Nucleophilic Displacements of *N*-Aryl and Heteroaryl Groups. Part 2.[1] Pyrylium-mediated Transformations of Anilines into Aryl-sulphur Functionality

Alan R. Katritzky * and Roland T. Langthorne
Department of Chemistry, University of Florida, Gainesville, Fla. 32611, U.S.A.

Carbon disulphide and methyl iodide converted the anhydrobases (3) into 8-[(methylthio)thiocarbonyl]-pyridinium iodides (4) which afforded new pyridinium anhydrobases (5) with ethoxide. These anhydrobases rearranged into the isomeric ketene *S,S*-dithioacetals (6), precursors for disulphides.

The functionalisation of aromatic amines *via* substituted pyridinium salts (as an alternative to the classical diazonium reaction) has received attention recently in our laboratories.[1] It is an extension of the transformations of alkyl and benzylamines already achieved *via* this medium.[2]

All previously known preparations of thiophenyls from arylamines require prior formation of the aryl diazonium salt. Various reagents have been employed in the transposition of the diazonium salt to the corresponding thiol: [3,4] Na_2S_2 (*via* ArSSAr), KSCSOEt (*via* ArSCSOEt), and R_2NCSNR_2 [*via* $ArS^+{=}C(NR_2)_2$].

Previously the amino group of primary alkyl and benzylamines has been replaced by various sulphur functionalities *via* *N*-substituted pyridinium salts; SCN,[5] SCSOEt,[5] $SCSNMe_2$,[5] SCOPh,[6] and $S^+C(NHMe)_2$.[6] However, only in one instance was the procedure successfully applied to arylamines: [7] to give aryl thiocyanates.

We have recently reported the conversion of anilines into phenols *via* intramolecular rearrangements of suitably substituted pyridinium anhydrobases.[1] The *N*-aryl bonds are cleaved under relatively mild conditions even when the aryl group is unactivated. This procedure has now been extended to demonstrate intramolecular nucleophilic substitution to sulphur.

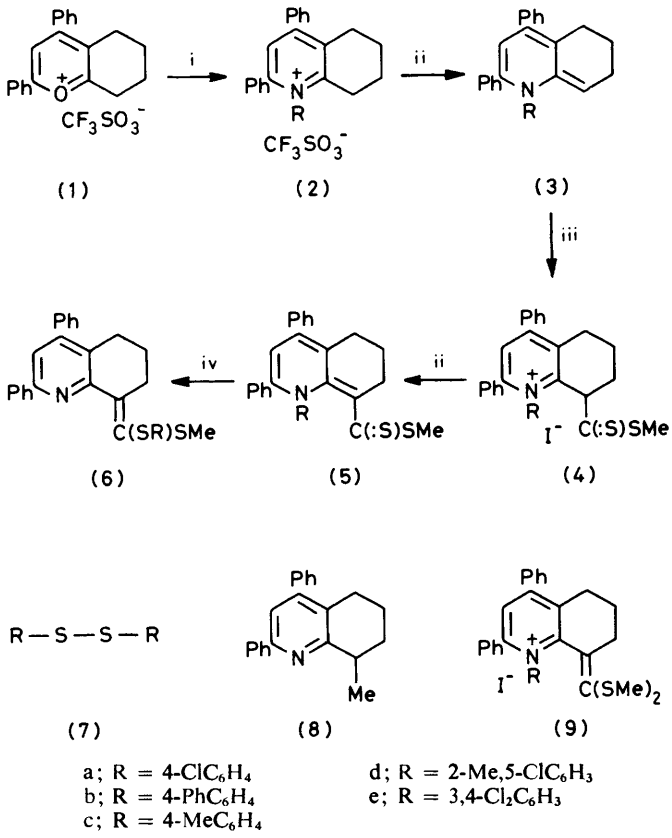
Treatment of the enamines (3) [1] with the thioacylating agent $PhCS_2CH_2CO_2H$ [8] in an analogous reaction failed. However, anhydrobases (or enamines) of various types are known to give adducts with CS_2.[9-11] This reactivity has been used to develop a novel synthetic sequence.

Conversion of Anilines into Ketene S-*Aryl*-S'-*methyldithioacetals*.—2,4-Diphenyl-5,6,7,8-tetrahydrochromenylium triflate (1) condensed readily with a series of aromatic amines to give the corresponding quinolinium salts (2). Treatment with sodium ethoxide generated the anhydrobases (3). Although, as previously reported, these anhydrobases decompose on attempted recrystallisation, satisfactory microanalyses were obtained on the crude material from the reaction media (see Experimental section).

The C=S moiety was introduced into the anhydrobase (3) by a modified procedure (*cf.* ref. 9); *in situ* treatment with carbon disulphide and methyl iodide generated the stable and characterisable pyridinium iodides (4) in high yields (Table 1). ^{1}H N.m.r. data are given in Table 2. In some instances small quantities of the bisthiomethyl adducts (9) were formed. Compounds of this type have also been previously reported.[10,11]

Base treatment of an ethanolic suspension of (4) gave tetrahydroquinolines (5) (Table 3). Characteristic changes in the ^{1}H n.m.r. spectra (Table 4) are a merging of the 5- and 7-CH_2 signals and an upfield shift (*ca.* δ 8.7 to *ca.* 6.9) of the 3-CH proton.

Internal aryl migration to yield the ketene *S,S*-acetal (6)



a; R = 4-ClC_6H_4
b; R = 4-PhC_6H_4
c; R = 4-MeC_6H_4
d; R = 2-Me,5-ClC_6H_3
e; R = 3,4-$Cl_2C_6H_3$

Scheme 1. *Reagents:* i, RNH_2; ii, NaOEt; iii, CS_2–MeI; iv, Heat

was effected thermally (Table 5). Use of dimethylformamide (b.p. 153 °C) (procedure A) gave, in general, higher yields than those obtained in toluene (b.p. 111 °C) (procedure B). The ^{1}H n.m.r. spectra (Table 6) showed distinct triplets for the 5- and 7-CH_2 protons; the 3-CH proton was hidden under the aromatic multiplet; a distinct multiplet (integrating for 2 protons) at δ 8.1 was apparent in all products. This may be assigned to the *ortho*-protons of the 2-phenyl substituent, the other protons resonating in the aromatic region (δ 7.0—7.6).

It is evident that electron-donating substituents considerably reduce the rate of intramolecular nucleophilic sulphur attack on the aryl ring. Where electron-withdrawing substituents are present [as in the 3,4-dichlorophenyl analogue (6e)] rearrangement occurs in higher yield in a shorter time and at a lower temperature.

For the *p*-tolyl derivative (5c) rearrangement could not be effected in toluene. In refluxing xylene some reaction occurred, but even in refluxing DMF the yield was low (see Table 5).

Table 1. Preparation of 8-[(methylthio)thiocarbonyl]-1-aryl-2,4-diphenyl-5,6,7,8-tetrahydroquinolinium iodides (4)

Compd.	Yield (%)	M.p. (°C)	Recryst. solvent *	Found (%) C	H	N	Molecular formula	Required (%) C	H	N
(4a)	97	148—150	EtOAc	56.6	4.1	2.2	$C_{29}H_{25}ClINS_2$	56.7	4.1	2.3
(4b)	96	157—159	PhMe	63.9	4.6	2.1	$C_{35}H_{30}INS_2$	64.1	4.6	2.1
(4c)	81	193—195	MeCN	60.6	4.8	2.3	$C_{30}H_{28}INS_2$	60.7	4.7	2.3
(4d)	72	143—145	Me_2CO–Et_2O	57.5	4.4	2.2	$C_{30}H_{27}ClINS_2$	57.4	4.3	2.2
(4e)	91	151—153	MeCN	53.5	3.8	2.1	$C_{29}H_{24}Cl_2INS_2$	53.7	3.7	2.1

* All compounds crystallised as prisms.

Table 2. ^{1}H N.m.r.[a] of 8-[(methylthio)thiocarbonyl]-1-aryl-2,4-diphenyl-5,6,7,8-tetrahydroquinolinium iodides (4)

Compd.	5-CH_2 (2 H, m) δ	6-CH_2 (2 H, m) δ	7-CH_2 (2 H, m) δ	8-CH (1 H, m) δ	8-CS_2CH_3 (3 H, s) δ	3-CH (1 H, m) δ	Aromatics (m) δ	H	Other δ
(4a)	3.0	2.0	2.3	5.1	2.5	8.5	6.5—8.0	14	—
(4b)	2.9	1.9	2.2	5.2	2.4	8.9	6.7—7.9	19	—
(4c)	2.9	1.9	2.1	5.2	2.4	8.7	6.5—7.7	14	2.2 (3 H, s)
(4d)	3.1	1.8 [b]	2.4	3.5	2.2	8.5	7.1—7.9	13	1.8 (3 H, s)
(4e)	3.0	1.9	2.2	5.1	2.5	8.9	6.8—7.8	13	—

[a] δ($CDCl_3$). [b] Signal hidden under CH_3 singlet.

Table 3. Preparation of 8-[(methylthio)thiocarbonyl]-1-aryl-2,4-diphenyl-1,5,6,7-tetrahydroquinolines (5)

Compd.	Yield (%)	M.p. (°C)	Recryst. solvent *	Found (%) C	H	N	Molecular formula	Required (%) C	H	N
(5a)	95	182—184	EtOH	71.4	5.1	2.8	$C_{29}H_{24}ClNS_2$	71.7	4.9	2.9
(5b)	95	167—169	EtOH	79.4	5.6	2.6	$C_{35}H_{29}NS_2$	79.7	5.5	2.7
(5c)	88	181—183	c-C_6H_{12}	77.4	5.9	3.0	$C_{30}H_{27}NS_2$	77.4	5.8	3.0
(5d)	67	164—166	c-C_6H_{12}	72.1	5.3	2.8	$C_{30}H_{26}ClNS_2$	72.1	5.2	2.8
(5e)	69	173—175	EtOH	66.9	4.5	2.7	$C_{29}H_{23}Cl_2NS_2$	66.9	4.4	2.7

* All compounds recrystallised as prisms.

Table 4. ^{1}H N.m.r.[a] of 8-[(methylthio)thiocarbonyl]-1-aryl-2,4-diphenyl-1,5,6,7-tetrahydroquinolines (5)

Compd.	5-CH_2, 7-CH_2 (4 H, m) [b] δ	*J*	6-CH_2 (2 H, m) δ	8-CS_2CH_3 (3 H, s) δ	3-CH (1 H, s) δ	Aromatics (m) δ	*H*	Other δ
(5a)	2.7	6	1.8	2.3	6.9	7.0—7.6	14	—
(5b)	2.7	6	1.8	2.3	6.9	7.0—7.8	19	—
(5c)	2.7	6	1.8	2.25	*c*	6.8—7.6	15	2.15 (3 H, s)
(5d)	2.8	*d*	1.9	2.4	6.8	6.9—7.6	13	2.1 (3 H, s)
(5e)	2.8	5	1.8	2.3	6.8	7.0—7.6	13	—

[a] δ($CDCl_3$), *J* in Hz. [b] Two overlapping triplets. [c] Signal hidden under rest of aromatics. [d] Unresolved multiplet.

Although acceptable microanalysis figures were not obtained for the rearranged compound (6c), it was characterised by ^{13}C n.m.r. and mass spectral comparisons and an accurate *m/z* determination. Attempted rearrangement of the 5-chloro-2-methylphenyl derivative (5d) gave a mixture of three products as shown by mass spectrometry.

25 MHz ^{13}C *N.m.r. Spectroscopy.*—^{13}C N.m.r. spectra were recorded for representative samples of the two series of compounds (5) and (6). The spectra were assigned using off-resonance decoupling to establish multiplicity. In the primary carbon region SMe resonated at 17.2—17.7 p.p.m. in all cases. The Ar-Me signal occurred at 21.2 p.p.m. in (6c). The three methylene signals appeared at 23.9, 28.0, and 32.7 p.p.m. in compound (5) and 23.0, 27.0, and 31.8 p.p.m. in compounds (6).

Resonances in the aromatic region were complex. However, compounds of type (5) displayed a doublet at 120.0 p.p.m. and singlets at 117.0, 132.5, 134.5, 137.0, 140.5, 146.0, 149.5, and 158.5 p.p.m. separated from the aromatic multiplet. In contrast, compounds of type (6) displayed a doublet at 119.5 p.p.m. and singlets at 137.5, 139.0, 143.0, 149.0, and 153.0 p.p.m. in the quaternary region. The stereochemistry shown in (6) is assumed to result from the mechanism postulated.

Mass Spectra.—Further evidence for the rearrangement of (5c) to (6c) was obtained from a comparison of their mass spectra. Compound (5c) has a base peak (*m/z* 418) corresponding to loss of SMe· with other main fragmentations from the molecular ion at *m/z* 465 assigned as follows (*m/z*, % intensity): (450,23) $-CH_3$·; (386,20) $-SCH_3$·, —S; (374,18) $-CS_2CH_3$·. The product (6c) has a base peak (*m/z* 450) cor-

Table 5. Preparation of 8-[arylthio(methylthio)methylene]-2,4-diphenyl-5,6,7,8-tetrahydroquinolines (6)

Compd.	Procedure [a] A Time (h)	A Yield (%)	B Time (h)	B Yield (%)	M.p. (°C)	Recryst. solvent [d]	Crystal form	Found (%) (Required %) C	H	N	Molecular formula
(6a)	8	80	20	90	142—144	EtOH	Prisms	71.6 (71.7	5.0 4.9	2.9 2.9)	$C_{29}H_{24}ClNS_2$
(6b)	8	85	16	78	88—90	MeOH	Prisms	79.6 (79.7	5.6 5.5	2.6 2.7)	$C_{35}H_{29}NS_2$
(6c)	7	25	14	15 [b]	57—59	n-C_6H_{14}	Prisms	— (—	— —	c —)	$C_{30}H_{27}NS_2$
(6e)	2.5	75	4.5	65	127—129	EtOH	Needles	66.8 (66.9	4.5 4.4	2.6 2.7)	$C_{29}H_{23}ClNS_2$

[a] A: Reflux in DMF, B: reflux in toluene. [b] Reaction in xylene. [c] Compound characterised by m.s. and ^{13}C n.m.r.

Table 6. ^1H N.m.r.[a] of 8-[arylthio(methylthio)methylene]-2,4-diphenyl-5,6,7,8-tetrahydroquinolines (6)

Compd.	5-CH_2 (2 H, t) δ	5-CH_2 (2 H, t) J	6-CH_2 (2 H, m) δ	7-CH_2 (2 H, t) δ	7-CH_2 (2 H, t) J	8=C–SCH_3 (3 H, s)	Aromatics and 3-CH (2 H, m) δ	δ	H
(6a)	3.0	6	1.8	2.7	6	2.3	8.1	7.2—7.6	13
(6b)	3.0	6	1.8	2.7	6	2.3	8.1	7.0—7.6	18
(6c)	3.0	6	1.8	2.7	6	2.3 [b]	8.1	7.0—7.6	13
(6e)	3.0	6	1.8	2.7	6	2.3	8.1	7.1—7.6	12

[a] δ($CDCl_3$); J in Hz. [b] δ 2,3, 6 H, overlapped singlet, due to combination with 4-CH_3 substituent.

responding to loss of Me·. Subsequent diagnostic peaks from the molecular ion (*m/z* 465) are (*m/z*, % intensity): (418,16) $-SCH_3$·; (374,13) $-C_7H_7$·; (359,11) $-CH_3$·, $-C_7H_7$·; (342,7) $-SC_6H_4CH_3$·; (327,17) $-SCH_3$·, $-C_7H_7$·.

High-resolution mass spectrometry gave *m/z* 465.1617, $C_{30}H_{27}NS_2$ requires 465.1585.

Transformations of Ketene S-*Aryl*-S′-*methyldithioacetals*.—Ketene *S,S*-dithioacetals, and the reactions they undergo have been the subject of several studies. Cleavage of the carbon–sulphur bond [12] and, more specifically, Raney nickel hydrogenolysis,[13] have been reviewed (though no mention of the vinyl compounds was made). Oxidation to sulphoxides and sulphones and hydrolysis to thiols are the most documented reactions.[14] In a review on ' umpolung ' of the reactivity of carbonyl compounds through sulphur-containing reagents,[15] useful transformations *via* ketene *S,S*-dithioacetals were surveyed. Some specific transformations of ketene *S,S*-dithioacetals include oxidation and base hydrolysis,[16] and acid hydrolysis and displacement with aryl hydrazine.[17]

Although *S,S*-dialkyldithioacetals and bis(phenylthio)-ketenes are well documented in the literature no previous reports of mixed *S*-aryl-*S*′-methyldithioacetals were apparent. Attempted oxidation with hydrogen peroxide, potassium permanganate, or 3-chloroperbenzoic acid gave mixtures of products. The mixed aryl, alkyl dithioacetals were stable to trifluoroacetic acid. Acid hydrolysis of (6b) and (6e) in the presence of bromine gave the corresponding aryl disulphides (7b) and (7e). Reductive demethylthiolation using sodium borohydride–nickel chloride gave a mixture of *S*-aryl and *S*′-methyl reduced products. Raney nickel desulphurisation of (6b) gave biphenyl and 8-methyltetrahydroquinoline (8).

Experimental

^1H N.m.r. spectra (60 MHz) were recorded with a Varian EM 360L spectrometer using internal $SiMe_4$ as a standard. ^{13}C N.m.r. spectra (25 MHz) were recorded on a Jeol JNM-FX100 spectrometer. I.r. spectra were obtained using NaCl plates on a Perkin-Elmer 283 B spectrophotometer as solutions in $CHBr_3$. Mass spectral measurements were recorded on a AEI MS 30 spectrometer, with Kratos OS 55 data system. Melting points were recorded on a Kofler hot-stage apparatus and are uncorrected.

2,4-Diphenyl-5,6,7,8-tetrahydrochromenylium trifluoromethanesulphonate (31%), m.p. 182—184 °C (lit.,[9] m.p. 187 °C) was prepared using the literature procedure quoted.

General Procedures for Preparation of N-*Aryl*-2,4-*diphenyl*-5,6,7,8-*tetrahydroquinolinium Trifluoromethanesulphonates* (2). —*Procedure A*. The chromenylium salt (1.0 g, 2.3 mmol), arylamine (2.3 mmol), and triethylamine (0.23 g, 2.3 mmol), were treated in dichloromethane (50 ml) as previously described.[1] Compounds (2a, b, and c) were prepared in this manner.

Procedure B. The chromenylium salt (1.0 g, 2.3 mmol) was added portionwise to the molten arylamine (10 mmol) and the deep red solution heated at 100 °C in an oil-bath until the evolution of water vapour ceased (30—90 min.). The residue was triturated with ether (2 × 75 ml) to remove excess of arylamine. Crystallisation with water (25 ml) afforded the quinolinium salt as white prisms. Prepared in this manner were the following. N-(5-*Chloro*-2-*methylphenyl*)-2,4-*diphenyl*-5,6,7,8-*tetrahydroquinolinium trifluoromethanesulphonate* (2d), (90%), m.p. 162—164 °C after trituration with Et_2O (Found: C, 62.3; H, 4.5; N, 2.4. $C_{29}H_{25}ClF_3NO_3S$ requires C, 62.2; H, 4.5; N, 2.5%).

N-(3,4-*Dichlorophenyl*)-2,4-*diphenyl*-5,6,7,8-*tetrahydroquinolinium trifluoromethanesulphonate* (2e) (76%), m.p. 160—162 °C after trituration with Et_2O (Found: C, 58.0; H, 3.8; N, 2.4. $C_{28}H_{22}Cl_2F_3NO_3S$ requires C, 57.9; H, 3.8; N, 2.4%).

General Procedure for Preparation of N-*Aryl*-2,4-*diphenyl*-1,5,6,7-*tetrahydroquinolines* (3).—The quinolinium salt (2.3

mmol) in absolute ethanol (50 ml) was treated with 99% sodium hydride (0.11 g, 4.6 mmol) as previously described.[1] Novel tetrahydroquinolines prepared in this manner were as follows. N-(*5-Chloro-2-methylphenyl*)-2,4-*diphenyl*-1,5,6,7-*tetrahydroquinoline* (3d) (86%), m.p. 144—146 °C after trituration with EtOH (Found: C, 81.9; H, 5.9; N, 3.4. $C_{28}H_{24}ClN$ requires C, 82.1; H, 5.9; N, 3.4%); δ([$^2H_5$]pyridine) 7.6—7.0 (13 H, m), 5.4 (1 H, s), 3.8 (1 H, t, *J* 5 Hz), 2.5 (2 H, t, *J* 6 Hz), 2.3 (3 H, s), 2.1 (2 H, m), and 1.5 (2 H, m).

N-(3,4-*Dichlorophenyl*)-2,4-*diphenyl*-1,5,6,7-*tetrahydroquinoline* (3e) (67%), m.p. 119—121 °C after trituration with EtOH (Found: C, 75.2; H, 5.0; N, 3.2. $C_{27}H_{21}Cl_2N$ requires C, 75.3; H, 4.9; N, 3.3%); δ($CDCl_3$) 7.5—6.8 (13 H, m), 5.3 (1 H, s), 3.9 (1 H, t, *J* 5 Hz), 2.5 (2 H, t, *J* 6 Hz), 2.1 (2 H, m), and 1.6 (2 H, m).

General Procedure for Preparation of 8-[(*Methylthio*)*thiocarbonyl*]-N-*aryl*-2,4-*diphenyl*-5,6,7,8-*tetrahydroquinolinium Iodides* (4).—The enamine (4 mmol) was added portionwise to carbon disulphide (30 ml) at −10 °C with stirring. The mixture was allowed to warm to 0 °C to ensure complete reaction (30 min). Methyl iodide (0.62 g, 4.4 mmol) was added dropwise at −10 °C and the mixture stirred for 2 h, whilst warming to room temperature. The solvent was removed under reduced pressure (15 mmHg) and the residue washed with ether to afford yellow prisms (Table 1).

General Procedure for Preparation of 8-[(*Methylthio*)*thiocarbonyl*]-1-*aryl*-2,4-*diphenyl*-1,5,6,7-*tetrahydroquinolines* (5).—The quinolinium iodide (3 mmol) suspended in absolute ethanol (50 ml) was treated dropwise with a solution of sodium ethoxide (4.5 mmol) in absolute ethanol (5 ml). After the mixture had been stirred for 30 min any insoluble material was filtered off and the solvent removed under reduced pressure (15 mmHg). The residue was washed with water (2 × 25 ml) and dried *in vacuo* (0.5 mmHg) over phosphorus pentoxide (Table 3).

General Procedure for Preparation of 8-[*Arylthio*(*methylthio*)*methylene*]-2,4-*diphenyl*-5,6,7,8-*tetrahydroquinolines* (6).—The tetrahydroquinoline (1 mmol) was refluxed in either dimethylformamide (procedure A) or toluene (procedure B) until completion of reaction as indicated by t.l.c. (silica gel, EtOAc). The solvent was removed under reduced pressure (1 and 15 mmHg respectively) and the residue crystallised from methanol. Times of reaction and yields are given in Table 5. The material insoluble in ethanol from the preparation of compounds (5a, b, and d) was characterised as the corresponding bisthiomethyl salts.

8-[*Bis*(*thiomethyl*)*methylene*]-1-(4-*chlorophenyl*)-2-,4-*diphenyl*-5,6,7,8-*tetrahydroquinolinium iodide* (9a) (12%); yellow prisms from MeCN, m.p. 241—243 °C (Found: C, 57.25; H, 4.3; N, 2.2. $C_{30}H_{27}ClINS_2$ requires C, 57.37; H, 4.30; N, 2.23%), δ($CDCl_3$) 8.4 (1 H, m), 7.9—7.0 (14 H, m), 3.0 (4 H, m), 2.4 (2 H, m), and 2.1 and 1.9 (both 3 H, s).

1-*Biphenyl*-4-*yl*-8-[*bis*(*thiomethyl*)*methylene*]-2,4-*diphenyl*-5,6,7,8-*tetrahydroquinolinium iodide* (9b) (5%); yellow prisms from MeCN, m.p. 245—247 °C (Found: C, 64.5; H, 4.8; N, 2.1. $C_{36}H_{32}INS_2$ requires C, 64.6; H, 4.8; N, 2.1%), δ($CDCl_3$) 8.6 (1 H, m), 7.9—7.0 (19 H, m), 3.2 (4 H, m), 2.3 (2 H, m), and 2.1 and 1.8 (both 3 H, s).

8-[*Bis*(*thiomethyl*)*methylene*]-1-(5-*chloro*-2-*methylphenyl*)-2,4-*diphenyl*-5,6,7,8-*tetrahydroquinolinium iodide* (9d) (7%); yellow prisms from EtOH, m.p. 169—171 °C (Found: C, 57.7; H, 4.5; N, 2.1. $C_{31}H_{29}ClINS_2$ requires C, 57.9; H, 4.5; N, 2.2%); δ($CDCl_3$) 8.4 (1 H, s), 7.7—7.0 (13 H, m), 3.2 (4 H, m), 2.2 (2 H, m), and 2.3, 2.1, and 1.7, all three 3 H, s).

Bis(*biphenyl*-4-*yl*) *Disulphide* (7b).—The 8-[biphenyl-4-ylthio(methylthio)methylene]-2,4-diphenyl-5,6,7,8-tetrahydroquinoline (6b) (0.5 g, 1 mmol) in acetic acid (5 ml) was treated with 15% HCl (1 ml) and heated to 50 °C. Bromine in acetic acid (1.6 g of 20% solution) was added dropwise and the mixture heated 1 h on a steam-bath. After storage overnight at room temperature, the mixture was filtered to give the *disulphide* (0.11 g, 62%); white prisms from MeCN, m.p. 147—148 °C (lit.,[18] m.p. 128—130 °C) (Found: C, 77.6; H, 4.9; S, 17.2. $C_{24}H_{18}S_2$ requires C, 77.8; H, 4.9; S, 17.3%).

Bis(3,4-*dichlorophenyl*) *Disulphide* (7e).—The 3,4-dichlorophenyl analogue (6e) (0.25 g, 0.5 mmol) was treated as described above. Filtration gave the disulphide (0.035 g, 39%); white prisms from Et_2O, m.p. 83—85 °C (lit.,[19] m.p. 87—89 °C).

8-*Methyl*-2,4-*diphenyl*-5,6,7,8-*tetrahydroquinoline* (8).—The 8-[biphenyl-4-ylthio(methylthio)methylene]-2,4-diphenyl-5,6,7,8-tetrahydroquinoline (6b) (0.5 g, 1 mmol) in absolute ethanol (30 ml) was added to a suspension of Raney nickel (excess) in absolute ethanol (30 ml). The suspension was stirred under reflux for 14 h, filtered, concentrated under reduced pressure (15 mmHg) and the residue dissolved in Et_2O. Trifluoromethanesulphonic acid (0.3 g, 2 mmol) precipitated the 8-*methylquinolinium salt* (0.26 g, 58%); white prisms from trituration with ether, m.p. 115—117 °C (Found: *m*/*z* 299.1662. Calc. for $C_{22}H_{21}N$: *m*/*z* 299.1674), δ($CDCl_3$) 8.2 (2 H, m), 7.3—7.7 (9 H, m), 3.2 (1 H, m), 2.6 (2 H, t, *J* 5 Hz), 1.8 (4 H, m), and 1.5 (3 H, d, *J* 8 Hz).

The ether filtrate was evaporated under reduced pressure (15 mm Hg) and the residue sublimed at 120 °C (15 mmHg) for 1 h to give biphenyl (0.05 g, 32%), m.p. 65—67 °C (lit.,[20] m.p. 72 °C), δ($CDCl_3$) 7.8—7.4 (10 H, m).

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