

SHORT
COMMUNICATIONS

Iodoalkoxylation, Iodohydroxylation, and Iodoacetoxylation of Alkenes Catalyzed by $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$

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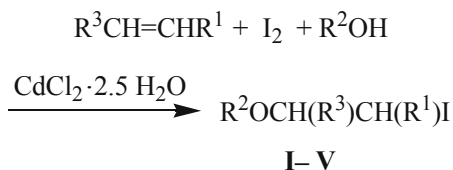
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Reactions of alkenes with iodine in alcohol, water, or carboxylic acid in the presence of catalysts $\{\text{Cu}(\text{OAc})_2$ [1], $\text{Ce}(\text{SO}_3\text{CF}_3)_4$ [2], ZnCl_2 [3], or iodosobenzene dichloride [4] $\}$ provide a convenient procedure for preparation of iodoethers, iodohydrins, and iodoacetates.

Cadmium chloride is applied as catalyst in a wide range of organic reactions [5]. However no published information exists on its use in reactions of iodoalkoxylation, iodohydroxylation, and iodoacetoxylation.

We established that the reaction of alkenes with propargyl alcohol, water, or acetic acid and crystalline iodine catalyzed by $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ was a convenient preparation procedure for propargyl β -iodoethers [6, 7], iodohydrine [2, 8], and iodoacetate [1, 2, 9] obtained in 75–85% yield.

1-Propargyloxy-2-iodocyclohexane (I). Into a stirred



$\text{R}^1, \text{R}^3 = (\text{CH}_2)_4$ (**I, IV, V**); $\text{R}^1 = \text{H}, \text{R}^3 = \text{Ph}$ (**II**), Bu (**III**), $\text{R}^2 = \text{CH}_2\text{C}\equiv\text{CH}$ (**I–III**), H (**IV**), Ac (**V**).

mixture of 14 g (0.25 mol) of propargyl alcohol and 20.5 g (0.25 mol) of cyclohexene cooled to 5–10°C was added 22 g (0.12 mol) of $\text{CdCl}_2 \cdot 2.5 \text{H}_2\text{O}$, then was added by portions of 1 g 63 g (0.25 mol) of finely dispersed crystal-line iodine. The reaction mixture was stirred at room temperature for 3 h, filtered, the filtrate was diluted with 5% solution of NaHCO_3 , treated with 10% $\text{Na}_2\text{S}_2\text{O}_3$

solution, and extracted with ether. Ether was removed, the residue was distilled in a vacuum. Yield 52.7 g (80%), bp 114–115°C (1 mm Hg), d_4^{20} 1.5218, n_D^{20} 1.5503 {yield 62%, bp 115°C (1 mm Hg), d_4^{20} 1.5215, n_D^{20} 1.5500 [6]}. ^1H NMR spectrum (CDCl_3), δ , ppm: 1.2–2.2 m [8H, $(\text{CH}_2)_4$, ring protons], 2.5 t (1H, $\equiv\text{CH}$), 3.60 m (1H, CHO), 4.20 m (1H, ICH), 4.25 d (2H, $\text{OCH}_2\text{C}\equiv\text{C}$). Found, %: C 40.49; H 4.58; I 48.52. $\text{C}_9\text{H}_{13}\text{IO}$. Calculated, %: C 40.91; H 4.96; I 48.07.

6-Iodo-5-phenyl-4-oxa-1-hexyne (II) was similarly obtained from propargyl alcohol, styrene, and iodine. Yield 60.7 g (85%), bp 93–94°C (1 mm Hg), d_4^{20} 1.5812, n_D^{20} 1.5902 {yield 73%, bp 93°C (1 mm Hg), d_4^{20} 1.5816, n_D^{20} 1.5900 [7]}. ^1H NMR spectrum (CDCl_3), δ , ppm: 2.5 t (1H, $\equiv\text{CH}$), 3.8 d (2H, OCH_2), 3.38 d (2H, ICH₂), 4.21 d (2H, $\text{OCH}_2\text{C}\equiv\text{C}$), 4.25 m (1H, CHI), 7.30 m (5H, C_6H_5). Found, %: C 46.12; H 3.60; I 44.12. $\text{C}_{11}\text{H}_{11}\text{IO}$. Calculated, %: C 46.17; H 3.87; I 44.30.

5-Iodomethyl-4-oxa-1-nonyne (III) was similarly obtained from propargyl alcohol, 1-hexene, and iodine. Yield 51.8 g (78%), bp 83°C (1 mm Hg), d_4^{20} 1.4588, n_D^{20} 1.5143 {yield 53%, bp 83°C (1 mm Hg), d_4^{20} 1.4585, n_D^{20} 1.5140 [7]}. ^1H NMR spectrum (CDCl_3), δ , ppm: 2.5 t (1H, $\equiv\text{CH}$), 3.60 m (1H, CHO), 3.38 m (2H, ICH₂), 4.01 d (2H, $\text{OCH}_2\text{C}\equiv\text{C}$), 0.85–1.25 m [9H, CH_3 , $(\text{CH}_2)_3$]. Found, %: C 38.45; H 5.4; I 50.52. $\text{C}_9\text{H}_{15}\text{IO}$. Calculated, %: C 38.12; H 5.2; I 50.34.

2-Iodocyclohexanol (IV) was similarly obtained from water, cyclohexene, and iodine within 6 h. Yield 42.3 g (75%), mp 42–43°C (H_2O) (mp 42°C [2, 8]).

1-Acetoxy-2-iodocyclohexane (V) was similarly obtained from cyclohexene, acetic acid, and iodine. Yield 67 g (85%), d_4^{20} 1.6115 (d_4^{20} 1.61 [2]). ^1H NMR spectrum (CDCl_3), δ , ppm: 1.2–2.3 m [8H, $(\text{CH}_2)_4$, ring protons], 2.3 s (3H), 4.25 m (1H, CHI), 3.60 m (1H, CHO). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 170.3, 71.3, 67.4, 38.3, 32.0, 27.4, 23.9, 21.6. Found, %: C 35.4; H 4.75; I 47.00. $\text{C}_8\text{H}_{13}\text{IO}_2$. Calculated, %: C 35.8; H 4.88; I 47.15.

NMR spectra were registered on a spectrometer Bruker DRX 300 M [300 (^1H), 75 (^{13}C) MHz].

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