[3 + 2] CYCLOADDITION OF CHIRAL AZOMETHINE YLIDES FROM AMINOSUGAR N-OXIDES. ENANTIOSELECTIVE SYNTHESIS OF 3,4-DISUBSTITUTED PYRROLIDINES

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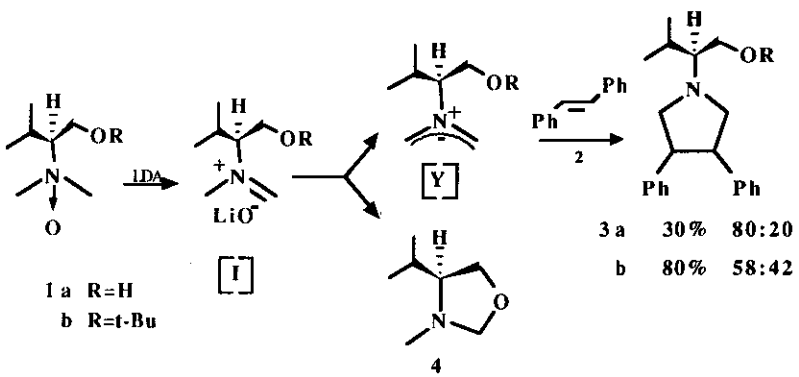
Abstract-The base deprotonation method, applied to amino-sugar *N*-oxides prepared from methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (**8**) and methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**9**), allows the easy generation of complex and very reactive sugar azomethine ylides. Fair yields of the major diastereomeric pyrrolidines resulting from [3+2] cycloaddition to stilbene are thus obtained with good asymmetric induction. The easy elimination of the chiral appendage as starting epoxides gives access to the enantiomerically enriched 3,4-diphenylpyrrolidines.

1,3-Dipolar cycloaddition of azomethine ylides to olefins represents a powerful access to pyrrolidines.[1] Nevertheless, until recently,[2,3] little was known about the asymmetric 1,3-dipolar cycloaddition of chiral azomethine ylides to achiral dipolarophiles.



Scheme 1

As an extension of our investigation on highly reactive non-stabilized azomethine ylides [Y] generated from tertiary amine *N*-oxides,[4a] we studied the asymmetric induction in 1,3 dipolar cycloaddition of chiral dipoles with nonactivated olefins.[4b] When using (*S*)-1-hydroxymethyl-2-methylpropylamine-*N*,*N*-dimethylamine *N*-oxide (**1a**) and *trans* -stilbene (**2**) as the dipolarophile, a mixture of diastereomeric *trans* -3,4-diphenylpyrrolidines (**3a**) was formed with good diastereoselectivity (de = 60%) but in low yield, due to the concomitant formation of the oxazolidine (**4**) resulting from intramolecular trapping of the iminium salt intermediate [I] by the lithium alkoxide (Scheme 1).[4b, 5]

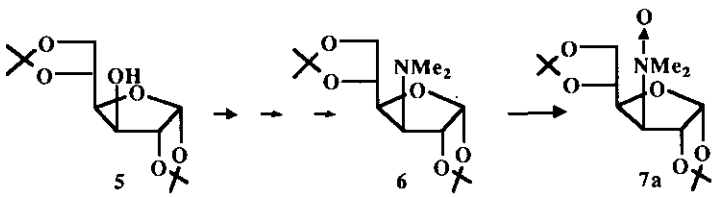
In order to avoid this unwanted reaction, the hydroxy function was protected as a *t*-butyl ether in the starting *N*-oxide (**1b**). The yields of the resulting pyrrolidines (**3b**) were highly increased, at the expense of diastereoselectivity.

We then turned towards aminosugar *N*-oxides as chiral ylide precursors, having in mind that such structures, unlike (**1b**), could be rigid enough to allow diastereofacial control while preventing the oxazolidine formation.

RESULTS AND DISCUSSION

Cycloaddition Reactions

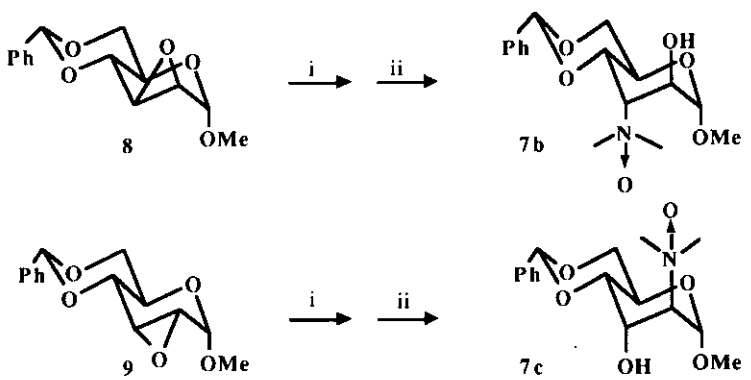
In a preliminary experiment we have studied the behavior of *N*-oxide (**7a**) resulting from the oxidation of the corresponding tertiary amine (**6**) , prepared in six steps from (**5**) (Scheme 2).[6]



Scheme 2

When *N*-oxide (**7a**) was treated with LDA at -78°C in the presence of *trans*-stilbene (**2**), 30% of expected diastereomeric pyrrolidines (**10a**) and (**11a**) were formed in a 75:25 ratio (Table 1, entry 1).

Despite the low yields of isolated products, this result is of importance since it shows that it is possible to generate a reactive ylide by amino-sugar *N*-oxide deprotonation, and that this **non-stabilized** dipole is so reactive that it adds to stilbene, a dipolarophile which is inert towards the corresponding ylides generated by other



i $NHMe_2$; ii H_2O_2

Scheme 3

ways.[1] The cycloadddition occurs even at -78°C with a much better diastereoselectivity than **1b**.

We then studied amino sugar *N*-oxide derivatives (**7b**)[7] and (**7c**), easily prepared by oxidation of the corresponding tertiary amines obtained from ring opening of methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-mannopyranoside (**8**)[8] and methyl 2,3-anhydro-4,6-*O*-benzylidene-α-D-allopyranoside (**9**)[9] by dimethylamine (Scheme 3).

In these derivatives the *N*-oxide functionality is *trans*-diaxial with respect to the free hydroxy function. Such a geometry was designed to prevent the intramolecular trapping of the intermediate iminium salt and the ensuing

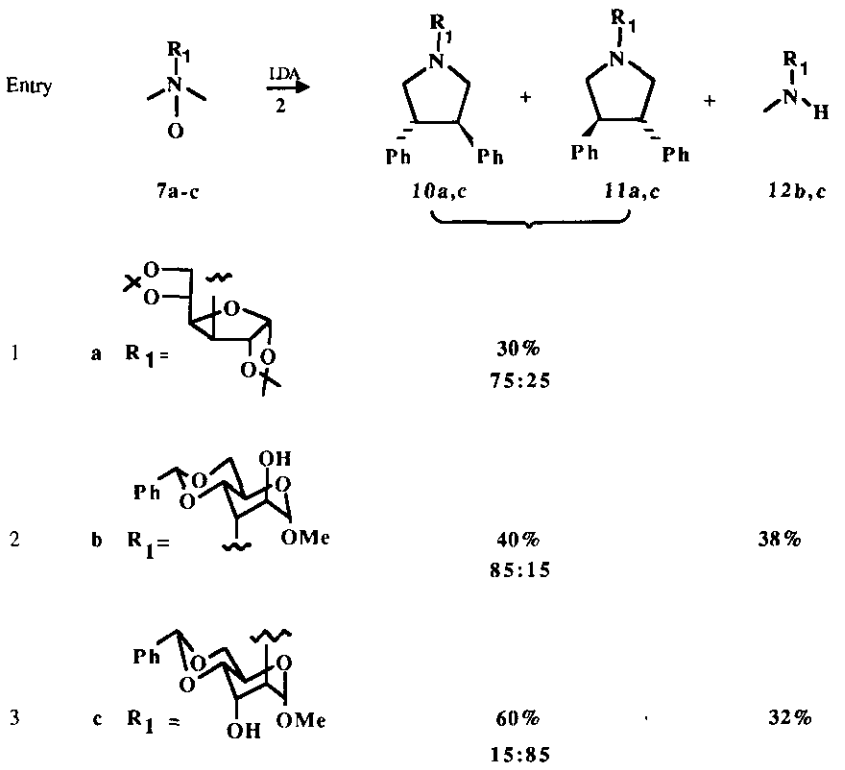


Table 1. Yields and Diastereomeric Ratios in the Reaction between (**7a-c**) and Stilbene (**2**)

oxazolidine formation. The structural features of the expected aminosugar pyrrolidines (**10b, c**), and (**11b, c**) were anticipated to allow for easy access to enantiomerically enriched 3,4-disubstituted pyrrolidines (**15**) and (**16**) of known absolute configuration[10] by removal of the sugar part as starting epoxides (**7** and **8**), according to the method described by Castedo[11] and successfully used in our previous work.[5]

When *N*-oxide (**7b**) was treated at 0°C for four hours with LDA in the presence of *trans*-stilbene (**2**), 40% of a mixture of diastereomeric *trans* -3,4-diphenylpyrrolidines (**10b**) and (**11b**) was isolated in a 85:15 ratio (Table 1, entry 2). When the reaction was carried out on *N*-oxide (**7c**), pyrrolidines (**10c**) and (**11c**) were formed in 60% yield, with the same diastereoselectivity which was independent of the reaction temperature. The competitive formation of demethylated amines [**12b**(38%) and **12c** (32%)], respectively, from (**7b**) and (**7c**) is reminiscent of previous observations in our laboratory.[4c]

Access to Optically Active *trans*-3,4-Diphenylpyrrolidines (15) and (16)

Pure diastereomers (**10b, c**) and (**11b, c**) were obtained by preparative hplc. Cleavage of the chiral auxiliary was achieved on the mixture of diastereomers by treating each couple with 50% NaOH in $CHCl_3$ in the presence of tetrabutylammonium bromide.[11] N-C bond breaking results from the formation of the epoxides (**8**) and (**9**), and enantiomerically enriched *N*-formyl derivatives (**13**) and (**14**) were obtained after work-up. Their hydrolysis yielded the corresponding *trans*-3,4-diphenylpyrrolidines (**15**) and (**16**) whose optical rotation sign allowed the

determination of their absolute configuration by comparison with literature data.[10] The optical rotation values measured, $[\alpha]_D^{25}$ -138° (c 1.2, $CHCl_3$) and $[\alpha]_D^{25}$ +142° (c 1.0, $CHCl_3$) for enriched NH-pyrrolidines (**15**) and (**16**), respectively, were in accordance with the expected enantiomeric excess. It was thus established that *N*-oxide (**7b**) led preferentially to (-)-(3*R*, 4*R*)-3,4-diphenylpyrrolidine (**15**), whereas (**7c**) gave antipodal compound (**16**). The quantitative recovering of corresponding epoxides (**8**) and (**9**) shows the importance of these compounds as chiral auxiliaries in the asymmetric [3 + 2] cycloaddition of azomethine ylides with olefins (Table 2).

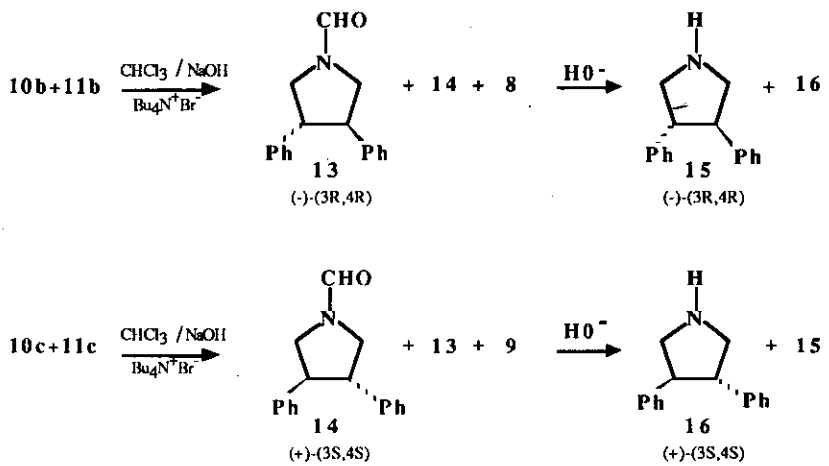
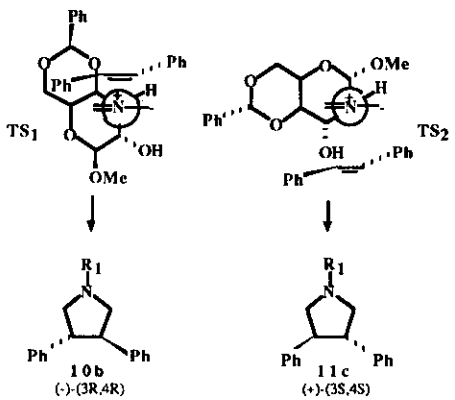


Table 2. Access to the Enantiomerically Enriched NH-Pyrrolidines.

The selectivity observed in the cycloaddition results from a diastereofacial control exerted by the sugar skeleton. The transition states of the reactions between stilbene (**2**) and the *N*-oxides (**7b,c**) are schematically represented as TS_1 and TS_2 (Scheme 4) in which the dipole terminii are as far as possible from, respectively, the OMe group, and the oxygen of the sugar skeleton. They are consistent with an approach of dipolarophiles to the ylide with phenyl groups being located so as to minimize the steric interactions with the sugar moiety.



Scheme 4

CONCLUSION

The base deprotonation method applied to amino-sugar *N*-oxides (**7b, c**) allows the easy generation of complex but very reactive sugar azomethine ylides. Fair yields of major diastereomeric pyrrolidines (**10b**) and (**11c**) resulting from [3+2] cycloaddition with stilbene are thus obtained with fair asymmetric induction. Enantiomerically enriched 3,4-diphenylpyrrolidines (**15**) and (**16**) are easily recovered by removal of the chiral appendage as starting epoxides (**8**) and (**9**).

Further studies are in progress with other dipolarophiles.[12]

EXPERIMENTAL SECTION

General. Hnmr or Cnmr spectra were recorded in $CDCl_3$, on a Bruker WP 200-54 (200 MHz); chemical shifts from tetramethylsilane are given in δ. Mass spectra (ms) were obtained on a AEI-MS-50 spectrometer; cims and fab were recorded on AEI-MS-9 spectrometer. The reactions were monitored by thin layer chromatography (tlc) and Hnmr. Purifications were achieved by column chromatography (elution), preparative thin layer chromatography (tlc, elution), and high pressure liquid chromatography (hplc).

General procedure. Amine *N*-oxides (**7a-c**) (1 mmol) were dried just before use, by heating under vacuum at 30°C for 6 h,in a three necked flask equipped with rubber septum. The dipolarophile (**2**) (198 mg, 1.1 mmol) in anhydrous THF (50 ml) was then added *via* a syringe and the suspension was cooled to the desired temperature before LDA (4 eq.) was introduced. The reaction was monitored by vpc and tlc. The diastereomeric ratios were determined, on the crude mixture, by hplc and Hnmr.

Oxidation of 1,2;5,6-di-*O*-isopropylidene-3-deoxy-3-*N*-dimethylamino-α-D-glucofuranose (6): acces to *N*-oxide (7a). Oxidation of the tertiary amine (**6**)[6] (870 mg, 3.02 mmol) by 30% H_2O_2, yielded hygroscopic *N*-oxide (**7a**) as an oil (820 mg, 90%). Hnmr δ 1.20 (s, 6H), 1.43 (s, 3H), 1.50 (s, 3H), 3.10 (s, 3H), 3.42 (s, 3H), 3.85 (d, *J* = 5 Hz, 1H), 3.98-4.02 (m, 1H), 4.19-4.29 (dd, *J* = 9, 6 Hz, 1H), 4.30-4.33 (m, 1H), 5.61-5.63 (d, *J* = 4 Hz, 1H), 5.85-5.87 (d, *J* = 4 Hz, 1H); fab m/z 304, 288.

1,2;5,6-Di-*O*-isopropylidene-3-deoxy-3-*N*-(3,4-*trans*-diphenylpyrrolidine)-α-D-glucofuranose (10a) and (11a). *N*-oxide (**7a**) (680 mg, 2.24 mmol) in THF (100 ml) treated at -78°C by LDA (10 mmol) in the presence of *trans* stilbene (440 mg, 2.44 mmol) yielded pyrrolidines (**10a**) and (**11a**) as an oil, in a 75:25 ratio (260 mg, 30%); Hnmr (400 MHz), δ 1.36 (s, 3H), 1.43 (s, 3H), 1.46 (s, 3H), 1.50 (s, 3H), 2.83-3.13 (m, 2H), 2.23-3.43 (m, 5H), 3.98-4.03 (dd, *J* = 8, 4 Hz, 1H), 4.07-4.12 (dd, *J* = 8, 4 Hz, 1H), 4.36-4.50 (m, 1H), 4.83 (d, *J* = 4 Hz, 1H), 5.80 (d, *J* = 4 Hz, 1H), 7.08-7.28 (m, 10H); Cnmr δ 25.83, 26.14, 26.77, 26.96, 52.62, 52.84, 59.70, 60.03, 65.84, 68.09, 72.78, 72.96, 79.69, 81.99, 105.03, 111.10, 115.03, 126.51, 127.53, 128,56, 143.92; cims m/z 465. Anal. Calcd for $C_{28}H_{35}NO_5$: C, 72.17; H, 7.57. Found: C, 71.92; H, 7.32.

Oxidation of methyl 4,6-*O*-benzylidene-3-deoxy-3-*N*-dimethylamino-α-D-altropyranoside: access to *N*-oxide (7b). The tertiary amine (1.30 g, 4.20 mmol), obtained in 74% yield by ring opening of epoxide (**8**) by dimethylamine, was oxidized by 30% H_2O_2 (7 ml) in MeOH (7 ml) to yield (**7b**) (1.30 g, 94%); Hnmr δ 3.38 (s, 3H), 3.40 (s, 3H), 3.45 (s, 3H), 3.63-3.89 (m, 3H), 3.96-4.19 (m, 1H), 4.22-4.49 (m, 2H), 4.64 (s, 1H), 5.20 (s, 1H), 5.51 (s, 1H), 7.29 (m, 5H); cims m/z 325; mp 148°C (from CH_2Cl_2); lit.,[7] 149°C.

Oxidation of methyl 4,6-*O*-benzylidene-2-deoxy-2-*N*-dimethylamino-α-D-altro-pyranoside: access to *N*-oxide (7c) The tertiary amine (3.09 g, 10 mmol) obtained in 74% yield by epoxide (**9**) ring opening by dimethylamine, was oxidized by H_2O_2 30% (10 ml) in MeOH (10 ml) to yield *N*-oxide (**7c**) (2.60 g,

80%); Hnmr δ 3.17 (s, 3H), 3.29 (s, 3H), 3.47 (s, 3H), 3.33-3.49 (m, 1H), 3.69-3.83 (m, 1H), 3.84-3.97 (m, 1H), 4.13-4.37 (m, 3H), 4.53-4.65 (d, J = 2.9 Hz, 1H), 5.70 (s, 1H), 7.27-7.39 (m, 3H), 7.43-7.57 (m, 2H); Cnmr δ 55.78, 57.53, 58.11, 59.45, 64.60, 70.05, 77.67, 83.95, 97.11, 103.22, 127.54, 129.06, 130.00, 138.99; ms m/z 309, 307; fab m/z 326, 310, 278; mp 199°C (from CH_2Cl_2). Anal. Calcd for $C_{16}H_{23}NO_6$: C, 59.06; H, 7.13. Found: C, 59.07; H,7.16.

Methyl 4,6-*O*-benzylidene-3-deoxy-3*N*-[3(R)-4(R)-*trans*-diphenylpyrrolidine]-α-D-altropyranoside (10b). Methyl 4,6-*O*-benzylidene-3-deoxy-3-*N*-[3(S)-4(S)-*trans*-diphenylpyrrolidine]-α-D-altropyranoside (11b) and Methyl 4,6-*O*-benzylidene-3-deoxy-3-*N*-methylamino-α-D-altroside (12b). *N*-Oxide (**7b**) (290 mg, 0.92 mmol) and *trans*-stilbene (**2**) (180 mg, 1.02 mmol) were treated with LDA (4 mmol) at 0°C. They yielded, after usual work up and chromatography on silica gel, (**10b**) and (**11b**) (270 mg, 38%, pentane-AcOEt 80:20) as a mixture of diastereomers (**10b/11b** = 85/15) separated by preparative hplc (MeOH-H_2O 80:20 + 0.5% Et_3N) and (**12b**)[13] (100 mg, 38%, pentane-AcOEt 60:40).

(**10b**) as an oil; Hnmr δ 2.99-3.67 (m + s, 10H), 3.67-3.87 (dt, J = 10 Hz, 1H), 4.17-4.43 (m, 3H), 4.44-4.57 (m, 1H), 4.59 (s, 1H), 5.50 (s, 1H), 6.99-7.49 (m, 15H); fab m/z 488, 470, 364, 336. Anal. Calcd for $C_{30}H_{33}NO_5$: C, 73.92: 6.82. Found: C, 73.58; H, 6.52.

(**11b**) as an oil; Hnmr δ 3.43 (s, 3H), 4.67 (s, 1H), 5.67 (s, 1H), 6.79-6.73 (m, 15H).

(**12b**) as an oil; Hnmr δ 2.53 (s, 3H), 2.99-3.17 (m, 1H), 3.37 (s, 3H), 3.39-3.49 (m, 1H), 3.67-3.87 (m, 2H), 3.92-4.07 (m, 1H), 4.07-4.23 (m, 1H), 4.23-4.37 (m, 2H), 4.57 (s, 1H), 5.53 (s, 1H), 7.07-7.67 (m, 5H); mass m/z 296.

Methyl 4,6-*O*-benzylidene-2-deoxy-2-*N*-[3(S)-4(S)-*trans*-diphenylpyrrolidine]-α-D-altropyranoside (11c); Methyl 4,6-*O*-benzylidene-2-deoxy-2-*N*-[3(R)-4(R)-*trans*-diphenylpyrrolidine]-α-D-altropyranoside (10c) and Methyl 4-6-*O*-benzylidene-2-deoxy-2-*N*-methylamino-α-D-altropyranoside (12c). *N*-Oxide (**7c**) (100 mg, 0.31 mmol) and *trans*-stilbene (**2**) (68.4 mg, 0.38 mmol) were treated with LDA (1.2 mmol) at 0°C.They yielded, after usual work up and chromatography on alumina, (**11c**) and (**10c**) (87.7 mg, 58%, CH_2Cl_2) as a mixture of diastereomers [(**11c/10c**) = 85/15)] separated by preparative hplc (MeOH-H_2O 80:20) and (**12c**) (29.6 mg, 32%, CH_2Cl_2-MeOH 99:1).

(**11c**). Hnmr δ 2.83-3.09 (m, 3H), 3.29-3.73 (m + s, 8H), 3.83-4.05 (m, 1H), 4.07-4.47 (m, 4H), 4.95 (s, 1H), 5.65 (s, 1H), 7.07-7.57 (m, 15H); Cnmr δ 52.29, 52.32, 56.00, 59.07, 60.79, 61.19, 67.74, 67.95, 69.65, 77.20, 100.15, 102.54; fab m/z 488, 382, 352, 265, 237, 91; mp 83°C (from AcOEt). Anal. Calcd for $C_{30}H_{33}NO_5$: C, 73.92, H, 6.82. Found: C, 73.64, H, 6.76.

(**10c**) as an oil; Hnmr δ 3.47 (s, 3H), 4.90 (s, 1H), 5.70 (s, 1H); fab 488, 413, 391, 237, 149.

(**12c**) as an oil; Hnmr δ 2.50 (s 3H), 2.88-2.97 (d, J = 3 Hz, 1H), 3.43 (s, 3H), 3.73-3.90 (m, 2H), 4.05-4.43 (m, 4H), 4.65 (s, 1H), 5.62 (s, 1H), 7.13-7.67 (m, 5H), Cnmr δ 35.32, 55.73, 58.64, 62.92, 68.16, 69.46, 76.95, 101.07, 102.67, 126.38, 127.51, 128.36, 128.63, 129.18, 137.47.

***N*-Formyl-*trans*-3,4-diphenylpyrrolidines (13) and (14).** The mixture of diastereomeric pyrrolidines (**10b**) and (**11b**) (28.3 mg, 0.06 mmol) was treated with 50% NaOH (0.5 ml) in $CHCl_3$ (6 ml), in the presence of catalytic amounts of TBABr. It yielded, after usual work up and preparative tlc (heptane-AcOEt 50:50), epoxide (**8**) identical with an authentic sample[8] (15.0 mg, 99%) and the enantiomerically enriched (3R,4R)-(**13**) (12.4 mg, 82%).

(**13**) as an oil; Hnmr δ 3.27-3.73 (m, 4H), 3.93-4.17 (m, 2H), 6.99-7.39 (m, 10H), 8.27 (s, 1H); Cnmr δ 50.34, 50.58, 51.18, 53.13, 127.29, 127.41, 127.54, 128.85, 138.51, 160.88; ms m/z 251, 180 178, 147, 104; $[\alpha]_D^{25}$ -75.7° (c 0.90, $CHCl_3$).

The same reaction run with the diastereomeric pyrrolidines (**10c**) and (**11c**) (78 mg, 0.16 mmol) yielded, after usual work-up and chromatography on alumina, epoxide (**9**) (39mg, 90%, pentane-AcOEt 3:1) and the enantiomerically enriched (**3S,4S**)-(**14**) as an oil, (38 mg, 94%). Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.81. Found: C, 80.92; H, 6.91. $[\alpha]_D^{25}$ +76° (c 1.1, $CHCl_3$).

***trans*-(3R,4R)-Diphenylpyrrolidine (15).** Hydrolysis of (**13**) (31 mg, 0.12 mmol) with KOH (55mg, 1 mmol) in EtOH(0.5ml) yielded enantiomerically enriched (**15**) after usual work up (24 mg, 90%). Hnmr δ 3.17-4.07 (m, 7H), 6.89-7.50 (m, 10H); ms m/z 223, 105, 91; $[\alpha]_D^{25}$-138° (c 1.3, $CHCl_3$)[10]; lit.,[10] $[\alpha]_D^{20}$ -226° ($CHCl_3$).

***trans*-(3S,4S)-Diphenylpyrrolidine (16).** Hydrolysis of **14** (19.8 mg, 0.08 mmol) with KOH (45mg, 0.8 mmol) in EtOH (0.5 ml) yielded (**16**) after usual work-up (16.7 mg, 95%); $[\alpha]_D^{25}$ +142° (c 0.8, $CHCl_3$)

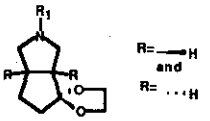
REFERENCES AND NOTES

1. (a) R. Huisgen, "1,3-Dipolar Cycloaddition. Introduction, Survey and Mechanism" in "1,3-Dipolar Cycloaddition Chemistry," ed. by A. Padwa, Wiley, New-York, **1986**, pp. 1-163; (b) E. Vedejs, "Advances in Cycloaddition" Vol. **33**, ed. by D. P. Curran, JAI Press Inc., Greenwich, **1988**, p. 33. (c) O. Tsuge and S. Kanemasa, Advances Heterocycl. Chem., **1989**, 45, 231.
2. (a) A. Padwa, Y. Chen, V. Chiacchio and W. Dent, Tetrahedron, **1985**, 41, 3529. (b) J. Rouden, J. Royer and H. P. Husson, Tetrahedron Lett., **1989**, 30, 5133. (c) P. Deprez, J.Royer and H. P. Husson, Tetrahedron Asymmetry, **1991**, 2, 1189. (d) P. Deprez, J. Rouden, A. Chiaroni, C. Riche, J. Royer and H. P. Husson, Tetrahedron Lett., **1991**, 32, 7531. (e) A. S. Anslow, L. M. Harwood, H. Phillips, D. Watkin and L. F. Wong, Tetrahedron Asymmetry, **1991**, 2, 1343.
3. For recent results concerning 1,3-dipolar cycloaddition of achiral azomethine ylides to homochiral activated olefinic dipolarophiles, see A. G. H. Wee, J. Chem. Soc., Perkin Trans. I, **1989**, 1363; S. Kanemasa and H.Yamamoto, Tetrahedron Lett., **1990**, 31, 3633; R. Annunziata, M. Cinquini, F. Cozzi, L. Raimondi and T. Pilati, Tetrahedron Asymmetry, **1991**, 2, 1329.
4. (a) R. Beugelmans, L. Benadjila-Iguertsira, J. Chastanet, G. Negron, and G. Roussi, Can. J. Chem., **1985**, 728; G. Roussi and J. Zhang, Tetrahedron, **1991**, 47, 5161 and references cited herein. (b) G. Negron and G. Roussi, Heterocycles, **1992**, 34, 293. (c) The formation of a demethylated amine has already been observed with dimethylaniline-*N*-oxide.[1a] We do not think that these byproducts could have come from hydrolysis of the unreacted corresponding ylides **Y** or iminiums **I**, because their yields are unaffected by the reaction times. Experiments are in progress to determine the origin of these compounds.
5. G. Roussi and J. Zhang, Tetrahedron Lett. , **1991**, 32, 1443.
6. M. Yamada, K.Tachibana, T. Kuroda,and T. Sakakibara, Carbohydrate Res., **1983**, 112, 189.
7. R. D. Guthrie and M. A. Prior, Carbohydrate Res., **1971**, 18, 373.
8. D. R. Hicks and B. Fraser-Reid, Synthesis, **1974**, 203.
9. N. K. Richtmyer, Methods Carbohydr. Chem., **1962**, 107.
10. K. Tomioka, M. Nakajima, and K. Koga, Chem. Lett., **1987**, 65. We thank Prof. Tomioka for a gift of reference compound (**15**). The measured optical rotation value of the enantiomerically enriched pyrrolidines **15** {$[\alpha]_D^{25}$ -138° (c 1.3, $CHCl_3$)} and (**16**) {$[\alpha]_D^{25}$ +142° (c 0.8, $CHCl_3$)}, instead of -

158° expected, is doubtless due to the fact that **(15)** and **(16)** were obtained in small quantities which did not allow complete purification.

11. L. Castedo, J. L.Castro, and K. Riguera, Tetrahedron Lett., **1984**, 25, 1205.

12. In a preliminary experiment, the cycloaddition has been performed with cyclopenten-1-one ethylene ketal as dipolarophile. The expected diastereomeric pyrrolidines were obtained in 30% yield in a 65:35 ratio. No separation was attempted. Amine **(12b)** was competitively formed. The difference in selectivity can be accounted by the fact that, in this case, the dipolarophile bears only one substituent able to induce asymmetry.



13. E. Conway, R. D. Guthrie, S. D. Gero, G. Lukacs and A. M. Sepulchre, J. Chem. Soc., Perkin Trans. II, **1974**, 542.

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