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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 ($\text{X} = \text{Cl}, \text{OAc}, \text{OCOCF}_3, \text{X}_2 = \text{CO}_3$, etc.)³. Although there were several ways to get triarylbismuth 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 unconveniently.

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 temperature with good yields (Table 1).

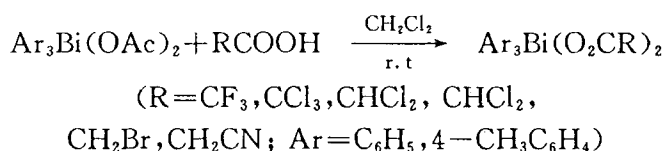


Table 1. Triarylbismuth Dihaloacetates through Carboxylic group—Translation

| Entry | Product | | Reaction time (min) | M. P. (°C) | | Yield (%) |
|-------|---|--------------------|------------------------|------------|-------------------|-----------|
| | Ar | R | | Found | Lit. ⁶ | |
| a | C ₆ H ₅ | CF ₃ | 30 | 143–4 | 133 | 95 |
| b | C ₆ H ₅ | CCl ₃ | 60 | 160 | 158 | 91 |
| c | C ₆ H ₅ | CHCl ₂ | 60 | 119–119.5 | 118.9 | 82 |
| d | C ₆ H ₅ | CH ₂ Cl | 60 | 169(dec) | 166 | 82 |
| e* | 4-CH ₃ C ₆ H ₄ | CF ₃ | 30 | 178(dec) | | 81.5 |
| f* | 4-CH ₃ C ₆ H ₄ | CH ₂ Br | 60 | 146–7 | | 80.7 |
| g | C ₆ H ₅ | CH ₂ Br | 60 | 167–9 | 171–2 | 81 |
| h | C ₆ H ₅ | CH ₂ CN | 60 | 126–7 | 125–4 | 80 |

* Satisfactory elemental analysis results 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, $\text{Ar}_3\text{Bi}(\text{O}_2\text{CR})_2$

| Ertry | IR(KBr, cm^{-1}) | ^1H -NMR(CDCl_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) |

Triphenylbismuthine, tris (4 — methylphenyl) 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 ($\text{CH}_2\text{Cl}_2/\text{pet. ether}$) to give crystals after being cooled in a refrigerator, 0.63g, mp143—4°C, yield: 95%.

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