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

ORGANOINDIUM DERIVATIVES
I. REACTIONS OF SOME ORGANOINDIUM COMPOUNDS WITH SULPHUR DIOXIDE

A. T. T. HSIEH
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Great Britain)

(Received September 16th, 1970; in revised form October 16th, 1970)

SUMMARY

The preparations of the polymeric $(RSO_2)_3In$ (R = Me, Et, Ph or p-MeC_6H_4), dimeric $(MeSO_2InMe_2)_2$ and monomeric $PhSO_2InPh_2$ are reported and the reaction of liquid sulphur dioxide with some dimethylindium(III) alkoxides, phenoxide and pentafluorophenoxide is described. The possible structures of the complexes are discussed in relation to their vibrational, NMR and mass spectra.

INTRODUCTION

Recently, considerable interest[1,2] has been focussed on the nature of the bonding of metal sulphinates, which, as a result of severe lack of structural information, still remains a subject of much speculation. Sulphinates of main group metals have, in general, been prepared either by sulphur dioxide insertion into metal–carbon bonds, or from the reaction of a metal halide with sodium arenesulphinates. Sulphur dioxide insertion reactions have been extensively investigated in systems such as Zn[3], Hg[3-7], Al[8-10], Ga[10,11], Tl[12], Sn[13-16] and Pb[17-19], whereas the metathetical reaction has only been used very recently in the preparation of sulphinates of Zn[20], Cd[20], Hg[20,21], Tl[22] and Sn[23].

In contrast, only one previous report described the formation of $(PhSO_2InMe_2)_2$ from the reaction of trimethylindium with benzenesulphinic acid[24]. As part of a continued study of the reactions of organoindium compounds, we have prepared some sulphinato complexes of indium by sulphur dioxide insertion into the indium–carbon bonds and others by the reaction of indium(III) chloride with sodium arenesulphinates. We have also investigated the reaction of sulphur dioxide with some organoindium compounds containing indium–oxygen bonds. A preliminary account has already been published[25]. Since the completion of this work, one appeared[10] describing the preparation and vibrational and mass spectra of the complex $(MeSO_2InMe_2)_2$ which we have similarly prepared.

RESULTS AND DISCUSSION

Reaction of sulphur dioxide with trimethylindium

Trimethylindium reacts smoothly with liquid sulphur dioxide from −45° to room temperature during 1 h to give a white air-stable solid, analysed as $Me_3In(SO_2)_3$. It is insoluble in most common organic solvents and hence its molecular weight could not be determined. It is also passive towards hydrolysis but is decomposed by hydrochloric acid to give indium(III) chloride and methanesulphinic acid.

Its vibrational spectra can be readily interpreted by comparison with the known spectra of trimethylindium[26] and tris(methanesulphinato)aluminium[10]. As expected, $\nu_s(InC_3)$ (467 cm^{-1} in the Raman spectrum) and $\nu_{as}(InC_3)$ (500 and 495 cm^{-1} in the IR and Raman spectrum respectively) modes in trimethylindium are absent in the vibrational spectra of this complex. Its IR spectrum shows two intense absorptions at 997 and 967 cm^{-1}. For the latter, a corresponding peak at 974 cm^{-1} in the Raman spectrum is also observed. Hence these bands, which lie within the range of sulphur–oxygen stretching frequencies of *O*- or *O,O'*-sulphinates[25], may accordingly be assigned as chiefly the asymmetric and symmetric stretching modes.

While a higher value (>1.100) of the $\nu_{as}(SO_2)/\nu_s(SO_2)$ ratio has been observed for *S*-sulphinates[21], it is sometimes possible to distinguigh an *O*-sulphinate from an *O,O'*-sulphinate on the basis of both the peak positions and the $\nu_{as}(SO_2)/\nu_s(SO_2)$ ratio, which is usually much smaller for the bidentate *O,O'*-sulphinate. However, it is not possible to distinguish, on these grounds, the intermolecular from the intramolecular structure. In this case, the presence of *O,O'*-sulphinato groups is indicated by a low $\nu_{as}(SO_2)/\nu_s(SO_2)$ ratio (1.031).

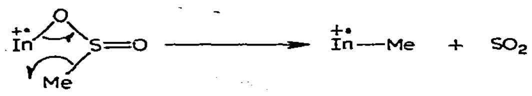
The proton NMR spectrum of tris(methanesulphinato)indium in pyridine, in which it is only slightly soluble, shows two singlets (τ 7.40 and 7.74) of intensity ratio 1/2. They may be attributed to the methyl protons on the intermolecular and intramolecular *O,O'*-sulphinato groups or *vice versa*.

These observations, together with the low solubility and low volatility of the compound, suggest a polymeric structure involving intermolecular *O,O'*-sulphinato groups, analogous to that in the aluminium complexes $(RSO_2)_3Al$ ($R = Me^{10}$ or Et^{8-10}). This is consistent with its mass spectrum (taken at a source temperature of 180°) which exhibits, in addition to the molecular ion $Me_3(SO_2)_3In^+$ (*m/e* 352), peaks attributable to $Me_4(SO_2)_4In^+$ (*m/e* 431), $Me_n(SO_2)_3In^+$ ($n=2$ or 4), $Me_n(SO_2)_2In^+$ ($n=0$, 1 or 2), $Me_n(SO_2)In^+$ ($n=0$, 1–3), $InSO^+$ (*m/e* 163) and Me_nIn^+ ($n=0$, 1–3), although no ions containing two indium atoms are observed. Among others, the following could be an important process in the fragmentation leading to some otherwise unexpected ions such as $Me_3(SO_2)In^+$ and Me_3In^+:

$$Me_4(SO_2)_4In^+ \xrightarrow{-SO_2} Me_4(SO_2)_3In^+ \xrightarrow{-Me} \underset{(M^+)}{Me_3(SO_2)_3In^+}$$

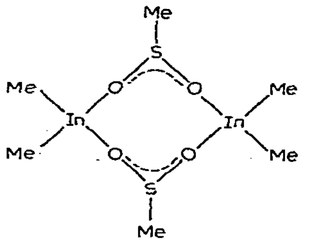
$$\xrightarrow{-SO_2} Me_3(SO_2)In^+ \xrightarrow{-SO_2} Me_3In^+$$

The formation of these unexpected ions by loss of sulphur dioxide molecules prior to the loss of methyl groups could be the result of a rearrangement involving a four-membered cyclic transition state:



It is essential to emphasize that the loss of methyl groups or sulphur dioxide molecules need not be stepwise.

Under carefully controlled conditions, trimethylindium reacts with only one mole of sulphur dioxide at −50° to give the moisture-sensitive Me_3InSO_2. Its identity was established by analysis and by its mass spectrum which shows, in addition to the molecular ion, dimeric species of the type $Me_n(SO_2)_2In_2^+$ ($n=1$–5) and $Me_n(SO_2)In_2^+$ ($n=1$, 3 or 5). Its solid state IR spectrum shows strong absorptions at 1028 and 1001, and at 975 (sh) and 950 cm^{-1} which may be attributed to the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ modes respectively. Again, a low $\nu_{as}(SO_2)/\nu_s(SO_2)$ ratio (~1.03) clearly indicates an *O,O'*-sulphinate structure (I). Since the sulphur–oxygen stretching frequencies in dichloromethane solution [1027 and 1003 and 976 (sh) and 952 cm^{-1}] have not shifted significantly from those in the solid state, it is reasonable to assume that the dimeric structure is retained in solution. Weidlein[10] has very recently prepared this compound from the reaction of a 1/1 molar ratio of trimethylindium and sulphur dioxide at −50° and has described its vibrational and mass spectra which are in general agreement with ours. Its proton NMR spectrum exhibits two singlets of intensity ratio 1/2 at τ 7.93 and 10.03 which may be assigned to the CH_3–S and CH_3–In protons respectively. This evidence lends further support to the stoicheiometry of the complex and its probable structure in solution.



(I)

Reaction of sulphur dioxide with triethylindium

Triethylindium reacts rapidly with an excess of sulphur dioxide at low temperature to give a white powder of $Et_3In(SO_2)_3$. The monosulphinate, Et_3InSO_2, could not be isolated even at −78° or using a deficiency of sulphur dioxide.

The vibrational spectra of the complex are compared with the known spectra of triethylindium[27] and tris(ethanesulphinato)aluminium[10]. The intense absorptions at 1005 and 968 cm^{-1} in the IR spectrum and correspondingly at 1001 and 968 cm^{-1} in the Raman spectrum may be assigned as chiefly the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ modes respectively. The presence of *O,O'*-sulphinato groups is indicated by a low $\nu_{as}(SO_2)/\nu_s(SO_2)$ ratio of 1.038.

It is insoluble in most common organic solvents and too involatile for mass spectral studies. Thus, its molecular weight could not be determined. The proton NMR spectrum in a saturated pyridine solution is complex but may be roughly described as two closely overlapping sets of triplets (at ca. τ 9.0) and quartets (at ca. τ 7.5) with an approximate intensity ratio of 3/2. By analogy with tris(methanesulphinato)indium, this complex may well possess a polymeric structure with intermolecular and intramolecular *O,O'*-sulphinato groups.

Reaction of sulphur dioxide with triphenylindium

At low temperatures, triphenylindium reacts with sulphur dioxide to give the unstable Ph_3InSO_2, which loses sulphur dioxide slowly *in vacuo* and more rapidly when heated. From the residue of the thermal decomposition, triphenylindium may be recovered in fair yield. The white air-sensitive monosulphinate is soluble in common organic solvents with rapid dissociation of the sulphur dioxide molecule.

Its IR spectrum in the solid state and in solution is compared with that of triphenylindium. In the solid state spectrum of the complex, absorptions at 1053, 854 and 586 cm^{-1} which are absent in that of triphenylindium, may be unambiguously assigned as chiefly the $\nu_{as}(SO_2)$, $\nu_s(SO_2)$ and $\delta(SO_2)$ modes. This is consistent with an *O*-sulphinate structure [*cf.* the corresponding frequencies of the *O*-sulphinate isomer of phenyl(benzenesulphinato)mercury[5]] and presumably monomeric. Other major peaks in the spectrum are mainly due to vibrations of the phenyl groups which may be readily identified and assigned by comparison with that of triphenylindium, phenyl(benzenesulphinato)mercury[5] and chlorobenzene[28] using the nomenclature of Whiffen[28].

Other indium(III) arenesulphinates

Since prolonged reaction of triphenylindium with sulphur dioxide at room temperature leads to extensive decomposition with the deposition of metallic indium, tris(benzenesulphinato)indium is therefore prepared from the reaction of indium(III) chloride with sodium benzenesulphinate in aqueous or alcoholic solution:

$$InCl_3 + 3\ PhSO_2Na \longrightarrow (PhSO_2)_3In + 3\ NaCl$$

The *p*-toluenesulphinate, $(p\text{-}MeC_6H_4SO_2)_3In$, was similarly prepared. These white solids are air-stable and sparingly soluble in and unaffected by water. In this respect, they are similar to tris(ethanesulphinato)aluminium[8-10] or -indium, but contrary to other sulphinates such as tris(benzenesulphinato)thallium[29] and bis(benzenesulphinato)tin[23,29] which are rapidly hydrolysed by moisture.

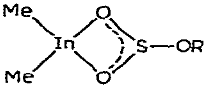
The IR spectrum of tris(benzenesulphinato)indium may be readily interpreted by comparison with that of sodium benzenesulphinate dihydrate[5,21], triphenylindium and bis(benzenesulphinato)mercury[21]. The indium–carbon stretching modes are, as expected, absent. In the sulphur–oxygen stretching region, the two strong absorptions at 963 and 930 cm^{-1} are ascribed as mainly the asymmetric and symmetric modes respectively. The positions of the bands and a low $\nu_{as}(SO_2)/\nu_s(SO_2)$ ratio (1.035) again suggest an *O,O'*-sulphinate structure. The low solubility and involatility of this complex prevent further investigations of such physical properties as its molecular weight in solution and its mass spectrum.

The properties of the *p*-toluenesulphinate is entirely analogous. Strong IR absorptions at 969, 930 and 591 cm^{-1} are respectively attributed to the $\nu_{as}(SO_2)$, $\nu_s(SO_2)$ and $\delta(SO_2)$ vibrations and an *O,O'*-sulphinate structure is indicated by the $\nu_{as}(SO_2)/\nu_s(SO_2)$ ratio of 1.042.

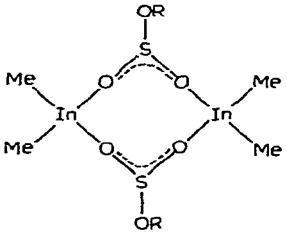
Reaction of sulphur dioxide with some indium–oxygen bonded compounds

Dimethylindium(III) alkoxides react readily with liquid sulphur dioxide at room temperature to give the white moisture-sensitive complexes RSO_3InMe_2 (R = Me or Et). The presence of two hydrolysable methyl groups implies that the insertion of sulphur dioxide is not between indium and a methyl group. Further evidence is furnished by the IR spectra in which strong absorptions assignable to the $\nu_{as}(InC_2)$ and $\nu_s(InC_2)$ modes are present in the expected region (550–460 cm^{-1}). Other major absorptions in the spectra can be assigned by comparison with those of dimethylindium(III) complexes[30] and dimethyl(ethanesulphonato)thallium[12].

Although the molecular ion, $EtSO_3InMe_2{}^+$, is not observed in its mass spectrum (taken at a source temperature of 100°), multiplets attributable to the monomeric ions $Me_2(SO_3)In^+$ (m/e 225), $Me_n(SO_2)In^+$ (n=0–2) and Me_nIn^+ (n=0–2) are present together with dimeric species such as $Me_n(SO_3)(SO_2)In_2^+$ (n=2 or 4), $Me_n(SO_3)In_2^+$ (n=2 or 4), $Me_4(SO_2)In_2^+$ (m/e 354) and $Me_2In_2^+$ (n=1, 2 or 4). On the basis of this observation, the monomeric structure (II) may be excluded and these complexes therefore appear to have the structure (III). It is of interest to compare this with the trimeric structure of $(MeSO_3MMe_2)_3$ (M = Al or Ga)[24] and the monomeric structure of $EtSO_3TlMe_2$[12].



(II)



(III)

Dimethylindium(III) phenoxide reacts with liquid sulphur dioxide in an analogous manner to yield the white air-stable complex $PhSO_3InMe_2$. Its IR spectrum shows strong absorptions at 1247 and 1228 and at 1027 and 1001 cm^{-1} which may be respectively assigned as chiefly the $\nu_{as}(SO_3)$ and $\nu_s(SO_3)$ modes. In the mass spectrum of $PhSO_3InMe_2$, neither the molecular ion nor any dimeric species is observed and these seem to indicate a monomeric structure [(II), R = Ph], at least in the gas phase.

Dimethylindium(III) pentafluorophenoxide behaves rather differently towards sulphur dioxide. At room temperature, it takes up two moles of sulphur dioxide to form a white, air-stable and involatile solid, analysed as $C_6F_5OInMe_2{,}2SO_2$. Absence of intense absorptions in its IR spectrum in the $\nu_{as}(SO_3)$ and $\nu(InC_2)$ regions (1250–1100 and 550–460 cm^{-1} respectively) suggests that the insertion occurred at the indium–carbon bonds. Indeed, very strong bands are observed in the 1040–950 cm^{-1} region, characteristic of an *O*- or *O,O'*-sulphinate. It is evident from a comparison with the IR spectra of the compounds C_6F_5X (X = Cl, Br, I[31] or OH[32,33]) and of dimethylindium(III) derivatives[30] that other vibrations such as the ν(C–F) and $\rho(CH_3–S)$ modes and possibly some combinations and overtones also absorb in this region. Hence, no unambiguous assignments can be made.

EXPERIMENTAL

General

All manipulations were performed under nitrogen or using a conventional

Pyrex vacuum line. Reactions involving organoindium compounds were carried out in Rotaflo greaseless tap-ampoules.

The IR spectra of the complexes were measured on a Perkin–Elmer 457 grating spectrophotometer with samples prepared in KBr discs or in nujol and hexachlorobutadiene mulls between CsBr plates. Solution spectra were taken in dichloromethane in 0.5 mm balanced NaCl cells. Helium–neon excited laser Raman spectra were registered on a Coderg PH-1 spectrometer using solid samples sealed in evacuated capillary tubes. Mass spectra were recorded on an A.E.I. MS9 spectrometer with an ionising energy of 70 eV, an ionising current of 100 μA and a source pressure of 2×10^{-7} mm. NMR spectra were obtained on a Perkin–Elmer R 10 or a Varian Associate HA-100 instrument operating at 60 and 100 MHz respectively. Calibration was made by internal reference to tetramethylsilane or a solvent peak where appropriate.

Trimethylindium[34,35] and triethylindium[34] were prepared by the Grignard method and purified by trap-to-trap condensation. The purity of the samples was checked tensiometrically. Triphenylindium was prepared by the metal exchange reaction between metallic indium and diphenylmercury[36] and was recrystallised from chloroform. Its IR spectrum shows the following absorptions: 1579 w, 1478 m, 1433 s, 1200 w, 1087 m, 1070 m, 1030 m, 1003 mw, 913 w, 741 vvs, 736 vvs, 701 vvs, 680 m (sh), 618 m, 473 s (sh) and 470 vs cm^{-1}.

Dimethylindium alkoxides[37], phenoxide and pentafluorophenoxide[38] were prepared from trimethylindium and the corresponding alcohol or phenol. Laboratory reagent grade liquid sulphur dioxide (BDH) was fractionated before use.

Preparation of tris(methanesulphinato)indium

Excess sulphur dioxide was condensed (−196°) into an ampoule containing 467 mg (2.82 mmole) of trimethylindium and the mixture was allowed to warm up to room temperature from −45°. During 1 h, a white precipitate was produced leaving a colourless solution. Fractionation of this mixture gave the unreacted sulphur dioxide (8.5 mmole consumed) as the only volatile material and a fine white powder of the product in nearly quantitative yield. (Found: C, 10.53; H, 2.66; S, 27.50. $C_3H_9InO_6S_3$ calcd.: C, 10.23; H, 2.58; S, 27.31%.)

Its IR spectrum (KBr disc) shows absorptions at 2998 w, 2916 w, 1625 w, 1407 ms, 1295 m, 1160 vw, 1066 m (sh), 995 vs, 965 vs, 897 s (sh), 692 s, 673 m (sh), 546 s, 495 vw (sh), 436 w (sh) and 390 m cm^{-1}. The following absorptions are observed in its Raman spectrum: 1743 vw, 1512 w, 1410 w, 1293 s (br), 974 s (br), 819 ms, 701 vs, 686 m (sh) 550 w, 497 vs, 439 w, 422 w and 392 m cm^{-1}.

Preparation of dimethyl(methanesulphinato)indium

A mixture of trimethylindium (386 mg, 2.42 mmole) and an excess of sulphur dioxide was shaken at −50° for 1 min and the excess sulphur dioxide was quickly removed *in vacuo* while cooling to −78°. After 1 h, it was allowed to warm up to room temperature and further evacuated for 15 min, leaving a white powder of the product (Yield 90%). (Found: C, 16.44; H, 3.85; hydrolysable methyl groups, 13.4. $C_3H_9InO_2S$ calcd.: C, 16.08; H, 4.05; hydrolysable methyl groups, 13.42%.)

Further reaction of the complex with excess sulphur dioxide at room temperature gave tris(methanesulphinato)indium in good yield.

Preparation of tris(ethanesulphinato)indium

Excess sulphur dioxide reacted with triethylindium (453 mg, 2.83 mmole) during ½ h at −50° to give tris(ethanesulphinato)indium as a white solid (Yield 96%). (Found: C, 18.62; H, 3.85; S, 23.8. $C_6H_{15}InO_6S_3$ calcd.: C, 18.28; H, 3.84; S, 24.4%.)

Its IR spectrum (KBr disc) shows absorptions at 2987 m, 2977 ms, 2879 w, 2860 w (sh), 1460 ms, 1452 m, 1413 m, 1400 w (sh), 1381 m, 1370 w (sh), 1265 m, 1072 s (sh), 1056 s, 1005 vs, 968 vs, 789 ms, 683 s, 674 m (sh), 608 ms, 540 s, 478 w, 463 vw (sh), 413 s and 395 m (sh) cm^{-1}. Its Raman spectrum exhibits the following peaks: 1459 w, 1452 vw, 1375 s, 1263 m, 1073 m, 1056 ms, 1035 s, 1001 vs, 968 vs, 942 s, 790 m, 761 m, 684 m, 679 s, 605 s, 542 s, 480 m, 462 s, 415 s and 399 w cm^{-1}.

Preparation of diphenyl(benzenesulphinato)indium

Excess sulphur dioxide was condensed (−196°) into an ampoule containing 424 mg (1.22 mmole) of triphenylindium and the mixture was allowed to warm up to −45° while being agitated until all the solid had dissolved. It was then maintained at −55° for ½ h after which all the excess sulphur dioxide was pumped off at that temperature, leaving a white solid of diphenyl(benzenesulphinato)indium in 98% yield. (Found: C, 52.28; H, 3.74; S, 7.28. $C_{18}H_{15}InO_2S$ calcd.: C, 52.70; H, 3.69; S, 7.82%.)

Its IR spectrum (mull) shows the following peaks: 1579 w, 1478 m, 1433 s, 1201 w, 1087 ms, 1071 m, 1053 ms, 1030 s, 1003 m, 913 w, 854 ms, 740 vvs, 736 vvs, 700 vs, 685 m (sh), 620 m, 586 ms, 473 s (sh), and 469 vs cm^{-1}.

Preparation of tris(arenesulphinato)indium

A saturated aqueous solution of $PhSO_2Na \cdot 2H_2O$ (2.0 g, 10.0 mmole) was added to an aqueous solution of $InCl_3 \cdot 3H_2O$ (0.9 g, 3.27 mmole). The white solid precipitated was filtered, washed with water (2 x 25 ml) followed by acetone (10 ml) and dried *in vacuo* for 1 h (Yield 97%). (Found: C, 39.75; H, 2.97; S, 17.44. $C_{18}H_{15}InO_6S_3$ calcd.: C, 40.16; H, 2.81; S, 17.87%.)

Its IR spectrum (mull) shows the following peaks: 1583 vw, 1479 m, 1449 vs, 1331 w, 1250 vw (br), 1175 w (sh), 1162 w, 1089 s, 1070 m, 1025 m (sh), 1003 s, 963 vvs, 930 vs, 850 w (br), 756 vs, 702 vs, 690 vs, 618 m (sh), 599 vs, 523 w and 422 mw cm^{-1}.

Tris(*p*-toluenesulphinato)indium was similarly prepared from $p\text{-}MeC_6H_4SO_2Na,4\ H_2O$ and $InCl_3,3\ H_2O$ in aqueous or alcoholic solution. (Yield 95%). (Found: C, 43.09; H, 3.66; S, 16.42. $C_{21}H_{21}InO_6S_3$ calcd.: C, 43.46; H, 3.65; S, 16.58%.)

Reaction of sulphur dioxide with dimethylindium(III) alkoxides

Dimethylindium methoxide, $(Me_2InOMe)_3$, (448 mg, 0.85 mmole) was dissolved in liquid sulphur dioxide (4 ml) at −50° to give a clear colourless solution. The mixture was then allowed to warm up slowly to room temperature with agitation, during which a white precipitate of dimethyl(methanesulphonato)indium was produced. (Yield 87%). (Found: hydrolysable methyl groups, 12.2. $C_3H_9InO_3S$ calcd.: hydrolysable methyl groups, 12.53%.)

Its IR spectrum (mull) shows absorptions at 1418 ms (sh), 1408 ms, 1301 m, 1170 m (sh), 1146 s (sh), 1102 s (sh), 1070 s, 966 vvs (br), 723 s (sh), 702 vs, 570 m (sh), 528 s (br), 471 m, 422 w and 406 m cm^{-1}.

Dimethylindium ethoxide reacted with sulphur dioxide in an analogous way to give dimethyl(ethanesulphonato)indium in 85% yield. (Found: hydrolysable methyl groups, 11.6. $C_4H_{11}InO_3S$ calcd.: hydrolysable methyl groups, 11.84%.)

Its IR spectrum (mull) shows absorptions at 1475 s, 1460 m, 1408 mw, 1381 s, 1297 w (sh), 1292 ms, 1169 s, 1162 ms (sh), 1115 m (sh), 1094 s, 1062 s (sh), 1045 vs, 999 vvs, 887 vs, 864 s, 845 s (sh), 820 s, 724 vs (br), 560 m (sh), 532 s (br), 485 m, 465 m, 445 w, 423 m and 402 m cm^{-1}.

Reaction of sulphur dioxide with dimethylindium(III) phenoxide and pentafluorophenoxide

Excess sulphur dioxide reacted with dimethylindium phenoxide during 10 min at room temperature to give a white solid of dimethyl(benzenesulphonato)indium in 90% yield. (Found: C, 31.55; H, 3.72; S, 10.17. $C_8H_{11}InO_3S$ calcd.: C, 31.81; H, 3.67; S, 10.62%.) Its IR spectrum shows the following absorptions: 1594 s, 1489 vs, 1440 ms, 1410 mw, 1293 mw, 1247 s (sh), 1228 vs, 1170 ms, 1157 m, 1073 m, 1027 s (sh), 1001 vs, 932 s, 897 s, 853 s, 769 vs, 758 s (sh), 726 s, 697 vs, 624 w, 576 ms, 554 s, 518 m, 495 mw, 414 ms and 377 mw cm^{-1}.

Under similar conditions, dimethylindium pentafluorophenoxide reacted to give a white solid of $(MeSO_2)_2InOC_6F_5$ in 93% yield. (Found: C, 21.19; H, 1.33; S, 14.34. $C_8H_6F_5InO_5S_2$ calcd.: C, 21.08; H, 1.33; S, 14.06%.) Its IR spectrum shows the following absorptions: 1637 w, 1535 m (sh), 1511 vs, 1417 m, 1409 m (sh), 1312 m, 1302 ms, 1249 mw, 1169 m, 1154 ms, 1018 vvs (sh), 999 vvs, 968 vs (sh), 960 vs, 940 s, 845 mw (br), 742 m, 700 ms, 679 w and 632 ms cm^{-1}.

ACKNOWLEDGEMENTS

I thank Dr. M. J. Mays for his interest in this work, Dr. A. G. Lee for a helpful discussion and the British Council for an award.

REFERENCES

1 M. F. Lappert, *Advan. Organometal. Chem.*, 5 (1967) 225.
2 W. Kitching and C. W. Fong, *Organometal. Chem. Rev. A*, 5 (1970) 281.
3 N. A. D. Carey and H. C. Clark, *Can. J. Chem.*, 46 (1968) 649.
4 G. B. Deacon and P. W. Felder, *J. Amer. Chem. Soc.*, 90 (1968) 493, 6895.
5 G. B. Deacon and P. W. Felder, *Aust. J. Chem.*, 22 (1969) 549.
6 P. J. Pollick, J. P. Bibler and A. Wojcicki, *J. Organometal. Chem.*, 16 (1969) 201.
7 W. Kitching, B. Hegarty, S. Winstein and W. G. Young, *J. Organometal. Chem.*, 20 (1969) 253.
8 E. B. Baker and H. H. Sisler, *J. Amer. Chem. Soc.*, 75 (1953) 5193.
9 K. Ziegler, K. Krupp, K. Weyer and W. Larbig, *Justus Liebigs Ann. Chem.*, 629 (1960) 251.
10 J. Weidlein, *J. Organometal. Chem.*, 24 (1970) 63.
11 J. Weidlein, *Z. Anorg. Allg. Chem.*, 366 (1969) 22.
12 A. G. Lee, *Chem. Commun.*, (1968) 1614; *J. Chem. Soc. A*, (1970) 467.
13 N. A. D. Carey and H. C. Clark, *Can. J. Chem.*, 46 (1968) 643.
14 W. Kitching, C. W. Fong and A. J. Smith, *J. Amer. Chem. Soc.*, 91 (1969) 767.
15 C. W. Fong and W. Kitching, *J. Organometal. Chem.*, 22 (1970) 95, 107.
16 E. Lindner, U. Kunze, G. Ritter and A. Haag, *J. Organometal. Chem.*, 24 (1970) 119.
17 R. Gelius, *Z. Anorg. Allg. Chem.*, 349 (1966) 22.
18 F. Huber and F.-J. Padberg, *Z. Anorg. Allg. Chem.*, 351 (1967) 1.
19 C. W. Fong and W. Kitching, *J. Organometal. Chem.*, 21 (1970) 365.
20 E. Lindner and G. Vitzthum, *Angew. Chem. Int. Ed. Engl.*, 9 (1970) 160.
21 G. B. Deacon, *Aust. J. Chem.*, 20 (1967) 1367.

22 G. B. DEACON AND V. N. GARG, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 717.
23 E. LINDNER, U. KUNZE, G. VITZTHUM, G. RITTER AND A. HAAG, *J. Organometal. Chem.*, 24 (1970) 131.
24 G. E. COATES AND R. N. MUKHERJEE, *J. Chem. Soc.*, (1964) 1295.
25 A. T. T. HSIEH, *Inorg. Nucl. Chem. Lett.*, 6 (1970) 767.
26 J. R. HILL, L. A. WOODWARD AND E. A. V. EBSWORTH, *Spectrochim. Acta*, 20 (1964) 1249.
27 F. OSWALD, *Fresenius' Z. Anal. Chem.*, 197 (1963) 309.
28 D. H. WHIFFEN, *J. Chem. Soc.*, (1956) 1350.
29 A. T. T. HSIEH, unpublished results.
30 H. C. CLARK AND A. L. PICKARD, *J. Organometal. Chem.*, 8 (1967) 427.
31 D. A. LONG AND D. STEELE, *Spectrochim. Acta*, 19 (1963) 1955.
32 J. M. BIRCHALL AND R. N. HASZELDINE, *J. Chem. Soc.*, (1959) 13.
33 T. GRAMSTAD AND G. VAN BINST, *Spectrochim. Acta*, 22 (1966) 1681.
34 F. RUNGE, W. ZIMMERMANN, H. PFEIFFER AND I. PFEIFFER, *Z. Anorg. Allg. Chem.*, 267 (1951) 39.
35 E. TODT AND R. DÖTTER, *Z. Anorg. Allg. Chem.*, 321 (1963) 120.
36 H. GILMAN AND R. G. JONES, *J. Amer. Chem. Soc.*, 62 (1940) 2353.
37 G. E. COATES AND R. A. WHITCOMBE, *J. Chem. Soc.*, (1956) 3351.
38 A. T. T. HSIEH, to be published.