

Stereochemistry of Sulphur Organic Compounds. Part 11.† A Conformational Study of Some 2-Thio-derivatives of *N*-Phenyl-1-phenylethylamine

Ernesto Brunet, M. Carmen Carreño, M. Teresa Gallego, and José L. García Ruano*

Departamento de Química Orgánica, Fac. Ciencias, Universidad Autónoma de Madrid, Madrid 34, Spain

Felipe Alcludia

Departamento de Química Orgánica, Fac. Farmacia, Universidad de Sevilla, Spain

The syntheses and a conformational study of *N*-phenyl-2-*Y*-1-phenylethylamine [*Y* = SCH₃, SOCH₃ (two diastereoisomers), SO₂CH₃, and ⁺S(CH₃)₂] are reported. Conformational preferences have been established from changes in the vicinal coupling constants induced by protonation at the amine nitrogen. This determines the electrostatic character of the interactions between the two heteroatoms functions. In addition, the configurational assignment for diastereoisomeric sulfoxides is also reported.

The conformational analysis of several series of acyclic compounds with oxygen and sulphur functions at adjacent carbons has been previously reported.^{1,2} In addition to steric effects, these studies indicated that electrostatic interactions and intramolecular hydrogen bonding determined the population of the different rotamers in the conformational equilibria.

Our present interest is to study the conformational preferences of a series of acyclic β-nitrogenated thio-derivatives, in order to understand the influence of sulphur–nitrogen interactions upon conformational stability. Nitrogenated functions are available with a positive or negative charge density on the heteroatom. This fact implies that β-nitrogenated thio-derivatives can be better models than the oxygenated ones to study the role of electrostatic interactions between the heteroatoms. In the present paper, the syntheses and conformational analysis of *N*-phenyl-2-thio-derivatives of 1-phenylethylamine (1)–(4) are reported. An additional point of interest in this series is that the amine nitrogen can be easily protonated. The change in the sign of charge density on the nitrogen may induce significant variations in the conformational equilibria.

Results and Discussion

The synthesis of compound (2) was achieved by condensation of *N*-phenylbenzylideneamine with sodium dimethylsulphanyl carbanion, generated by the reaction of dry DMSO with NaH.³ This reaction yielded a 1 : 1 mixture of diastereoisomers (2α + 2β) ‡ which were separated by crystallization. The highest m.p. isomer was designated as (2α). The sulphide (1) was obtained by reduction of (2) with Ph₃P–CCl₄. Reaction of (1) with methyl toluene-*p*-sulphonate yielded the sulphonium salt (4). The oxidation of compound (1) with sodium metaperiodate did not affect the nitrogen function but yielded sulphoxide (2) as a 1 : 1 mixture of diastereoisomers. Attempts to obtain sulphone (3) by oxidation of (1) or (2) with excess of sodium metaperiodate were unsuccessful. This compound was obtained by condensation of *N*-phenylbenzylideneamine with sodium dimethylsulphonyl carbanion, generated from dimethyl sulphone and NaH in DMSO as solvent. This reaction yielded a mixture of sulphoxide (2) and sulphone (3), separated by chromatography.

The staggered rotamers of compounds (1)–(4) are given in

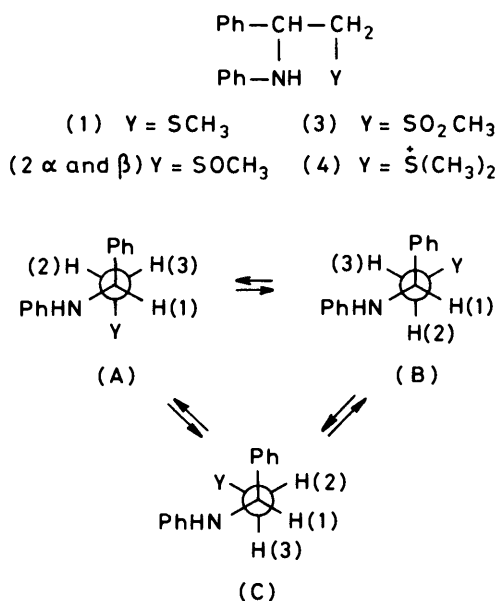


Figure 1. Rotamers around the C–C bond in compounds (1)–(4)

Figure 1. The conformation of the carbon skeleton is approximated from the relative values of the n.m.r. vicinal coupling constants $J_{1,2}$ and $J_{1,3}$. Large differences between them are indicative of a marked preference for conformations (A) or (B), whereas similar values reveal weighted means of the above rotamers. On the other hand, the increase of population of conformation (C) in the equilibrium will decrease $J_{1,2}$, $J_{1,3}$, and therefore $(J_{1,2} + J_{1,3})$.

In order to establish the preferred conformation it is necessary to assign H(2) and H(3) unequivocally in the ¹H n.m.r. spectra. In related β-hydroxylated thio-derivatives^{2,4,5} this assignment was carried out by use of the long-range coupling constants between the methylene and hydroxylic protons. In compounds (1)–(4) no long range coupling constant was observed. In similar cases^{6,7} we predicted first the favoured conformations on the basis of the existing interactions in every rotamer and so we assigned H(2) and H(3). Afterwards, it was necessary to check this assignment with the experimental results.

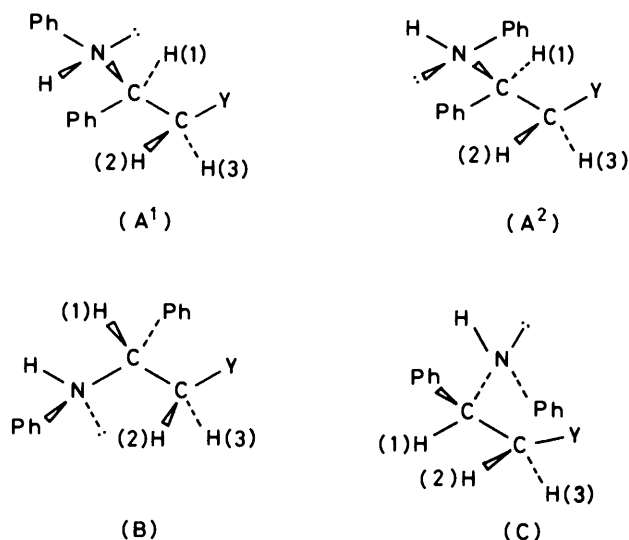
From steric factors, Figure 1 suggested that conformation (A) would be the most stable. Nevertheless, the spatial arrangement of the substituents around the CH–NH bond

† Part 10, F. Alcludia, C. Carreño, J. L. García Ruano, and P. Prados, *An. Quim.*, in the press.

‡ The diastereoisomer ratio was established from the methyl signals in the ¹H n.m.r. spectra of the reaction mixtures.

Table 1. ¹H N.m.r. parameters of compounds (1)–(4)

Compound	Solvent	Concentration (% w : v)	Chemical shift (δ)				Coupling constants (J/Hz)		
			H(1)	H(2)	H(3)	CH ₃ -S	J _{1,2}	J _{1,3}	J _{2,3}
(1)	CDCl ₃	20	4.39	2.92	2.75	1.96	4.68	8.90	-13.55
		10	4.41	2.96	2.79	2.01	4.65	8.95	-13.68
	[² H ₆]DMSO CF ₃ CO ₂ H	5	4.42	2.98	2.81	1.98	4.52	8.97	-13.68
		5	4.51	2.79	2.93	2.04	5.79	8.04	-13.27
		5	4.73	3.42	3.29	2.26	9.66	5.24	-15.00
(2α)	CDCl ₃	2	5.02	3.15	3.00	2.59	8.86	3.08	-13.34
	[² H ₆]DMSO	2	4.84	3.16	2.96	2.59	11.47	3.04	-13.04
	CF ₃ CO ₂ H	2	5.43	3.83	4.29	3.01	7.90	4.82	-14.88
(2β)	CDCl ₃	1	4.90	3.18	2.93	2.77	9.22	5.47	-13.27
	[² H ₆]DMSO	1	4.79	3.23	3.10	2.62	7.81	7.10	-12.83
	CF ₃ CO ₂ H	1	5.36	4.24	3.90	3.09	7.18	7.08	-13.61
(3)	CDCl ₃	1	5.01	3.49	3.39	2.79	8.70	4.27	-14.31
	[² H ₆]DMSO	1	4.96	3.70	3.38	3.00	9.47	3.80	-14.49
	CF ₃ CO ₂ H	1	5.40	4.48	4.22	3.00	8.10	5.56	-14.75
CF ₃ CO ₂ H-(3) ^a	CDCl ₃		5.06	4.70	3.71	3.08	9.76	3.64	-14.74
(4)	CDCl ₃	2	4.75	4.30	3.77	2.88	11.03	3.78	-12.52
	CDCl ₃ -[² H ₆]DMSO (4 : 3)		4.95	3.95	3.79	2.98	10.70	3.78	-12.61
	CF ₃ CO ₂ H	2	5.30	4.58	4.71	3.05–2.68	4.20	11.22	-12.97

^a CF₃CO₂H : (3) molar ratio = 3.**Figure 2.** Significant rotamers of *N*-phenyl-2-*Y*-1-phenylethylamine [Y = SCH₃, SOCH₃, SO₂CH₃, and S⁺(CH₃)₂]

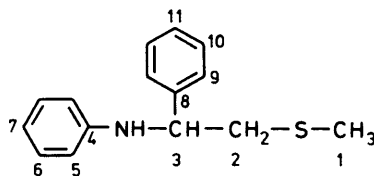
produces large variations in the stability of rotamers. As it can be seen from Figure 2, conformation A¹ has a (Ph-Ph)_{1,2-g} interaction, in addition to (PhNH-Y)_{1,2-g} shown in Figure 1, whereas conformation A² exhibits (Ph-Y)_{1,3-p}. This interaction probably makes the (A²) rotamer less stable than (A¹). On the other hand, conformations (B) and (C) have (Ph-H)_{1,3-p} in addition to those observed in Figure 1. According to this, on steric grounds, the population of (B) could be higher than that of (A). However polar factors may stabilize the (NH-Y)_{1,2-g} interaction and invert the conformational preference. Thus the different steric and electrostatic interactions for every compound have to be considered.

The ¹H n.m.r. parameters of compounds (1)–(4) are given

in Table 1. The analysis of the spectra were carried out using the LAOCOON-III program.^{8,9} Coupling constants of the sulphide (1) in CDCl₃ indicated that there exists a conformational preference for rotamers (A) or (B). Two opposed interactions may be operative in rotamer (A). (i) The destabilizing (NH-SCH₃)_{1,2-g} interaction, due to the unshared electron pairs of both heteroatoms¹⁰ or to the electrostatic repulsion between them and (ii) the stabilizing intramolecular hydrogen bonding (NH ··· S). Table 1 shows that there is little influence of the concentration on the coupling constant in CDCl₃. On the other hand, when the solvent polarity increased (increasing the DMSO-CDCl₃ ratio) the preference of the initially favoured rotamer slightly decreased [(J_{1,2} - J_{1,3}) diminishes whereas (J_{1,2} + J_{1,3}) remains constant].* Both factors suggested that polar effects (electrostatic and hydrogen bonding interactions) scarcely influenced the conformational equilibrium. Therefore, steric effects must be the determining factor for rotamer stability. This suggests a preference for rotamer (B). However a definitive assignment could not yet be made.

Protonation at the nitrogen must increase the stability of rotamer (A) with respect to (B), because of the stabilizing electrostatic (N⁺-SCH₃)_{1,2-g} interactions. Thus, the study of protonated compounds can shed new light on conformational preferences. Due to the existence of two basic centres in compound (1) (S and N) it was necessary to ascertain the protonation site. ¹³C Chemical shifts of compounds (1)–(4) in CDCl₃ in different conditions (the molar ratios CF₃CO₂H: compound are indicated) are collected in Table 2. The chemical shifts for C-1 remained almost unchanged whereas carbons directly bonded to nitrogen (C-3 and C-4) and those in

* The assignment of protons when the solvent is changed was made by correlations using CDCl₃-DMSO mixtures of increasing polarity and different CF₃CO₂H : substrate molar ratios in CDCl₃. The resulting parameters, omitted from Table 1 are available as Supplementary Publication, No. SUP 23580 (4 pp.) (see *J. Chem. Soc., Perkin Trans. 2*, 1983, xvii for details).

Table 2. ¹³C Chemical shifts in compounds (1)–(4) (in CDCl₃)

Compound	Molar ratio	Chemical shift (δ)										
		C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11
(1)		15.4	42.5	56.4	147.2	113.7	128.9	117.7	142.6	126.2	128.6	127.3
CF ₃ CO ₂ H : (1)	1.61	15.8	36.9	66.3	135.5	122.2	129.5	127.7	133.7	128.3	128.8	129.5
(2 α)		38.7	61.7	54.1	146.2	113.7	128.9	117.8	141.0	126.2	128.9	127.6
CF ₃ CO ₂ H : (2 α)	1.55	37.5	57.4	57.4	140.2	118.3	119.4	123.5	136.3	127.2	129.1	129.1
(2 β)		39.6	61.8	56.2	146.4	114.0	129.0	118.1	141.7	126.1	129.0	127.9
CF ₃ CO ₂ H : (2 β)	1.48	38.4	56.1	61.3	140.7	120.2	129.3	125.9	134.3	127.8	129.0	129.8
(3)		42.0	61.1	54.3	146.1	114.4	129.4	118.9	140.4	126.4	129.4	128.4
CF ₃ CO ₂ H : (3)	1.45	42.2	58.0	58.9	139.2	119.3	129.8	124.9	135.3	127.7	129.5	129.8
(4)		24.0	50.0	53.4	146.1	114.4	129.0	118.4	139.1			
		(25.8) ^a										
CF ₃ CO ₂ H : (4)	5	26.1	45.9	62.6	133.4	122.7	130.0	128.8	131.1			
		(26.0) ^a										

^a Methyl groups appear at different field.

'ortho' and 'para' positions with respect to it (C-5 and C-7) in the phenylamine ring experienced a substantial modification. It allowed us to conclude that protonation by CF₃CO₂H mainly occurred at nitrogen and not at the sulphur function in all studied cases. In addition, $\Delta\delta$ induced by CF₃CO₂H in C-2 can be also attributed to protonation at nitrogen rather than at the sulphur function, because similar variations are observed for C-8.

The favoured rotamer for compound (1) in CF₃CO₂H (see Table 1) is different to that in CDCl₃ [the observed variations in J_{vic} from the spectra of mixtures CF₃CO₂H : (1) at different molar ratios, indicated a progressive inversion of the conformational preference as the CF₃CO₂H proportion was increased]. It could not be attributed to changes in medium polarity according to the results above mentioned in CDCl₃-[²H₆]DMSO mixtures. Therefore, as protonation at nitrogen produced a relative stabilization of rotamer (A), its participation in the equilibrium might be larger as the CF₃CO₂H : (1) molar ratio was increased. Thus, it can be assumed that (B) was the favoured conformation of (1) in CDCl₃. Now we can explain the slight differences in coupling constants as the medium polarity was increased (see values in [²H₆]DMSO) on the basis of a decrease of the repulsive (NH-SCH₃)_{1,2-g} electrostatic interaction, which destabilized conformation (A) in CDCl₃.

From Table 1 it can be seen that compound (4) in CDCl₃ shows a marked conformational preference, as indicated by the observed high ($J_{1,2} - J_{1,3}$) value, the later being hardly affected by an increase of the medium polarity. Protonation at nitrogen (see Table 1) determines an inversion of conformational preference as can be deduced from the observed changes in $J_{1,2}$ and $J_{1,3}$. These changes can be explained by taking into account the fact that protonation must generate an [⁺N/S(CH₃)₂]_{1,2-g} interaction which would destabilize conformation (A) with respect to (B). Therefore, it can be concluded that the observed changes in conformational preference are only compatible with the predominance of rotamer (A) in CDCl₃ and a gradually increasing preference for (B) as the CF₃CO₂H proportion increased.

In the diastereoisomeric sulphoxides (2 α and β) the sulphur atom bears a positive charge density, being able to interact

favourably with the amine nitrogen. In addition, an intramolecular hydrogen bond, N-H...O-S, can be formed. Both considerations suggested that the (NH-SOCH₃)_{1,2-g} interaction was stabilizing and so it was reasonable to accept that the different $J_{1,2}$ and $J_{1,3}$ values observed in CDCl₃ were due to a predominance of rotamer (A) in the equilibrium for both diastereoisomers. Besides this assumption, which will be demonstrated later, the distinct behaviour shown when the solvent was changed from CDCl₃ to [²H₆]DMSO must be undoubtedly attributed to the different configuration of the chiral centres for each diastereoisomer.^{11,12}

From Table 1 the following facts can be discovered. Isomer (2 β) displays a larger ($J_{1,2} + J_{1,3}$) value than (2 α) in CDCl₃, i.e., participation of (C) in the equilibrium was lower for (2 β) than for (2 α). (ii) When the solvent polarity was increased, the sum ($J_{1,2} + J_{1,3}$) is almost invariant for isomer (2 β), whereas it was increased for isomer (2 α), i.e., participation of (C) in the equilibrium was hardly affected for isomer (2 β) but diminished for (2 α) as the polarity was increased.

These features made possible an attempt at configurational assignment on the basis of the most significant conformations for both diastereoisomers (Figure 3). The existence of a destabilizing (Ph-CH₃)_{1,3-p} interaction* in conformation (C) would determine its low or zero participation in the conformational equilibrium for the (RS,SR) isomer in any solvent. However, the absence of such interaction in (C') made it possible for this rotamer to be considered in the equilibrium for the (RR,SS) isomer in CDCl₃ solution. Therefore, the (RS,SR) diastereoisomer would exhibit a larger ($J_{1,2} + J_{1,3}$) value than that for (RR,SS) in CDCl₃. On the other hand, loss of intramolecular hydrogen bonding in [²H₆]DMSO must lower the participation of (C') in this solvent because of the resulting (O-NHPh)_{1,3-p} interaction, and so the ($J_{1,2} + J_{1,3}$) value would increase in [²H₆]DMSO for the (RR,SS) isomer. These considerations would agree with the experimental results shown in Table 1 if compound (2 α) is assigned to configuration (RR,SS) and compound (2 β) to configuration (RS,SR).

* This interaction has been estimated to be 17 kJ mol⁻¹ in compounds with a carbon skeleton.¹³

higher participation of the favoured rotamer, which decreases when $\text{CF}_3\text{CO}_2\text{H}$ is used as solvent.

The slight differences observed in the coupling constants of compound (3) under different conditions did not allow the unequivocal assignment of the favoured rotamer nor an understanding of the conformational changes. However, since (A) is the predominant rotamer in (2α and β), this preference has to be maintained in sulphone (3). This conclusion can be justified by observing the stability changes introduced by the substitution of the sulphur unshared electron pair by an oxygen atom (see Figure 3). The transformation of sulphoxide (2α) in sulphone (3) would destabilize (B) [(O-Ph)_{1,3-p} interaction] more than (A) [(O-H)_{1,3-p} in (A₁) and (O-NH)_{1,3-p} in (A₂)]. Thus, the latter has still to be predominant. On the other hand, rotamer (C) of (3) ought to be slightly more stable than that of (2β) [it has a (Ph-O)_{1,3-p} interaction instead of a (Ph-CH₃)_{1,3-p} one] which could explain why ($J_{1,2} + J_{1,3}$) in CDCl_3 is lower for (3) [higher participation of (C)] than for (2β).

It was difficult to explain the increased proportion of (A) when the medium becomes more polar (see values in [$^2\text{H}_6$]DMSO), since it was not accompanied, as for (2α), by a decrease in the participation of (C). On the contrary, it changes very little as indicated by the slight variation of ($J_{1,2} + J_{1,3}$).

N-Protonation of the sulphoxides and sulphone (see Table 2), induced by the addition of $\text{CF}_3\text{CO}_2\text{H}$, introduces an electrostatic stabilizing interaction in rotamer (A) [(N⁺-O⁻)_{1,3-p}, see before]. This fact could explain the increasing preference of rotamer (A), when the molar ratio $\text{CF}_3\text{CO}_2\text{H}$: (3) was increased. The lower values of ($J_{1,2} - J_{1,3}$) observed in neat $\text{CF}_3\text{CO}_2\text{H}$ may be due to the increase in medium polarity.

The arguments in this paper rest on the assumption that the vicinal coupling constants, $J_{1,2}$ and $J_{1,3}$, vary only with the dihedral angle in the CH-CH₂ system. However, it is well known that among other factors electronegativity contributes to coupling constants but with an effect much smaller than that resulting from the stereochemistry of the protons involved.

An extreme situation emerges when the coupling constants of the amines in CDCl_3 were compared with those of the protonated derivatives in $\text{CF}_3\text{CO}_2\text{H}$. The question is whether the effect on J_{vic} of the electronegativity change, induced by protonation, could substantially modify our conclusions based only on stereochemical grounds. As the observed variations reach ± 7 Hz in some cases the answer must be negative. In order to confirm this, we evaluated the vicinal constants for every possible rotamer of Figure 1 using the equation generalized by Altona *et al.*,¹⁴ which takes into account the electronegativity as well as the orientation of the substituents attached to a CH-CH₂ fragment. The NH electronegativity (obviously larger than that for nitrogen) was calculated from models using Muller's equation¹⁵ and the value, extrapolated to Higgins' scale, was lower than 3.30 units (the value for nitrogen is 3.00).

The differences between the calculated J_{vic} from the aforementioned values of 3.00 and 3.30, never became larger than 0.4 Hz. Furthermore, the molar fractions of the different rotamers evaluated from the calculated and experimental J_{vic} values, were only modified by *ca.* 3% at a maximum if the differences in electronegativity between NH and N were considered. These results suggested to us that the introduction of substituent electronegativity would not add to a qualitative discussion of the shift of conformational equilibria induced by protonation.

The main conclusions from this work are as follows.

(1) Polar interactions between the sulphur functions and the amine nitrogen are similar to those observed previously between hydroxy-oxygen and sulphur functions. These interactions are stabilized when the sulphur atom has a positive charge density, as in the case of sulphoxide, sulphone, and sulphonium salt.

(2) The electrostatic interactions between NH and the S-O group in sulphoxides and sulphones depends on the relative spatial arrangement of these atoms and contributes to the differentiation of the behaviour of both diastereoisomeric sulphoxides.

(3) The easy protonation of the amine nitrogen generates strong electrostatic interactions with the sulphur functions which can substantially modify the conformational behaviour of these systems. The possibility of controlling the extent of protonation should allow control of the conformational populations. This fact may be useful for the study of other systems of wide biological interest with different heteroatoms in the N-C-C-X grouping.¹⁶

Experimental

M.p.s are uncorrected. ¹H N.m.r. spectra were recorded on a 100 MHz Varian XL-100-15 spectrometer by the Fourier transform technique using 16 K of core in a Nicolet 1180 stored program computer. The signal of the deuteriated solvent was employed as the deuterium field frequency lock with tetramethylsilane as internal reference. Analysis of the spectra were carried out using the LAOCOON III program on a Nicolet 1180 computer. We estimate the reliability of all values as ± 0.1 Hz and the root mean square deviations for the calculated and the experimental lines were usually better than 0.05 Hz. I.r. spectra were recorded on a Pye-Unicam SP 1100 spectrometer. Mass spectra were obtained on a Hitachi-Perkin-Elmer RMU-6MG spectrometer. Column chromatography was performed on silica gel 60 (60—230 mesh; Merck).

N-Phenyl-2-methylsulphinyl-1-phenylethylamine (2).—This compound was obtained as a 1 : 1 mixture of diastereoisomers ($2\alpha + \beta$), following the procedure reported by Corey.³ Isolation of (2α) was carried out by repeated recrystallization from ethyl acetate, m.p. 173—175° (Found: C, 69.45; H, 6.6; N, 5.65. $\text{C}_{15}\text{H}_{17}\text{NOS}$ requires C, 69.45; H, 6.6; N, 5.4%; ν_{max} (Nujol) 3 340, 1 605, 1 530, 1 500, 1 020, 795, 755, 750, and 700 cm^{-1} ; $\delta(\text{CDCl}_3)$ 2.60 (s, CH_3SO), 2.89—3.40 (m, CH_2SO), 4.96—5.20 (m, CHN and NH), and 6.54—7.46 (m, $\text{C}_6\text{H}_5\text{N}$ and $\text{C}_6\text{H}_5\text{C}$). The mother liquors contained the isomer (2β), which was purified by recrystallization from benzene, m.p. 122—124° (Found: C, 69.45; H, 6.8; N, 5.35%; ν_{max} (Nujol) 3 325, 1 610, 1 530, 1 505, 1 035, 755, and 700 cm^{-1} ; $\delta(\text{CDCl}_3)$ 2.82 (s, CH_3SO), 3.08—3.58 (m, CH_2SO), 4.86br (s, NH), 5.06—5.20 (m, CHN), and 6.76—7.66 (m, $\text{C}_6\text{H}_5\text{N}$ and $\text{C}_6\text{H}_5\text{C}$).

N-Phenyl-2-methylthio-1-phenylethylamine (1).—A solution of *N*-phenyl-2-methylsulphinyl-1-phenylethylamine (0.5 g, 2.0 mmol) and triphenylphosphine (0.99 g, 3.7 mmol) in CCl_4 (20 ml) was refluxed for 30 min. The solution was concentrated to dryness and the resulting material was chromatographed (benzene-ethyl acetate 1 : 1) to yield compound (1) (0.36 g, 72%) as an oil, ν_{max} (liquid film) 3 425, 1 605, 1 505, 750, 740, 700, and 695 cm^{-1} ; $\delta(\text{CDCl}_3)$ 1.98 (s, CH_3S), 2.62—3.04 (m, CH_2S), 4.32—4.46 (m, CHN), 4.68br (s, NH), and 6.46—7.38 (m, $\text{C}_6\text{H}_5\text{C}$ and $\text{C}_6\text{H}_5\text{N}$); *m/e* 243 (2%), 195 (4), 183 (20), 182 (100), 104 (19), 91 (6), and 77 (36).

Oxidation of N-Phenyl-2-methylthio-1-phenylethylamine.—A solution of (1) (0.36 g, 1.5 mmol) and sodium metaperiodate (0.32 g, 1.5 mmol) in water (50 ml) was stirred at 0° for 4 h and then allowed to stand overnight at room temperature. The solution was extracted with chloroform, dried (MgSO₄), and evaporated to dryness, giving a 1 : 1 mixture of (2 α and β) (0.18 g, 47%).

N-Phenyl-2-methylsulphonyl-1-phenylethylamine (3).—A solution of dimethyl sulphone (4.3 g, 45.7 mmol) in dimethyl sulphoxide (20 ml) was slowly added to sodium hydride (0.55 g, 22.9 mmol) under nitrogen. The mixture was stirred for 45 min at 70° and diluted with tetrahydrofuran (20 ml). A solution of *N*-phenylbenzylideneamine (2.07 g, 11.4 mmol) in tetrahydrofuran (10 ml) was added to the resulting suspension at 0°. The mixture was stirred for 30 min at room temperature, hydrolysed with ice-water (150 ml), and allowed to stand overnight. The filtered solid was a 1 : 1 mixture of (2) and (3). Separation by chromatography (benzene-ethyl acetate 1 : 1) yielded *N*-phenyl-2-methylsulphonyl-1-phenylethylamine (3) (1.3 g, 10%) which was recrystallized from benzene, m.p. 145–147° (Found: C, 65.5; H, 6.1; N, 5.3; S, 11.9. C₁₅H₁₇NO₂S requires C, 65.45; H, 6.2; N, 5.1; S, 11.6%); ν_{\max} (Nujol) 3 410, 1 605, 1 525, 1 505, 1 300, 1 130, 790, 750, 705, and 695 cm⁻¹; δ (CDCl₃) 2.74 (s, CH₃SO₂), 3.48 (m, CH₂SO₂), 4.74 (m, NH), 5.02 (m, CHC), and 6.58–7.48 (m, C₆H₅N and C₆H₅C); *m/e* 277 (2.5%), 276 (7.5, M⁺) 275 (29.4), 196 (3.7), 183 (19.3), 182 (100), 105 (5.8), 104 (45), 93 (13.7), and 77 (27.0).

2-Phenylamino-2-phenylethyl(dimethyl)sulphonium (4). *Toluene-p-sulphonate.*—A mixture of *N*-phenyl-2-methylthio-1-phenylethylamine (1 g, 4.1 mmol) and methyl toluene-*p*-sulphonate (0.76 g, 4.9 mmol) was stirred overnight at 60°. CH₂Cl₂ (15 ml) was then added and the resulting solid filtered. Recrystallization from CH₂Cl₂ afforded the *toluene-p-sulphonate salt* (4) (0.5 g, 30%), m.p. 83–85° (Found: C, 61.75; H 6.5; N, 3.15. C₂₃H₂₇NO₃S₂·H₂O requires C, 61.7; H, 6.55;

N, 3.1%); ν_{\max} (Nujol) 3 340, 1 605, 1 495, 1 190, 1 120, 1 030, 1 010, 810, 750, 720, 690, and 680 cm⁻¹; δ (DMSO) 2.25 (s, CH₃Ph), 2.98 (s, CH₃S), 3.35 (s, NH), 3.62–3.84 (m, CH₂S), 4.90–5.20 (CHN), and 6.50–7.62 (m, C₆H₅N, C₆H₅C, and CC₆H₄S).

References

- 1 L. Cassidei, V. Fiandanese, G. Marchese, and O. Sciacovelli, *J. Chem. Soc., Perkin Trans. 2*, 1980, 1642.
- 2 F. Alcudia, J. L. García Ruano, J. H. Rodríguez, and F. Sánchez, *Can. J. Chem.*, 1979, **57**, 2426.
- 3 E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 1965, **87**, 1345.
- 4 F. Alcudia, F. Fariña, J. L. García Ruano, and F. Sánchez, *J. Chem. Soc., Perkin Trans. 2*, 1978, 412.
- 5 F. Alcudia, F. Fariña, J. L. García Ruano, J. H. Rodríguez, and F. Sánchez, *J. Chem. Soc., Perkin Trans. 2*, 1979, 564.
- 6 F. Alcudia, F. Fariña, J. L. García Ruano, J. H. Rodríguez, and F. Sánchez, *An. Quim.*, 1978, **74**, 482.
- 7 F. Alcudia, J. L. García Ruano, P. Prados, and J. H. Rodríguez, *An. Quim.*, in the press.
- 8 A. A. Bothner-By and S. M. Castellano, *J. Chem. Phys.*, 1964, **41**, 3863.
- 9 S. M. Castellano, 'LAOCN3 in Computer Programs for Chemistry,' ed. D. F. Detar, Benjamin, New York, 1968, vol. 1, p. 10.
- 10 N. S. Zefirov, *Tetrahedron*, 1977, **24**, 3193.
- 11 C. A. Kingsbury and R. A. Anerbach, *J. Org. Chem.*, 1971, **36**, 1737.
- 12 F. Alcudia, E. Brunet, J. L. García Ruano, J. H. Rodríguez, and F. Sánchez, *J. Chem. Res.*, 1982 (S) 284, (M) 2826.
- 13 M. Lasperas, A. P. Rubalcaba, and M. L. Quiroga, *Tetrahedron*, 1980, **36**, 3403.
- 14 C. A. G. Hassnoot, F. A. A. M. de Leeuw, and C. Altona, *Tetrahedron*, 1980, **36**, 2783.
- 15 J. C. Muller, *Bull. Soc. Chim. Fr.*, 1964, 1815.
- 16 'Burger's Medicinal Chemistry,' ed. M. E. Wolff, Wiley, New York, 1981, 4th edn., Part III, p. 487.

Received 2nd August 1982; Paper 2/1333