Sulphonamidomercuriation of Olefins and Subsequent Reductive Demercuriation or Bromodemercuriation †

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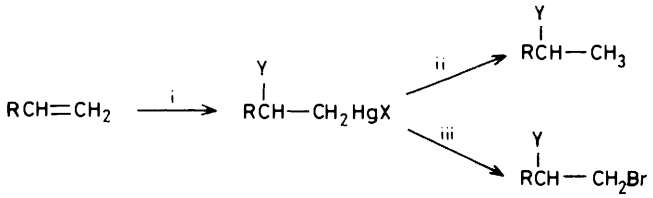
The addition of toluene-*p*-sulphonamide to olefins in the presence of anhydrous mercury(II) nitrate and subsequent sodium borohydride reduction leads to the corresponding *N*-alkylsulphonamides. The sulphonamidomercuriation–demercuriation of 1,4- and 1,5-dienes yields saturated nitrogen-containing heterocycles. A possible mechanism for the stereoselective synthesis of *cis*-2,5-dimethyl-*N*-tosylpyrrolidine is proposed. The treatment of the intermediate organomercurials, isolated as the sodium salts of their bromomercurio derivatives, with bromine gives the corresponding 2-bromoalkylsulphonamides through a regiospecific bromodemercuriation process.

The solvomercuriation of olefins has been widely employed for their Markovnikov functionalization. The intermediate β-substituted organomercurials can be demercuriated by reduction with sodium borohydride in alkaline media[1] or bromodemercuriated to the corresponding β-substituted alkyl bromides[2] (Scheme 1). Many different nucleophiles, HY, can be

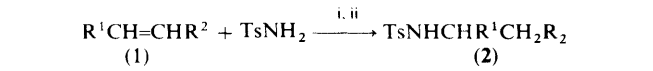


Scheme 1. *Reagents:* i, $HY–HgX_2$; ii, $NaBH_4$–NaOH; iii, Br_2

used in the mercuriation step, *e.g.* water, alcohols, hydroperoxides, carboxylic acids, amines, nitriles, and azide and nitrite ions.[3] We have recently reported the first example of the addition of carboxamides and related compounds to olefins using mercury(II) nitrate.[4,5] Continuing with our studies on mercuriation reactions, in this paper we report that toluene-*p*-sulphonamide ($TsNH_2$) can also be used as a good nucleophilic reagent in the mercuriation of alkenes and dienes using mercury(II) nitrate.

Results and Discussion

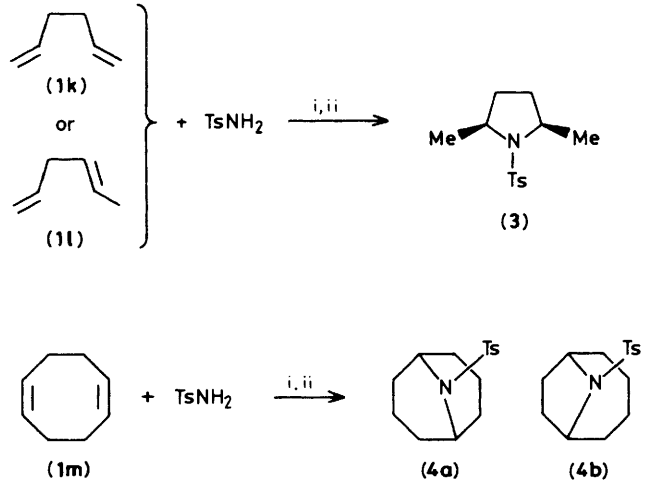
Sulphonamidomercuriation–Demercuriation of Unsaturated Systems.—When toluene-*p*-sulphonamide was allowed to react with different mono-olefins (**1**) in the presence of anhydrous mercury(II) nitrate in methylene dichloride, followed by *in situ* demercuriation with sodium borohydride in aqueous sodium hydroxide and n-butylamine as co-solvent, the corresponding *N*-substituted sulphonamides (**2**) were obtained (Scheme 2 and Table 1).



Scheme 2. *Reagents:* i, $Hg(NO_3)_2$; ii, $NaBH_4$

The use of $Hg(NO_3)_2·H_2O$ as the mercury(II) salt leads to lower yields; for instance, the sulphonamidomercuriation–demercuriation of compound (**1g**) gave product (**2g**) in only 39% yield (*cf.* Table 1). The addition does not take place using (*a*) branched olefins *e.g.* α-methylstyrene or t-butylethylene, probably because of steric requirements; or (*b*) functionalized olefins such as allylamines, allyl sulphides, or alkenylsilanes, probably because of the oxidative properties of the mercury(II) nitrate.

The sulphonamidomercuriation–demercuriation of hexa-1,4-diene (> 95% *E*-isomer from ^{13}C n.m.r. spectroscopy) and hexa-1,5-diene affords (stereoselectively) *cis*-2,5-dimethyl-*N*-tosylpyrrolidine (**3**) (Scheme 3 and Table 1). The configuration of compound (**3**) was deduced by comparison of its n.m.r. data with those of the *N*-aryl analogues.[12]



Scheme 3. *Reagents:* i, $Hg(NO_3)_2$; ii, $NaBH_4$

The hexa-1,5-diene cyclization which leads to the *cis*-pyrrolidine (**3**) apparently takes place through the following mechanism. First, after the addition to one of the double bonds, the nitrogen electron pair interacts with the mercury atom added. In a second step another mercury(II) ion from additional mercury(II) nitrate is similarly complexed by the electrons of the nitrogen atom, requiring approach from the same side and resulting in a *cis* configuration for both mercurial groups (Figure 1). It is noteworthy that the preliminary electronic interaction seems to be required since if the first mercury atom is absent a *trans* addition takes place. Thus, the intramolecular amidomercuriation of *N*-(1-methylpent-4-enyl)carboxamides affords mainly *trans*-2,5-dimethylpyrrolidine derivatives.[13] Furthermore, the basicity of the nitrogen atom must play an

† Preliminary communication, J. Barluenga, C. Jiménez, C. Nájera, and M. Yus, *J. Chem. Soc., Chem. Commun.*, 1981, 1178.

Table 1. *N*-Substituted toluene-*p*-sulphonamides (**2**), (**3**), and (**4**)

Olefin (**1**)				Yield (%)[a]				
	R^1	R^2	Product	Product[b]	Hg^0	M.p. (°C)	Lit. m.p. or b.p. [°C (mmHg)]	Ref.
(**1a**)	H	H	(**2a**)	77	100	56—58[c]	58	6
(**1b**)	CH_3	H	(**2b**)	95	100	112—114[d]		
(**1c**)	$[CH_2]_3$		(**2c**)	52	99	81—83[e]	84	7
(**1d**)	$[CH_2]_4$		(**2d**)	66 (66)	92	83—85[f]	85.7	8
(**1e**)	n-C_4H_9	H	(**2e**)	52 (82)	98	120—122[d]		
(**1f**)	n-C_5H_{11}	H	(**2f**)	46	61	123—125[g]	Oil	9
(**1g**)	n-C_6H_{13}	H	(**2g**)	74	79	121—123[d]	200 (10)	10
(**1h**)[h]	n-C_3H_7	n-C_3H_7	(**2h**)	81	100	148—150[i]		
(**1i**)	Ph	H	(**2i**)	31 (56)	68	80—82[j]	82—83	9
(**1j**)	$PhCH_2$	H	(**2j**)	73	98	67—69[g]	64—66	11
(**1k**)[k]			(**3**)	63 (95)	97	99—100[g]		
(**1l**)			(**3**)	80	99	98—100		
(**1m**)			(**4a**) + (**4b**)	73	90	146—147[f]		

[a] Based on mercury(II) nitrate. [b] Yields in the mercuriation–demercuriation process using compound (**5**) are given in parentheses. [c] From diethyl ether [d] From tetrachloromethane. [e] From chloroform. [f] From methanol. [g] From hexane–chloroform. [h] *trans*-Isomer. [i] From hexane. [j] From ethanol water. [k] More than 95% of the *trans*-isomer (from ^{13}C n.m.r. spectroscopy).

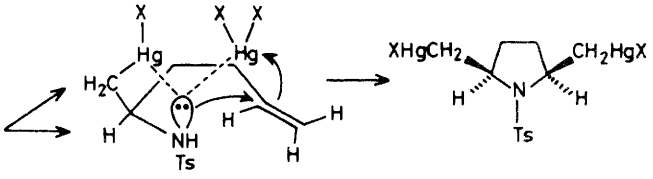
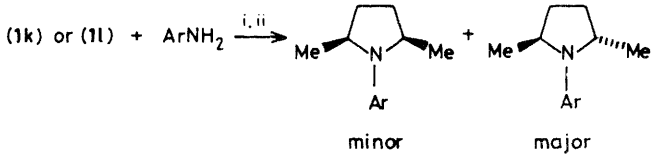


Figure 1.

important role since the intermolecular aminomercuriation of hexa-1,4- and -1,5-diene with aromatic amines also leads mainly to the *trans* isomer[12] (Scheme 4).

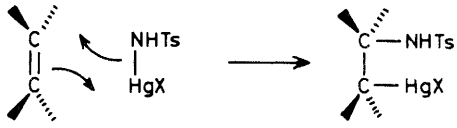


Scheme 4. *Reagents:* i, $Hg(OAc)_2$; ii, $NaBH_4$

Our claim that the mercury(II) salt adds to the same side as the electron pair of the nitrogen atom can be justified since the corresponding toluene-*p*-sulphonamide–mercury(II) nitrate compound[2] has been isolated and can be used in mercuriation reactions. Thus, the reaction of mercury(II) nitrate with toluene-*p*-sulphonamide (molar ratio 1:1) in methylene dichloride leads to compound (**5**). When the sulphonamidomercuriation of mono-olefins or dienes was carried out with compound (**5**) under the same conditions as above described, the same products, indeed with improved yields, were obtained (Table 1, footnote *b*).

$$TsNH{-}HgNO_3$$
(**5**)

The mercury–nitrogen interaction (Figure 1) invoked in order to explain the attack at the second double bond does not necessarily mean that the sulphonamidomercuriation takes place through a *cis* mechanism—as was proposed by Wright[14]—(Scheme 5), since the aminomercuriation of cyclohexane with urethane and mercury(II) nitrate leads to *trans*-*N*-(2-nitratomercuriocyclohexyl)urethane. The stereochemistry of this compound was deduced from the ^1H n.m.r. data of its chloromercurio derivative.*[15]



Scheme 5.

Concerning the stereoselective synthesis of compound (**3**) from hexa-1,4-diene, apparently the first amidomercuriation reaction takes place on the terminal double bond,† whilst the second addition of the mercury(II) salt, to the internal double bond, seems to take place on the less sterically hindered site (Figure 2). The steric requirement in the sulphonamidomercuriation of hexa-1,4-diene for introduction of the second mercury atom is more important than in the case of hexa-1,5-diene since the ring must bear a voluminous mercury-containing group. The different stereochemical results, described herein between sulphonamidomercuriation of hexa-1,4-diene and the corresponding aminomercuriation reaction, have to be attributed to the different nitrogen–mercury interactions.

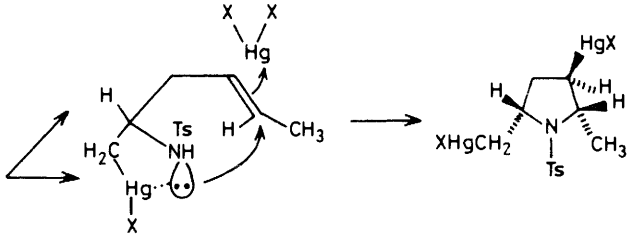


Figure 2.

* The corresponding study on the toluene-*p*-sulphonamide derivative was not possible owing to its very low solubility in common solvents.
† This fact was deduced from correlation with the results on the monoaminomercuriation–demercuriation of hexa-1,4-diene with *N*-methylaniline [diene:$Hg(NO_3)_2$ molar ratio 1:1] which leads exclusively to *N*-methyl-*N*-(1-methylpent-3-enyl)aniline.[15]

Table 2. Sulphonamidomercurials (**6**)

Compound		Yield[a] (%)	M.p.[b] (°C (decomp.)	Molecular formula	Analysis Found (Calc.) (%)		$\nu_{max.}$(Nujol) (cm^{-1})	
	R^1				Hg	N	SO_2	Ar
(**6a**)	H	70	213—215	$C_9H_{11}BrHgNNaO_2S$	39.4 (40.1)	2.6 (2.8)	1 280 1 130	810
(**6b**)	n-C_4H_9	80	198—200	$C_{13}H_{19}BrHgNNaO_2S$	35.1 (36.0)	2.2 (2.5)	1 270 1 130	810
(**6c**)	n-C_6H_{13}	83	220—222	$C_{15}H_{23}BrHgNNaO_2S$	33.7 (34.3)	2.2 (2.4)	1 270 1 130	820
(**6d**)	$PhCH_2$	69	248—250	$C_{16}H_{17}BrHgNNaO_2S$	33.4 (33.9)	2.1 (2.4)	1 290 1 140	820 760, 710

[a] Isolated yields based on mercury(II) nitrate. [b] Could not be recrystallized.

Table 3. 2-Bromoalkyltoluene-*p*-sulphonamides (**7**)

Compound		Yield[a] (%)	M.p. (°C)
	R^1		
(**7a**)	H	76	88—90[b,c]
(**7b**)	n-C_4H_9	96	77—79[d]
(**7c**)	n-C_6H_{13}	95	Oil
(**7d**)	$PhCH_2$	90	120—122[c]

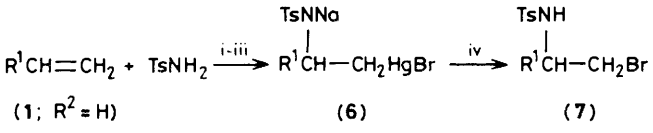
[a] Isolated yields based on compounds (**6**). [b] Lit.,[19b] m.p. 89—91 °C. [c] From hexane–acetone. [d] From hexane.

The sulphonamidomercuriation–demercuriation of cycloocta-1,5-diene yielded a mixture of both regioisomeric tosylated 9-azabicyclo[3.3.1]- and -[4.2.1]-nonanes (**4a**) and (**4b**) (Scheme 3 and Table 1). The isomer ratio was deduced from the ^1H and ^{13}C n.m.r. spectra of the reaction mixture.[16]

Nevertheless the sulphonamidomercuriation of 1,6-diene systems and *N*-allyltoluene-*p*-sulphonamide failed, although the aminomercuriation–demercuriation of such diene systems[17] and *N*-allylamines[18] leads to the expected nitrogen-containing saturated heterocycles.

Sulphonamidomercuriation–Bromodemercuriation of Olefins.—In order to extend the synthetic applicability of the sulphonamidomercuriation reaction, the subsequent bromodemercuriation was studied. This process was carried out by isolating the organomercurial intermediates, since bromination *in situ* failed. These intermediates were prepared by a sulphonamidomercuriation reaction and subsequent treatment of the reaction mixture with aqueous sodium hydroxide and sodium bromide. They can only be precipitated in alkaline media and were isolated as their *N*-sodium amides (**6**) (Scheme 6 and Table 2). Compounds (**6**) were treated with bromine in methylene dichloride to yield β-bromoalkylsulphonamides (**7**) (Scheme 6 and Table 3).

The regiospecific synthesis of compounds (**7**) has, in our opinion, an additional interest owing to the possibility of transforming β-bromoalkylsulphonamides into aziridines[19] and piperazines.[20]



Scheme 6. *Reagents:* i, $Hg(NO_3)_2$; ii, NaOH; iii, NaBr; iv, Br_2

Experimental

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 ^{13}C N.m.r. spectra were recorded on a Varian FT-80 spectrometer, with $SiMe_4$ as internal standard. Anhydrous mercury(II) nitrate is commercially available (Fluka) and was stored under argon.

Sulphonamidomercuriation–Demercuriation of Olefins and Dienes. General Procedure.—Anhydrous mercury(II) nitrate (10 mmol) was added to a stirred solution of the olefin or diene (10 or 5 mmol, respectively) and toluene-*p*-sulphonamide (60 mmol) in methylene dichloride (30 ml) and the mixture was heated under reflux for *ca.* 24 h. In the case of ethylene or propylene the olefin was bubbled through the reaction mixture under reflux for 8 h. The reaction mixture was cooled to 0 °C and then 10% aqueous sodium hydroxide (30 ml), n-butylamine (10 ml), and a solution of sodium borohydride (10 mmol) in 10% aqueous sodium hydroxide (10 ml) were added. The precipitated mercury(0) was filtered off, and the organic layer was separated and dried (Na_2SO_4) and the solvents were evaporated off. The residue was distilled at 0.001 Torr and/or recrystallized to yield products (**2**), (**3**), and (**4**). Data for these compounds are given in Table 4.

Preparation of TsNH–$HgNO_3$ (**5**).—Toluene-*p*-sulphonamide (1.7 g, 10 mmol) was added to a solution of anhydrous mercury(II) nitrate (3.25 g, 10 mmol) in methylene dichloride (20 ml). The resulting suspension was stirred for 1 h and the white precipitate was filtered off, washed with methylene dichloride, and dried *in vacuo* to give compound (**5**) (4.1 g, 95%), m.p. 185—187 °C; $\nu_{max.}$(Nujol) 3 300 (NH), 1 390 (NO_3), 1 260 and 1 140 (SO_2), and 820 cm^{-1} (Ar) [Found: Hg, 46.0; N (Kjeldahl), 3.0. $C_7H_8HgN_2O_5S$ requires Hg, 46.4; amidic N, 3.2%].

Sulphonamidomercuriation–Demercuriation using Compound (**5**).—To a solution of an olefin (**1**) (10 mmol) or hexa-1,5-diene (**1k**) (5 mmol) in methylene dichloride (30 ml) was added compound (**5**) (10 mmol). The reaction mixture was worked up as described above for products (**2**) and (**3**).

Isolation of the organomercurials (**6**). Once the sulphonamidomercuriation had taken place the methylene dichloride was removed under reduced pressure (15 mmHg) and the residue was dissolved in methanol (100 ml). The resulting solution was basified with 10% aqueous sodium hydroxide (50 ml) and a slight excess of sodium bromide (1:1.2 molar ratio) was added to the well stirred solution. The precipitate was filtered off, washed with methanol, and dried *in vacuo* (0.1

Table 4. Spectral data of substituted toluene-*p*-sulphonamides (**2**), (**3**), (**4**), and (**7**)

Compound	$\nu_{max.}$ (cm^{-1})[a] NH	SO_2	δ_H[b]	δ_C (p.p.m.)[b]
(**2a**)	3 280	1 330, 1 160[c]	0.95 (3 H, t, *J* 6 Hz, CH_2CH_3), 2.25 (3 H, s, $ArCH_3$), 2.8 (2 H, m, CH_2), 5.8 (1 H, br s, NH), 7.1 and 7.6 (together 4 H, 2 d, *J* 8 Hz, ArH)[d]	14.7, 21.2, 37.9, 127.1, 129.3, 137.6, 142.4[d]
(**2b**)[e]	3 280	1 310, 1 160	1.2 (6 H, d, *J* 6 Hz, 2 × $CHCH_3$), 2.5 (3 H, s, $ArCH_3$), 3.5 (1 H, m, CH), 5.8 (1 H, br s, NH), 7.3 and 7.9 (together 4 H, 2 d, *J* 8 Hz, ArH)[d]	21.2, 23.3, 45.9, 127.0, 129.5, 138.8, 142.7[d]
(**2c**)	3 250	1 350, 1 165	1.5 (8 H, m, 4 × CH_2), 2.4 (3 H, s, $ArCH_3$), 3.55 (1 H, m, CH), 6.1 (1 H, br s, NH), 7.25 and 7.8 (together 4 H, 2 d, *J* 8 Hz, ArH)	20.1, 22.2, 32.0, 54.2, 126.0, 128.4, 137.6, 141.8
(**2d**)	3 300	1 330, 1 170	0.95—1.9 (10 H, m, 5 × CH_2), 2.4 (3 H, s, $ArCH_3$), 3.1 (1 H, m, CH), 5.6 (1 H, br s, NH), 7.2 and 7.8 (together 4 H, 2 d, *J* 8 Hz, ArH)	21.0, 24.3, 24.9, 33.5, 52.4, 126.7, 129.3, 138.8, 142.6
(**2e**)[f]	3 260	1 330, 1 170	0.8 (3 H, t, *J* 6 Hz, CH_2CH_3), 1.0 (3 H, d, *J* 6 Hz, $CHCH_3$), 1.2 (6 H, m, 3 × CH_2), 2.4 (3 H, s, $ArCH_3$), 3.1 (1 H, m, CH), 5.7 (1 H, d, *J* 8 Hz, NH), 7.2 and 7.8 (together 4 H, 2 d, *J* 8 Hz, ArH)[d]	13.8, 21.3, 22.2, 27.5, 36.8, 49.4, 127.0, 129.0, 139.3, 141.7[d]
(**2f**)[g]	3 280	1 340, 1 170	0.8 (3 H, t, *J* 6 Hz, CH_2CH_3), 1.05 (3 H, d, *J* 6 Hz, $CHCH_3$), 1.15 (8 H, m, 4 × CH_2), 2.45 (3 H, s, $ArCH_3$), 3.2 (1 H, m, CH), 5.15 (1 H, d, *J* 8 Hz, NH), 7.25 and 7.8 (together 4 H, 2 d, *J* 8 Hz, Ar H)	13.5, 21.1, 21.4, 22.1, 24.9, 31.2, 37.3, 49.9, 126.9, 129.3, 138.8, 142.8
(**2g**)	3 300	1 340 1 170[c]	0.8 (3 H, t, *J* 6 Hz, CH_2CH_3), 1.0 (3 H, d, *J* 6 Hz, $CHCH_3$), 1.15 (10 H, m, 5 × CH_2), 2.4 (3 H, s, $ArCH_3$), 3.2 (1 H, m, CH), 5.5 (1 H, d, *J* 8 Hz, NH), 7.2 and 7.8 (together 4 H, 2 d, *J* 8 Hz, ArH)	13.5, 20.9, 21.1, 22.1, 25.1, 28.5, 31.3, 37.1, 49.6, 126.8, 129.1, 138.8, 142.4
(**2h**)[h]	3 280	1 320, 1 160	0.8 (6 H, t, *J* 6 Hz, 2 × CH_2CH_3), 1.2 (10 H, m, 5 × CH_2), 2.4 (3 H, s, $ArCH_3$), 3.1 (1 H, m, CH), 5.9 (1 H, br s, NH), 7.2 and 7.7 (together 4 H, 2 d, *J* 8 Hz, ArH)	12.6, 17.3, 20.1, 21.2, 26.3, 33.4, 36.0, 52.7 125.9, 128.1, 138.1, 141.4
(**2i**)	3 260	1 330, 1 170[c]	1.3 (3 H, d, *J* 6 Hz, $CHCH_3$), 2.35 (3 H, s, $ArCH_3$), 4.4 (1 H, q, *J* 6 Hz, CH), 5.1 (1 H, br s, NH), 7.0—7.9 (9 H, m, ArH)[d]	21.0, 23.1, 53.3, 125.9, 126.7, 126.8, 128.1, 129.0, 137.6, 142.1, 142.5
(**2j**)	3 290	1 330, 1 160[c]	1.0 (3 H, d, *J* 6 Hz, $CHCH_3$), 2.3 (3 H, s, $ArCH_3$), 2.65 (2 H, m, CH_2), 3.5 (1 H, m, CH), 5.45 (1 H, br s, NH), 6.7—7.9 (9 H, 2 m, ArH)	20.4, 20.7, 42.1, 50.7. 125.7, 126.3, 127.7, 128.7, 128.9, 137.2, 137.5, 142.3
(**3**)[i]		1 330, 1 160	1.3 (6 H, d, *J* 6 Hz, 2 × $CHCH_3$), 1.5 (4 H, m, 2 × CH_2), 2.4 (3 H, s, $ArCH_3$), 3.6 (2 H, m, 2 × CH), 7.3 and 7.7 (together 4 H, 2 d, *J* 8 Hz, ArH)[d]	21.2, 23.6, 31.9, 57.0, 127.4, 129.1, 135.8, 142.1[d]
(**4a**) + (**4b**)[j]		1 350, 1 170	1.25—2.2 (12 H, m, 6 × CH_2), 2.4 (3 H, s, $ArCH_3$), 4.05 and 4.25 (together 2 H, 2 m, 2 × CH), 7.2 and 7.7 (together 4 H, 2 d, *J* 8 Hz, ArH)	19.5, 21.1, 23.7, 29.0, 30.9, 35.5, 47.7, 58.6, 126.4, 126.6, 129.2, 129.3, 137.3, 139.0, 142.2, 142.6
(**7a**)	3 290	1 330, 1 160[k,l]	2.4 (3 H, s, $ArCH_3$), 3.35 (4 H, m, $BrCH_2$ and NCH_2), 6.0 (1 H, br s, NH), 7.2 and 7.7 (together 4 H, 2 d, *J* 8 Hz, ArH)[d]	20.8, 30.7, 43.9, 126.2, 129.2, 136.1, 142.9
(**7b**)[m]	3 250	1 320, 1 160[n]	0.7 (3 H, t, *J* 6 Hz, CH_2CH_3), 0.85—1.7 (6 H, m, 3 × CH_2), 2.3 (3 H, s, $ArCH_3$), 3.3 (3 H, m, $BrCH_2$ and CH), 4.8 (1 H, br s, NH), 7.2 and 7.7 (together 4 H, 2 d, *J* 8 Hz, ArH)	11.9, 19.7, 20.2, 25.5, 31.3, 36.0, 51.7, 125.2, 127.9, 136.1, 141.7
(**7c**)[o]	3 300	1 330, 1 160[c,l]	0.8 (3 H, t, *J* 6 Hz, CH_2CH_3), 1.2 (10 H, m, 5 × CH_2), 2.3 (3 H, s, $ArCH_3$), 3.35 (3 H, m, $BrCH_2$ and CH), 5.4 (1 H, br s, NH), 7.2 and 7.7 (together 4 H, 2 d, *J* 8 Hz, ArH)[d]	14.0, 21.4, 22.3, 25.0, 28.5, 31.5, 32.7, 37.8, 53.8, 127.0, 129.6, 138.1, 143.0[d]
(**7d**)[p]	3 290	1 290, 1 150[l]	2.3 (3 H, s, $ArCH_3$), 2.65 (2 H, m, $ArCH_3$), 3.3 (2 H, m, CH_2), 3.6 (1 H, m, CH), 5.3 (1 H, br s, NH), 6.7—7.8 (9 H, m, ArH)	21.4, 40.0, 45.6, 56.3, 127.5, 129.5, 130.1, 130.5, 138.8, 139.5, 143.7[q]

[a] In Nujol unless otherwise stated. [b] In $CDCl_3$ unless otherwise stated. [c] Film. [d] In CCl_4 with a D_2O capillary. [e] Found: C, 56.0; H, 7.3; N, 6.4. $C_{10}H_{15}NO_2S$ requires C, 56.3; H, 7.1; N, 6.6%. [f] Found: C, 61.6; H, 8.4; N, 5.4. $C_{13}H_{21}NO_2S$ requires C, 61.6; H, 8.3; N, 5.5%. [g] Found: C, 62.5; H, 8.5; N, 5.2. $C_{14}H_{23}NO_2S$ requires C, 62.4; H, 8.6; N, 5.2%. [h] Found: C, 63.3; H, 8.8; N, 4.7. $C_{15}H_{25}NO_2S$ requires C, 63.6; H, 8.9; N, 4.9%. [i] Found: C, 61.6; H, 7.5; N, 5.5. $C_{13}H_{19}NO_2S$ requires C, 61.6; H, 7.6; N, 5.5%; *m/z*, 253 (M^+). [j] Found: C, 64.6; H, 7.5; N, 5.1. $C_{15}H_{21}NO_2S$ requires C, 64.5; H, 7.6; N, 5.0%. [k] In $CHCl_3$. [l] ν_{C-Br} 670 cm^{-1}. [m] Found: C, 46.4; H, 6.2; N, 4.0. $C_{13}H_{20}BrNO_2S$ requires C, 46.7; H, 6.0; N, 4.2%; *m/z*, 333 (M^+). [n] ν_{C-Br} 680 cm^{-1}. [o] Found: C, 49.4; H, 6.5; N, 3.8. $C_{15}H_{24}BrNO_2S$ requires C, 49.7; H, 6.7; N, 3.9%. [p] Found: C, 52.0; H, 4.8; N, 3.6. $C_{16}H_{18}BrNO_2S$ requires C, 52.2; H, 4.9; N, 3.8%. [q] In [$^2H_6$]acetone.

mmHg) to afford products (**6**). Data for these compounds are given in Table 2.

Bromodemercuriation of Compounds (**6**). *General Procedure.*—To a suspension of a sulphonamidomercurial (**6**) (5 mmol) in methylene dichloride (30 ml) was added a solution of bromine (5 mmol) in methylene dichloride (10 ml). The mixture was refluxed for 3 h. The mercury(II) bromide was filtered off and the solution was washed successively with 1M aqueous sulphuric acid (10 ml), 20% aqueous sodium hydrogen sulphite (10 ml), and saturated aqueous sodium hydrogen carbonate (10 ml). The organic layer was dried with sodium sulphate and the solvent

was removed (15 mmHg) to yield the corresponding crude compound (**7**). These compounds were purified by recrystallization and their properties are given in Table 4.

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Received 3*rd May* 1983; *Paper* 3/690