## Arylation of aliphatic alcohols with tri-*p*-tolylbismuth and tri-*p*-tolylbismuth diacetate in the presence of a copper salt

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Tri-*p*-tolylbismuth diacetate in the presence of a catalytic amount of a copper(II) salt (1 : 0.02, mol/mol) and tri-*p*-tolylbismuth in the presence of copper diacetate (1 : 2) replace the hydrogen atom of the hydroxyl groups of methanol and butanol with a tolyl group at 80 °C in up to 90 % yields.

**Key words:** tri-*p*-tolylbismuth, tri-*p*-tolylbismuth diacetate, arylation; copper diacetate; methanol, butanol; alkyl tolyl ethers.

Triphenylbismuth diacylates phenylate aliphatic alcohols in the presence of catalytic amounts of copper(II) salts at ~20 °C (reaction (1)) to give the corresponding ethers in a high yields (up to 90 %).<sup>1,2</sup>

$$Ph_{3}Bi(OC(O)R)_{2} + R'OH \xrightarrow{Cat} R'OPh +$$
(1)  
+ RC(O)OH + Ph\_{2}BiOC(O)R

R = Me, Et, Ph; R' = Et, Bu, Pr<sup>i</sup>, C<sub>5</sub>H<sub>11</sub><sup>i</sup>, cyclo-C<sub>6</sub>H<sub>11</sub>, Ph, H

Aliphatic alcohols are phenylated (alkylated) by triphenyl-, tributyl-, and tribenzylbismuth in the presence of copper diacetate. However, these reactions only occur at a fixed molar ratio, *viz.*, OMC :  $Cu(OAc)_2 = 1 : 2$  (reaction (2)),<sup>3-5</sup> where OMC is an organometallic compound.

$$R_{3}Bi + R'OH + 2 Cu(OAc)_{2} \longrightarrow (2)$$

$$\longrightarrow R'OR + RH + RBi(OAc)_{2} + 2 CuOAc$$

$$= Ph, Bu, Bu', PhCH_{2}$$

R

The yields of alkyl phenyl ethers are close to 100 %, while dialkyl ethers are obtained in 10-25 % yields.

The purpose of the present work is to investigate the arylation of aliphatic alcohols with tri-*p*-tolylbismuth and tri-*p*-tolylbismuth diacetate. The latter was synthesized using the procedure described earlier<sup>6,7</sup> by the reaction of tri-*p*-tolylbismuth with acetic acid in the presence of *tert*-butylhydroperoxide at ~20 °C (reaction (3)).

$$p - \text{Tol}_{3}\text{Bi} \xrightarrow{\text{ButOOH}} [p - \text{Tol}_{3}\text{Bi}(\text{OH})\text{OBut}] \xrightarrow{2 \text{ AcOH}} p - \text{Tol}_{3}\text{Bi}(\text{OAc})_{2} + \text{ButOH} + \text{H}_{2}\text{O}$$
(3)  
$$(p - \text{Tol} = p - \text{MeC}_{6}\text{H}_{4})$$

Tri-*p*-tolylbismuth diacetate is a colorless crystalline compound soluble in chloroform and insoluble in hydrocarbons. In a capillary, this compound is noticeably decomposed in the 148–155 °C temperature range, although according to the published data<sup>8</sup> its m.p. is 162 °C. The product was characterized by elemental analysis data and IR spectrum, and its molecular weight was determined. In a solution of *o*-xylene at 80 °C, tri*p*-tolylbismuth diacetate decomposes after 8 h to give tolylacetate in a yield of 0.81 mol per mol of starting compound. Under similar conditions, but in the absence of a solvent, the yield of the ether was 0.21 mol. In the presence of a catalytic amount of copper diacetate (2 %), the decomposition is accelerated.

The obtained results indicate that the reductive decay of tri-*p*-tolylbismuth diacetate occurs (reaction (4)).

$$p - \text{Tol}_3 \text{Bi}(\text{OAc})_2 \longrightarrow p - \text{Tol}_2 \text{BiOAc} + p - \text{TolOAc}$$
 (4)

p-Tolylbismuth diacetate and tri-p-tolylbismuth were identified among the reaction products. These compounds form due to the symmetrization of di-p-tolylbismuth acetate.

The arylation activity of tri-*p*-tolylbismuth diacetate was studied using primary aliphatic alcohols, *viz.*, methanol and butanol, in the presence of a catalytic amount of copper(11). The results obtained are given in the Table 1. Under the reaction conditions, no products of the thermal decay of the starting OMC are formed, while the replacement of the active H atom in the alcohols with a tolyl group takes place to give the corresponding alkyl tolyl ether (the yield is 57–78 %) according to reaction (1). In the case of more effective catalyst, the copper dipelargonate, the yelds of ethers increase up to 71-90 % (see Table 1). In parallel to reaction (1), the dearylation of OMC of bismuth(111) with acetic acid occurs to yield toluene (reaction (5), see Table 1).

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**Table 1.** Products of the reaction of tri-*p*-tolylbismuth diacetate with alcohols in the presence of catalytic amounts of copper(II) salts (OMC :  $Cu^{II}$  salt = 1 : 0.02, mol/mol; 80 °C, 8 h)

Alcohol	Copper(II) salt	Yield of products (mol per mol of OMC)				
		p-TolOR	TolH	AcOH		
BuOH	Cu(OAc) <sub>2</sub>	0.57	1.37	0.86		
BuOH	$Cu(O_2C_9H_{17})_2$	0.71	1.15	0.61		
MeOH	$Cu(OAc)_2$	0.78	1.15	0.35		
MeOH	$Cu(O_2C_9\tilde{H}_{17})_2$	0.90	1.71	0.72		

## p-Tol<sub>2</sub>BiOAc + AcOH $\longrightarrow p$ -TolBi(OAc)<sub>2</sub> + TolH (5)

This reaction of bismuth phenyl derivatives has been studied earlier in detail,<sup>4</sup> and the factors affecting the competitive processes (1) and (5) have been revealed.

Similarly to tri-*p*-tolylbismuth diacetate, tri-*p*-tolylbismuth replaces the H atom in alcohols with a tolyl group in the presence of copper diacetate and when OMC :  $Cu^{II}$  salt = 1 : 2.

The data given in Table 2 indicate that the maximum yield of the alkyl tolyl ether (0.62 mol per mol of the starting OMC) is obtained in neat methanol; the yield of the ether in butanol is somewhat lower. A similar correlation of the activities of methanol and butanol was also observed in the case of their phenylation<sup>4</sup> and alkylation.<sup>5</sup>

We believe that, in both alkylation and arylation of alcohols, the reagent responsible for the formation of ethers is a copper(III) compound,  $RCu(OAc)_2$  (R = PhCH<sub>2</sub>, Ph, *p*-Tol), which forms during the reaction. According to the literature data,<sup>1,4</sup> this compound is formed as a result of the reaction between a bismuth(III,v) OMC and a copper(II) salt. The reaction of the Cu<sup>III</sup> compound with an alcohol yields an ether (reaction (6)).

$$[RCu(OAc)_2] + AlkOH \longrightarrow ROAlk + CuOAc + AcOH (6)$$

 $R = Ph, PhCH_2, p-Tol$ 

A comparison of the results obtained for the arylation and alkylation of alcohols with systems such as  $Ar_3Bi(OAc)_2 + Cu(OAc)_2$  (1 : 0.02), where Ar = Ph,

**Table 2.** Products of the reaction of tri-*p*-tolylbismuth with alcohols in the presence of copper diacetate (OMC :  $Cu^{II}$  salt = 1 : 2, mol/mol; 80 °C, 8 h)

Alcohol	Solvent	Yield of products (mol per mol of OMC)		
		p-TolOR	TolH	AcOH
МеОН		0.62	0.65	0.60
BuOH	_	0.38	1.02	1.10
MeOH	Toluene	0.38		0.48
BuOH	Toluene	0.09	_	0.28

*p*-Tol, and  $R_3Bi + Cu(OAc)_2$  (1 : 2), where R = Ph, *p*-Tol, PhCH<sub>2</sub>, shows that the reactivity of the tolyl derivatives is lower than the reactivity of the phenyl derivatives, but is higher than the reactivity of the benzyl analogs.

The obtained results are probably a reflection of the stability of the intermediate copper(III) compounds. In the case of the aryl derivatives, stabilization due to the transfer of the ring  $\pi$ -electrons to the vacant orbitals of the Cu atom takes place. In addition, the back transfer of the copper d-electrons to the anti-bonding  $\pi^*$ -orbitals of the aryl group occurs. Electron-donating substituents in the aromatic ring increase the energy of these orbitals<sup>9</sup> and thus retard back electron transfer. Therefore, the stability of the tolyl derivatives of copper(III) is lower than that of the phenyl analogs. In the case of a benzyl derivative, this stabilization does not take place.

## Experimental

**Tri-***p***-tolylbismuth diacetate.** A mixture of acetic acid (4 mmol) and *tert*-butylhydroperoxide (2 mmol) in benzene (5 mL) was quickly added dropwise to tri-*p*-tolylbismuth (2 mmol) in benzene (12 mL) with stirring and cooling to 0 °C. The reaction mixture was stirred for 1 h with cooling, 1 h at room temperature, and was stored for 24 h in a refrigerator. The liquid products were removed under reduced pressure, and the solid residue was dissolved in chloroform (6 mL). After adding hexane and cooling, tri-*p*-tolylbismuth diacetate was formed as crystals in 57 % yield. Found (%): C, 48.51; H, 4.45; Bi, 33.68; AcO, 18.70 (by hydrolysis with phosphorus acid<sup>10</sup>); M = 650. C<sub>25</sub>H<sub>27</sub>BiO<sub>4</sub>. Calculated (%): C, 50.00; H, 4.50; Bi, 34.80; AcO, 19.67; M = 600.

Thermal decay of tri-*p*-tolylbismuth diacetate. In an evacuated tube with a branch pipe, tri-*p*-tolylbismuth diacetate (1 mmol) was heated at 80 °C. The liquid reaction products (tolyl acetate, toluene) were collected in the branch of the tube, which was cooled with liquid nitrogen, and analyzed by GLC. The mixture of solid products (tri-*p*-tolylbismuth and *p*-tolylbismuth diacetate) was dissolved in warm pentane, and the insoluble *p*-tolylbismuth diacetate was isolated. The products were identified by their melting points.

Reaction of tri-*p*-tolylbismuth diacetate with butanol. In an evacuated tube, a mixture of tri-*p*-tolylbismuth diacetate (1 mmol), copper diacetate (0.02 mmol), and butanol (5 mL) was heated for 8 h at 80 °C. The liquid products were analyzed by GLC.

Using analogous procedures, the reaction of tri-*p*-tolylbismuth diacetate with methanol and the reaction of tri-*p*-tolylbismuth with methanol and butanol were carried out.

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