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Cadmium metal-mediated allylation of carbonyl compounds

Shuki Araki, Hirokazu Ito, and Yasuo Butsugan *

Department of Applied Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466 (Japan)

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Abstract

Metallic cadmium prompted Barbier-type coupling of carbonyl compounds and allylic halides. The reaction was regio-selective giving homoallylic alcohols coupled at the γ-position of allylic halides. α,β-Unsaturated carbonyl compounds underwent only 1,2-addition.

Introduction

Organocadmium reagents are usually prepared by the transmetallation of organomagnesium or organolithium reagents with cadmium halides, because cadmium metal is less reactive than magnesium and lithium toward oxidative addition to organic halides [1]. Metallic cadmium, therefore, has been scarcely used in synthetic chemistry. In 1966 it was found that alkyl iodides and allyl bromides react with cadmium metal to give organocadmium reagents in polar aprotic solvents such as hexamethylphosphoric triamide [2]. More recently, direct syntheses of organocadmium reagents from activated cadmium metal and organic halides have been reported. Klabunde has described the preparation of an active cadmium slurry by metal atom-solvent cocondensation from which an ethylcadmium reagent was synthesized [3]. Rieke has described three methods for the preparation of reactive cadmium powders and also showed their usefulness in synthetic chemistry [4]. We have found that a commercially available cadmium powder is effective for Barbier-type allylation of carbonyl compounds.

Results and discussion

The reaction of a commercial cadmium powder with carbonyl and allylic halide with the usual work-up under suitable conditions gave homoallylic alcohols in good

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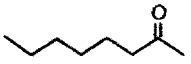
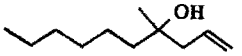
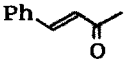
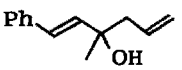
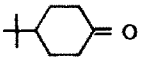
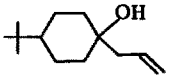
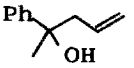
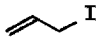
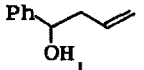
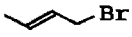
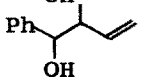
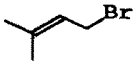
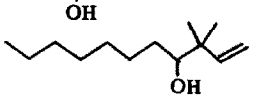
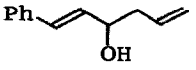
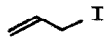
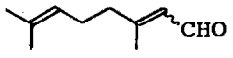
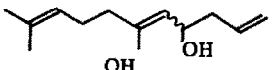
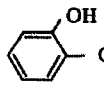
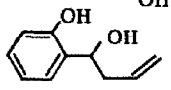
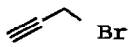
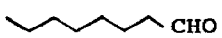
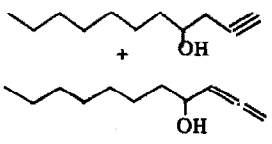
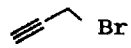
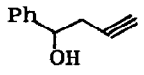
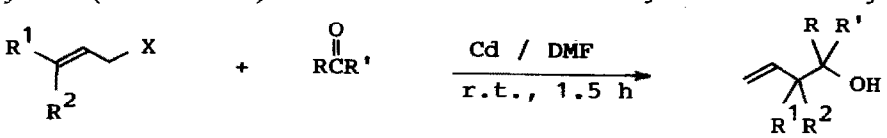
Table 1

Cadmium-mediated allylation of carbonyl compounds [a]

Entry	Allyl halide	Carbonyl compound	DMF (ml)	Product	Yield (%)
1			4		92
2		〃	4	〃	91
3			4		96
4			4		99 [b]
5		$PhCOCH_3$	2		83
6		PhCHO	2		78
7		〃	2		90 [c]
8			4		59
9			4		94
10			2		99
11			2		74
12			2		74 [d]
13		PhCHO	2		59

[a] All the reactions were carried out using allyl halide (3 mmol), carbonyl compound (2 mmol), and cadmium (3 mmol). [b] Axial/equatorial alcohol 80/20. [c] *Erythro/threo* 50/50. [d] Acetylene/allene 82/18.

yields (see Table 1). Various ketones and aldehydes react readily to give the



X = Br, I

corresponding homoallylic alcohols. Even salicylaldehyde which bears a hydroxyl group gave allylated product in 74% yield (entry 11). Allylation of 4-t-butylcyclohexanone gave a mixture of the axial and equatorial alcohols (80/20) (entry 4). α,β-Unsaturated carbonyl compounds gave only 1,2-addition products (entries 3, 9, and 10). 1-Bromo-2-butene (entry 7) and 1-bromo-3-methyl-2-butene (entry 8) coupled at their γ-terminus regio-selectively. The products from the reaction of 1-bromo-2-butene and benzaldehyde were a mixture of *erythro* and *threo* isomers (50/50). 3-Bromo-1-propyne, an example of a propargylic halide gave predominantly α-coupled products (entries 12 and 13). The reaction of benzoyl chloride with allyl iodide yielded a complex mixture of products, from which 4-phenyl-1,6-heptadien-4-ol was isolated in 35% yield. Ester and cyano groups were not allylated by this method. Attempted alkylation of benzaldehyde by ethyl iodide failed and 87% of the benzaldehyde was recovered unchanged.

In our reaction, *N,N*-dimethylformamide (DMF) was the solvent of choice; in other solvents such as tetrahydrofuran, the yields were considerably diminished. Although Barbier-type allylation of carbonyl compounds has been achieved with various metals and metal reductants [5], our cadmium-prompted reaction provides a unique example of the use of cadmium metal in synthetic organic chemistry.

Experimental

IR spectra were recorded on a Jasco A-102 spectrometer. ^{1}H NMR spectra were measured with a Hitachi R-24A (60 MHz) or a Varian XL-200 (200 MHz) spectrometer. The chemical shifts are given in δ with tetramethylsilane as an internal standard. DMF was dried over calcium hydride and distilled before use. Cadmium powder (99.999%, 60–80 mesh) was purchased from Nakarai Chemicals Co., Ltd. and used as received. All the reactions were conducted under argon.

Cadmium-prompted reaction of carbonyl compounds with allylic halides

The following reaction of 2-octanone with 3-bromo-1-propene (entry 2) is representative. To a suspension of cadmium powder (337 mg, 3.0 mmol) in DMF (3 ml) was added a solution of 2-octanone (256 mg, 2.0 mmol) and 3-bromo-1-propene (363 mg, 3.0 mmol) in DMF (1 ml), and exothermic reaction soon occurred. The mixture was stirred at room temperature for 1.5 h and the reaction was quenched by the addition of dilute (1 *N*) hydrochloric acid. The product was extracted with ether and the extracts were washed with water and brine, and then dried over anhydrous sodium sulfate. The solvent was removed under reduced pressure and the residue was chromatographed on silica gel (eluant: dichloromethane) to give 4-methyl-1-decen-4-ol (310 mg, 91%).

All other reactions were carried out similarly and the structures of the products were deduced from their spectral data. All products are known compounds [5], so only their IR and ^{1}H NMR data are given below.

4-Methyl-1-decen-4-ol. IR (neat): 3420, 3110, 2970, 2880, 1644, 1470, 1460, 1380, 1158, 1144, 1002, 918 cm^{-1}; ^{1}H NMR ($CDCl_3$): 0.89 (t, *J* 6 Hz, 3H, Me), 1.16 (s, 3H, Me), 1.23–1.60 (m, 11H, CH_2 and OH), 2.23 (d, *J* 7 Hz, 2H, CH_2), 5.06–5.23 (m, 2H, olefin H), 5.78–5.99 (m, 1H, olefin H).

(E)-3-Methyl-1-phenyl-1,5-hexadien-3-ol. IR (neat): 3420, 3085, 3075, 3035, 2980, 2935, 2820, 1640, 1598, 1494, 1446, 1434, 1370, 1272, 1102, 970, 916, 748, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$): 1.33 (s, 3H, Me), 2.25–2.45 (m, 2H, CH_2), 2.62 (bs, 1H, OH),

5.04–5.17 (m, 2H, olefin H), 5.72–5.94 (m, 1H, olefin H), 6.25 (d, *J* 16 Hz, 1 H, olefin H), 6.58 (d, *J* 16 Hz, 1H, olefin H), 7.12–7.38 (m, 5H, Ph).

1-Allyl-4-t-butylcyclohexanol (axial alcohol). IR (neat): 3400, 3080. 2975, 2950, 2875, 2850, 1638, 1476, 1440, 1390, 1364, 1234, 1188, 1140, 992, 952, 912 cm^{-1}; ^1H NMR ($CDCl_3$): 0.86 (s, 9H, Me), 1.24–1.79 (m, 10H, CH_2, CH, and OH), 2.18 (d, *J* 7 Hz, 2H, CH_2), 5.03–5.19 (m, 2H, olefin H), 5.79–6.00 (m, 1H, olefin H).

1-Allyl-4-t-butylcyclohexanol (equatorial alcohol). IR (neat): 3400, 3080, 2975, 2950, 2875, 1638, 1476, 1466, 1450, 1392, 1364, 1228, 1144, 1036, 990, 910 cm^{-1}; ^1H NMR ($CDCl_3$): 0.86 (s, 9H, Me), 1.08–1.86 (m, 10H, CH_2, CH, and OH), 2.31 (d, *J* 7 Hz, 2H, CH_2), 5.09–5.28 (m, 2H, olefin H), 5.80–6.02 (m, 1H, olefin H).

2-Phenyl-4-penten-2-ol. IR (neat): 3435, 3085, 3070, 3035, 2985, 2935, 1640, 1494, 1444, 1374, 1068, 1028, 998, 912, 764, 698 cm^{-1}; ^1H NMR ($CDCl_3$): 1.48 (s, 3H, Me), 2.39–2.69 (m, 3H, CH_2 and OH), 5.00–5.14 (m, 2H, olefin H), 5.51–5.74 (m, 1H, olefin H), 7.14–7.47 (m, 5H, Ph).

1-Phenyl-3-buten-1-ol. IR (neat): 3400, 3100, 3050, 2950, 2925, 1644, 1496, 1454, 1050, 1002, 918, 760, 702 cm^{-1}; ^1H NMR ($CDCl_3$): 2.44 (t, *J* 6 Hz, 2H, CH_2), 2.65 (bs, 1H, OH), 4.64 (t, *J* 6 Hz, 1H, CH), 5.10 (d, *J* 11 Hz, 1H, olefin H), 5.11 (d, *J* 16 Hz, 1H, olefin H), 5.66–5.86 (m, 1H, olefin H), 7.24–7.38 (m, 5H, Ph).

2-Methyl-1-phenyl-3-buten-1-ol (erythro and threo 1 / 1). IR (neat): 3420, 3075, 3030, 2980, 2935, 1638, 1494, 1452, 1010, 914, 762, 700 cm^{-1}; ^1H NMR ($CDCl_3$): 0.86 and 1.00 (each d, *J* 7, 6 Hz, 3H, Me), 2.11 and 2.26 (each bs, 1H, OH), 2.41–2.65 (m, 1H, CH), 4.36 and 4.59 (each d, *J* 8, 5 Hz, 1H, CH), 4.99–5.30 (m, 2H, olefin H), 5.67–5.91 (m, 1H, olefin H), 7.24–7.43 (m, 5H, Ph).

3,3-Dimethyl-1-undecen-4-ol. IR (neat): 3400, 3090, 2935, 2865, 1638, 1466, 1414, 1378, 1072, 910 cm^{-1}; ^1H NMR ($CDCl_3$): 0.88 (t, *J* 6 Hz, 3H, Me), 1.00 (s, 6H, Me), 1.16–1.74 (m, 13H, CH_2 and OH), 3.19–3.33 (m, 1H, CH), 5.06 (dd, *J* 16, 1 Hz, 1H, olefin H), 5.09 (dd, *J* 11, 1 Hz, 1H, olefin H), 5.85 (dd, *J* 16, 11 Hz, 1H, olefin H).

(E)-1-Phenyl-1,5-hexadien-3-ol. IR (neat): 3370, 3080, 3030, 2930, 2920, 1642, 1496, 1448, 1028, 968, 916, 746, 692 cm^{-1}; ^1H NMR ($CDCl_3$): 2.37 (t, *J* 6 Hz, 2H, CH_2), 3.00 (bs, 1H, OH), 4.30 (bq, *J* 6 Hz, 1H, CH), 5.11 (d, *J* 10 Hz, 1H, olefin H), 5.13 (d, *J* 16 Hz, 1H, olefin H), 5.72–5.96 (m, 1H, olefin H), 6.21 (dd, *J* 16, 6 Hz, 1H, olefin H), 6.56 (d, *J* 16 Hz, 1H, olefin H), 7.15–7.42 (m, 5H, Ph).

6,10-Dimethyl-1,5,9-undecatrien-4-ol. IR (neat): 3370, 3110, 3000, 2950, 1646, 1444, 1380, 1028, 1004, 916 cm^{-1}; ^1H NMR ($CDCl_3$): 1.61 (s, 3H, Me), 1.68 (bs, 6H, Me), 1.96–2.38 (m, 7H, CH_2 and OH), 4.43 (bq, *J* 7 Hz, 1H, CH), 5.06–5.32 (m, 4H, olefin H), 5.70–5.95 (m, 1H, olefin H).

1-(2-Hydroxyphenyl)-3-buten-1-ol. IR (neat): 3360, 3100, 3060, 3000, 2980, 2965, 1644, 1590, 1494, 1458, 1244, 1036, 990, 922, 754 cm^{-1}; ^1H NMR ($CDCl_3$): 2.52 (bt, *J* 7 Hz, 2H, CH_2), 4.04 (bs, 1 H, OH), 4.80 (t, *J* 7 Hz, 1 H, CH), 5.08 (d, *J* 11 Hz, 1 H, olefin H), 5.09 (d, *J* 16 Hz, 1H, olefin H), 5.64–5.85 (m, 1H, olefin H), 6.74–7.18 (m, 4H, aryl H), 8.36 (bs, 1 H, OH).

1-Undecyn-4-ol and 1,2-undecadien-4-ol (82 / 18 mixture). IR (neat): 3380, 3325, 2970, 2945, 2880, 2870, 2125, 1956, 1468, 1458, 1380, 1124, 1052, 1020, 992, 844 cm^{-1}; ^1H NMR ($CDCl_3$): 0.89 (t, *J* 6 Hz, 3H, Me), 1.15–1.69 (m, 12H, CH_2), 2.06 (t, *J* 2 Hz, 0.8 H, acetylene H), 2.30 (bs, 1H, OH), 2.33–2.47 (m, 1.6 H, CH_2), 3.70–3.84 (m, 0.8 H, CH), 4.12–4.27 (m, 0.2 H, allene H), 4.82–4.92 (m, 0.4 H, allene H), 5.25 (dd, *J* 13, 6 Hz, 0.2 H, allene H).

1-Phenyl-3-butyn-1-ol. IR (neat): 3425, 3320, 3080, 3025, 2930, 2130, 1648, 1620, 1496, 1452, 1344, 1192, 1052, 756, 702 cm^{-1}; ^1H NMR ($CDCl_3$): 2.03 (t, *J* 2 Hz, 1H, acetylene H), 2.58 (dd, *J* 7, 2 Hz, 2H, CH_2), 2.96 (bs, 1H, OH), 4.81 (bt. *J* 6 Hz, 1H, CH), 7.19–7.47 (m, 5H, Ph).

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