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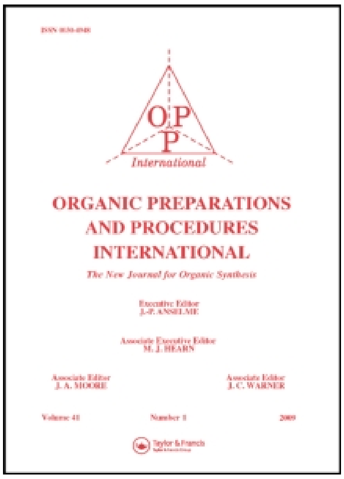

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A NOVEL SYNTHESIS OF TRIARYLBISMUTH DISULFONATES

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Morena, M. L. Sá e Melo and A. S. Campos Neves, *ibid.*, **34**, 353 (1993).

10. For example, the preparation of 6-azidoindole from 6-aminoindole has been reported: L. L. Melhado and N. J. Leonard, *J. Org. Chem.*, **48**, 5130 (1983).

11. In some cases crystallization began to occur during the reflux. In this case, more DMFDMA may be added to the reaction mixture to ensure complete reaction.

12. Aluminum amalgam was prepared from aluminum metal and mercuric chloride immediately prior to use, according to L. F. Fieser and M. Fieser, "*Reagents for Organic Synthesis*", Vol. 1, pp. 20-22, John Wiley & Sons, New York, NY, 1967.

13. Reaction times varied from 5-12 hrs depending on how well the aluminum was amalgamated. The reaction may be followed by TLC (elution with 9:1 CH_2Cl_2:ethanol) by the appearance of the product (R_f = 0.43-0.45) and disappearance of the starting material (R_f = 0.85, blue spot).

14. R. K. Brown and N. A. Nelson, *J. Am. Chem. Soc.*, **76**, 5149 (1954).

15. CuBr was freshly prepared prior to use, according to the procedure detailed in A. I. Vogel, "*Practical Organic Chemistry*", 3rd edn., p. 191, Longmans, Green and Co., London, England, 1956.

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A NOVEL SYNTHESIS OF TRIARYLBISMUTH DISULFONATES

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Pentavalent triarylbismuth compounds (Ar_3BiX_2, X-Cl, O_2CR, O_3SR, etc.) are a class of important organic bismuth reagents. They are especially useful in organic synthesis as mild and selective arylating agents.[1,2] Although there are several ways to prepare triarylbismuth diacetates,[3,4] to our knowledge triarylbismuth disulfonates have been prepared only by one method, *i. e.* the reaction of triarylbismuth carbonates with sulfonic acids.[2,5]

Usually. triarylbismuth carbonates have been synthesized by use of triarylbismuth dihalides as intermediates that are obtained from triarylbismuthine. Considering that triarylbismuth diacetates can be prepared directly from triarylbismuthines,[4b] we used triarylbismuth diacetates to react with sulfonic acids in order to develop a facile method for the synthesis of some new triarylbismuth disulfonates[3]. Since sulfonic acids are stronger than acetic acid, we believed that acid group transposition could occur easily. In fact the reaction of triarylbismuth diacetates with various sulfonic acids occurred readily to produce triarylbismuth disulfonates **3** in good yields. Thus, the present method constitutes a novel synthesis of triarylbismuth disulfonates[3] with the advantages of simple manipulations, mild reaction conditions and good yields.

$$\underset{\mathbf{1}}{Ar_3Bi(OAc)_2} + \underset{\mathbf{2}}{RSO_3H} \xrightarrow[\text{reflux}]{CH_3CN} \underset{\mathbf{3}}{Ar_3Bi(OSO_2R)_2}$$

a) Ar = C_6H_5, R = 4-$CH_3C_6H_4$
b) Ar = 4-$CH_3C_6H_4$, R = 4-$CH_3C_6H_4$
c) Ar = C_6H_5, R = 4-ClC_6H_4
d) Ar = 4-$CH_3C_6H_4$, R = 4-ClC_6H_4
e) Ar = C_6H_5, R = 4-BrC_6H_4
f) Ar = 4-$CH_3C_6H_4$, R = 4-BrC_6H_4
g) Ar = C_6H_5, R = CH_3
h) Ar = 4-$CH_3C_6H_4$, R = CH_3

TABLE. Synthesis of Triarylbismuth Disulfonates

Compd.	mp. (°C)	lit. mp. (°C)	Yield (%)	^{1}H NMR (δ)	Analysis Found (Calcd) C	H
3a	189-192	190-194[a]	88	2.25 (s, 6H); 6.83-7.23 (m, 8H); 7.47-8.27 (m, 15H)	49.05 (49.11)	3.72 (3.73)
3b	183-185	—	90	2.27 (s, 6H); 2.40 (s, 9H) 6.87-7.30 (m, 8H) 7.37-8.07 (m, 12H)	50.86 (50.97)	4.27 (4.28)
3c	173 (dec.)	—	83	6.80-7.35 (m, 8H) 7.55-8.30 (m, 15H)	43.68 (43.76)	2.80 (2.81)
3d	191 (dec.)		80	2.29 (s, 9H); 7.08-7.34 (m, 8H); 7.53-8.18 (m, 12H)	45.66 (45.79)	3.33 (3.38)
3e	180 (dec.)	—	86	7.13-7.73 (m,8H) 7.50-8.21 (m, 15H)	39.31 (39.49)	2.52 (2.54)
3f	210-212	—	85	2.40 (s, 9H); 7.05-7.30 (m, 8H); 7.34-8.10 (m,1 2H)	41.45 (41.53)	3.05 (3.06)
3g	170-172	—	81	2.44 (s, 6H) 7.10-7.50 (m, 15H)	38.02 (38.10)	3.34 (3.36)
3h	168-170	172[b]	78	2.43 (s, 15H) 7.40-8.25 (m, 12H)	41.02 (41.07)	4.06 (4.05)

a) Ref. 2. b) Ref. 5.

EXPERIMENTAL SECTION

Melting points were determined on a Delta Series DSC 7 apparatus and are uncorrected. ^{1}H-NMR spectra were recorded on Varian EM-360 and FX-90Q instruments using TMS as an internal standard. IR spectra were obtained as KBr disks on a Perkin Elmer 683 instrument. Elemental analyses were performed on a Carlo Erba 1106 instrument. Triphenylbismuthine, *tris*-(4-methylphenyl)bismuthine,[3] triphenylbismuth diacetate and *tris*-(4-methylphenyl)bismuth diacetate[4,6] were prepared according to the literature methods.

Typical Procedure: To a well stirred solution of triphenylbismuth diacetate (0. 562g, 1mmol) in acetonitrile (15 mL) was added a solution of *p*-toluenesulfonic acid (2.1mmol) in acetonitrile (10 mL). After having been refluxed for 1 hr, the reaction mixture was filtered to remove a small amount of insoluble substance. The solvent was evaporated from the filtrate, and the crude product that remained was recrystallized from a mixed solvent of dichloromethane with petroleum ether to give triphenylbismuth disulfonate (**3a**, 0.69g, 88%), mp. 189-192°, lit.[a] 190-194°.

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