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REACTIONS OF TRIETHYLINDIUM WITH HALOMETHANES: PREPARATIONS AND PROPERTIES OF DIETHYLINDIUM HALIDES

TAKAYOSHI MAEDA, HISASHI TADA, KIYOSHI YASUDA* AND ROKURO OKAWARA
Department of Applied Chemistry, Osaka University Yamadakami, Suita, Osaka (Japan)

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SUMMARY

Triethylindium, Et_3In, reacted with CH_2X_2 (X=I and Br) and CCl_4 (or $CHCl_3$) to give the corresponding diethylindium halide, Et_2InX (X=I, Br and Cl). These reactions are explained as proceeding through a carbenoid intermediate (Et_2InCH_2X) (I) (X=I and Br) and (Et_2InCCl_3) (II), respectively. Methylene from (I) was added to cyclohexene to give norcarane, whereas dichloromethylene from (II) was preferentially inserted into the In–C bond to give 2-pentene.

Et_2InX (X=I, Br and Cl) were found to have a dimeric structure with a non-linear C–In–C skeleton. Et_2InF was prepared from Et_3In and Et_3SnF and polymeric structure with linear C–In–C units is suggested for it.

INTRODUCTION

It has been known that some organometallic compounds react with polyhalomethanes[1] in various types of reactions. For instance, reactions of Et_3Al with halomethanes involve Friedel–Crafts[2], radical[3], reductive[4] and carbenoid[2] reactions.

The chemistry of organoindium compounds has not been extensively studied. In the course of our studies, we have briefly reported[5] the reactions of Et_3In with haloforms to give corresponding Et_2InX (X=Cl and Br). This paper reports the results of studies in which Et_3In was allowed to react with CH_2I_2, CH_2Br_2 and CCl_4 (or $CHCl_3$). The structures of Et_2InX including Et_2InF prepared from Et_3In and Et_3SnF, are also discussed.

EXPERIMENTAL

Triethylindium was prepared by the Grignard method[6], and was confirmed to be ether-free** by means of its PMR spectrum. All chemicals and solvents were obtained commercially, dried by standard methods, and nitrogen was bubbled through them just before use. All of the following reactions and physical measurements were carried out under an atmosphere of dry nitrogen.

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* Present address: Takeda Chemical Institute, Higashiyodogawa, Osaka, Japan.

** Presence of ether retards the reaction of Et_3In and CH_2Br_2.

Physical measurements

The IR spectra were obtained using a Hitachi EPI-2G and a Hitachi EPI-L spectrophotometer, both equipped with gratings. Molecular weights were determined ebulliometrically in an atmosphere of nitrogen. The PMR spectra were recorded on a Japan Electron Optics JNM-3H-60 spectrometer. GLC analyses were carried out using, for gaseous components, a 1 m column packed with 60–80 mesh activated charcoal, and for the other compounds, a 2 m column packed with 25 wt.% dinonyl phthalate on 40–60 mesh celite 545 or 5 wt.% silicone DC 550 on 80–100 mesh celite 545.

TABLE 1

THE REACTION OF TRIETHYLINDIUM WITH HALOMETHANES

Reagents g (mmole)				Solvent (ml)	Reaction time (days)	Conversion[a] of halomethane (%)	Products (% yield)[b]		
Halomethane		Et_3In	Cyclohexene				Norcarane[a] or 2-pentene[a]	EtX[c]	Et_2InX
CH_2I_2	4.72 (17.6)	3.51 (17.3)	3.2 (40)	n-Hexane (20)	1	100	Norcarane (22)	EtI (87)	Et_2InI (72)
CH_2Br_2	5.00 (28.7)	4.62 (22.9)	3.6 (40)		7	60	Norcarane (14)	EtBr (15)	Et_2InBr (62)
CH_2Cl_2	1.72 (20.2)	3.54 (17.5)	3.5 (43)		7	0[d]			
$CHCl_3$	1.40 (11.7)	7.30 (36.2)		Cyclohexane (25)	3	90	2-Pentene (11)	EtH (18)	Et_2InCl (63)
CCl_4	1.06 (6.88)	4.11 (20.3)	[e]	Cyclohexane (25)	3	100	2-Pentene (13)	EtCl [f]	Et_2InCl (94)

[a] By PMR spectrum. [b] On the basis of the Et_3In. [c] By GLC. [d] No reaction occurred even when the molar ratio CH_2Cl_2/Et_3In was 20/1. [e] The products were same when cyclohexene was present. [f] Not determined (see experimental section).

TABLE 2

PROPERTIES OF Et_2InX

X in Et_2InX	M.p. (°C) (reported)	Analysis found (calcd.) (%)			Mol. wt. in benzene		ν(In–C) (cm^{-1}), solid[a] (solution)[b]	
		C	H	In	Found (calcd.)	At wt.%	Asym.	Sym.
F	258–260	25.28 (25.03)	5.41 (5.25)	60.08 (59.82)	[c]		518 [c]	461 (vw) [c]
Cl	204–206 (202–205)[d]	23.51 (23.05)	4.84 (4.84)	55.92 (55.10)	477 (209)	2.00	515 (515)	460 (460)
Br	169–171 (168–170)[d]	19.21 (19.00)	3.99 (3.97)	46.30 (45.41)	466 (253)	1.75	510 (512)	456 (460)
I	171–173	16.31 (16.06)	3.28 (3.36)	38.68 (38.29)	654 (300)	1.46	506 (506)	455 (454)

[a] In Nujol mulls. [b] In dichloromethane solution at 1.5–2.0 wt.%. [c] Not determined because of limited solubility. [d] Ref. 5.

Reactions of triethylindium with halomethanes

The reaction conditions and the yields of the products are shown in Table 1, and the properties of the diethylindium halides obtained, are listed in Table 2. These reactions were carried out at room temperature. However, when the reaction was vigorous, Et_3In, diluted in an appropriate solvent, was mixed at 0° with the halomethane in the same solvent. The total amount of the solvent is also shown in Table 1.

(*i*). *With* CH_2X_2 ($X=I$, *Br and Cl*). Triethylindium in n-hexane was added dropwise to an ice-cooled mixture of an equivalent amount of CH_2I_2 and excess of cyclohexene in n-hexane with vigorous stirring. A white precipitate was formed. After the addition was completed, the mixture was allowed to warm up to room temperature and stirring was continued for one day. The precipitate was filtered and washed twice with n-hexane to give diethylindium iodide. This compound is soluble in tetrahydrofuran, and slightly soluble in dichloromethane and benzene. Ethyl iodide and norcarane in the filtrate were determined by GLC and PMR spectroscopy, respectively, adding a known amount of CH_2Cl_2 as an internal standard.

Triethylindium was dissolved in mixtures of cyclohexene and CH_2Cl_2 at room temperature, and PMR analysis showed that after standing for seven days there were no detectable changes in the mixtures even when a large excess of CH_2Cl_2 was employed.

(*ii*). *With* $CHCl_3$ *and* CCl_4. Triethylindium and $CHCl_3$ were mixed at room temperature in cyclohexane and the mixture was kept standing for 3 days. During this procedure, evolution of a gas and formation of a precipitate were observed. The gas was confirmed to be ethane containing a negligible amount of ethylene by GLC. The white precipitate was washed with n-hexane to give diethylindium chloride. The filtrate was found to contain 2-pentene and unreacted $CHCl_3$ by GLC. The amounts of these compounds were determined by PMR (Std.; benzene) spectra. 2-Pentene was also identified as its dibromide by GLC and PMR spectrum.

Triethylindium and CCl_4 in cyclohexene were mixed at 0°, and the mixture was allowed to react at room temperature for 3 days with stirring. The volatiles were removed by trap-to-trap distillation under vacuum. The residue was washed three times with n-hexane to give diethylindium chloride. The volatiles were found to contain ethyl chloride and 2-pentene by GLC and PMR (Std.; CH_2Br_2) analyses. The amount of ethyl chloride was not quantitatively determined, because a part of it escaped from the system during the above procedure.

The reaction in the presence of cyclohexene (CCl_4/Et_3In/cyclohexene; 2/1/10 molar ratio) was carried out as shown above. However, no 7,7-dichloronorcarane was detected; 2-pentene was present.

Methanolysis of the reaction mixture at low temperatures

Et_3In (3.11 g, 15.5 mmole) and CH_2I_2 (1.5 ml, 18.6 mmole) were mixed at −20° in 25 ml of ether. After 10 min, 8 ml of methanol was added and the mixture was warmed to room temperature. The volatiles were removed by trap-to-trap distillation under vacuum, and confirmed to contain ethyl iodide and methyl iodide which were converted to the corresponding ammonium iodide derivatives by adding triethylamine. The amount of methyltriethylammonium iodide (3 mmole, 20%) was determined by PMR spectroscopy.

The methanolysis (8 ml, CH_3OH) of the mixture of Et_3In (3.99 g, 19.7 mmole) and CCl_4 (4.1 g, 26.6 mmole) at −20°, was carried out as above. 2-Pentene, ethyl chloride, or $CHCl_3$, could not be detected in the trapped volatiles by GLC. From a similar reaction carried out at 5°, small amounts of 2-pentene and ethyl chloride were detected, but no $CHCl_3$.

Preparation of diethylindium fluoride from triethylindium and triethyltin fluoride

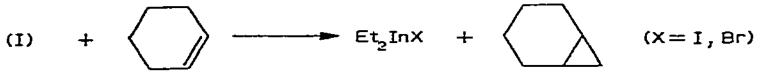
Et_3In (6 g; 30 mmole) was added to triethyltin fluoride[7] (6 g; 25 mmole) in 150 ml of tetrahydrofuran. The mixture was stirred for one day at room temperature. The volatiles were removed in vacuo and found to contain tetraethyltin by GLC. The residue was recrystallized from tetrahydrofuran to give fine needles of diethylindium fluoride (3.5 g; 73%), insoluble in dichloromethane and benzene, and slightly soluble in tetrahydrofuran.

RESULTS AND DISCUSSION

Reactions of triethylindium with halomethanes

The reaction of Et_3In with dihalomethanes (CH_2X_2: X = I and Br) in cyclohexene at room temperature gave norcarane and the corresponding ethyl halide and diethylindium halide. These results suggest that the cyclopropanation of the olefin proceeds through the carbenoid intermediate (I)*.

$$Et_3In + CH_2X_2 \longrightarrow \underset{(I)}{(Et_2InCH_2X)} + EtX$$



Existence of (I) was confirmed by methanolysis at −20° of the reaction mixture of Et_3In and CH_2I_2 to give an appreciable amount of methyl iodide.

$$(Et_2InCH_2I) + CH_3OH \rightarrow (Et_2InOCH_3) + CH_3I$$

On the basis of the reaction conditions shown in Table 1, it may be concluded that the apparent reactivity of the dihalomethanes towards Et_3In increases in the order; $CH_2Cl_2 < CH_2Br_2 < CH_2I_2$. This shows that the removal of one halogen atom from CH_2X_2 as positive halogen is more difficult when X is chlorine, which is in accord with the results found[1,11] in the reaction of tetrahalomethanes with n-BuLi (or MeLi).

As summarized in Table 1, the reaction** of Et_3In with CCl_4 (or $CHCl_3$) in a 3/1 molar ratio gave 2-pentene, ethyl chloride (or ethane) and diethylindium chloride. The formation of these products may be explained by assuming a carbenoid intermediate (II), which can react further with Et_3In, following a reaction scheme similar

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* $(ICH_2)_3In$, obtained by the reaction of CH_2N_2 and InI_3, was found to react with cyclohexene to give norcarane (1–2% yield)[8]. Various carbenoids of this type have been isolated. *e.g.* $(ICH_2)_2Zn \cdot ZnI_2$[9] and Et_2AlCH_2I[10].

** These reactions differ from the reductive reaction of Et_3Al with $CHCl_3(CCl_4)$ to give Et_2AlCl, $CH_2{=}CH_2$ and CH_2Cl_2 ($CHCl_3$)[4]. Et_3In has been reported to be a less reductive reagent than Et_3Al[12].

to that proposed for the reaction of halomethanes with n-BuLi[13], n-$C_6H_{13}MgBr$[14] and i-Bu_3Al[15].

$$\begin{aligned}
CCl_4(CHCl_3)+Et_3In &\rightarrow \underset{(II)}{(Et_2In{-}CCl_3)}+EtCl(EtH)\\
(II)+Et_3In &\rightarrow \underset{(III)}{(Et_2In{-}CCl_2{-}Et)}+Et_2InCl\\
(III)+Et_3In &\rightarrow \underset{(IV)}{(Et_2In{-}CClEt{-}Et)}+Et_2InCl\\
(IV) &\rightarrow CH_3CH_2CH{=}CHCH_3+Et_2InCl
\end{aligned}$$

$$\overline{}$$

$$CCl_4(CHCl_3)+3\ Et_3In \rightarrow CH_3CH_2CH{=}CHCH_3+EtCl(EtH)+3\ Et_2InCl$$

This scheme is also supported by the fact that the reaction with CCl_4 in which the conversion is complete, gave a 94% yield of diethylindium chloride.

The failure to obtain $CHCl_3$ by methanolysis of the reaction mixture of Et_3In and CCl_4 (described in the experimental section) indicates that intermediate (II) is formed with more difficulty than is (I) and, if formed, that it reacts immediately with Et_3In to give 2-pentene, before reacting with methanol. The fact that the reaction of Et_3In with CCl_4 in the presence of cyclohexene gave 2-pentene but no norcarane derivative may imply that such carbenoids as (II) interact preferentially* with the more anionic carbon atom attached to In (insertion**) than with that of cyclohexene (addition). These cases point out the remarkable difference between the natures of (I) and (II).

Properties of diethylindium halides, Et_2InX ($X=F$, Cl, Br and I)

Diethylindium chloride, bromide and iodide were obtained in good yield by the reactions of Et_3In with CCl_4, $CHCl_3$ [5], $CHBr_3$ [5], CH_2Br_2 and CH_2I_2.

These three diethylindium halides (Cl, Br and I) are dimeric in benzene solution (Table 2). In their IR spectra, both the In–C asymmetric and symmetric stretching bands were found; however, the band expected*** for In–Cl stretching was not observed down to 250 cm^{-1}. For these three compounds, therefore, halogen-bridged dimers with non-linear Et_2In moieties are the most probable structures, as reported[19] for dimethylindium halides.

The IR spectrum of the fluoride shows a strong band due to the In–C asymmetric stretching and that of a very weak In–C symmetric stretching. It has much higher m.p. than other three halides and it is sparingly soluble in dichloromethane and benzene. These results suggest that it may have a polymeric structure with

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* It has been reported[16] that dichlorocarbene is a more discriminating species than unsubstituted carbenes.

** A possible mechanism could not be excluded, which involves nucleophilic attack by CCl_2 at Et_3In as suggested in the case of the reactions of organoboranes with CCl_2 [17].

*** It has been reported[18] that for the hexacoordinated monomer, $InCl_3Py_3$, in the solid state, In–Cl stretching bands are found at 302 and 273 cm^{-1}.

approximately linear C–In–C moieties*, similar to that of diorganothallium halides, such as $(CH_3)_2TlCl$, which has linear C–Tl–C units[21].

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* It has been reported[20] that in water the dimethylindium cation has a linear C–In–C skeleton.