Comparative Arylation Reactions with Pentaphenylbismuth and with Triphenylbismuth Carbonate

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Summary Pentaphenylbismuth is a useful reagent for the specific *ortho*-phenylation of phenols under very mild conditions, a comparison of this reagent with triphenylbismuth carbonate being drawn; arylation reactions of the carbonate have been extended to include nitro-compounds and amides.

THE facile cleavage of the bismuth–phenyl bond in triphenylbismuth carbonate has enabled us to develop a useful method for direct arylation of the carbonyl group[1] and to achieve the arylation of 2-naphthol [arylation by 1-Ph, 76%, triphenylbismuth carbonate; 1-(*p*-tolyl), 72%, tri(*p*-tolyl)bismuth dibenzoate].

However, attempted introduction of a second phenyl group into 1-phenyl-2-naphthol leads to the formation of the unsymmetrical (^{13}C n.m.r.) yellow crystalline dimer (**1**) (91%), and reaction of 2,6-dimethylphenol with the carbonate gives 2,2′,6,6′-tetramethylbiphenoquinone[2] (92%), presumably by phenolic radical coupling.

Since these arylation reactions involve the possible intermediacy of a five-valent bismuth species (**2**, L = carbonate derived), it was of interest to investigate the influence of the fifth ligand (L) on the course of the reaction. We report herein a comparison of the reactivity between triphenylbismuth carbonate and pentaphenylbismuth. The latter reagent, readily prepared by the reaction of triphenyl-

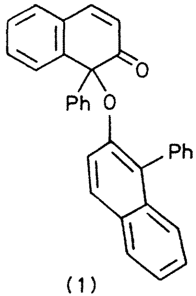
TABLE

Phenol	Products	Yield/%
2-Naphthol	1-Phenyl-2-naphthol[a]	61
1-Naphthol	2-Phenyl-1-naphthol[b]	48
2,6-Dimethylphenol	6-Phenyl-2,6 dimethylcyclohexa-2,4-dienone[c]	72
4-t-Butyl-2,6-dimethylphenol	4-t-Butyl-6-phenyl-2,6-dimethylcyclohexa-2,4-dienone	51
2,3,5,6-Tetramethylphenol	6-Phenyl-2,3,5,6-tetramethylcyclohexa-2,4-dienone	82
2,4-Dimethylphenol	2,4 Dimethyl-2,6-diphenylcyclohexa-2,4-dienone	21
	2,4-Dimethyl-6-phenylphenol[d]	26
(**3**)	2,4-Diphenylestrone	14
	4-Phenylestrone	13
	2,4-Diphenylestradiol	12
Estrone	4-Phenylestrone	18
	2,4-Diphenylestrone	41
p-Nitrophenol	4-Nitrophenyl phenyl ether	42

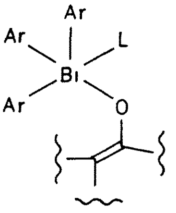
[a] R Huisgen, E A Leander, and P Otto, *Chem Ber*, 1969, **102**, 3405 [b] Characterised as the *p*-nitrobenzoate H Hopff and P Thalmann, *Chimica*, 1959, **13**, 101 [c] All new compounds were fully characterised by analytical and spectral data [d] The naphthylurethane derivative was prepared A Nickon and B R Aaronhoff, *J Org Chem*, 1962, **27**, 3379

bismuth dichloride with phenyl-lithium,[3] can be stored for several months at −20 °C Its chemistry has been little studied before

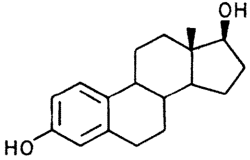
Accordingly, a variety of phenols (Table) were treated at room temperature in dichloromethane or benzene with pentaphenylbismuth On addition of the reagent, the purple colour was immediately discharged with presumed formation of intermediate (**2**, L = Ph) The isolation of 2-phenyl-1-naphthol is noteworthy, since reaction of 1-naphthol with triphenylbismuth carbonate led to an intractable mixture of products The method clearly provides a convenient route to a variety of 6-phenylcyclohexa-2,4-dienones, particularly for phenols possessing two *ortho*-methyl groups This class of compounds is not easy to prepare by known routes The reaction of 2,4-dimethylphenol occurs *via* the intermediacy of 2,4-dimethyl-6-phenylphenol Thus, the observed pattern of substitution and the marked regiospecificity for exclusive formation of *ortho*-cyclohexadienones distinguish the reagent from the more electrophilic aryl-lead tricarboxylates[4] Initial phenylation of estradiol (**3**) in the 4-position was confirmed by 400 MHz n m r spectra ($J_{1,2}$ 8 Hz) Interestingly, reaction of *p*-nitrophenol proceeded *via* reductive elimination of the intermediate and formation of 4-nitrodiphenyl ether The isolation of diphenyl ether by reaction of phenol with pentaphenylbismuth has been described[5]



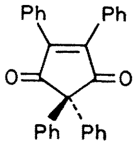
(1)



(2)



(3)



(4)

Although treatment of phloroglucinol with pentaphenylbismuth gave a complex mixture of products, reaction with an excess of triphenylbismuth carbonate yielded the perphenylated ene-dione (**4**) (60%) 2,4,6-Triphenylphloroglucinol was also isolated from this reaction and shown to be an intermediate

We have also briefly examined the behaviour of other functional groups with pentaphenylbismuth As noted in the phenylation of estradiol, we have confirmed an isolated report[5] that the reagent can function as an oxidant for the hydroxy-group Thus, oxidation of benzyl alcohol and cholestanol gave the corresponding carbonyl compounds in modest yield (45%) Interestingly, oxidation of 2-phenylethanol was followed by phenylation of the readily enolised aldehyde to give, ultimately, triphenylacetaldehyde[6] (14%) 2-Phenyl-2-ethoxycarbonylcyclohexanone can be readily prepared from the appropriate β-keto ester (57%) Additionally, we have now shown that both pentaphenylbismuth and triphenylbismuth carbonate react with 2-nitropropane to afford 2-phenyl-2-nitropropane[7] in 25 and 80% yield respectively The reaction of aryl thiols, RSH, with triphenylbismuth carbonate consistently yields the derived disulphide (R = Ph, 70%, *o*-tolyl, 90%, *p*-tolyl, 89%), whereas the intermediate formed from pentaphenylbismuth undergoes preferential reductive elimination to give the mixed diaryl sulphide RSPh (R = Ph, 65%, *o*-tolyl, 47%, *p*-tolyl, 32%)

Attempted phenylation of the potassium enolate of cholestanone with pentaphenylbismuth gave only minor amounts of phenylated product, thus indicating that the availability of a relatively acidic proton in the substrate is necessary for reaction with pentaphenylbismuth On the other hand, the carbonate, by possessing a leaving group capable of sustaining a negative charge, is not subject to such constraints We have therefore extended arylation reactions of triphenylbismuth carbonate to the amide group Treatment of the sodio-salt of acetanilide with the carbonate in refluxing dioxan gave *NN*-diphenylacetamide (90%) *N*-Phenyl-*N*-methylbenzamide was similarly prepared from *N*-methylbenzamide (90%).

It is thus apparent that a useful degree of control over product formation can be exercised in organobismuth chemistry by ligand variation

A facile arylation reaction of malonic acid derivatives with aryl-lead triacetates has recently been reported by Pinhey and Rowe[8]

We consider that the arylation reactions of Bi^V species do not involve free aryl radicals (no quenching with Et_3SiH) and support the mechanism previously presented.[1]

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