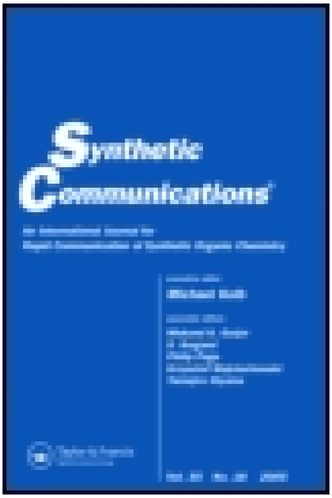

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

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To cite this article: J. Liming & H. Xian (1994) A Novel Synthesis of Triarylbismuth Dihaloacetates, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 24:7, 989-992, DOI: 10.1080/00397919408020774

To link to this article: http://dx.doi.org/10.1080/00397919408020774

SYNTHETIC COMMUNICATIONS, 24(7), 989-992 (1994)

A NOVEL SYNTHESIS OF TRIARYLBISMUTH DIHALOACETATES

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Abstract: Triarylbismuth dihaloacetates were prepared in good yields through carboxylic group — transformation. The method had advantages of simple manipulation, nonusage of silver salt and mild conditions.

Pentavalent organobismuth compounds are important reagents in organic synthesis. For example, the arylbismuth reagents of the type Ar_3BiX_2 are mild and efficient oxidizing agents for a wide range of primary, secondary, allylic, and benzylic alcohols.[1,2] However, it is notable that a mild and selective arylating method by bismuth reagents has been developed in the past ten years. The arylation of a variety of substrates, such as phenols, alcohols, enols and so on, have been realized by the arylbismuth derivatives, among which the Ar_3BiX_2 type was often used ($X = Cl, OAc, OCOCF_3, X_2 = CO_3$, etc.)[3]. Although there were several ways to get triarylbigmuth diacetates,[4,5] yet to our knowledge, triarylbismuth dihaloacetates were prepared by only one method in which triarylbismuth dihalides reacted with silver haloacetates.[6] The defect of the method is the usage of toxic silver salt that is usually made unconviently.

Because of easy achievement of triarylbismuth diacetates, we try to react halogenated acetic acid, which is strongly acidic, with the highvalent bismuth compounds directly in order to develop a novel synthesis of triarylbismuth dihaloacetates. Experiments showed that the following carboxylic group—transformation reaction took place readily at room temporature with good yields(Tabie 1).

$$Ar_3Bi(OAc)_2 + RCOOH \xrightarrow[r.t]{CH_2Cl_2} Ar_3Bi(O_2CR)_2$$

$$(R=CF_3, CCl_3, CHCl_2, CHCl_2, CH_2Br, CH_2CN;\ Ar=C_6H_5, 4-CH_3C_6H_4)$$

Table 1. Triarylbismuth Dihaloacetates through Carboxylic group—Translation

Entry	Product		Reatton time	M. P. (℃)		Yield(%)
	Ar	R	(min)	Found	Lit.[6]	
a	C_6H_5	CF_3	30	143—4	133	95
b	C_6H_5	CCl_3	60	160	158	91
c	C_6H_5	$CHCl_2$	60	119—119.5	118.9	82
d	C_6H_5	CH_2Cl	60	169(dec)	166	82
e*	$4-CH_3C_6H_4$	CF_3	30	178(dec)		81.5
f*	$4-CH_3C_6H_4$	CH_2Br	60	146—7		80.7
g	C_6H_5	CH_2Br	60	167—9	171—2	81
h	C_6H_5	CH_2CN	60	126—7	125—4	80

* Satisfactory elemental analysis resolts have been obtained;C±0.16, H±0.05

Compared with the reported method,[6] our present one has the advantages of mild conditions, manipulative convenience, good yields and the nonusage of toxic silver salt. So it would be convenient synthesis for triarylbismuth dihaloacetates.

Table 2. Spectral Data of the Products, $Ar_3Bi(O_2CR)_2$

Ertry	IR(KBr, cm—1)	^{1}H—NMR(CDCl$_3$3/TMS, ppm)
a	1685,1325	7.50—8.17(m. ArH)
b	1665,1320	17.50—8.22(m. ArH)
c	1635,1355	5.68(s,1H), 17.42—8.33(m,15H)
d	1650,1358	3.77(s,2H),7.45—8.17(m,15H)
e	1690,1315	2.40(s,9H);7.42—8.05(q,12H)
f	1645,1335	2.40(s,9H);3.10(s,4H)、7.37—8.05(q,12H)
g	1648,1345	3.13(s,4H);7.57—8.20(m.15H)
h	1630, 1345	3.62(s,4H). 7.53—8.22(m,15H)

Triphenylbimuthine, tris (4 — methylpbenyl) bismuthine,[4] triphenylbismuth diacetates and tris(4—methylphenyl)bismuth diacetates[5-7] were prepared by the reported methods.

Typical procedure: To a stirred turbid solution of triphenyl—bismuth diacetates(1mmol) in methylene dichloride(20mL) is added trifluoroacetic acid (2.1mml) at room temperature. The solution becomes clear gradually in 30 minutes and the reaction mixture is filtered to remove a small amount of insoluble substances. The solvent is distilled and the crude products are purified with recrystallization (CH_2Cl_2/pet. ether) to give crystals after being cooled in a refrigerator, 0.63g, mp143—4℃, yield: 95%.

Acknowledgment: This research was supported by the Natural Science Foundation of China and by the Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences.

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(Received in the UK 01 September 1993)