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Cadmium-Catalyzed Olefination of Aldehydes With α-Bromoacetic Ester in The Presence of Tri-n-butylarsine

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Summary: Cadmium-catalyzed olefination of aldehydes with α -bromoacetic ester in the presence of tri-n-butylarsine is described.

The reactions of cadmium and organocadmium compounds have been studied but most research in this area has been devoted to the application of organo- cadmium reagents in organic synthesis.¹ The main synthetic use was in the preparation of ketones from acid chlorides and anhydrides², and generally has a limited scope. However, to the best of our knowledge, cadmium as a catalyst has not been reported previously. We now wish to report a cadmium-catalyzed reaction of α -bromoacetic ester with aldehydes in the presence of tri-n-butyl arsine leading to the conversion of aldehyde to alkenes. The reaction sequence is shown in Scheme 1.

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Scheme 1

A catalytic amount of cadmium powder was added into a mixture of equivalent amount of methyl bromoacetate, aldehyde and tri-n-butyl arsine under nitrogen. The mixture was stirred and heated at 100-110° for several hours (see Table 1). After the aldehyde was completely disappeared (¹H NMR or TLC monitor), the product was obtained by chromatography of the reaction mixture on silica gel in 68-89% yields exclusively in E form. The results are summarized in Table 1.

It is noteworthy that the characteristic feature of this reaction is only one step, the experimental procedure is simplified, and no base and solvent is need. The starting material and cadmium powder are commercially available. The reaction is of wide scope. The aldehyde may be aliphatic, aromatic or heterocyclic. Thus, the reaction would have its potentially for the synthesis of the α,β -unsaturated ester as well as the intermediates of some natural products.

Experimental:

All boiling and melting points were uncorrected. ¹H NMR spectra were recorded on Varian EM360-A (60 MHz) or Jeol FX-902 (90 MHz) instrument with TMS as external reference and are reported in units (J value with Hz).

General procedure: Aldehyde (2.0 mmol), tri-n-butyl arsine (2.0 mmol), cadmium powder (0.2 mmol) and methyl bromoacetate (2.0 mmol) were stirred

Compound	R	Condition		Yield ^a
		Temp.(°C)	Time(hr.)	(%)
2a	C ₆ H ₅	100	20	87
2b	p-CH ₃ C ₆ H ₄	100	20	81
2c	p-CH ₃ OC ₆ H ₄	100	22	84
2d	p-ClC ₆ H ₄	100	16	87
2e	p-FC ₆ H ₄	100	16	85
2f	p-NO ₂ C ₆ H ₄	100	10	76
2g	CH ₃ (CH ₂) ₅	110	20	68
2h	2-Furanyl	100	20	89

Table 1. Cadmium-catalyzed Oelfination of Aldehydes.

a) Isolated yields. All products were characterized by spectroscopy and all double bonds formed were exclusively in E form.

and heated under nitrogen. After the aldehyde disappeared (¹H NMR or TLC identifies), the reaction mixture was column chromatography on silica gel eluting with petroleum ether (60-90⁰)/ethyl acetate (10/1) to give the product, which is in E-isomer as judged on the basis of their ¹H NMR data.

Methyl 3-phenyl-2E-propenoate (2a)³.

87% yield; ¹NMR (TMS/CCl₄) 3.78 (s,3H), 6.35 (d, 1H , J=16Hz), 7.15-7.50 (m, 5H), 7.60 (d, 1H, J= 16Hz). M.P. 34-35°C.

Methyl 3-(4-methyl-phenyl)-2E-propenoate (2b)⁴:

- 81% yield; ¹H NMR (TMS/CCl₄): 2.30 (s, 3H), 3.65 (s, 3H), 6.17 (d, J = 16
- Hz, 1 H),7.05-7.30 (m, 4H), 7.47 (d, J =16 Hz, 1H). M.P. 56-57^oC.
- Methyl 3-(4-methoxy-phenyl)-2E-propenoate (2C)⁴;
- 84% yield; ¹H NMR (TMS /CCl₄) ppm; 3.55 (s, 3H), 3.60 (s, 3H), 6.00 (d, J = 16 Hz, 1H), 6.63 (d, 2H, J = 8Hz), 7.23 (d, J = 8Hz), 7.38 (d, J = 16 Hz, 1H). M.P. : 88-89°C.
- Methyl 3-(4-Chloro-phenyl)-2E-propenoate (2d)⁴;
- 87% Yield; ¹H NMR (TMS/CCl₄) ppm; 3.65 (s, 3H), 6.20 (d, J = 16 Hz, 1H),
- 7.18-7.57 (m, 4H), 7.57 (d, J = 16 Hz, 1H). M.P.; 73-75°C.
- Methyl 3-(4-fluoro-phenyl)-2E-propenoate (2e)⁵;

85% Yield; ¹H NMR (TMS/CCl₄); 3.68 (s,3H), 6.23 (d, J = 16 Hz, 1H), 6.83-7.65 (m, 5H). M.P.; 58-59°C.

Methyl 3-(4- nitro-phenyl)-2E-propenoate (2f)⁴;

76% yield; ¹H NMR (TMS/CCl₄) ppm; 3.78 (s, 3H), 6.50 (d, J = 16 Hz), 7.65 (d, J = 8 Hz, 2H), 7.70 (d, J = 16 Hz), 8.22 (d, J = 8 Hz, 2H). M.P., 160-161°C.

Methyl 2E-nonenoate $(2g)^6$:

68% yield; ¹H NMR (TMS/CCl₄): 0.90-1.50 (m, 11H), 1.97-2.35(m, 2H),

3.65 (s,3H), 5.65 (d, J = 16 Hz), 6.80 (dt, J = 16 Hz, 7.0 Hz, 1H).

Methyl 3-(2-furanyl)-2E-propenoate (2h)⁷:

89% yield; ¹H NMR (TMS/CCl₄) : 3.50(s, 3H), 6.03(d, J = 16 Hz, 1H), 6.15-6.37 (m, 2H), 7.17 (d, J = 16 Hz), 7.23 (brs, 1H). M.P.: 25-26°C.

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