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Organobismuth(III) and organobismuth(V) carboxylates and their evaluation as paint driers

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A range of bismuth and organobismuth carboxylates has been prepared (e.g. $Bi(carboxylate)_3$; $PhBi(carboxylate')_2$; and $Ph_3Bi(carboxylate'')_2$ where carboxylate = octanoate, i.e. 5-ethylhexanoate; carboxylate' = acetate and monomaleate; carboxylate'' = acetate, propionate, benzoate, 5-ethylhexanoate, and 0.5 oxalate. A combination of IR (solid) and NMR (solution) studies suggests that in the case of the bismuth(V) compounds the carboxylates may be inequivalent in the crystalline forms but equivalent in solution. The compounds have been tested as driers in two paint formulations, Synolac 50W (linseed-based) and Sorbal P470 (linoleic-rich). Although initially promising results were obtained for Synolac 50W, the shelf life of the bismuth driers was poor. With Sorbal P470, bismuth driers were inferior to established formulations. However, a combination of $Bi(OOCH_7H_{15})_3$ with tris(diethyldithiocarbamato)bismuth(III) out-performed established driers.

Keywords: Organobismuth, carboxylate, paint driers

INTRODUCTION

Modern paints are complex mixtures designed to meet the increasingly stringent expectations of customers. A rapidly drying paint is appreciated, provided that the drying is even. To this end additives known as driers are present in paint formulations and often mixtures of metal soaps (metal salts of long-chain carboxylic acids) in hydrocarbon solvents such as white spirit are effective. Indeed, a mixture of calcium(II) and lead(II) soaps was extensively used, the combination being superior to each component separately. This observation suggests the posibility that an anionic complex of lead(II) could be implicated.

Lead is not an acceptable ingredient of paint, even in the relatively low concentrations involved in drier formulations. Acceptable alternatives are now in commercial use but there is interest in identifying other possibilities, particularly if the level of toxicity is low. Compounds of bismuth have low toxicity and, in a sense, $RBi(OOCR')_2$ and $R_3Bi(OOCR')_2$ may be regarded as analogues of $Pb(OOCR')_2$. Hence it was decided to examine the possibility of using various bismuth and organobismuth carboxylates in drier formulations. This paper makes a brief report of the results of these investigations.

EXPERIMENTAL

Preparation of bismuth compounds

Triphenylbismuthine was prepared by a Grignard route; phenylbismuth dimaleate[1] and phenylbismuth diacetate[2] were prepared by literature methods.

Further reactions with maleic acid
In addition to phenylbismuth dimaleate[1] the reaction of Ph_3Bi with maleic acid affords a second product of m.p. 282–284 °C which has an analysis close to that required for bis(diphenylbismuth) maleate, i.e. $(Ph_2Bi(OOCH{=}CHCOO)BiPh_2$. Found: C, 36.1; H, 1.0 %. $C_{28}H_{22}Bi_2O_4$ requires C, 35.5; H, 3.2 %. (A very low hydrogen figure was noted for all the organobismuth(III) carboxylates studied. No satisfactory explanation can be offered.)

Phenylbismuth dichloride
This was prepared *in situ* by the reactin of triphenylbismuthine (1.0 g, 2.3 mmol) in dry acetone (20 cm^3) with a solution of bismuth trichloride (1.5 g, 4.6 mmol) in dry acetone (20 cm^3). The solution was used for further synthesis following reflux under dinitrogen for 3 h.

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Table 1 Triphenylbismuth dicarboxylates synthesized by a phase-transfer catalytic method

		Analysis (%)					
		Found			Requires		
Compound	M.p. (°C)	C	H	Bi	C	H	Bi
Ph_3Bi(oxalate)	151			39.9			39.6
$Ph_3Bi(OOCCH_3)_2$	162–164	47.1	4.01	37.2	47.3	3.80	37.5
$Ph_3B_i(OOCC_2H_5)_2$	160–161	49.2	4.20	35.5	49.2	4.30	35.7
$Pa_3Bi(OOCPh)_2$	165–166	56.1	3.70	30.5	56.3	3.80	30.7
Ph_3Bi(5-ethylhexanoate)$_2$	98–99	56.0	4.20	28.5	56.2	4.10	28.8

Syntheses with phenylbismuth dichloride

The above solution of phenylbismuth dichloride was reacted with potassium acetate in acetone but no phenylbismuth diacetate was isolated.

Phenylbismuth dichloride prepared as described above was reacted with 2 molar equivalents of potassium octanoate (viz. potassium 5-ethylhexanoate). The solution was refluxed for 3 h under dinitrogen. A white precipitate was identified as potassium chloride. The filtrate was stored under dinitrogen for a period of 2 days to allow further precipitation of potassium chloride. The solution was centrifuged at 4 000 rpm for 10 min, the acetone layer was decanted and the solvent was removed by evaporation under reduced pressure. The liquid product was stored in a vacuum desiccator where it slowly converted to a waxy solid. Found: Bi, 31.5%. $PhBi(OOC.C_7H_{15})_2$ requires: Bi; 36.5%; $Bi(OOC.C_7H_{15})_3$ requires: Bi, 32.7 %.

The ^{13}C NMR spectrum confirmed the absence of an aryl group.

Triphenylbismuth dichloride

This compound was made by the following adaptation of literature methods.[3,4] A solution of triphenylbismuthine (3.0 g, 6.8 mmol) in petroleum ether (40–60 °C) (40 cm^3) was treated dropwise with a solution of sulphuryl chloride (1.0 g, 7.4 mmol) in petroleum ether (40–60 °C) (20 cm^3) under dinitrogen. The mixture was stirred at ambient temperature for 30 min. A white product was filtered, washed with cold petroleum ether (40–60) and recrystallized from benzene. Yield 87 %, m.p. 146 °C (lit.[4] 142 °C). Found: C, 40.4; H, 2.80; Bi, 39.9 %. $C_{18}H_{15}BiCl_2$ requires: C, 42.2; H, 2.94; Bi, 40.9 %.

The metathesis of Ph_3BiCl_2 with sodium carboxylate or potassium carboxylate gave very poor yields of product. A method involving phase-transfer catalysis (PTC) was therefore developed.

Triphenylbismuth oxalate

A benzene (100 cm^3) solution of triphenylbismuth dichloride (1.0 g, 2.0 mmol) and an aqueous (50 cm^3) solution of sodium oxalate (0.3 g, 4.0 mmol) were added to a conical flask and a small quantity of t-butyltriethylamonium bromide was added. The flask was stoppered and set on a Stuart flask-shaker for 48 h. The layers were separated and the aqueous layer was extracted with three aliquots of benzene (20 cm^3); the combined benzene solutions were concentrated under reduced pressure to give the crude product. The crude material was recrystallized from a benzene/petroleum ether mixture (60 : 40, v/v). This methodology was used to prepare a range of triphenylbismuth carboxylates which, together with supporting analytical data, constitute Table 1.

Physical measurements

Infrared spectra were recorded on a Perkin–Elmer FTIR 1710 spectrometer. Samples were examined as potassium bromide discs in the range 4 000–220 cm^{-1}; some data are listed in Table 2. NMR spectra: (routine ^1H and ^{13}C were obtained with a Bruker Spectrospin AC300 instrument) representative data are in Table 3. Microanalyses for carbon and hydrogen were obtained with a Carlo Erba 1106 elemental analyser. Bismuth was determined by atomic absorption on a Perkin–Elmer 360 instrument following decomposition of organic matter by treatment of a 3 : 2 mixture of concentrated sulphuric and nitric acids in a quartz tube.

Crystallography

Attempts were made to determine the crystal structures of two compounds, Ph_3Bi(oxalate) and

Table 2 ν(COO) frequencies for bismuth(III) and bismuth(V) carboxylate compounds

	ν(COO) (cm^{-1})		
Compound	ν$_{as}$(COO)	ν$_{s}$(COO)	Δν(cm^{-1})
$PhBi(OOCCH{=}CHCOOH)_2$	1585	1261	324
	1533	1297	236
$\{Ph_3Bi\}_2(OOCCH{=}CHCOO)$	1588	1395	193
	1483	1253	120
$Ph_3Bi(oxalate)$	1636	1253	319 (av.)
$Ph_3Bi(OOCCH_3)_2$	1588	1385	203
	1572	1331	241
$Ph_3Bi(OOCC_2H_5)_2$	1596	1377	230 (av.)
		1356	
$Ph_3Bi(OOCPh)_2$	1600	1351	249
	1560	1326	234
Ph_3Bi(5-ethylhexanoate)$_2$	(Overlapping complex vibrational modes)		

$Ph_3Bi(OOCC_2H_5)_2$ (Enraf–Nonius 4 circle diffractometer). The crystal of the oxalate degraded in the X-ray beam and insufficient data could be collected for a structure determination. Some information on the unit cell (monoclinic, *P*) was obtained:

$$\alpha = 90.0440(10), \quad \beta = 90.1202(3), \quad \gamma = 89.9680(7)$$

$$a = 9.2263(20), \quad b = 22.3969(5), \quad c = 17.2195(4)$$

Even after repeated recrystallization the crystals of $Ph_3Bi(OOCC_2H_5)_2$ proved to have surface imperfections which prevented structure determination.

Dry time measurements for paints

The time required for a film of paint of standard thickness to dry was determined using a Beck Koller drying time recorder which has six needles which traverse a fixed length of paint film over a predetermined time. A 12 in × 1 in (30 cm × 2.5 cm) glass slide was coated with the test paint using a 38 μm or 76 μm applicator cube, the needles were dropped onto the film and the power switched on. A track such as that shown in Fig. 1 was formed.

Interpretation of track

AB (Stage 1)

The paint is still fluid and flows back into the track created by the needle. Solvent evaporation occurs and driers begin to promote the cross linking reactions. At point B the viscosity is such that the paint no longer flows back.

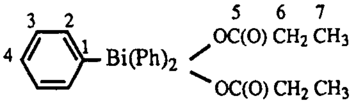
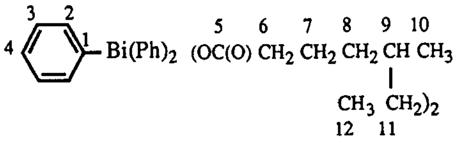
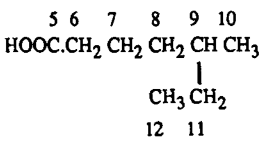
BC (Stage 2)

Evaporation of solvents is complete, primary driers are effective; the end of this stage is recognizable by the beginning of a tear in the film.

CD (Stage 3)

The surface forms a skin but the main body is still wet; the needle pulls the skin away leaving tear marks.

Table 3 Some ^{13}C NMR data[a] for $Ph_3Bi(OOCR)_2$ where $R{=}OOCCH_2CH_3$ and $OOCCH_2CH_2CH_2CH(CH_3)CH_2CH_3$

^{13}C chemical shift (w.r.t. Me_4Si)	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	C11	C12
	161.0	133.1	131.0	130.5	—	28.8	10.1					
	161.7	134.1	130.6	130.3	182.7	32.6	29.3	26.2	47.9	13.8	22.6	11.5
 $HOOC.CH_2CH_2CH_2CH(CH_2CH_3)CH_3$					183.0	31.2	29.3	24.9	46.9	13.5	22.4	11.4

[a] All data are for $CDCl_3$ solutions.

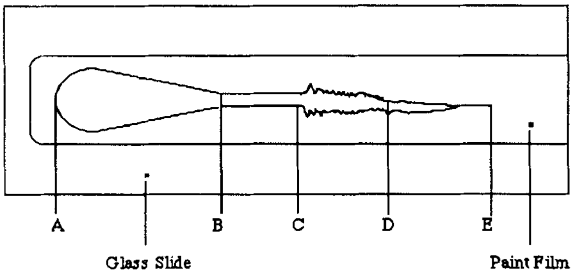


Figure 1 Schematic representation of 'dry time' measurement for paint films (see text).

DE (Stage 4)
The paint hardens and the needle tack becomes a faint line.

Evaluation of bismuth compounds as driers

Two paints were used in the evaluation, Synolac 50W and Sorbal P470. Bismuth compounds were added such that the concentrations gave 0.1 % bismuth in 100 g paint. Standard commercial driers were used for comparison, e.g. Cozirc 69 (0.06 % Co, 0.09 % Zr, 0.02 % Ca per 100 g paint) and EP9138 (0.04 % Co, 0.02 % Li, 0.133 % Ca per 100 g paint).

Synolac 50W
Synolac 50W is a linseed-oil-based paint with white spirit as solvent and contains 75% nonvolatiles. Driers were evaluated for films of 38 μm and 76 μm. Little difference in performance was noted for the 38 μm film but for the thicker film some bismuth driers were more effective: for example,

Bismuth trioctanoate (8.5 h)

< EP.9138 (13.5 h) < Cozirc 69 (18.5 h)

< Ph_3Bi(5-ethylhexanoate)

After storage (eight months) or accelerated storage (six weeks at 50 °C) the paint containing the bismuth driers showed 'loss of dry' indicating a poor shelf-life.

Sorbal P470
Sorbal P470 is a linoleic-rich paint with white spirit as solvent and contains 70 % non-volatiles. The bismuth driers were inferior to the standard driers in both the 38 μm and 76 μm films; they also experienced greater 'loss of dry' on storage than was the case for Synolac 50W. However, the addition of tris(diethyldithiocarbamato)bismuth, $Bi(dedtc)_3$, synthesized by the metathesis of bismuth trichloride and Nadedtc at a level provided by 5 cm^3 of a 0.003 g solution in 250 cm^3 of butanol/white spirit (50:50, v/v) produced a dramatic improvement in performance. Thus Bi(5-ethylhexamnoate)$_3$ had a Stage 3 drying time of 2.6 h when mixed with $Bi(dedtc)_3$, compared with 5.5 h for Cozirc 69. When Stage 4 drying times are considered, other organobismuth–$Bi(dedtc)_3$ combinations accelerated the final phase of drying; $Ph_3\,Bi(OOC.C_2H_5)_2 + Bi(dedtc)_3$ had the best time of just under 8 h (cf. Cozirc, 12.6 h); all organobismuth compounds used in combination with $Bi(dedtc)_3$ compared well with the standard drier formulations. More complete details of these evaluations are available.[5]

DISCUSSION

Organobismuth compounds

The purpose of this investigation was to evaluate organobismuth compounds as driers in paint formulations. Generally derivatives containing long alkyl chains are more compatible with paint solvents. Hence, although the literature synthesis[2] of $PhBi(OOCCH_3)_2$ was successfully repeated, the target bismuth(III) compounds contained carboxylate groups such as maleate and octanoate. The bismuth(V) compounds selected, $Ph_3Bi(OOCR)_2$, contained a more catholic choice of R groups.

Attempts to prepare compounds of the type $PhBi(OOCR)_2$ met with limited sucess. Although $PhBi(OOCCH{=}CHCOOH)_2$ was isolated[1] from the reaction of maleic acid and Ph_3Bi, a second product was also obtained: $Ph_2Bi(OOCCH{=}CHOO)BiPh_2$. When $PhBiCl_2$ (prepared *in situ*) was reacted with octanoic acid, Bi(5-ethylhexanoate)$_3$ resulted; reaction of the solution of $PhBiCl_2$ with 2,2′-bipyridyl gave $PhBiCl_2$(bipy) (found: C, 37.2; H, 2.91; Bi, 40.5; N, 5.39%; $C_{16}H_{13}BiCl_2N_2$ requires: C, 37.4; H, 2.72; Bi, 40.7; N, 5.95%) which established that the dichloride was present. Elemental analyses of the new bismuth(III) materials were poor (others have commented on such problems[2]), but routine scans of ^1H and ^{13}C NMR spectra support the proposed formulations both by identifying groups that are present (or absent) and, from integration of the ^1H NMR data, by establishing the analytical ratios of the organic groups. Full details of the spectra are available.[5] Neither of the maleate derivatives was suitable for crystallographic studies.

Structural data for $RBi(OOCR')_2$ is sparse and that for $R_2Bi(OOCR')$ not much more plentiful, although recently a crystal structure of $Ph_2Bi(O_2CCH_2NHCOPh)$ was determined showing a ψ-trigonal–bipyrimidal bismuth atom with two phenyl groups and a lone pair constituting the equatorial plane and the axial positions occupied by oxygen atoms of bridging carboxylate groups.[6] IR spectroscopy can be valuable in determining the mode of coordination of carboxylate groups.[7] In particular, the difference, $\Delta\nu$, in frequency between the antisymmetric (ν_{as}) and symmetric (ν_s) (COO) frequencies will be greater for monodentate (which are more 'ester'-like) than for symmetrically bidentate and symmetrically bridging groups (which are more 'salt'-like in symmetry terms). Unsymmetrical chelating or bridging modes will give intermediate values of $\Delta\nu$. Some relevant data are shown in Table 2, which includes related information for bismuth(V) compounds. The data for $PhBi(OOCCH{=}CHCOOH)_2$ show very clearly the presence of the —COOH group [$\nu(OH) = 3428\,cm^{-1}$; $\Delta\nu(COO) = 324\,cm^{-1}$) and of either a monodentate or, more probably, unsymmetrically bidentate bridging $—COO^-$ ($\Delta\nu = 236\,cm^{-1}$). Unfortunately these limited data do not permit further structural speculation. Deacon *et al.*[2] showed that $PhBi(OOCCH_3)_2$ changed with time in solution, but the ^1H NMR spectrum of a dimethylsulphoxide solution of phenylbismuth bis-(monomaleate) was invariant over 12 h. However, the ^{13}C spectrum did suggest that the solution species contained *two* phenyl environments.

The bismuth(V) derivatives synthesized using a phase-transfer catalyst were generally better characterized, at least in the sense that no analytical problems were encountered. Attempts to obtain X-ray structural information on two compounds were frustrated by the decomposition of Ph_3Bi(oxalate) in the X-ray beam and by persistent surface imperfections on crystals of $Ph_3Bi(OOCC_2H_5)_2$. The IR data (Table 2) give some information on the nature of the carboxylate bondng in the solids. It is interesting that there is evidence of inequivalence of the groups in $Ph_3Bi(OOCR)_2$ ($R{=}CH_3$, C_2H_5, Ph), however ^{13}C NMR data[5] indicate that, in solution, the carboxylate groups are equivalent. The IR spectra were determined as potassium bromide discs; hence bromide–carboxylate exchange reactions may provide an explanation for two sets of COO vibrations. However, disc spectra did not vary with time, nor were the observed bands characteristic of $RCOO^-$, the expected product of the ligand exchange reaction. The environment of bismuth in Ph_3Bi(furan-2-carboxylate)$_2$ is significantly distorted due to an effective coordination number of 7.[8] This illustrates the presence of some Lewis acidity which could be satisfied in the solid by weak, and possibly differential, coordination of the second oxygen of each carboxylate group. In soluton the ^{13}C NMR data are consistent with the equivalence of the three phenyl groups and show a single set of resonances from the carboxylate group, an observation consistent with a trigonal–bipyramidal structure for $Ph_3Bi(OOCR)_2$ in deuteriochloroform ($CDCl_3$) solution.

Organobismuth compounds as driers

There is little that need be added to the informatin in the Experimental section. However promising they had been in initial studies, the organobismuth compounds investigated showed a poor shelf-life. A promising exception was the combination of some triphenybismuth dibarboxylates [e.g. $Ph_3Bi(OOCC_2H_2]$ with tris(diethyldithiocarbamato)bismuth. There appears to be some synergism between the reagents which could suggest the formation of anionic complexes. If further work is carried out in this field, a sensible direction would be the development of driers in which the organobismuth compound is coupled with carboxyates of more electropositive metals.

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