170, 1110, 1024, 958, 915, 723 cm^{-1}.

(E)-5-acetoxy-3-octene[10]: oil, ^{1}HNMR δ 6.0 (dt, *J*=16.4, 1H), 5.24 (ddt, *J*-16.2, 8.3, 2.1, 1H), 5.03 (dt, 1H), 1.96 (s, 3H), 1.71–1.22 (m, 6H), 1.20–0.87 (m, 6H); IR (film) 3321, 2965, 2871, 1736, 1664, 1456, 1015, 965, 941, 823 cm^{-1}.

(E)-1-propyl-2-pentenyl benzoate[10]: oil, ^{1}HNMR δ 8.02–7.11 (m, 5H), 6.10 (dt, *J*=16.2, 1H), 5.22 (ddt, *J*=16.1, 8.1, 2.0 1H), 5.04 (dt, 1H), 1.68–1.22 (m, 6H); 1.20–0.87 (m, 6H) IR (film) 2930, 1710, 1650, 1602, 1585, 1491, 1450, 1312, 1270, 1168, 1112, 1070, 1025, 1010, 967, 715 cm^{-1}.

(E)-5-methoxy-3-octene[11]: oil, ^{1}HNMR δ 5.60 (dt, *J*=16.4, 1H), 5.20 (ddt, *J*=16.1, 80, 2.1), 3.40 (dt, 1H), 3.28 (s, 3H), 2.20–1.91 (m, 2H), 1.8–1.2 (m, 4H), 1.2–0.8 (m, 6H); IR (film) 3323, 2931, 2885, 1663, 1465, 1377, 1120, 1071, 1026, 991 cm^{-1}.

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