Aryllead Triacetates: Regioselective Reagents for *N*-Arylation of Amines

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Aryllead triacetates have been found to be regioselective reagents for the mono *N*-arylation of a range of aromatic, heterocyclic and aliphatic amines under mild and neutral conditions in a reaction catalysed by copper diacetate. The arylation of arylamines was unaffected by the steric hindrance of the arylamine but was dependent on the arylamine basicity. In addition, the position of oxidisable substituents on both the aryllead triacetate and the arylamine was found to be important due to a competing oxidation–reduction reaction. The arylation of heterocyclic amines proceeded in modest to good yields whilst aliphatic amines were arylated in poor to modest yields. The mechanism proposed for these reactions involves transfer of the aryl group onto copper forming a copper(III) intermediate which subsequently undergoes ligand coupling to give the *N*-arylated amine and the catalytic Cu^{I} species.

The mild, neutral, regioselective mono *N*-arylation of aromatic, heterocyclic and aliphatic amines is a desirable reaction for the preparation of diarylamines, *N*-arylated heterocyclic and *N*-arylated aliphatic amines, respectively. Diarylamines are an important class of compounds which act as antioxidants,[1] antifungal agents,[2] as well as intermediates in the synthesis of carbazoles[3] and fluoran dyes.[4] Only a very limited range of diarylamines can be prepared from diphenylamine itself and a number of practical methods are available for their direct synthesis. Diarylamines prepared by the reaction of activated fluoroarenes with arylamines containing electron-donating groups[5,6] are limited to electron-donating groups in one ring and electron-withdrawing groups in the second. The displacement of fluorine, nitro groups[7] and the other halogens by arylamines containing electron-withdrawing groups produces diarylamines containing electron-withdrawing groups in each ring. The Ullmann reaction has proven useful primarily for the preparation of diarylamines containing NO_2 or COOR groups.[8] In the Goldberg reaction,[9] an aryl bromide reacts with an acetanilide in the presence of K_2CO_3 and copper iodide to give an *N*-acetyldiarylamine, which is hydrolysed to the corresponding diarylamine. Aryl bromides containing two *ortho*-substituents give low yields of *N*-acetyldiarylamines,[10] which furthermore are resistant to hydrolysis. However, the major limitations of the Goldberg reaction are its applicability only to arylamines containing electron-withdrawing groups and the need for drastic reaction conditions. The synthesis of diarylamines *via* the Chapman rearrangement[11,12] is generally applicable to diarylamines containing electron-donating substituents in one ring and electron-withdrawing in the other. A series of diarylamines was prepared by the reaction of an arene with aryl azides in the presence of $AlCl_3$,[13] or TFA.[14] Diarylamines were prepared by the reaction of aryl halides in the presence of alkali amides,[15] or complex bases,[16] giving a mixture of *para*- and *meta*-substituted diphenylamines. The limitations of this method, which involves an aryne intermediate, are its lack of regioselectivity, its non-applicability to base-sensitive substrates and that *ortho*-substituted diphenylamines may not be prepared. Diaryliodonium salts arylated amines in poor yields.[17] Thus, the need for a milder and more general synthesis of diarylamines is obvious and, in particular, the preparation of diarylamines containing electron-donating substituents in both rings.

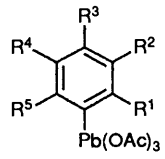
N-Aryltetrahydroisoquinolines possess antispasmodic properties[18] and exhibit antirhinoviral activity.[19] The major mode of preparation of these compounds involves the condensation of an *ortho*-haloethylbenzyl halide with substituted anilines.[20,21] Yields are good, but the preparation of the *ortho*-halobenzyl halide is difficult. Arylation at nitrogen of the preformed 1,2,3,4-tetrahydroisoquinoline ring would be a more favourable approach to these compounds. A variety of methods are available for the preparation of the piperidine ring and most of these feature intramolecular closure at the nitrogen atom.[22,23] Ethanolic tetracarbonyl hydridoferrate solution combined with glutaraldehyde[24] is efficient for the selective transformation of an amino group into a piperidine ring, although *ortho*-substituents exhibit an inhibitory effect. Pentane-1,5-diol was found to react with aromatic primary amines, in the presence of a ruthenium catalyst modified with phosphine ligands, to give *N*-substituted piperidines in good yields.[25]

More recently, it has been found that organobismuth reagents phenylate aliphatic and aromatic amines under copper catalysis in a mild and high yielding reaction.[26] The reaction was found to be essentially independent of the aromatic amine basicity and steric hindrance, although steric effects did play a role in the phenylation of aliphatic primary amines. Trivalent organobismuth reagents also phenylate amines in the presence of copper diacylate in a reaction that was found to be dependent on the amine basicity and steric effects.[27] The applicability of the catalysed *N*-phenylation by organobismuth reagents was extended to the phenylation of indolic derivatives[28] and α-amino acid derivatives.[29] The possibility for copper catalysed *N*-arylation of amines exists although the range of easily accessible triarylbismuth diacetates is limited due to difficulty in their preparation.

Phenyllead triacetate **1** was found[30] to successfully phenylate both aromatic and aliphatic amines under copper catalysis in a reaction that was dependent on the amine basicity. In a previous communication,[31] we have reported the arylation of various aromatic, heterocyclic and aliphatic amines by methoxy-substituted phenyllead triacetates under copper diacetate catalysis. We would now like to report on the extensions of our studies in this area.

Aryllead triacetates are a class of organometallic reagents which efficiently α-arylate phenols,[32] β-diketones,[33] β-keto esters,[34] enamines,[35] nitronate salts[36] and α-hydroxymethylene

Table 1 Aryllead triacetates



$ArPb(OAc)_3$	R^1	R^2	R^3	R^4	R^5
1	H	H	H	H	H
2	OMe	H	H	H	H
3	H	OMe	H	H	H
4	H	H	OMe	H	H
5	H	H	Me	H	H
6	OMe	H	OMe	H	H
7	OMe	H	H	OCH_3	H
8	H		OCH_2O	H	H
9	OMe	H	OMe	H	OMe

Table 2 *N*-Arylation of anilines by aryllead reagents

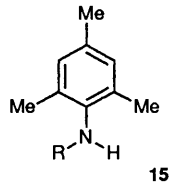
Amine	$ArPb(OAc)_3$	Time/h	Product (%)	
10	**2**	2	**11** (95)	
10	**3**	2.5	**12** (84)	
10	**4**	2.5	**13** (76)	
10	**5**	2	**14** (92)	
10	**6**	2	**15** (74)	
10	**7**	2.5	**16** (70)	
10	**8**	2.5	**17** (91)	
10	**9**	2	**18** (18)	**19** (48)
20	**4**	2	**21** (72)	
20	**6**	2.5	**22** (78)	
20	**9**	2	**23** (0)[a]	**19** (60)
24	**2**	0.5	**25** (85)	
24	**3**	0.5	**26** (74)	
24	**4**	0.5	**27** (91)	
24	**5**	0.5	**28** (92)	
24	**6**	0.5	**29** (25)	**30** (60)
24	**7**	0.5	**31** (25)	
32	**1**	2	**22** (34)	
32	**6**	4	**33** (0)[a]	**30** (68)
34	**6**	48	**35** (0)	
36	**6**	48	**37** (0)	
38	**2**	4	**39** (64)	
38	**3**	4	**40** (56)	
41	**2**	4	**42** (90)	
41	**7**	6	**43** (77)	
44	**4**	3	**28** (89)	
44	**5**	2	**45** (94)	
44	**8**	2	**46** (97)	

[a] $Cu(OAc)_2$ added to a solution of amine and aryllead triacetate at 0–5 °C.

ketones[37,38] in high yields under mild conditions. More recently, we have shown their usefulness in the facile preparation of a series of 3-aryl-4-hydroxycoumarins, an important sub-class of isoflavonoid natural products.[39] In contrast to the arylbismuth(v) reagents, aryllead triacetates with varying substitution patterns can be readily prepared.

Aryllead triacetates **2**–**9** were prepared either by plumbylation[40] or by tin–lead exchange.[41] The former, used to prepare aryllead triacetates **4**, **5**, **6** and **9** in reasonable yields, is a short route, with the formation of only one isomer, but is however applicable to the preparation of a limited number of aryllead triacetates. The latter, used to prepare aryllead triacetates **2**, **3**, **7** and **8** involves the reaction of an aryltributylstannane with $Pb(OAc)_4$ under $Hg(OAc)_2$ catalysis and is a more general route of wider applicability.

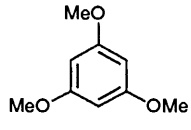
The steric hindrance of the substrate amine has no effect on the yields of hindered diarylamines produced. The yields of the coupling of mesitylamine **10** with a series of aryllead triacetates in the presence of a catalytic amount of $Cu(OAc)_2$ are high in all cases with the exception of the formation of the extremely hindered *N*-(2,4,6-trimethylphenyl)-2,4,6-trimethoxyaniline **18**. In this case, 1,3,5-trimethoxybenzene **19** (48% based on 2,4,6-



10 R = H
11 R = 2-$MeOC_6H_4$
12 R = 3-$MeOC_6H_4$
13 R = 4-$MeOC_6H_4$
14 R = 4-MeC_6H_4
15 R = 2,4-$(MeO)_2C_6H_3$
16 R = 2,5-$(MeO)_2C_6H_3$
17 R = 3,4-$(OCH_2O)C_6H_3$
18 R = 2,4,6-$(MeO)_3C_6H_2$

trimethoxyphenyllead triacetate **9**) was also isolated, and its formation suggests that the reduction of **9** with oxidation of **10** is a competing reaction to the *N*-arylation observed in all other cases. Attempts to increase the yield of **18** by increasing the molar ratio **9**–**10** to 2.2:1.0 failed and a similar yield was obtained. Isomerisation did not occur in any case, *i.e.*, nitrogen bonds to the carbon of the aryl ring which was bonded to lead, and this 100% regiospecificity in the *ipso*-substitution of the aryllead reagents is noteworthy.

As the yield of *N*-phenylated diarylamines produced in the coupling reaction with **1** was dependent on the arylamine basicity,[30] the effect of the latter was investigated in the coupling reactions with aryllead triacetates. Variously substituted anilines **20**, **24**, **32**, **34** and **36** differing in their basicity were used. Aniline **20** was found to react well with 4-methoxyphenyllead triacetate **4** and 2,4-dimethoxyphenyllead triacetate **6** to give *N*-phenyl-*p*-anisidine **21** and *N*-phenyl-2,4-dimethoxyaniline **22** in good yield. However, reaction with **9** gave **19** even with variation of the reaction conditions, *e.g.*, addition of $Cu(OAc)_2$



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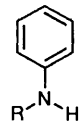
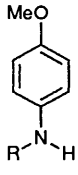
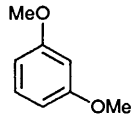


20 R = H
21 R = 4-$MeOC_6H_4$
22 R = 2,4-$(MeO)_2C_6H_3$
23 R = 2,4,6-$(MeO)_3C_6H_2$



24 R = H
25 R = 2-$MeOC_6H_4$
26 R = 3-$MeOC_6H_4$
27 R = 4-$MeOC_6H_4$
28 R = 4-MeC_6H_4
29 R = 2,4-$(MeO)_2C_6H_3$
31 R = 2,5-$(MeO)_2C_6H_3$



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to a solution of **9** and **19** in methylene dichloride at room temperature or at 0–5 °C. *para*-Anisidine **24** was found to give high yields of diarylamines in much shorter reaction times: 30 min compared with 2 h for **20**. The arylation of **24** by **6** was accompanied by oxidation–reduction as indicated by the isolation of 1,3-dimethoxybenzene **30**. The starting arylamine was consumed to give polymeric materials which were not further investigated. Interestingly, there were no such problems

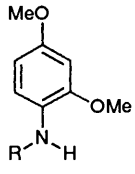
Table 3 *N*-Arylation of heterocyclic amines by aryllead reagents

Amine	$ArPb(OAc)_3$	Time/h	Product (%)
47	**4**	16	**48** (39)
47	**5**	16	**49** (35)
47	**6**	16	**50** (60)
47	**8**	16	**51** (38)
47	**9**	16	**52** (36)
53	**4**	12	**54** (43)
53	**6**	12	**55** (67)
53	**9**	12	**56** (55)
57	**5**	24	**58** (59)
57	**6**	24	**59** (25)

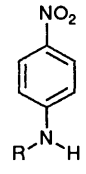
Table 4 *N*-Arylation of aliphatic amines by aryllead reagents

Amine	$ArPb(OAc)_3$	Time/h	Product (%)
60	**6**	48	**61** (0)
62	**5**	24	**63** (39)
62	**6**	24	**64** (35)
65	**6**	24	**66** (19)
65	**9**	24	**67** (0)
68	**6**	48	**69** (0)

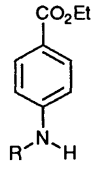
encountered in the formation of diarylamine **31** which suggests that an *ortho,para*-methoxylated aryllead triacetate undergoes reduction rather than *N*-arylation when coupled with **24**. 2,4-Dimethoxyaniline **32** coupled with **1** to give diarylamine **22** but none of diarylamine **33** with **6**. Diarylamine **22** was prepared by the coupling of **20** and **6** in 78% yield whereas phenylation of **32** by **1** gave **22** in poor yield (34%). This suggests that in the preparation of arylphenylamines, it is better to arylate aniline **20** rather than phenylate the arylamine, as oxidation–reduction is preferred in the latter case. However, as noted above, there is a limitation on the arylating agent (*e.g.*, **9**) which may be used. Both of the electron-poor arylamines **34** and **36** were found to



32 R = H
33 R = 2,4-$(MeO)_2C_6H_3$



34 R = H
35 R = 2,4-$(MeO)_2C_6H_3$

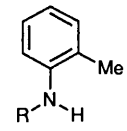


36 R = H
37 R = 2,4-$(MeO)_2C_6H_3$

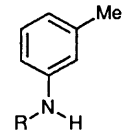
be totally unreactive towards **6**, which is comparable to the non-reactivity of **34** with **1** as previously reported.[30] Furthermore, **34** and **36** were isolated after reaction and no reduction products were observed. Thus, the arylation of amines by aryllead triacetates is dependent on the arylamine basicity and on the position of oxidisable substituents on both the aryllead triacetate and arylamine, but more so the latter.

The dependence of the reaction on the substitution pattern of the substrate arylamine was next investigated by reaction of various aryllead triacetates with *ortho*-, *meta*- and *para*-toluidine (**38**, **41** and **44**, respectively).

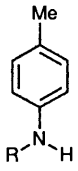
Varying the position of the methyl substituent of the arylamine has little effect on the yields obtained, although the yields of diarylamines produced on the arylation of **38** were lower than for the other two isomers. However, the presence of an *ortho*-substituent on the arylamine cannot have a major effect, as mesitylamine **10** gave high yields of diarylamines. The yield of *N*-(*p*-tolyl)-*p*-anisidine **28** was only slightly lower (89%) compared to that obtained (92%) from the coupling of **24** with 4-methylphenyllead triacetate **5**. When both the arylamine and the aryllead reagent have non-oxidisable substituents, the yields of diarylamines are almost quantitative, *e.g.*, di(*p*-tolyl)amine **45** and *N*-(*p*-tolyl)-3,4-methylenedioxyaniline **46** were obtained in 94% and 97%, respectively. Again, 100% regioselectivity was observed.



38 R = H
39 R = 2-$MeOC_6H_4$
40 R = 3-$MeOC_6H_4$

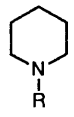


41 R = H
42 R = 2-$MeOC_6H_4$
43 R = 2,5-$(MeO)_2C_6H_3$

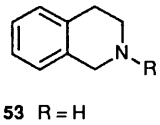


44 R = H
45 R = 4-MeC_6H_4
46 R = 3,4-$(OCH_2O)C_6H_3$

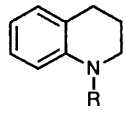
The *N*-arylating potential of these aryllead reagents was applied to the *N*-arylation of heterocyclic amines and the results are outlined in Table 3. The *N*-arylation of piperidine **47** proceeds in modest yields, even after 16 h. 1,2,3,4-Tetrahydroisoquinoline **53** was arylated by aryllead reagents **4**, **6** and **9** in good yields. The isomeric 1,2,3,4-tetrahydroquinoline **57** was



47 R = H
48 R = 4-$MeOC_6H_4$
49 R = 4-MeC_6H_4
50 R = 2,4-$(MeO)_2C_6H_3$
51 R = 3,4-$(OCH_2O)C_6H_3$
52 R = 2,4,6-$(MeO)_3C_6H_2$



53 R = H
54 R = 4-$MeOC_6H_4$
55 R = 2,4-$(MeO)_2C_6H_3$
56 R = 2,4,6-$(MeO)_3C_6H_2$



57 R = H
58 R = 4-MeC_6H_4
59 R = 2,4-$(MeO)_2C_6H_3$

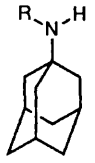
also arylated in modest yields although the reaction times were longer than for **53**. The tetrahydroquinoline **57** behaves like an aromatic secondary amine whereas **53** behaves like a more strongly basic aliphatic secondary amine. This explains the longer reaction time and the poorer yield of 1-(2,4-dimethoxyphenyl)-1,2,3,4-tetrahydroquinoline **59** compared to 2-(2,4-dimethoxyphenyl)-1,2,3,4-tetrahydroisoquinoline **55**. The modest yields of *N*-arylated tetrahydroisoquinolines are comparable to those observed when **53** was phenylated by **1** as previously reported.[30] The competing oxidation–reduction reaction was not observed in any of the above examples.

The *N*-arylation of aliphatic amines was also investigated and the results are outlined in Table 4. Benzylamine **62** was arylated in modest yields after 24 h. After this reaction time, some **62** remained unconsumed as did some of the aryllead reagents **5** and **6**, as indicated by thin-layer chromatography of the reaction mixture. Butylamine **65** was arylated by lead reagent **6** in poor yield (19%) and was found to be unreactive towards lead reagent **9**. Furthermore 1-adamantylamine **60** and *tert*-butylamine **68** were inert towards lead reagent **6**, which confirms the steric influence of the alkyl substituent as previously reported.[30] The yields of *N*-arylaliphatic amines are far inferior to the near quantitative yields of *N*-phenylated amines obtained using organobismuth reagents.[26] Further reactions where only oxidation–reduction was observed are outlined in Table 5.

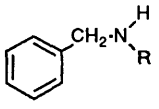
Table 5 Oxidation–reduction reactions observed during *N*-arylation studies[a]

Amine	$ArPb(OAc)_3$	Product (%)
32	**9**	**19** (85)
32	**9**	**19** (22)[b]
44	**13**	**19** (54)
70	**9**	**19** (58)[c]
71	**6**	**30** (70)
71	**9**	**19** (59)
—	**9**	**9** (100)

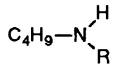
[a] Aryllead reagent was added to a suspension of copper diacetate and amine in methylene dichloride and was stirred under these conditions for 24 h. [b] Aryllead reagent added to a solution of amine in methylene dichloride at room temperature in the absence of copper diacetate. [c] Reaction carried out in the dark.



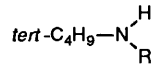
60 R = H
61 R = 2,4-$(MeO)_2C_6H_3$



62 R = H
63 R = 4-MeC_6H_4
64 R = 2,4-$(MeO)_2C_6H_3$

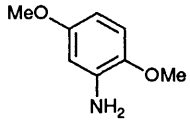


65 R = H
66 R = 2,4-$(MeO)_2C_6H_3$
67 R = 2,4,6-$(MeO)_3C_6H_2$



68 R = H
69 R = 2,4-$(MeO)_2C_6H_3$

Aryllead reagent **9** is most susceptible to reduction under the reaction conditions employed and almost complete reduction occurred when reacted with arylamine **32**. In fact, a slow oxidation of **32** occurred even in the absence of $Cu(OAc)_2$. 2,5-Dimethoxyaniline **70** was also oxidised, in a reaction carried out in the dark due to its light sensitivity. Diethylamine **71** was



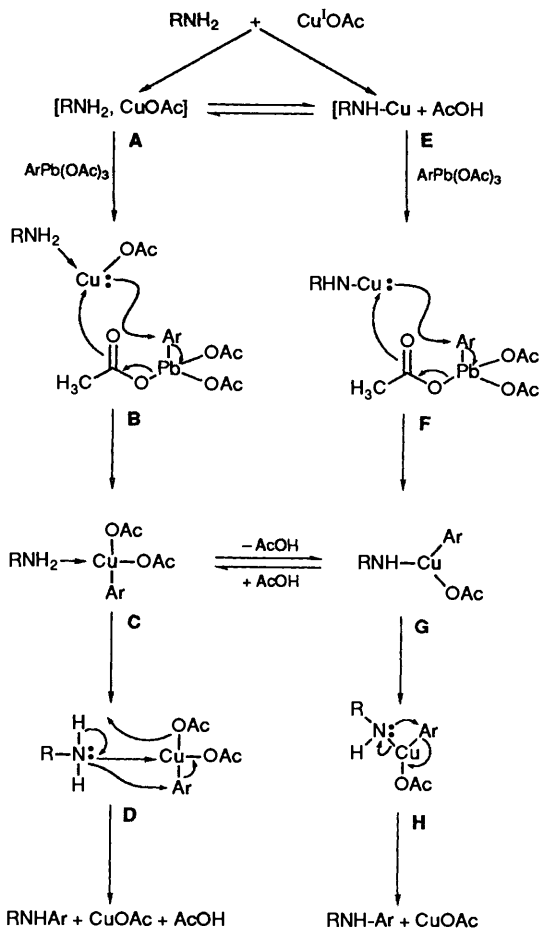
70

Et_2NH

71

oxidised by both aryllead reagents **6** and **9**. The aryllead reagent **9** was unreactive towards $Cu(OAc)_2$ and this result has mechanistic implications. As noted earlier, the consumption of amines resulted in the formation of polymeric materials which were not further investigated.

Indole-type derivatives and phenols were found to be inert towards arylation under these conditions. This is a limitation of the method, but these substrates may be arylated using organobismuth reagents as previously reported.[28,42] The mechanism that we postulate for this copper catalysed *N*-arylation is outlined in Scheme 1. As aryllead reagents are unreactive towards $Cu(OAc)_2$, the first step appears to involve the formation of an amine–copper complex. This complex may either involve a dative nitrogen-to-copper bond **A** or a covalent nitrogen-to-copper bond **E**. Oxidative addition of the aryllead triacetate, which might involve a Π-aryl complex to copper, gives an intermediate **B** or **F**. In both cases, reduction of the aryllead triacetate occurs with transfer of the aryl group onto copper to form a copper(III) intermediate **C** or **G**. At this stage, ligand coupling occurs to give the *N*-arylated amine and the



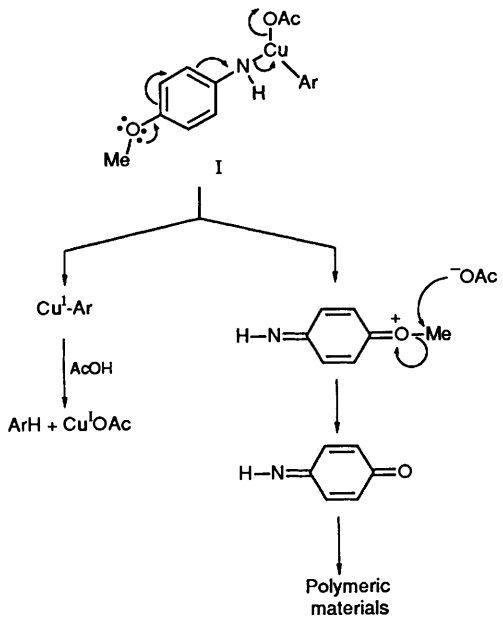
Scheme 1

catalytic Cu^I species. The inertness and non-consumption of the electron-deficient arylamines **34** and **36** suggests non-formation of the amine–copper complex **A** or **E** or the inability of such a complex to reduce the aryllead triacetate. However, no colour change was observed on the addition of $Cu(OAc)_2$ to a solution of either **34** or **36** which is in contrast to all other experiments performed, where a colour change, assigned to the formation of the amine–copper complex, was observed. Thus, the latter explanation would seem to be ruled out.

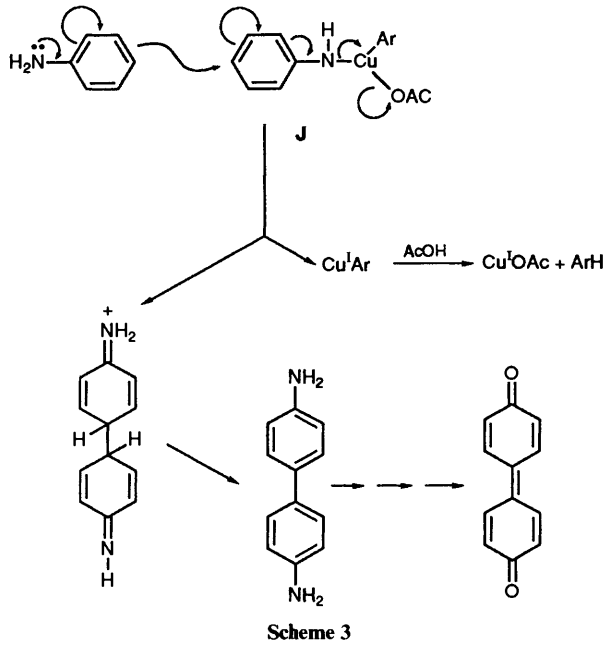
The oxidation–reduction reactions also observed may be explained as in Scheme 2. When an easily oxidisable aniline is involved in the Cu^{III} intermediate **I**, it is oxidised with elimination of acetate ion from copper to give a Cu^I aryl species which upon acetolysis yields the catalytic species Cu^IOAc and arene.

In the case of arylamine **20**, which was oxidised by aryllead reagent **9**, oxidative dimerisation as outlined in Scheme 3 is postulated to occur. Attack of a second molecule of **20** on the Cu^{III} intermediate **J** occurs with elimination of acetate ion and the formation of biaryls which ultimately give quinones after subsequent oxidation. The Cu^IAr species again is thought to undergo acetolysis forming arene and Cu^IOAc. The fact that arylamine **32** was slowly oxidised by aryllead reagent **9** in the absence of copper diacetate may be explained as in Scheme 4. Direct nucleophilic attack of the electron-rich arylamine **32** on the electrophilic lead atom with loss of AcOH gives an intermediate of type **K**, which, after oxidation and elimination of acetate ion, gives the aryllead(II) acetate. This undergoes acetolysis to form arene **19** and lead diacetate. As seen from Table 5, this process is slower in the absence of copper diacetate.

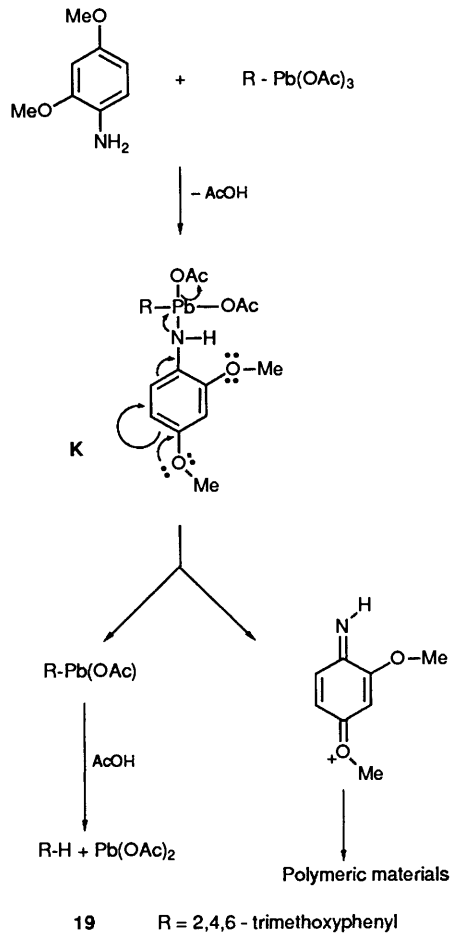
In the case of the present and preceding[26,42] copper catalysed



Scheme 2



Scheme 3



19 R = 2,4,6 - trimethoxyphenyl

Scheme 4

reactions, addition of large amounts of 1,1-diphenylethene had no effect on the arylation reaction. Hence a free-radical mechanism is excluded although the possibility of an inner-sphere radical mechanism cannot be discounted.

Aryllead triacetates are a class of reagents which regiospecifically mono *N*-arylate amines under mild and neutral conditions. The yields of diarylamines are high and are independent of the steric hindrance of the arylamine and the substitution pattern of arylamines containing non-oxidisable substituents. A large dependence on the arylamine basicity exists.

This method compares favourably to the drastic conditions employed in the Ullmann, Goldberg and Chapman methods by the mild conditions used. It is superior to arynic methods by the neutral conditions employed, useful for the arylation of base-sensitive substrates and by its regioselectivity for the synthesis of *ortho*-substituted diarylamines which cannot be made *via* aryne methods. However, polymethoxylated diarylamines are not easily prepared by this method due to competing oxidation–reduction reactions. The *N*-arylation of heterocyclic amines proceeds in modest yields whilst *N*-arylated aliphatic amines are obtained in poor yield. Thus, aryllead triacetates possess possible chemoselective properties as preferential *N*-arylation of amines would occur in the presence of an alkylamine.

Experimental

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were determined for solutions in deuteriochloroform with tetramethylsilane as internal standard on Varian Gemini-200[a] and JEOL JNM-PMX60[b] instruments. All *J* values are given in Hz. IR spectra were recorded on a Perkin-Elmer 881 spectrophotometer* and a Perkin-Elmer 1710 Infra-red Fourier Transform spectrophotometer.† Mass spectra were recorded on a VG Analytical 705 high resolution double focusing magnetic sector mass spectrometer with attached VG 11/2505 data system in the EI mode* and on a VG Analytical 770 mass spectrometer with attached INCOS 2400 data system in the EI mode.† UV spectra were recorded on a Beckman DU-7 spectrophotometer. Chromatographic separations were performed using Aldrich silica gel 130–270 mesh 60 Å (column chromatography). Separation by preparative thin layer chromatography was found to be undesirable due to the facile oxidation of the *N*-arylated amines produced. Phenyllead

* Texas A&M University.
† University College, Dublin.

triacetate **1** is available commercially (Alfa). Ether refers to diethyl ether. All solvents were purified by standard techniques.

Preparation of Aryllead Triacetates.—4-Methoxyphenyllead triacetate **4**, 4-methylphenyllead triacetate **5**, 2,4-dimethoxyphenyllead triacetate **6** and 2,4,6-trimethoxyphenyllead triacetate **9** were prepared by plumbylation.[40] 2-Methoxyphenyllead triacetate **2**, 3-methoxyphenyllead triacetate **3** and 2,5-dimethoxyphenyllead triacetate **7** were prepared by tin–lead exchange.[41]

3,4-*Methylenedioxyphenyllead triacetate* **8**. Butyllithium (1.6 mol dm^{-3} in hexane, 31.6 cm^3, 0.051 mol) was added to a stirred solution of 4-bromo-(1,2-methylenedioxy)benzene (9.24 g, 0.046 mol) in dry THF (50 cm^3) under nitrogen at −78 °C and was stirred at this temperature for 30 min. Tributyltin chloride (21.05 g, 0.065 mol) was added and the reaction mixture was stirred for 30 min at −78 °C. After this time, the reaction mixture was added to saturated aqueous ammonium chloride (40 cm^3) and then to H_2O (250 cm^3). This was extracted with ether (2 × 200 cm^3), washed with brine (2 × 100 cm^3), dried and concentrated to yield an oil which upon distillation gave (3,4-methylenedioxyphenyl)tributylstannane (15.21 g, 80.5%, b.p. 166–169 °C at 0.8 mmHg) as a colourless oil, $\nu_{max}(CHCl_3)/cm^{-1}$ 3040, 925 and 887; δ 7.12–6.94 (3 H, m, 2-H, 5-H, 6-H), 5.84 (2 H, s, OCH_2O) and 1.94–0.84 (27 H, m, 3 × C_4H_9); *m/z* 411 [3,4-$(OCH_2O)C_6H_3Sn^+Bu_3$, 3%], 355 [3,4-$(OCH_2O)C_6H_3Sn^+Bu_2$, 100], 299 [3,4-$(OCH_2O)C_6H_3Sn^+Bu$, 14], 240 [3,4-$(OCH_2O)C_6H_3Sn^+$, 82] and 120 [Sn^+, 9] based on ^{120}Sn, Sn satellites also occur (Found: C, 55.60; H, 7.75. $C_{19}H_{32}O_2Sn$ requires C, 55,50; H, 7.85%).

Lead tetraacetate (10.72 g, 24.2 mmol) was stirred in chloroform (40 cm^3) at 40 °C with (3,4-methylenedioxyphenyl)-tributylstannane (10.28 g, 24 mmol) and mercuric acetate (0.382 g, 1.2 mmol) for 4 h. After this time, the reaction mixture was filtered through Celite, the solvent removed under reduced pressure, and a yellow solid resulted. Light petroleum (25 cm^3) was added and the yellow solid was collected and washed with light petroleum (2 × 15 cm^3) to give 3,4-methylenedioxyphenyllead triacetate **8** (12.54 g, 99.2%) m.p. 126.5–130 °C ($CHCl_3$–ether–light petroleum), $\nu_{max}(CHCl_3)/cm^{-1}$ 3019, 1555, 1473, 1213, 776 and 668; $\lambda_{max}(CHCl_3)/nm$ 254.5 (ε 6576) and 280.5 (6123); δ 7.34–7.08 (2 H, m, 2-H, 6-H), 6.98 (1 H, d, *J* 8.5, 5-H), 6.05 (2 H, s, OCH_2O) and 2.10 (9 H, s, 3 × OAc); *m/z* 571 [3,4-$(OCH_2O)C_6H_3Pb^+(OAc)_3$, 1%], 447 [3,4-$(OCH_2O)C_6H_3Pb^+(OAc)_2$, 1], 388 [3,4-$(OCH_2O)C_6H_3Pb^+$-(OAc), 0.5], 329 [3,4-$(OCH_2O)C_6H_3Pb^+$, 1.2], 267 [$Pb^+OAc$, 100], 242 [3,4,3′,4′-bismethylenedioxybiphenyl, 9], 208 [Pb^+, 4] and 121 [3,4-$(OCH_2O)C_6H_3^+$, 90] based on ^{208}Pb isotope, ^{207}Pb and ^{209}Pb satellites also occur (Found: C, 31.05; H, 2.85. $C_{13}H_{14}O_8Pb$ requires C, 30.90; H, 2.80%).

General Procedure for the N-*Arylation of Amines Under Copper Catalysis.*—Aryllead triacetate (0.55 mmol) was added to a well-stirred solution of amine (0.50 mmol) and copper diacetate (0.009 g, 0.05 mmol) in dry methylene dichloride (5 cm^3) at room temperature under an atmosphere of argon and was stirred under these conditions for the length of time indicated in the tables (Tables 2–5). The reaction mixture was then filtered through Celite, concentrated and purified by column chromatography. The eluent system used was methylene dichloride–hexane (4:1), unless otherwise indicated. The solid diarylamines prepared recrystallised as colourless needles from ethyl alcohol, unless otherwise stated.

N-*Mesityl*-o-*anisidine* **11**. 2-Methoxyphenyllead triacetate **2** (0.270 g) and mesitylamine **10** (0.067 g) gave **11** (0.114 g, 95%) as an orange solid, m.p. 97.5–99 °C (lit.,[14] 100–100.5 °C).

N-*Mesityl*-m-*anisidine* **12**. 3-Methoxyphenyllead triacetate **3** (0.270 g) and mesitylamine **10** (0.067 g) gave **12** (0.100 g, 84%) as a yellow solid, m.p. 79–80 °C, $\nu_{max}(CHCl_3)/cm^{-1}$ 3419, 3020, 1599, 1495 and 756; δ 7.05 (1 H, t, *J* 8.10, 4-H), 6.93 (2 H, s, 3′-H, 5′-H), 6.29 (1 H, dd, *J* 8.13 and 2.40, 5-H), 6.13 (1 H, dd, *J* 8.01 and 2.20, 3-H), 6.02 (1 H, t, *J* 2.12 and 2.38, 2-H), 5.12 (1 H, br s, N-H), 3.73 (3 H, s, 3-OCH_3), 2.30 (3 H, s, 4′-CH_3) and 2.17 (6 H, s, 2′-CH_3, 6′-CH_3); *m/z* 241 (M^+, 100%), 226 (23), 224 (8), 211 (8), 208 (4) and 134 (9) (Found: C, 79.70; H, 8.00; N, 5.70. $C_{16}H_{19}NO$ requires C, 79.60; H, 7.95; N, 5.80%).

N-*Mesityl*-p-*anisidine* **13**. 4-Methoxyphenyllead triacetate **4** (0.270 g) and mesitylamine **10** (0.067 g) gave **13** (0.091 g, 76%) as a solid, m.p. 96–97 °C, $\nu_{max}(CHCl_3)/cm^{-1}$ 3413, 3005, 1506, 1484 and 823; δ 6.91 (2 H, s, 3′-H, 5′-H), 6.72 (2 H, d, *J* 8.99, 2-H, 6-H), 6.45 (2 H, d, *J* 9.03, 3-H, 5-H), 4.92 (1 H, br s, N-H), 3.72 (3 H, s, 4-OCH_3), 2.28 (3 H, s, 4′-CH_3) and 2.14 (6 H, s, 2′-CH_3, 6′-CH_3); *m/z* 241 (M^+, 100%), 226 (86), 208 (5), 119 (17), 113 (9) and 91 (9) (Found: C, 79.60; H, 7.85; N, 5.70. $C_{16}H_{19}NO$ requires C, 79.60; H, 7.95; N, 5.80%).

N-(p-*Tolyl*)-2,4,6-*trimethylaniline* **14**. 4-Methylphenyllead triacetate **5** (0.260 g) and mesitylamine **10** (0.067 g) gave **14** (0.103 g, 92%) as a solid, m.p. 64.5–66 °C (lit.,[14] 66–67 °C).

N-*Mesityl*-2,4-*dimethoxyaniline* **15**. 2,4-Dimethoxyphenyllead triacetate **6** (0.287 g) and mesitylamine **10** (0.067 g) gave **15** (0.100 g, 74%) as a solid, m.p. 111–112.5 °C, $\nu_{max}(CHCl_3)/cm^{-1}$ 3417, 3019, 1510 and 1224; δ 6.92 (2 H, s, 3′-H, 5′-H), 6.52 (1 H, d, *J* 2.60, 3-H), 6.25 (1 H, dd, *J* 8.56 and 2.66, 5-H), 6.03 (1 H, d, *J* 8.55, 6-H), 5.28 (1 H, br s, N-H), 3.91 (3 H, s, 4-OCH_3), 3.73 (3 H, s, 2-OCH_3), 2.29 (3 H, s, 4′-CH_3) and 2.16 (6 H, s, 2′-CH_3, 6′-CH_3); *m/z* 271 (M^+, 100%), 256 (55), 241 (37), 224 (11) and 136 (6) (Found: C, 75.30; H, 7.75; N, 5.00. $C_{17}H_{21}NO_2$ requires C, 75.25; H, 7.80; N, 5.20%).

N-*Mesityl*-2,5-*dimethoxyaniline* **16**. 2,5-Dimethoxyphenyllead triacetate **7** (0.287 g) and mesitylamine **10** (0.067 g) gave **16** (0.094 g, 70%) as a solid, m.p. 81–82 °C, $\nu_{max}(CHCl_3)/cm^{-1}$ 3418, 3018, 1604, 1511, 1212 and 733; δ 6.93 (2 H, s, 3′-H, 5′-H), 6.75 (1 H, d, *J* 8.61, 3-H), 6.18 (1 H, dd, *J* 8.61 and 2.93, 4-H), 5.75 (1 H, d, *J* 2.91, 6-H), 5.60 (1 H, br s, N-H), 3.90 (3 H, s, 2-OCH_3), 3.64 (3 H, s, 5-OCH_3), 2.29 (3 H, s, 4′-CH_3) and 2.17 (6 H, s, 2′-CH_3, 6′-CH_3); *m/z* 271 (M^+, 100%), 256 (51), 241 (61), 240 (14), 238 (16), 224 (15), 198 (7), 136 (9), 128 (5), 121 (13) and 91 (6) (Found: C, 74.90; H, 7.70; N, 4.90. $C_{17}H_{21}NO_2$ requires C, 75.25; H, 7.80; N, 5.20%).

N-*Mesityl*-3,4-*methylenedioxyaniline* **17**. 3,4-Methylenedioxyphenyllead triacetate **8** (0.278 g) and mesitylamine **10** (0.067 g) gave **17** (0.116 g, 91%) as a solid, m.p. 77–79 °C, $\nu_{max}(CHCl_3)/cm^{-1}$ 3417, 3024, 2780, 1504, 932 and 861; δ 6.91 (2 H, s, 3′-H, 5′-H), 6.60 (1 H, d, *J* 8.33, 5-H), 6.09 (1 H, d, *J* 2.16, 2-H), 5.95–5.91 (1 H, m, 6-H), 5.83 (2 H, s, OCH_2O), 4.92 (1 H, br s, N-H), 2.28 (3 H, s, 4′-CH_3) and 2.15 (6 H, s, 2′-CH_3, 6′-CH_3); *m/z* 255 (M^+, 100%), 240 (14), 210 (20), 196 (18), 181 (10), 133 (13) and 91 (12) (Found: C, 75.45; H, 6.95; N, 5.15. $C_{16}H_{17}NO_2$ requires C, 75.25; H, 6.70; N, 5.50%).

N-*Mesityl*-2,4,6-*trimethoxyaniline* **18**. 2,4,6-Trimethoxyphenyllead triacetate **9** (0.304 g) and mesitylamine **10** (0.067 g) gave **18** (0.027 g, 18%) as a solid, m.p. 71–73 °C, $\nu_{max}(CHCl_3)/cm^{-1}$ 3420, 3019, 2780, 1505, 1233, 857 and 850; δ 6.75 (2 H, s, 3′-H, 5′-H), 6.11 (2 H, s, 3-H, 5-H), 4.80 (1 H, br s, N-H), 3.72 (3 H, s, 4-OCH_3), 3.60 (6 H, s, 2-OCH_3, 6-OCH_3), 2.21 (3 H, s, 4′-CH_3) and 2.10 (6 H, s, 2′-CH_3, 6′-CH_3); *m/z* 301 (M^+, 100%), 286 (32), 271 (27), 255 (20), 254 (43) and 91 (10) (Found: C, 72.00; H, 7.75; N, 4.50. $C_{18}H_{23}NO_3$ requires C, 71.75; H, 7.70; N, 4.65%). Also isolated was 1,3,5-trimethoxybenzene **19** (0.045 g, 49%).

N-*Phenyl*-p-*anisidine* **21**. 4-Methoxyphenyllead triacetate **4** (0.270 g) and aniline **20** (0.047 g) gave **21** (0.072 g, 72%) as a solid, m.p. 105 °C (lit.,[43] 104–105 °C).

N-*Phenyl*-2,4-*dimethoxyaniline* **22**. 2,4-Dimethoxyphenyllead triacetate **6** (0.287 g) and aniline **20** (0.047 g) gave **22** (0.089 g, 78%) as an oil, lit.,[43] b.p. 191–195 °C at 6 mmHg) (Found: C,

73.45; H, 6.40; N, 6.00. Calc. for $C_{14}H_{15}NO_2$: C, 73.35; H, 6.60; N, 6.10%).

N-(2-*Methoxyphenyl*)-p-*anisidine* **25**. 2-Methoxyphenyllead triacetate **2** (0.270 g) and *p*-anisidine **24** (0.062 g) gave **25** (0.097 g, 85%) as a solid, m.p. 66.5–67.5 °C (lit.,[44] 71–72 °C).

N-(3-*Methoxyphenyl*)-p-*anisidine* **26**. 3-Methoxyphenyllead triacetate **3** (0.270 g) and *p*-anisidine **24** (0.062 g) gave **26** (0.085 g, 74%) as a solid, m.p. 61.5–62.5 °C (lit.,[45] 68 °C).

4,4′-*Dimethoxydiphenylamine* **27**. 4-Methoxyphenyllead triacetate **4** (0.270 g) and *p*-anisidine **24** (0.062 g) gave **27** (0.105 g, 91%) as a solid, m.p. 101–103 °C (lit.,[46] m.p. 102–103 °C).

N-(p-*Tolyl*)-p-*anisidine* **28**. 4-Methylphenyllead triacetate **5** (0.260 g) and *p*-anisidine **24** (0.062 g) gave **28** (0.089 g, 89%) as a solid, m.p. 82–83 °C (lit.,[47] m.p. 83–84 °C).

N-(4-*Methoxyphenyl*)-2,4-*dimethoxyaniline* **29**. 2,4-Dimethoxyphenyllead triacetate **6** (0.287 g) and *p*-anisidine **24** (0.062 g) gave **29** (0.032 g, 25%) as an oil, $\nu_{max}(CHCl_3)/cm^{-1}$ 3447, 3020, 1424, 1214, 878 and 774; δ 7.10–6.80 (5 H, m, 2′-H, 3′-H, 5′-H, 6′-H, 6-H), 6.50–6.20 (2 H, m, 3-H, 5-H), 3.84 (3 H, s, 2-OCH_3) and 3.73 (6 H, s, 4-OCH_3, 4-′OCH_3); *m*/*z* 259 (M^+, 100%), 244 (96), 229 (8), 213 (37), 201 (10) and 129 (10) (Found: C, 69.10; H, 6.80; N, 5.75. $C_{15}H_{17}NO_2$ requires C, 69.45; H, 6.60; N, 5.40%). 1,3-Dimethoxybenzene **30** (0.045 g, 60%) was also isolated.

N-(4-*Methoxyphenyl*)-2,5-*dimethoxyaniline* **31**. 2,5-Dimethoxyphenyllead triacetate **7** (0.287 g) and *p*-anisidine **24** (0.062 g) gave **31** (0.032 g, 25%) as an oil, $\nu_{max}(CHCl_3)/cm^{-1}$ 3423, 3024, 1510, 1225 and 734; δ 7.12 (2 H, d, *J* 8.95, 2′-H, 6′-H), 6.86 (2 H, d, *J* 8.87, 3′-H, 5′-H), 6.74 (1 H, d, *J* 7.75, 3-H), 6.62 (1 H, d, *J* 2.93, 6-H), 6.26 (1 H, dd, *J* 7.75 and 2.93, 4-H), 5.99 (1 H, br s, N-H), 3.84 (3 H, s, 2-OCH_3), 3.78 (3 H, s, 4′-OCH_3) and 3.69 (3 H, s, 5-OCH_3); *m*/*z* 260 (16%), 259 (M^+, 100), 244 (93), 213 (52), 186 (8) and 130 (7) (Found: C, 70.00; H, 6.95; N, 5.80. $C_{15}H_{17}NO_3$ requires C, 69.55; H, 6.60; N, 5.40%).

N-*Phenyl*-2,4-*Dimethoxyaniline* **22**. Phenyllead triacetate **1** (0.249 g) and 2,4-dimethoxyaniline **32** (0.077 g) gave **22** (0.039 g, 34%) as an oil, identical with an authentic sample.

N-(o-*Tolyl*)-o-*anisidine* **39**. 2-Methoxyphenyllead triacetate **2** (0.270 g) and *o*-toluidine **38** (0.054 g) gave **39** (0.068 g, 64%) as an oil[48] (Found: C, 78.35; H, 7.25; N, 6.45. Calc. for $C_{14}H_{15}NO$: C, 78.85; H, 7.10; N, 6.60%).

N-(o-*Tolyl*)-m-*anisidine* **40**. 3-Methoxyphenyllead triacetate **3** (0.270 g) and *o*-toluidine **38** (0.054 g) gave **40** (0.060 g, 56%) as an oil, $\nu_{max}(CHCl_3)/cm^{-1}$ 3441, 3014, 1200, 788, 752 and 690; δ 7.27–7.11 (4 H, m, 3′-H, 4′-H, 5′-H, 6′-H), 6.98–6.90 (1 H, m, 5-H), 6.55–6.43 (3 H, m, 2-H, 4-H, 6-H), 5.38 (1 H, br s, N-H), 3.75 (3 H, s, 3-OCH_3) and 2.25 (3 H, s, 2′-CH_3); *m*/*z* 213 (M^+, 100%), 198 (27), 182 (16), 167 (11), 154 (8), 106 (10) and 45 (20) (Found: C, 78.60; H, 6.95; N, 6.40. $C_{14}H_{15}NO$ requires C, 78.85; H, 7.10; N, 6.60%).

N-(m-*Tolyl*)-o-*anisidine* **42**. 2-Methoxyphenyllead triacetate **2** (0.270 g) and *m*-toluidine **41** (0.054 g) gave **42** (0.095 g, 90%) as an oil, $\nu_{max}(CHCl_3)/cm^{-1}$ 3424, 1587, 1236, 887, 794 and 688; δ 7.33–7.26 (1 H, m, 4-H), 7.18–7.12 (1 H, m, 2′-H), 6.96–6.73 (6 H, m, 3-H, 5-H, 6-H, 4′-H, 5′-H, 6′-H), 6.11 (1 H, br s, N-H), 3.86 (3 H, s, 2-OCH_3) and 2.31 (3 H, s, 3′-CH_3); *m*/*z* 213 (M^+, 100%), 198 (46), 183 (79), 170 (6), 154 (13) and 77 (12) (Found: C, 78.85; H, 7.30; N, 6.30. $C_{14}H_{15}NO$ requires C, 78.85; H, 7.10; N, 6.60%).

N-(m-*Tolyl*)-2,5-*dimethoxyaniline* **43**. 2,5-Dimethoxyphenyllead triacetate **7** (0.287 g) and *m*-toluidine **41** (0.054 g) gave **43** (0.082 g, 77%) as an oil, $\nu_{max}(CHCl_3)/cm^{-1}$ 3422, 3025, 1588, 1526, 1212 and 893; δ 7.21–7.13 (1 H, m, 5-H), 7.03–6.97 (2 H, m, 4′-H, 6′-H), 6.91 (1 H, d, *J* 2.93, 6-H), 6.78 (1 H, d, *J* 8.71, 4-H), 6.75 (1 H, d, *J* 2.84, 2′-H), 6.33 (1 H, dd, *J* 8.79 and 2.93, 3-H), 6.15 (1 H, br s, N-H), 3.83 (3 H, s, 2-OCH_3), 3.73 (3 H, s, 5-OCH_3) and 2.31 (3 H, s, 3′-CH_3); *m*/*z* 243 (M^+, 88%), 228 (100), 213 (52), 197 (10) and 184 (7) (Found: C, 74.15; H, 7.25; N, 5.40. $C_{15}H_{17}NO_2$ requires C, 74.05; H, 7.05; N, 5.80%).

N-(p-*Tolyl*)-p-*anisidine* **28**. 4-Methoxyphenyllead triacetate **4** (0.270 g) and *p*-toluidine **44** (0.054 g) gave **28** (0.092 g, 92%).

N-(p-*Tolyl*)-p-*toluidine* **45**. 4-Methylphenyllead triacetate **5** (0.260 g) and *p*-toluidine **44** (0.054 g) gave **45** (0.092 g, 94%) as a solid, m.p. 78–79 °C (lit.,[49] 79 °C).

N-(p-*Tolyl*)-3,4-*methylenedioxyaniline* **46**. 3,4-Methylenedioxyphenyllead triacetate **8** (0.274 g) and *p*-toluidine **44** (0.054 g) gave **46** (0.108 g, 96%) as an oil, $\nu_{max}(CHCl_3)/cm^{-1}$ 3428, 3013, 931 and 816; δ 7.15–6.64 (4 H, m, 2′-H, 3′-H, 5′-H, 6′-H), 6.60 (1 H, d, *J* 2.50, 5-H), 6.43 (1 H, dd, *J* 8.50 and 2.51, 6-H), 5.86 (2 H, s, OCH_2O), 5.02 (1 H, br s, N-H) and 2.29 (3 H, s, 4′-CH_3); *m*/*z* 228 (15%), 227 (M^+, 100), 198 (13), 168 (22), 154 (18), 91 (12) and 84 (10) (Found: C, 73.95; H, 5.85; N, 6.05. $C_{14}H_{13}NO_2$ requires C, 73.95; H, 5.75; N, 6.20%).

1-(4-*Methoxyphenyl*)*piperidine* **48**. 4-Methoxyphenyllead triacetate **4** (0.270 g) and piperidine **47** (0.042 g) gave **48** (0.038 g, 39%) as an oil (eluent: methylene dichloride–hexane, 8:1), lit.,[25] b.p. 88 °C at 0.9 mmHg (Found: C, 75.20; H, 9.10; N, 7.15. Calc. for $C_{12}H_{17}NO$: C, 75.35; H, 8.95; N, 7.30%).

1-(4-*Tolyl*)*piperidine* **49**. 4-Methylphenyllead triacetate **5** (0.260 g) and piperidine **47** (0.042 g) gave **49** (0.038 g, 39%) as an oil (eluent: methylene dichloride–hexane, 8:1), lit.,[22] b.p. 140–143 °C at 15 mmHg (Found: C, 82.00; H, 9.70; N, 7.95. Calc. for $C_{12}H_{17}N$: C, 82.20; H, 9.75; N, 8.00%).

1-(2,4-*Dimethoxyphenyl*)*piperidine* **50**. 2,4-Dimethoxyphenyllead triacetate **6** (0.287 g) and piperidine **47** (0.042 g) gave **50** (0.067 g, 60%) as an oil (eluent: methylene dichloride), $\nu_{max}(CHCl_3)/cm^{-1}$ 2940, 1509, 1235 and 888; δ 6.87 (1 H, d, *J* 8.54, 6′-H), 6.49–6.39 (2 H, m, 3′-H, 5′-H), 3.84 (3 H, s, 2′-OCH_3), 3.78 (3 H, s, 4′-OCH_3), 2.90 (4 H, t, *J* 5.41, H_2C-N-CH_2) and 1.82–1.47 (6 H, m, 3-CH_2, 4-CH_2, 5-CH_2); *m*/*z* 221 (M^+, 85%), 220 (60), 206 (100), 192 (5), 164 (10), 150 (40), 110 (8), 79 (10) and 41 (19) (Found: C, 70.70; H, 8.80; N, 6.05. $C_{13}H_{19}NO_2$ requires C, 70.55; H, 8.65; N, 6.35%).

1-(3,4-*Methylenedioxyphenyl*)*piperidine* **51**. 3,4-Methylenedioxyphenyllead triacetate **8** (0.278 g) and piperidine **47** (0.042 g) gave **51** (0.039 g, 38%) as an oil (eluent: methylene dichloride), $\nu_{max}(CHCl_3)/cm^{-1}$ 3023, 2858, 1631, 1384, 952, 936 and 832; δ 6.74 (1 H, d, *J* 8.5, 5′-H), 6.44 (1 H, d, *J* 2.5, 2′-H), 6.37 (1 H, dd, *J* 8.5 and 2.5, 6-H), 5.85 (2 H, s, OCH_2O), 3.18–2.92 (4 H, m, H_2C-N-CH_2) and 1.88–1.58 (6 H, m, 3-CH_2, 4-CH_2, 5-CH_2); *m*/*z* 205 (M^+, 87%), 204 (100), 190 (5), 176 (9), 164 (14), 149 (40), 148 (30), 91 (12), 65 (21) and 41 (17) (Found: C, 69.95; H, 7.40; N, 6.40. $C_{12}H_{15}NO_2$ requires C, 70.20; H, 7.35; N, 6.80%).

1-(2,4,6-*Trimethoxyphenyl*)*piperidine* **52**. 2,4,6-Trimethoxyphenyllead triacetate **9** (0.304 g) and piperidine **47** (0.042 g) gave **52** (0.045 g, 36%) as a solid (eluent: methylene dichloride–hexane, 8:1), m.p. 86.5–88 °C, $\nu_{max}(CHCl_3)/cm^{-1}$ 3036, 2937, 1201 and 857; δ 6.15 (2 H, s, 3′-H, 5′-H), 3.80 (3 H, s, 4′-OCH_3), 3.76 (6 H, s, 2′-OCH_3, 6′-OCH_3), 3.16–2.91 (4 H, m, H_2C-N-CH_2) and 1.80–1.52 (6 H, m, 3-CH_2, 4-CH_2, 5-CH_2); *m*/*z* 251 (M^+, 100%), 250 (97), 236 (53), 220 (11), 194 (11), 180 (48), 69 (22) and 41 (43) (Found: C, 66.95; H, 8.45; N, 5.25. $C_{14}H_{21}NO_3$ requires C, 66.90; H, 8.40; N, 5.55%).

2-(4-*Methoxyphenyl*)-1,2,3,4-*tetrahydroisoquinoline* **54**. 4-Methoxyphenyllead triacetate **4** (0.270 g) and 1,2,3,4-tetrahydroisoquinoline **53** (0.067 g) gave **54** (0.051 g, 43%) as a solid (eluent: methylene dichloride–hexane, 8:1), m.p. 93–94 °C (lit.,[21] 93–95 °C).

2-(2,4-*Dimethoxyphenyl*)-1,2,3,4-*tetrahydroisoquinoline* **55**. 2,4-Dimethoxyphenyllead triacetate **6** (0.287 g) and 1,2,3,4-tetrahydroisoquinoline **53** (0.067 g) gave **55** (0.090 g, 60%) as a solid (eluent: methylene dichloride), m.p. 61–63 °C (lit.,[19] 62–64 °C).

1,2,3,4-*Tetrahydro*-2-(2,4,6-*trimethoxyphenyl*)*isoquinoline* **56**. 2,4,6-Trimethoxyphenyllead triacetate **9** (0.304 g) and 1,2,3,4-tetrahydroisoquinoline **53** (0.067 g) gave **56** (0.082 g, 55%) as an oil (eluent: methylene dichloride), $\nu_{max}(CHCl_3)/cm^{-1}$ 2943,

1600, 1234, 857 and 764; δ 7.14–6.97 (4 H, m, 5-H, 6-H, 7-H, 8-H), 6.17 (2 H, s, 3′-H, 5′-H), 4.27 (2 H, s, 1-CH_2), 3.82 (3 H, s, 4′-OCH_3), 3.80 (6 H, s, 2′-OCH_3, 6′-OCH_3), 3.34 (2 H, t, *J* 6.0, 3-CH_2) and 2.90 (2 H, t, *J* 6.0, 4-CH_2); *m/z* 299 (M^+, 38%), 298 (34), 282 (19), 184 (100), 169 (30), 141 (12) and 43 (19) (Found: C, 71.95; H, 7.25; N, 4.40. $C_{18}H_{21}NO_3$ requires C, 72.20; H, 7.05; N, 4.65%).

1,2,3,4-*Tetrahydro*-1-(4-*tolyl*)*quinoline* **58**. 4-Methylphenyllead triacetate **5** (0.257 g) and 1,2,3,4-tetrahydroquinoline **57** (0.067 g) gave **58** (0.066 g, 59%) as an oil, $\nu_{max}(CHCl_3)/cm^{-1}$ 3007, 2930, 1510 and 831; δ 7.14 (4 H, m, 2′-H, 3′-H, 5′-H, 6′-H), 7.04–6.84 (2 H, m, 5-H, 8-H), 6.69–6.60 (2 H, m, 6-H, 7-H), 3.58 (2 H, t, *J* 5.65, 2-CH_2), 2.85 (2 H, t, *J* 6.84, 4-CH_2), 2.34 (3 H, s, 4′-CH_3) and 2.04 (2 H, m, 3-CH_2); *m/z* 223 (M^+, 100%), 222 (54), 207 (5), 194 (7), 96 (8) and 91 (8) (Found: C, 85.85; H, 7.95; N, 5.85. $C_{16}H_{17}N$ requires C, 86.05; H, 7.65; N, 6.90%).

2-(2,4-*Dimethoxyphenyl*)-1,2,3,4-*tetrahydroquinoline* **59**. 2,4-Dimethoxyphenyllead triacetate **6** (0.287 g) and 1,2,3,4-tetrahydroquinoline **57** (0.067 g) gave **59** (0.034 g, 25%) as an oil (eluent: methylene dichloride–hexane, 8:1), $\nu_{max}(CHCl_3)/cm^{-1}$ 3013, 2936, 1602, 1230, 882 and 728; δ 7.12 (1 H, d, *J* 8.40, 6′-H), 6.99–6.84 (2 H, m, 5-H, 8-H), 6.60–6.45 (3 H, m, 5′-H, 6-H, 7-H), 6.17 (1 H, d, *J* 7.10, 3′-H), 3.83 (3 H, s, 2′-OCH_3), 3.75 (3 H, s, 4′-OCH_3), 3.49 (2 H, m, 2-CH_2), 2.86 (2 H, t, *J* 6.21, 4-CH_2) and 2.08 (2 H, m, 3-CH_2); *m/z* 269 (M^+, 100%), 254 (27), 226 (6), 194 (2), 167 (5), 117 (12) and 91 (3) (Found: C, 75.70; H, 7.30; N, 5.10. $C_{17}H_{19}NO_2$ requires C, 75.80; H, 7.10; N, 5.20%).

N-*Benzyl*-p-*toluidine* **63**. 4-Methylphenyllead triacetate **5** (0.270 g) and benzylamine **62** (0.054 g) gave **63** (0.038 g, 39%) as an oil, lit.,[50] b.p. 160–162 °C at 4 mmHg) (Found: C, 85.55; H, 7.60; N, 6.65. Calc. for $C_{14}H_{15}N$: C, 85.20; H, 7.65; N, 7.15%).

N-*Benzyl*-2,4-*dimethoxyaniline* **64**. 2,4-Dimethoxyphenyllead triacetate **6** (0.287 g) and benzylamine **62** (0.054 g) gave **64** (0.043 g, 35%) as an oil, $\nu_{max}(CHCl_3)/cm^{-1}$ 3441, 1599, 1219, 1046, 780 and 671; δ 7.34 (5 H, s, C_6H_5), 6.53–6.39 (3 H, m, 3′-H, 5′-H, 6′-H), 4.31 (2 H, s, CH_2), 3.86 (3 H, s, 2′-OCH_3) and 3.76 (3 H, s, 4′-OCH_3); *m/z* 243 (M^+, 100%), 228 (20), 152 (52), 124 (17), 91 (87) and 65 (18) (Found: C, 73.90; H, 6.95; N, 5.60. $C_{15}H_{17}NO_2$ requires C, 74.05; H, 7.05; N, 5.80%).

N-*Butyl*-2,4-*dimethoxylaniline* **66**. 2,4-Dimethoxyphenyllead triacetate **6** (0.287 g) and butylamine **65** (0.037 g) gave **66** (0.020 g, 19%) as an oil, $\nu_{max}(CHCl_3)/cm^{-1}$ 3441, 1599, 1219, 1046, 780 and 671; δ 6.80–6.38 (3 H, m, 3′-H, 5′-H, 6′-H), 3.78 (3 H, s, 2′-OCH_3), 3.70 (3 H, s, 4′-OCH_3) and 1.92–0.84 (9 H, s, C_4H_9); *m/z* 209 (M^+, 49%), 194 (17), 166 (100) and 151 (42) (Found: C, 68.75; H, 9.05; N, 6.80. $C_{12}H_{19}NO_2$ requires C, 68.85; H, 9.15; N, 6.70%).

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References

1 D. C. Thompson, R. H. Baker and R. W. Brownlow, *Ind. Eng. Chem.*, 1952, **44**, 850.
2 S. Sakai, K. Minoda, G. Saito, Y. Iida, A. Ueno and A. Sato, *J. Sci. Research Inst. (Tokyo)*, 1956, **50**, 175.
3 B. Akermark, L. Eberson, E. Jonsson and E. Pettersson, *J. Org. Chem.*, 1975, **40**, 1365.
4 H. Sensui, S. Suzuka, M. Gonda and T. Ohara, Jap P 60 214 763 (*Chem. Abstr.*, 1986, **104**, 109187h).
5 R. Lantz and P. Obellianne, *Bull. Soc. Chim. Fr.*, 1956, 311.
6 J. J. Kulagowski and C. W. Rees, *Synthesis*, 1980, 215.
7 J. H. Gorvin, *J. Chem. Soc., Chem. Commun.*, 1985, 238.
8 F. Ullmann and H. Kipper, *Ber. Dtsch. Chem. Ges.*, 1905, **38**, 2120.
9 I. Goldberg, *Ber. Dtsch. Chem. Ges.*, 1907, **40**, 4541.
10 H. S. Freeman, J. R. Butler and L. D. Freedman, *J. Org. Chem.*, 1978, **43**, 4975.
11 J. W. Schulenberg and S. Archer, *Organic Reactions*, 1965, **14**, p. 1.
12 C. G. McCarthy and L. A. Garner, in *The Chemistry of Amidines and Imidates*, ed. S. Patai, Wiley, New York, 1975, p. 189–240.
13 K. Nakamura, A. Ohno and S. Oka, *Synthesis*, 1974, 882.
14 R. J. Sundberg and K. B. Sloan, *J. Org. Chem.*, 1973, **38**, 2052.
15 H. Heaney, *Chem. Rev.*, 1962, **62**, 81.
16 M. F. Moreau-Hochu and P. Caubère, *Tetrahedron*, 1977, **33**, 955.
17 A. Varvoglis, *Synthesis*, 1984, 714 and references therein.
18 F. Dengel, USP 2 951 013/1960 (*Chem. Abstr.*, 1961, **55**, 4545i).
19 H. F. Hodson, J. F. Batchelor, J. W. T. Selway, J. G. Vinter and R. Iyer, EP Appl. 25 598/1981 (*Chem. Abstr.*, 1981, **95**, 42938d).
20 B. P. Das and U. P. Basu, *Indian J. Chem.*, 1965, **3**, 268.
21 A. Rieche and E. Höft, *J. Prakt. Chem.*, 1962, **17**, 293.
22 A. N. Bourns, H. W. Embleton and M. K. Hansuld, *Can. J. Chem.*, 1952, **30**, 1; *Organic Synthesis*, 1954, **34**, 79 and references therein.
23 A. C. Cope, H. L. Dryden and C. F. Howell, *Organic Synthesis*, Coll. Vol. IV, 1963, p. 816.
24 Y. Watanabe, S. C. Shim, T. Mitsudo, M. Yamashita and Y. Takegami, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2302.
25 Y. Tsuji, K. T. Huh, Y. Ohsugi and Y. Watanabe, *J. Org. Chem.*, 1985, **50**, 1365.
26 D. H. R. Barton, J.-P. Finet and J. Khamsi, *Tetrahedron Lett.*, 1986, **27**, 3615.
27 D. H. R. Barton, J.-P. Finet and J. Khamsi, *Tetrahedron Lett.*, 1987, **28**, 887.
28 D. H. R. Barton, J.-P. Finet and J. Khamsi, *Tetrahedron Lett.*, 1988, **29**, 1115.
29 D. H. R. Barton, J.-P. Finet and J. Khamsi, *Tetrahedron Lett.*, 1989, **30**, 937.
30 D. H. R. Barton, N. Yadav-Bhatnagar, J.-P. Finet and J. Khamsi, *Tetrahedron Lett.*, 1987, **28**, 3111.
31 D. H. R. Barton, D. M. X. Donnelly, J.-P. Finet and P. J. Guiry, *Tetrahedron Lett.*, 1989, **30**, 1377.
32 H. C. Bell, J. T. Pinhey and S. Sternhell, *Aust. J. Chem.*, 1979, **32**, 1551.
33 J. T. Pinhey and B. A. Rowe, *Aust. J. Chem.*, 1979, **32**, 1561.
34 J. T. Pinhey and B. A. Rowe, *Aust. J. Chem.*, 1980, **33**, 113.
35 G. L. May and J. T. Pinhey, *Aust. J. Chem.*, 1982, **35**, 1859.
36 R. P. Kozyrod and J. T. Pinhey, *Aust. J. Chem.*, 1985, **38**, 713.
37 J. T. Pinhey and B. A. Rowe, *Aust. J. Chem.*, 1983, **36**, 789.
38 D. J. Collins, J. D. Cullen, G. D. Fallon and B. M. Gatehouse, *Aust. J. Chem.*, 1984, **37**, 2279.
39 D. H. R. Barton, D. M. X. Donnelly, J.-P. Finet and P. J. Guiry, *Tetrahedron Lett.*, 1989, **30**, 1539.
40 D. De Vos, W. A. A. Van Barneveld, D. C. Van Beelen, H. O. Van Der Kooi, J. Wolters and A. Van Der Gen, *Recl. Trav. Chim. Pays-Bas*, 1975, **94**, 97 and references therein.
41 R. P. Kozyrod, J. Morgan and J. T. Pinhey, *Aust. J. Chem.*, 1985, **38**, 1147.
42 D. H. R. Barton, J.-P. Finet, J. Khamsi and C. Pichon, *Tetrahedron Lett.*, 1986, **27**, 3619.
43 R. Willstätter and H. Kubli, *Ber. Dtsch. Chem. Ges.*, 1909, **42**, 4135.
44 I. G. C. Coutts and M. Hamblin, *J. Chem. Soc., Perkin Trans. 1*, 1975, 2445.
45 J. Schmitt, FrP 1 173 121/1959 (*Chem. Abstr.*, 1962, **56**, 479f).
46 P. Pratesi and G. Castorina, *Il Farmaco (Pavia) Ed. Sci.*, 1954, **9**, 144.
47 A. B. Sen and A. K. Sen Gupta, *J. Indian Chem. Soc.*, 1957, **34**, 413.
48 T. Ohta, N. Miyata and M. Hirobe, *Chem. Pharm. Bull.*, 1981, **29**, 1221.
49 B. C. Saunders and P. J. G. Mann, *J. Chem. Soc.*, 1940, 769.
50 A. M. Osman, M. Z. A. Badr and A. E. Abdel-Rahman, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2611.

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