Tetraphenylbismuth Monotrifluoroacetate: a New Reagent for Regioselective Aryl Ether Formation

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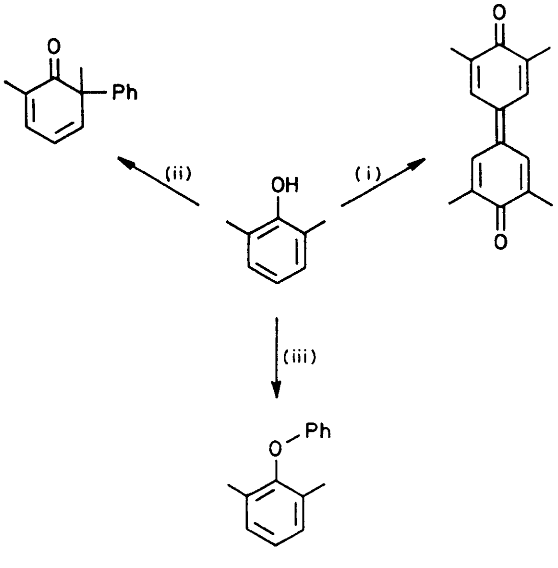
Summary Tetraphenylbismuth trifluoroacetate is a useful new reagent for selective formation of the aryl–oxygen bond, and in its reactivity complements the behaviour of other Bi^{V} arylating agents.

WE have recently shown that triphenylbismuth carbonate[1] and pentaphenylbismuth[2] are efficient arylating agents for enolates, phenols, and a variety of other ambident anions. Interestingly, the nature of the product formed is determined by the choice of organobismuth reagent as exemplified by the reactions of 2,6-dimethylphenol (Scheme). In order to account for the *ortho* specificity in the reaction of phenols with pentaphenylbismuth we have suggested the initial formation of the intermediate (**1**). We have also noted[2] that pentaphenylbismuth reacts with *p*-nitrophenol to give the diaryl ether. Consideration of these facts suggested to us that intermediates of type (**1**) (L = electron-withdrawing group) should undergo preferential reductive elimination and hence formation of an aryl–oxygen bond. We report herein the reactivity of tetraphenylbismuth trifluoroacetate which gives (**1**, L = $OCOCF_3$).



SCHEME. *Reagents:* i, Ph_3BiCO_3 (92%); ii, Ph_5Bi (72%); iii, $Ph_4BiOCOCF_3$ (58%).

Crystalline tetraphenylbismuth trifluoroacetate was readily prepared by addition (0 °C, 5 min) of trifluoroacetic acid (1 equiv.) to a solution of pentaphenylbismuth in benzene. The phenol was then added and the solution was heated (Table). The results confirm that smooth O-arylation is the principal reaction, in contrast with the results obtained before (Scheme). We have thus developed a convenient synthesis of unsymmetrical diaryl ethers.

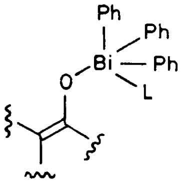
The intermediates (**1**, L = $OCOCF_3$) from reactions with tetraphenylbismuth trifluoroacetate were more stable thermally than those derived from reaction with pentaphenylbismuth (**1**, L = Ph). Thus, in the case of *p*-nitrophenol the same intermediate could be generated either by reaction with the trifluoroacetate or by sequential treatment with pentaphenylbismuth followed by trifluoroacetic acid (1 equiv.). The latter procedure gave an improved yield of aryl ether (70%).

TABLE. Reaction of phenols with tetraphenylbismuth monotrifluoroacetate in benzene.

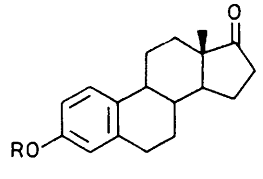
Phenol	T/°C	t/h	Product yield[a]/%
2-Naphthol	80	140	77[b,c]
2,6-Dimethylphenol	70	72	58[d,e]
2,3,5,6-Tetramethylphenol	80	24	57
Estrone (**2**)	80	12	68[f]
p-Nitrophenol	70	72	51[e]

[a] Yield of *O*-phenyl ether. [b] Product was 2-naphthyl phenyl ether (R. Huisgen and W. D. Zahler, *Chem. Ber.*, 1963, **96**, 747. [c] 1-Phenyl-2-naphthol (4%) also formed (R. Huisgen, E. A. Leander, and P. Otto, *Chem. Ber.*, 1969, **102**, 3405). [d] All new compounds were fully characterized by analytical and spectral data. [e] Starting material also recovered. [f] Estrone phenyl ether (**3**).

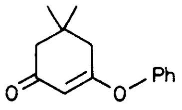
We have also studied the behaviour of other readily enolisable compounds. Although dimedone gave the expected monoaryl enol ether[3] (**4**) (55%), 2-ethoxycarbonylcyclohexanone yielded a mixture of the ether (36%) and 2-phenyl-2-ethoxycarbonylcyclohexanone (7%) by arylation on carbon. Reaction of the same β-keto-ester with tetraphenylbismuth acetate led only to the C-arylated product (40%), thus emphasising the role of the powerful electron-withdrawing trifluoroacetoxy-group.



(1)



(2) R = I
(3) R = Ph



(4)

Improved yields of mixed diaryl sulphides are obtained by reaction of aryl thiols with the monotrifluoroacetate, when compared with those reported with pentaphenylbismuth[2] (R = Ph, 70%; *o*-tolyl, 78%; *p*-tolyl, 80%).

Toluene-*p*-sulphinic acid reacts with either pentaphenylbismuth or with the derived trifluoroacetate at 80 °C to give high yields of *p*-tolyl phenyl sulphone (87 and 76% respectively). Remarkably, the same product can also be prepared by treatment of an *aqueous* solution of the sodium salt at 80 °C with triphenylbismuth carbonate (27%), the yield being limited by the instability of the sodium salt,[1] but not by that of the carbonate, in water.

A variety of procedures are now available for arylation reactions including the recently developed aryl lead tricarboxylates method[4] and the arylation of enolates by the $S_{RN}1$ mechanism,[5] both of which are economical in terms of aryl group transfer. We consider, however, that the formation of covalent Bi^{V} intermediates and the potential for controlled ligand variation allow the development of useful and regioselective reactions for those cases where the aryl group is inexpensive. In addition, Bi^{V} reagents permit the synthesis of highly hindered perphenylated compounds.[1,6]

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[3] I. Ia. Neiland, G. Ia. Vanag, and E. Iu. Gudrinietse, *Zh. Obshch. Khim.*, 1958, **28**, 1201.

[4] H. C. Bell, J. T. Pinhey, and S. Sternhell, *Aust. J. Chem.*, 1979, **32**, 1551; H. C. Bell, G. L. May, J. T. Pinhey, and S. Sternhell, *Tetrahedron Lett.*, 1976, 4303; J. T. Pinhey and B. A. Rowe, *Aust. J. Chem.*, 1979, **32**, 1561; *Tetrahedron Lett.*, 1980, **21**, 965; *Aust. J. Chem.*, 1980, **33**, 113; R. P. Kozyrod and J. T. Pinhey, *Tetrahedron Lett.*, 1981, **22**, 783.

[5] See *inter alia* R. Beugelmans and G. Roussi, *J. Chem. Soc., Chem. Commun.*, 1979, 950; R. Beugelmans and H. Ginsburg, *ibid.*, 1980, 508; R. Beugelmans, B. Boudet, and L. Quintero, *Tetrahedron Lett.*, 1980, **21**, 1943 and references there cited.

[6] D. H. R. Barton, W. B. Motherwell, and M. T. Barros Papoula, in preparation.