Pergamon

Tetrahedron Letters, Vol. 38, No. 3, pp. 365-366, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(96)02305-2

The Chemistry of Pentavalent Organobismuth Reagents. New Preparative Methods for Aryl Bismuth (V) Carboxylates and Sulfonates.

Thomas Arnauld, Derek H. R. Barton* and Eric Doris

Department of Chemistry, Texas A&M University, College Station, TX 77843-3255 (USA)

***Abstract*:** Two new methods for the preparation of aryl bismuth (V) carboxylates and sulfonates are reported. The first strategy involves an acid catalysed ligand exchange from triphenyl bismuth diacetate, while the second utilizes an oxidative addition of dibenzoyl peroxide catalyzed by $BF_3.OEt_2$.

The arylation of organic substrates remains an arduous task for the synthetic chemist. Using bismuth reagents,[1] a wide range of functional groups can be arylated and, in some cases, alkylated. The effect of copper salts, or in some instances of metallic copper, permits the arylation of amines and alcohols.[2] In appropriate cases, very hindered compounds can be prepared in good yields.[3]

During our studies on the preparation of new bismuth (V) species as arylating reagents, we have found that the readily accessible $Ph_3Bi(OAc)_2$ [4] easily undergoes ligand exchange [5] in the presence of a strong carboxylic or sulfonic acid [6] (Scheme 1). A number of examples are listed in the table.

$$Ar_3Bi(OAc)_2 \quad + \quad 2\,XH \quad \xrightarrow[\text{r.t.}]{CH_2Cl_2} \quad Ar_3BiX_2$$

$$\boxed{XH : CF_3CO_2H,\ CH_3SO_3H,\ TosOH}$$

Scheme 1

Table: Examples of Ligand Exchange from $Ph_3Bi(OAc)_2$.

Entry	$Ar_3Bi(OAc)_2$	XH	Product	Yield
1	$Ph_3Bi(OAc)_2$	CF_3CO_2H	$Ph_3Bi(OC(O)CF_3)_2$	87%
2	$Ph_3Bi(OAc)_2$	CH_3SO_3H	$Ph_3Bi(OSO_2CH_3)_2$	82%
3	$Ph_3Bi(OAc)_2$	TosOH	$Ph_3Bi(OTos)_2$	75%

The pathway developed above offers the advantage over the "classical one" [7] ($Ph_3Bi \rightarrow Ph_3BiCl_2 \rightarrow Ph_3BiCO_3 \rightarrow Ph_3BiX_2$) in that it requires fewer steps from the commercially available Ph_3Bi. Furthermore, the direct conversion of Ph_3BiCl_2 into the di-carboxylate, using the sodium or potassium salt of the corresponding acid,[8] necessitates extended periods of reaction. This method is therefore an improvement over existing methodologies by providing a shorter, more efficient route to the desired Bi (V) species.

We also conceived that the oxidation rate of aryl bismuth (III) by dibenzoyl peroxide should be enhanced in the presence of a catalytic amount of boron trifluoride etherate ($BF_3.OEt_2$).[9] While the previously reported method of Dodonov [10] needs prolonged reaction time (300 hours), the addition of 0.1 equivalents of $BF_3.OEt_2$ allows a much faster process (24 hours) (Scheme 2) in accordance with our conception with a satisfactory yield of easily purified product.

$$Ar_3Bi \quad + \quad (PhC(O))_2O_2 \quad + \quad BF_3.OEt_2\ \text{cat.} \quad \xrightarrow[\text{r.t.}]{C_6H_6} \quad Ar_3Bi(OBz)_2$$

Scheme 2

Acknowledgments: We thank the Welch Foundation, the N.I.H., and the Schering-Plough Corporation for financial assistance. We also thank Dr D.M.T. Chan (DuPont Agricultural Products) for a copy of his important article [2] prior to publication.

References and Notes:

1- For reviews on bismuth chemistry, see: Freedman, L. D.; Doak, G. O. *Chem. Rev.* **1982**, *82*, 15-57. Finet, J. P. *Chem. Rev.* **1989**, *89*, 1487-1501.

2- Barton, D. H. R.; Finet, J. P. *Pure Appl. Chem.* **1987**, *59*, 937-946. For recent developments, see: Chan, D. M. T. *Tetrahedron Lett.* **1996**, in press.

3- Barton, D. H. R.; Blazejewski, J. C.; Charpiot, B.; Finet, J. P.; Motherwell, W. B.; Barros Papoula, M. T.; Stanforth, S. P. *J. Chem. Soc. Perkin Trans 1* **1985**, 2667-2675.

4- $Ph_3Bi(OAc)_2$ was prepared by direct oxidation of Ph_3Bi with peracetic acid, a new procedure introduced by: Sinclair, P. J.; Wong, F.; Wyvratt, M.; Staruch, M. J.; Dumont, F. *Bioorg. Med. Chem. Lett.* **1995**, *5*, 1035-1038.

5- Acidolysis of aryl bismuth (III) by carboxylic acids, leading to ligand exchange, has already been reported, see: Deacon, G. B.; Jackson, W. R.; Pfeiffer, J. M. *Aust. J. Chem.* **1984**, *37*, 527-535.

6- **Experimental Procedure for the Preparation of $Ph_3Bi(OMes)_2$:** All operations were performed under Ar. CH_3SO_3H (0.26 mL, 2.2 eq.) was added dropwise to a stirred solution of $Ph_3Bi(OAc)_2$ (1 g, 1.79 mmoles, 1 eq.) in 18 mL anhydrous CH_2Cl_2 at room temperature. The reaction was stirred overnight and the volatiles were removed *in vacuo*. The crude product was then recrystallized from CH_2Cl_2, over which hexanes had been layered, to afford $Ph_3Bi(OSO_2CH_3)_2$ [11] (0.92 g, 82%) (m.p. 166-170°C).

7- Barton, D. H. R.; Kitchin, J. P.; Lester D. J.; Motherwell, W. B.; Barros Papoula, M. T. *Tetrahedron*, **1981**, *37* (suppl. 1), 73-79.

8- Gilman, H.; Yale, H. L. *J. Am. Chem. Soc.* **1951**, *73*, 4470-4471.

9- **Experimental Procedure for the Preparation of $Ph_3Bi(OBz)_2$:** All operations were performed under Ar. $BF_3.OEt_2$ (0.05 mL, 0.1 eq.) was added dropwise to a stirred solution of Ph_3Bi (2 g, 4.54 mmoles, 1 eq.) and dibenzoyl peroxide (1.31 g, 1.2 eq.) in 20 mL anhydrous C_6H_6 at room temperature. The reaction was stirred 24 h in the dark, the volatiles were removed *in vacuo*. The precipitate was then taken in Et_2O and filtered. The crude product was recrystallized from CH_2Cl_2, over which hexanes had been layered, to afford $Ph_3Bi(OBz)_2$ (2.29 g, 75%, m.p. 167-169°C, lit.[10] 169°C).

10- Dodonov, V. A.; Gushchin, A. V.; Brilkina, T. G. *J. Gen. Chem. USSR.* **1985**, 63-68.

11- Selected spectral data for $Ph_3Bi(OSO_2CH_3)_2$:
^{1}H NMR ($CDCl_3$, 200 MHz): δ 2.41 (s, 6H), 7.60 (t, J = 7.3 Hz, 3H), 7.78 (dd, J = 7.3 Hz and 8.5 Hz, 6H), 8.23 (d, J = 8.5 Hz, 6H).
^{13}C NMR ($CDCl_3$, 50 MHz): δ 39.8, 132.4, 132.7, 134.7, 157.1.
IR (KBr): cm^{-1} 1468, 1438, 1282, 984, 930, 725.
Anal: Calcd for $C_{20}H_{21}BiO_6S_2$: C, 38.10; H, 3.36; S, 10.17. Found: C, 38.00; H, 3.34; S, 10.10.

(*Received in USA* 7 *October* 1996; *revised* 14 *November* 1996; *accepted* 18 *November* 1996)