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Indium-mediated Reaction of 1,3-Dichloro- and 1,3-Dibromopropenes with Carbonyl Compounds. Generation of Novel 3,3-Diindiopropene

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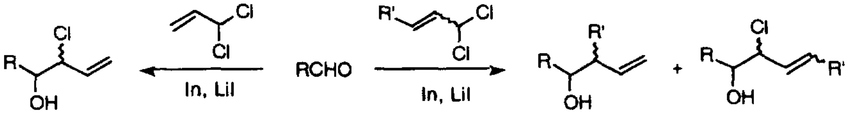
Abstract: Indium-mediated reaction of 1,3-dichloropropene with aldehyde gave *syn*-chlorohydrin predominantly. A similar reaction of 1,3-dibromopropene gave vinyloxirane and homoallyl alcohol; the former is formed from γ-bromoallylindium via the corresponding bromohydrin, and the latter is considered to be derived from a unique allylic diindium reagent, 3,3-diindiopropene.

INTRODUCTION

Recently, there has been increasing interest in the use of organoindium reagents in selective organic synthesis.[1] Our previous paper reported[2] that the indium-mediated reaction of 3,3-dichloropropene with carbonyl compounds gives the corresponding chlorohydrins, whereas 1-substituted 3,3-dichloropropenes give homoallyl alcohols exclusively or predominantly (Scheme 1). In the latter reaction, an allylic diindium species was postulated as the intermediate leading to the homoallyl alcohols. Very recently, an indium-mediated reaction of 1,3-dibromopropene with aldehydes in an aqueous medium was described,[3] and this paper prompted us to publish here our independent results on the indium-mediated reactions with 1,3-dichloro- and 1,3-dibromopropenes in organic solvents, which proceed via a different reaction pathway from that in water, consequently giving different products.



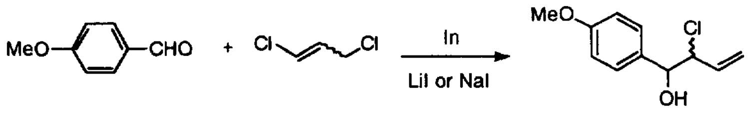
Scheme 1

RESULTS AND DISCUSSION

a. Reaction with 1,3-dichloropropene.

In the presence of lithium iodide or sodium iodide, indium was found to mediate readily the coupling of 1,3-dichloropropene with aldehyde, and chlorohydrin **1** was obtained as the sole product. Without the iodide salts, no reaction occurred. Table 1 summarizes the results with *p*-anisaldehyde in various solvents. With increasing the solvent polarity, the diastereoselectivity (*syn*/*anti* ratio) increased. The effect of reaction temperature on diastereoselectivity was examined in the reaction with benzaldehyde (Table 2), which shows that tem-

Table 1. Reaction of *p*-Anisaldehyde with 1,3-Dichloropropene in Various Solvents[a]

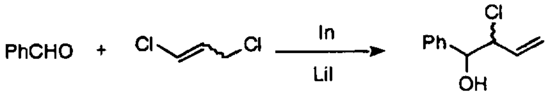


1a

Solvent	Additive	Yield/%	*syn*:*anti*
CH_2Cl_2	LiI	0	---
acetone	NaI	58	69:31
t-BuOH	LiI	56	71:29
THF	LiI	67	73:27
DMF	LiI	75	75:25
THF/H_2O (3:1)	LiI	93	81:19
MeOH	LiI	58	82:18
MeOH/H_2O (1:1)	LiI	45	90:10
H_2O[b]	LiI	26	80:20

[a] All reactions carried out with *p*-anisaldehyde (1 mmol), 1,3-dichloropropene (2 mmol), lithium (or sodium) iodide (2 mmol), and indium (1 mmol) at room temperature for 3 h. [b] Reaction time 15 h.

Table 2. Reaction of Benzaldehyde with 1,3-Dichloropropene[a]

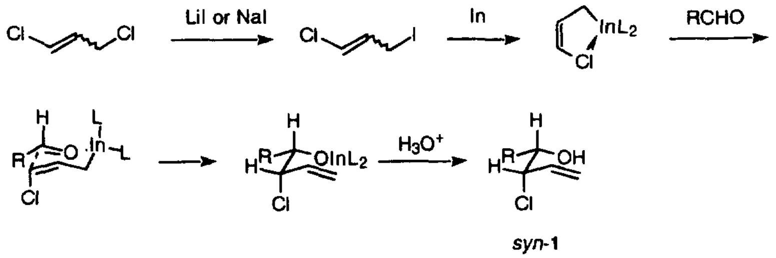


1b

Solvent	Temp./°C	Yield/%	*syn*:*anti*
THF	0	88	79:21
THF	-78	59	81:19
MeOH	0	31	85:15
MeOH	-78	47	86:14
DMF	0	52	84:16
DMF	-60 to -30	83	92: 8

[a] All reactions carried out with benzaldehyde (1 mmol), 1,3-dichloropropene (2 mmol), lithium iodide (2 mmol), and indium (1 mmol) for 2 h.

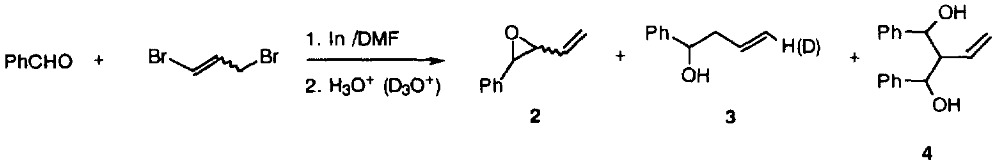
perature did not affect significantly the diastereoselectivity. It is noted that, in contrast to the above reactions, the reactions of γ-alkyl substituted allylindium reagents, such as cinnamyl- and crotylindium reagents, with carbonyl compounds give *anti*-adducts predominantly.[4] The *syn*-selectivity observed in the present reaction may be explained by the fact that the intermediate γ-chloroallylindium reagent has a *Z*-configuration with an intramolecular chelation of the chlorine atom to the indium. Although the starting 1,3-dichloropropene was an *E*/*Z*-mixture (*E*/*Z*=68/32), *E*/*Z*-isomerization is possible during the oxidative addition of indium.[4] A chair-like cyclic transition state in which the chlorine atom adopts an axial-position furnishes the *syn*-adduct **1** (Scheme 2).



Scheme 2

b. Reaction with 1,3-dibromopropene.

The indium-mediated reaction of 1,3-dibromopropene with benzaldehyde was examined in DMF (Scheme 3). When the reaction was conducted in a Barbier-type manner (1,3-dibromopropene, benzaldehyde, and indium all mixed together at the same time), the products were vinyloxirane **2** (56% yield) and homoallyl alcohol **3** (12%). Recently, the same reaction in water was reported and *gem*-bisallylation adduct **4** was obtained as the major product.[3] However, the formation of compound **4** was only modest (< 5%) in our reaction in DMF. A similar reaction with excess indium in a Grignard-type manner (preformation of the organoindium reagent from 1,3-dibromopropene and indium followed by the addition of benzaldehyde) gave an increased proportion of **3** (**2**: 19%, **3**: 41% yield), though prolonging the reaction time of 1,3-dibromopropene with indium did not change the ratio **2** : **3**. When the reaction was quenched with DCl/D_2O, (*E*)-**3**-*d* (74% *d*) was obtained, whereas no deuterium was incorporated in **2**. These results suggest that two different organoindium compounds are formed from 1,3-dibromopropene and indium: one is a monoindium compound which leads to **2** and the other is a diindium compound leading to **3**.



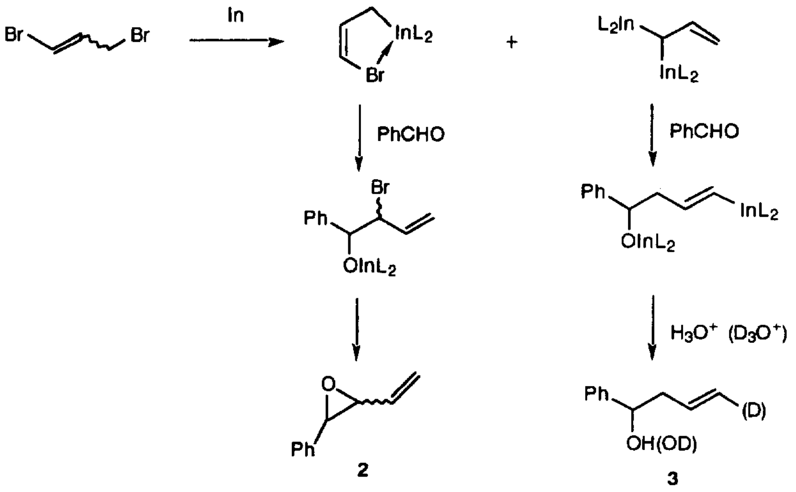
Scheme 3

Based on these observations, a plausible reaction scheme is illustrated in Scheme 4. The vinyloxirane **2** obtained in this reaction was *cis* rich (*cis*:*trans*=86:14), indicating again the bromine-chelation of the intermediate allylic monoindium species. If the allylic diindium compound couples with the aldehyde at the γ-carbon as is the case with simple allylic indium reagents,[4,5] the predominant structure may be 3,3-diindiopropene as depicted in Scheme 4. Such an allylic *gem*-diindium reagent is a rare example of the little studied organodiindium compounds.[6]

TYPICAL EXPERIMENTAL PROCEDURES

a. Reaction of 1,3-dichloropropene with p*-anisaldehyde.*

p-Anisaldehyde (0.12 cm^3, 1.0 mmol), 1,3-dichloropropene (0.23 cm^3, 2.0 mmol), indium powder (0.11 g, 1.0 mmol), and lithium iodide (0.27 g, 2.0 mmol) were stirred in DMF (3.0 cm^3) at room temper-



Scheme 4

ature for 3 h. Usual workup and column chromatography on silica gel (CH_2Cl_2) gave 2-chloro-1-(4-methoxyphenyl)-3-buten-1-ol (75% yield).

b. Reaction of 1,3-dibromopropene with benzaldehyde.

Barbier-type reaction: Benzaldehyde (0.35 cm^3, 3.4 mmol), 1,3-dibromopropene (0.10 cm^3, 1.0 mmol), and indium powder (0.12 g, 1.0 mmol) were stirred in DMF (2 cm^3) at 0 °C for 3 h. After being quenched with aqueous sodium hydroxide (1 N, 2 cm^3), the products were extracted with ether. Column chromatographic separation gave **2** (*cis*:*trans*=86:14, 56% yield), **3** (12%), and **4** (5%).

Grignard-type reaction: 1,3-Dibromopropene (0.10 cm^3, 1.0 mmol) and indium powder (0.58 g, 5.0 mmol) were stirred in DMF (2 cm^3) at 0 °C for 1 h. To the resulting organoindium reagent was added benzaldehyde (0.35 cm^3, 3.4 mmol), and the mixture was further stirred at 0 °C for 3 h. Column chromatography gave **2** (*cis*:*trans*=83:17, 19% yield) and **3** (41%). Compound **4** was not found in this reaction. A prolonged reaction time (3 h) of 1,3-dibromopropene with indium did not change the ratio **2** : **3**.

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