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Enantioselective Reactions of 2-Bromopropanamides with Primary, Secondary, or Tertiary Amines. Synthesis of some Alaninamides.

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Abstract: Enantiomeric 2-bromopropanamides react with primary, secondary, or tertiary aliphatic amines in toluene at room temperature, yielding the corresponding secondary or tertiary amino, or quaternary ammonium amide. If the reacting amines are good nucleophiles, either product is obtainable in high yield and e.e., by running the reaction either in the presence or absence of Ag_2O. With a less nucleophilic amine, Ag_2O or Ag^+ promotes the formation either of an optically active amine derivative, or a high diastereomeric excess of a dimeric derivative, whose structure was ascertained by X-ray analysis.

In the configurational alteration or modification of the amino group of a natural amino acid through the classic sequence of deamination-substitution (retention)-nucleophilic substitution of the resulting 2-haloacid (inversion), relatively few nucleophiles were used: among these, ammonia and methylamine have been widely reported.[1]

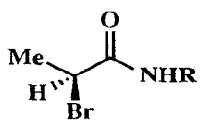
As a part of our continuing research on 2-haloamides, we have been studying the stereochemistry of reactions of (S)-2-bromopropanamides with amines, to obtain N,N'-substituted alaninamides. This appproach would provide a more general application than the alkylation of an aminoacid,[2] towards modified chiral aminoacids and their derivatives, as candidates for biological or other studies.

In preliminary tests, the two enantiomers of 2-aminoamide **2d** were obtained, under satisfactory enantioselectivity control, from (S)-N-benzyl-2-bromopropanamide **1b** and benzylamine, in the presence or absence of Ag_2O.[3]

In the present research, (S)-2-bromopropanamides (**1a-c**) have been allowed to react in toluene, at room temperature, with primary, secondary, or tertiary amines, either without a promoter, or in the presence of Ag_2O or Ag^+.

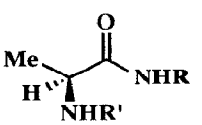
From (S)-2-bromo-N-phenylpropanamide (**1a**) and a primary or secondary amine endowed with good nucleophilic character,[4] the corresponding 2-alkylamino- or 2-dialkylamino-propanamide (**2a,b; 3a,b, Scheme**), were obtained with yields and optical activities as reported in **Table 1**, and the following approximate rate trend: pyrrolidine > benzylamine > diethylamine > t.buylamine. Conversely, when the same reacting systems were sonicated in the presence of an equimolecular amount of the insoluble promoter Ag_2O, each N,N'-substituted alaninamide was obtained faster (1-3h), with an optical rotation of the same magnitude, but of opposite sign. Our experiments and literature data (see further considerations below) suggest that the enantiomers arising either in the absence or presence of Ag_2O result from inversion or retention of configuration, respectively.

Scheme



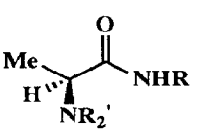
1

	R
a	Ph
b	CH_2Ph
c	tBu



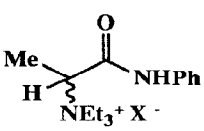
2

	R	R'
a	Ph	tBu
b	Ph	CH_2Ph
c	CH_2Ph	tBu
d	CH_2Ph	CH_2Ph
e	tBu	tBu
f	tBu	CH_2Ph



3

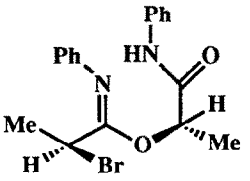
	R	R'
a	Ph	Et
b	Ph	$(CH_2)_4$
c	CH_2Ph	Et
d	tBu	Et
e	Ph	iPr



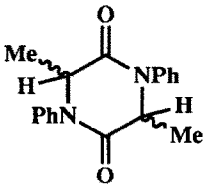
4

	X^-
a	$CF_3SO_3^-$
b	Br^-

Formulae **2**, **3** depict the (S)-configuration and formula **5** depicts the (S,S)-configuration assigned to the products obtained in the presence of Ag_2O.



5



6

Table 1. Reactions of (S)-(-)-2-bromo-N-phenylpropanamide (1a) [a]

Coreagents: mol per mol of **1a**			Time (h)	Product %	$[\alpha]_D^{20}$		Recov. **1a**	Dimeric
	Ag_2O	Ag^+			$CHCl_3$	EtOH	%	product (%)
$tBuNH_2$				**2a**				
5	-	-	50	92	+49			
2	1	-	2	86	-50			
$PhCH_2NH_2$				**2b**				
5	-	-	8	94	+9.3			
2	1	-	3	91	-9			
2	-	1	3	75	+9.2			
Et_2NH				**3a**				
5	-	-	10	86	-62	-28		
2	1	-	3	90	+59	+27		
2	-	1	1.5	94	-65			
$(CH_2)_4NH$				**3b**				
2-5	-	-	2 - 1.5	100	-0.8	-32		
2-5	1	-	1 - 0.7	95	+0.8	+31		
iPr_2NH				**3e**				
5		-	1320	-			100	
0	1	-	17	-			7	**5** (57)
5	1	-	2.5	72	+48.4			**5**(10)
2		1	65	6	+45	+30	42	**5** (8)
Et_3N								
5	-	-	900	-			100	
				4a				
2		1	180	75	-43			
				4b				
2	1		7.5	11[b]				

[a] G. Snatzke and M. M. El Abadelah, Chem. Ber., 1973, 106, 2072.

[b] The dioxopiperazines **6** and 2-hydroxypropananilide were also formed (See Exptl).

Table 2. Reactions of (S)-(-)-2-bromo-N-benzyl-propanamide (1b) [3]

Coreagents: mol per mol of **1b**			Time (h)	Product %	$[\alpha]_D^{20}$		Recov. **1b**
	Ag_2O	Ag^+			$CHCl_3$	EtOH	%
$tBuNH_2$				**2c**			
10	-	-	700	43	+8	+8	
2	1	-	3.5	87	-9.4		
$PhCH_2NH_2$				**2d**[a]			
2	-	-	72	90	+4.2		
2	1	-	2.5	94	-4.2		
2	-	1	10	90	+3.8		7
Et_2NH				**3c**			
2	-	-	12	96	-38.4		
2	1	-	4	100	+37.5		

[a] **2d** was previously obtained either in (R)- or (S)- form, in ethyl ether.[3] In the present reaction with Ag_2O, sonication shortened the reaction time.

Table 3. Reactions of (S)-(-)-2-bromo-N-t.butyl-propanamide (1c) [b]

Coreagents: mol per mol of **1c**			Time (h)	Product %	$[\alpha]_D^{20}$		Recov. **1c**
	Ag_2O	Ag^+			$CHCl_3$	EtOH	% (e.e.)
$tBuNH_2$				**2e**			
10	-	-	100	<10			
2	1	-	4.5	91	-26.5	-26	
2	-	1	700	53	+20.5		41
$PhCH_2NH_2$				**2f**			
2	-	-	40	87	+3.6	-7	
2	1	-	16	90	-3.8	+7	
2	-	1	30	65	+3,8		29 (98)
Et_2NH				**3d**			
2	-	-	80	96	-62,8		
2	1	-	12	95	+62,7		

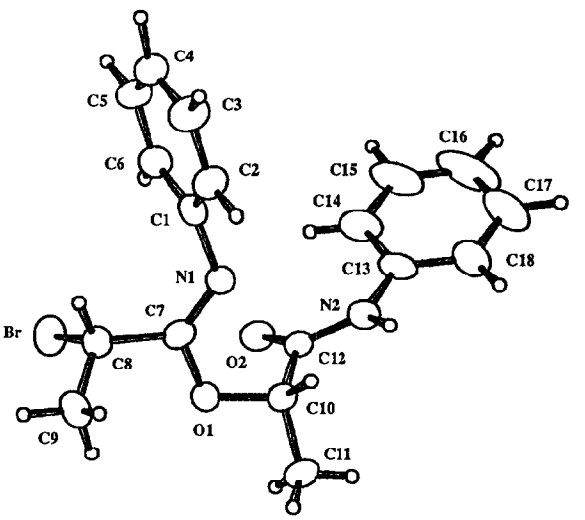
[b] For racemic compound, see: R. S. Safir, H. Dalalian, W. Fanshawe, K. Cyr, R. Lopresti, R Williams, S. Upham, L. Goldman, and S. Kusher, *J. Am. Chem. Soc.*, 1955, 77, 4840; for the enantiomeric compound, see ref. **11**.

N-Benzyl- and N-tbutyl-2-bromopropanamides (**1b, c**) displayed a trend similar to that of 2-bromoamide **1a**, leading to both enantiomeric N,N'-substituted alaninamides (**2c-f**; **3c, d, Tables 2, 3**). Reactions run in the presence of Ag_2O are fast and offer the more promising synthetic strategy.

In order to get indirect information on the behaviour of Ag_2O, several reactions in the presence of toluene-soluble silver trifluoromethanesulfonate were performed. In several cases, Ag^+ accelerated the substitution of bromine by the amine, and led to a product having the same optical activity of the sample produced by the amine with no promoter.

Whereas a chiral 2-bromoamide (**1a-c**) reacts enantioselectively with the above mentioned primary or secondary amines according to the experimental conditions, a different trend was observed with diisopropylamine or triethylamine. Observations were limited to 2-bromopropananilide (**1a**). In the absence of a promoter, **1a** remained unchanged even after prolonged contact with either amine. Addition of Ag_2O or Ag^+ provided, respectively, 2-diisopropylaminopropananilide (**3e**), or the quaternary ammonium trifluoromethanesulfonate (**4a**), of unknown optical purities. In the presence of Ag_2O, two types of self-condensation products of **1a** formed competitively: i) 3,6-dimethyl-1,4-diphenyl-2,5-dioxopiperazine(s); ii) the halide-imidoether-amide (S,S)-**5**, arising in high diastereomeric eccess, as proved by comparison with the diastereomeric mixture obtained from racemic **1a**. An X-ray analysis fully described the structure and configuration of **5** (**Figure**).

Figure. X-ray structure of the dimeric compound (S,S)-5



Configurational aspects of **3e**, **4** and the dioxopiperazine derivative(s), as well as conformational and hydrogen-bonding properties of representative products, deserve further studies. We wish to comment here upon the enantioselectivity observed when a primary or secondary amine gives a prevailing enantiomeric derivative, and on the diastereoselectivity observed when the chiral 2-bromopropanamide (**1a**) provides both the nucleophile and the alkylating agent to afford the dimeric compound **5**.

A sufficiently reactive primary or secondary amine would react in the absence of a promoter, according to an S_N2 mechanism, favoured by the neighbouring amide carbonyl. Ag^+ would give electrophilic assistance in some cases.[5] Accordingly, we assign to the resulting 2-aminoamides a configuration opposite to the one present in the parent 2-bromoamide, independently of the sign of the optical rotation.

Turning to the reactions in the presence of Ag_2O, we cannot conclude whether Ag_2O behaves more as a base, by abstracting a proton from the amide moiety, or as a Lewis acid, by offering electrophilic assistance. From a practical point of view, the results would be in agreement with a neighbouring group mechanism causing a double inversion, and resulting in 2-aminoamides with the same configuration of the parent 2-bromoamides, independently of the sign of optical rotation. Interactions between Ag_2O and the solution-species would make the mechanism a complex one, deserving proper studies. In any case, the mechanism operating in toluene in the presence of Ag_2O must stand on a chirality carrying species, and would formally encompass a labile aziridinone (α-lactam). Aziridinones were previously isolated from 2-haloamides,[6] and an optically active aziridinone of undefined configuration was isolated from a chiral, configurationally unstable, 2-chloroamide.[7] On the other hand, in silver promoted reactions in an α-haloacid and its derivatives [8] or in α-haloketones [9] and α-haloimines,[10] competition between S_N2 or S_N1 mechanisms or competitive substitutions or rearrangements via α-acyl- or related carbenium ions were demonstrated to occur. We consistently obtained samples of 2-aminoamides displaying optical activities of the same magnitude but opposite sign, and assume that two mechanisms operate at mutual exclusion. For example, the fast reactions occurring between **1a** and pyrrolidine with or without Ag_2O, suggest that the exclusion is due to peculiar features of the mechanism with Ag_2O. As to possible deviations from quantitative e.e. (see Expt.), we expect that they are due more to a low e.e. in the parent compound rather than to a leak between the two mechanisms.

Concerning this point, a recent study on the optical purity of 2-haloacids obtained through diazotization-substitution, included derivatization to 2-haloamides. In the case of insufficient control of temperature and amine concentration, some racemisation of the 2-haloamide was observed.[11]

By deliberate choice, we caused some systems to react in adverse conditions, and observed that racemisation may compete with substitution. On the other hand, from reacting systems under carefully controlled conditions,

we recovered only minor amounts of unreacted 2-bromopropanamides showing low or no loss of optical activity.

In order to rationalize the diastereoselective formation of bromodimer (S,S)-**5** from **1a** in the presence of Ag_2O, we assume that the conjugate base of **1a**, a bromoamidate anion,[12] would behave as an ambident nucleophile and undergo alkylation at the oxygen atom [13] by a second molecule of **1a**.[14] The (S,S) configurations of the two sp^3 carbons are rationalized as follows: i) CBr retains its configuration since it undergoes no reaction; ii) the alkylating centre shows unchanged configuration due to two inversions occurring through a neighbouring group-like mechanism discussed above.

Current research aims are to measure the e.e.s accurately enough to ascertain whether the trend of occasional deviations may be related to the reaction partners;[15] to find whether the observed enantioselectivity and diastereoselectivity control holds for other systems; to study the reaction mechanisms, and to look for broader synthetic applications.

Experimental

2-Bromo-N-phenyl (-N-benzyl; -N-tbutyl)propanamide (**1a-c**) having the S-configuration were used throughout.[3] A sonicator Branson 3200 was used in all reactions with Ag_2O. Specific rotations [α] were measured using a Perkin-Elmer 241 polarimeter operating at λ = 589 nm (sodium D line) at 20°C. Concentration was 1-2% in chloroform or ethanol. A high e.e. was measured in both enantiomers of **2a**, as was the case for **2d**,[3] by ^1H NMR in the presence of tris-[3-(trifluoromethylhydroxymethylene)-(+)-camphorato] europium (III) (Aldrich, Eu $(hfc)_3$). However, in this paper, we limited our analysis to the (opposite) optical activities of aminoamides (**2, 3**) and the d.e. and X-ray analysis of bromodimer **5**; all e.e.s are under proper analysis by chiral GC and HPLC.[15] ^1H and ^{13}C NMR spectra were determined on a Bruker AC 200 (200 MHz) instrument, in $CDCl_3$; chemical shifts are reported as δ units (ppm) downfield from tetramethylsilane. I.R. spectra were registered on a Perkin-Elmer 299 B instrument equipped with NaCl cells (1mm), in $CHCl_3$. Melting points were measured using a Reichter-Kofler instrument and are uncorrected. Elemental analyses are reported for compounds **4** and **5**; other products gave C,H,N with errors of $\pm$ 0.5 %. Rf_1 and Rf_2 refer to thin layer chromatography (Merck plates 0.25 mm) with the solvent mixture ethyl acetate-n.hexane (1:1) or (1:4), unless otherwise indicated. Spots were revealed with iodine vapors. In column chromatography, silica gel and the above solvent mixtures were used.

The new products obtained are listed below. Additional data are in **Tables 1-3**. Examples of preparations are reported for: (S)-**3a**; (R)-**3a**; **3e**; **4**; (S,S)-**5**.

2-tButylamino-N-phenylpropanamide (2a). M.p. 70-71. Rf_1 0.43. ^1H NMR: 1.13 (s, 9H, tBu), 1.38 (d, 3H,CH_3), 2.04 (br. s, 1H, NH), 3.38 (q, 1H, CH), 7.09-7.61 (m, 5H, Ph) 9.82 (br.s,1H, NHCO).

2-Benzylamino-N-phenylpropanamide (2b). M.p. 87-89. Rf_1 0.31. ^1H NMR: 1.41 (d, 3H, CH_3), 1.64 (br. s, 1H, NH), 3.37 (q, 1H, CH), 3.82 (s, 2H, CH_2), 7.10-7.61 (m, 5H, Ph), 9.82 (br.s, 1H, NHCO).

(S)-2-Diethylamino-N-phenylpropanamide (3a). To a solution of 2-bromo-N-phenylpropanamide (1a) (228 mg, 1mmol) in toluene (5 ml), Ag_2O (232 mg, 1 mmol) and diethylamine (146 mg, 2 mmol) were added successively. The mixture was sonicated 3h, filtered through Celite, and the solid was washed with ethyl acetate (3 ml for 3 times). The solution and washings were concentrated to constant weight. Oil. [α] +59 ($CHCl_3$). Rf_1 0.55. ^1H NMR: 1.11 (t, 6H, $2CH_3$), 1.27 (d, 3H, CH_3), 2.56 (m, 4H, $2CH_2$), 3.48 (q, 1H, CH), 7.04-7.60 (m, 5H, Ph), 9.59 (br. s, 1H, NH).

(R)-2-Diethylamino-N-phenylpropanamide (3a). To a solution of **1a** (114 mg, 0.5 mmol) in toluene (3 ml), $Ag^+CF_3SO_3^-$ (128 mg, 0.5 mmol) and diethylamine (73 mg, 1 mmol) were added successively. The supernatant was pipetted from the formed AgBr and $Et_2NH_2^+CF_3SO_3^-$, concentrated, and purified by column chromatography. Oil. [α] -65 ($CHCl_3$).

N-Phenyl-2-pyrrolidinopropanamide (3b). M.p. 40-43. Rf_1 0.43. ^1H NMR: 1.38 (d, 3H, CH_3), 1.83 (m, 4H, $2CH_2$), 2.64 (m, 4H, $2CH_2N$), 3.04 (q, 1H, CH), 7.10-7.60 (m, 5H, Ph), 8.99 (br. s, 1H, NH). IR: 3010 (NH), 1680 (CO), 1600, 1520, 1440, 1130.

2-Diisopropylamino-N-phenylpropanamide (3e). A solution of **1a** (228 mg, 1mmol) in toluene (5 ml) was treated with Ag_2O (232 mg, 1 m.mol) and diisopropylamine (ml 1.4, 10 mmol). Work up as for (S)-**3a** gave **3e** (188 mg, 76%). Oil. Rf_2 0.54. ^1H NMR: 1.12 and 1.15 (2d, 12H, $4CH_3$), 1.45 (d, 3H, CH_3), 3.20 (m, 2H, 2CH), 3.61 (q, 1H, CH), 7.07-7.58 (m, 5H, Ph), 9.75 (br. s, 1H, NH). IR: 3290 (NH), 1680 (CO), 1600, 1510, 1440, 1150, 1040.

Further elution gave some compound **5** (32 mg, 17%) (see below).

N-Benzyl-2-tbutylaminopropanamide (2c). Oil. Rf 0.5 (hexane-acetone 1/1). ^1H NMR: 1.03 (s, 9H, tBu), 1.33 (d, 3H, CH_3), 3.33 (q, 1H, CH), 4.43 (d, 2H, CH_2), 7.24-7.34 (m, 5H, Ph), 8.06 (br. s, 1H,NHCO).

N-Benzyl-2-diethylaminopropanamide (3c). Oil. Rf_1 0.3. ^1H NMR: 0.98 (t, 6H, $2CH_3$), 1.23 (d, 3H, CH_3), 2.47 (m, 4H, $2CH_2$), 3.40 (q, 1H, CH), 4.44 (2AB, 2H, CH_2Ph), 7.22-7.37 (m, 5H, Ph), 7.78 (br. s, 1H, NHCO).

2-tButylamino-N-tbutylpropanamide (2e). M.p. 53-54. Rf_1 0.2. ^1H NMR: 1.06 (s, 9H, tBu amine), 1.33 (s, 9H, tBu amide), 1.25 (d, 3H, CH_3), 3.10 (q, 1H, CH_3), 7.65 (br. s, 1H, NHCO). IR: 3320 (NH), 2980, 1660 (CO), 1530.

2-Benzylamino-N-tbutylpropanamide (2f). Oil. Rf_1 0.14. ^1H NMR: 1.34 (s, 9H, tBu), 1.29 (d, 3H, CH_3), 1.60 (br. s, 1H, NH), 3.11 (q, 1H, CH), 3.72 (s, 2H, CH_2), 7.26-7.32 (m, 5H, Ph), 7.17 (br. s, 1H, NHCO).

N-tButyl-2-diethylaminopropanamide (3d). Oil. Rf_1 0.2. ^1H NMR: 1.34 (s, 9H, tBu), 1.03 (s, 6H, $2CH_3$), 1.14 (d, 3H, CH_3), 2.46 (m, 4H, $2CH_2$), 3.24 (q, 1H, CH), 7.42 (br. s, 1H, NHCO).

2-Triethylammonium-N-phenylpropanamide, trifluoromethanesulfonate (4a). To a solution of **1a** (228 mg, 1 mmol) and $Ag^+CF_3SO_3^-$ (257 mg, 1mmol) in toluene (5 ml), triethylamine (0.5 g, 5 mmol) was added and the mixture was magnetically stirred for eight days. The filtrate and washings (ethyl acetate) gave, on concentration, a dark solid that was triturated with petrol ether (4 ml, 2 times) and ethyl ether (3 ml, 4 times) to remove soluble impurities. The undissolved solid (300 mg, 75 %), taken up with ethyl acetate (1 ml), gave colorless prisms. M.p. 110-113. ^1H NMR: 1.46 (t, 9H, 3CH3), 1.73 (d, 3H, CH_3), 3.68 (m, 6H, $3CH_2$), 4.69 (q, 1H, CH), 7.15-7.70 (m, 5H, Ph), 8.06 (br. s, 1H, NH). ^{13}C NMR: 9.15 ($3CH_3$), 14.37 (CH_3), 54.30 ($3CH_2$), 67.06 (CH), 117.27 (2 Ar), 123.62 (1 Ar), 128.99 (2 Ar), 137.13 (1 Ar), 165.31(CO). Anal. Calcd.for $C_{16}H_{25}F_3N_2SO_4$: C, 48.23, H, 6.32, F, 14.3, N, 7.03, S, 8.05. Found: C, 48.17, H, 6.46, F, 14.6, N, 7.03, S, 8.08.

A racemic sample of **1a** remained unchanged when treated with triethylamine (5 mol; 900 h) in the absence of a promoter. However, upon sonication with triethylamine (2 mol), Ag_2O (1 mol), and molecular sieves 4 A, **1a** gave the following compounds (^1H NMR comparison with **4a** and other authentic specimens): **4b** (11%); cis- and trans-3,6-dimethyl-1,4-diphenyl-2,5-dioxopiperazine **6** (61%); 2-hydroxypropananilide[12] (19%).

(S,S)-5-Bromo-2-methyl-N-phenyl-4-phenylimino-3-oxahexanamide (5). A solution of **1a** (684 mg, 3 m.mol) in toluene (15 ml) was treated with Ag_2O (696 mg, 3 m.mol) and the mixture was sonicated 17 h. Filtration and evaporation of the solvent gave an oil that was purified through column chromatography. Colourless prisms: 323 mg (57%); m. p. 140-142; [α] +213 (c 1.2, CHCl3); +170 (c 1.3, EtOH).Rf_2 0.45 brown, discolouring to grey-violet. ^1H NMR: 1.53 (d, 3H, CH_3CO), 1.78 (d, 3H, CH_3CBr), 4.53 (q, 1H, CHO), 5.21 (q, 1H, CHBr), 6.70-7.63 (m, 10H, 2Ph), 9.87 (s, 1H, NH). ^{13}C NMR: 17.57(C_6), 22.52 (CH_3-

C_2), 37.31 (C_5), 71.54 (C_2), 119.26 (2 Ar), 120.27 (2 Ar), 124.06 (1 Ar), 124.50 (1 Ar), 129.07 (2 Ar),129.34 (2 Ar), 137.49 (1 Ar), 146.04 (1 Ar), 157.38 (C_4), 169.35 (C_1). IR: 3400 (NH), 1680 (CO), 1600, 1530, 1440, 1260, 1150, 1050. Anal. Calcd. for $C_{18}H_{19}BrN_2O_2$: C, 57.61, H, 5.10, Br, 21.29, N, 7.46. Found: C, 57.64, H, 5.18, Br, 21.20, N, 7.42.

^{1}H NMR of the crude oil revealed: unreacted **1a** (6%); 2-hydroxypropananilide (20%); minor unidentified product(s).

Diastereoisomer of bromodimer 5. A reaction identical to the one above, where racemic **1a** was used, gave a diastereomeric mixture. ^{1}H NMR allowed to assign to the non isolated diastereoisomer (R,S)-**5** the following signals: 1.66(d, 3H, CH_3CO), 1.84 (d, 3H, CH_3Br), 4.51(q, 1H, CHO), 5.51(q, 1H, CHBr), 6.70-7.70 (m, 10H, 2Ph), 8.40 (br. s, 1H, NH).

Crystal data of (S,S)-**5**: $C_{18}H_{19}BrN_2O_2$, M_r = 375.3, orthorombic, $P2_12_12_1$, a = 8.285(3), b = 13.957(2), c = 15.912(2) A, V = 1840.0(8) A^3, z = 4, D_x = 1.355 g cm^{-3}, monochromated MoKα (λ = 0.71069 A), μ = 22.20 cm^{-1}, F(000) = 848, T = 295 K, Enraf-Nonius CAD4 diffractometer; 2287 unique reflections measured; 1221 reflection observed ($I \geq 2\sigma$ (I)); solution by direct methods (MULTAN81: Main, P.; Hull, S.E.; Lessinger, L.; Germain, P.;Declercq, J.-P; Woolfson, M.M. (1981) Universities of York, England and Louvain, Belgium); full matrix least-squares refinement; non-hydrogen atoms anisotropic, hydrogen atoms included at calculated positions except HN2 which was refined isotropically. Both enantiomorphous structures were refined with final disagreement factors R_1 = 0.045 and $R_1(W)$ = 0.043, and R_2 = 0.061 and $R_2(W)$ = 0.060 for the two enantiomers respectively. The correct absolute configuration was assigned to the enantiomer displaying the lower values of the disagreement factors. The structure shown in the Figure presents a short intramolecular contact of 2.824(6) A between imine N1 and carbonyl C12 atoms. The molecules in the crystal are connected head-to-tail by means of N2-HN2---O2 hydrogen bond (N2-HN2 =.0.92(5) A, N2---O2 (x+1/2, 3/2-y, 1-z) = 2.958(6) A, N2-HN2---O2 = 170(4)°). Atomic coordinates, thermal parameters, bond lenghts and angles are available from the Cambridge Crystallographic Data Centre.

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