Stereochemistry of Imino-group Reduction. Part 3.[1] The Hydride Reduction of Achiral Benzil Monoimines

Benito Alcaide, Carmen López-Mardomingo, Rafael Pérez-Ossorio,* and Joaquin Plumet
Departamento de Química Orgánica, Facultad de Química, Universidad Complutense, Madrid-3, Spain

The *RR,SS*:*RS,SR* ratio of diastereoisomeric amino-alcohols obtained from the lithium aluminium hydride reduction of the monoimines prepared by reaction of benzil and various aliphatic and aromatic achiral amines has been determined. Stereochemical results are analysed in terms of competition between two reaction routes involving respectively preliminary reduction of the oxo group and the imino group. The influence of polar and steric factors of the nitrogen substituent is discussed as is also that of solvent polarity. The reduction of some monoimines with sodium borohydride has also been studied. An interpretation of the ratios *RR,SS*:*RS,SR* is provided.

We have previously reported [1] the stereochemistry of the lithium aluminium hydride (LAH) reduction of the monoimines prepared by reaction of benzils and 1-phenylethylamine.[2] We also described the catalytic hydrogenation of the monoimine prepared from unsubstituted benzil, and the LAH reduction of the resulting amino-ketone. It was shown that the stereochemistry of the latter two-step reduction differs markedly from that of the direct reduction. Both types of reduction are useful synthetic methods for the preparation of amino-alcohols with three chiral centres since both are highly stereoselective. The stereochemical course of these reactions is expected to be influenced by the presence of a chiral centre in the starting imino-ketone. In order to gain a deeper insight into the mechanism of these processes it seems desirable to study similar reductions in the absence of such a chiral centre. Thus, we have studied both types of reduction in simple benzil monoimines, PhCOC(Ph)=NR (1), in which R is an achiral group. The stereochemical course is easily followed, since only two pairs of racemic diastereoisomeric amino-alcohols are obtained in each case.

The *N*-phenylimine (1a) (R = Ph) was chosen for initial study. Since LAH behaves as a rather hard reagent,[3] polar influences may modify the stereochemical course of the reaction. Thus, the influence of electron-donating substituents in the *N*-aryl group was subsequently examined by carrying out the LAH reduction of (1b) (R = *p*-$Me_2NC_6H_4$), (1c) (R = *p*-$MeOC_6H_4$), (1d) (R = *p*-MeC_6H_4), (1e) (R = *p*-ClC_6H_4), (1f) (R = *p*-BrC_6H_4), (1g) (R = *p*-IC_6H_4), and (1h) (R = *p*-FC_6H_4). In order to ascertain the possible incidence of steric factors, the imines (1i) (R = $PhCH_2$) and (1j) (R = Ph_2CH) were also studied. In addition the influence of solvent polarity on stereochemistry was also investigated in the LAH reduction of (1a). Finally, as an extension to other reducing agents, comparison of the stereochemical results of the LAH reduction of (1a, i, and j) with those obtained in the $NaBH_4$ reduction is also reported.

Results and Discussion

The results of the various reduction reactions are collected in Table 1.

Assignment of Configuration to N-*Substituted* 2-*Amino*-1,2-*diphenylethanols* (2).—This was based mainly on ^1H n.m.r. data (Table 2); high-dilution i.r. spectroscopy was also used. As can be seen in Table 3 fairly high values of $\Delta\nu$ [$\nu_{OH(free)} - \nu_{OH(associated)}$] indicative of a high degree of intramolecular association were obtained. The importance of this hydrogen-bond association for the conformational analysis of the amino-alcohols is thus shown. Then, from consideration of the ^1H n.m.r. data and using conformational arguments similar to those previously reported [1] the *RR,SS* configuration was assigned to the isomer having the highest coupling constant $J_{a,b}$ and the *RS,SR* configuration to the compound with the lowest value of $J_{a,b}$. Although the differences in $J_{a,b}$ between both isomers are only 1—2 Hz the assignment is justified by comparison with known, well established systems (see ref. 1 and references quoted therein). Alternatively, the *RS.SR* configuration for the amino-alcohols has been established by ring-opening of *trans*-stilbene oxide with the appropriate amine.[4,5]

Catalytic Hydrogenation of (1) *to Amino-ketones* (3) *and Subsequent LAH Reduction to* (2).—The catalytic hydrogenation of (1a—j) led to amino-ketones (3) as already reported [6] for (1a, i, and j). This may be explained as a reflection of the soft nature of the reducing agent.[3] Other factors may affect the results of this hydrogenation. It is commonly supposed that in catalytic hydrogenation the absorption of material onto the surface is often the critical step. However, the hydrogenation of the imino-ketones PhCOC(Ph)=NCH(Ph)R with different sizes of R group (and then with different ease of absorption) yields in all cases the related amino-ketones.[6] Subsequent LAH reduction of (3) yielded the *RS,SR*-isomer of (2). Total stereoselectivity was also observed in the $NaBH_4$ reduction of (3). These results have been accounted for by the Pérez-Ossorio model for the stereoselective reduction of carbonyl compounds bearing polar α-substituents.[7] The spectral properties of *RS,SR*-(2) were subsequently determined.

LAH Reduction of Benzil Monoimines (1) *to Aminoethanols* (2).—The mechanistic possibilities for the LAH reduction of imino-ketones are shown in Scheme 1. The simultaneous reduction of both imino and carbonyl groups through a cyclic transition state *via* double co-ordination between aluminium and the imino and carbonyl groups can be discarded since in an achiral system the reaction would produce no stereoselectivity at all.

On the other hand, LAH reduction of *N*-(1-phenylethyl)-α-aminodeoxybenzoin yields a stereochemical result opposite to that of LAH reduction of *N*-(1-phenylethyl)-1-benzoylbenzylideneamine.[1] This is an indication that with LAH the carbonyl group is attacked preferently and that route *a* will be followed.

This preferential attack by LAH on the carbonyl group can be accounted for since the monoimines of 1,2-dicarbonyl compounds are ambident electrophiles, the carbonyl and imino groups being respectively the hard and soft sites of the reacting system. The results of the reductions of these compounds with reducing agents of variable hardness are in agreement with this.[3]

Table 1. Reduction of *N*-substituted 1-benzoylbenzylideneamines (1)

Compound	Reducing agent and reaction conditions	Reaction time (h)	Product	Yield [b]	*RR,SS* [a] / *RS,SR*
(1a)		10	(3a)	95	
(1b)		0.5	(3b)	71	
(1c)		0.5	(3c)	76	
(1d)	H_2–Pd(C)–AcOEt–Room temp.	1	(3d)	92	
(1e)		1	(3e)	96	
(1f)		1.5	(3f)	94	
(1i)		2.5	(3i)	98	
(1j)		10	(3j)	93	
(1a)		4	(2a)	95	1.8
(1b)		1	(2b)	100	⩾20 [c]
(1c)		1	(2c)	100	>20 [d]
(1d)		1	(2d)	100	5.0
(1e)	$LiAlH_4$–Et_2O–Room temp.	1	(2e)	100	2.6
(1f)		1	(2f)	100	2.3
(1g)		1	(2g)	100	1.3
(1h)		1	(2h)	100	8.6
(1i)		3	(2i)	80	2.0
(1j)		4	(2j)	100	3.9
(1a)		4.5	(2a)	82	0.9
(1i)	$NaBH_4$–EtOH–b.p.	3	(2i)	100	0.5
(1j)		8	(2j)	100	2.8

[a] Determined from conveniently enlarged ^{1}H n.m.r. spectra taken in $CDCl_3$ at 60 MHz. [b] Difference from 100% is starting material or fission compounds. In crude product (^{1}H n.m.r.). [c] Only the *RR,SS*-isomer was observed. [d] The amount of *RR,SS*-isomer was 95 ± 3%.

Table 2. ^{1}H N.m.r. spectral data (δ) of *N*-substituted 2-amino-1,2-diphenyl ethanols [a] $Ph^aCHOH^bCH(Ph)NHR$ (2)

Compound	Isomer	CH-a	CH-b	$J_{1,2}$/Hz	R[b]	OH and NH
(2a)	*RR,SS*	4.83	4.50	6.0		3.0—4.2
	RS,SR	5.03	4.67	5.0		3.5—3.8
(2b)	*RR,SS*	4.73	4.36	7.0	2.80	3.4—3.6
	RS,SR	4.95	4.55	5.0	2.80	3.6—4.0
(2c)	*RR,SS*	4.73	4.40	7.0	3.50	3.2—4.0
	RS,SR	4.97	4.53	5.0	3.50	3.3—3.7
(2d)	*RR,SS*	4.73	4.40	7.0	2.20	3.3—3.6
	RS,SR	4.93	4.58	5.0	2.20	3.3—3.6
(2e)	*RR,SS*	4.80	4.43	6.0		4.2—5.0
	RS,SR	4.97	4.55	4.5		4.3—5.0
(2f)	*RR,SS*	4.76	4.40	6.0		3.2—3.8
	RS,SR	4.96	4.53	4.5		3.4—3.8
(2g) [a]	*RR,SS*	4.77	4.40	6.0		3.5—4.4
	RS,SR	4.95	4.52	5.0		
(2h) [c]	*RR,SS*	4.73	4.36	6.0		3.1—3.8
	RS,SR	4.97	4.53	5.0		
(2i)	*RR,SS*	4.57	*d*	8.0	*d*	*d*
	RS,SR	4.83	3.90	6.0	3.60	1.6—2.8
(2j)	*RR,SS*	*e*	3.50	8.0	*e*	2.2—4.0
	RS,SR	4.66	3.60	6.0	4.50	1.8—2.7

[a] In $CDCl_3$ at 60 MHz. Magnetic parameters were directly read from conveniently enlarged spectra. [b] Aromatic protons not shown. [c] Magnetic parameters were read from the spectra of the reaction crude from $LiAlH_4$ reduction. [d] The five protons give a complex unresolved signal at δ 3.3—3.8. [e] Both protons appear as a complex unresolved signal at δ 4.3—4.5.

From the results above we can tentatively conclude that the varying stereoselectivity observed in the LAH reductions of (1) (Table 1) may depend on the relative operativity of routes *a* and *b* (Scheme 1) which in turn yield respectively the *RR,SS*- and *RS,SR*-isomers of (2) as discussed later.

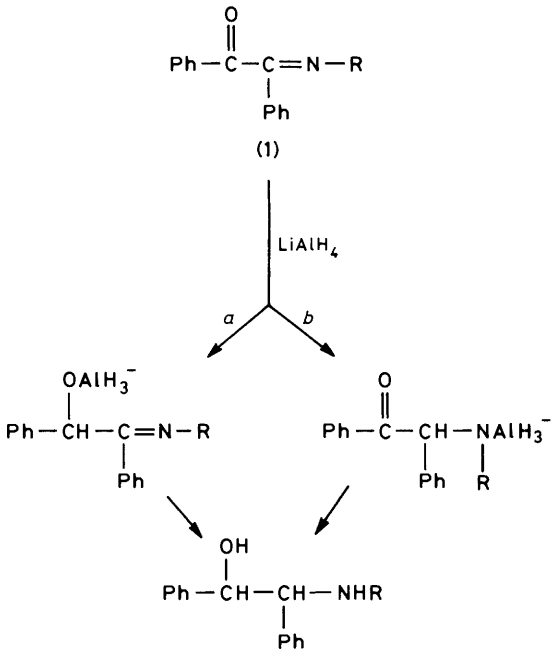
Some support to this conclusion has been found by studying the influence of *para*-substitution in the *N*-aryl ring on the isomeric alcohols ratio in the LAH reduction of *N*-aryl-1-benzoylbenzylideneamines [Table 1, entries (1a—h)]. Electron-releasing substituents will tend to soften the imino group.* Thus, operativity of route *a* will increase as also will the proportion of the *RR,SS*-alcohol. The linear correlation observed between σ_0^R and the *RR,SS*:*RS,SR* ratio is particularly significant for all cases, except (2d), and taking into account a value of log (*RR,SS*/*RS,SR*) = 1.7 (98% of *RR,SS*) for (2b). This correlation is given by $\sigma_0^R = -0.30$ [log (*RR,SS*/*RS,SR*)] − 0.04 (*r* 0.913). If (2a) is excluded the correlation is even better, $\sigma_0^R = -0.26$ [log (*RR,SS*/*RS,SR*)] − 0.01 (*r* 0.995). In

* Electron release will increase electron density on the imine nitrogen atom; consequently electron donation by the carbon atom will decrease and the charge density on this atom will also be lowered.

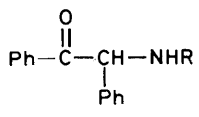
Table 3.[a] Absorption frequencies for free and intramolecularly associated hydroxy groups in *N*-substituted 2-amino-1,2-diphenylethanols (2)

Compound	R	Isomer	ν_{OH} (free)	ν_{OH} (associated)	$\Delta\nu$
(2a)[b]	Ph	*RR,SS*	3 620	3 580	40
		RS,SR	3 605	3 550	55
(2i)	$PhCH_2$	*RR,SS*	3 600	3 444	156
		RS,SR	3 604	3 445	159
(2j)	Ph_2CH	*RR,SS*	3 592	3 444	148
		RS,SR	3 596	3 444	152

[b] Measurements were carried out at 10^{-1}, 10^{-2}, and 10^{-3}-M concentrations in $CHCl_3$; the last are shown. The range 3 300—4 000 cm^{-1} was scanned. Assignment of the bands was based on their change of dilution. [b] For the possible origin of association in this case see ref. 4.

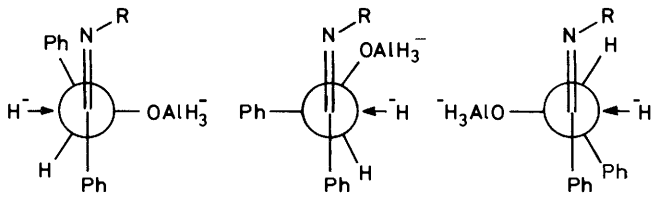


Scheme 1.



any case, these data should be considered as an additional contribution to the above interpretation and should not be overestimated.

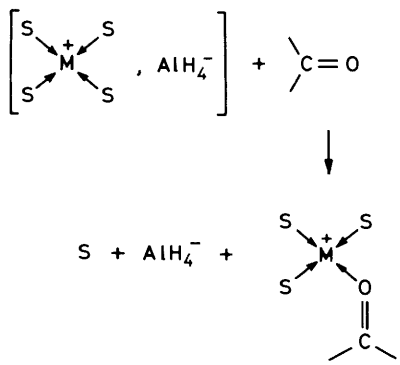
The exclusive formation of the *RR,SS*-alcohol in the LAH reduction of the imino-alkoxides (route *a*, Scheme 1) has been previously accounted for by application of the Pérez-Ossorio and Felkin models.[1] Transition state (I) of Scheme 2 was selected. To the arguments already advanced it may be added that antiperiplanarity effects [8] would favour transition states (I) and (III) but the latter would be destabilized by Ph–Ph crowding. On the other hand, rotation of (III) to give a



Scheme 2.

Table 4. Solvent effect on the stereochemistry of LAH reduction of PhCOCH(Ph)=NPh (1a)

Entry	Solvent	*RR,SS*: *RS,SR*	DN
1	Et_2O	1.8	19.2
2	THF	1.6	20.0
3	Bu^n_2O	1.2	
4	Pr^i_2O	0.5	
5	Et_3N	0.3	61.0



Scheme 3.

Karabatsos-type conformation will increase phenyl hindrance to hydride attack.

The effect of aryl-substituted *N*-alkyl groups [(1i and j)] is again an increase in the *RR,SS*: *RS,SR* ratio. Besides the effects already mentioned, steric influences may also operate, since, in any case, it seems reasonable that the bulkier the R group the more favoured will be route *a*.

The effects of solvent on the stereochemistry of the reduction process should supply some additional mechanistic information. This effect has been studied for the LAH reduction of (1a) (Table 4).

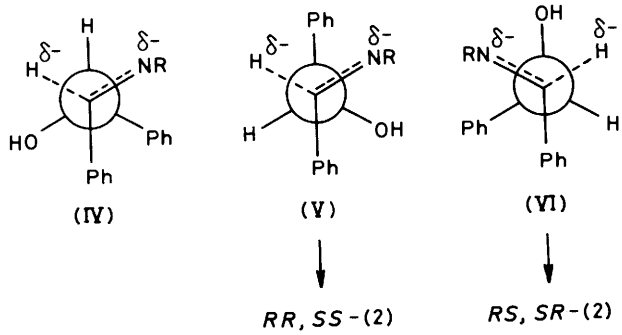
The mechanism of ketone reduction by complex metallic hydrides involves a decisive role of the metallic cation in the transition state of the process. It has been proposed [9] that the reducing agent forms a solvent-separated ion pair with the metallic counterion (Scheme 3).

Before the attack by the nucleophile, the carbonyl group co-ordinates to the metal ion by displacing a molecule of solvent.[10] According to Ahn *et al.*[8,11] activation of the carbonyl group by the metal ion is a consequence of the decrease in energy of the LUMO of the former by co-ordination with M^+. The orbital interaction HOMO (nucleophile) — LUMO (C = O) thus becomes favoured.

Apparently Li^+ co-ordination still plays a dominant role in the carbonyl reduction when this occurs in close proximity to the imino group. If so, any effect that tends to decrease such co-ordination would favour route *b* (Scheme 1) over *a* and

Table 5. Preparation of *N*-substituted 1-benzoylbenzylideneamines PhCOC(Ph)=NR (1)

Compound	Reagents (mmol)	Solvent (ml)	Reaction time (h)	Crystallized from	M.p. (°C)	Yield (mmol; %)	i.r. (KBr) ν(C=O) ν(C=N)	^{1}H N.m.r. δ(CDCl$_3$)	Analysis (%) Calc.; Found
(1b)	31	Toluene (45)	1	MeOH	134—136	21; 68	1 660 1 609	2.83 (s, 6 H) 6.50 (d, 2 H, $J_{1,2}$ 9 Hz) 6.93 (d, 2 H, $J_{1,2}$ 9 Hz) 7.2—8.0 (m, 10 H)	C, 80.5; 80.35 H, 6.1; 6.2 N, 8.55; 8.6
(1c)	26	Xylene (50)	6	EtOH	114—116	21; 80	1 678 1 609	3.60 (s, 3 H) 6.2—7.8 (m, 14 H)	C, 80.0; 80.15 H, 5.3; 5.55 N, 4.45; 4.3
(1d)	31	Xylene (48)	6	MeOH	110	21.7; 70	1 662 1 618	2.20 (s, 3 H) 6.2—7.8 (m, 14 H)	C, 84.3; 84.15 H, 5.7; 5.7
(1e)	26	Xylene (54)	8	MeOH	98—100	19.5; 75	1 668 1 625 1 619(sh)	6.2—7.8 (m, 14 H)	C, 75.1; 75.35 H, 4.4; 4.6 N, 4.4; 4.3 Cl, 11.1; 10.8
(1f)	24	Xylene (40)	6	MeOH	95—96	17.6; 73	1 668 1 627 1 620(sh)	6.2—7.8 (m, 14 H)	C, 65.95; 65.8 H, 3.85; 3.85 N, 3.85; 3.9 Br, 21.95; 22.05
(1g)	19	Toluene (40)	15	MeOH	122—123	12; 65	1 668 1 612	6.3—7.7 (m, 14 H)	C, 58.4; 58.5 H, 3.4; 3.55 N, 3.4; 3.3
(1h)	28	Xylene (45)	6	MeOH	107—108	17; 62	1 662 1 619	6.3—7.8 (m, 14 H)	C, 79.2; 79.15 H, 4.6; 4.55 N, 4.6; 4.55



Scheme 4.

would increase the proportion of the *RS,SR*-alcohol. In fact, comparison of entries 1,3, and 4 (Table 4) shows that the increase in size and/or co-ordination ability of solvent would hinder the approach of the carbonyl group to the cation solvation shell and its substitution for a solvent molecule. Thus the amount of *RS,SR*-alcohol would increase, as observed.

Entries 1, 2, and 5 (Table 4) also show that the degree of solvation as measured by the 'donation number' DN [12] agrees satisfactorily with the isomer ratio. A large DN value means a tight solvation shell and a lesser opportunity for activation of the carbonyl group.

Sodium Borohydride Reduction of (1) *to* (2).—The stereoselectivity observed in sodium borohydride reductions are appreciably lower than in LAH reduction and the formation of the *RS,SR*-alcohol is more favoured. The two routes for the $NaBH_4$ reduction are similar to Scheme 1. Two questions arise: the possible different behaviour of both reducing agents in the selection of either route *a* or *b* and also the possible stereochemical differences for LAH and $NaBH_4$.

With respect to regioselectivity it has been previously shown [3] that LAH reduction of *N*-(1-phenylethyl)-1-benzoylbenzylideneamine occurs only by route *a* but with $NaBH_4$ both routes *a* and *b* are followed; these results have been interpreted in connexion with the relative hardness of both reagents.

Important differences in the stereochemical course of both types of reduction have been recently pointed out by Wigfield.[13] In this respect, it should be emphasized that in reductions with $NaBH_4$, the final products are the alcohols and that the transition states are, very probably, product-like.

In connection with route *b* we have already reported the stereochemistry of the $NaBH_4$ reduction of amino-ketones in hydroxylic solvents which yields exclusively the *RS,SR*-alcohol. With respect to route *a* the three product-like transition states shown in Scheme 4 may be envisaged for the reduction of imino-alcohols; (IV) can be discarded on account of steric crowding not compensated by OH–NR association and the relative stabilization of (VI) due to that association may explain together with the occurrence of route *b* the lower stereoselectivity observed in this reaction compared with LAH reduction.

Experimental

M.p.s are uncorrected. ^{1}H N.m.r. spectra were recorded with a Varian T 60-A apparatus. I.r. spectra were recorded on a Beckmann 4240 spectrophotometer, for the 10^{-1} and 10^{-2}M solutions; for the 10^{-3}M solutions a Perkin-Elmer 621 spectrophotometer provided with a variable-thickness cell was used.

N-*Substituted* 1-*Benzoylbenzylideneamines* (1).—These were prepared by direct condensation of equimolar amounts of benzil and the appropriate amine in toluene or xylene in the presence of catalytic amounts of $ZnCl_2$–1-phenylethylamine complex.[2] The imines (1a),[4] (1i),[4] and (1j) [2a] have been previously reported. Data for the remaining imines, reaction conditions, yields, physical properties, and analyses are gathered in Table 5. Imines (1c—e) have been also described [14] but are included in Table 5 where additional data are given.

N-*Substituted* 2-*Amino*-1,2-*diphenylethanols* (2).—The *RS*,-*SR*-isomers were obtained through the route (1) ⟶ (3) ⟶ (2) using either LAH or $NaBH_4$ for the last reduction. Compound *RS*,*SR*-(2a) had m.p. 121—122 °C (from EtOH) (Found: C, 83.15; H, 6.7; N, 4.7. $C_{20}H_{19}NO$ requires C, 83.05; H, 6.55; N, 4.85%). Compound *RS*,*SR*-(2i) had m.p. 149—150 °C (from Et_2O–EtOH, 5 : 1) (Found: C, 83.2; H, 7.1; N, 4.7. $C_{21}H_{21}NO$ requires C, 83.15; H, 6.95; N, 4.6%). Compound *RS*,*SR*-(2j) had m.p. 126—128 °C (from n-hexane) (Found: C, 85.5; H, 6.5; N, 3.75. $C_{27}H_{25}NO$ requires C, 85.5; H, 6.6; N, 3.7%).

The *RR*,*SS*-isomers were isolated from the alcohol mixture obtained by LAH reduction of (1) as reported below. Compound *RR*,*SS*-(2a) had m.p. 107—108 °C (from C_6H_6–n-hexane, 1 : 5) (Found: C, 83.2; H, 6.5; N, 4.65%). Compound *RR*,*SS*-(2i), m.p. 127—128 °C (from EtOH) (Found: C, 83.1; H, 7.0; N, 4.7%). Compound *RR*,*SS*-(2j) had m.p. 102—104 °C (from EtOH) (Found: C, 85.65; H, 6.5; N, 3.8%).

The remaining alcohols (2b—h) were not isolated. Composition of the mixtures was deduced from ^1H n.m.r. data. Spectra showed no other signals than those expected for the amino-alcohols.

LAH Reductions of (1) *in* Et_2O.—The imine (0.75 mmol) dissolved in anhydrous Et_2O (35 ml) was added to a suspension of LAH (1.50 mmol) in Et_2O (10 ml). Addition was carried out with stirring at 0 °C in *ca.* 30 min. Stirring was continued for another 30 min at room temperature. After hydrolysis with the minimum amount of water, aluminium salts were filtered off and the solution dried ($MgSO_4$). After filtration and elimination of solvent the mixture of isomeric alcohols was worked up as before. The *RS*,*SR*-alcohol was isolated and crystallized as already quoted.

Acknowledgements

We thank Dr. A. I. Blanch for i.r. spectra recording.

References

1 Part 2, B. Alcaide, R. Fernández de la Pradilla, C. López-Mardomingo, R. Pérez-Ossorio, and J. Plumet, *J. Org. Chem.*, 1981, **46**, 3234.
2 For the synthesis and structure of this type of compounds, see (*a*) J. L. García Ruano, R. Haro, C. Pascual, R. Pérez-Ossorio, and J. Plumet, *An. Quim.*, 1979, **75**, 165; (*b*) S. García Blanco, I. Fonseca, and S. Martínez Carrera, *Acta Crystallogr., Sect. B*, 1979, **35**, 2643; (*c*) J. L. García Ruano, M. A. Henao, D. Molina, R. Pérez-Ossorio, and J. Plumet, *Tetrahedron Lett.*, 1979, 3123; (*d*) J. L. García Ruano, M. A. Henao, D. Molina, R. Pérez-Ossorio, and J. Plumet, *An. Quim.*, 1980, **76C**, 260.
3 B. Alcaide, C. López-Mardomingo, R. Pérez-Ossorio, and J. Plumet, *An. Quim.*, 1982, **78C**, 278.
4 R. Mathis, M. T. Maurette, Ch. Godechot, and A. Lattes, *Bull. Soc. Chim. Fr.*, 1970, 3047.
5 B. Alcaide, C. López-Mardomingo, R. Pérez-Ossorio, and J. Plumet, *J. Heterocycl. Chem.*, 1982, **19**, 45.
6 B. Alcaide, G. Escobar, R. Pérez-Ossorio, and J. Plumet, *Org. Prep. Proceed. Int.*, 1982, **14**, 220.
7 B. Alcaide, G. Escobar, J. L. González-Simó, C. López-Mardomingo, R. Pérez-Ossorio, and J. Plumet, *Tetrahedron Lett.*, 1982, **23**, 2033. See also O. Arjona, R. Pérez-Ossorio, A. Pérez-Rubalcaba, and M. L. Quiroga, *J. Chem. Soc., Perkin Trans. 2*, 1981, 597 and references therein.
8 N. T. Ahn and O. Eisenstein, *Nouv. J. Chim.*, 1976, **1**, 61.
9 (*a*) E. C. Ashby and J. R. Boone, *J. Org. Chem.*, 1976, **41**, 2890; E. C. Ashby, F. R. Dobbs, and H. P. Hopking, *J. Am. Chem. Soc.*, (*b*) 1973, **95**, 2823; (*c*) 1975, **97**, 3158.
10 E. C. Ashby and J. R. Boone, *J. Am. Chem. Soc.*, 1976, **98**, 5524.
11 (*a*) N. T. Ahn and O. Eisenstein, *Tetrahedron Lett.*, 1976, 155; (*b*) N. T. Ahn, *Top. Curr. Chem.*, 1980, **88**, 196. See also E. D'Incan, A. Loupy, A. Restelli, J. Seyden-Penne, and P. Viout, *Tetrahedron*, 1982, **38**, 1755.
12 C. Reichardt in ' Solvent Effects in Organic Chemistry,' Verlag, 1979, p. 14.
13 D. C. Wigfield, *Tetrahedron*, 1979, **35**, 449.
14 B. Alcaide, M. A. León-Santiago, R. Pérez-Ossorio, J. Plumet, M. A. Sierra, and M. C. de la Torre, *Synthesis*, 1982, 989.

Received 4th January 1983; *Paper* 3/002