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SHORT PAPER

Samarium(II)-induced coupling of acid chlorides with allylic halides

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Samarium(II)-induced coupling of acid chlorides with allylic halides gave diallylated tertiary alcohols. Monoallylated allylic ketones could not be obtained.

Keywords: Samarium(II) iodide, allylic halides, allylation, tertiary alcohols

INTRODUCTION

Samarium(II) iodide, readily obtainable from samarium metal and 1,2-diiodoethane in tetrahydrofuran (THF), has been proved to be useful for the reduction of activated olefins, halides, epoxides, aldehydes, and ketones, and also for Barbier–Grignard-type coupling of organic halides with carbonyl compounds.[1] This reagent is also effective for reductive dimerization of allylic halides,[1] aldehydes and ketones,[2] and acid chlorides.[3] However, cross-coupling between acid chlorides and organic halides has not to our knowledge been reported so far. Here, we describe the samarium(II)-induced coupling of acid chlorides with allylic and benzylic compounds.

RESULTS AND DISCUSSION

When a mixture of octanoyl chloride and allyl iodide was added to a solution of samarium(II) iodide in THF, the characteristic blue–green color of samarium(II) turned yellow–green within 1 min. The reaction was quenched by the addition of water and the product was purified by column chromatography on silica gel. From the spectroscopic data, the product was confirmed to be the tertiary alcohol, 4-heptylhepta-1,6-dien-4-ol (**1**). The isolated yield of **1** was 56%. The compound **1** is considered to be formed via undec-1-en-4-one, which however could not be found in the reaction mixture. The yield of **1** improved to 72% when a 2:1 mole ratio of allylic iodide to octanoyl chloride was used. When allyl bromide or allyl diphenylphosphate was used in place of allyl iodide, the cross-coupling competed with the homo-coupling of the acid chloride;[3] consequently lower yields of **1** were obtained. Thus, in these cases considerable amounts of the keto-alcohol, 9-hydroxyhexadecan-8-one (**2**) were produced. Compound **2** is considered to be produced by the reduction of the initially formed hexadecane-8,9-dione.[3] Similar reactions of octanoyl chloride with β-methallyl halides, and benzyl bromide gave the corresponding tertiary alcohols **3** and **4**, respectively (Table 1). In the latter reaction, **2** as well as bibenzyl were isolated. The reaction of benzoyl chloride with allyl iodide gave benzil in 50% yield and the yield of the cross-coupling product (**5**) was poor (18%)

EXPERIMENTAL

General

Infrared spectra were recorded on a JASCO IRA-1 spectrophotometer. ^{1}H NMR spectra were recorded on a Hitachi R-24A spectrometer (60 MHz) or on a Varian XL-200 spectrometer (200 MHz) with Me_4Si as an internal standard. Mass spectra were determined using a Hitachi M-52 instrument at 20 eV. Elemental analyses were performed at the Elemental Analysis Center

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Table 1 Samarium(II)-induced coupling of acid chlorides with allylic compounds[a]

Compound	Acid chloride	Allylic compound	Cross-coupling product (Yield, %)[b]	Homo-coupling product (Yield, %)[b]
1	$Me(CH_2)_6\overset{O}{\overset{\|}{C}}Cl$	$CH_2{=}CHCH_2I$	$Me(CH_2)_6C(OH)(CH_2CH{=}CH_2)_2$ **1** (72)	—
2	$Me(CH_2)_6\overset{O}{\overset{\|}{C}}Cl$	$CH_2{=}CHCH_2Br$	**1** (23)	$Me(CH_2)_6\overset{O}{\overset{\|}{C}}{-}\overset{OH}{\overset{\mid}{C}}H(CH_2)_6Me$ **2** (36)
3	$Me(CH_2)_6\overset{O}{\overset{\|}{C}}Cl$	$CH_2{=}CHCH_2O\overset{O}{\overset{\|}{P}}(OPh)_2$	**1** (19)	**2** (35)
4	$Me(CH_2)_6\overset{O}{\overset{\|}{C}}Cl$	$CH_2{=}\overset{Me}{\overset{\mid}{C}}CH_2Br$	$Me(CH_2)_6C(OH)(CH_2\overset{Me}{\overset{\mid}{C}}{=}CH_2)_2$ **3** (29)	**2** (36)
5	$Me(CH_2)_6\overset{O}{\overset{\|}{C}}Cl$	$CH_2{=}\overset{Me}{\overset{\mid}{C}}CH_2Cl$	**3** (3)	**2** (24)
6	$Me(CH_2)_6\overset{O}{\overset{\|}{C}}Cl$	$PhCH_2Br$	$Me(CH_2)_6C(OH)(CH_2Ph)_2$ **4** (53)	**2** (18) + $PhCH_2CH_2Ph$ (52)[c]
7	$Ph\overset{O}{\overset{\|}{C}}Cl$	$CH_2{=}CHCH_2I$	$PhC(OH)(CH_2CH{=}CH_2)_2$ **5** (18)	$Ph\overset{O}{\overset{\|}{C}}{-}\overset{O}{\overset{\|}{C}}Ph$ (50)

[a] All the reactions were carried out in THF at room temperature using acid chloride, allylic compound, and SmI_2 in the ratio of 1:2:4. [b] Based on the acid chloride used. [c] Yield of crude material, based on benzyl bromide used.

of Kyoto University. For Kugelrohr distillation, a Shibata GTO-250R glass tube oven was used. THF was freshly distilled from sodium benzophenone ketyl. All the reactions were carried out under an argon atmosphere.

Samarium(II)-induced coupling of acid chlorides with allylic compounds

The following reaction of octanoyl chloride with allyl iodide is representative. To a solution of samarium(II) iodide, prepared from samarium metal (397 mg, 2.64 mmol) and 1,2-diiodoethane (620 mg, 2.20 mmol) in THF (20 cm^3) according to a literature method,[1] was added a mixture of octanoyl chloride (83 mg, 0.51 mmol) and allyl iodide (205 mg, 1.22 mmol) in THF (1 cm^3) at room temperature. The color of the mixture turned from blue–green to yellow–green within 1 min. The mixture was further stirred for 20 min and the reaction was quenched by the addition of water. The product was extracted with ether and the extracts were successively washed with water, aqueous $Na_2S_2O_3$, water, and brine, and then dried ($MgSO_4$). The solvent was evaporated and the residue was column chromatographed on silica gel (benzene). Kugelrohr distillation furnished pure 4-heptylhepta-1,6-dien-4-ol (**1**; 77 mg, 72%) as a colorless oil.

All the other experiments were similarly carried out and the products were separated by column chromatography on silica gel; the structures were deduced by their spectral and analytical data.

4-Heptylhepta-1,6-dien-4-ol (1)[4]

B.p. 105–115°C/4.2 Torr (1 Torr ≈ 133.322 Pa); IR (neat) 3430, 3080, 2970, 2940, 2870, 1642, 1466, 1444, 1380, 1145, 995 and 913 cm^{-1}; ^1H NMR ($CDCl_3$) 0.89 (*t*, $J = 6$ Hz, 3H, Me), 1.20–1.47 (m, 12H, CH_2), 1.57 (bs, 1H, OH), 2.24 (d, $J = 7$ Hz, 4H, CH_2), 5.14 (dd, $J = 19$, 2 Hz, 2H, olefin H), 5.15 (dd, $J = 10$, 2 Hz, 2H, olefin H), 5.77–5.98 (m, 2H, olefin H); MS: m/z (rel. intensity) 192 ($M^+ - H_2O$, 1), 169 (16), 128 (11), 127 (100), 69 (15), 57 (51).

9-Hydroxyhexadecan-8-one (2)[5]

B.p. 150–160°C/4.2 Torr; IR (neat) 3495, 2970, 2930, 2870, 1712, 1466, 1402, 1378, 1124, 1086, 1016, and 720 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.88 (t, $J=6$ Hz, 6H, Me), 1.23–1.90 (m, 22H, CH_2), 2.46 and 2.48 (each t, $J=7$ Hz, 2H, CH_2), 3.51 (bs, 1H, OH), 4.15–4.24 (m, 1H, CH); MS: m/z (rel. intensity) 256 (M^+, 5), 158 (22), 129 (88), 128 (41), 127 (63), 111 (81), 69 (100), 57 (26).

4-Heptyl-2,6-dimethylhepta-1,6-dien-4-ol (3)

B.p. 125–135°C/2.8 Torr; IR (neat) 3570, 3500, 3080, 2930, 2870, 1643, 1452, 1366, 1124, 1074, 888 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.88 (t, $J=6$ Hz, 3H, Me), 1.22–1.49 (m, 12H, CH_2), 1.69 (bs, 1H, OH), 1.85 (s, 6H, Me), 2.22 (s, 4H, CH_2), 4.77 (bs, 2H, olefin H), 4.94 (bs, 2H, olefin H); MS: m/z (rel. intensity) 183 (14), 128 (9), 127 (100), 57 (49). Found: C, 80.50; H, 12.73%. Calcd for $C_{16}H_{30}O$: C, 80.61; H, 12.68%.

2-Benzyl-1-phenylnonan-2-ol (4)

B.p. 190–200°C/4.0 Torr; IR (neat) 3580, 3480, 3070, 3035, 2930, 2870, 1600, 1498, 1452, 1376, 1122, 1083, 1030, 883, 750, 719, and 699 cm^{-1}; ^{1}H NMR ($CDCl_3$) 0.88 (t, $J=6$ Hz, 3H, Me), 1.17–1.56 (m, 13H, CH_2 and OH), 2.81 (s, 4H, CH_2), 7.22–7.42 (m, 10H, Ph); MS: m/z (rel. intensity) 292 ($M^+ - H_2O$, 1), 220 (17), 219 (100), 128 (22), 91 (12). Found: C, 85.27: H, 10.02%. Calcd for $C_{22}H_{30}O$: C, 85.11; H, 9.74%.

4-Phenylhepta-1,6-dien-4-ol (5)[6]

B.p. 91–97°C/5.1 Torr; IR (neat) 3570, 3480, 2985, 2940, 2920, 1641, 1496, 1448, 1341, 1056, 1030, 1000, 916, and 701 cm^{-1}; ^{1}H NMR ($CDCl_3$) 1.78 (bs, 1H, OH), 2.47–2.78 (m, 4H, CH_2), 5.13 (dd, $J=17$, 1 Hz, 2H, olefin H), 5.15 (dd, $J=10$, 1 Hz, 2H, olefin H), 5.53–5.75 (m, 2H, olefin H), 7.29–7.49 (m, 5H, Ph); MS: m/z (rel. intensity) 170 ($M^+ - H_2O$, 1), 147 (46), 129 (10), 105 (100).

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