Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

STUDIES OF ORGANOINDIUM COMPOUNDS
REACTIONS OF TRIETHYLINDIUM WITH THIOBENZOPHENONE, BENZOPHENONE, BENZALDEHYDE, PHENYLISOCYANATE AND BENZONITRILE

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(Received October 15th, 1968)

SUMMARY

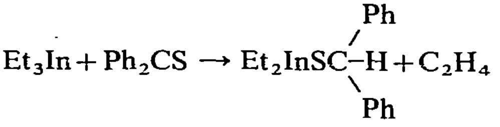
Triethylindium reacted with thiobenzophenone, benzophenone, benzaldehyde, phenyl isocyanate and benzonitrile, forming colored complexes at low temperature. With elevation of temperature, these complexes, except that of benzonitrile (V), rearranged, giving hydrogen migration products (I) and (II) and ethyl group migration products (III) and (IV) exclusively. These diethylindium compounds were isolated and identified and a possible explanation for these selective rearrangements is discussed on the basis of the steric hindrance about the carbon atom of the functional group of the organic reagents.

The fairly thermally stable benzonitrile complex was forced to partially decompose at more elevated temperatures, giving ethyl group migration and a small amount of hydrogen migration products and the trimer of benzonitrile.

INTRODUCTION

Previous studies of the reactions of triethylindium have been limited to those with compounds having active hydrogens[1], dimethyltin sulfide[2], halomethyl compounds[2] and dithiocyanogen[3].

We have already reported that the reaction of triethylindium with thiobenzophenone gives diethylindium benzhydrylmercaptide and ethylene almost quantitatively[4].



$$Et_3In + Ph_2CS \longrightarrow Et_2InSC(Ph)_2H + C_2H_4$$

This report describes the reaction of triethylindium with some reagents having polar multiple bonds: thiobenzophenone, benzophenone, benzaldehyde, phenyl isocyanate and benzonitrile.

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EXPERIMENTAL

Reagents and general comments

Triethylindium was prepared by the Grignard method[1] and confirmed to be ether-free by its PMR spectrum. Thiobenzophenone was prepared from benzophenone and hydrogen sulfide. Commercial benzophenone was used without purification. The other organic reagents were obtained commercially and purified by distillation over sodium wire or P_2O_5, and nitrogen was bubbled just before use. All the following reactions and physical measurements were carried out under an atmosphere of dry nitrogen.

TABLE 1

PMR DATA AND COLOR OF THE TRIETHYLINDIUM COMPLEXES

A mixture of 5 mole % of triethylindium and 5 mole % of the reagent in CH_2Cl_2, at -40 to $-50°$; chemical shifts are given in ppm upfield from CH_2Cl_2.

Reagent	$\delta_1{}^c$	$\delta_2{}^c$	$\Delta = (\delta_2 - \delta_1)$	Color
[a]	3.99	4.73	0.74	
[b]	4.00	4.75	0.75	
PhCHO	4.01	4.80	0.79	Orange
Ph_2CO	4.01	4.83	0.82	Wine red
PhNCO	3.99	4.83	0.84	Pale yellow
PhCN	4.00	4.88	0.88	Yellow
Ph_2CS	4.03	4.92	0.89	Red

[a] 5 Mole % of Et_3In. [b] 10 Mole % of Et_3In. [c] Chemical shift of methyl protons (δ_1) and methylene protons (δ_2) of ethyl groups attached to indium.

TABLE 2

THE REACTIONS OF TRIETHYLINDIUM

Reactants	(g)	(mMole)	Solvent (ml)	Reaction conditions	Reaction products	Yield (%)
Et_3In	5.15	25.95	20	15°	C_2H_4	70
Ph_2CS	5.25	25.95	80	2–3 min	$(Et_2InSCHPh_2)_2$ (I)	78
			(n-hexane)			
Et_3In	3.78	18.7	20	98°	C_2H_4	96
Ph_2CO	3.41	18.7	40	28 h	$(Et_2InOCHPh_2)_2$ (II)	79
			(n-heptane)			
Et_3In	3.78	18.7	20	69°	$(Et_2InOCHPhEt)_2$(III)	99[a]
PhCHO	1.99	18.7	20	3 h		
			(n-hexane)			
Et_3In	7.76	38.4	20	48°	$(Et_2InNPhCOEt)_2$(IV)	6
PhNCO	4.58	38.4	60	6 h		89[b]
			(petroleum ether)			
Et_3In	2.52	12.4	20	111°	$Et_3In \cdot NCPh$ (V)	89
PhCN	1.42	13.6	20	30 h		
			(toluene)			

[a] By PMR spectrum. [b] Yield of hydrolysis product.

TABLE 3

CHEMICAL AND PHYSICAL DATA FOR REACTION PRODUCTS

No.	M.p.	Analyses			Mol.wt.		PMR data[a]		
	(°C)		Found	Calcd.	Found	Calcd.	τ (ppm)	Rel.int.	Multipl.[b]
(I)	130–131	C	55.29	54.85	729	372	2.85	10	m
		H	5.49	5.69	738		4.60	1	s
		In	37.21	37.29			8.95	6	t
		S	8.53	8.61			9.45	4	q
(II)	146–148	C	57.02	57.33	1068	356	2.79	10	m
		H	5.95	5.94			4.20	1	s
		In	32.24	32.24			8.91	6	t
							9.62	4	q
(III)	44.5[c]	C	49.71	50.67	675	308	2.71	5	s
		H	6.79	6.87			5.39	1	t
		In	37.18	37.26			8.29	2	q
							8.81	6	t
							9.4	7	c
(IV)	50–52	In	36.31	35.75	783	321	2.90	5	m
							7.82	2	q
							8.5–9.4	13	c
(V)	[d]	In	37.71	37.63	280	305	2.40	5	s
							8.59	9	t
							9.42	6	q

[a] Measured in CCl_4 except the compound (V) in CH_2Cl_2, using TMS as an internal standard. [b] Multiplicity: m, multiplet; s, singlet; t, triplet; q, quartet; c, complex. [c] B.p. 171–172°(10^{-3} mm): [d] B.p. 72° (10^{-3} mm).

A mixture of triethylindium and the reagents shown in Table 1 in non-polar organic solvents at low temperature took on a characteristic color. The color disappeared, in general, with elevation of temperature, and in some cases evolution of gas and the formation of a precipitate were observed. The reaction conditions to complete the decomposition of these complexes and the yields of products are summarised in Table 2. The properties of the organoindium compounds obtained are shown in Table 3.

Reaction of triethylindium with thiobenzophenone[4] *and benzophenone*

The solution of benzophenone and triethylindium in n-heptane evolved ethylene upon heating at 98°. Subsequent removal of n-heptane yielded crystals which upon repeated recrystallizations from a mixture of dichloromethane and petroleum ether gave diethylindium benzhydryloxide (II). The m.p. of this compound was depressed to 104–110° after being exposed to air for an hour. In the hydrolysis product of the reaction mixture in several runs, we could identify only diphenylcarbinol by its PMR spectrum, but not diphenylethylcarbinol.

Reaction of triethylindium with benzaldehyde

In this reaction there was no gas evolution. After the solvent was removed, the residual viscous liquid was distilled in high vacuum to give colorless hygroscopic crystals of diethylindium 1-phenyl-n-propoxide (III). The hydrolysis of the product gave only phenylethylcarbinol, which was identified as its derivative, 1-phenyl-n-propyl *N*-(1-naphthyl)carbamate (m.p. 100–101° ; lit.[5] 102°).

Reaction of triethylindium with phenyl isocyanate

The reaction, which proceeded without gas evolution, gave a small amount of colorless, unknown crystals. The filtrate was evaporated and the residue was recrystallized from n-hexane twice to give very hygroscopic crystals of *N*-(diethylindium)-*N*-phenylpropionamide (IV). In one run hydrolysis of the filtrate gave propionanilide (m.p. 107–108° ; lit.[6] 105°). IR spectrum of (IV) in nujol mull showed a strong band due to C=O stretching at 1667 cm^{-1}*. This suggests that diethylindium group is attached to the nitrogen and the migrated ethyl group is attached to the carbon of the isocyanate group.

Reaction of triethylindium with benzonitrile

An adduct of triethylindium benzonitrile (V) was obtained by mixing the two reagents. Even after prolonged heating in the conditions shown in Table 2, this adduct did not decompose and was recovered almost quantitatively with a small amount of metallic indium. IR spectrum of (V) in liquid film showed a band due to C≡N stretching at 2252 cm^{-1}.

Thermal decomposition of triethylindium–benzonitrile adduct

The adduct (V) (8.05 g, 26.4 mmole), heated at 125–137° for 37 h, gave about 200 ml (8.35 mmole) of gas (ethylene/ethane, 79/21), which was identified and measured by GLC (2 m column packed with activated charcoal), 0.009 g (0.08 mmole) of metallic indium and a dark reddish-brown reaction mixture. From this mixture, crystals of 2,4,6-triphenyltriazine (2.73 g, yield, 10%**) were obtained which were recrystallized from toluene, m.p. 229°, lit.[8] 231°. (Found: C, 81.53; H, 4.89; N, 13.58%. $C_{21}H_{15}N_3$ calcd.: C, 81.97; H, 4.81; N, 13.14%.)

The filtrate was distilled in vacuum to give 3.52 g (11.5 mmole) of the unreacted adduct (V) and a non-volatile, reddish-brown tar. The IR spectrum of the tar showed a strong band at 1660 cm^{-1}, suggesting the presence of the C=N bond. Hydrolysis of the tar with 0.1 *N* hydrochloric acid gave 1.58 mmole (6%**) of propiophenone and 0.45 mmole (2%**) of benzaldehyde, which were confirmed by GLC (1 m column packed with 25 wt % dinonyl phthalate on a 40–60 mesh celite 545) by adding a known amount of benzonitrile as an internal standard. Propiophenone was also identified as its derivative, 2,4-dinitrophenylhydrazone (m.p. 190°; lit.[5] 191°). Thus the presence in the tar of the ethyl migration product, $Et_2InNCPhEt$, and the hydrogen migration product, $Et_2InNCPhH$, can be assumed.

Thermal decomposition of triethylindium in an excess of benzonitrile

A yellow mixture of triethylindium (0.40 g, 2.30 mmole) and benzonitrile

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* In the case of $Me_2Al{-}O{-}C(Me){=}N{-}Ph$, a band due to C=N group appeared at 1575 cm^{-1} (ref. 7).

** Percentage calculated on the amount of adduct used.

(1.43 g, 12.0 mmole) was heated for 22 h at 140° to give a gray reddish-brown solution. The needles which appeared on standing at room temperature, were recrystallized from toluene to yield 0.50 g of 2,4,6-triphenyltriazine (*ca.* 211 % calculated on the amount of triethylindium used).

Physical measurements

Molecular weights in benzene solution were determined cryoscopically or by using a Mechrolab vapor pressure osmometer model 302 under nitrogen. The IR spectra in liquid films were obtained using a Hitachi EPI-2G spectrophotometer equipped with gratings. The PMR spectra were recorded on a Japan Electron Optics JNM-3H-60 spectrometer 60 MHz at various temperatures using TMS as an internal standard.

RESULTS AND DISCUSSION

The characteristic colors, which appeared in the first stage of every reaction, may be due to complex formation analogous to yellow complexes between benzophenone and aluminum alkyls[9]. The increment of the internal shift of the ethyl proton magnetic resonance of the mixture in comparison with that of free triethylindium at low temperature, as shown in Table 1, seems to support this assumption, for similar shifts have been reported for triethylaluminum[10] and triethylgallium[11].

These complexes except (V) rearranged at elevated temperatures in organic solvents as shown in Table 2. It is remarkable that we could isolate exclusively hydrogen migration products (I) and (II), or ethyl group migration products (III) and (IV) almost quantitatively, for in the reactions of triethylaluminum with benzophenone[9] and benzaldehyde[12], the simultaneous presence of both types of products* has been reported.

In general, based on the ratio of both types of products, the mechanism of the reactions of triethylaluminum with organic reagents has been discussed with relation to the steric hindrance of the reagents, dimeric nature of triethylaluminum[13] and an ability of decomposition of triethylaluminum to diethylaluminum hydride and ethylene[14]. We have not enough knowledge of triethylindium or its complexes in the organic solvents used for our reactions. However, considering the monomeric nature of triethylindium in benzene[1] and the difficulty of spontaneous decomposition of it to diethylindium hydride and ethylene under these conditions, it is straightforwardly concluded that the controlling factor of our reactions may be the steric hindrance about the carbon atom in the functional group of the organic reagents.

The triethylindium–benzonitrile complex (V) is remarkable in its thermal stability in comparison with the analogous complex of triethylgallium[15] and the other complexes which were studied in this report. However, the complex (V) can be forced to partially decompose at more elevated temperatures to give ethylene (6 %), 2,4,6-triphenyltriazine (10 %) and non-volatile reddish-brown tar. Since ethyl group migration and a small amount of hydrogen migration primary products appear to be present in the tarry reaction product, as shown in the experimental section, we can

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* In these cases, the presence of both types of compounds containing aluminum have been assumed through their hydrolysis products.

assume concurrent occurrence of an additional decomposition reaction of triethylindium to ethylene and diethylindium hydride at higher temperature as in the case of triethylaluminum–benzonitrile complex[14].

The trimerisation of benzonitrile to triazine seems to be catalysed by triethylindium, for more than two moles of benzonitrile were consumed per mole of triethylindium. Analogous catalytic reactions have been found for some other organometallic compounds of Groups I[16], II[16,17] and III[15,18].

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