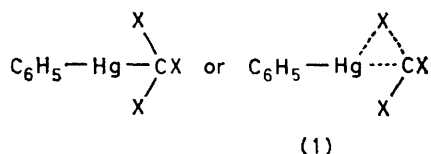


Alkylidene Transfer from Monochloroalkylmercury(II) Compounds to Aromatic Amines; Selective C-Alkylation¹

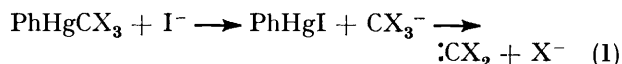
By Jose Barluenga,* Pedro J. Campos, Miguel A. Roy, and Gregorio Asensio, Departament de Química Orgánica, Facultad de Ciencias, Universidad de Oviedo, Oviedo, Spain

α,α -Diarylalkane derivatives have been synthesized from monochloroalkylmercury(II) compounds in a non-carbenoid alkylidene transfer reaction which takes place selectively on the aromatic ring. A mechanism is suggested for this process. Intermediate products are prepared by alternative routes to ascertain their participation in the course of the reaction. As a consequence, two different aryl groups can be successively incorporated into the alkane molecule.

THE synthesis and chemical properties of polyhalogenoalkylmercury(II) compounds have been extensively studied in the last thirteen years. They have been found to be excellent halogenocarbene sources under mild reaction conditions.²⁻⁴ Their most useful application has been the synthesis of cyclopropanes from alkenes.^{5,6} A few reactions with nucleophiles containing lone electron pairs have also been described; with alcohols and aliphatic or aromatic secondary amines they lead to products derived from carbene insertion on the O-H⁷ or the N-H⁸ bonds. The reaction of polyhalogenoalkylmercurials with tertiary aromatic amines has been shown to lead to a complex mixture of products⁹ difficult to rationalize but explained as a result of the interaction of the amine with a dihalogenocarbene. When halogenoalkylmercurials behave as divalent carbon-transfer reagents to alkenes, alcohols, and amines *via* a free carbene or a carbenoid path in the reactions above mentioned, the mercury remains in oxidation state II throughout the process. Seyferth proved² that a concerted $:\text{CCl}_2$ extrusion process takes place *via* a cyclic transition state (1) in the reactions where cyclopropanes are generated, excluding the possibility of the formation of a CX_3^- free anion as carbene precursor.¹⁰ However,



trihalogenomethide ions do act as the intermediate when the carbene insertion reaction is catalysed by iodide ion¹¹ [reaction (1)] which promotes the ionic rupture of the mercurial.

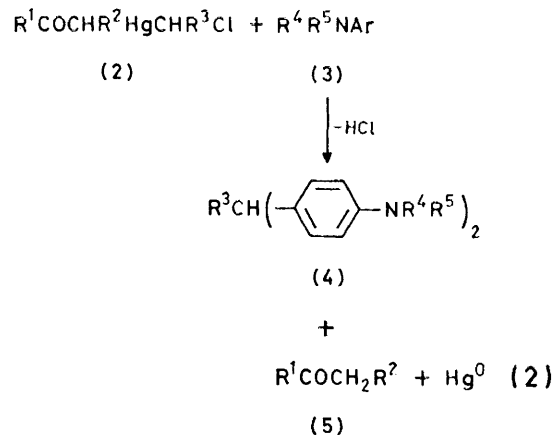


Monohalogenoalkylmercurials have received little attention,¹² and only a few reactions in which $:\text{CH}_2$ is transferred from HgCH_2Hal to olefins to give cyclopropanes,¹³ and substitution reactions of halogen for tertiary aliphatic amines to give mercuriated ammonium salts,¹⁴ have been reported. Recently we described the systematic preparation of monohalogenoalkylmercurials¹⁵ and our preliminary results on their reactivity

towards alcohols¹⁵ and amines.¹ Only in these two latter types of reaction the mercury is reduced to the elemental state, this fact clearly suggesting that a different non-carbenoid reaction mechanism might be operative.

RESULTS AND DISCUSSION

The reaction of monohalogenoalkylmercurials (2) with aromatic amines (3) in a molar ratio of 1:4 gave bis-(4-aminophenyl)alkanes (4), an organic compound (5) derived from substitution of mercury for hydrogen in the starting mercurial (2), and mercury(0) (reaction 2, Table 1). However, products of insertion in the N-H,



$\text{C}_\alpha\text{-C}$ or C-N bonds, which might be expected to result from a carbene-amine interaction,¹⁶ were not observed. The diamines (4) were not contaminated with any other positional isomers. Only in the case of the reaction of aniline with a monochloromethylmercury(II) compound [*e.g.* (2a)], *N*-(4-aminobenzyl)aniline was isolated by column chromatography as a side-product in <1% yield. This product obviously results from a very minor partial competitive alkylation at the nitrogen site.

Bis(chloromethyl)mercury (6) also reacts with aromatic amines to give diamines (4) and elemental mercury, but methyl chloride, which should be generated in this case in the place of the carbonyl compound (5), could not be detected. Instead, *N*-methyl derivatives of both the diamine (4) and an excess of the starting amine (3) were isolated (reaction 3, Table 2). Steric reasons justify the

TABLE 1

Synthesis of bis-(4-aminophenyl)alkanes (4) from monochloroalkylmercurials (2) (reaction 2)

R ¹	R ²	R ³	(2)	R ⁴	R ⁵	Ar	(3)	Temp. (°C)	Time	(4); Yield (%)	(5); Yield (%)	Yield of Hg ⁰ (%)
H	H	H	a	H	H	Ph	a	20	20 min	a 88	(a) 41	91
Me	H	H	b	H	H	Ph	a	20	20 min	a 79	(b) 79	94
Ph	H	H	c	H	H	Ph	a	20	1 h	a 39	(c) 87	45
Ph	Me	H	d	H	H	Ph	a	20	1 h	a 42	(d) 73	47
Me	H	H	b	H	H	<i>o</i> -Tolyl	b	20	40 min	b 49	(b) 80	93
Me	H	H	b	H	H	2,6-Xylyl	c	20	30 min	c 74	(b) 86	99
H	H	H	a	Me	H	Ph	d	20	30 min	d 53	(a) 39	85
Me	H	H	b	Me	H	Ph	d	20	30 min	d 60	(b) 83	93
Me	H	H	b	Et	H	Ph	e	20	30 min	e 62	(b) 73	80
MeO	H	H	e	Ph	H	Ph	f	70 *	1 h	f 43	(e) 51	84
H	H	H	a	Me	Me	Ph	g	125	2 h	g 55	(a) 31	83
Me	H	H	b	Me	Me	Ph	g	125	2 h	g 78	(b) 53	96
Me	H	H	b	Et	Et	Ph	h	125	2 h	h 45	(b) 60	90
Me	H	H	b	CH ₂ Ph	H	Ph	i	70 *	5 h	i 43	(b) 42	60
Me	H	Me	f	H	H	Ph	a	20	30 min	j 39	(b) 72	95
H	H	Me	g	Et	H	Ph	e	20	30 min	k 32	(a) 29	97
Me	H	Et	h	Me	Me	Ph	h	125	2 h	l 69	(b) 67	75

* In THF solution.

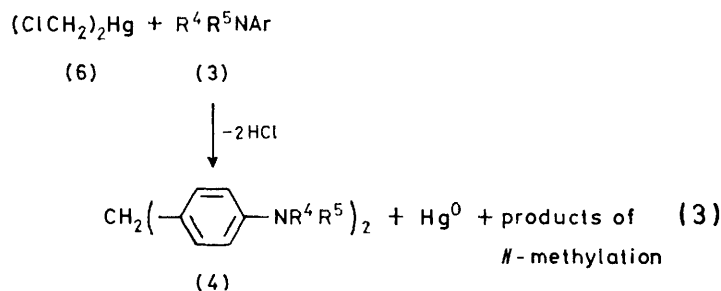
lack of *N*-methylation or *NN*-dimethylation encountered on 2,6-dimethylaniline and 2-toluidine respectively. The contamination of compounds (4) with their *N*-methyl derivatives and the loss of a methylene group make bis(chloromethyl)mercury (6) a poor starting material for the synthesis of (4) compared with unsymmetrical mercurials of type (2).

The course of the reaction of aromatic amines with

all of them are always stabilized by the presence of an α-carbonyl group.

In fact, other examples have been reported in which organomercurials undergo a base-promoted heterolytic cleavage to give a mercuric or organomercuric ion and a carbanion stabilized by inductive¹¹ (reaction 1) or conjugative effects.¹⁷

The observed trends of the reaction speed for different



monochloroalkylmercury(II) compounds (2) can be explained according to the sequence of reactions suggested in Scheme 1.

The first step (reaction 4) implies that the amine basic nitrogen interacts with the mercury(II) in (2) promoting the selective heterolytic cleavage of the α-carbonyl C-Hg bond. The selectivity of this rupture is obviously predetermined by the relative stability of the two possible carbanionic species which can be generated. In our study

amines clearly shows that this is governed mainly by both the co-ordination ability of the amine nitrogen and the existence of N-H bonds. The enhancement of the amine basicity greatly accelerates the reaction since aliphatic amines react, in general, much faster than do aromatic amines with equal numbers of substituents on the nitrogen.¹

The abstraction of a proton from the amine to give the carbonyl compound (5) was established by the formation

TABLE 2

Reactions of bis(chloromethyl)mercury (6) with aromatic amines (3) (reaction 3)

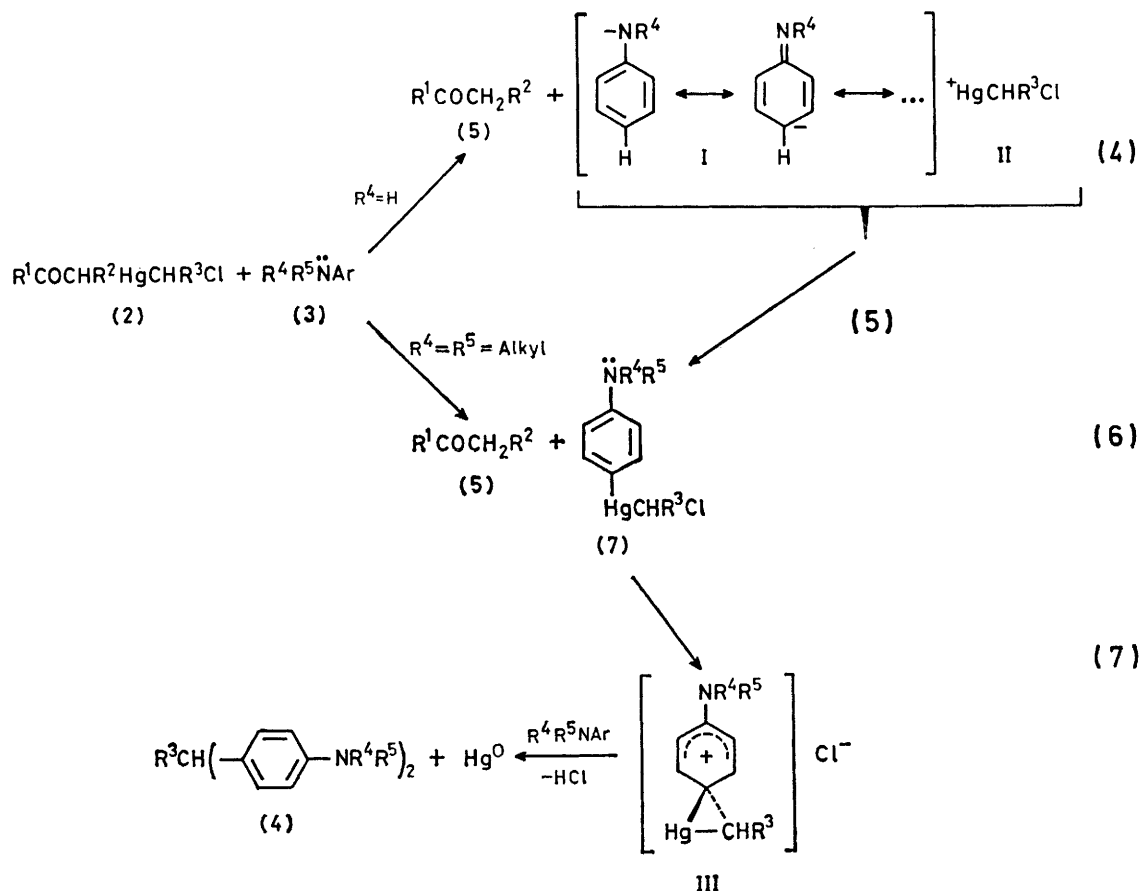
Amine	Temp. (°C)	Time	Solvent	Diamine; Yield (%)	Yield of Hg ⁰ (%)	<i>N</i> -methylation of (3) (%)	<i>NN</i> -dimethylation of (3) (%)
(3a)	20	12 h	THF	(4a) 84	99	18	14
(3b)	20	20 h	THF	(4b) 86	89	32	0
(3c)	20	20 h	THF	(4c) 99	99	0	0
(3d)	20	36 h	THF	(4d) 66	85	42	
(3e)	20	36 h	THF	(4e) 78	100	46	
(3f)	70	72 h	THF	(4f) 22	84	52	
(3g)	100	48 h	Bu ₂ O	(4g) 96	100		
(3h)	100	48 h	Bu ₂ O	(4h) 99	88		

of α -deuteriopropiophenone in the reaction of (2d) with *NN*-dideutioaniline (reaction 8). On the other hand, when tertiary aromatic amines were used the proton must be abstracted from the *para*-position of the amine aromatic ring (reaction 6) and, indeed, reactions took place at a lower speed (Table 1).

The heterolytic cleavage of (2) also accounts for the different chemical behaviour of the two chloromethyl

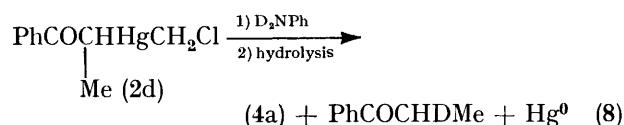
and found that the substitution takes place exclusively at the *para*-position to the amino-group when reaction times < 5 min are used.

Several *para*-mercuriated amines (7) were prepared by an alternative route [e.g. *NN*-diethyl-4-chloromethylmercurioaniline (7d); reaction 9] in order to prove that these compounds really act as intermediates in the synthesis of (4). The preparation and characterization



SCHEME 1

groups of bis(chloromethyl)mercury (6); while one of them plays the role of R^1 and gives rise to the appearance of *N*-methylated products (reaction 3), the second

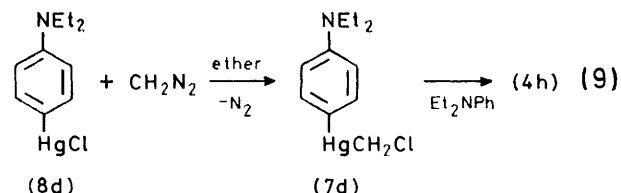


behaves as the 'normal' chloromethyl group of a monochloromethylmercury(II) compound (2).

The formation of the *C*-mercuriated intermediate product (7) (reactions 5 and 6) is similar to the mercuriation of aromatic amines which is reported to proceed in the ring *via* rearrangement of *N*-mercuriated products, except when weak electrophiles [e.g. phenylmercury(II) hydroxide] are used.¹⁸ We have re-investigated the mercuriation of aromatic amines with mercury(II) acetate

of stable 4-chloromethylarylamines (7; $R^4, R^5 = \text{alkyl}$) derived from tertiary aromatic amines have already been reported.¹⁵

The transformation of (7) to (4) can, at first, be envisaged to take place through two alternative general



reaction paths (Scheme 2). The first would involve the transference of a 'free' alkylidene group (CHR^3) (path *a*) from (7) to two new molecules of amine; the second (path *b*) supposes that the alkylidene group reacts with an

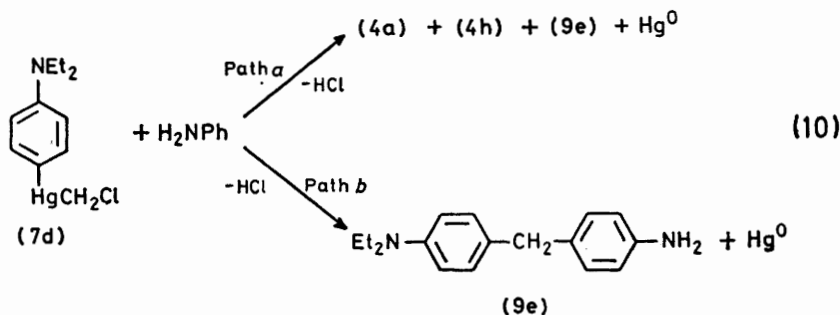
amine while remaining attached to the original aromatic ring throughout the process. The first possibility (path *a*) was easily ruled out by means of an experiment (reaction 10) in which *NN*-diethyl-4-chloromethylmercurioaniline (7d) was allowed to react with an excess of aniline (molar ratio 1 : 2) to afford the asymmetric diamine (9e) and only trace amounts of 4a and 4h. The intramolecular reductive cleavage of (7) to give elemental mercury and diamines (4) (reaction 7) might occur through an intermediate σ -bridged mercurioalkyl-

on a Varian Aerograph-2800 (column Chrom. G, 1.5% OV-101).

Monochloroalkylmercurials (2a–h),¹⁵ *NN*-diethyl-4-chloromethylmercurioaniline (7d),¹⁵ and bis(chloromethyl)mercury (6)²⁰ were prepared according to the literature methods.

Reaction of Monochloroalkylmercurials (2) with Aromatic Amines.—The following description is typical of the method used.

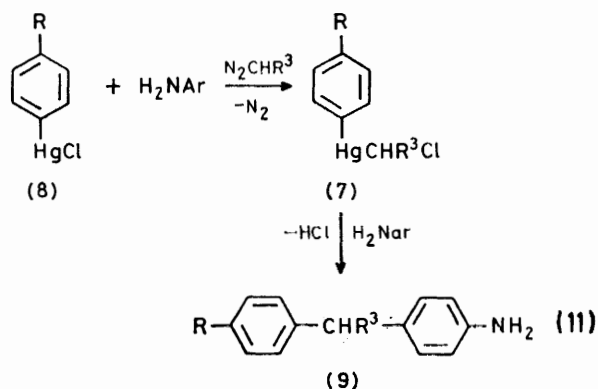
Reaction between chloromethylmercurioacetaldehyde (2a) and aniline. To a 100-ml flask, (2a) (14.7 g, 50 mmol) and



SCHEME 2

idenebenzenium ion [(III), Scheme 1] resulting from the elimination of chloride. The ion (III) would be greatly stabilized by the electron-donor effect¹⁹ of the *para*-amino-group.

The process above described (reaction 10) could be generalized to chloroalkylmercurioarenes¹⁵ in which the



para-amino-group in (7) is substituted for an alkyl group or even hydrogen. In this way, asymmetric derivatives of the α,α -diarylalkanes (9) were easily synthesized. When these reactions were carried out only for synthetic purposes, chloroalkylmercurioarenes (7) were prepared *in situ* from the corresponding *para*-chloromercurioarene (8)¹⁵ and diazoalkane in the presence of the appropriate aromatic amine (reaction 11, Table 3).

EXPERIMENTAL

I.r. spectra were recorded on a Pye-Unicam SP-1000 instrument. ¹H N.m.r. spectra were recorded on a Varian EM-390 spectrometer in deuteriochloroform or carbon tetrachloride, with tetramethylsilane as an internal lock. Gas-liquid chromatographic analyses (g.l.c.) were performed

on a Varian Aerograph-2800 (column Chrom. G, 1.5% OV-101). Aniline (18.6 g, 200 mmol) were added with stirring. After 2–3 min the temperature of the reaction mixture rose spontaneously, a precipitate of elemental mercury appeared, and the evolution of gaseous acetaldehyde was observed. Acetaldehyde was collected and characterized as the dimedone adduct (yield 6.2 g; 41%; m.p. 138 °C; lit.,²¹ 139 °C). The reaction mixture was hydrolysed after 20 min with 1*N* potassium hydroxide, the elemental mercury was filtered off (yield 9.12 g, 91%) and the resulting clear solution extracted with ether and the organic layer dried (Na₂SO₄). Solvents and the excess of amine were removed *in vacuo* (10⁻² Torr) and the residue was purified by column chromatography (silica; chloroform–ether 80 : 20) to give two fractions. The main fraction was recrystallized from hexane–chloro-

TABLE 3

Synthesis of asymmetric derivatives of α,α -diphenylalkanes (9) (reaction 11)

R	(8)	R ³	(7)	Ar in (3)	(9); Yield (%)	Yield of Hg ⁰ (%)
NH ₂	a	H	a	<i>o</i> -Tolyl	(a) 70	82
NH ₂	a	H	a	2,6-Xylyl	(b) 45	60
NHMe	b	H	b	Ph	(c) 69	85
NHEt	c	H	c	Ph	(d) 62	81
NEt ₂	d	H	d	Ph	(e) 71	94
H	e	H	e	Ph	(f) 66	62
Bu ^t	f	H	f	Ph	(g) 42	80
NEt ₂	d	Me	g	Ph	(h) 62	60

form and characterized as bis-(4-aminophenyl)methane (4a) (yield 7.8 g, 88%). For physical data and elemental analyses see Tables 4 and 5. The other fraction was identified as *N*-(4-aminobenzyl)aniline (yield 0.1 g, 1%); m.p. 48–49 °C (lit.,²² 49–50 °C); ν_{max} (film) 690, 740, 820, 1 360, 1 510, 1 600, and 3 380 cm⁻¹; δ (CCl₄) 3.65 (s, NH₂ and NH), 4.20 (s, CH₂), and 6.50–7.30 (m, aromatic) (Found: C, 78.49; H, 7.21; N, 14.31. C₁₃H₁₄N₂ requires C, 78.75; H, 7.12; N, 14.13).

Modifications to this general procedure have to be intro-

duced for the analysis of (5) in the reaction mixture when this product is not acetaldehyde. Acetone (5b) and methyl acetate (5e) were determined by distillation *in vacuo* of the reaction mixture prior to the hydrolysis and analysis of the distillate by g.l.c. Acetophenone (5c) and propiophenone (5d) appeared, following the general procedure, in the distillate which contained the excess of amine; they were determined by g.l.c. analysis.

Details of the products obtained (4a—l) and reaction conditions are summarised in Tables 1, 4, and 5.

analysed by g.l.c. and was a mixture of aniline, *N*-methyl-aniline (yield 0.95 g, 18%) and *NN*-dimethylaniline (yield 0.83 g, 14%). The oily residue was purified by column chromatography [silica; cyclohexane–benzene–diethylamine (75 : 15 : 10)] to give (4a) (yield 8.24 g, 84%). Other fractions were mixtures of different *N*-methyl derivatives of (4a) and were not further purified.

When tertiary aromatic amines were used (*e.g.* *NN*-dimethylaniline) the presence of trimethylphenylammonium chloride was detected in the aqueous layer by ^1H n.m.r.

TABLE 4
Physical data of compounds (4) and (9)

Compound	M.p. (°C)	Lit. m.p. (°C)	Formula	Molecular weight	Analysis			$\nu_{\text{max.}}$ /cm $^{-1}$ (N = nujol; f = film)
					Calc. (Found)			
					C	H	N	
(4a)	91—92	92—93 ^a	C ₁₃ H ₁₄ N ₂	(198.27)	78.75 (78.7)	7.2 7.0	14.13 14.0	810, 1 250, 1 510, 1 630, 3 400 (f)
(4b)	86—88		C ₁₅ H ₁₈ N ₂	(226.32)	79.60 (79.3)	8.02 8.15	12.38 12.5	840, 1 270, 1 510, 1 580, 1 620, 3 400 (N)
(4c)	114—115		C ₁₇ H ₂₂ N ₂	(254.37)	80.27 (80.1)	8.72 8.7	11.01 10.85	890, 1 390, 1 470, 1 500, 1 630, 3 390, 3 470 (N)
(4d)	56—57	56—57 ^b	C ₁₅ H ₁₈ N ₂	(226.32)	79.60 (79.8)	8.02 7.9	12.38 12.15	810, 1 180, 1 270, 1 320, 1 430, 1 615, 3 420 (N)
(4e)	75—77		C ₁₇ H ₂₂ N ₂	(254.37)	80.27 (80.15)	8.72 8.65	11.01 11.2	820, 1 210, 1 320, 1 520, 1 615, 2 980, 3 440 (f)
(4f)	112—113	113	C ₂₅ H ₂₂ N ₂	(350.46)	85.68 (85.6)	6.33 6.2	7.99 7.85	695, 750, 820, 1 310, 1 500, 1 595, 2 900, 3 020, 3 390 (f)
(4g)	90—91	91—92 ^a	C ₁₇ H ₂₂ N ₂	(254.37)	80.27 (80.3)	8.72 8.6	11.01 10.9	810, 1 180, 1 360, 1 460, 1 530, 1 620 (N)
(4h)	40—42	42.5 ^d	C ₂₁ H ₃₀ N ₂	(310.48)	81.24 (81.55)	9.74 9.65	9.02 8.85	805, 1 260, 1 360, 1 520, 1 610, 2 980 (f)
(4i)	110—112		C ₂₇ H ₂₆ N ₂	(378.51)	85.67 (85.25)	6.92 7.0	7.40 7.95	710, 740, 810, 1 500, 1 600, 3 410 (N)
(4j)	Oil		C ₁₄ H ₁₆ N ₂	(212.29)	79.21 (79.0)	7.59 7.5	13.19 13.5	770, 860, 1 160, 1 320, 1 510, 1 605, 2 980, 3 420 (f)
(4k)	Oil		C ₁₈ H ₂₄ N ₂	(268.40)	80.55 (80.95)	9.01 8.95	10.44 10.1	780, 1 460, 1 505, 1 610, 2 670, 2 980 (f)
(4l)	Oil		C ₁₉ H ₂₆ N ₂	(282.43)	80.80 (80.5)	9.28 9.30	9.92 10.15	820, 1 180, 1 360, 1 545, 1 630, 2 840, 2 920, 3 010 (f)
(9a)	127	127—128 ^e	C ₁₄ H ₁₆ N ₂	(212.29)	79.21 (79.15)	7.60 7.7	13.19 13.15	770, 830, 1 280, 1 320, 1 510, 1 620, 2 920, 3 380 (f)
(9b)	Oil		C ₁₅ H ₁₈ N ₂	(226.32)	79.60 (79.85)	8.02 7.95	12.38 12.2	780, 1 280, 1 315, 1 495, 1 610, 2 930, 3 390 (f)
(9c)	Oil		C ₁₄ H ₁₆ N ₂	(212.29)	79.21 (79.05)	7.59 7.65	13.19 13.3	750, 810, 1 310, 1 505, 1 595, 3 370 (f)
(9d)	Oil		C ₁₅ H ₁₈ N ₂	(226.32)	79.60 (79.45)	8.02 8.10	12.38 12.45	820, 1 270, 1 380, 1 470, 1 610 (f)
(9e)	Oil		C ₁₇ H ₂₂ N ₂	(254.37)	80.27 (80.1)	8.72 8.7	11.01 11.25	755, 815, 1 200, 1 270, 1 520, 1 615, 2 970, 3 360 (f)
(9f)	35—36	34—35 ^f	C ₁₃ H ₁₃ N	(183.25)	85.21 (85.6)	7.15 6.9	7.64 7.45	700, 765, 830, 1 325, 1 520, 1 610, 3 020, 3 400 (f)
(9g)	Oil		C ₁₇ H ₂₁ N	(329.36)	85.31 (85.7)	8.84 8.7	5.85 5.6	830, 1 280, 1 475, 1 510, 1 620, 2 970, 3 430 (f)
(9h)	Oil		C ₁₈ H ₂₄ N ₂	(268.40)	80.55 (80.35)	9.01 8.9	10.44 10.7	700, 760, 1 160, 1 275, 1 510, 1 610, 2 980, 3 430 (f)

^a Beilstein, vol. 13, Band 2, p. 111. ^b Beilstein, vol. 13, p. 239. ^c Beilstein, vol. 13, Band 1, p. 73. ^d Beilstein, vol. 13, p. 242. ^e Beilstein, vol. 13, p. 254. ^f Beilstein, vol. 12, p. 1323.

Reaction of Bis(chloromethyl)mercury (6) with Aromatic Amines.—The following description is typical of the method used.

Reaction between (6) and aniline. In a 100-ml flask, (6) (14.98 g, 50 mmol) was dissolved in THF (30 ml) and aniline (18.6 g, 200 mmol) was added with stirring. After 12 h at room temperature the reaction mixture was hydrolysed with 1*N* potassium hydroxide and the elemental mercury (yield 9.9 g, 99%) was filtered off. The resulting clear solution was extracted with ether, the ether layer dried (Na₂SO₄), and the solvents and the excess of amine were evaporated *in vacuo* (10⁻² Torr). The distillate was

analysis after D₂O hydrolysis of the reaction mixture; δ (D₂O) 3.57 (s, PhMe₃N⁺).

Details of the products obtained (4a—h) and reaction conditions are summarised in Tables 2, 4, and 5.

Reaction of α -Chloromethylmercuriopropiophenone (2d) with NN-Dideuterioaniline.—To a 25-ml flask, (2d) (3.8 g, 10 mmol) and *NN*-dideuterioaniline (2.8 g, 30 mmol) were added with stirring. After 1 h at room temperature the reaction mixture was distilled *in vacuo* (10⁻² Torr) and the distillate, analysed by ^1H n.m.r. and g.l.c., was found to be a mixture of deuteriated anilines and α -deuteriopropiophenone contaminated with the regular ketone (yield 0.94 g,

69%), δ (CCl_4) 1.10 (broad d, MeCHD), 2.90 (q, MeCHD), and 7.30–8.10 (m, Ph). The residue was treated following the general method already described to give elemental mercury (yield 0.92 g, 46%) and (4a) (yield 0.81 g, 41%).

4-Aminophenylmercury Chloride (8a).—The mercuriation of aniline according to the methods previously reported²³ led to mixtures of mercuriated amines and, for this reason, (8a) was prepared as follows. To a solution of mercury(II) acetate (15.9 g, 50 mmol) in water (80 ml), aniline (9.7 g, 105 mmol) was added with vigorous stirring. After 5 min the resultant white solid was removed by filtration, washed with water and then dissolved in methanol and precipitated as the chloromercury derivative upon addition of a solution

TABLE 5

¹H N.m.r. data for compounds (4) and (9)
(δ in p.p.m. from SiMe_4 , ¹J/Hz)

(4a)	3.40 (s, NH_2), 3.80 (s, CH_2), 6.60–7.40 (m, C_6H_4)
(4b)	2.10 (s, Me), 3.33 (s, NH_2), 3.70 (s, CH_2), 6.50–7.20 (m, C_6H_3)
(4c)	2.10 (s, Me), 3.33 (s, NH_2), 3.65 (s, CH_2), 6.72 (s, C_6H_4)
(4d)	2.65 (s, Me), 3.40 (s, NH), 3.73 (s, CH_2), 6.40–7.20 (m, C_6H_4)
(4e)	1.10 (t, MeCH_2 , <i>J</i> 7.5), 3.00 (q, MeCH_2 , <i>J</i> 7.5), 3.27 (s, NH), 3.74 (s, CH_2), 6.50–7.10 (m, C_6H_4)
(4f)	3.86 (s, CH_2), 5.30 (br s, NH), 6.80–7.30 (m, aromatic)
(4g)	2.80 (s, Me), 3.83 (s, CH_2), 6.60–7.10 (m, C_6H_4)
(4h)	1.10 (t, MeCH_2 , <i>J</i> 7.0), 3.25 (q, MeCH_2 , <i>J</i> 7.0), 3.70 (s, CH_2), 6.40–7.10 (m, C_6H_4)
(4i)	3.65 (s, NH), 3.70 (s, CH_2), 4.20 (s, CH_2N), 6.50–7.20 (m, aromatic)
(4j)	1.10 (d, MeCH , <i>J</i> 7.5), 3.40 (m, MeCH), 3.70 (br s, NH_2), 6.20–7.40 (m, C_6H_4)
(4k)	1.15 (d, MeCH , <i>J</i> 7.5), 1.40 (t, MeCH_2 , <i>J</i> 7.5), 3.30 (q, MeCH_2 , <i>J</i> 7.5), 3.55 (q, MeCH , <i>J</i> 7.5), 7.00–7.70 (m, C_6H_4), 8.80 (s, NH)
(4l)	0.83 (t, MeCH_2CH , <i>J</i> 7.0), 1.96 (m, MeCH_2CH), 2.80 (s, MeN), 3.56 (t, MeCH_2CH , <i>J</i> 7.5), 6.40–7.10 (m, C_6H_4)
(9a)	2.10 (s, MeN), 4.15 (s, CH_2), 4.43 (s, NH_2), 6.40–7.20 (m, aromatic)
(9b)	2.15 (s, Me), 3.66 (s, CH_2), 4.60 (s, NH_2), 6.50–7.20 (m, aromatic)
(9c)	2.65 (s, MeN), 3.70 (s, NH, NH_2), 4.10 (s, CH_2), 6.00–7.50 (m, aromatic)
(9d)	1.20 (t, MeCH_2 , <i>J</i> 7.0), 3.10 (q, MeCH_2 , <i>J</i> 7.0), 3.75 (s, CH_2), 5.23 (s, NH, NH_2), 6.40–7.30 (m, aromatic)
(9e)	1.15 (t, MeCH_2 , <i>J</i> 7.5), 3.28 (q, MeCH_2 , <i>J</i> 7.5), 3.65 (s, NH_2), 3.80 (s, CH_2), 6.40–7.40 (m, aromatic)
(9f)	3.50 (s, NH_2), 3.78 (s, CH_2), 6.10–7.70 (m, aromatic)
(9g)	1.25 (s, Me), 3.90 (s, NH_2), 4.10 (s, CH_2), 6.30–7.60 (m, aromatic)
(9h)	1.13 (t, MeCH_2N , <i>J</i> 7.0), 1.95 (d, MeCH , <i>J</i> 7.5), 3.33 (q, MeCH_2N , <i>J</i> 7.0), 4.30 (q, MeCH , <i>J</i> 7.5), 4.80 (s, NH_2), 6.30–7.60 (m, aromatic)

of potassium chloride (3.8 g, 50 mmol) in water (20 ml). After recrystallization from methanol (yield 3.3 g, 20%) it had m.p. 209–210 °C, (lit.,²³ 188 °C); ν_{max} (Nujol) 810, 1 020, 1 470, 1 595, 1 600, 2 960, 3 200, and 3 250 cm^{-1} ; δ ($[\text{H}_6]$ DMSO) 5.10 (broad s, NH_2), and 6.40–7.20 (m, *p*- C_6H_4) (Found: Hg, 60.30. $\text{C}_6\text{H}_6\text{ClHgN}$ requires Hg, 61.13).

4-Methylaminophenylmercury Chloride (8b).—This was prepared following the general method described for (8a); it had m.p. 180–181 °C; ν_{max} (Nujol) 810, 1 190, 1 380, 1 470, 1 500, 1 590, and 3 410 cm^{-1} ; δ ($[\text{H}_6]$ DMSO) 2.73 (s, Me), 5.30 (br s, NH), and 6.30–7.25 (m, *p*- C_6H_4) (Found: Hg, 57.80. $\text{C}_7\text{H}_8\text{ClHgN}$ requires Hg, 58.62).

4-Ethylaminophenylmercury Chloride (8c).—This was prepared following the general method described for (8a); it had m.p. 143–145 °C; ν_{max} (Nujol) 820, 1 195, 1 295,

1 490, 1 590, and 3 390 cm^{-1} ; δ ($[\text{H}_6]$ DMSO) 1.16 (t, MeCH_2N , *J* 7.5 Hz), 3.00 (q, MeCH_2N , *J* 7.5 Hz), 5.40 (s, NH), and 6.35–7.27 (m, *p*- C_6H_4) (Found: Hg, 55.71. $\text{C}_8\text{H}_{10}\text{ClHgN}$ requires Hg, 56.31).

4-Diethylaminophenylmercury Chloride (8d).—To a solution of mercury(II) chloride (13.6 g, 50 mmol) in water-methanol 1:1 (120 ml), *NN*-diethylaniline (17.1 g, 115 mmol), dissolved in methanol (10 ml), was added with vigorous stirring. After 6 h the resulting white solid was removed by filtration, washed with methanol and ether, dried, and recrystallized from methanol (yield 10.9 g, 57%), m.p. 160–162 °C; ν_{max} (Nujol) 805, 1 210, 1 275, 1 360, 1 410, 1 510, 1 600, and 2 900 cm^{-1} ; δ ($[\text{H}_6]$ DMSO) 1.12 (t, MeCH_2N , *J* 7.5 Hz), 3.20 (q, MeCH_2N ; *J* 7.5 Hz), and 6.30–7.30 (m, *p*- C_6H_4) (Found: Hg, 52.05. $\text{C}_{10}\text{H}_{14}\text{ClHgN}$ requires Hg, 52.20).

4-*t*-Butylphenylmercury Chloride (8f).—This was prepared by the method used by Dimroth for the mercuriation of toluene;²⁴ (8f) had m.p. 170–171 °C; ν_{max} (Nujol) 825, 1 020, 1 385, 1 470, and 2 950 cm^{-1} ; δ ($[\text{H}_6]$ DMSO) 1.25 (s, Me), and 7.30–7.50 (m, *p*- C_6H_4) (Found: Hg, 54.0. $\text{C}_{10}\text{H}_{13}\text{ClHg}$ requires Hg, 54.32).

Reaction between *NN*-Diethyl-4-chloromethylmercurioaniline (7d) and *NN*-Diethylaniline.—In a 100-ml flask, (7d)¹⁵ (19.90 g, 50 mmol) was dissolved in THF (20 ml) and *NN*-diethylaniline (8.19 g, 55 mmol) was added with stirring. After 12 h at room temperature the reaction mixture was hydrolysed with 1*N* potassium hydroxide, the elemental mercury (yield 8.22 g, 82%) was filtered off, the resulting clear solution was extracted with ether, and the organic layer dried (Na_2SO_4). Solvents and the excess of amine were removed *in vacuo* (10^{-2} Torr) and the oily residue was purified by column chromatography [silica; cyclohexane-benzene-diethylamine (75:15:10)] to give (4h) (yield 9.76 g, 63%). Details of the product are given in Tables 4 and 5.

Reaction between *NN*-Diethyl-4-chloromethylmercurioaniline (7d) and Aniline.—In a 100-ml flask, (7d)¹⁵ (19.90 g, 50 mmol) was dissolved in THF (20 ml), and aniline (9.31 g, 100 mmol) was added with stirring. After 12 h at room temperature the reaction mixture was hydrolysed with 1*N* potassium hydroxide, the elemental mercury (yield 9.03 g, 90%) was filtered off, the resulting clear solution was extracted with ether, and the organic layer dried (Na_2SO_4). Solvents and the excess of amine were removed *in vacuo* (10^{-2} Torr) and the oily residue was purified by column chromatography [silica; cyclohexane-benzene-diethylamine (75:15:10)] to give two fractions. The main fraction was an oil which could not be crystallized and was identified as *NN*-diethylbis-(4-aminophenyl)methane (9e) (yield 9.27 g, 73%). In the other fraction (0.15 g) the presence of (4a) and (4h) was detected by t.l.c. [silica; cyclohexane-benzene-diethylamine (75:15:10)]. Details of these products are summarized in Tables 4 and 5.

Reactions of 4-Chloromercurioarenes (8) with Diazoalkanes and Aromatic Amines.—The following description is typical of the method used.

Reaction of 4-aminophenylmercury chloride (8a) with diazomethane and 2-toluidine. In a 250-ml flask, (8a) (16.40 g, 50 mmol), 2-toluidine (5.11 g, 55 mmol), and THF (50 ml) were placed and then an ether solution of diazomethane (55 mmol) was added dropwise. After stirring at room temperature for 12 h the reaction mixture was heated in an oil bath at 50 °C for 12 h. The resultant mixture was hydrolysed with 1*N* potassium hydroxide and the elemental mercury (yield 8.22 g, 82%) was filtered off. The resulting

clear solution was extracted with ether, the organic layer dried (Na_2SO_4), and the solvents were removed at reduced pressure (0.15 Torr). The residue was purified by column chromatography [silica; cyclohexane–benzene–diethylamine (75 : 15 : 10)] to give an oil which was recrystallized from hot hexane and characterized as 2-methylbis-(4-aminophenyl)methane (9a) (yield 7.40 g, 70%), m.p. 127 °C.

Details of the products obtained (9a–h) and reaction conditions are collected in Tables 3–5.

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