The Chemistry of Pentavalent Organobismuth Reagents. Part 7.† The Possible Role of Radical Mechanisms in the Phenylation Process for Bismuth(V), and Related Lead(IV), Iodine(III), and Antimony(V) Reagents

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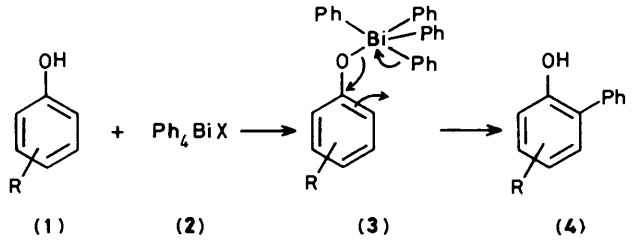
The phenylation reactions of bismuth(V), lead(IV), and iodine(III) have been examined to test the presence or absence of phenyl radicals. In the case of several bismuth(V) reactions the presence of phenyl radicals has been detected, but it has been shown, by use of a large excess of radical trapping agent, that these radicals have nothing to do with the phenylation process. In the same way, the other phenylation reactions fail to respond to a large excess of a radical trap.

We have recently shown that reagents based on arylated Bi^V can arylate, in particular phenylate, many anions with remarkable efficiency.[1-3] Two mechanisms have been proposed. The first involves the formation of an O–Bi bonded intermediate and has been well demonstrated in the case of phenols (Scheme 1). Thus

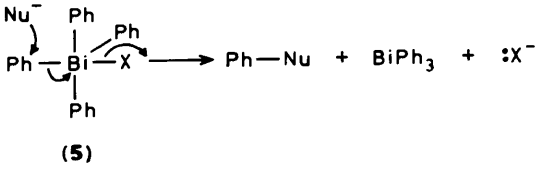


(1) (2) (3) (4)

Scheme 1.

a phenol (**1**) in the presence of base reacts with a Bi^V reagent like (**2**; X = $OCOCF_3$) to give an intermediate (**3**). In certain cases the intermediate has been fully characterised. When heated, the intermediate (**3**) decomposes to give (**4**) with exclusive phenylation in the *ortho* position. However, when the phenol contains electronegative groups the intermediate undergoes a different rearrangement to give *O*-phenylated compounds.

A second mechanism occurs in the absence of base and leads to *O*-phenylation without formation of an intermediate. It can be represented by the nucleophilic substitution shown in Scheme 2.



(5)

Scheme 2.

These two mechanisms were not proposed without consideration being given to the possible involvement of phenyl radicals, especially as such a mechanism has been proposed in diphenyliodonium chemistry [4] (*vide infra*).

A standard technique for the detection of phenyl radicals is to add a spin trap like phenyl-t-butylnitrone and to examine any trapped radical in the e.s.r. spectrum. We started with the base-catalysed phenylation[3] of tetraphenylacetone (**6**) to give pentaphenylacetone (**7**) using tetraphenylbismuth toluene-*p*-sulphonate as phenylating agent in tetrahydrofuran (THF) under argon at room temperature. The base used was *N*-t-butyl-*N'*,*N''*-tetramethylguanidine (BTMG).[5] A good yield of pentaphenylacetone (88%) was obtained (Table 1.).

Table 1. Phenylation of 1,1,3,3-tetraphenylacetone (**6**) with tetraphenylbismuth tosylate (**2**; X = Ts)[a]

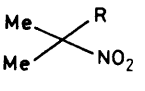
Entry	Substrate (**6**) (Equiv.)	(**2**; X = Ts) and BTMG (Equiv.)	PhNO (Equiv.)	(**7**) (%)	PhNHAc (%)	Ph_2NAc (%)
1	1	2	0	88		
2	1	2	2	90	83[b,c]	3[b,c]
3	0	2	2		87[b,c]	3[b,c]

[a] All reactions were performed in anhydrous THF at room temperature under argon with *N*-t-butyl-*N'*,*N''*-tetramethylguanidine (BTMG) as base. [b] Yields of (**7**) are isolated yields. Yields of PhNHAc and of Ph_2NAc are after reductive acetylation (see Experimental section). [c] All e.s.r. studies were done in the dark.

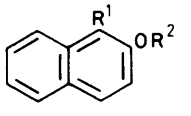
When phenyl-t-butylnitrone was added to this reaction in benzene a triplet of doublets was seen in the e.s.r. spectrum (g = 2.0061 ± 0.0004, A_N = 14.49 ± 0.05, A_H = 2.25 ± 0.05). This spectrum was identical with the spectrum obtained by phenyl radical addition.[6] In addition, the same spectrum was seen in the absence of the tetraphenylacetone, but was not observed in

(**6**) R = H
(**7**) R = Ph

(**8**) R = H
(**9**) R = Ph



(**13**) R = H
(**14**) R = Ph



(**10**) R^1 = R^2 = H
(**11**) R^1 = Ph, R^2 = H
(**12**) R^1 = H, R^2 = Ph

† Part 6, D. H. R. Barton, N. Yadav Bhatnagar, J.-P. Finet, and W. B. Motherwell, *Tetrahedron*, 1986, **42**, 3111.

the absence of the Bi^V reagent. A similar spectrum was also obtained when the reaction was performed in THF (g = 2.0062 ± 0.0004, A_N = 14.52 ± 0.05, A_H = 2.48 ± 0.05).

This is, of course, evidence for the generation of phenyl radicals, but does not indicate the quantity generated nor the role that they play in the phenylation process. We decided to use a large excess of a suitable trap, such that the phenyl radicals would all be diverted and little or no formation of pentaphenylacetone would be seen.[7]

For reasons of analytical convenience we took nitrosobenzene as trap and worked out a procedure whereby reductive acetylation of the total product with iron–acetic acid–acetic anhydride gave acetanilide, from unchanged nitrosobenzene, and *N*,*N*-diphenylacetamide from spin trapped phenyl radicals ($Ph_2NO\cdot$). It was easy to separate the products.

As can be seen from Table 1 the percentage of phenyl trapped as radical is very low, both in the presence and absence of the ketone. The yield of phenylated ketone is, however, unchanged. In the absence of the ketone the yield of phenyl radical adduct with nitrosobenzene is time-dependent: 3% after 3 h and 11% after 12 h. We conclude, therefore, that phenyl radicals, although present in small quantity, are *not* involved in the phenylation mechanism.

In the case of entries 2 and 3 (Table 1) the spin concentration was measured in the e.s.r. spectrum and compared with an authentic solution of diphenylpicrylhydrazyl (DPPH). The signal increased steadily during the reaction and after 3 h represented 2—3% yield in agreement with the quantity of *N*,*N*-diphenylacetamide isolated. The signal observed in the phenylation reaction (g = 2.0061 ± 0.0004, A_N = 9.78 ± 0.05, A_{H_o} = 1.85 ± 0.05, A_{H_m} = 0.83 ± 0.05) was identical with that of diphenylnitroxyl[8] prepared by a known method. We checked that nitrosobenzene in the dark gave no signal and also that the substrate (**6**) with nitrosobenzene and BTMG behaved likewise. However, at a higher gain, a poorly resolved triplet appeared which was similar to that seen from BTMG and nitrosobenzene in tetrahydrofuran (THF).[9]

The second phenylation process that we examined was the conversion[3] of 2-ethoxycarbonylcyclohexanone (**8**) to its 2-phenyl derivative (**9**) (Table 2). Two phenylating reagents were used, pentaphenylbismuth and tetraphenylbismuth tosylate (**2**; X = Ts) in the presence of *N*-t-butyl-*N*′,*N*″-tetramethylguanidine (BTMG). The phenylation with pentaphenylbismuth in benzene (neutral conditions) gave no evidence of a radical process. In 1 h the reaction was complete with or without a large excess of nitrosobenzene. Phenylation under basic conditions with tetraphenylbismuth tosylate also gave no indication of the participation of phenyl radicals.

The extensive work of Beringer and his colleagues[10] on arylation with diaryl (especially diphenyl) iodonium salts suggests that radicals are readily generated in this system. We noted the careful work[11] of McEwen *et al.* showing the existence of two mechanisms, one an induced radical-chain process producing aromatic hydrocarbon (Ar·→ArH) and another of the type indicated in (**5**) (Scheme 2) affording ArOEt by a non-radical S_N2 process. The radical-chain process was inhibitable by radical traps like 1,1-diphenylethylene.

Because the reaction with diphenyliodonium salts is much slower than phenylation with Bi^V reagents, reactions must be carried out at a higher temperature (boiling t-butyl alcohol, 83 °C). The results in Table 3 (entries 1—3) are comparable to those reported[10] by Beringer *et al.* giving 50—60% of phenylation. At 83 °C nitrosobenzene decomposes rapidly and cannot be used as a spin trap. We, therefore, followed the precept of McEwen[11] and of Walborsky[12] and used 1,1-diphenylethylene. As already reported[11] this trap improved the reaction and gave an 80% yield of phenylated product. We agree with the literature[11] that this phenylation reaction does not involve radicals. It is radical induced decomposition of the reagent which takes place in the absence of a trap. A signal is observed in the presence of the trap (g = 2.0027 ± 0.0004, $A_{H\text{-}\beta}$ = 9.40 ± 0.05) and can be attributed to the expected radical[13] from Ph· addition to 1,1-diphenylethylene. However, we have used an excess of trap which has been largely recovered (87%). A phenyl radical mechanism is thus excluded.

Since *N*-nitrosoacetanilide (NNA) decomposes in solution by two competing routes (ionic and radical), addition of a radical trap promotes the ionic pathway.[14] 1,1-Diphenylethylene (DPE) is the most efficient trap. When 1,1-diphenylethylene was added to a solution of NNA in THF, triphenylethylene was isolated from the mixture, although in a low yield (2% with 2 equiv. of DPE, and 5% with 3 equiv. of DPE). The trapping

Table 2. Phenylation of 2-ethoxycarbonylcyclohexanone (**8**) with Bi^V reagents[a]

Entry	(**8**) (Equiv.)	BTMG (Equiv.)	Bi^V (Equiv.)	PhNO (Equiv.)	Solvent	(**9**) (%)	PhNHAc (%)[b]	Ph_2NAc (%)[b]
1	1	0	(**2**; X = Ph) (1.5)	0	PhH	91		
2	1	0	(**2**; X = Ph) (1.5)	2	PhH	80	88	5
3	0	0	(**2**; X = Ph) (1.5)	2	PhH		84	1
4	1	1.5	(**2**; X = Ts) (1.5)	0	THF	91		
5	1	1.5	(**2**; X = Ts) (1.5)	2	THF	83	89	2
6	0	1.5	(**2**; X = Ts) (1.5)	2	THF		90	1

[a] All reactions were performed in anhydrous solvents for 1 h at room temperature under argon. [b] Yields of products after reductive acetylation (see Experimental section).

Table 3. Phenylation of 2-ethoxycarbonylcyclohexanone (**8**) with diphenyliodonium salts

Entry	(**8**) (Equiv.)	Base (Equiv.)	$Ph_2I^+X^-$ X (Equiv.)	DPE[c]	Reaction time (h)	(**9**) (%)	Recovered trap (%)
1	1	BTMG (1.5)	Cl (3)		4	63	
2	1	HMDS,Na[b] (2)	Cl (2.5)		20	60	
3	1	BTMG (1.1)	AcO (2)		2	55	
4	1	BTMG (1.1)	AcO (2)	2	2	80	87

[a] All reactions performed in t-butyl alcohol, under reflux. [b] HMDS,Na = sodium bis(trimethylsilyl)amide. [c] DPE = 1,1-diphenylethylene.

efficiency of nitrosobenzene was proven when NNA was decomposed in its presence. After reductive elimination, *N,N*-diphenylacetamide was obtained in a yield corresponding to 40% trapped phenyl radicals. The efficiency of 1,1-diphenylethylene as a phenyl radical trap was better indicated when phenyldiazonium tetrafluoroborate was treated with metallic copper and 1,1-diphenylethylene in DMF. A 43% yield of triphenylethylene was then obtained.

An important series of papers[15] by J. T. Pinhey and his collaborators has shown the value of aryl-lead tricarboxylates for the electrophilic phenylation of oxoesters like (**8**) and *its* congeners. To aid comparison we used phenyl-lead triacetate and studied the phenylation of (**8**) in the presence of pyridine with chloroform as solvent as used by Pinhey *et al.*[15] The results are shown in Table 4. The reaction was slow at 40 °C and required 15 h. The yield was the same in the presence and in the absence of a large excess of 1,1-diphenylethylene as spin trap. Again a radical mechanism is excluded.

2-Nitropropane is phenylated efficiently by Bi^V reagents under basic conditions.[3] We examined in the usual way (Table 5) the effect of 1,1-diphenylethylene and of oxygen at 20 °C on this reaction using the usual guanidine base and tetraphenylbismuthtoluene-*p*-sulphonate or triphenylbismuth dichloride. The 2-phenyl derivative was formed in excellent yield and the two traps had no effect on the reaction.

We have studied extensively the arylation of phenols by Bi^V reagents.[2] We selected 2-naphthol (**10**) as a suitable phenol for radical-trapping experiments. Under basic conditions it is phenylated in high yield[2] to 1-phenyl-2-naphthol (**11**). The results are summarised in Table 6. Phenylation in the presence of the guanidine base at room temperature gave a high yield of (**11**) in 1 h. The addition of an excess of nitrosobenzene did not alter the yield and the usual small percentage of trapping of phenyl radicals is seen in the amount of *N,N*-diphenylacetamide isolated.

Under neutral conditions *O*-phenylation to give phenyl 2-naphthyl ether (**12**) is expected.[2] This reaction is much slower and requires heating in benzene under reflux for 15 h. We used, therefore, 1,1-diphenylethylene as spin trap and in large excess. Again, it had no effect on the reaction and again a radical mechanism is excluded. Similarly, 3,5-di-t-butylphenol (**16**) and tetraphenylbismuth trifluoroacetate gave the phenyl ether (**17**), with the same yield in the presence or absence of 1,1-diphenylethylene (70—71%).

Diphenyliodonium chloride reacted also with (**16**) in the presence of BTMG to give the phenyl ether (**17**) (82%). The high yield shows that the competing radical pathway does not interfere significantly, as in the reaction with alkoxides.[10] Triphenylsulphonium bromide reacted also with (**16**) in the presence of BTMG to give the phenyl ether (40%). In the presence of 1,1-diphenylethylene a higher yield was obtained (65%)

In all these reactions, a radical mechanism can be excluded, and in the reaction of phenols with tetraphenylbismuth trifluoroacetate under neutral conditions, we favour[2] the mechanism shown in (**5**).

However *O*-phenylation of phenols substituted by electron-withdrawing groups in the *para* position with Bi^V reagents (Ph_5Bi or Ph_4BiX under basic conditions) occurs through a covalent Bi–O intermediate.[2] 4-Nitrophenoxytetraphenylbismuth gave 4-nitrodiphenyl ether (95%) in the presence or absence of 1,1-diphenylethylene. 4-Nitrophenoxytriphenylbismuth trifluoroacetate did not give the phenyl ether, but biphenyl (65%). When the thermal decomposition was performed in the presence of 1,1-diphenylethylene, the yield of biphenyl was not significantly modified (52% after ozonolysis). A radical mechanism can be again excluded, the reductive elimination must occur by a concerted process similar to the one involved in *C*-phenylation.

The sodium anion of 3-methylindole (**18**) reacted with

Table 4. Phenylation of 2-ethoxycarbonylcyclohexanone (**8**) with phenyl-lead triacetate in $CHCl_3$ at 40 °C

Entry	(**8**) (Equiv.)	$PhPb(OAc)_3$ (Equiv.)	Pyridine (Equiv.)	DPE (Equiv.)	Time (h)	(**9**) (%)
1	1	1.1	1.1	0	15	78
2	1	1.1	1.1	2	15	76

Table 5. Phenylation of 2-nitropropane (**13**) with Bi^V reagents

Expt. no.	(**13**) (Equiv.)	BTMG (Equiv.)	Bi^V (Equiv.)	Trap (Equiv.)	Time (h)	(**14**) (%)
1	1	1.5	(**2**; X = Tos) 1.5	0	2[a]	86
2	1	1.5	(**2**; X = Tos) 1.5	DPE (2)	2[a]	89
3	1	1.5	(**2**; X = Tos) 1.5	O_2[b]	2[a]	82
4	1	1.5	(**15**) 1.2	0	2	77
5	1	1.5	(**15**) 1.2	DPE (2)	2	78

[a] Reaction performed in THF at 40 °C, under argon; otherwise at room temperature. [b] A flow of oxygen was bubbled through the reaction mixture at a rate of 1 ml/s.

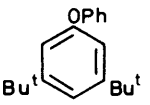
Table 6. Phenylation of 2-naphthol (**10**)

Entry	Base (Equiv.)	Bi^V (Equiv.)	Trap (Equiv.)	Solvent	Temp. (°C)	Time (h)	(**11**) (%)	(**12**) (%)	PhNHAc	Ph_2NAc
1	BTMG (1.5)	(**2**; X = Tos) (1.5)	0	THF	R.t.*	1	90	0		
2	BTMG (1.5)	(**2**; X = Tos) (1.5)	PhNO (2)	THF	R.t.	1	87	0	90	5
3	0	(**2**; X = CF_3CO_2) (1.5)	0	PhH	80	15	0	82		
4	0	(**2**; X = CF_3CO_2) (1.5)	DPE (2)	PhH	80	15	0	85		

* R.t. = room temp.

(15)

(16)



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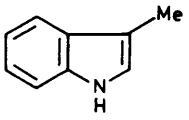

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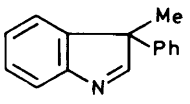

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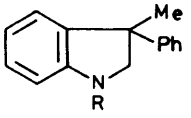

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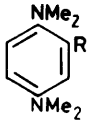
(21) R = Bz



(22) R = H
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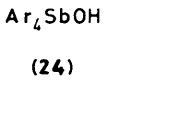

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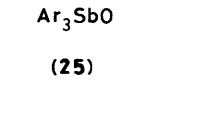

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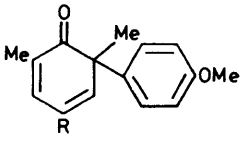
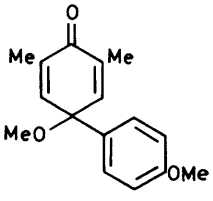


(26) R = Me
(27) R = OMe



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triphenylbismuth dichloride to give the 3-phenyl derivative (**19**) (51%). Addition of 1,1-diphenylethylene, again, did not change the yield (49%).

A quantitative yield was obtained in the reaction of 3-methylindole (**18**) with (**2**; X = Tos) and BTMG in the presence or absence of 1,1-diphenylethylene (95—98%). As a N–Bi covalently bonded intermediate cannot give the 3-phenyl derivative (**19**) and as free radicals are not involved, the reaction must have another mechanism. In an interesting reaction, *N,N,N',N'*-tetramethylphenylene-1,4-diamine (**22**) reacted with triphenylbismuth dichloride and BTMG to produce the 2-phenyl derivative (**23**) (19%). Again the presence of 1,1-diphenylethylene slightly improved the yield (23%). The same product was obtained with triphenylbismuth carbonate,[16] with or without 1,1-diphenylethylene (16—17%). A radical mechanism can again be excluded.

Phenylhydroxylamine reacted with triphenylbismuth carbonate[16] under neutral or basic conditions (BTMG) to give after reductive acetylation, *N,N*-diphenylacetamide (29—33%). Addition of 1,1-diphenylethylene did not alter the yield. The reaction does not proceed by oxidation to nitrosobenzene followed by phenylation, as nitrosobenzene was not phenylated under such conditions. This reaction is another case of phenylation without formation of radicals.

Finally, we turned our attention to the thermal decomposition of tetra-arylstibonium hydroxide (**24**) to triarylstibine oxide[17] (**25**). McEwen *et al.*[11] postulated a radical mechanism to explain this reaction, based on kinetic experiments and product distribution. However, when the reaction was performed in the presence of various amounts of 1,1-diphenylethylene, no significant change was observed in the yield of benzene, and a radical mechanism is seemingly excluded.

Although an e.s.r. study of some of the organobismuth reactions indicated the presence of phenyl radicals, the chemical trapping procedure (with PhNO or with 1,1-diphenylethylene) clearly excludes any participation of phenyl radicals in the *O*-, *C*-, or *N*-phenylation reactions with various pentavalent organobismuth reagents. The formation of phenyl radicals can be explained as a side reaction involving BTMG and the bismuth reagent, as shown by a series of blank experiments. By the same arguments aryl radicals do not seem to be present in alternative arylation procedures either.

It is now possible to compare Bi^{V}, Pb^{IV}, and I^{III} reagents in their various phenylating capacities. The iodonium (I^{III}) salts are not readily available and do not give such good yields of phenylated products as the other reagents. Both Bi^{V} and Pb^{IV} are efficient arylating reagents and can give very high yields. The Bi^{V} reagents react faster at lower temperatures than the corresponding Pb^{IV} derivatives and give good yields (where needed) of very hindered products. On the other hand the Pb^{IV} reagents of Pinhey[15] have only one aryl group which is meaningfully used in the reaction. Bi^{V} reagents waste several aryl groups in each reaction. If one works with very valuable compounds this, of course, is not important.

Amongst Bi^{V} reagents Ph_4BiOTs, $Ph_4BiOCOCF_3$, and Ph_3BiCl_2 all react quickly under mild basic conditions and often at room temperature. $BiPh_5$ reacts more slowly. Since Ph_3BiCl_2 is very easy to prepare, it is a preferred reagent for practical synthesis.

The formation of Bi^{V} intermediates in the base-catalysed arylation of phenols has been thoroughly demonstrated. We have not sought for such intermediates in Pb^{IV} chemistry, but we noted in the excellent work of Pinhey[15] there was one case of *p*-methoxyphenylation where the *para*-position was preferred. Thus *p*-methoxyphenylation of 2,6-dimethylphenol gave exclusively the cyclohexa-2,4-dienone (**26**) in high yield. However, *p*-methoxyphenylation of 4-methoxy-2,6-dimethylphenol afforded only 26% of the 2,4-dienone (**27**) and the major product was the 2,5-dienone (**28**) (58%). We repeated this work and found only the 2,4-dienone (**27**) in good yield (85%). Thus the reactions of aryl-lead triacetates with phenols probably involve an intermediate of the same type as that seen with bismuth(v).*

Kinetic studies at present underway support the mechanistic proposals made in this paper and will be presented in due course.

Experimental

M.p.s were determined with a Kofler hot-stage apparatus and are uncorrected. I.r. spectra were recorded on a Perkin-Elmer 257 apparatus. N.m.r. spectra were determined for solutions in deuteriochloroform with $SiMe_4$ as internal standard on Varian T-60 and Varian EM-360 instruments. Mass spectra were recorded with an AEI MS-9 or MS-50 instrument. E.s.r. spectra were recorded on Bruker ER-420 and ER-100D apparatus equipped with Bruker ER-400 X-RL or TR-4102 cavities. Deaerated solutions of the samples were maintained under argon in a quartz tube. All solvents and reagents were purified and dried by standard techniques. Chromatographic separations were performed using Merck Kieselgel 60 GF 254 (preparative t.l.c.) and Merck Kieselgel 60 H (column chromatography). G.c. analyses were performed on a Intersmat IGC 15 apparatus with a LTT 4200 integrator.

* See note added in proof on p. 248.

Preparation of Organobismuth Reagents.—Pentaphenylbismuth, tetraphenylbismuth, trifluoroacetate, and tetraphenylbismuth tosylate were prepared as previously reported.[1]

Preparation of Iodonium Reagents.—Diphenyliodonium chloride was prepared by reaction of sodium iodiate with benzene in sulphuric acid.[18] Diphenyliodonium acetate was prepared from the chloride.[4]

Preparation of α-Phenyl-N-(t-butyl)nitrone (**PBN**).—α-Phenyl-N-(t-butyl)nitrone was prepared by reaction of t-butylamine with benzaldehyde, followed by oxidation with perbenzoic acid[19] and thermal isomerisation (34%), m.p. 73—74 °C (light petroleum) (lit.,[20] 75—76 °C) (Found: C, 74.45; H, 8.6. Calc. for $C_{11}H_{15}NO$: C, 74.54; H, 8.53%).

Synthesis of Tetraphenylacetone (**6**).—1,1,3,3-Tetraphenylacetone (**6**) was prepared by reaction of diphenylacetyl chloride with potassium diphenylmethanide, according to Kantor and Hauser's procedure,[21] in a 65% yield, m.p. 130—134 °C, (lit.,[21] 134 °C); $\nu_{max.}(CHCl_3)$ 2 900, 1 710, and 1 590 cm^{-1}; $\delta(CDCl_3)$ 7.3 (20 H, m, ArH) and 5.3 (2 H, s, Ph_2CH); *m/z* 362 (M^+), 195 ($M^+ - Ph_2CH$), and 167 ($M^+ - Ph_2CHCO$) (Found: C, 89.35; H, 6.3. Calc. for $C_{27}H_{22}O$: C, 89.50; H, 6.07%).

Phenylation of Tetraphenylacetone (**6**) *with Tetraphenylbismuth Tosylate* (**2**; X = Ts).—A solution of (**2**; X = Ts) (0.688 g) in anhydrous THF (10 ml) was added to a solution of (**6**) (0.181 g) and *N*-t-butyl-*N'*,*N''*-tetramethylguanidine (**BTMG**) (0.170 g) in THF (10 ml) under argon, at room temperature. The mixture was stirred for 3 h. A drop of 10% aqueous HCl was added and the solvent distilled under reduced pressure. Preparative t.l.c. of the residue (eluant: hexane–ether, 9:1) afforded pentaphenylacetone (**7**) (0.190 g, 88%) as a white powder, m.p. 179—183 °C (ether) (lit.,[21] 180 °C); $\nu_{max.}(CHCl_3)$ 2 835, 1 710, 1 660, and 1 590 cm^{-1}; $\delta(CDCl_3)$ 7.63—7.20 (25 H, m, ArH) and 5.23 (1 H, s, Ph_2CHCO); *m/z* 438 (M^+), 243 ($M^+ - Ph_2CHCO$), and 167 ($M^+ - Ph_3CCO$) (Found: C, 90.2; H, 5.95. Calc. for $C_{33}H_{26}O$: C, 90.41; H, 5.94%).

Phenylation of (**6**) *with* (**2**; X = Ts) *in the Presence of Nitrosobenzene.*—A solution of (**2**; X = Ts) (0.688 g) and nitrosobenzene (0.107 g) in anhydrous THF (10 ml) was added to a solution of (**6**) (0.181 g) and **BTMG** (0.170 g) in THF (10 ml) under argon and kept in the dark at room temperature. The mixture was stirred for 3 h. A drop of 10% aqueous HCl was then added, followed by acetic anhydride (1 ml). The mixture was slowly added to a stirred suspension of iron powder (0.230 g) in acetic acid (1 ml) heated at 100 °C with distillation of THF. After the mixture had been stirred for 3 h, the precipitate was filtered off and washed with ether. The filtrate and the ethereal phase were treated together with aqueous sodium hydroxide solution until basic. The organic phase was then washed with brine, dried (Na_2SO_4), and distilled under reduced pressure. Preparative t.l.c. of the residue [two elutions: hexane–ether (9:1) followed by CH_2Cl_2–MeOH (98:2)] gave (**7**) (0.197 g, 90%), acetanilide (0.112 g, 83%), and *N*,*N*-diphenylacetamide (0.006 g, 3%), all identical with authentic samples.

Reductive Acetylation of Nitrosobenzene.—A solution of nitrosobenzene (0.107 g) in THF (5 ml) was added to a suspension of iron powder (0.230 g) in acetic acid (1 ml) and acetic anhydride (1 ml) at 100 °C. After 2.5 h, the reaction mixture was worked-up as before. Preparative t.l.c. (eluant: CH_2Cl_2–MeOH 98:2) afforded acetanilide (0.127 g, 94%).

Blank Experiment on the Acetylation of Diphenylamine under the Reductive Acetylation Conditions.—A mixture of diphenylamine (0.169 g), iron powder (0.230 g) in acetic acid (2 ml), and acetic anhydride (1 ml) was stirred at 100 °C for 2.5 h. Work-up and preparative t.l.c. afforded *N*,*N*-diphenylacetamide (0.189 g, 90%).

Blank Experiment on the Stability of Pentaphenylacetone (**4**) *under the Reductive Acetylation Conditions.*—A mixture of pentaphenylacetone (**7**) (0.030 g) and iron powder (0.010 g) in acetic acid (0.25 ml) and acetic anhydride (0.25 ml) was stirred at 100 °C for 3 h. Work-up and preparative t.l.c. afforded (**4**) (0.03 g, 100%) with no trace of 1,1,1,3,3-pentaphenylpropan-2-ol.

Blank Experiment of the Phenylation Reaction in the Absence of (**6**) *and* (**7**).—(i), *BTMG, Nitrosobenzene, and* (**2**; X = Tos). A mixture of (**2**; X = Ts) (0.688 g), **BTMG** (0.170 g), and nitrosobenzene (0.107 g) in anhydrous THF (20 ml) was stirred under argon for 3 h at room temperature, in the dark. After addition of 10% aqueous HCl (1 drop) and acetic anhydride (1 ml), the mixture was added to a suspension of iron powder (0.230 g) in acetic acid (1 ml), at 100 °C, with distillation of THF. After 3 h, the mixture was worked up as before to yield, after preparative t.l.c. [eluant: CH_2Cl_2–MeOH (98:2)] acetanilide (0.117 g, 87%) and *N*,*N*-diphenylacetamide (0.007 g, 3%).

(ii) When the reaction was performed for 15 h instead of 3 h reductive acetylation afforded acetanilide (0.062 g, 46%) and *N*,*N*-diphenylacetamide (0.024 g, 11%).

(iii) *Nitrosobenzene and* (**2**; X = Tos). A solution of (**2**; X = Tos) (0.688 g) and nitrosobenzene (0.107 g) in anhydrous THF (10 ml) was stirred under argon overnight at room temperature. Reductive acetylation and work-up afforded acetanilide (0.099 g, 73%) and *N*,*N*-diphenylacetamide (0.002 g, 1%).

(iv) *Nitrosobenzene and BTMG.* Reaction as above performed on **BTMG** (0.170 g) and nitrosobenzene (0.107 g) afforded, after reductive acetylation, acetanilide (0.108 g, 80%).

(v) *Nitrosobenzene alone.* Nitrosobenzene (0.107 g) submitted to the same conditions gave acetanilide (0.11 g, 82%).

(vi) **BTMG** *and* (**2**; X = Tos). A solution of (**2**; X = Tos) (0.688 g) and BTMG (0.170 g) in anhydrous THF (10 ml) was stirred under argon overnight at room temperature. The solvent was distilled off under reduced pressure. Preparative t.l.c. of the residue afforded triphenylbismuth (0.280 g, 64%).

Phenylation of 2-Ethoxycarbonylcyclohexanone (**8**). (i) *With pentaphenylbismuth.* A solution of (**8**) (0.085 g) and pentaphenylbismuth (0.445 g) in anhydrous benzene (10 ml) was stirred under argon for 1 h at room temperature. After distillation under reduced pressure, preparative t.l.c. [eluant: hexane–ether (4:1)] gave 2-ethoxycarbonyl-2-phenylcyclohexanone (**9**) (0.112 g, 91%) as a colourless oil, identical with an authentic sample.[3]

(ii) *With pentaphenylbismuth in the presence of nitrosobenzene.* A solution of (**8**) (0.085 g), nitrosobenzene (0.107 g), and pentaphenylbismuth (0.450 g) in anhydrous benzene (10 ml) was stirred in the dark under argon for 1 h at room temperature. Acetic anhydride (1 ml) was added and the mixture slowly introduced into a suspension of iron powder (0.230 g) in acetic acid (1 ml) at 100 °C. The mixture was stirred for 4 h at 100 °C. After filtration, the precipitate was washed with ether (50 ml) and the organic phase neutralised with concentrated aqueous sodium hydroxide, washed with brine, dried (Na_2SO_4), and distilled under reduced pressure. Preparative t.l.c. of the residue [eluant: hexane–ether (4:1) followed by CH_2Cl_2–MeOH (98:2)] afforded 2-ethoxycarbonyl-2-phenylcyclohexanone (0.099 g, 80%), acetanilide (0.119 g, 88%), and diphenylacetamide (0.010 g, 5%).

(iii) *Blank experiment with pentaphenylbismuth and nitroso-*

benzene. The previous experiment without (**8**) gave acetanilide (0.114 g, 84%) and diphenylacetamide (0.002 g, 1%).

(iv) *With tetraphenylbismuth tosylate and BTMG*. A mixture of (**8**) (0.085 g), BTMG (0.130 g), and (**2**; X = Ts) (0.520 g) in THF (10 ml) was stirred in the dark under argon for 1 h at room temperature. After addition of 10% aqueous HCl (one drop) distillation under reduced pressure and preparative t.l.c. gave (**9**) (0.112 g, 91%).

(v) *With tetraphenylbismuth tosylate, BTMG and nitrosobenzene*. A mixture of (**8**) (0.085 g), BTMG (0.130 g), nitrosobenzene (0.107 g), and (**2**; X = Ts) (0.520 g) in THF (10 ml) was stirred in the dark under argon for 1 h at room temperature. After addition of 10% aqueous HCl (one drop) and acetic anhydride (1 ml) the solution was introduced slowly into a suspension of iron powder (0.230 g) in acetic acid (1 ml) at 100 °C, with distillation of THF. After 3 h at 100 °C, the mixture was filtered, the residue washed with ether, and the organic phases neutralised with concentrated aqueous sodium hydroxide. The solution was extracted with ether, washed with brine, dried (Na_2SO_4), and distilled under reduced pressure. Preparative t.l.c. of the residue [eluant: hexane–ether (4:1) followed by CH_2Cl_2–MeOH (98:2)] yielded (**9**) (0.103 g, 83%), acetanilide (0.120 g, 89%), and diphenylacetamide (0.004 g, 2%).

(vi) *With phenyl-lead triacetate*. A solution of (**8**) (0.051 g) and pyridine (24 μl, 0.023 g) in $CHCl_3$ (0.5 ml) was stirred under argon for 0.5 h at room temperature. Phenyl-lead triacetate (0.150 g) was then added, and the mixture stirred for 15 h at 40 °C. Addition of aqueous 10% HCl (one drop), distillation under reduced pressure, and preparative t.l.c. of the residue [eluant: hexane–ether (4:1)] afforded (**9**) (0.058 g, 78%).

(vii) *With phenyl-lead triacetate in the presence of* 1,1-*diphenylethylene*. A solution of (**8**) (0.051 g), pyridine (24 μl, 0.023 g), 1,1-diphenylethylene (0.107 g), and phenyl-lead triacetate (0.150 g) was stirred as above for 14 h at 40 °C. Work-up and column chromatography (eluant: hexane) followed by preparative t.l.c. [eluant: hexane–ether (4:1)] gave (**9**) (0.056 g, 76%).

(viii) *With diphenyliodonium acetate and BTMG*. A mixture of (**8**) (0.085 g), BTMG (0.1 g), and diphenyliodonium acetate (0.374 g) in anhydrous t-butyl alcohol (1 ml) was stirred under argon for 2 h under reflux. After addition of 10% aqueous HCl (one drop) and distillation under reduced pressure preparative t.l.c. of the residue [eluant: hexane–ether (4:1)] afforded (**9**) (0.066 g, 55%).

(ix) *With diphenyliodonium acetate, BTMG and* 1,1-*diphenylethylene*. (*a*) A mixture of (**8**) (0.085 g), BTMG (0.095 g), 1,1-diphenylethylene (0.180 g) and diphenyliodonium acetate (0.374 g) in t-butyl alcohol (1 ml) was treated and worked up as above to give (**9**) (0.098 g, 80%). (*b*) When the reaction was performed with 5 equiv. of 1,1-diphenylethylene (0.45 g instead of 0.180 g) (**9**) was isolated in a 76% yield (0.093 g).

Reaction of 2-*Nitropropane* (**13**).—(i) *With tetraphenylbismuth tosylate and BTMG*. Compound (**2**; X = Ts) (0.520 g) was added to a solution of 2-nitropropane (0.045 g) and BTMG (0.127 g) in anhydrous THF (1 ml), stirred under argon for 10 min at room temperature. The mixture was stirred for 2 h at 40 °C. After addition of 10% aqueous HCl (one drop) and distillation under reduced pressure, preparative t.l.c. [eluant: hexane–ether (4:1)] afforded α-nitrocumene (**14**) (0.071 g, 86%) as a yellow oil, identical with an authentic sample;[22] *m/z* 165 (M^+) and 119 ($M^+ - NO_2$).

(ii) *With tetraphenylbismuth tosylate, BTMG and* 1,1-*diphenylethylene*. A reaction as above performed in the presence of 1,1-diphenylethylene (0.176 μl) yielded (**14**) (0.073 g, 89%).

(iii) *With tetraphenylbismuth tosylate and BTMG under a flow of oxygen*. When the reaction was performed with bubbling of oxygen (flow rate: 1 ml/s), (**14**) was obtained (0.068 g, 82%) as before.

(iv) *With triphenylbismuth dichloride and BTMG*. Triphenylbismuth dichloride (0.310 g) was added to a solution of 2-nitropropane (0.045 g) and BTMG (0.127 g) in anhydrous THF (5 ml) stirred under argon for 10 min at room temperature. The mixture was stirred for 2 h. After addition of 1M aqueous HCl (2 drops) and distillation under reduced pressure, preparative t.l.c. [eluant: hexane–ether (4:1)] afforded α-nitrocumene (**14**) (0.064 g, 77%).

(v) *With triphenylbismuth dichloride, BTMG and* 1,1-*diphenylethylene*. A reaction as above performed in the presence of 1,1-diphenylethylene (0.175 μl) yielded (**14**) (0.065 g, 78%) and 1,1-diphenylethylene (0.155 g, 86%).

Phenylation of 2-*naphthol* (**10**).—(i) *With tetraphenylbismuth tosylate and BTMG*. A solution of (**10**) (0.072 g), BTMG (0.130 g), and (**2**; X = Ts) (0.520 g) in anhydrous THF (10 ml) was stirred under argon for 1 h at room temperature. Acidification with 10% aqueous HCl, distillation under reduced pressure, and preparative t.l.c. [eluant: hexane–ether (9:1)] gave 1-phenyl-2-naphthol (0.099 g, 90%), m.p. 89—90 °C (methylene dichloride–pentane).

(ii) *With tetraphenylbismuth tosylate, BTMG and Nitrosobenzene*. A solution of (**10**) (0.144 g), BTMG (0.130 g), (**2**; X = Tos) (1.04 g), and nitrosobenzene (0.214 g) was treated as above in the dark. After acidification, the first half of the reaction mixture was worked up as above to yield (**11**) (0.096 g, 87%). Acetic anhydride (1 ml) was added to the second half and the solution was then introduced slowly into a suspension of iron powder (0.230 g) in acetic acid (1 ml) at 100 °C, with distillation of THF. After being stirred at 100 °C for 3 h, the mixture was filtered, the precipitate washed with ether, and the filtrate neutralised with concentrated aqueous sodium hydroxide. The organic phase was washed with brine, dried (Na_2SO_4) and distilled under reduced pressure. Preparative t.l.c. [eluant: CH_2Cl_2–MeOH (98:2)] gave acetanilide (0.119 g, 88%) and diphenylacetamide (0.008 g, 4%).

(iii) *With tetraphenylbismuth trifluoroacetate*. A solution of (**10**) (0.072 g) and (**2**; X = CF_3CO_2) (0.470 g) in anhydrous benzene (3 ml) was stirred under argon for 15 h under reflux. The mixture was treated with trichloroacetic acid, washed with water, dried (Na_2SO_4), and the organic phase distilled under reduced pressure. Preparative t.l.c. of the residue afforded phenyl-2-naphthyl ether (**12**) (0.090 g, 82%), m.p. 45—46 °C.

(iv) *With tetraphenylbismuth trifluoroacetate and* 1,1-*diphenylethylene*. A solution of 2-naphthol (0.072 g), tetraphenylbismuth trifluoroacetate (0.470 g), and 1,1-diphenylethylene (0.180 g) in anhydrous benzene (3 ml) was stirred as above for 15 h under reflux. Work-up as above yielded phenyl-2-naphthyl ether (**12**) (0.093 g, 85%). 1,1-Diphenylethylene was recovered (0.146 g, 85%).

Phenylation of 3,5-*Di-t-butylphenol* (**16**).—(i) *With tetraphenylbismuth trifluoroacetate*. A solution of (**16**) (0.103 g), tetraphenylbismuth trifluoroacetate (0.472 g) in anhydrous benzene (2 ml) was stirred under argon for 4 h under reflux. The mixture was treated with 1M aqueous HCl (a few drops), washed with water, dried (Na_2SO_4), and the organic phase distilled under reduced pressure. Preparative t.l.c. of the residue (eluant: hexane) afforded 3,5-di-t-butylphenyl phenyl ether (**17**) (0.100 g, 71%), m.p. 71—73 °C (lit.,[3] 72—73 °C).

(ii) *With tetraphenylbismuth trifluoroacetate and* 1,1-*diphenylethylene*. A reaction as above performed in the presence of 1,1-diphenylethylene (0.180 μl) yielded (**17**) (0.098 mg, 70%).

(iii) *With triphenylsulphonium bromide and BTMG*. A solution of (**16**) (0.103 g) and BTMG (0.093 g) in t-butyl alcohol (10 ml) was stirred under argon for 10 min at room temperature.

After addition of triphenylsulphonium bromide (0.257 g), the reaction mixture was stirred under reflux for 48 h. 1M Aqueous HCl (1 drop) was added, followed by a 1M aqueous sodium periodate. The solution was extracted with ether, and the organic phase dried ($MgSO_4$) and distilled under reduced pressure. Preparative t.l.c. of the residue (eluant: hexane) yielded (**17**) (0.044 g, 40%).

(iv) *With triphenylsulphonium bromide, BTMG and* 1,1-*diphenylethylene* (**17**). A reaction as above performed in the presence of 1,1-diphenylethylene (180 μl) gave (**17**) (0.071 g, 65%) and 1,1-diphenylethylene (0.065 g, 36%).

(v) *With diphenyliodonium chloride and BTMG.* A solution of (**16**) (0.109 g) and BTMG (0.213 g) in t-butyl alcohol (5 ml) was stirred under argon for 10 min at room temperature. Diphenyliodonium chloride (0.396 g) was added and the reaction mixture was stirred under reflux for 15 h. After addition of 1M aqueous HCl (a few drops), the mixture was extracted with ether, and the organic phase washed with water, dried ($MgSO_4$), and distilled under reduced pressure. Preparative t.l.c. of the residue (eluant: hexane) gave (**17**) (0.115 g, 82%).

Thermal Decomposition of 4-*Nitrophenoxy-tri- and -tetraphenylbismuth Derivatives.*—(i) 4-*Nitrophenoxytetraphenylbismuth.* A solution of 4-nitrophenoxytetraphenylbismuth[3] (0.655 g) in anhydrous toluene (5 ml) was stirred under argon for 5 h under reflux. The solvent was distilled off under reduced pressure and column chromatography of the residue (eluant: ether–hexane gradient) afforded triphenylbismuth (0.347 g, 79%) and 4-nitrodiphenyl ether (0.205 g, 95%), m.p. 55—56 °C (ether–hexane) (lit.,[23] 56 °C).

(ii) 4-*Nitrophenoxytetraphenylbismuth and* 1,1-*diphenylethylene.* A reaction as above performed in the presence of 1,1-diphenylethylene (350 μl) afforded 1,1-diphenylethylene (0.340 g, 95%), triphenylbismuth (0.310 g, 70%), and 4-nitrodiphenyl ether (0.206 g, 96%).

(iii) 4-*Nitrophenoxytriphenylbismuth trifluoroacetate.* A solution of 4-nitrophenoxytriphenylbismuth trifluoroacetate[3] (0.345 g) in anhydrous benzene (10 ml) was stirred under argon for 50 h under reflux. Distillation under reduced pressure of the solvent and column chromatography of the residue (eluant: hexane) afforded biphenyl (0.050 g, 65%) as the only non-bismuth product.

(iv) 4-*Nitrophenoxytriphenylbismuth trifluoroacetate and* 1,1-*diphenylethylene.* A solution of 4-nitrophenoxytriphenylbismuth trifluoroacetate (0.345 g) and 1,1-diphenylethylene (180 μl) in anhydrous benzene (10 ml) was stirred under argon for 50 h under reflux. The solvent was distilled off under reduced pressure. Ozonolysis of the residue dissolved in methylene dichloride, at −78 °C for 15 min, followed by bubbling of oxygen until the reaction temperature reached room temperature followed by distillation of the solvent and preparative t.l.c. (eluant: hexane), afforded biphenyl (0.040 g, 52%). A blank experiment of ozonolysis of biphenyl under similar conditions gave an 80% recovery of biphenyl.

Phenylation of 3-*Methylindole.*—(i) *With triphenylbismuth dichloride and* NaH. A mixture of 3-methylindole (0.065 g) and sodium hydride (50% suspension in oil; 0.060 g washed with THF) in anhydrous THF (5 ml) was stirred under argon at room temperature for 1 h. Triphenylbismuth dichloride (0.380 g) was then added and the mixture stirred for a further 3 h at room temperature. After addition of 1M aqueous HCl (a few drops), the mixture was extracted with ether, and the organic phase washed with water, dried ($MgSO_4$), and distilled under reduced pressure. Preparative t.l.c. of the residue [eluant: hexane–ether (4:1)] afforded 3-methyl-3-phenyl-3*H*-indole (0.053 g, 51%) as a yellow oil; $\nu_{max.}(CHCl_3)$ 2 950, 2 850, 1 600, 1 560, and 1 440 cm^{-1}; $\delta(CDCl_3)$ 8.3 (1 H, s, 2-H), 8.1—7.0 (9 H, m, ArH), and 1.7 (3 H, s, CH_3); *m/z* 207 (M^+). Reduction of 3-methyl-3-phenyl-3*H*-indole by $NaBH_4$ in methanol, followed by benzoylation with benzoyl chloride in anhydrous ether in the presence of triethylamine afforded *N*-benzoyl-3-methyl-3-phenyl-2,3-dihydroindole, m.p. 135—137 °C (lit.,[24] 139—140 °C); $\nu_{max.}(CHCl_3)$ 2 950, 1 640, 1 480, and 1 400 cm^{-1}; $\delta(CDCl_3)$ 8—6.9 (14 H, m, ArH), 4.17 and 4.00 (2 H, 2 d, *J* 16 Hz, 2-H), and 1.8 (3 H, s, CH_3) (Found: C, 84.25; H, 6.2. Calc. for $C_{22}H_{19}NO$: C, 84.32; H, 6.11%).

(ii) *With triphenylbismuth dichloride,* NaH *and* 1,1-*diphenylethylene.* A reaction as above performed in the presence of 1,1-diphenylethylene (0.180 μl) gave 3-methyl-3-phenyl-3*H*-indole (0.051 g, 49%) and 1,1-diphenylethylene (0.165 g, 90%).

(iii) *With tetraphenylbismuth tosylate and BTMG.* A solution of 3-methylindole (0.065 g) and BTMG (0.170 g) was stirred under argon at room temperature for 10 min. Compound (**2**; X = Tos) (0.516 g) was added and the mixture stirred for 2.5 h. After addition of 1M aqueous HCl (a few drops) and extraction with ether, the organic phase was washed with water, dried ($MgSO_4$), and distilled under reduced pressure. Column chromatography of the residue (eluant: ether gradient in hexane) afforded 3-methyl-3-phenyl-3*H*-indole (0.098 g, 95%).

(iv) *With tetraphenylbismuth tosylate, BTMG and* 1,1-*diphenylethylene.* A reaction as above performed in the presence of 1,1-diphenylethylene (0.180 μl) gave, after column chromatography, 3-methyl-3-phenyl-3*H*-indole (0.101 g, 98%).

Phenylation of N,N,N′,N′-*Tetramethylphenylene*-1,4-*diamine.*—(i) *With triphenylbismuth dichloride and BTMG.* A solution of *N,N,N′,N′*-tetramethylphenylene-1,4-diamine (**22**) (0.082 g) and BTMG (0.175 g) in anhydrous benzene (3 ml) was stirred under argon for 10 min at room temperature. Triphenylbismuth dichloride (0.383 g) was added and the reaction mixture stirred overnight at room temperature. After addition of 1M aqueous HCl (a few drops), the solvent was distilled off under reduced pressure. Column chromatography of the residue [eluant: hexane–ether (7:3)] afforded 2-*phenyl*-N,N,N′,N′-*tetramethylphenylene*-1,4-*diamine* (**23**) (0.023 g, 19%), m.p. 56—58 °C (hexane); $\nu_{max.}(CHCl_3)$ 2 850, 1 600, 1 490, and 1 320 cm^{-1}; $\delta(CDCl_3)$ 7.86—6.77 (8 H, m, ArH), 2.96 (6 H, s, 2-CH_3), and 2.53 (6 H, s, 2-CH_3); *m/z* 240 (M^+), and 225 ($M^+ - CH_3$) (Found: C, 80.2; H, 8.4. $C_{16}H_{20}N$ requires C, 79.95; H, 8.39%).

(ii) *With triphenylbismuth dichloride, BTMG and* 1,1-*diphenylethylene.* A reaction as above performed in the presence of 1,1-diphenylethylene (180 μl) yielded (**23**) (0.028 g, 23%).

(iii) *With tetraphenylbismuth tosylate and BTMG.* A solution of *N,N,N′,N′*-tetramethylphenylene-1,4-diamine (0.082 g), BTMG (0.130 g), and (**2**; X = Tos) (0.516 g) was stirred under argon for 5 h at room temperature. The solvent was distilled off under reduced pressure. Column chromatography of the residue (eluant: ether–hexane gradient) afforded triphenylbismuth (0.140 g, 65%) and (**23**) (0.009 g, 8%).

(iv) *With triphenylbismuth carbonate.* A mixture of (**22**) (0.164 g) and triphenylbismuth carbonate (1.5 g) in benzene (3 ml) was stirred under argon for 3 days at room temperature. The solvent was distilled off under reduced pressure and column chromatography of the residue afforded (**23**) (0.040 g, 16%) and triphenylbismuth (0.260 g, 59%).

(v) *With triphenylbismuth carbonate and* 1,1-*diphenylethylene.* A reaction as above performed in the presence of 1,1-diphenylethylene (350 μl) yielded (**23**) (0.041 g, 17%).

Phenylation of Phenylhydroxylamine.—(i) *With triphenylbismuth carbonate.* A mixture of phenylhydroxylamine (0.109 g) and triphenylbismuth carbonate (1 g) in anhydrous THF (3 ml) was stirred under argon for 30 min at room temperature. T.l.c. indicated the absence of unchanged phenylhydroxylamine. Reductive acetylation of the mixture [iron powder (0.230 g),

acetic acid (1 ml), and acetic anhydride (1 ml) at 100 °C for 2.5 h], work-up, and preparative t.l.c. of the residue [eluant: methylene dichloride–ether (4:1)] afforded *N,N*-diphenylacetamide (0.044 g, 33%) and acetanilide (0.106 g, 50%).

(ii) *With triphenylbismuth carbonate and* 1,1-*diphenylethylene.* A reaction as above performed in the presence of 1,1-diphenylethylene (350 µl), for 1 h at room temperature followed by reductive acetylation, yielded *N,N*-diphenylacetamide (0.077 g, 36%) and acetanilide (0.037 g, 28%).

(iii) *With triphenylbismuth carbonate and BTMG.* A mixture of phenylhydroxylamine (0.109 g), BTMG (30 µl), and triphenylbismuth carbonate (1 g) in anhydrous THF (10 ml) was stirred under argon for 30 min at room temperature. Reductive acetylation and work-up as above gave *N,N*-diphenylacetamide (0.058 g, 27%) and acetanilide (0.039 g, 29%).

(iv) *Blank experiment of phenylation of nitrosobenzene.* A mixture of nitrosobenzene (0.107 g) and triphenylbismuth carbonate (1 g) in anhydrous benzene (3 ml) was stirred under argon for 15 h at room temperature. Reductive acetylation and work-up afforded acetanilide (0.110 g, 81%) and no trace of *N,N*-diphenylacetamide.

Thermal Decomposition of Tetraphenylantimony Hydroxide.—(i) *Without* 1,1-*diphenylethylene.* A solution of tetraphenylantimony hydroxide (0.223 g) in anhydrous chlorobenzene (10 ml) was stirred under argon for 48 h at 110 °C. G.c. analysis (column DC 200, 1.5 m) of the mixture indicated the presence of benzene (100%) by comparison with a standard solution of benzene in chlorobenzene. The solvent was distilled off under reduced pressure to give a white solid (0.184 g, 100%) of triphenylantimony oxide, m.p. 305 °C (lit.,[25] m.p. 221.5—222 °C); *m/z* 738 [$(Ph_3SbO)_2$] and 368 (Ph_3SbO). The difference in m.p. can be due to the polymeric nature of our precipitate.

(ii) *With* 1,1-*diphenylethylene.* When the reaction was performed with 1,1-diphenylethylene (180 µl), benzene (93%) was detected. With 450 µl, 107% of benzene and with 900 µl, 97% of benzene were detected.

Decomposition of N-*Nitrosoacetanilide.*—(i) *In the presence of nitrosobenzene.* A solution of *N*-nitrosoacetanilide (0.082 g)[26] and nitrosobenzene (0.107 g) in anhydrous THF (10 ml) was stirred under argon at room temperature for 6 h in the dark. Reductive acetylation followed by work-up and column chromatography [eluant: methylene dichloride–ether (7:3)] afforded acetanilide (0.089 g, 66%) and *N,N*-diphenylacetamide (0.042 g, 20%).

(ii) *In the presence of* 1,1-*diphenylethylene.* A solution of *N*-nitrosoacetanilide (0.082 g, 0.5 mmol) and 1,1-diphenylethylene (180 µl, 1 mmol) in anhydrous THF (10 ml) was stirred under argon, in the dark, overnight at room temperature. The solvent was distilled off and preparative t.l.c. of the residue (eluant: hexane) afforded 1,1-diphenylethylene (0.161 g, 88%) and triphenylethylene (0.005 g 2%) identical with an authentic sample. When the reaction was performed with 1.5 mmol (0.240 g) of N-nitrosoacetanilide, 1,1-diphenylethylene (0.104 g, 57%), and triphenylethylene (0.013 g, 5%) were recovered.

Decomposition of Phenyldiazonium Tetrafluoroborate, in the Presence of Cu *and* 1,1-*Diphenylethylene.*—Anhydrous DMF (20 ml) was added under argon to a mixture of phenyldiazonium tetrafluoroborate[27] (4.5 g), powdered copper (1.26 g), and 1,1-diphenylethylene (360 µl). The mixture was stirred for 48 h at room temperature and then filtered and extracted with ether. The organic phase was washed with water and dried ($MgSO_4$). Distillation of the solvent and column chromatography of the residue (eluant: hexane) afforded 1,1-diphenylethylene (0.085 g, 23%) and triphenylethylene (0.222 g, 43%).

p-*Methoxyphenylation of* 4-*Methoxy*-2,6-*dimethylphenol* (**26**).—The above phenol (0.113 g) was added to a solution of *p*-methoxyphenyl-lead triacetate (0.367 g) in chloroform (4 ml) containing pyridine (68 µl) and the solution was kept at room temperature for 24 h. The solvents were distilled off under reduced pressure and preparative t.l.c. of the residue [eluant: hexane–ether (3:1)] afforded (**27**) (0.140 g, 85%) as an oil; $\lambda_{max.}$ 284 (2 500, 277 (2 590), and 240 (7 282); $\nu_{max.}$($CHCl_3$) 1 655 and 1 605 cm^{-1}; δ($CDCl_3$) 7.25 and 6.81 (4 H, AA′BB′, *J* 8 Hz, 2′-H, 6′-H, and 3′-H, 5′-H), 6.80—6.65 (1 H, m, 3-H), 5.21 (1 H, d, *J* 3 Hz, 5-H), 3.77 (3 H, s, 4′-OMe), 3.64 (3 H, s, 4-OMe), 1.85 (3 H, br s, 2-Me), and 1.62 (3 H, s, 6-Me); *m/z* 258 (M^+), 243 ($M^+ - CH_3$), 230 ($M^+ - CO$), and 215 ($M^+ - COCH_3$).

* *Added in proof* (2.10.86). Dr. J. T. Pinhey (University of Sydney), has now informed us (10.7.86) that he agrees that the product is exclusively (**27**). We thank Dr. Pinhey cordially for his collaboration.

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