Pergamon

Tetrahedron Vol. 51, No. 22, pp. 6285-6292, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4020/95 $9.50+0.00

0040-4020(95)00283-9

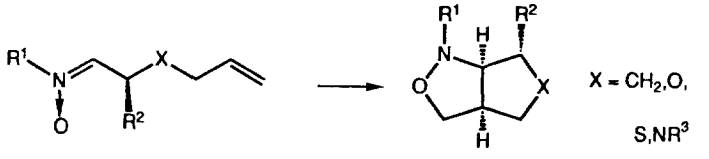
The Enolate Group as Dipolarophile in Intramolecular Cycloaddition of Nitrones

Hans Günter Aurich*, Heiner Köster

Fachbereich Chemie der Philipps-Universität Marburg, D-35032, Germany

Abstract: Nitrones **5** were prepared starting from N-benzylalaninol **3**. Michael addition of **3** to 3-butenone-2 afforded alcohol **4** which was converted to **5** by Swern oxidation and subsequent treatment of the resulting aldehyde with N-alkylhydroxylamines. The enolate group of nitrones **6** generated by treatment of **5** with LDA acted as dipolarophile attacking the nitrone group to give the bicyclic compounds **7** by a spontaneous intramolecular cycloaddition. This took place with high diastereoselectivity affording only one diastereomer in 23 to 65% yield. The two substituents at position 4 give rise to a change in conformation of compounds **7** compared to compounds **8** unsubstituted at this position

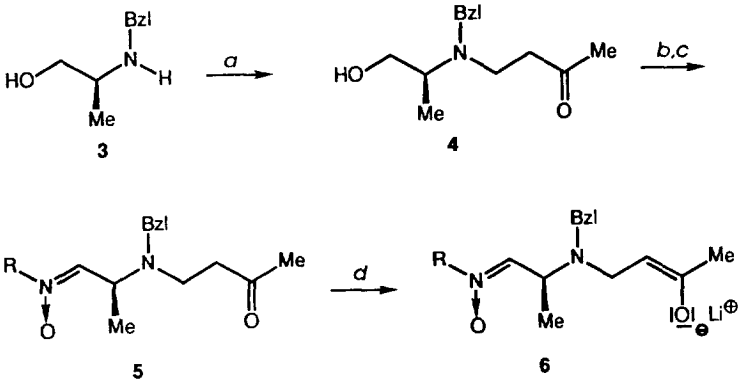
The synthetic potential of the intramolecular cycloaddition of alkenyl nitrones discovered by Le Bel[1] in 1959 has rapidly increased in last years.[2] In particular, the cycloaddition of C-4-alkenyl nitrones (5-hexenyl-imin-N-oxides) **1** X = CH_2 has been of growing interest, since it proceeds usually with high regio- and stereoselectivity.[3] Furthermore, a particularly high asymmetric induction arises if the carbon atom at position 2 is a chiral center.[4] Introduction of a hetero atom in the tether of **1** between nitrone and alkene moiety extends the scope of this reaction additionally.[2b,5] So far we have studied the intramolecular cycloaddition of 5-hexenyl-imine-N-oxides **1** in which the methylene group at position 3 is replaced by a heteroatom such as nitrogen, oxygen or sulfur.[5a]



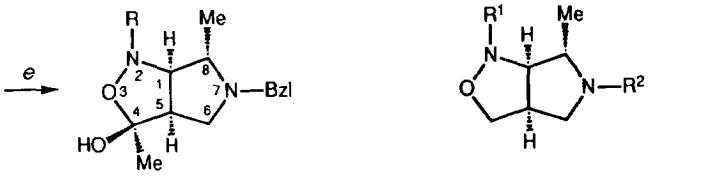
1 **2**

In this paper we report on the intramolecular cycloaddition of nitrones in which an enolate group operates as dipolarophile instead of a simple alkene group. As far as we know an enolate group generated from a keto group by proton abstraction has never been used as dipolarophile in this reaction.

The nitrones **5** were synthesized as follows: At first (S)-(+)-5-benzyl-7-hydroxy-6-methyl-5-azaheptanone-2 (**4**) was prepared by nucleophilic addition of N-benzylalaninol (**3**) to 3-butenone-2. Swern oxidation[6] of **4** gave the corresponding aldehyde which was treated with N-alkylhydroxylamines without isolation to afford the nitrones **5a-c**.



3 **4** **5** **6**



7 **8**

a : R = tBu
b : R = Bzl
c : R = Me

a : R^1 = tBu, R^2 = Bzl
b : R^1 = R^2 = Bzl
c : R^1 = tBu, R^2 = Allyl

a: CH_2=CH—COMe *b*: DMSO, $(COCl)_2$, Et_3N *c*: R—NHOH
d: LDA, THF, -78°C *e* : -78°C → rt, 4h

These were converted to lithium enolates **6** by reaction with lithium diisopropylamide in tetrahydrofuran at -78°C. When the reaction mixture was allowed to warm up to room temperature intramolecular cycloaddition of the enolate group to the nitrone moiety occurred affording the 4-hydroxy-4-methyl-3-oxa-2.7 diazabicyclo[3.3.0]octanes 7 in 23 to 65% yield.

Compounds **7** were obtained as diastereomerically pure optically active substances. The constitution of compounds 7 followed from their ^{13}C NMR data. The most conspicuous signal is that of C-4 at 101.2-102.4 ppm[7] confirming the existence of the semiketal group.

With the exception of the specific substituent R there were only negligible deviations in the ^{1}H and ^{13}C NMR spectra of the three compounds **7a-c**, suggesting that the same configuration must be ascribed to them. The configuration at C-4 was detected by NOE difference spectroscopy[8] of **7a**. Upon irradiation with the frequency of the methyl group at C-4 the intensity of the signals of 5-H (2.3%) and 6β-H (0.6%) increased. Thus the methyl group and 5-H must be cis-orientated.

Further information on the configuration of compounds **7a-c** comes from the coupling constants J 1-H/8-H which are smaller than one hertz. This is only in accordance with a trans orientation of these protons. Since both five-membered rings can only be cis-fused for steric reasons and the configuration at C-8 is given by the starting compound (S)-alanine, compounds **7** must be described as (1R,4S,5R,8S)-3-oxa-2.7-diazabicyclo[3.3.0]octanes. The high diastereoselectivity of the intramolecular cycloaddition of lithium enolates **6** may be explained by the following arguments.

Since an attack of the alkene moiety to the nitrone group from the Si side would give rise to a stronger steric interaction between nitrone oxygen and methyl group at position 2, the attack from the Re side with a minor steric interaction between oxygen and hydrogen is more favorable (Figure 1). Thus the trans-orientation at positions 1 and 8 in bicyclic compounds **7** is determined. The position of the hydroxy group in the product is presumably determined by a favorable chelation between the oxygen of the nitrone group and the lithium atom in the transition state as illustrated in Figure 1.

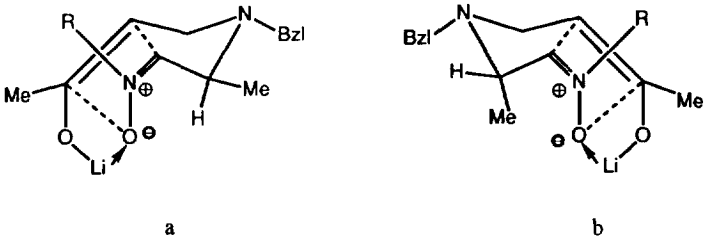


Figure 1. Nitrone group is attacked a) from the Re side b) from the Si side

Whereas 3-oxa-2.7-diazabicyclo[3.3.0]octanes **8** which are unsubstituted at position 4 exist in conformation B as was confirmed by X-ray analyses as well as by the ^{1}H NMR coupling constants[9] the bicyclic compounds **7** prefer conformation A (Figure 2). This is revealed by comparison of the ^{1}H NMR data, in particular the coupling constants, of **7** and **8** (Table 1).

Table 1. Comparison of some ^{1}H NMR Data of Compounds **7** and **8**

		1-H	5-H	6-Hα	6-Hβ	8-H	CH_3	J1/5	1/8	5/6α	5/6β
7	a R^1=tBu	3.23	2.66	2.56	2.82	3.15	0.92	9.7	<1	5.6	<1
	b R^1=Bzl	3.09	2.85	2.54	2.83	2.72	0.58	9.4	<1	5.9	<1
8	a R^1=tBu	3.47	3.02	3.14	2.01	2.31	1.24	9.2	7.0	9.1	7.7
	b R^1=Bzl	3.29	3.16	3.19	1.99	2.26	1.04	7.5	7.5	8.3	7.9

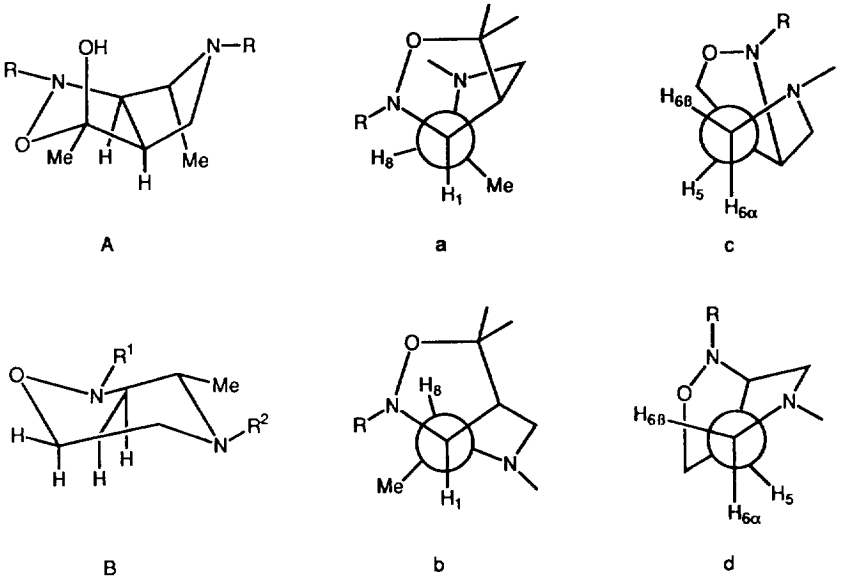


Figure 2. Possible conformations of compounds **7**. a) A: view along C-1/C-8 bond. b) B: view along C-1/C-8 bond. c) A: view along C-6/C-5 bond. d) B: view along C-6/C-5 bond

Most informative is the difference of J 1/8 between the two types of bicyclic compounds. From molecular models it can be seen that in conformation A the dieder angle H_1-C_1-C_8-H_8 should be about 90° (Figure 2a). In accordance with this prediction the coupling constants for **7a-c** are smaller than 1Hz. In contrast, the coupling constants J 1/8 of **8a** and **8b** are 7.0 and 7.5 Hz, respectively, according to an angle of approximately 150-160° (Figure 2b) as can be derived with the aid of the Karplus equation.[10] A similar situation arises for the coupling constants 5/6β. In **7** the protons 5- and 6β-H are approximately perpendicular orientated (Figure 2c), hence their coupling constants are again smaller than 1 Hz. On the other hand, the coupling constants of corresponding protons of **8a** and **b** fall in the range of 7.7-7.9 Hz, indicating an angle of about 155-160° (Figure 2d) which is roughly in agreement with the model. The conspicuous differences in the chemical shift of

6-Hα and 6-Hβ are also plausible. In **8** the 6-Hβ is opposite to the free electron pair of the adjacent nitrogen atom. Thus a considerable shift to higher field is caused. In contrast, in conformation A which compounds **7** adopt the 6-Hα is in a similar position. This is the reason for its high field shift, whereas the signal of the 6-Hβ which is now in a quasi-equatorial position undergoes a low field shift.

Since the 6-Hβ as well as the methyl group at position 4 are both in a quasi-equatorial position a small increase of the signal of 6-Hβ arises in the NOE experiment mentioned above.

Last not least, the high-field shift of the signal of the methyl group at C-8 on comparison of **8** and **7** is caused by the change from a quasi-equatorial position in **8** to a quasi-axial position in **7**.

Quite similar results concerning the dependence of conformation on the position of substitution were obtained by Hassner et al.[11], although the situation of the 3-oxa-2.7-diazabicyclo[3.3.0]octanes they studied was somewhat different insofar as they were unsubstitued at 2-position. However, in general they found that a substituent at position 8 favors conformation B, whereas substitution at position 4 favors conformation A, even if there is a substituent at C-8.

Experimental Part

Elemental analyses were performed by the division Routine Analytik, Fachbereich Chemie, University of Marburg. Spectra were recorded with following instruments: ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz): Bruker AC 300; Solvent $CDCl_3$, internal standard residue of ^{1}H (δ = 7.25 ppm) or of ^{13}C (δ = 77.0 ppm). - MS: Varian CH 7 (EI) and 711 (FD). - IR: Beckman IR 33 and Bruker IFS 88-FT-IR. Optical rotation: Polarimeter Perkin Elmer 241, at 589 nm.

(S)-(+)-5-Benzyl-7-hydroxy-6-methyl-5-azaheptanone-2 (**4**): N-Benzylalanine[12] was reduced to the corresponding alcohol **3** by the procedure described by Giannis and Sandhoff[13]. A solution of **3** (1.65 g, 10 mmol) and 3-butenone-2 (0.77 g, 11 mmol) in chloroform (50 mL) was stirred for 24 h at room temperature. After removal of the solvent **4** was obtained in 98% yield (2.30 g). Colourless liquid $[\alpha]_D^{25}$ = 48.2 - $C_{14}H_{21}NO_2$ (235.2) Calcd. C 71.53, H 8.93 N 5.95 Found C 71.31 H 9.02 N 5.82 - MS (EI): m/z (%) = 235 (100, M^+) - IR (neat): 3450 (OH), 1720 cm^{-1} (C=O). - ^{1}H NMR: δ = 0.84 (d, ^{3}J = 6.7 Hz, 3H, CH_3); 1.87 (s, 3H, CH_3); 2.47 (m, 3H, 3-H, 3-H', 4-H); 2.82 (m, 1H, 4-H'); 2.90 (dqd, ^{3}J = 10.8, 6.7, 5.0 Hz, 1H, 6-H); 3.28 (dd, ^{2}J = 16.0, ^{3}J = 5.0 Hz, 1H, 7-H); 3.32 (d, ^{2}J = 13.8 Hz, 1H, CH_2Ph); 3.35 (dd, ^{2}J = 16.0, ^{3}J = 10.8 Hz, 1H, 7-H'); 3.66 (d, ^{2}J = 13.8 Hz, 1H, CH_2Ph); 7.17-7.27 (m, 5H, ArH). - ^{13}C NMR: δ =9.1 (CH_3), 30.0 (C-1), 42.6 and 43.6 (C-3 and C-4); 54.2 (CH_2Ph); 56.7 (C-6); 63.2 (C-7); 126.8, 128.0, 128.6, 139.7 (Ar); 208.0 (C-2).

Formation of nitrones **5**: A solution of DMSO (0.60 mL, 8.6 mmol) in CH_2Cl_2 (5 mL) was dropped at -78°C to a stirred solution of $(COCl)_2$ (0.64 g, 5 mmol) in CH_2Cl_2 (50 mL). After 15 min a solution of **4** (4.2 mmol) in CH_2Cl_2 (20 mL) was added in drops. Stirring was continued at -78°C for 1 h, then Et_3N (2.26 mL,

16.2 mmol) was added. After 5 min the reaction mixture was allowed to warm up to 0°C. Subsequently water (20 mL), N-alkylhydroxylamine (4.62 mmol) and anhydrous $MgSO_4$ (10g) were added. The mixture was stirred for 12 h, then the organic layer was washed with water and subsequently dried with $MgSO_4$. After removal of the solvent at reduced pressure the crude material which easily decomposes was subjected to cycloaddition without further purification.

5a: yield 85%, colourless oil. - MS (EI): m/z (%) = 304 (100, M^+) - IR (neat): 1730 cm^{-1}. - ^1H NMR: δ = 1.19 (d, J = 6.7 Hz, 3H, CH_3); 1.39 (s, 9H, $C(CH_3)_3$); 1.97 (s, 3H, CH_3); 2.50 (t, J = 7.1 Hz, 2H, 3-H); 2.77 (t, J = 7.1 Hz, 2H, 4-H); 3.51 (d, ^2J = 14.4 Hz, 1H, CH_2-Ph); 3.59 (d, ^2J = 14.4 Hz, 1 H, CH_2-Ph); 4.10 (qd, J = 6.7, J = 6.5 Hz, 1H, 6-H); 6.83 (d, J = 6.5 Hz, 1H, 7-H); 7.10-7.25 (m, 5H, Ar-H); - ^{13}C NMR: δ = 13.6 (CH_3), 28.0 [$C(\underline{C}H_3)_3$]; 30.5 (C-1); 42.1 (C-3); 46.3 (C-4); 53.3 (C-6); 55.6 (CH_2Ph); 69.5 [$\underline{C}(CH_3)_3$]; 136.6 (C-7); 208.2 (C-2); 127.1, 128.4, 140.1 (Ar).

5b: yield 85%, brown-red oil. - MS (EI): m/z (%) = 338 (100, M^+) - IR (neat): 1740, 1720 cm^{-1}. - ^1H NMR: δ = 1.16 (d, J = 6.8 Hz, 3H, CH_3); 1.91 (s, 3H, 1-H); 2.44 (dt, ^2J = 7.2, ^3J = 6.8 Hz, 1H, 4-H); 2.71 (m, 2H, 3-H); 2.90 (td, ^3J = 7.3, ^2J = 7.2 Hz, 1H, 4-H'); 3.46 (d, ^2J = 14.2 Hz, 1H, CH_2-Ph); 3.59 (d, ^2J = 14.2 Hz, 1H, CH_2-Ph); 4.10 (quint., J = 6.8 Hz, 1H, 6-H); 4.75 (s, 2H, CH_2-Ph); 6.73 (d, J = 6.8 Hz, 1H, 7-H); 7.10-8.14 (m, 10H, Ar-H); - ^{13}C NMR: δ = 13.8 (CH_3), 30.2 (C-1); 41.9 (C-3); 45.9 (C-4); 52.5 (C-6); 55.3 (CH_2Ph); 69.5 (CH_2-Ph); 140.9 (C-7); 207.9 (C-2); 126.6, 128.1, 128.3, 128.7, 128.9, 133.0, 139.5 (Ar).

5c: yield 90%, red oil. - MS (EI): m/z (%) = 262 (29, M^+) - IR (neat): 1750 cm^{-1}. - ^1H NMR: δ = 1.19 (d, J = 6.8 Hz, 3H, CH_3); 1.96 (s, 3H, CH_3); 2.48 (m, 2H, 3-H); 2.75 (m, 2H, 4-H); 3.52 (d, ^2J = 14.2 Hz, 1H, CH_2-Ph); 3.55 (s, 3H, CH_3); 3.63 (d, ^2J = 14.2 Hz, 1 H, CH_2-Ph); 4.07 (qd, J = 6.8 and 6.7 Hz, 1H, 6-H); 6.71 (d, J = 6.7 Hz, 1H, 7-H); 7.08-7.30 (m, 5H, Ar-H); - ^{13}C NMR: δ = 13.4 (CH_3), 30.3 (C-1); 40.1 (C-3); 45.8 (C-4); 52.7 (C-6); 52.7 (CH_3); 55.4 (CH_2Ph); 141.9 (C-7); 207.9 (C-2); 126.7, 128.2, 139.6 (Ar).

Formation of the bicyclic compounds **7**: An 1.6 molar solution of n-butyllithium in hexane (12.5 mL, 20 mmol) was dropped to a solution of diisopropylamine (2.8 mL, 20 mmol) in THF at -78°C. After an interval of 15 min. a solution of nitrone **5** (15 mmol) in THF (20 mL) was added drop by drop. The reaction mixture was stirred for an hour at -78°C and then warmed up to room temperature during a period of 4 h. Then a saturated aqueous solution of NH_4Cl (8 mL) was added and the solvent was removed. The residue was dissolved in diethyl ether (100 mL) and washed with saturated solutions of NH_4Cl and NaCl, successively. Thereafter the organic layer was dried with $MgSO_4$. After removal of the solvent the crude product was purified by column chromatography on silica gel.

(1R,4S,5R,8S)-(+)-7-Benzyl-2-tert-butyl-4.8-dimethyl-4-hydroxy-3-oxa-2.7-diazabicyclo[3.3.0]octane (**7a**): Brown oil in 65% yield from chromatography (SiO_2, CH_3Cl/EtOAc 4:1, R_f = 0.26). $[\alpha]_D^{25}$ = 26.6° $C_{18}H_{28}N_2O_2$ (304.2) Calcd. C 71.10 H 9.20 N 9.20 Found C 71.27 H 9.25 N 9.18. - MS (FD): m/z (%) = 304 (100, M^+) - IR (neat): 3370 cm^{-1} (OH). - ^1H NMR: δ = 0.92 (d, 3H, CH_3); 1.07 (s, 9H, $C(CH_3)_3$); 1.35 (s, 3H,

CH_3); 2.56 (dd, 1H, 6-Hα); 2.66 (dd, 1H, 5-H); 2.82 (d, 1H, 6-Hβ); 3.15 (q, 1H, 8-H); 3.23 (d, 1H, 1-H); 3.60 (d, 1H, CH_2Ph); 3.71 (d, 1H, CH_2Ph), 7.20-7.31 (m, 5H, Ar-H); J 1/5 = 9.7, J 1/8 <1, J 5/6α = 5.6, J 5/6β <1, J 8/CH_3 = 6.9, ^{2}J 6α/β = 9.7, ^{2}J CH_2Ph = 13.1 Hz. - ^{13}C NMR: δ = 9.7 (CH_3), 22.8 (CH_3), 25.5 [C($\underline{C}H_3$)$_3$]; 49.5 (C-6); 53.9 (CH_2Ph); 54.9 (C-5); 57.4 [$\underline{C}(CH_3)_3$]; 62.2 (C-8); 70.2 (C-1); 101.2 (C-4), 127.2, 128.5, 138.2 (Ar).

(1R,4S,5R,8S)-(+)-2.7-Dibenzyl-4.8-dimethyl-4-hydroxy-3-oxa-2.7-diazabicyclo[3.3.0]octane (**7b**): Brown oil in 23% yield from chromatography (SiO_2, $CHCl_3$/EtOAc 3:1, R_f = 0.49 - $[\alpha]_D^{25}$ = 15.2° - MS (EI): m/z (%) = 338 (54, M^+) - IR (neat): 3400 cm^{-1} (OH). - ^{1}H NMR: δ = 0.58 (d, 3H, CH_3); 1.44 (s, 3H, CH_3); 2.54 (dd, 1H, 6-Hα); 2.72 (q, 1H, 8-H); 2.83 (d, 1H, 6-Hβ); 2.85 (dd, 1H, 5-H); 3.09 (d, 1H, 1-H); 3.57 (d, 1H, CH_2Ph); 3.62 (d, 1H, CH_2Ph), 3.80 (d, 1H, CH_2Ph); 4.42 (d, 1H, CH_2Ph), 7.20-7.50 (m, 10H, Ar-H); J 1/5 = 9.4, J 1/8 <1, J 5/6α = 5.9, J 5/6β <1, J 8/CH_3 = 6.9, ^{2}J 6α/β= 9.8, ^{2}J CH_2Ph = 13.2, ^{2}J CH_2Ph = 12.2 Hz. - ^{13}C NMR: δ = 9.2 (CH_3), 22.6 (CH_3), 49.2 (C-6); 53.5 (CH_2Ph); 54.7 (C-5); 60.1 (C-8); 62.4 (CH_2Ph); 76.9 (C-1); 102.1 (C-4), 125.5, 127.1, 128.0, 128.2, 128.4, 128.5, 132.6, 138.2 (Ar).

(1R,4S,5R,8S)-(+)-7-Benzyl-4-hydroxy-2.4.8-trimethyl-3-oxa-2.7-diazabicyclo[3.3.0]octane (**7c**): Brown oil in 45% yield from chromatography (SiO_2, $CHCl_3$/EtOAc 3:1, R_f = 0.39 - $[\alpha]_D^{25}$ = 18.3° - MS (EI): m/z (%) = 262 (100, M^+) - IR (neat): 3350 cm^{-1} (OH). - ^{1}H NMR: δ = 0.89 (d, 3H, CH_3); 1.35 (s, 3H, CH_3); 2.52 (dd, 1H, 6-Hα); 2.68 (s, 3H, CH_3); 2.78 (d, 1H, 6-Hβ); 2.82 (d, 1H, 1-H); 2.84 (dd, 1H, 5-H); 3.12 (q, 1H, 8-H); 3.60 (d, 1H, CH_2Ph), 3.65 (d, 1H, CH_2Ph); 7.20-7.35 (m, 5H, Ar-H); J 1/5 = 8.9, J 1/8 <1, J 5/6α = 5.2, J 5/6β <1, J 8/CH_3 = 6.9, ^{2}J 6α/β = 9.9, ^{2}J CH_2Ph = 13.1Hz. - ^{13}C NMR: δ = 10.2 (CH_3), 22.7 (CH_3), 45.0 (CH_3); 49.6 (C-6), 53.9(CH_2Ph); 55.2 (C-5); 59.6 (C-8); 79.7 (C-1); 102.4 (C-4), 127.3, 128.5, 138.3 (Ar).

Acknowledgement: We thank the Fonds der Chemischen Industrie for financial support.

References

1. Le Bel, N.A.; Whang, J.J., *J. Am. Chem. Soc.* **1959**, *81*, 6334-6335.
2. a) Torssell, K.B.G.; *Nitrile Oxides, Nitrones and Nitronates in Organic Synthesis*, VCH Publishers, **1988**, Chapter 5; b) Annuntiata, R.; Cinquini,M.; Cozzi, F.; Raimondi, L. *Gazz. Chim. Ital.* **1989**, *119*, 253, see pp. 266-268.
3. Wade, P.A. In *Comprehensive Organic Synthesis*, Trost, B.M.; Fleming, I.; Semmelhack, M.E. Eds.; Pergamon Press, Oxford **1991**, Vol. 4, pp. 1113-1114.
4. Bernet, B.; Vasella, A. *Helv. Chim. Acta* **1979**, *62*, 2411-2431.

5. a) Aurich, H.G.; Ruiz Quintero, J.-L. *Tetrahedron* **1994**, *50*, 3929-3942 and references cited there; b) Chiacchio, U.; Buemi, G.; Casuscelli, F.; Procopio, A.; Rescifina, A.; Romeo, R. *Tetrahedron* **1994**, *50*, 5503-5514; c) Wovkulich, P.M.; Baggiolini, E.G.; Hennessy, B.M.; Uskokovic, M.R.; *Heterocycles* **1993**, *35*, 791-806; d) Black, D.St.C.; Craig, D.C.; Deb-Das, R.B.; Kumar N. Aust. J. *Chem.* **1993**, *46*, 603-622; e) Tamura, O.; Yamaguchi, T.; Noe, K.; Sakamoto, M. *Tetrahedron Lett.* **1993**, *34*, 4009-4010; f) Tamura, O.; Yamaguchi, T.; Okabe, T.; Sakamoto, M. *Synlett* **1994**, 620-622; g) Rong, J.; Roselt, P.; Plavec, J.; Chattopadhyaya, J. *Tetrahedron* **1994**, *50*, 4921-4936; h) Tamura, O.; Okabe, T.; Yamaguchi, T.; Gotanda, K.; Noe, K.; Sakamoto, M. *Tetrahedron* **1995**, *51*, 107-118; i) Tamura, O.; Okabe, T.; Yamaguchi, T., Kotani, J.; Gotanda, K.; Sakamoto, M. *Tetrahedron* **1995**, *51*, 119-128.
6. a) Omura, K.; Swern, D. *Tetrahedron* **1978**, *34*, 1651-1660; b) Marx, M.; Tidwell, T.T. *J. Org. Chem.* **1984**, *49*, 788-793.
7. For simple acetals or ketals the signals of the carbon atom fall in the range from 99.3-109.9. Kalinowski, H.-O.; Berger, S.; Braun, S. *^{13}C-NMR-Spektroskopie*, Georg Thieme Verlag Stuttgart, **1984**, pp. 168-169.
8. Hesse, M.; Meier, H.; Zeeh, B. *Spektroskopische Methoden in der organischen Chemie*, Georg Thieme Verlag Stuttgart, **1991**, pp. 130-131.
9. a) Aurich, H.G.; Frenzen, G.; Gentes, C. *Chem. Ber.* **1993**, *126*, 787-795; b) Gentes, C. Dissertation, University of Marburg 1994, Verlag Shaker Aachen, pp. 26-29.
10. Reference 8 pp. 105
11. Hassner, A.; Maurya, R.; Friedman, O.; Gottlieb, H.E. *J. Org. Chem.* **1993**, *58*, 4539-4546.
12. Quitt, P.; Hellerbach, J.; Vogler, K. *Helv. Chim. Acta* **1963**, *46*, 327-333.
13. Giannis, A.; Sandhoff, K. *Angew. Chem.* **1989**, *101*, 220-222; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 218-220.

(*Received in Germany* 27 *March* 1995; *accepted* 5 *April* 1995)