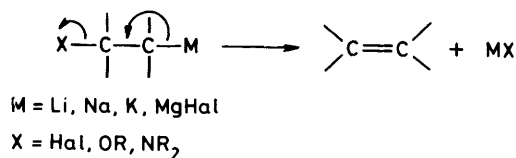


β -Substituted Organoalkaline Tri- and Tetra-anions; Preparation, Stability, and Reactivity

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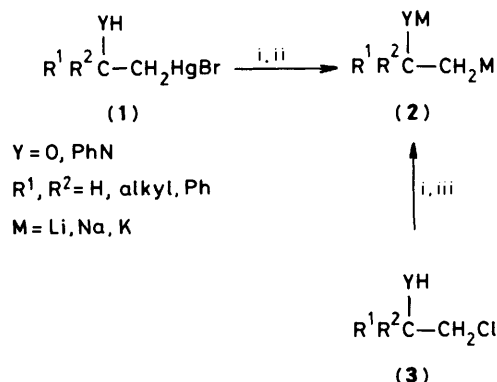
New β,γ -, β,β' -disubstituted organometallic trianions of the type $C(\bar{Y})C(\bar{Y}')\bar{C}$ (**8**) and $C(\bar{Y})\bar{C}C(\bar{Y}')$ (**18**) ($Y = \text{or } \neq Y' = O, \text{PhN}$), β -substituted organodimetallic trianions of the type $\bar{C}C(\text{PhN})\bar{C}$ (**25**) with alkali-metal cations (Li, Na, and K), and a lithiated tetra-anion of the type $\bar{C}C(\text{PhN})C(\text{PhN})\bar{C}$ (**32**) are obtained from the corresponding substituted organomercury(II) compounds *via* low-temperature mercury-alkali metal transmetallation. The starting organomercurials can be obtained by solvomercuriation from suitable unsaturated systems. These polyanion derivatives are stable species only at temperatures in the range -78 to -100 °C; at higher temperatures rapid decomposition takes place *via* either a β -elimination process or proton abstraction from the reaction media. The new polyanionic compounds are characterized by transformation into their deuterio derivatives with deuterium oxide at low temperature. The thermal decomposition of these organometallic intermediates is also reported. The reactivity of the lithiated trianion derived from isopropylaniline (**25a**) with different agents (ethyl bromide, dimethyl disulphide, and trimethylchlorosilane) in a successive or simultaneous way is studied; this process occurs in a regioselective manner.

The preparation of β -substituted organometallic compounds derived from main group elements is greatly hindered by the tendency of these systems to undergo β -elimination reactions which lead to the formation of olefins (Scheme 1). In fact, the β -elimination of β -substituted organometallic compounds obtained from starting materials other than olefins represents a convenient method for obtaining alkenes.¹



Scheme 1.

Recently, β -substituted organometallic compounds (**2**) derived from lithium,^{2a,b,d} sodium,^{2c} and potassium,^{2c} in which the metal is linked to an sp^3 hybridized carbon atom, have been prepared by mercury-alkali metal transmetallation at low temperatures from β -substituted organomercury compounds (**1**). The lithium dianions can also be obtained by direct metallation with lithium naphthalenide at low temperature from chlorohydrins (**3**)³ (Scheme 2). These dianionic



Scheme 2. Reagents: i, PhM or BuLi; ii, M; iii, $C_{10}H_8^- Li^+$.

intermediates are stable at low temperatures owing to the loss of electronegativity of the heteroatom at the β -position with respect to the metal atom, thus hindering the β -elimination.

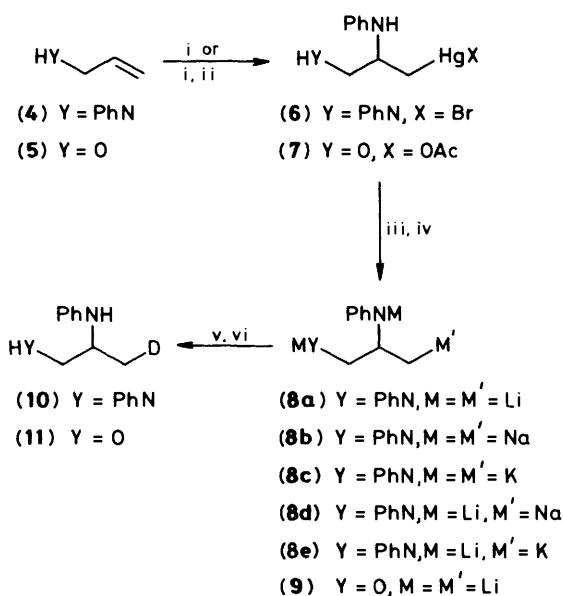
We now report the preparation for the first time of new trianion derivatives of the type $C(\bar{Y})C(\bar{Y}')\bar{C}$, $C(\bar{Y})\bar{C}C(\bar{Y}')$, and $\bar{C}C(\bar{Y})\bar{C}$ (respectively, β,γ -, β,β' -disubstituted organoalkali metal and β -substituted organodialkali metal compounds) and a tetra-anion derivative of the type $\bar{C}C(\bar{Y})C(\bar{Y}')\bar{C}$ from the suitable organomercury compounds *via* mercury-alkali metal transmetallation.

Results and Discussion

β,γ -Disubstituted Organoalkali Metal Compounds.—Successive treatment of the diaminomercurial (**6**) [obtained by mercuriation of allylaniline (**4**) with aniline-mercury(II) acetate⁴ and further metathesis with potassium bromide] with phenyl-lithium⁵ and lithium powder at -78 °C yielded the corresponding trianion derivative (**8a**). This compound was characterized by transformation into its deuterio-derivative (**10**) with deuterium oxide at low temperature. The same process using phenylsodium⁶–sodium naphthalenide,⁷ or phenyl-potassium⁸–potassium[†] to give the trianion derivatives (**8b**) and (**8c**) required a reaction temperature of -100 °C to avoid decomposition. The heterometallic trianions (**8d**) and (**8e**), which are more stable than the homosodium and homopotassium derivatives, were obtained using phenyl-lithium–sodium naphthalenide or phenyl-lithium–potassium at -78 °C. Compounds (**8b–e**) were again characterized by deuteriolysis and spectroscopic analysis of the product (**10**) (Scheme 3 and Table 1).

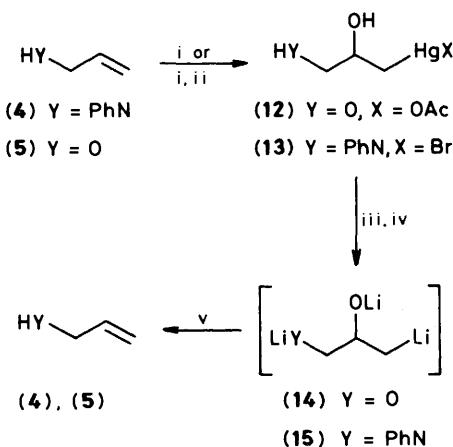
When the hydroxyaminomercurial (**7**) [obtained by aminomercuriation of allyl alcohol (**5**) with aniline-mercury(II) acetate] was treated successively with phenyl-lithium and lithium powder at -78 °C the corresponding trianion derivative (**9**) was obtained. The characterization of the compound (**9**) was made as above by deuteriolysis and spectroscopic analysis of the corresponding deuterio-derivative (**11**) (Scheme 3 and Table 1).

[†] Sodium and potassium were used as metal plates prepared by dissolution of the metal in liquid ammonia at -50 °C followed by evaporation at 0.1 mmHg.



Scheme 3. Reagents: i, $\text{PhNH}_2\text{-Hg(OAc)}_2$; ii, KBr; iii, PhM; iv, M' ; v, D_2O ; vi, $\text{HCl-H}_2\text{O}$.

Treatment of the dihydroxymercurial (12) [obtained by mercuriation of allyl alcohol (5) with water-mercury(II) acetate] with phenyl-lithium and lithium powder at -78°C led to the trianion derivative (14), which under the prevailing

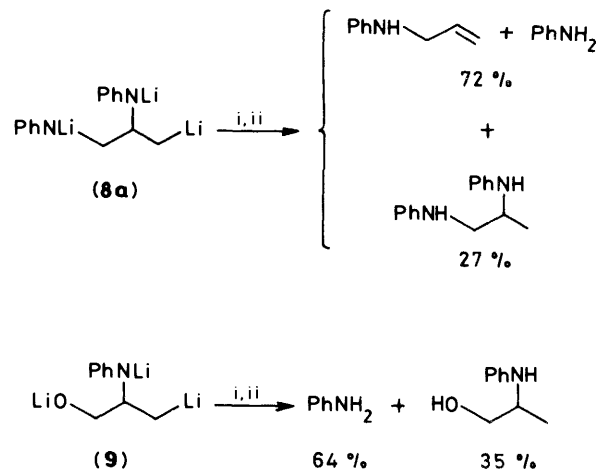


Scheme 4. Reagents: i, $\text{H}_2\text{O-Hg(OAc)}_2$; ii, KBr; iii, PhLi; iv, Li; v, $\text{HCl-H}_2\text{O}$.

reaction conditions decomposed *via* β -elimination to yield allyl alcohol [(5), 90%]. Propane-1,2-diol was not found as a reaction product (Scheme 4). A similar result was obtained by successive treatment of the aminohydroxymercurial (13) [prepared by mercuriation of allylaniline (4) with water-mercury(II) acetate and further metathesis with potassium bromide] with phenyl-lithium and lithium powder at -78°C : the initially obtained trianion derivative (15) undergoes β -elimination leading to allylaniline [(4), 85%] (Scheme 4). We can conclude from the behaviour of the trianions (14) and (15) that when a metal-oxy group is present in the β -position with respect to the metal in the β,γ -disubstituted organoalkali metallic compounds, the trianion intermediates are very

unstable and undergo β -elimination to yield the corresponding unsaturated products.

Finally, the thermal stability of the trilithium trianions (8a) and (9) was studied. When the temperature was allowed to rise to -50°C , decomposition of these trianions occurred; thus, together with a β -elimination reaction there was also a proton abstraction from the reaction media, probably from the solvents⁹ (Scheme 5). Here we have found a different behaviour



Scheme 5. Reagents and conditions: i, -78 to -50°C ; ii, $\text{HCl-H}_2\text{O}$.

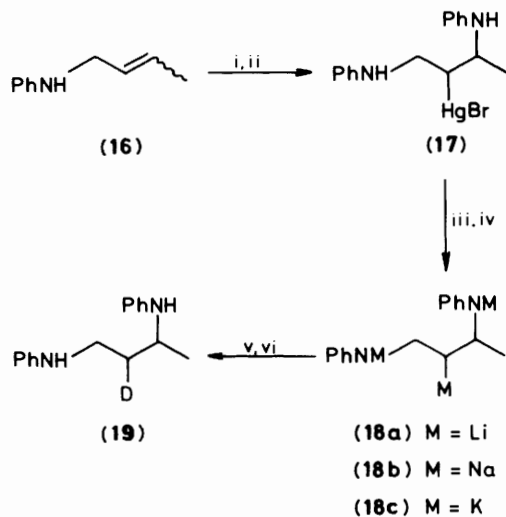
of the trianions (8a) and (9) compared with that of the β -oxygenated trianions (14) and (15), which suffer only β -elimination and no proton abstraction.

β,β' -Disubstituted Organoalkali Metal Compounds.—Successive treatment of the compound (17) [obtained by amino-mercuriation of *N*-but-2-enylaniline (16)¹⁰ with aniline-mercury(II) acetate and further metathesis with potassium bromide¹¹] with phenyl-lithium and lithium powder at -78°C yielded the corresponding trianion derivative (18a). Use of phenylsodium-sodium* or phenylpotassium-potassium* to give the corresponding trianion derivatives (18b) and (18c) required a reaction temperature of -100°C to avoid β -elimination. These intermediates (18a-c) were characterized by transformation into their deuterio-derivative (19) by deuteriolysis with deuterium oxide at low temperature and spectroscopic analysis of compound (19) (Scheme 6 and Table 1).

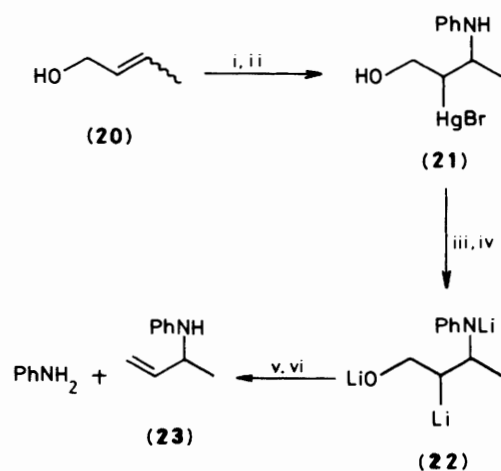
The same process as above starting from but-2-enyl alcohol (20)¹¹ yielded the corresponding trianion, which decomposed readily at low temperature by β -elimination. Thus the lithiated trianion (22) obtained at -78°C led after hydrolysis only to products from β -elimination [20% aniline and 71% *N*-(1-methylallyl)aniline (23)] without incorporation of deuterium to (22) (Scheme 7 and Table 1).

In the case of the intermediate (18a), increasing the temperature to -50°C after preparation caused its decomposition to give only the corresponding products of β -elimination [20% *N*-but-2-enylaniline (16), 19% *N*-(1-methylallyl)aniline (23), and 33% aniline]; no trace of *N,N'*-diphenylbutane-1,3-diamine was detected as a reaction product (Scheme 8).

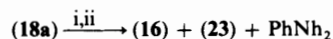
* Sodium and potassium were used as metal plates prepared by dissolution of the metal in liquid ammonia at -50°C followed by evaporation at 0.1 mmHg.



Scheme 6. Reagents: i, $\text{PhNH}_2\text{-Hg(OAc)}_2$; ii, KBr ; iii, PhM ; iv, M ; v, D_2O ; vi, $\text{HCl-H}_2\text{O}$.



Scheme 7. Reagents: i, $\text{PhNH}_2\text{-Hg(OAc)}_2$; ii, KBr ; iii, PhLi ; iv, Li ; v, D_2O ; vi, $\text{HCl-H}_2\text{O}$.



Scheme 8. Reagents and conditions: i, -78 to -50 °C; ii, $\text{HCl-H}_2\text{O}$.

The observed behaviour when obtaining (22) and in the thermal decomposition of (18a) differs from that of the dianions of type (2), where capture of a proton from the reaction medium occurs preferentially.^{1,9} On the other hand, the greater instability observed for the intermediates (18) related to (2) must be assigned to the secondary character of the trianions (18) reported in this paper.

β -Substituted Organodialkali Metal Compounds*.—The successive reaction of the aminomercurial (24) [obtained by the *in situ* aminomercuriation¹² of diallylmercury¹³ with aniline-mercury(II) acetate and further metathesis with potassium bromide] with phenyl-lithium and lithium powder at -78 °C yielded the corresponding trianion derivative (25a). This compound was characterized by transformation into its

Table 1. Synthesis of the trianion derivatives (8), (9), (14), (15), (18), and (22)

Trianion	Reaction conditions		% Yield	
	$t/^\circ\text{C}^a$	Time (s)	Hg ^{ob}	(10), (11), or (19) ^c
(8a)	-78	10 min (8 h)	90	78
(8b)	-100	2 h (6 h) ^d	50	44
(8c)	-100	2 h (6 h)	80	52
(8d)	-78	10 min (8 h) ^d	60	60
(8e)	-78	10 min (8 h)	66	46
(9)	-78	10 min (8 h)	64	52
(14)	-78	10 min (8 h)	75	<i>e</i>
(15)	-78	10 min (8 h)	80	<i>e</i>
(18a)	-78	10 min (8 h)	75	52
(18b)	-100	2 h (8 h)	68	31
(18c)	-100	2 h (6 h)	80	23
(22)	-78	10 min (8 h)	70	<i>e</i>

^a Bath temperature. ^b Based on amount of starting mercurial (6), (7), (12), (13), (17), or (21) used. ^c Yield of isolated product, based on Hg⁰ precipitated. ^d Sodium naphthalene was used in the metallation step. ^e Only products from β -elimination (4), (5), or (23) were obtained.

Table 2. Preparation of the starting mercurials (6), (7), (12), (13), (17), and (21)

Mercurial	Reaction time	% Yield ^a
(6)	1 h	63
(7)	4 h	61
(12)	10 min	82
(13)	5 min	89
(17)	1 h	42
(21)	1.5 h	28

^a Based on amount of starting unsaturated material (4), (5), (16), and (20)

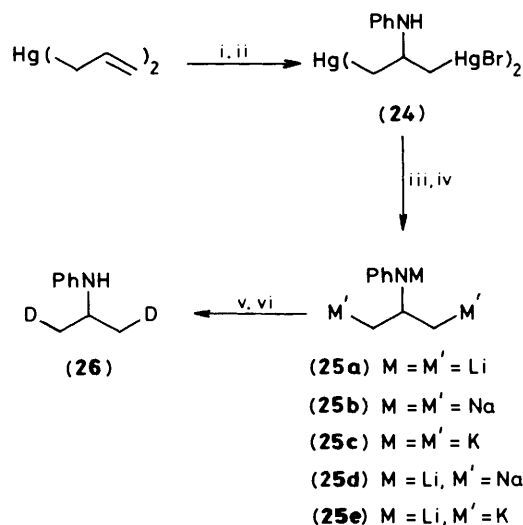
dideuterio-derivative (26) with deuterium oxide at low temperature. Use of the phenylsodium-sodium[†] or phenyl-potassium-potassium[†] to give the corresponding trianion derivatives (25b) and (25c) required a reaction temperature of -100 °C to avoid β -elimination. The heterometallic trianion derivatives [(25d) and (25e)], which are more stable than the homosodium (25b) and homopotassium (25c) derivatives, were obtained using phenyl-lithium-sodium or phenyl-lithium-potassium, respectively, at -78 °C. Compounds (25b–e) were again characterized by deuteriolysis and spectroscopic analysis of compounds (26) (Scheme 9 and Table 3).

Increasing the temperature to -50 °C after preparation of (25a) caused decomposition of the trianion to give allyl-lithium. The latter was isolated by reaction with benzaldehyde and further hydrolysis (75% yield); no trace of isopropylamine was found as a reaction product (Scheme 10).

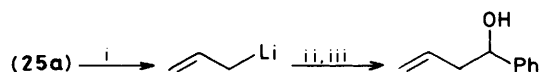
The reactivity of the lithiated trianion (25a) with different electrophiles under several reaction conditions was studied. Intermediate (25a) was allowed to react at -78 °C with an electrophile E^1 (ethyl bromide, dimethyl disulphide, or trimethylchlorosilane) in stoichiometric ratio followed by hydrolysis at the same temperature with aqueous hydrochloric acid and the corresponding products (27) were obtained. Products (27) were slightly contaminated (<19%) with compounds (28) coming from the reaction of both lithiated

* Preliminary communication, J. Barluenga, J. Villamaña, F. J. Fañanás, and M. Yus, *J. Chem. Soc., Chem. Commun.*, 1982, 355.

[†] Sodium and potassium were used as metal plates prepared by dissolution of the metal in liquid ammonia at -50 °C followed by evaporation at 0.1 mmHg.

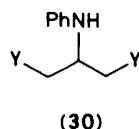


Scheme 9. Reagents: i, $\text{PhNH}_2\text{-Hg(OAc)}_2$; ii, KBr ; iii, PhM ; iv, M' ; v, D_2O ; vi, $\text{HCl-H}_2\text{O}$.



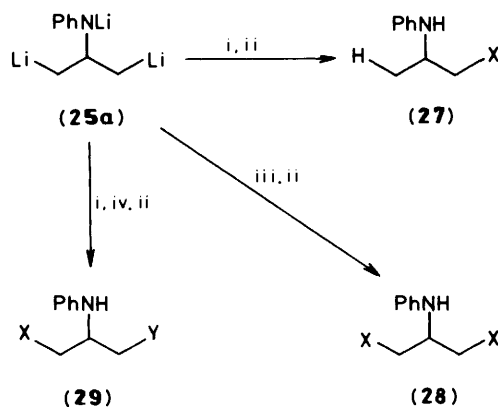
Scheme 10. Reagents and conditions: i, -78 to -50 °C; ii, PhCHO ; iii, $\text{HCl-H}_2\text{O}$.

carbon atoms with the electrophile E^1 . When the reaction of the trianion (25a) at -78 °C was carried out with an excess of the electrophile E^1 (3:1) and this was followed by hydrolysis with aqueous hydrochloric acid the major product was the disubstituted compound (28), which was mixed with appreciable amount (<29%) of the mono-substituted products (27). Finally, a tandem addition of two different electrophiles E^1 and E^2 was studied: the successive treatment of the trianion (25a) with a stoichiometric amount of an electrophile E^1 at -78 °C, and an excess of the second electrophile E^2 (deuterium oxide, ethyl bromide, or trimethylchlorosilane) at the same temperature led to the mixed product (29). This compound was contaminated with variable amounts of products (28) (<12%) and (30) (<33%) (Scheme 11 and Table 4). The isolation and purification of all compounds (27), (28), and (29) was carried out by distillation under reduced pressure.

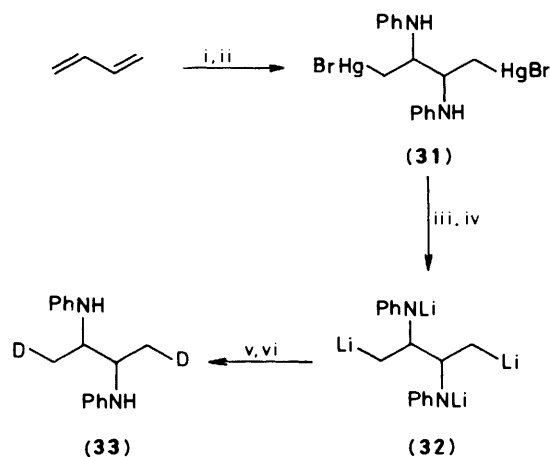


In all above described reactions of the trianion (25a) with electrophilic agents an estimated *ca.* 20% of β -elimination was found as a consequence of the important tendency of this synthon to undergo elimination.

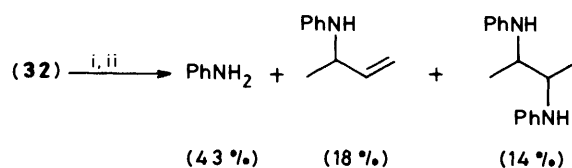
Tetra-anion Derived from *N,N'*-Diphenylbutane-2,3-diamine.—Successive treatment of 1,4-bis(bromomercuro)-*N,N'*-diphenylbutane-2,3-diamine (31)¹⁴ [obtained by the amino-mercuriation of butadiene with aniline-mercury(II) acetate and further double decomposition with potassium bromide] with phenyl-lithium and lithium powder at -78 °C yielded the corresponding tetra-anion derivative (32). This compound was



Scheme 11. Reagents: i, $\text{E}^1 = \text{EtBr}, \text{Me}_2\text{S}_2, \text{Me}_3\text{SiCl}$ (stoichiometric); ii, $\text{HCl-H}_2\text{O}$; iii, E^1 (excess 3:1); iv, $\text{E}^2 = \text{D}_2\text{O}, \text{EtBr}, \text{Me}_3\text{SiCl}$ (excess 3:1).



Scheme 12. Reagents: i, $\text{PhNH}_2\text{-Hg(OAc)}_2$; ii, KBr ; iii, PhLi ; iv, Li ; v, D_2O ; vi, $\text{H}_2\text{O-HCl}$.



Scheme 13. Reagents and conditions: i, -78 to -50 °C; ii, $\text{H}_2\text{O-HCl}$.

Table 3. Synthesis of the trianions (25)

Trianion	Reaction conditions		
	$t/^\circ\text{C}^a$	Time (s)	% Yield
		PhM (M')	
(25a)	-78	10 min (8 h)	90 55
(25b)	-100	2 h (6 h)	94 60
(25c)	-100	2 h (6 h)	78 63
(25d)	-78	10 min (8 h)	92 59
(25e)	-78	10 min (8 h)	92 54

^a Bath temperature. ^b Based on amount of (24) used. ^c Yield of isolated product, based on Hg^0 precipitated.

Table 4. Synthesis of compounds (27), (28), and (29) from the trianion derivative (25a)

Product	E ¹	E ²	X	Y	% Yield		B.p. t/°C (p/mmHg)
					Hg ^{0a}	Product ^b	
(27a)	EtBr		Et		78	45 (8) ^c	65—67 (0.1) ^d
(27b)	Me ₂ S ₂		MeS		82	70 (15) ^c	64—65 (0.001) ^e
(27c)	Me ₃ SiCl		Me ₃ Si		80	71 (19) ^c	51—53 (0.001) ^f
(28a)	EtBr		Et		70	65 (29) ^g	96—99 (0.1)
(28b)	Me ₂ S ₂		MeS		75	76 (22) ^g	172—176 (0.001)
(28c)	Me ₃ SiCl		Me ₃ Si		80	72 (26) ^g	105—108 (0.001)
(29a)	Me ₂ S ₂	D ₂ O	MeS	D	82	54 (11) ^c (33) ^h	85—89 (0.001)
(29b)	Me ₂ S ₂	EtBr	MeS	Et	70	46 (10) ^c (12) ^h	95—98 (0.001)
(29c)	Me ₂ S ₂	Me ₃ SiCl	MeS	Me ₃ Si	70	44 (7) ^c (19) ^h	110—112 (0.001)
(29d)	Me ₃ SiCl	D ₂ O	Me ₃ Si	D	81	53 (12) ^c (28) ^h	65—68 (0.001)
(29e)	Me ₃ SiCl	EtBr	Me ₃ Si	Et	72	40 (5) ^c (22) ^h	72—74 (0.001)

^a Based on amount of (24). ^b Yield of isolated product, based on (25a). ^c Yield of compound (28) determined by g.l.c. analysis with an internal standard, based on (25a). ^d Lit.,¹⁸ b.p. 242 °C (760 mmHg). ^e Lit.,^{2d} 64—65 °C (0.001 mmHg). ^f Lit.,^{2b} b.p. 50—52 °C (0.001 mmHg). ^g Yield of compound (27) determined by g.l.c. analysis with an internal standard, based on (25a). ^h Yield of compound (30) determined by g.l.c. analysis with an internal standard, based on (25a).

characterized by transformation into its dideuterio-derivative (33)* with deuterium oxide at low temperature (Scheme 12).

Increasing the temperature to -50 °C after preparation of (32) caused decomposition of the tetra-anion to give the corresponding products from β -elimination [aniline (43%)[†] and *N*-(1-methylallyl)aniline (18%)[†]] and from a proton abstraction from the reaction medium⁹ [*N,N'*-diphenylbutane-2,3-diamine (14%)[†]] (Scheme 13).

Experimental

General.—M.p.s are uncorrected and were measured on a Büchi-Tottoli capillary melting point apparatus. I.r. spectra were determined with a Pye-Unicam SP-1000 spectrometer. ¹H and ¹³C N.m.r. spectra were recorded on a Varian ET-80 spectrometer, with SiMe₄ as internal standard; when carbon tetrachloride was used as solvent a D₂O capillary was employed as lock reference. The purity of volatile distilled products and the chromatographic analysis were determined with a g.l.c. Varian Aerograph 2800 instrument equipped with an OV-101 Chromosorb column. Elemental analysis of the organic compounds obtained was carried out with a Perkin-Elmer 240 Elemental Analyzer; nitrogen and mercury in the mercurials were determined, respectively, by Kjeldahl's method¹⁵ and by gravimetric analysis.¹⁵ Ether refers to diethyl ether. Starting reactants were of the best commercial grade available (Aldrich, Fluka) and were used without further purification. Phenyl-lithium,⁵ phenylsodium,⁶ phenylpotassium,⁸ and sodium naphthalenide⁷ were prepared as already described. Lithium powder was commercially available (<20 μ , Koch Licht); sodium and potassium were used as metal plates.‡ Ether (referring to diethyl ether) was dried successively with anhydrous calcium chloride, sodium sulphate, sodium, and finally a K-Na (K₃Na) liquid alloy¹⁶ under argon reflux, and was then distilled and stored under argon. Tetrahydrofuran (THF) was dried successively with anhydrous calcium chloride and sodium sulphate; it was then refluxed with potassium, distilled, and stored under argon. All reactions (except the mercuriation reactions) were carried out under argon and all glassware was dried before use.

* Isolated as a diastereoisomeric mixture (¹³C n.m.r.).

† From g.l.c. analysis.

‡ Sodium and potassium were used as metal plates prepared by dissolution of the metal in liquid ammonia at -50 °C followed by evaporation at 0.1 mmHg.

N-But-2-enylaniline (16)¹⁰ was prepared from aniline by successive treatment with phenyl-lithium and a mixture of *Z/E*-but-2-enyl bromide (80%), b.p. 116—118 °C/15 mmHg (lit.,¹⁰ b.p. 116—118 °C/15 mmHg); ν_{\max} (neat) 3 410 (NH), 3 080, 1 620, 1 520, 770, 710 (Ph), and 1 670 cm⁻¹ (C=C); δ_{H} (CCl₄) 1.7 (3 H, d, *J* 5 Hz, CH₃), 3.35 (1 H, s, NH), 3.55 (2 H, m, CH₂), 5.55 (2 H, m, 2 \times CH), and 6.3—7.2 p.p.m. (5 H, m, Ph).

Preparation of the Mercurials (6), (13), (17), and (21): General Procedure.—Mercury(II) acetate (31.8 g, 100 mmol) was added slowly to a stirred solution of the corresponding allylic or but-2-enylic compound [(4), (5), (16), or (20)] (100 mmol) and water or aniline (50 ml) in THF (100 ml) and the mixture was stirred (see Table 2). The solvents were removed (15 and 0.001 mmHg) and the oily residue was dissolved in methanol (100 ml). To this solution was added a solution of potassium bromide (18 g, 150 mmol) in water (50 ml). The resulting precipitate was filtered off (G-3), washed (water, methanol, and ether) and dried (0.1 mmHg). Compounds (6), (13), (17), and (21) were prepared by this method. 2,3-Bis(phenylamino)propylmercury bromide (6), m.p. 112 °C (Found: Hg, 39.6; N, 5.6. C₁₅H₁₇BrHgN₂ requires Hg, 39.66; N, 5.54); ν_{\max} (Nujol) 3 500 (NH), 3 010, 1 610, 1 500, 760, and 700 cm⁻¹ (Ph).

2-Hydroxy-3-(phenylamino)propylmercury bromide (13), m.p. 134—137 °C (Found: Hg, 46.4; N, 3.3. C₉H₁₂BrHgNO requires Hg, 46.57; N, 3.25); ν_{\max} (Nujol) 3 400 (OH, NH), 3 010, 1 600, 1 500, 760, and 700 cm⁻¹ (Ph).

2-Bromomercurio-*N,N'*-diphenylbutane-1,3-diamine (17), m.p. 97—100 °C (decomp.) (Found: Hg, 38.4; N, 5.4. C₁₆H₁₉BrHgN₂ requires Hg, 38.59; N, 5.39); ν_{\max} (Nujol) 3 380 (NH), 3 010, 1 600, 1 500, 760, and 700 cm⁻¹ (Ph).

2-Bromomercurio-3-phenylaminobutan-1-ol (21), m.p. 118—120 °C (decomp.) (Found: Hg, 45.2; N, 3.2. C₁₀H₁₄BrHgNO requires Hg, 45.10; N, 3.15); ν_{\max} (Nujol) 3 390 (OH, NH), 3 010, 1 600, 1 500, 760, and 700 cm⁻¹ (Ph).

Preparation of Mercurials (7) and (12): General Procedure.—Once the mercuriation reaction had been carried out as described above (see Table 2) the solvents were removed (15 and 0.001 mmHg) and the resulting oil was dissolved in chloroform; the resulting solution was washed with aqueous sodium hydrogen carbonate and dried (Na₂SO₄). The solvent was removed (15 mmHg) and the resulting oil was dried (0.001 mmHg). Compounds (7) and (12) were prepared by this method. 3-Hydroxy-2-(phenylamino)propylmercury acetate (7)

(Found: Hg, 49.1; N, 3.45. $C_{11}H_{15}HgNO_3$ requires Hg, 48.94; N, 3.42); v_{max} (neat) 3 400 (OH, NH), 3 010, 1 600, 1 500, 750, 690 (Ph), and 1 560 cm^{-1} (C=O).

2,3-Dihydroxypropylmercury acetate (12) (Found: Hg, 59.9. $C_5H_{10}HgO_4$ requires Hg, 59.93); v_{max} (neat) 3 300 (OH) and 1 550 cm^{-1} (C=O).

Preparation and Deuteriolysis of the Trianion Derivatives (8), (9), and (18): General Procedure.—Phenylalkali metal (an ether solution of phenyl-lithium, or solid phenylsodium or phenylpotassium, 20 mmol) was added to a stirred solution of the corresponding aminomercurial [(6), (7), or (17)] (10 mmol) in THF (125 ml) at low temperature (see Table 1) under argon, and the mixture was stirred for 10 min or 2 h (see Table 1). The corresponding metal (lithium powder, sodium naphthalenide,⁷ sodium or potassium plates,* 60 mmol) was then added and the reaction mixture was stirred for 6–8 h (see Table 1) at the same temperature. Deuterium oxide (2.0 ml) was added to the reaction mixture and then the temperature was allowed to rise to room temperature overnight. The resulting mixture was hydrolysed with water, neutralized with hydrochloric acid, and then extracted with ether; the organic extract was then washed with water and dried (Na_2SO_4). Elemental mercury was filtered off and weighed. The solvents were removed (15 mmHg) and the resulting residue was distilled to give the products (10), (11), or (19). 3-Deuterio-N,N'-diphenylpropane-1,2-diamine (10), b.p. 129–131 °C (0.001 mmHg) [lit.,⁴ for the undeuteriated compound, b.p. 135–138 °C (0.001 mmHg)] (Found: C, 79.3; H/D, 8.5; N, 12.3. $C_{15}H_{17}DN_2$ requires C, 79.25; H/D, 8.42; N, 12.32); v_{max} (neat) 3 360 (NH), 3 060, 3 030, 3 010, 1 600, 1 500, 760, and 700 cm^{-1} (Ph); $\delta_H(CCl_4)$ 1.15 (2 H, d, J 6 Hz, CH_2D), 2.7–3.3 (2 H, m, CH_2N), 3.4–3.9 (3 H, m, CH and $2 \times NH$), and 6.2–7.1 (10 H, m, $2 \times Ph$); $\delta_C(CCl_4)$ 18.34 (t, J_{CD} 19 Hz, CH_2D), 47.89 (CH_2N), 48.96 (CH), 112.83, 113.46, 117.17, 117.31, 129.07, 147.37, and 148.2 p.p.m. (Ph).

3-Deuterio-2-(phenylamino)propanol (11), b.p. 80–83 °C (0.001 mmHg) (Found: C, 71.1; H/D, 9.3; N, 9.2. $C_9H_{12}DNO$ requires C, 71.02; H/D, 9.27; N, 9.20); v_{max} (neat) 3 400 (OH, NH), 3 060, 3 010, 1 600, 1 500, 760, and 700 cm^{-1} (Ph); $\delta_H(CDCl_3)$ 1.0 (2 H, d, J 6 Hz, CH_2D), 3.1–3.5 (3 H, m, CH_2O and CH), 3.5–3.8 (2 H, br s, OH and NH), and 6.2–7.3 (5 H, m, Ph); $\delta_C(CDCl_3)$ 16.90 (t, J_{CD} 19 Hz, CH_2D), 50.16 (CH), 65.36 (CH_2O), 113.60, 117.45, 128.95, and 147.22 p.p.m. (Ph).

2-Deuterio-N,N'-diphenylbutane-1,3-diamine (19), b.p. 148–150 °C (0.001 mmHg) (Found: C, 79.4; H/D, 8.8; N, 11.5. $C_{16}H_{19}DN_2$ requires C, 79.68; H/D, 8.77; N, 11.61); v_{max} (neat) 3 400 (NH), 3 030, 3 010, 1 600, 1 500, 780, and 710 cm^{-1} (Ph); $\delta_H(CCl_4)$ 0.9 (3 H, d, J 6 Hz, CH_3), 1.3–1.7 (1 H, m, CHD), 2.9 (2 H, d, J 6 Hz, CH_2), 3.0–3.7 (3 H, m, CHN and $2 \times NH$), and 6.2–7.0 (10 H, m, $2 \times Ph$); $\delta_C(CCl_4)$ 20.61 (CH_3), 35.86 (t, J_{CD} 19.5 Hz, CH_2D), 40.66 (CH_2N), 46.47 (CHN), 112.53, 113.16, 117.00, 128.86, 128.97, 147.19, and 148.10 p.p.m. (Ph).

Attempted Preparation of the Trianions (14), (15), and (22).—Once the transmetallation reaction from the corresponding mercurial [(12), (13), and (21)] was carried out as described above for trianions (8), (9), or (18) the reaction mixture was hydrolysed and worked up as above. Elemental mercury was weighed (see Table 1). The reaction residue was condensed (0.001 mmHg, 50–100 °C bath temperature) and the condensate was analyzed by g.l.c. (see text).

Thermal Decomposition of the Trianions (8a), (9) and (18a).—Once the trianions (8a), (9), and (18a) were prepared as described above the temperature was allowed to rise to –50 °C for ca. 2 h, and then the reaction mixture was worked up as above. Elemental mercury was weighed [80, 66, and 70%, respectively, for (8a), (9), and (18a)]. The reaction residue was condensed (0.001 mmHg, 100–150 °C bath temperature) and the collecting condensate was analyzed by g.l.c. (see text).

Bis-(3-bromomercurio-2-phenylaminopropyl)mercury (24).—Mercury(II) acetate (63.7 g, 200 mmol) was added to a stirred solution of diallylmercury¹³ (28.6 g, 100 mmol) in THF (125 ml) and aniline (93 g, 1 mol) and the mixture stirred for 15 min. The solvents were removed (15 and 0.001 mmHg) and the oily residue was dissolved in methanol (100 ml). To this solution was added potassium bromide (36 g, 300 mmol), and the resulting precipitate was filtered off (G-3), washed (water, methanol, and ether), and dried (0.1 mmHg) (84.0 g, 82%), m.p. 129–131 °C (Found: Hg, 58.7; N, 2.7. $C_{18}H_{22}Br_2Hg_3N_2$ requires Hg, 58.54; N, 2.72); v_{max} (Nujol) 3 380 (NH), 3 060, 3 020, 1 610, 1 510, 770, and 700 cm^{-1} (Ph).

Preparation and Deuteriolysis of the Trianion Derivatives (25) Isolation of 1,3-Dideuterio-N-phenylpropan-2-amine (26): General Procedure.—Phenylalkali metal (an ether solution of phenyl-lithium, or solid phenylsodium or phenylpotassium, 20 mmol) was added to a mechanically stirred solution of bis-(bromomercurio-2-phenylaminopropyl)mercury (24) (10.3 g, 10 mmol) in THF (125 ml) at low temperature (see Table 3) under argon, and the mixture was stirred for 10 min or 2 h (see Table 3). The corresponding metal (lithium powder, sodium or potassium plates,* 180 mmol) was then added and the reaction mixture was stirred for 6–8 h (see Table 3) at the same temperature. Deuterium oxide (4.0 ml) was added to the resulting mixture which was then stirred for 2 h. The mixture was hydrolysed with water, neutralized with hydrochloric acid, and then extracted with ether; the organic extract was then washed with water and dried (Na_2SO_4). Elemental mercury was filtered off and weighed. The solvents were removed (15 mmHg) and the resulting residue was distilled, b.p. 72–76 °C (15 mmHg) [lit.,¹⁷ for *N*-isopropylaniline, b.p. 72–75 °C (14 mmHg)] (Found: C, 78.7; H/D, 11.1; N, 10.2. $C_9H_{11}D_2N$ requires C, 78.78; H/D 11.02; N, 10.21); v_{max} (neat) 3 360 (NH), 3 050, 3 010, 1 600, 1 500, 750, and 690 cm^{-1} (Ph); $\delta_H(CDCl_3)$ 1.15 (4 H, d, J 6 Hz, $2 \times CH_2$), 3.4 (1 H, br s, NH), 3.55 (1 H, q, J 6 Hz, CH), and 6.4–7.3 (5 H, m, Ph); $\delta_C(CDCl_3)$ 21.66 (t, J_{CD} 19 Hz, CH_2D), 43.22 (CH), 112.53, 116.10, 128.21, and 146.75 p.p.m. (Ph); m/z 137 (M^+).

Thermal Decomposition of the Trianion (25a): Isolation of 1-Phenylbut-3-en-1-ol.—The trianion (25a) was obtained (30 mmol) as described above, the temperature being allowed to rise from –78 to –50 °C. The reaction mixture was filtered off (G-3) at the same temperature, and benzaldehyde (3.2 g, 30 mmol) was added to the resulting solution; the mixture was then stirred for 6 h. After this time the reaction mixture was hydrolysed with water, neutralized with hydrochloric acid, and extracted with ether; the organic extract was then washed with water and dried (Na_2SO_4). Elemental mercury was weighed (6.75 g, 75%). The solvents were removed (15 mmHg) and the residue was distilled (2.5 g, 75%), b.p. 88–92 °C (0.1 mmHg) (Found: C, 80.9; H, 8.2. $C_{10}H_{12}O$ requires C, 81.04; H, 8.16); v_{max} (neat) 3 400 (OH), 3 000, 1 600, 1 490, 760, 700 (Ph), and 1 660 cm^{-1} (C=C); $\delta_H(CCl_4)$ 2.3 (2 H, t, J 6 Hz, CH_2C), 3.6 (1 H, br s, OH), 4.4 (1 H, t, J 6 Hz, CHO), 4.75–5.1 (2 H, m, $CH_2=C$), 5.3–5.9 (1 H, m, CH=C), and 6.9–7.2 p.p.m. (5 H, m, Ph).

* Sodium and potassium were used as metal plates prepared by dissolution of the metal in liquid ammonia at –50 °C followed by evaporation at 0.1 mmHg.

Reaction of the Trianion (25a) with Electrophiles E¹ (Molar Ratio 1:1) and Isolation of Compounds (27): General Procedure.—To a filtered solution of the trianion (25a) (20 mmol), obtained as described above, the corresponding electrophile E¹ (20 mmol) was added at -78°C and the reaction mixture stirred for 30 min. The resulting mixture was hydrolysed and worked up as for compound (26). *N*-(1-Methylbutyl)aniline (27a),¹⁸ ν_{max} (neat) 3 400 (NH), 3 060, 3 020, 1 600, 1 500, 760, and 700 cm^{-1} (Ph); $\delta_{\text{H}}(\text{CCl}_4)$ 0.95 (3 H, t, *J* 6 Hz, CH_3CH_2), 1.15 (3 H, d, *J* 6 Hz, CH_3CH), 1.3—1.55 (4 H, m, $2 \times \text{CH}_2$), 3.2 (1 H, br s, NH), 3.3—3.6 (1 H, m, CH), and 6.35—7.15 (5 H, m, Ph); $\delta_{\text{C}}(\text{CCl}_4)$ 13.69 (CH_3CH_2), 18.92 (CH_2CH_3), 20.37 (CH_3CH), 39.20 (CH_2CH), 47.89 (CH), 113.00, 116.47, 128.79, and 147.60 p.p.m. (Ph).

1-Methylthio-*N*-phenylpropane-2-amine (27b),^{2d} ν_{max} (neat) 3 350 (NH), 3 040, 3 010, 1 600, 1 500, 760, and 700 cm^{-1} (Ph); $\delta_{\text{H}}(\text{CDCl}_3)$ 1.3 (3 H, d, *J* 6 Hz, CH_3CH), 2.1 (3 H, s, CH_3S), 2.5—2.8 (2 H, m, CH_2), 3.7—3.9 (2 H, m, CH and NH), and 6.4—7.3 (5 H, m, Ph); $\delta_{\text{C}}(\text{CCl}_4)$ 15.94 (CH_3S), 19.90 (CH_3C), 40.66 (CH_2), 48.08 (CH), 113.30, 117.09, 129.02, and 147.18 p.p.m. (Ph).

1-Trimethylsilyl-*N*-phenylpropane-2-amine (27c),^{2b} ν_{max} (neat) 3 390 (NH), 3 060, 3 030, 3 000, 1 600, 1 500, 750, 700 (Ph), and 850 cm^{-1} (CSi); $\delta_{\text{H}}(\text{CCl}_4)$ 0.15 (9 H, s, $3 \times \text{CH}_3\text{Si}$), 0.85 (2 H, t, *J* 6 Hz, CH_2), 1.2 (3 H, d, *J* 6 Hz, CH_3C), 3.2 (1 H, br s, NH), and 3.4—3.7 (1 H, m, CH); $\delta_{\text{C}}(\text{CCl}_4)$ -0.88 (CH_3Si), 23.97 (CH_3C), 26.53 (CH_2), 45.99 (CH), 113.14, 116.97, 128.95, and 146.89 p.p.m. (Ph).

Reaction of the Trianion (25a) with Electrophiles E¹ (Molar Ratio 1:3) and Isolation of Compounds (28): General Procedure.—To a filtered solution of the trianion (25a) (20 mmol), obtained as described above, the corresponding electrophile E¹ (60 mmol) was added at -78°C ; the reaction mixture was then hydrolysed and worked up as for compound (26). *N*-(1-Propylbutyl)aniline (28a) (Found: C, 81.6; H, 11.1; N, 7.3. $\text{C}_{13}\text{H}_{21}\text{N}$ requires C, 81.61; H, 11.06; N, 7.32); ν_{max} (neat) 3 380 (NH), 3 070, 3 030, 3 000, 1 600, 1 510, 760, and 700 cm^{-1} (Ph); $\delta_{\text{H}}(\text{CCl}_4)$ 0.9 (6 H, t, *J* 6 Hz, $2 \times \text{CH}_3$), 1.2—1.5 (8 H, m, $4 \times \text{CH}_2$), 3.0—3.5 (2 H, m, CH and NH), and 6.2—7.3 (5 H, m, Ph); $\delta_{\text{C}}(\text{CCl}_4)$ 13.90 (CH_3), 18.85 (CH_2CH_3), 37.42 (CH_2CH), 52.23 (CH), 112.71, 116.54, 128.83, and 147.86 p.p.m. (Ph).

1,3-Bis(methylthio)-*N*-phenylpropane-2-amine (28b) (Found: C, 58.2; H, 7.6; N, 6.1. $\text{C}_{11}\text{H}_{17}\text{NS}_2$ requires C, 58.10; H, 7.53; N, 6.16); ν_{max} (neat) 3 360 (NH), 3 060, 3 000, 1 600, 1 500, 760, and 700 cm^{-1} (Ph); $\delta_{\text{H}}(\text{CCl}_4)$ 2.0 (6 H, s, $2 \times \text{CH}_3$), 2.6—2.8 (4 H, m, $2 \times \text{CH}_2$), 3.4—3.85 (2 H, m, CH and NH), and 6.3—7.2 (5 H, m, Ph); $\delta_{\text{C}}(\text{CDCl}_3)$ 16.40 (CH_3), 38.10 (CH_2), 52.52 (CH), 113.69, 118.04, 129.32, and 146.80 p.p.m. (Ph).

N-Phenyl-1,3-bis(trimethylsilyl)propane-2-amine (28c) (Found: C, 64.3; H, 10.4; N, 5.1. $\text{C}_{15}\text{H}_{29}\text{NSi}$ requires C, 64.44; H, 10.46; N, 5.01); ν_{max} (neat) 3 390 (NH), 3 040, 3 030, 3 000, 1 600, 1 500, 760, 690 (Ph), and 850 cm^{-1} (CSi); $\delta_{\text{H}}(\text{CCl}_4)$ 0.15 (18 H, s, $6 \times \text{CH}_3$), 0.6—0.9 (4 H, m, $2 \times \text{CH}_2$), 3.1 (1 H, br s, NH), 3.35—3.75 (1 H, m, CH), and 6.2—7.2 (5 H, m, Ph); $\delta_{\text{C}}(\text{CDCl}_3)$ -0.67 (CH_3), 27.43 (CH_2), 47.83 (CH), 113.23, 116.88, 129.14, and 147.13 p.p.m. (Ph).

Tandem Reactions of the Trianion (25a) with two Different Electrophiles E¹ and E² and Isolation of Compounds (29): General Procedure.—To a filtered solution of the trianion (25a) (20 mmol), obtained as described above, the electrophile E¹ (20 mmol) was added at -78°C ; the reaction mixture was then stirred for 30 min. The second electrophile E² (60 mmol) was then added at the same temperature and the mixture stirred for 3 h. The resulting mixture was hydrolysed and worked up as for compound (26). 1-Deuterio-*N*-phenyl-3-methylthiopropene-2-

amine (29a) (Found: C, 65.8; H/D, 8.9; N, 7.6. $\text{C}_{10}\text{H}_4\text{DNS}$ requires C, 65.88; H/D, 8.85; N, 7.68); ν_{max} (neat) 3 390 (NH), 3 080, 3 050, 3 020, 1 610, 1 510, 760, and 710 cm^{-1} (Ph); $\delta_{\text{H}}(\text{CCl}_4)$ 1.1 (2 H, d, *J* 6 Hz, CH_2D), 1.95 (3 H, s, CH_3), 2.5—2.7 (2 H, m, CH_2S), 3.3—3.7 (2 H, m, CH and NH), and 6.3—7.2 (5 H, m, Ph); $\delta_{\text{C}}(\text{CCl}_4)$ 16.02 (CH_3), 19.71 (t, J_{CD} 19.5 Hz, CH_2D), 40.69 (CH_2S), 47.94 (CH), 113.27, 117.22, 128.64, and 146.89 p.p.m. (Ph).

1-Methylthio-*N*-phenylpropane-2-amine (29b) (Found: C, 68.7; H, 9.1; N, 6.7. $\text{C}_{12}\text{H}_{19}\text{NS}$ requires C, 68.85; H, 9.15; N, 6.69); ν_{max} (neat) 3 380 (NH), 3 020, 3 010, 1 600, 1 500, 760, and 690 cm^{-1} (Ph); $\delta_{\text{H}}(\text{CCl}_4)$ 0.95 (3 H, t, *J* 6 Hz, CH_3C), 1.2—1.7 (4 H, m, $2 \times \text{CH}_2\text{C}$), 2.0 (3 H, s, CH_3S), 2.5—2.7 (2 H, m, CH_2S), 3.4—3.8 (2 H, m, CH, and NH), and 6.3—7.3 (5 H, m, Ph); $\delta_{\text{C}}(\text{CCl}_4)$ 13.79 (CH_3C), 18.97 (CH_2CH_3), 36.30 (CH_2CH), 39.16 (CH_2S), 52.34 (CH), 113.12, 116.95, 128.94, and 147.40 p.p.m. (Ph).

1-Methylthio-*N*-phenyl-3-trimethylsilylpropane-2-amine (29c) (Found: C, 61.5; H, 9.1; N, 5.6. $\text{C}_{13}\text{H}_{23}\text{NSSi}$ requires C, 61.60; H, 9.15; N, 5.53); ν_{max} (neat) 3 400 (NH), 3 070, 3 050, 3 030, 3 000, 1 600, 1 510, 770, 680 (Ph), and 840 cm^{-1} (CSi); $\delta_{\text{H}}(\text{CCl}_4)$ 0.15 (9 H, s, $3 \times \text{CH}_3\text{Si}$), 0.7—1.0 (2 H, m, CH_2Si), 2.0 (3 H, s, CH_3S), 2.4—2.6 (2 H, m, CH_2S), 3.35—3.7 (2 H, m, CH and NH), and 6.2—7.2 (5 H, m, Ph); $\delta_{\text{C}}(\text{CCl}_4)$ -0.93 (CH_3Si), 16.22 (CH_3S), 22.85 (CH_2Si), 42.13 (CH_2S), 50.07 (CH), 113.7, 117.36, 129.05, and 146.65 p.p.m. (Ph).

1-Deuterio-*N*-phenyl-3-trimethylsilylpropane-2-amine (29d) (Found: C, 69.0; H/D, 10.6; N, 6.7. $\text{C}_{12}\text{H}_{20}\text{DNSi}$ requires C, 69.15; H/D, 10.64; N, 6.72); ν_{max} (neat) 3 390 (NH), 3 060, 3 030, 3 000, 1 600, 1 500, 750, 700 (Ph), and 850 cm^{-1} (CSi); $\delta_{\text{H}}(\text{CCl}_4)$ 0.15 (9 H, s, $3 \times \text{CH}_3\text{Si}$), 0.85 (2 H, t, *J* 6 Hz, CH_2Si), 1.2 (2 H, d, *J* 6 Hz, CH_2D), 3.2 (1 H, br s, NH), 3.4—3.7 (1 H, m, CH), and 6.3—7.2 (5 H, m, Ph); $\delta_{\text{C}}(\text{CCl}_4)$ -0.86 (CH_3Si), 23.10 (t, J_{CD} 19 Hz, CH_2D), 26.07 (CH_2Si), 45.61 (CH), 113.01, 116.73, 128.99, and 147.04 p.p.m. (Ph).

N-Phenyl-1-trimethylsilylpentane-2-amine (29e) (Found: C, 71.3; H, 10.8; N, 6.0. $\text{C}_{14}\text{H}_{25}\text{NSi}$ requires C, 71.42; H, 10.70; N, 5.95); ν_{max} (neat) 3 410 (NH), 3 060, 3 030, 3 010, 1 600, 1 510, 780, 690 (Ph), and 840 cm^{-1} (CSi); $\delta_{\text{H}}(\text{CCl}_4)$ 0.15 (9 H, s, $3 \times \text{CH}_3\text{Si}$), 0.7—1.1 (5 H, m, CH_3C and CH_2Si), 1.3—1.6 (4 H, m, CH_2CH_2), 3.15 (1 H, br s, NH), 3.35—3.7 (1 H, m, CH), and 6.3—7.2 (Ph); $\delta_{\text{C}}(\text{CCl}_4)$ 0.17 (CH_3Si), 14.89 (CH_3C), 19.80 (CH_2CH_3), 24.81 (CH_2Si), 41.37 (CH_2CH), 50.92 (CH), 113.95, 117.66, 129.95, and 148.50 p.p.m. (Ph).

Preparation and Deuteriolysis of the Tetra-anion (32).—A 0.8M-etheral solution of phenyl-lithium (50 ml, 40 mmol) was added to a solution of the aminomercurial (31)¹⁴ (10.1 g, 20 mmol) in THF (125 ml) at -78°C under argon. After the mixture had been stirred for 10 min lithium powder (1.68 g, 240 mmol) was added and the stirring continued for 8 h at -78°C . Deuterium oxide (3.0 ml) was added to the resulting mixture which was then stirred overnight, the temperature being allowed to rise to 20°C . The reaction mixture was then hydrolysed with water, neutralized with hydrochloric acid, and extracted with ether; the organic extract was then washed with water and dried (Na_2SO_4). The mercury(o) precipitated was filtered off and weighed (6.2 g, 78%). The solvents were removed (15 mmHg) and the resulting residue distilled (3.5 g, 72%), b.p. 155—158 $^{\circ}\text{C}$ (0.001 mmHg) (Found: C, 79.3; H/D, 9.2; N, 11.5. $\text{C}_{16}\text{H}_{18}\text{D}_2\text{N}_2$ requires C, 79.29; H/D, 9.15; N, 11.56); ν_{max} (neat) 3 460 (NH), 3 060, 3 040, 3 020, 1 610, 1 510, 770, and 710 cm^{-1} (Ph); $\delta_{\text{H}}(\text{CCl}_4)$ 0.8—1.2 (4 H, m, $2 \times \text{CH}_2$), 3.1—3.7 (4 H, m, $2 \times \text{CH}$ and $2 \times \text{NH}$), and 6.2—7.3 (10 H, m, $2 \times \text{Ph}$); $\delta_{\text{C}}(\text{CCl}_4)$ 15.66 (t, J_{CD} 19.9 Hz, CH_2D), 52.32, 52.45 (CH),

113.71, 113.81, 117.35, 129.15, and 147.74 p.p.m. (Ph)*; m/z 242 (M^+).

Thermal Decomposition of the Tetra-anion (32).—Once the tetra-anion had been prepared as described above, the temperature was allowed to rise to -50°C for ca. 2 h. The reaction mixture was then worked up as above and the residue condensed (0.001 mmHg, 100°C bath temperature) and analysed (g.l.c.) (see Scheme 13).

* See footnote * on p. 2689.

References

- (a) J. Barluenga, M. Yus, and P. Bernad, *J. Chem. Soc., Chem. Commun.*, 1978, 847; (b) J. Barluenga, M. Yus, J. M. Concellón, and P. Bernad, *J. Chem. Res.*, 1980 (S), 41; (M), 677; (c) J. Barluenga, M. Yus, J. M. Concellón, and P. Bernad, *J. Chem. Res.*, 1980, (S), 324; (d) J. Barluenga, M. Yus, J. M. Concellón, and P. Bernad, *J. Org. Chem.*, 1981, **46**, 2721; (e) J. Barluenga, M. Yus, J. M. Concellón, and P. Bernad, *J. Org. Chem.*, 1983, **48**, 609; (f) J. Barluenga, M. Yus, J. M. Concellón, and P. Bernad, *J. Org. Chem.*, 1983, **48**, 3116.
- (a) J. Barluenga, F. J. Fañanás, M. Yus, and G. Asensio, *Tetrahedron Lett.*, 1978, 2015; (b) J. Barluenga, F. J. Fañanás, and M. Yus, *J. Org. Chem.*, 1979, **44**, 4798; (c) J. Barluenga, F. J. Fañanás, and M. Yus, *J. Org. Chem.*, 1981, **46**, 1281; (d) J. Barluenga, F. J. Fañanás, J. Villamaña, and M. Yus, *J. Org. Chem.*, 1982, **47**, 1560.
- (a) J. Barluenga, J. Flórez, and M. Yus, *J. Chem. Soc., Chem. Commun.*, 1982, 1153; (b) J. Barluenga, J. Flórez, and M. Yus, *J. Chem. Soc., Perkin Trans. I*, 1983, 3019.
- J. Barluenga, C. Jiménez, C. Nájera, and M. Yus, *Synthesis*, 1981, 201.
- H. Gilman and W. Morton, *Org. React.*, 1954, **8**, 286.
- J. F. Nobis and L. F. Moormeir, *Ind. Eng. Chem.*, 1954, **46**, 539.
- H. Normant and B. Angelo, *Bull. Soc. Chim. Fr.*, 1960, 354.
- A. Maerker and J. D. Roberts, *J. Am. Chem. Soc.*, 1966, **88**, 1742.
- (a) R. B. Bates, L. M. Kroposki, and D. E. Potter, *J. Org. Chem.*, 1972, **37**, 560; (b) N. S. Mills, J. Shapiro, and M. Hollingsworth, *J. Am. Chem. Soc.*, 1981, **103**, 1263.
- C. Nájera, Ph.D. Thesis, University of Oviedo, 1979.
- On the regioselectivity in the mercuriation of but-2-enyl alcohol see: H. C. Brown and G. J. Lynch, *J. Org. Chem.*, 1981, **46**, 531; H. Hodjat-Kachani, J. J. Perie, and A. Lattes, *Chem. Lett.*, 1976, 409.
- J. Barluenga, C. Jiménez, C. Nájera, and M. Yus, *Synthesis*, 1982, 414, and references therein.
- 'The Organic Chemistry of Mercury,' L. G. Macarova and A. N. Nesmeyanov, North Holland, Amsterdam, 1967, p. 28.
- V. Gómez-Aranda, J. Barluenga, M. Yus, and F. Aznar, *Rev. Acad. Ciencias Zaragoza*, 1974, **29**, 321 (*Chem. Abstr.*, 1976, **85**, 20716w).
- A. I. Vogel, 'Text Book of Quantitative Inorganic Analysis,' Longmans, Green and Co., 1951, ch. III, p. 20 and ch. IV, p.16.
- H. Gilman and R. W. Young, *J. Org. Chem.*, 1936, **1**, 315.
- 'Handbook of Tables for Organic Compounds Identification,' CRC Press, Cleveland, Ohio, 1976.
- R. C. Elderfield and B. V. Meyer, *J. Am. Chem. Soc.*, 1954, **76**, 1887.

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