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Preliminary communication

SYNTHESIS OF METALLOCHIRAL TRIORGANOBISMUTHINES

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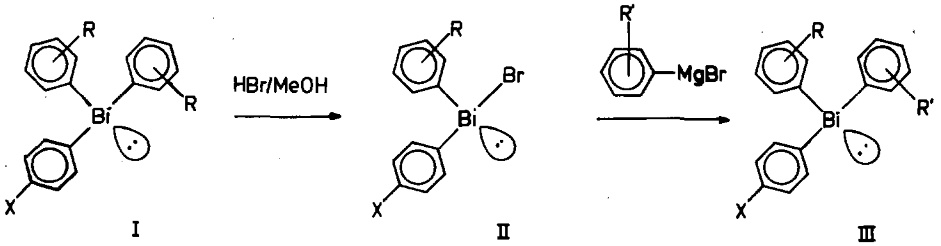
Summary

Triorganobismuthines containing a chiral centre at the metal atom have been prepared by selective bromodearylation of mixed triarylbismuthines, followed by reaction of the resulting chiral diarylbromobismuthines with arylmagnesium bromides. The NMR spectra of some of the new compounds exhibit diastereotopic effects, associated with the chirality, indicating that the bismuthines have a stable pyramidal configuration.

Selective heterolytic cleavage of carbon—metal bonds has been successfully used in the synthesis of chiral organometallic compounds such as chiral tetraorganotin [1] and tetraorganolead [2] compounds. We have found that the reaction of certain mixed triarylbismuthines (I) with hydrogen bromide in methanol proceeds with sufficient selectivity to be used for the synthesis of chiral diarylbromobismuthines (II). Reaction of compounds II with arylmagnesium bromides provides a novel type of compound, the metallochiral triorganobismuthines (III) (Scheme 1).

The synthesis of II was carried out by adding slowly a solution of hydrogen bromide in methanol (0.2—0.5 *M*) at 0—20°C to a solution of I in dichloro-



SCHEME 1

TABLE 1

SYNTHESIS OF CHIRAL BISMUTHINES: $(\mathrm{Ar})_2(\mathrm{Ar}')\mathrm{Bi} \xrightarrow[\text{(2) Ar}''\text{MgBr}]{\text{(1) HBr/MeOH}} (\mathrm{Ar})(\mathrm{Ar}')(\mathrm{Ar}'')\mathrm{Bi}$

Starting compound		Product		Yield (%)	M.P. (°C (uncorr.))
Ia	$(4\text{-BrC}_6\text{H}_4)(\alpha\text{-C}_{10}\text{H}_7)_2\text{Bi}^{a,b}$	IIIa	$(4\text{-BrC}_6\text{H}_4)(\text{C}_6\text{H}_5)(\alpha\text{-C}_{10}\text{H}_7)\text{Bi}$	44	129—130
Ib	$(4\text{-ClC}_6\text{H}_4)(2\text{-CH}_3\text{C}_6\text{H}_4)_2\text{Bi}^{a,c}$	IIIb	$(4\text{-ClC}_6\text{H}_4)[2\text{-(CH}_3)_2\text{CHOC}_6\text{H}_4](2\text{-CH}_3\text{C}_6\text{H}_4)\text{Bi}$	10	70—70.5
Ic	$(4\text{-ClC}_6\text{H}_4)(\alpha\text{-C}_{10}\text{H}_7)_2\text{Bi}^{a,d}$	IIIc	$(4\text{-ClC}_6\text{H}_4)[2\text{-(CH}_3)_2\text{CHOC}_6\text{H}_4](\alpha\text{-C}_{10}\text{H}_7)\text{Bi}$	39	130—133
Id	$(4\text{-ClC}_6\text{H}_4)[2,4,6\text{-(CH}_3)_3\text{C}_6\text{H}_2]_2\text{Bi}^{a,e}$	IIId	$(4\text{-ClC}_6\text{H}_4)[2\text{-(CH}_3)_2\text{CHOC}_6\text{H}_4][2,4,6\text{-(CH}_3)_3\text{C}_6\text{H}_2]\text{Bi}$	45	110—112
Id	$(4\text{-ClC}_6\text{H}_4)[2,4,6\text{-(CH}_3)_3\text{C}_6\text{H}_2]_2\text{Bi}^{a,e}$	IIIe	$(4\text{-ClC}_6\text{H}_4)(2\text{-C}_6\text{H}_5\text{CH}_2\text{OC}_6\text{H}_4)[2,4,6\text{-(CH}_3)_3\text{C}_6\text{H}_2]\text{Bi}$	55	103—104

[a] Prepared by adding 2 eq. of ArMgBr to $\text{Ar}'\text{BiCl}_2$ in THF at 0° C; $\text{Ar}'\text{BiCl}_2$ was prepared from $\text{Ar}'_3\text{Bi}$ and 2 eq. of BiCl_3 in toluene/ether [3]; $(4\text{-BrC}_6\text{H}_4)_3\text{Bi}$ was synthesized from $4\text{-BrC}_6\text{H}_4\text{Li}$ and BiCl_3 in ether (yield 67%, m.p. 145° C (uncorr.)) (lit 145° C[3]). [b] Yield 67%, m.p. 133—136° C (uncorr.). [c] 78%, 80—83° C. [d] 63%, 135° C; [e] 50%, 130—131° C.

methane or chloroform (0.2—0.5 *M*). Bismuthine IIb (X = Cl, R = 2-CH_3) precipitated after partial evaporation of the solvent and was obtained pure by filtration. The other bismuthines, sometimes as a mixture with the hydrocarbon formed, were isolated by complete evaporation of the solvent. The products thus obtained were used directly in the next step.

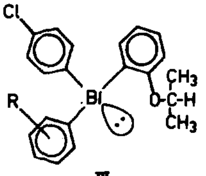
Compounds III were synthesized by treating II in tetrahydrofuran at 0°C with an excess of arylmagnesium bromide. The bismuthines were purified by crystallization from chloroform/ethanol and their structures were established by ^1H and ^{13}C NMR spectroscopy. The results are presented in Table 1*.

The selectivity of the reaction with hydrogen bromide is in agreement with the variations in reactivity found for electrophilic substitution in benzenoid compounds containing $(R)_nE$ (E = Si, Ge, Sn, Pb, Hg etc.) as the leaving group [4].

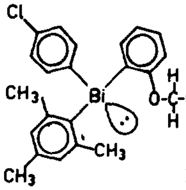
Some PMR data for the prochiral isopropoxy group of IIIb,c,d and the prochiral benzyloxy group of IIIe are listed in Table 2. For both groups diastereotopic effects are observed as a consequence of the chirality of the bismuthines.

TABLE 2

PMR DATA FOR TRIARYLBISMUTHINES



IIIb,c,d



IIIe

Bismuthine	R	Solvent	δ-$C(CH_3)_2$ [a] (ppm, vs TMS)		$\Delta\delta$ (ppm)
IIIb	2-CH_3	$CDCl_3$	1.20	1.19 [b]	0.015
IIIc	2,3-benzo	$CDCl_3$	1.17 [b]		0
IIId	2,4,6-$(CH_3)_3$	$CDCl_3$	1.25	1.14 [b]	0.112
IIId	2,4,6-$(CH_3)_3$	C_6D_6	0.87	0.99 [c]	0.12
IIId	2,4,6-$(CH_3)_3$	acetone-d_6	1.19	1.05 [c]	0.14
IIId	2,4,6-$(CH_3)_3$	DMSO-d_6	1.11	0.96 [c]	0.15
			$\delta(CH_2)$ [d] (ppm, vs TMS)		
IIIe		$CDCl_3$	5.03	5.01 [b]	0.021

[a] ^3J(H—H) 6 Hz. [b] Bruker WM-300. [c] JEOL PS 100. [d] ^2J(H—H) 12 Hz.

The influence of *ortho*-substitution (R) in the other aryl group of the bismuthine on the diastereotopic effect is remarkable. For the methyl protons of the isopropoxy group of IIIb (R = 2-CH_3) this effect is small ($\Delta\delta$ 0.015 ppm in $CDCl_3$), and in IIc (R = 2,3-benzo) it could not even be observed. In IIId (R = 2,4,6-$(CH_3)_3$), however, the effect is significant ($\Delta\delta$ 0.11 ppm in $CDCl_3$, 0.15 ppm in DMSO-d_6).

The ^{13}C spectrum of IIId also exhibits a diastereotopic effect for the methyl carbons of the isopropoxy group ($\Delta\delta$ 0.27 ppm). For the methylene protons of IIIe a diastereotopic effect of 0.021 ppm and a geminal coupling constant of 12 Hz is found (in $CDCl_3$).

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*This is not a general method. In some cases (e.g. X = Cl, R = 4-CH_3, R' = 4-CH_3O or 4-C_2H_5) this reaction leads to inseparable mixtures, consisting of at least three different triarylbismuthines, as was shown by 300 MHz PMR. Possibly redistribution reactions occur in these cases (e.g. 2 $Ar_2BiX \rightarrow Ar_3Bi + ArBiX_2$ or $Ar_2Ar'Bi + Ar_2BiX \rightarrow ArAr'BiX + Ar_3Bi$).

These data strongly suggest that these chiral bismuthines possess a stable, pyramidal configuration.

More detailed information on the synthesis and the spectral properties of this novel class of organobismuth compounds will be published separately.

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