A New Route to Arsonium, Stibonium, and Bismuthonium 2,2-Dimethyl-4,6-dioxo-1,3-dioxanides – The Crystal Structures of $Ph_3E\text{-}C_6H_6O_4$ (E = As, Sb, Bi) [1]

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Dedicated to Professor Heinrich Nöth on the Occasion of his 75th Birthday

Abstract. The ylides $Ph_3E\text{-}C_6H_6O_4$ [**3**; E = As (**a**), Sb (**b**), Bi (**c**)] have been prepared through the reaction of Ph_3E and 5-bromo-2,2-dimethyl-4,6-dioxo-1,3-dioxin (**4**) followed by addition of triethylamine in good yields. The crystal structures of **3** are reported.

Keywords: Arsenic; Antimony; Bismuth; Ylides; Crystal structure

Ein neuer Weg zu Arsonium- Stibonium- und Bismutonium-2,2-Dimethyl-4,6-dioxo-1,3-dioxamiden – die Kristallstrukturen von $Ph_3E\text{-}C_6H_6O_4$ (E = As, Sb, Bi) [1]

Inhaltsübersicht. Die Ylide $Ph_3E\text{-}C_6H_6O_4$ [**3**; E = As (**a**), Sb (**b**), Bi (**c**)] wurden durch Reaktion von Ph_3E und 5-Bromo-2,2-dimethyl-4,6-dioxo-1,3-dioxin (**4**) und anschließende Zugabe von Triethylamin in guter Ausbeute hergestellt. Die Kristallstrukturen von **3** werden mitgeteilt.

Introduction

There has been increasing attention for the chemistry of the heavier group 15 element ylides starting with the pioneering discovery of their cyclopentadienides **1** (E = As [2], Sb [3], Bi [4]) by *Lloyd*. In the past years, the investigation of bismuth ylides by *Barton* [5] and *Suzuki* [6, 7] opens up new routes in organic synthesis. As well known from phosphorus ylide chemistry [8], methylene fragments containing π-acceptor substituents cause an excellent stabilization thus dimedone and *Meldrum's* acid derivatives (**2**, **3**) being expected to be their most stable representatives.

Recently, we reported on a new route to *Meldrum's* acid derivatives starting from 5-bromo-2,2-dimethyl-4,6-dioxo-1,3-dioxin (**4**) and nucleophiles in the presence of bases [1]. In the following part, we describe a new synthesis for the ylides **3** and their structural characterization. **3a** [9] and **3c** [6, 10] have been prepared by other procedures formerly.

Syntheses and Structures of the Ylides $Ph_3E\text{-}C_6H_6O_4$ (3)

In general, there are two well known routes to give stabilized ylides of the heavier group 15 elements. While *Lloyd* investigated the reaction of diazomethane derivatives with triorganopnictides [2–4, 9, 11], additional reports deal with the ylide synthesis starting from CH-acidic organyls and R_3EX type compounds (X = CO_3, O, Cl_2 [5–7, 10]).

In fact, the reactions of **4** with Ph_3E (E = As, Sb, Bi) followed by addition of triethylamine give the title compounds as stable crystalline solids in good yields. On comparison with other *Meldrum's* acid derivatives, the spectroscopic data (see experimental part) are in the expected range.

To get more insight into their bonding, we have determined the crystal structures of **3** (Tables 1–5, Figures 1–3). Surprisingly, the ylides do not form isotypic crystals as a consequence both from different orientations of the Ph_3E fragments with respect to the heterocyclic ring [**3a** 179.2(3); **3b** 176.4(3); **3c** 166.1(2)°] and from the relative orientation of the phenyl rings. The ylidic E-C bond lengths are in the range of short single bonds [**3a** 1.859(2), **3b** 2.044(2), **3c** 2.139(7) Å] on comparison with the corresponding E-Ph distances. There are only minor differences in the structural parameters of the dioxin fragments (for details see table 5) including the folding angle along the axis of the endocyclic oxygen atoms [**3a** 42.6(2), **3b** 43.4(3), **3c** 41.9(4)°]. The enolate nature of the heterocyclic ring apparently causes a marked oxygen basicity which is revealed by short contacts between the pnictogen atoms and one of the exocyclic oxygen atoms [**3a** 2.926, **3b** 3.010, **3c** 3.162 Å]. Apparently, the C-O and C-C bond lengths of the dioxin fragment are not influenced by these interactions.

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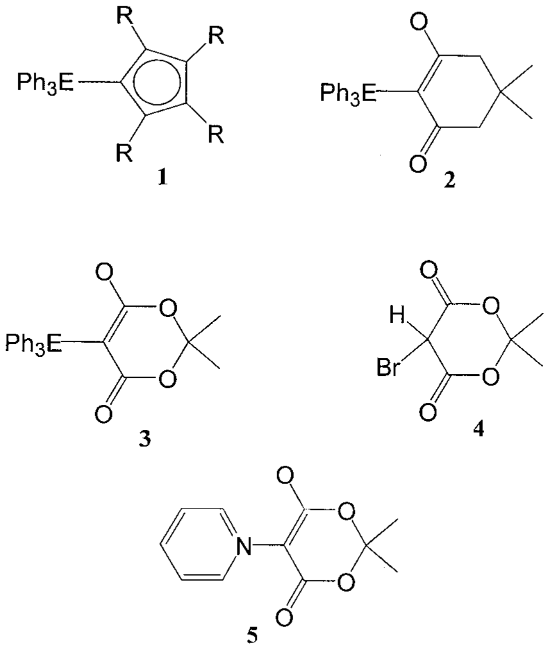

E = As (a), Sb (b), Bi (c)
R = Ph

Scheme 1

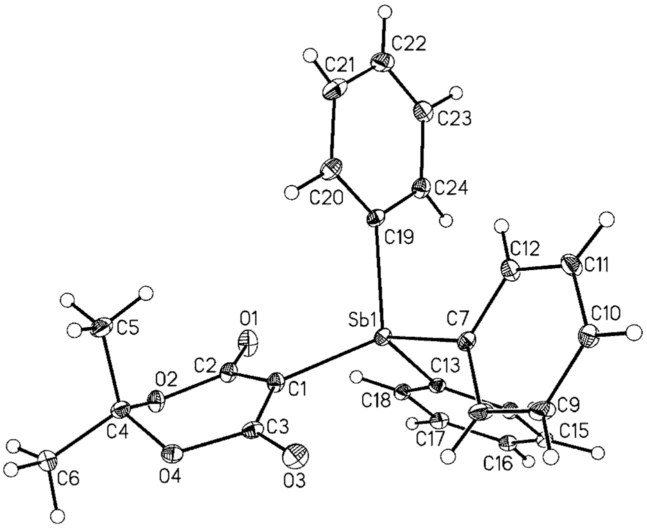

Fig. 2 The structure of Ph_3Sb-$C_6H_6O_4$ (**3b**) in the crystal.

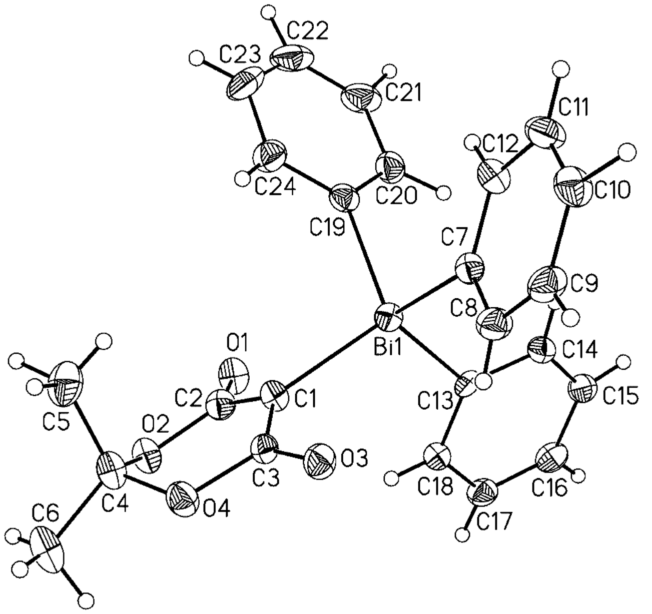

Fig. 3 The structure of Ph_3Bi-$C_6H_6O_4$ (**3c**) in the crystal.

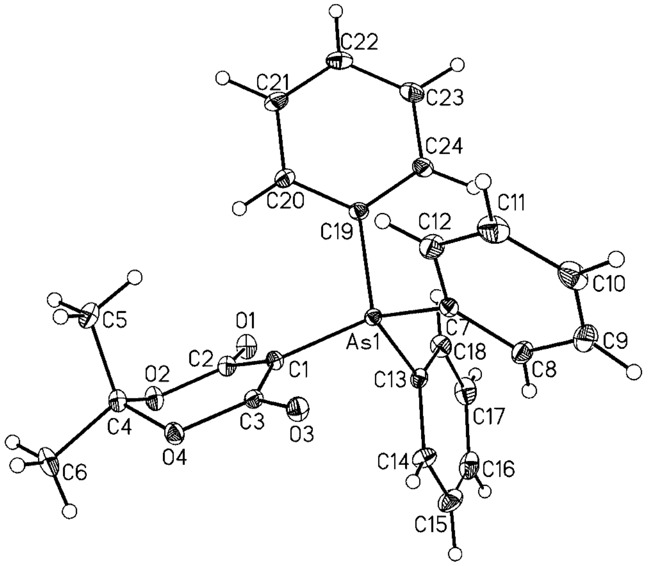

Fig. 1 The structure of Ph_3As-$C_6H_6O_4$ (**3a**) in the crystal.

Concluding Remarks

As expected, the crystal structures demonstrate **3** to be stabilized ylides, and no marked differences are observed going from arsenic to its heavier neighbours. Small deviations may be influenced by packing effects. The structure of their dioxin fragments are very close to that of its pyridine adduct **5** [1] which underlines the betaine nature of **3**.

A comparison of **3** with the structures of the dimedone derivatives **2** [12] reveals only minor differences in the ability of the heterocyclic framents to stabilize charge separation. In fact, the central E-C bond lengths are a little bit shorter for **3**.

Surprisingly, triphenylphosphane does not give an ylide of the type **3** on the reaction with **4** under the conditions mentioned below, triphenylphosphane oxide being the only phosphorus containing product detected. We are investiga-

Table 1 Crystal data of the compounds $Ph_3E-C_6H_6O_4$ (**3**)

	3a (E=As)	**3b** (E=Sb)	**3c** (E=Bi)
Unit cell dimension:			
a/Å	9.728(3)	9.586(5)	12.013(2)
b/Å	10.334(3)	9.743(6)	12.943(3)
c/Å	11.654(4)	12.287(6)	14.555(3)
α/°	64.69(2)	73.63(4)	
β/°	80.70(2)	69.37(2)	105.62(3)
γ/°	78.02(2)	84.13(4)	
Cell volume / $Å^3$	1032.5(6)	1030(1)	2179.6(8)
Z	2	2	4
density [calc.]/g/cm^{-3}	1.442	1.596	1.775
crystal system	triclinic	triclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$
measurement device	Siemens P4		CAD-4
wave length	0.71073	0.71073	1.54184
temperature/°C	−100	−100	−60
theta range/θ	2.15−29.50	2.18−27.50	2.36−24.69
reflections:			
collected	7930	9430	4677
observed $[F_0>4\sigma(F_0)]$	5538	4723	3692
refinement	full matrix least-squares method on F^2		
parameter	347	347	347
solution and refinement	ShelXTL V5.1 (NT)		
R_1-Value $[I>2\sigma(I)]$	0.0294	0.0295	0.0342
wR2-Value $[I>2\sigma(I)]$	0.0733	0.0776	0.0818
$_1R$-Value [all data]	0.0300	0.0300	0.0495
wR2-Value [all data]	0.0762	0.0782	0.0876
largest difference peak and hole/e·$Å^3$	+0.88, −1.11	+1.40, −1.68	+1.15, −1.02

Table 2 Atomic coordinates (x 104) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $Ph_3As-C_6H_6O_4$ (**3a**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
As(1)	3821(1)	1879(1)	1751(1)	20(1)
O(1)	874(1)	1725(1)	2757(1)	33(1)
O(2)	855(1)	−648(1)	3661(1)	31(1)
O(3)	4874(1)	−1563(1)	2373(1)	32(1)
O(4)	2868(1)	−2284(1)	3442(1)	30(1)
C(1)	3018(1)	203(2)	2660(1)	22(1)
C(2)	1553(1)	514(2)	3011(1)	25(1)
C(3)	3697(2)	−1204(2)	2791(1)	23(1)
C(4)	1708(2)	−2032(2)	4290(2)	27(1)
C(5)	2233(2)	−2102(2)	5475(2)	34(1)
C(6)	765(2)	−3144(2)	4574(2)	43(1)
C(7)	5782(1)	1513(2)	1238(1)	23(1)
C(8)	6274(2)	1948(2)	−36(2)	33(1)
C(9)	7730(2)	1761(3)	−357(2)	45(1)
C(10)	8662(2)	1146(3)	592(3)	47(1)
C(11)	8154(2)	693(3)	1863(3)	47(1)
C(12)	6710(2)	880(2)	2193(2)	37(1)
C(13)	2828(1)	3095(2)	271(1)	25(1)
C(14)	2624(2)	2455(2)	−517(2)	35(1)
C(15)	1821(2)	3270(3)	−1554(2)	46(1)
C(16)	1232(2)	4698(3)	−1794(2)	45(1)
C(17)	1460(2)	5332(2)	−1028(2)	44(1)
C(18)	2260(2)	4534(2)	18(2)	34(1)
C(19)	3796(2)	2847(2)	2840(1)	25(1)
C(20)	3277(2)	2218(2)	4111(2)	32(1)
C(21)	3364(2)	2859(2)	4929(2)	38(1)
C(22)	3926(2)	4134(2)	4466(2)	38(1)
C(23)	4451(2)	4759(2)	3202(2)	37(1)
C(24)	4402(2)	4111(2)	2382(2)	31(1)

Table 3 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $Ph_3Sb-C_6H_6O_4$ (**3b**). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Sb(1)	6650(1)	7575(1)	6696(1)	21(1)
O(1)	8512(2)	4957(2)	6317(2)	37(1)
O(2)	8975(2)	4011(2)	8037(2)	28(1)
O(3)	7064(2)	7263(2)	9425(2)	39(1)
O(4)	8121(2)	5126(2)	9629(2)	28(1)
C(1)	7521(2)	6127(2)	7855(2)	24(1)
C(3)	7503(2)	6264(3)	8984(2)	25(1)
C(2)	8325(3)	5040(2)	7338(2)	25(1)
C(4)	8285(2)	3796(3)	9318(2)	25(1)
C(5)	6786(3)	3077(3)	9745(3)	36(1)
C(6)	9366(3)	2906(3)	9887(3)	35(1)
C(7)	5311(2)	9174(2)	7438(2)	22(1)
C(8)	5722(3)	9912(3)	8101(3)	33(1)
C(9)	4748(3)	10909(3)	8594(3)	36(1)
C(10)	3383(3)	11179(3)	8432(2)	29(1)
C(11)	2978(3)	10457(3)	7773(3)	32(1)
C(12)	3941(3)	9455(3)	7272(2)	29(1)
C(13)	8230(2)	8676(2)	5058(2)	21(1)
C(14)	8143(2)	10164(2)	4733(2)	23(1)
C(15)	9136(3)	10948(3)	3658(2)	26(1)
C(16)	10223(3)	10246(3)	2906(2)	27(1)
C(17)	10322(3)	8764(3)	3249(2)	27(1)
C(18)	9332(3)	7959(3)	4319(2)	24(1)
C(19)	5091(2)	6595(2)	6296(2)	23(1)
C(20)	4054(3)	5643(3)	7218(2)	31(1)
C(21)	2897(3)	5150(3)	6991(3)	39(1)
C(22)	2781(3)	5597(3)	5845(3)	38(1)
C(23)	3822(3)	6520(3)	4928(3)	35(1)
C(24)	4981(3)	7037(3)	5147(2)	28(1)

Table 4 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for $Ph_3Bi-C_6H_6O_4$ (*3c*). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Bi(1)	8710(1)	4208(1)	2333(1)	45(1)
O(1)	7727(5)	6448(5)	1738(4)	61(2)
O(2)	9102(5)	7240(4)	1253(4)	57(1)
O(3)	11339(5)	4938(4)	2096(4)	59(1)
O(4)	10902(5)	6451(4)	1400(4)	61(2)
C(1)	9415(7)	5511(6)	1781(6)	49(2)
C(2)	8674(7)	6374(6)	1599(6)	51(2)
C(3)	10579(7)	5553(6)	1778(5)	46(2)
C(4)	10015(8)	7076(7)	812(7)	60(2)
C(5)	9543(13)	6581(12)	−158(8)	81(3)
C(6)	10550(15)	8121(10)	764(13)	89(4)
C(7)	9637(7)	2734(6)	2309(5)	45(2)
C(8)	10817(8)	2656(8)	2573(7)	62(2)
C(9)	11325(10)	1725(8)	2486(8)	67(3)
C(10)	10667(9)	882(7)	2132(8)	70(3)
C(11)	9478(9)	951(7)	1862(8)	72(3)
C(12)	8959(8)	1890(7)	1953(7)	57(2)
C(13)	8504(6)	4573(6)	3757(5)	42(2)
C(14)	8129(8)	3828(7)	4277(6)	51(2)
C(15)	7961(9)	4085(8)	5147(6)	63(2)
C(16)	8177(8)	5071(8)	5486(7)	60(2)
C(17)	8584(8)	5801(7)	4986(6)	60(2)
C(18)	8733(7)	5566(6)	4103(6)	50(2)
C(19)	6977(7)	3899(6)	1389(6)	52(2)
C(20)	6108(8)	3585(7)	1777(7)	65(2)
C(21)	5015(10)	3409(9)	1163(10)	87(3)
C(22)	4808(12)	3523(9)	211(11)	95(4)
C(23)	5663(14)	3807(10)	−171(8)	90(4)
C(24)	6777(11)	4009(8)	410(7)	69(3)

ting therefore the mechanism of this reaction and will report on our results in due course.

Experimental Section

All experiments have been performed in purified solvents under argon. 5-Bromo-2,2-dimethyl-4,6-dioxo-1,3-dioxin (**4**) has been prepared according to a published procedure [13]. Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre (**3a**: CCDC 205373, **3b**: CCDC 205372, **3c**: CCDC 205371). Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union

Table 5 Selected bond lengths /Å and angles /° for $Ph_3E\text{-}C_6H_6O_4$ (**3**).

	3a (E=As)	**3b** (E=Sb)	**3c** (E=Bi)
E−C(1)	1.859(2)	2.044(2)	2.139(7)
E−C(7)	1.915(2)	2.116(2)	2.214(7)
E−C(13)	1.915(2)	2.113(2)	2.205(7)
E−C(19)	1.917(2)	2.113(2)	2.200(8)
C(2)−O(1)	1.222(2)	1.228(3)	1.212(9)
C(2)−O(2)	1.368(2)	1.377(3)	1.384(2)
C(3)−O(3)	1.219(2)	1.213(3)	1.205(9)
C(3)−O(4)	1.386(2)	1.381(3)	1.385(9)
C(4)−O(4)	1.434(2)	1.429(3)	1.425(10)
C(4)−O(2)	1.442(2)	1.438(3)	1.428(10)
C(1)−C(2)	1.426(2)	1.410(3)	1.408(11)
C(1)−C(3)	1.421(2)	1.424(3)	1.401(11)
C(4)−C(5)	1.512(2)	1.516(3)	1.507(15)
C(4)−C(6)	1.516(2)	1.516(3)	1.515(15)
C(1)−E−C(7)	113.51(6)	114.13(9)	115.0(3)
C(1)−E−C(13)	109.83(6)	115.3(1)	109.9(3)
C(1)−E−C(19)	109.21(7)	111.0(1)	108.2(3)
C(7)−E−C(13)	109.00(7)	105.83(9)	112.6(3)
C(7)−E−C(19)	103.42(6)	100.94(9)	103.2(3)
C(13)−E−C(19)	111.76(7)	108.53(9)	107.4(3)
C(2)−O(2)−C(4)	116.66(11)	115.55(18)	116.6(6)
C(3)−O(4)−C(4)	108.00(12)	117.94(18)	118.1(6)
C(2)−C(1)−C(3)	122.75(13)	122.6(2)	123.4(7)
C(2)−C(1)−E	124.2010)	111.55(16)	113.7(6)
C(3)−C(1)−E	112.08(10)	125.41(17)	121.9(6)
O(1)−C(2)−O(2)	117.82(13)	118.0(2)	117.1(7)
O(1)−C(2)−C(1)	125.45(14)	125.4(2)	127.3(8)
O(2)−C(2)−C(1)	116.71(13)	116.5(2)	115.6(7)
O(3)−C(3)−O(4)	117.02(13)	116.5(2)	116.3(7)
O(3)−C(3)−C(1)	128.56(14)	128.4(2)	128.8(7)
O(4)−C(3)−C(1)	114.37(12)	115.0(2)	114.8(7)
O(2)−C(4)−O(4)	110.66(12)	110.7(2)	110.8(7)
O(2)−C(4)−C(5)	110.18(14)	109.8(2)	106.0(8)
O(4)−C(4)−C(5)	110.64(13)	110.7(2)	106.1(10)
O(2)−C(4) C(6)	105.25(13)	106.5(2)	110.0(9)
O(4)−C(4)−C(6)	106.81(15)	106.3(2)	110.6(8)
C(5)−C(4)−C(6)	113.15(15)	112.8(2)	113.2(11)

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General procedure for the synthesis of 3. 5 mmols of Ph_3E were added to a solution of 1.115 g (5 mmol) of **4** in 30 ml of dichloromethane, and the mixture was stirred at room temp. for 1 h. After addition of 0.90 ml (6.5 mmol) of triethylamine and stirring for further 1 h, the solution was extracted with 10 ml of water. The organic layer was dried over Na_2SO_4 and evaporated *in vacuo* to dryness. The residue was recrystallized from dichloromethane to give the ylides **3** as stable crystals.

$Ph_3As\text{-}C_6H_6O_4$ (3a). 1.45 g (95 %) yield, colourless crystals, m.p. 215-216 °C. Elemental analysis for $C_{24}H_{21}AsO_4$ (448.35 g/mol): found (calc.) C 64.16 (64.29), H 4.58 (4.72) %.

^{1}H-NMR ($CDCl_3$): δ = 1.78 (s, 6 H, Me), 7.45-7.65 (m, 15 H, Ph).
^{13}C-NMR ($CDCl_3$): δ = 26.0 (Me), 57.4 (C5), 103.2 (C2), 126.4, 129.5, 132.3, 132.7 (Ph), 165.3 (C4,6).
IR (KBr): ν_{CO} = 1648 cm^{-1}.
MS (FAB): *m/z* (%) = 449 [6, $M^+ + H$], 391 [100, $M^+ - Me_2CO$], 347 [30, $M^+ - Me_2CO$, CO_2] and further fragments.

$Ph_3Sb\text{-}C_6H_6O_4$ (3b). 1.59 g (90 %) yield, colourless crystals, m.p. 110-113 °C. Elemental analysis for $C_{24}H_{21}O_4Sb$ (495.18 g/mol): found (calc.) C 58.13 (58.21), H 3.93 (4.27) %.

^{1}H-NMR ($CDCl_3$): δ = 1.80 (s, 6 H, Me), 7.38-7.75 (m, 15 H, Ph).
^{13}C-NMR ($CDCl_3$): δ = 26.4 (Me), 58.3 (C5), 103.7 (C2), 128.9, 130.0, 132.8, 135.7 (Ph), 165.8 (C4,6).
IR (KBr): ν_{CO} = 1658 cm^{-1}.
MS (FAB): *m/z* (%) = 504 [100, $M^+ + Na, -Me$], 437 [28, $M^+ - Me_2CO$], 393 [8, $M^+ - Me_2CO$, CO_2] and further fragments.

$Ph_3Bi\text{-}C_6H_6O_4$ (3c). 1.60 g (55 %) yield, pale yellow crystals, m.p. 90-91 °C. Elemental analysis for $C_{24}H_{21}BiO_4$ (582.41 g/mol): found (calc.) C 48.90 (49.50), H 3.25 (3.63) %.

^{1}H-NMR ($CDCl_3$): δ = 1.78 (s, 6 H, Me), 7.48-7.67 (m, 15 H, Ph).
^{13}C-NMR ($CDCl_3$): δ = 26.5 (Me), 57.8 (C5), 103.7 (C2), 126.4, 130.1, 132.8, 133.2 (Ph), 165.8 (C4,6).
IR (KBr): ν_{CO} = 1581 cm^{-1}.
MS (FAB): *m/z* (%) = 552 [3, $M^+ - 2$ Me], 525 [8, $M^+ - Me_2CO$], 363 [36, Ph_2Bi^+], 286 [66, $PhBi^+$], 209 [100, Bi^+] and further fragments.

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