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PREPARATION OF DIETHYLINDIUM THIOBENZOATE AND ITS NOVEL REACTIONS ON HYDROLYSIS AND PYROLYSIS

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SUMMARY

The preparation of diethylindium thiobenzoate (I) is reported. This compound is a monomer in benzene and its structure is suggested to be a thiol type with carbonyl chelation.

Hydrolysis of (I) under either acidic or basic conditions gives both thiobenzoic acid and benzoic acid. Pyrolysis of (I) gives ethane, monoethylindium sulfide and 1,1-dibenzoylethane (II). This novel reaction has not been reported for other organometallic systems and a possible explanation is discussed.

INTRODUCTION

During our studies of the reactions of triethylindium with various unsaturated polar compounds[1-3], we have treated ethylindium derivatives containing In–O, In–N, or In–S bonds, and found that ethylindium compounds with an In–S bond such as ethylindium sulfide[4,5], diethylindium benzhydrylmercaptide[1] are fairly stable toward hydrolysis. We were interested in this finding and tried to synthesize diethylindium thiobenzoate which is expected to be fairly stable. Organometallic thiocarboxylates of the Group IIIB elements have not been reported, whereas those of the Group IVB[6,7] and VB[8] elements are known to be either thione or thiol type depending on the nature of the element.

We report here on the preparation of diethylindium thiobenzoate (I) and its structure as deduced from IR spectra and its novel reactivity on hydrolysis and pyrolysis.

EXPERIMENTAL

The general preparative methods for organoindium compounds and the preparation of triethylindium have been described[2]. Thiobenzoic acid, propiophenone and n-octane were of reagent-grade and were purified by distillation. The NMR (TMS as an internal standard) and IR spectral measurements were made using the same instruments described in the previous report[2]. Mass spectra were recorded on a Hitachi RMU-6 spectrometer using an ionization voltage of 70eV. Gas analysis was performed by GLC (2m column packed with activated charcoal).

Preparation of diethylindium thiobenzoate (I).

When thiobenzoic acid (6.21 g) in ether (40 ml) was added to triethylindium (9.1 g) in ether (40 ml), ethane was evolved. The solution was heated under reflux for 30 min, and the ether was removed under reduced pressure to give a white precipitate, which was recrystallized from n-hexane/ether to give (I) (7.52 g), m.p. 106–107°; NMR (in CCl_4): τ, 2.3 (multiplet, aromatic protons), 8.8 (multiplet, ethyl protons), the relative intensity 5/10; IR (in nujol), 1520 (sh) and 1464 s (br)* [ν(C=O)], 331 m [ν(In–S)]; (in 5 wt% of cyclohexane), 1547 (sh) and 1472 s (br)** [ν(C=O)], 347 m cm^{-1} [ν(In–S)]. [Found: C, 42.60; H, 4.91; In, 37.61; mol.wt., 374, 398 (cryoscopically in benzene under nitrogen at concentrations 1.78 and 4.00 wt%, respectively). $C_{11}H_{15}OSIn$ calcd.: C, 42.60; H, 4.87; In, 37.02%; mol.wt., 310.]

Hydrolysis of (I) at room temperature.

A representative example is as follows. Sulfuric acid (ca. 1 *N*) was added to 0.485 g of (I) in ether (30 ml) with stirring. Ethane was evolved and the ether layer became yellow. In the product, presence of 0.075 (30%) of benzoic acid and 0.079 g (37%) of thiobenzoic acid was estimated***. Similarly, from a hydrolysis of (I) in potassium hydroxide (ca. 1 *N*), the presence of 0.143 g (36%) of benzoic acid and 0.184 g (41%) of thiobenzoic acid was estimated.

Pyrolysis of (I) in n-octane and in propiophenone.

When a mixture as shown in Table 1 was allowed to react under stirring, ethane was slowly evolved and a white precipitate was formed. The precipitate was identified

TABLE 1

PYROLYSIS OF DIETHYLINDIUM THIOBENZOATE (I) AT 120° IN n-OCTANE OR PROPIOPHENONE FOR 15 H

Run	(I) (g)	Solvent (ml)	Products[a]				
			EtInS (g) [(%)]	(II) (g) [(%)]	EtH (%)	Thiobenzoic[b] acid (g) [(%)]	Benzoic[b] acid (g) [(%)]
1	1.228	n-Octane (35)	0.193 (28)	0.109 (12)	60	0.145 (27)	0.108 (22)
2	2.221	Propiophenone (40)	1.033 (81)	1.410 (82)	109	0.040 (2)	0.051 (6)

[a] Yield in % was calculated on the basis of (I) used. [b] Derived from the unreacted (I) (see hydrolysis section).

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* In hexachlorobutadiene.

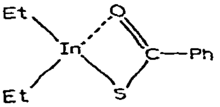
** In 5 wt% of carbon tetrachloride.

*** The estimation of the product was carried out as follows. The ether layer and the ether extracts of the separated aqueous layer were combined and oxidized over aqueous hydrogen peroxide (3%). The ether layer was neutralized by aqueous sodium bicarbonate and dried over anhydrous sodium sulfate. Upon evaporating the ether, dibenzoyl disulfide was obtained. The neutralized aqueous layer was acidified with sulfuric acid (ca. 1 *N*) and extracted with ether. The ether was dried and evaporated to give benzoic acid. For a reference experiment, thiobenzoic acid was oxidized under the same conditions. It was found that thiobenzoic acid changed into a small amount of benzoic acid (yield 15%) and dibenzoyl disulfide (yield 82%).

as ethylindium sulfide by its IR spectrum[5]. After removing the solvent from the filtrate under reduced pressure, the residue was dissolved in ether and hydrolysed with aqueous sulfuric acid (ca. 1 *N*). The organic layer was washed with water, then with aqueous sodium bicarbonate (10%). From the combined aqueous layer, the amounts of benzoic acid and thiobenzoic acid were estimated as described above. Evaporation of ether from the organic layer gave a pale yellow solid, which was recrystallized from ether–petroleum ether giving 1,1-dibenzoylethane (II), m.p. 82–83°. A mixture melting point with an authentic sample prepared by the method of Hauser[9] showed no depression. The IR spectrum of (II) was identical with that of the authentic sample [ν(C=O) was found at 1687 and 1664 cm^{-1} in KBr disc]. NMR (in CCl_4): τ, 2.15 (multiplet, aromatic protons), 2.65 (multiplet, aromatic protons), 4.94 (quartet, methine proton), 8.49 [doublet (*J* 7.0 Hz), methyl protons], the relative intensity 4/6/1/3; Mass spectrum *m/e* 238 (M^+, $C_{16}H_{14}O_2$). [Found: C, 80.85; H, 5.89; mol.wt., 228 and 230 (in benzene by a vapor pressure osmometer at concentrations 0.271 and 0.418 wt%, respectively). $C_{16}H_{14}O_2$ calcd.: C, 80.65; H, 5.92%; mol.wt., 238.]

DISCUSSION

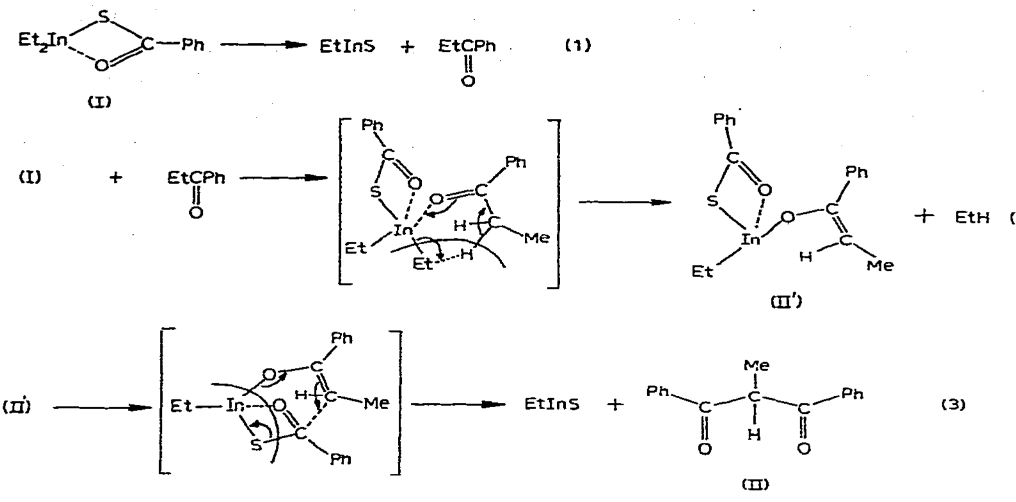
The assignments of the relevant IR bands of diethylindium thiobenzoate listed in experimental part are made in a straightforward manner comparing those of the diethylindium halides[10], monoethylindium sulfide[5] and some metal thiocarboxylates[8,11]. Since (I) is a monomer in non-polar solvents, the following structure is proposed. However, in the solid state small shifts of the frequencies for both ν(In–S) and ν(C=O) were observed.


(I)

Diethylindium thiobenzoate is one of the rare examples of monomeric diorganoindium compounds containing bidentate ligands[12,13] and this property may be ascribed to the sulfur atom having the proper size and a deformable valency angle[14].

While most metal thiobenzolates give only thiobenzoic acid on hydrolysis[15-17], (I) gave thiobenzoic acid and a considerable amount of benzoic acid both under acidic and basic conditions. This result may be attributed to the fact that chelation of the carbonyl group induces a high electrophilicity on the benzoyl carbon of (I) hence it is reactive under basic conditions. On the other hand, because of possible π-interaction between the indium and sulfur atoms[12], the sulfur may have a lower nucleophilicity than that of the chelating oxygen atom which is more readily attacked under acidic conditions.

As shown in Table 1, pyrolysis of diethylindium thiobenzoate in n-octane (run 1) gave ethane, monoethylindium sulfide and the unexpected 1,1-dibenzoylethane (II). A plausible scheme is shown in Scheme 1. Although propiophenone was not obtained in run 1, its formation as an intermediate [eqn. (1)] and its participation to form (II) [eqns. (2)–(3)] are supported by the fact that the yields of the three products increased and the amount of unreacted (I), decreased remarkably when (I) was pyrolysed in propiophenone (run 2). These reactions [eqns. (2)–(3)] may be associated with the



SCHEME 1

tendency for one In–C bond of diethylindium compounds to be cleaved easily[5,18], to the stability of the In–S bond and to the insolubility of monoethylindium sulfide.

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