

Preliminary communication

ORGANOBISMUTH COMPOUNDS

I. METALLOCHIRALITY IN DIARYLHALOBISMUTHINES

P. BRAS, H. HERWIJER and J. WOLTERS

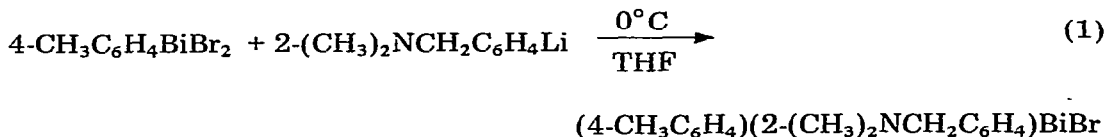
Gorlaeus Laboratories, Division of Organometallic Chemistry, University of Leiden, P.O. Box 9502, 2300 RA Leiden (The Netherlands)

(Received March 4th, 1981)

Summary

The preparation of some bismuthines containing a chiral centre at the bismuth atom is reported and their structures are established by NMR spectroscopy.

Metallochirality in organobismuth compounds has not been reported previously [1]. After our successful preparation of chiral organolead compounds [2] we have now developed a synthetic route to a novel class of organobismuth compounds: metallochiral bismuthines. Configurational stability was achieved by use of a built-in ligand. Such a ligand can be introduced with 2-(dimethylaminomethyl)phenyllithium (I) [3, 4] which was shown by Noltes and Van Koten [5] to be a valuable reagent in the synthesis of organocopper and chiral organotin compounds, and was later used in the preparation of chiral organosilicon and -germanium compounds [6]. The aryldibromobismuthine 4-CH₃C₆H₄BiBr₂ was treated at 0°C in THF with the reagent 2-(CH₃)₂NCH₂-C₆H₄Li (I) to give the chiral bismuthine (4-CH₃C₆H₄)(2-(CH₃)₂NCH₂C₆H₄)BiBr (II) in 70% yield (m.p. 126°C (uncorr.) after recrystallization from CHCl₃/EtOH).



Another example of a chiral bismuthine was prepared using 2-CH₃OCH₂C₆H₄MgBr (III). Reaction of III with aryldibromobismuthine 4-CH₃C₆H₄BiBr₂

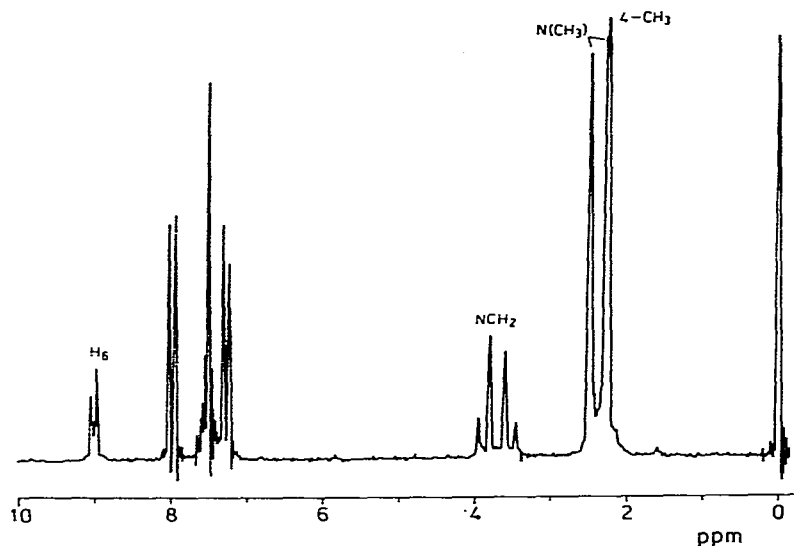


Fig. 1. PMR spectrum of $(4\text{-CH}_3\text{C}_6\text{H}_4)(2\text{-(CH}_3)_2\text{NCH}_2\text{C}_6\text{H}_4)\text{BiBr}$ (II), in CDCl_3 at 27°C .

yielded the chiral compound $(4\text{-CH}_3\text{C}_6\text{H}_4)(2\text{-CH}_3\text{OCH}_2\text{C}_6\text{H}_4)\text{BiBr}$ (IV) (31%, m.p. $123\text{--}124^\circ\text{C}$ (uncorr.) after recrystallization from $\text{CHCl}_3/\text{EtOH}$).

The PMR spectrum of II shown in Fig. 1, displays two signals for the benzylic protons which are diastereotopic as a consequence of the metalochirality. The presence of a doublet for the $(\text{CH}_3)_2\text{N}$ protons indicates intramolecular coordination between the N and Bi atoms (see Fig. 2), the N atom now being a prochiral centre and so giving diastereotopic CH_3 groups. ^{13}C NMR spectroscopy confirmed the PMR results: $\delta(^{13}\text{C}(\text{N}(\text{CH}_3)_2))$: 45.9 and 46.5 ppm (vs. TMS in CDCl_3).

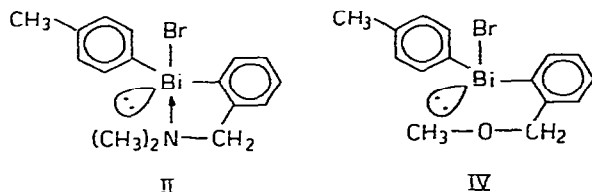


Fig. 2. Intramolecular coordination leading to configurational stability in the bismuthines II and IV.

PMR data for the compounds II and IV in several solvents are given in Tables 1 and 2. They reveal a solvent dependence of the diastereotopic effect for the $\text{N}(\text{CH}_3)_2$ and NCH_2 protons of compound II. In a strongly coordinating solvent such as DMSO the built-in ligand no longer prevents inversion at the Bi centre and the diastereotopic effect for both types of protons disappears. A diastereotopic effect has also been found for the methylene protons of compound IV. The Bi—O interaction is assumed to be weaker than the Bi—N interaction.

TABLE 1

PMR DATA^a OF (4-CH₃C₆H₄)₂(2-(CH₃)₂NCH₂C₆H₄)BiBr (II)

Solvent	$\delta(\text{N}(\text{CH}_3)_2)$	$\delta(\text{NCH}_2)^b$	$\delta(4\text{-CH}_3)$	$\delta(\text{H}(6))^c$	$\delta(\text{H}(\text{Arom}))$
CDCl ₃	2.27	3.55	2.25	9.00	7.24–8.08
	2.49	3.87			
CD ₃ COCD ₃	2.30	3.56	2.22	8.96	7.25–8.06
	2.49	4.04			
C ₆ D ₆	1.64	3.01	2.02	9.55	7.24–8.08
	1.76	3.17			
CD ₃ SOCD ₃	2.36	3.78	2.22	8.86	7.26–8.08

^aJEOL PS 100; ppm, internal reference TMS; concentration ~ 20% w/v. ^b $J(\text{H}-\text{H})$ 14 Hz. ^c(2-(CH₃)₂-NCH₂C₆H₄).

TABLE 2

PMR DATA^a OF (4-CH₃C₆H₄)₂(2-CH₃OCH₂C₆H₄)BiBr (IV)

Solvent	$\delta(\text{OCH}_3)$	$\delta(\text{OCH}_2)^b$	$\delta(4\text{-CH}_3)$	$\delta(\text{H}(6))^c$	$\delta(\text{H}(\text{Arom}))$
CDCl ₃	3.36	4.46	2.14	8.92	7.26–8.08
		4.64			
CD ₃ COCD ₃	3.44	4.64	2.24	8.85	7.26–8.12
		3.85			
C ₆ D ₆	2.56	3.85	1.97	9.40	6.94–8.12

^aJEOL PS 100; ppm, internal reference TMS; concentration ~ 20% w/v. ^b $J(\text{H}-\text{H})$ 12.5 Hz. ^c(2-CH₃OCH₂C₆H₄).

Studies of the synthesis, reactions, and the stereochemistries of metallochiral bismuthines are in progress.

Acknowledgement. The authors thank Miss. S. Amadio for valuable comments.

References

- 1 M. Wieber, *Gmelin Handbuch der Anorganischen Chemie*, Bd 47, Bismut-Organische Verbindungen, Springer Verlag, Berlin 1977.
- 2 H.O. van der Kooi, J. Wolters and A. van der Gen, *Rec. Trav. Chim. Pays-Bas*, 98 (1979) 353.
- 3 F.N. Jones and C.R. Hauser, *J. Org. Chem.*, 27 (1962) 4389.
- 4 G. Bähr and H. Zohm, *Angew. Chem.*, 75 (1963) 94.
- 5 G. van Koten and J.G. Noltes, *J. Amer. Chem. Soc.*, 98 (1976) 5393.
- 6a R.J.P. Corriu, G. Royo and A. De Saxe, *J. Chem. Soc. Chem. Commun.*, (1980) 892.
- b C. Breliere, F. Carre, R.J.P. Corriu, A. De Saxe, M. Poirier and G. Royo, *J. Organometal. Chem.*, 205 (1981) C1.