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STABLE ARYLSILVER COMPOUNDS CONTAINING DIMETHYLAMINO, (DIMETHYLAMINO)METHYL OR METHOXY GROUPS AT THE ARYL NUCLEUS*

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SUMMARY

The following organosilver compounds have been prepared from the corresponding lithium compounds and silver bromide: {2-[(dimethylamino)methyl]-phenyl}silver, {2-[(dimethylamino)methyl]phenyl}silver · silver bromide, bis{[2-(dimethylamino)phenyl]silver} · silver bromide, (2,6-dimethoxyphenyl)silver and (2,4,6-trimethoxyphenyl)silver. These substituted phenylsilvers, which have been characterized by elemental analysis, mol. wt. determinations, IR and PMR spectroscopy and by degradation reactions, show greater thermal, oxidative and hydrolytic stability than phenylsilver. In general the compounds decompose between 100° and 200° and react slowly with oxygen and water.

INTRODUCTION

The chemistry of σ-bonded alkyl- and arylsilver compounds is very poorly developed**. This is probably connected with the low intrinsic stability of the silver–carbon σ-bond. In general, alkylsilver compounds decompose between $-80°$ and $-50°$, while arylsilver compounds decompose between $-70°$ and $25°$ (ref. 2). However, in the related field of organocopper chemistry we have found[3] that *pure* phenylcopper is more stable than was previously reported[4]: it is stable for several days at room temperature and decomposes at about 100°***. Moreover, we have shown[6,7] that introduction of suitable substituents at the aryl nucleus of arylcopper compounds results in a further increase of the stability. Obviously, the stability of the organocoppers depends strongly both on the purity of the compounds and on the character of the organic group bound to the metal atom. These observations induced us to synthesize some substituted phenylsilver compounds and to study their stabilities.

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* Part of this work has been presented at the Vth International Conference on Organometallic Chemistry, Moscow 1971 (ref. 1).

** For a review see ref. 2.

*** Quite recently a similar observation was made for pure phenylsilver (decompn. temp. about 80°)[5].

RESULTS AND DISCUSSION

{2-[(Dimethylamino)methyl]phenyl}silver

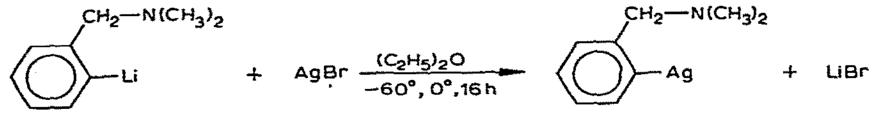
Reaction of {2-[(dimethylamino)methyl]phenyl}lithium with silver bromide in diethyl ether afforded an almost colourless benzene-soluble compound which according to elemental analysis (Table 1, run no. 1) appeared to be {2-[(dimethylamino)methyl]phenyl}silver (I) (61% yield) contaminated with a small amount of benzyldimethylamine:

TABLE 1

ANALYTICAL DATA FOR SUBSTITUTED PHENYLSILVER COMPOUNDS

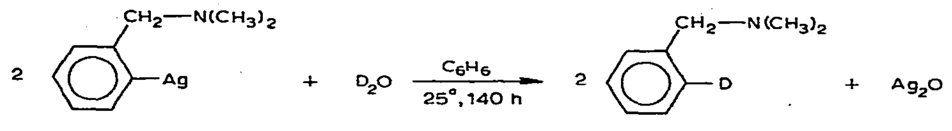
Run no.	*Formula*	*Analysis found (calcd.) (%)*			
		C	*H*	*Ag*	*N*
1	$C_9H_{12}AgN \cdot 0.07\ C_9H_{13}N$	46.1 (45.98)	5.4 (5.17)	43.3 (42.88)	6.0 (5.96)
2	$C_9H_{12}AgN$	44.3 (44.66)	5.2 (5.00)	44.5 (44.56)	5.9 (5.76)
3	$C_9H_{12}AgN$	44.9 (44.66)	5.1 (5.00)	43.6 (44.56)	5.7 (5.76)
4	$C_9H_{12}Ag_2BrN$[a]	24.8 (25.15)	3.0 (2.81)	50.1 (50.19)	3.3 (3.26)
5	$C_{16}H_{20}Ag_3BrN_2 \cdot 0.33\ C_6H_6$[b]	32.4 (32.25)	3.5 (3.31)	48.4 (48.33)	4.3 (4.18)
6	$C_{16}H_{20}Ag_3BrN_2 \cdot 0.33\ C_6H_6$	32.5 (32.25)	3.1 (3.31)		4.2 (4.18)
7	$C_{16}H_{20}Ag_2BrCuN_2$[c]	32.3 (32.05)	3.7 (3.36)	34.4 (35.98)	4.9 (4.67)
8	$C_8H_9AgO_2$	38.8 (39.22)	4.1 (3.70)	46.8 (44.02)	
9a	$C_9H_{11}AgO_3 \cdot 0.2\ C_6H_6$[d]	42.1 (42.15)	4.3 (4.35)		
9b	$C_9H_{11}AgO_3 \cdot 0.1\ C_6H_6$[e]	40.5 (40.76)	4.3 (4.13)		

[a] Found: Br, 18.5. Calcd.: Br, 18.59%. [b] Found: Br, 11.8. Calcd.: Br, 11.93%. [c] Found: Br, 13.1; Cu, 11.6. Calcd.: Br, 13.33; Cu, 10.60%. See also Experimental. [d] Found: O, 16.5. Calcd.: O, 16.51%. [e] Found: O, 16.7. Calcd.: O, 16.97%.



(I)

The compound (mol. wt. 835, $C_9H_{12}AgN$ calcd.: mol. wt. 242) is very stable for an organosilver compound: it does not show any visible changes upon heating to 150–160°; between 160–180° it turns black and melts at about 180°. Treatment with D_2O gave (2-deuteriobenzyl)dimethylamine (II) in almost quantitative yield:

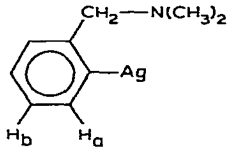


(I) (II)

In a second experiment a pink-coloured product was obtained, which again analyzed correctly for (I) (Table 1, run no. 2). This compound decomposed at about 106°; the mol. wt. was found to be 1215. In two other preparations colourless products were obtained which decomposed at 195° (Table 1, run no. 3; mol. wt. 880) and 190° (mol. wt. 940), respectively. PMR data of the products obtained in run no. 2 and 3 are shown in Table 2, and reveal that at least two R_nAg_n species [(Ia) and (Ib)] are present in the solution. The PMR and molecular weight data together suggest that these products differ in their degree of association [R_nAg_n, n(Ia) < n(Ib)]. The corresponding organocopper[8], organocopperlithium[9] and organosilverlithium[10] compounds have recently been found to be well-defined tetranuclear species (R_4Cu_4, $R_4Cu_2Li_2$ and $R_4Ag_2Li_2$) with aryl groups bridging the metal atoms. Bridging aryl groups may also be present in the oligomers (Ia) and (Ib). The observed pattern [broad (≈20 Hz) unresolved signal] for the *ortho*-proton H_a of both (Ia) and (Ib) in the PMR spectrum is in agreement with such a structure (*ortho*-coupling of H_a with H_b, ^{107}Ag and ^{109}Ag of about the same magnitude[10]).

TABLE 2

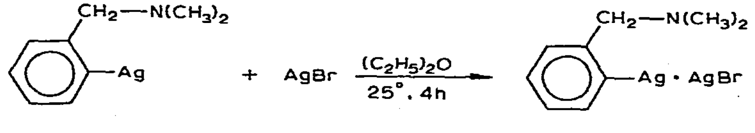
PMR DATA FOR {2-[(DIMETHYLAMINO)METHYL]PHENYL}SILVER[a]



Run no.	*Mol. wt.*	*Chemical shifts (ppm)*[b]			*Assignment*	*Ratio (Ia)/(Ib)*[c]
		$\delta(NCH_3)$	$\delta[N(CH_2)]$	δH_a		
2	1215	s 1.97	s 3.06	8.2 (br)	(Ia)	⩽1
		s 1.86	d 3.7, d 2.5[d]	8.0 (br)	(Ib)	
3	880	s 1.98	s 3.08	8.2 (br)	(Ia)	⩾2
		s 1.88	[e]	[e]	(Ib)	

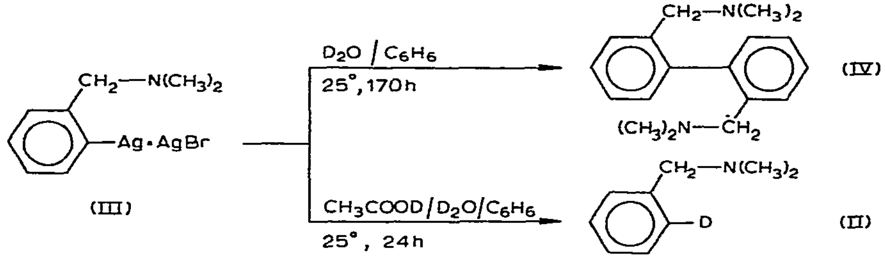
[a] Solvent C_6D_6; room temperature. [b] Downfield from TMS internal; s, singlet; d, doublet; (br), broad. [c] Calcd.: from the NCH_3 peak areas. [d] $J(H-H) \approx 12$ Hz. [e] Only very weak signals.

Reaction of silver bromide with a slight excess of (I) afforded the rust-brown 1/1 complex (III) (yield 95%; decompn. at 108°; see also Table 1, run no. 4):



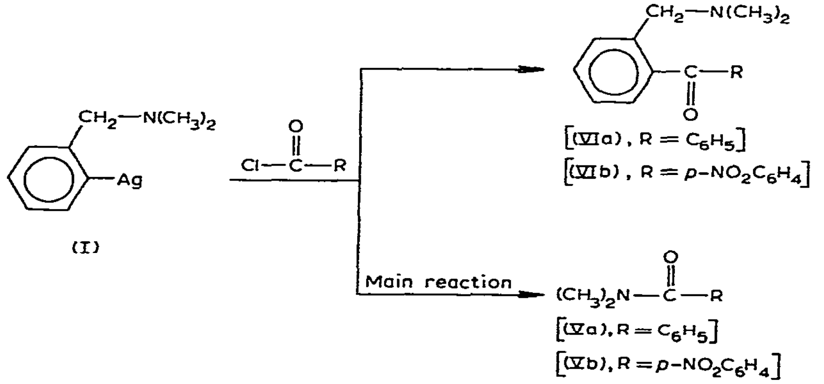
(I) (III)

Exposure of (III) to the atmosphere (and daylight) for 10 days did not change the colour; the decomposition temperature decreases from 108° to 104–106° after 3 days, to 102–104° after 5 days, and to 100–103° after 10 days, indicating a slow decomposition. Surprisingly, treatment with D_2O (nitrogen atmosphere) did not yield (II) but the dimeric product (IV) (100 % yield); treatment with CH_3COOD gave (II) in quantitative yield:



The reaction of (I) with cuprous bromide (1/1 ratio) took an unexpected course: a purple solid (mainly inorganic materials) and the dimeric product (IV) (80 % yield) were isolated.

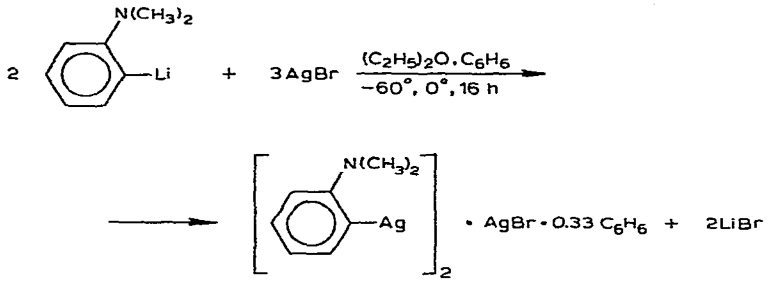
Reaction of phenylsilver with acid chlorides has been reported[11] to yield phenyl ketones, albeit in rather low yields. The reaction of (I) with benzoyl chloride and with *p*-nitrobenzoyl chloride afforded the corresponding amides (Va) and (Vb) in about 80 % yield. The expected coupling products (VIa) and (VIb) were present in about 10 % yield:



The amide (Va) is also formed in the reaction of benzyldimethylamine with benzoyl chloride[12]. The observation that the nitrogen atom of (I) is more susceptible to electrophilic attack than the carbon atom attached to silver may be connected with the special nature of the metal–carbon bond in this type of cluster compound[8-10,13].

[2-(*Dimethylamino*)*phenyl*] *silver*

From the reaction of [2-(dimethylamino)phenyl]lithium with silver bromide (1/1 ratio) a grey-black compound was obtained. Elemental analysis pointed to a complex (or mixture) of [2-(dimethylamino)phenyl]silver, silver bromide and benzene in a ratio of about 2/1/0.33. This experiment was repeated using two equivalents of silver bromide. From the resulting mixture a yellow benzene-soluble solid was isolated, which according to elemental analysis (Table 1, run no. 5) contains the organosilver compound, silver bromide and benzene in the same ratio as above (48% yield; decompn. between 110–140°, melting at about 140°):



(VII)

In a third experiment (ratio R'Li/AgBr 1/2) the same complex (VII) was isolated (Table 1, run no. 6) which starts to decompose at about 125° and melts at 140°. The mol. wt. of (VII) (in benzene) was found to be 1260. $C_{16}H_{10}Ag_3BrN_2$ calcd.: 644; this means that the complex is dimeric ($R'_4Ag_6Br_2$) and thus contains 6 silver atoms.

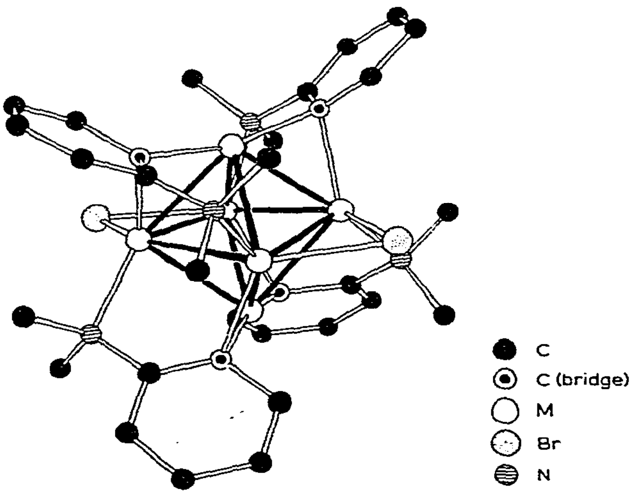
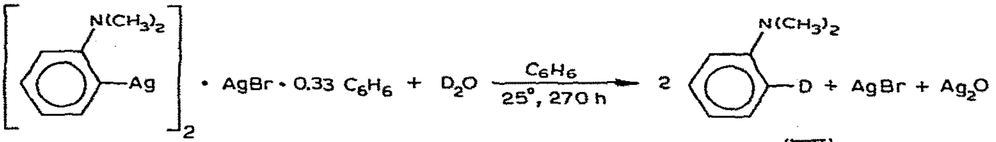


Fig. 1. Structure of $R'_4M_6Br_2$ for M=Cu (ref. 13).

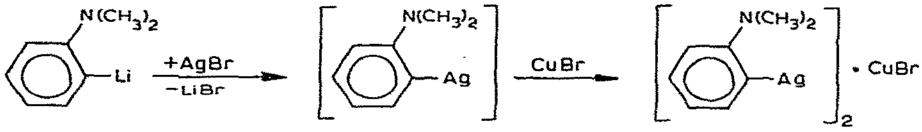
The corresponding copper complex $R'_4Cu_6Br_2$ likewise is dimeric both in solution[7] and in the solid state[13]. A structure for the $R'_4Ag_6Br_2$ complex with the two bromine atoms and the four aryl groups bridging the six silver atoms similar to that recently demonstrated for the $R'_4Cu_6Br_2$ complex[13] (Fig. 1, M=Cu) therefore seems likely.

Treatment of (VII) with D_2O afforded 2-deuterio-*N,N*-dimethylaniline (VIII) in low yield:


(VII) (VIII)

After a reaction period of 270 h the hydrolysis was still incomplete, so the complex is very stable in this respect. Even with deuterated acetic acid the reaction is very slow; after 16 h (20°) only 41 % of (VIII) could be detected.

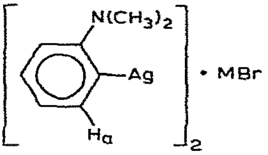
With the aim of obtaining a mixed-metal complex of the $R'_4M_6Br_2$ type, the reaction of the organosilver compound (not isolated as such) with cuprous bromide was carried out:


(IX)

The benzene-soluble light-brown complex (IX) isolated from this reaction (80% yield; decompn. between 115° and 170°) analyzed correctly for a 2/1 complex (Table 1, run no. 7). Again the complex was found to be dimeric. (Found: mol. wt., 1099; $C_{16}H_{10}Ag_2BrCuN_2$ calcd.: mol. wt., 599.5). PMR data of (VII) and (IX) have been presented in Table 3. The complex pattern of the spectrum of (IX), especially in the $N(CH_3)$ region, indicates the presence of several types of compounds. Most probably complexes of the type $R'_4Ag_mCu_nBr_2$ ($n+m=6$, overall composition approximately $R'_4Ag_4Cu_2Br_2$) are present. This means that in the hexanuclear silver complex (see

TABLE 3

PMR DATA OF BIS{[2-(DIMETHYLAMINO)PHENYL]SILVER}·METAL BROMIDE COMPLEXES[a]



Run no.	Metal bromide	Chemical shifts (ppm)[b]	
		$\delta(NCH_3)$	$\delta\ H_a$
5	AgBr	s 2.42	8.15–8.35 (vbr)
7	CuBr	s 1.94 (br)[c]	8.2–8.4 (vbr)[d]
		2.1–2.8 (vbr)	m 8.4–8.6
		s 2.42[d]	
		s 2.94 (br)[c]	

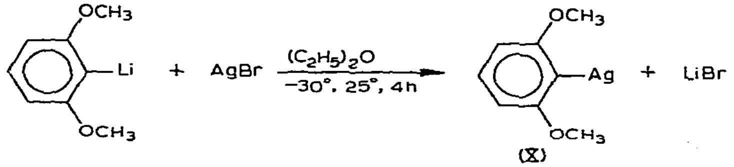
[a] Solvent C_6D_6; room temperature. [b] Downfield from TMS internal; s, singlet; m, multiplet; (br), broad; (vbr), very broad. [c] Ratio areas of signals at 1.94 and 2.94 ppm: ≈1/1. [d] Weak signals.

Fig. 1, M=Ag) one or more silver atoms have been replaced by copper atoms. The weak signals at 2.42 and 8.20–8.30 ppm in the PMR spectrum of (IX) point to the presence of a small amount of $R'_4Ag_6Br_2$(VII).

Treatment of (IX) with CH_3COOD afforded (VIII) in about 95% yield. Exposure of (IX) to the atmosphere for 2 days resulted in a small colour change of the surface of the solid (pale brown → brown), but the behaviour upon melting remained the same.

*(2,6-Dimethoxyphenyl)silver and (2,4,6-trimethoxyphenyl)silver**

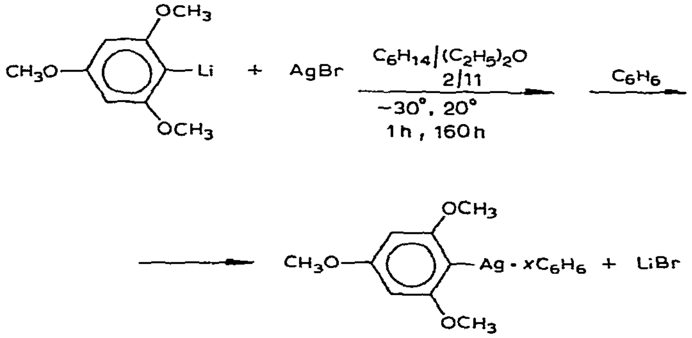
Reaction of (2,6-dimethoxyphenyl)lithium with silver bromide furnished a grey-black benzene-insoluble fraction (65% yield, decompn. between 140–160°) and a pale grey benzene-soluble fraction (21% yield, decompn. between 150–170°). The benzene-soluble fraction (Table 1, run no. 8) consists of almost pure (2,6-dimethoxyphenyl)silver (X).



(X)

Treatment of (X) with D_2O gave 2-deuterio-1,3-dimethoxybenzene (XI) in 40% (benzene-insoluble fraction) and 65% (benzene-soluble fraction) yield; after the reaction period used (44 h) the degradation was still incomplete; that means that (X) is rather stable in this respect.

A similar method was used for the preparation of (2,4,6-trimethoxyphenyl)silver (XII). Again two fractions were obtained: a benzene-insoluble fraction (31% yield, pale brown, decompn. 175–182°) and a benzene-soluble fraction (40% yield, pale brown, decompn. 115–120°). The IR spectra of these fractions are almost identical;



(XII)

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* Recently Wennerström[14] reported on the preparation of (2,6-dimethoxyphenyl)silver and (2,4,6-trimethoxyphenyl)silver. (2,6-Dimethoxyphenyl)silver, isolated in poor yield, was found to melt with decomposition between 135 and 140°; impure (2,4,6-trimethoxyphenyl)silver (not identified) was described to be rather unstable towards air, light and moisture.

both fractions contain a small amount of benzene (absorption at 676 cm^{-1}). Obviously both fractions consist of the desired compound (XII) contaminated with some benzene. Elemental analysis (Table 1, run no. 9a and 9b) and degradation reactions confirm this picture. The large differences in the decomposition temperatures and in the solubilities of the two fractions may be due to differences in the degree of association.

Treatment of (XII) with deuterated acetic acid in D_2O/benzene for 40 h afforded about 90% of 2-deuterio-1,3,5-trimethoxybenzene (XIII); the presence of benzene in (XII) was demonstrated by decomposition in D_2O/diethyl ether.

EXPERIMENTAL

General

All reactions were carried out in an atmosphere of dry oxygen-free nitrogen. Solvents were carefully purified, dried, and distilled before use under nitrogen. The organolithium compounds were prepared by standard procedures*.

PMR spectra, which were run by Miss L. Veldstra, were recorded on a Varian Associates HA-100 NMR spectrometer. IR spectra, which were run by Mrs. H. de Ridder-Alberda, were recorded on a Grubb–Parsons Spectromaster. Elemental analyses were carried out under supervision of Mr. W. J. Buis at the Analytical Department of this Institute. The silver and bromine analyses of the compounds containing both these elements were developed by Drs. J. Agterdenbos and J. P. S. Haarsma of the Laboratory of Analytical Chemistry, State University, Utrecht.

{2-[(*Dimethylamino*)*methyl*]*phenyl*}*silver* (*I*)

Synthesis (*run no.* 1)

Benzyldimethylamine (8.5 g, 63 mmoles) was added to a mixture of 47 ml of a 1.35 *M* solution of butyllithium (63 mmoles) in hexane and 250 ml of diethyl ether. After stirring for 65 h at room temperature the resulting suspension of {2-[(dimethylamino)methyl]phenyl} lithium (Colour test II on butyllithium was negative) was cooled to −60° and silver bromide (10.6 g, 56.5 mmoles) was added. After 1 h the mixture was allowed to warm to room temperature and stirred for 15 h. The brown precipitate was isolated by filtration, washed with ether (4 × 70 ml) until no bromide ions could be detected in the filtrate, and then with pentane (60 ml), and extracted with benzene (6 × 80 ml), to give almost colourless benzene solutions and a grey insoluble residue (3.7 g, decompn. at about 130°). The benzene was removed from the combined extracts by low-temperature distillation at reduced pressure to give 8.3 g of a colourless product A, (I), melting with decompn. at about 180° (yield 61%). (Found: C, 46.1; H, 5.2. $C_9H_{12}AgN \cdot 0.07\ C_9H_{13}N$ calcd.: C, 45.98; H, 5.17%.) IR (KBr): characteristic absorptions at 846 s (group vibration), 745 vs (*ortho*-disubstituted benzene) and 699 w (monosubstituted benzene, presence of a small amount of benzyldimethylamine) cm^{-1}.

Product A was washed with pentane (2 × 15 ml) to give 7.5 g of product B with the same characteristics (melting behaviour, IR spectrum) as A. Product B was

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* For a review see ref. 15.

treated with pentane (3 × 100 ml), and dried *in vacuo* to give 7.1 g of a colourless product C, again with the same characteristics as A and B and melted with decompn. at 180°; IR (Nujol): 844 s, 744 vs and 698 vw cm^{-1}. Qualitative tests for Li and Br were negative. Mol. wt. cryoscopic in benzene: 884, 843, 776. Elemental analysis: Table 1, run no. 1.

Reaction with D_2O. A mixture of 0.808 g (3.38 mmoles) of product C, 10 ml of benzene and 1 ml of D_2O was stirred for 140 h at room temperature. The resulting brown-black suspension was filtered; the filtrate was concentrated to a small volume, dried over sodium sulphate and analyzed (GLC, internal standard decane): 3.37 (100%) mmoles of (II). IR (neat): identical to an analytically pure sample of (II); only a very weak absorption at 699 cm^{-1} due to non-deuterated product was present. NMR (CCl_4, TMS internal): δ 2.15 [s, 6 H, $N(CH_3)_2$], 3.33 (s, 2 H, $N-CH_2-$) and 6.17 (m, 4 H, C_6H_4D) ppm.

Reaction with acid chlorides. A solution of 0.360 g (2.55 mmoles) of benzoyl chloride in 10 ml of benzene was added to a solution of 0.618 g (2.55 mmoles) of compound C in 40 ml of benzene. The mixture was stirred for 3 h at room temperature and for 3 h at 70°, and then 5 ml water and 10 ml of 4 *N* HCl were added. The resulting mixture was filtered; the benzene layer of the filtrate was dried over sodium sulphate, filtered, and concentrated to give 0.50 g of an oil containing mainly *N,N*-dimethylbenzamide (Va) (GLC, NMR, IR). The water layer of the filtrate was made alkaline and extracted with ether; the ether extract was dried over sodium sulphate, filtered and concentrated, yielding 0.10 g of an oil containing (Va) and 2-[(dimethylamino)-methyl]benzophenone (VIa). NMR (VIa) (CCl_4): δ 1.91 [s, 6 H, $N(CH_3)_2$], 3.36 (s, 2 H, $N-CH_2-$) and 7.1–7.7 (m, 9 H, C_6H_5 and C_6H_4) ppm. Overall yield: ≈80% of (Va) and ≈10% of (VIa).

Similar results were obtained in the reaction of (I) with *p*-nitrobenzoyl chloride. NMR (VIb) (CCl_4): δ 1.85 [s, 6 H, $N(CH_3)_2$], 3.36 (s, 2 H, $N-CH_2-$], 7.1–7.4 (m, 4 H, o-C_6H_4), 7.79 and 8.22 (2 × d, $J \approx 8.5$ Hz, 2 × 2 H, p-C_6H_4) ppm.

Synthesis (run no. 2)

Silver bromide (56.5 mmoles) was treated with a reaction mixture obtained from equimolar amounts (60 mmoles) of butyllithium and benzyldimethylamine as described above. The solvent was removed from the grey-black suspension by decantation and the remaining solid was washed with ether (5 × 80 ml, until the test for bromide ions was negative). Benzene (100 ml) was added to the solid, the solution obtained was decanted, and the benzene was transferred back to the remaining solid by low-temperature distillation and again decanted. By repetition of this procedure the solid was extracted six times, to give, after removal of the solvent *in vacuo*, 12.3 g of a pink product decomposing at about 130–135°. This product was extracted with 100 ml of benzene (7 ×) as described above, affording 11.6 g (yield 85%) of pink-coloured (I) decomposing between 105 and 108°. Qualitative tests on the presence of Li and Br were negative. IR (Nujol): characteristic absorptions at 842 s and 743 vs cm^{-1}; the weak absorption at 698 cm^{-1} (trace of benzyldimethylamine) observed in the product of run no. 1 (see above) was absent. NMR: Table 2. Mol. wt. cryoscopic in benzene: 1223, 1180, 1222. Elemental analysis: Table 1, run no. 2.

Reaction with D_2O. See above; 30 mmoles (I) in 11 ml benzene/D_2O 10/1 v/v, 130 h, room temperature: 82% of (2-deuteriobenzyl)dimethylamine (II) and 7% of

2,2'-bis[(dimethylamino)methyl]biphenyl (IV). NMR (IV) (CCl_4): δ 2.04 [s, 6 H, $N(CH_3)_2$], 3.01 and 3.06 (2 × d, J 13.5 Hz, 2 H, $N{-}CH_2{-}$), ≈ 7.1 and 7.5 (2 × m, 4 H, C_6H_4) ppm.

{2-[(Dimethylamino)methyl]phenyl}silver · silver bromide (III)

{2-[(Dimethylamino)methyl]phenyl}silver (3.5 mmoles) and silver bromide (3.2 mmoles) were mixed at 0° and ether (15 ml) was added. The resulting mixture was stirred for 1 h at room temperature to give a brick-red suspension. Benzene (10 ml) was added, and stirring was continued for 3 h. The solvent was removed (decantation), 60 ml of benzene were added to the residue, and after stirring for a short period the benzene was decanted. The solid was extracted with 60 ml of benzene (3 ×, decantatation–low temperature distillation procedure, see above) leaving rust-brown (III), decomposing at 108° (yield 95%). IR (Nujol): 842 vs, 752 vs and 678 vw (presence of trace of benzene) cm^{-1}. Elemental analysis: Table 1, run no. 4.

Reaction with D_2O. (III) (1.25 mmoles) in 11 ml benzene/D_2O 10/1 v/v, 170 h, room temperature: 100% of 2,2'-bis[(dimethylamino)methyl]biphenyl (IV).

Reaction with CH_3COOD. (III) (1.00 mmoles) in 11 ml benzene/10 N CH_3COOD in D_2O 10/1 v/v, 24 h, room temperature: 100% (2-deuteriobenzyl)dimethylamine (II).

Bis{[2-(dimethylamino)phenyl]silver} · silver bromide (VII)

A solution of 17.9 mmoles of [2-(dimethylamino)phenyl]lithium (prepared from the corresponding aryl bromide and lithium) in ether (50 ml) was added dropwise to a suspension of 6.7 g (35.8 mmoles) of silver bromide in ether (60 ml) kept at −60°. At the end of the addition the colour of the suspension changed from yellow to grey. After stirring for 16 h at 0° the dark coloured suspension was filtered. The remaining solid was washed with ether (4 × 25 ml, until bromide could no longer be detected in the filtrate) and extracted with 100 ml of benzene (8 × by the decantation–low temperature distillation procedure). Evaporation of the benzene extract *in vacuo* afforded 3.8 g of yellow (VII) decomposing between 110–140° and melting at 140° (yield 48%). IR (Nujol): characteristic absorptions at 923 s, 772 s, 763 m, 747 m, 718 s and 687 m (benzene?) cm^{-1}. NMR: Table 3. Elemental analysis: Table 1, run no. 5.

This experiment was repeated, to give 46% of (VII), decomposing between 125°–140° and melting at 140°. IR and NMR: same as in run no. 5. Elemental analysis: Table 1, run no. 6. Mol. wt. osmometric in benzene: 1260.

Reaction with D_2O. (VII) (1.0 mmole) in 11 ml benzene/D_2O 10/1 v/v, 270 h, room temperature: 12% of 2-deuterio-N,N-dimethylaniline (VIII). NMR (CCl_4): δ 2.88 [s, 6 H, $N(CH_3)_2$], 6.55 (m, 2 H, o/p-C_6H_4D) and 7.10 (m, 2 H, m-C_6H_4D) ppm. Considerable amounts of organosilver were still present as was evident from the formation of black precipitates and silver mirrors in the dark but clear solutions.

Reaction with CH_3COOD. (VII) (1.15 mmoles) in 11.5 ml benzene/10 N CH_3COOD in D_2O 10/1.5 v/v, 16 h, room temperature: 38–41% of (VIII).

Reaction with CuBr. A solution of 16.8 mmoles of [2-(dimethylamino)phenyl]lithium in ether (50 ml) was added dropwise to a suspension of 3.1 g (16.8 mmoles) of silver bromide in ether (70 ml) kept at −50°. After stirring for 1 h at −30° and 16 h at room temperature the mixture was filtered and the solid washed with ether (4 × 40 ml, until the test for bromide ion was negative). The black residue was suspended in ether (80 ml), 1.6 g (11 mmoles) of cuprous bromide was added and the resulting yellow mixture was stirred for 40 h at room temperature. The solvent was removed by distillation *in vacuo* and the residue was extracted with 100 ml of benzene (4 × by the decantation–low temperature distillation procedure). Evaporation of the benzene extract *in vacuo* afforded 4.0 g of pale brown (IX) decomposing between 115° and 170° (yield 80%). IR (Nujol): 992 s, 778 (sh), 772 s, 763 m, 750 m and 719 s cm^{-1}. NMR: Table 3. Elemental analysis: Table 1, run no. 7. (Found: C, 32.3; H, 3.7; Ag, 34.4; Br, 13.1; Cu, 11.6; N, 4.9; mol. wt. osmometric in benzene; 1099. $C_{16}H_{20}Ag_2N_2 \cdot BrCu$ calcd.: C, 32.05; H, 3.36; Ag, 35.98; Br, 13.33; Cu, 10.60; N, 4.67; mol. wt., 599.54. $C_{16}H_{20}Ag_{1.67}Cu_{0.33}N_2 \cdot BrCu$ calcd.: C, 32.86; H, 3.45; Ag, 30.74; Br, 13.67; Cu, 14.49; N, 4.79%; mol. wt., 584.76). Treatment with CH_3COOD: 1.00 mmole of (IX) in 11.5 ml benzene/10 *N* CH_3COOD in D_2O 10/1.5 v/v, 72 h, room temperature; yield: 95% of (VIII).

(2,6-*Dimethoxyphenyl*)*silver*

Silver bromide (3.4 g, 18 mmoles) was added at −30° to a solution of (2,6-dimethoxyphenyl)lithium [prepared from 16.2 ml of a 1.23 *N* solution of butyllithium in hexane and 2.76 g (20 mmoles) of 1,3-dimethoxybenzene in 85 ml of ether]; after stirring for 2 h at −30° and for 2 h at room temperature the almost black coloured suspension was filtered. The remaining solid was washed with ether (100 ml) and extracted with benzene (5 × 30 ml) yielding a grey-black insoluble fraction (Xa) (2.85 g, yield 65%, decompn. temp. 140–160°) and a yellow extract. Evaporation of the latter *in vacuo* afforded a pale grey fraction (Xb) (0.95 g, yield 21%, decompn. temp. 155–170°). IR (KBr): characteristic absorption at 786 s cm^{-1}. Elemental analysis: Table 1, run no. 8.

Reaction with D_2O. (Xa) (1.3 mmoles) in 11 ml C_6H_6/D_2O 11/1 v/v, 44 h, room temperature: 40% of 2-deuterio-1,3-dimethoxybenzene (XI).

1.5 mmoles of (Xb) was similarly treated; 44 h: 65% of (XI); after 132 h: 72% of (XI). NMR (CCl_4): δ 3.69 [s, 6 H, $(OCH_3)_2$], 6.34 (d, $J \approx 8.0$ Hz, 2 H) and 7.02 (t, 1 H) ppm.

(2,4,6-*Trimethoxyphenyl*)*silver*

Silver bromide (18 mmoles) was added at −30° to a solution of (2,4,6-trimethoxyphenyl)lithium (prepared from 20 mmoles of butyllithium and 20 mmoles of 1,3,5-trimethoxybenzene) in 100 ml ether/hexane 85/15. After stirring for 1 h at −30° and for 160 h at room temperature the solvent was decanted, the remaining pale brown solid was washed with ether (2 × 40 ml) and extracted with 100 ml of benzene (7 ×, decantation–low temperature distillation procedure). Evaporation of the extract yielded 4.1 g of a pale brown solid decomposing at 165–180°. Extraction of this solid with 70 ml of benzene (2 ×) afforded a benzene-insoluble fraction (XIIa) (1.55 g, yield 31%, decompn. temp. 175–182°) and a benzene-soluble fraction (XIIb) (2.0 g, yield 40%, decompn. temp. 115–120°). IR (Nujol): (XIIa) 943 s, 826 s, 815 s, 803 s, 785 m and 677 s cm^{-1}; (XIIb) 944 s, 830 s, 815 s, 802 s, 784 w and 678 w cm^{-1}. NMR (C_6D_6): (XIIb) δ 3.33 (s, 3H, 4-OCH_3), 3.72 [s, 6 H, 2,6-$(OCH_3)_2$] and 6.14 (s, 2 H, C_6H_2) ppm. Elemental analysis: Table 1, run no. 9a (XIIa) and 9b (XIIb).

Reaction with CH_3COOD. (XIIa) (2.0 mmoles) in 11.5 ml C_6H_6/10 *N* CH_3COOD in D_2O 10/1.5 v/v, 40 h, room temperature: 93% of 2-deuterio-1,3,5-trimethoxybenzene (XIII). NMR (CCl_4): δ 3.65 [s, 9 H, $(OCH_3)_3$] and 5.92 (s, 2 H, C_6H_2D) ppm.

(XIIb) (2.3 mmoles) treated as above during 40 h: 87 % of (XIII); 1.6 mmoles of (XIIb) treated with an ether/CH_3COOD/D_2O mixture during 42 h: 0.32 mmoles of benzene, *i.e.* 20 mole %.

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