1.5 h, the reaction was cooled to room temperature and allowed to stand overnight. The reaction mixture was worked up by rinsing the $CHCl_3$ solution with saturated $NaHCO_3$, followed by saturated brine. The $CHCl_3$ solution was then dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed by rotary evaporation to give 90 mg of a clear oil. GLC analysis showed that no starting material remained, and two new products in the approximate ratio of 1:1 were present. Samples of each were collected by GLC, and submitted to NMR analysis.

15: ^{1}H NMR (ppm from Me_4Si) 5.39 (s, 2 H), 3.79 (d, 2 H), 3.53 (d, 2 H), 1.83 (m, 2 H), 1.79 (s, 6 H), 1.65–1.32 (m, 4 H); MS, M^+ 190, 175, 145 (base), 131, 115, 105, 91.

17: ^{1}H NMR 5.45 (s, 1 H), 4.98 (br s, 1 H), 4.85 (d, 1 H), 3.77 (d, J = 7.5 Hz, 1 H), 3.70 (d, J = 7.5 Hz, 1 H), 3.61 (d, J = 2.5 Hz, 1 H), 3.58 (d, J = 2.5 Hz, 1 H), 2.39 (d, 1 H), 2.26 (d, 1 H), 1.87 (allylic doublet, 3 H), 1.80–1.55 (m, 6 H); MS, M^+ 190, 175, 158, 145 (base), 131, 117, 105, 91.

Epoxidation of 13 at 0 °C. To 20 mg of **13** in 15 mL of CH_2Cl_2 at 0 °C under N_2 was added 20 mg of MCPBA in 5 mL of the same solvent. The reaction mixture was stirred at 0 °C for about 72 h, after which time it was worked up as described above. GLC analysis demonstrated that all of the **13** had been consumed, and that only a trace of the dienes (**15** and **16**) were present. The major products (1:1) were collected by GLC and identified as the epoxides **18** and **19**.

17: ^{1}H NMR 3.69 (d, 2 H)8 3.27 (d, 2 H), 2.01 (d, 2 H), 1.88 (d, 2 H), 1.85 (m, 2 H), 1.55–1.30 (m, 4 H), 1.27 (s, 6 H); MS, M^+ 208, 193, 177, 163, 151, 145 (base), 135, 121, 109; HRMS calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1476.

18: ^{1}H NMR 3.73 (d, 2 H), 3.57 (d, 2 H), 1.96 (d, 2 H), 1.67 (d, 2 H), 1.70–1.40 (m, 6 H), 1.29 (s, 6 H); HRMS calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1443.

Epoxidation of 14. Treatment of 60 mg of **14** with 65 mg of MCPBA for 24 h at 20 °C in 20 mL of chloroform gave 66 mg (100%) of a clear liquid that was analyzed by GLC (10% DEGS, 10 ft × $^1/_8$ in., 180 °C), demonstrating the presence of two products (**19** and **20**) in the ratio of 53.1:46.9, respectively.

19: ^{1}H NMR 3.66 (d, 2 H), 3.37 (d, 2 H), 3.14 (dd, 2 H), 2.10 (ddd, 2 H), 1.93 (dd, 2 H), 1.82 (m, 2 H), 1.65–1.45 (m, 4 H); MS, 180, 162, 149, 132, 117, 91, 79 (base); HRMS calcd for $C_{11}H_{16}O_2$ 180.1150, found 180.1163.

20: ^{1}H NMR 3.73 (d, 2 H), 3.57 (d, 2 H), 3.13 (dd, 2 H), 2.19 (ddd, 2 H), 1.77 (dd, 2 H), 1.70–1.40 (m, 6 H); MS, 180, 162, 149, 132, 117, 91, 79 (base); HRMS calcd for $C_{11}H_{16}O_2$ 180.1150, found 180.1155.

Oxymercuration of 14. To a magnetically stirred solution of 1 equiv (0.29 g) of $Hg(OAc)_2$ in 10 mL of MeOH was added 0.15 of **15**, followed by *one drop* of concentrated HNO_3. After stirring for 18 h, 1 equiv (48.6 mg) of NaOMe was added and the solution was stirred an additional hour. Then 0.5 M NaOH (5 mL) was added, followed by excess $NaBH_4$. The reaction was stirred briefly and then allowed to settle before being filtered through Celite. Removal of solvent afforded 0.17 g (95%) of a yellow liquid that by GLC (10 ft × $^1/_8$ in., 10% DEGS, 150 °C, 40 psi He) showed only two peaks in a 1:1 ratio.

21: ^{1}H NMR 3.75 (dd, 2 H), 3.68 (dd, 2 H), 3.32 (d, 3 H), 2.00–1.20 (m, 10 H); MS 196, 168, 166, 149, 137 (base); 119, 93, 91, 79; HRMS calcd for $C_{12}H_{20}O_2$ 196.1463, found 196,1456.

22: ^{1}H NMR 3.68 (dd, 2 H), 3.61 (dd, 2 H), 3.31 (s, 3 H), 2.00–1.10 (m, 10 H); MS, 196, 168, 166, 149, 119, 93, 91, 79; HRMS calcd for $C_{12}H_{20}O_2$ 196.1463, found 196.1466.

Acknowledgment. The support of the NSF (ISP-801149) for this work is gratefully acknowledged, as its partial support toward acquisition of the NMR and mass spectrometers used in this study. The partial support of the Murdock Foundation toward acquisition of our mass spectrometers is also acknowledged.

Registry No. **13**, 88316-98-7; **14**, 15405-07-9; **15**, 91631-44-6; **16**, 91631-45-7; **17**, 91631-46-8; **18**, 91738-60-2; **19**, 91631-47-9; **20**, 91738-61-3; **21**, 91631-48-0; **22**, 91738-62-4.

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^{15}N and ^{13}C NMR Study of *N*-Methyl-*N*-nitrosoaniline and Its Ring-Substituted Derivatives

Robert Kupper,[†] Bruce D. Hilton,[‡] Marilyn B. Kroeger-Koepke,[†] Steven R. Koepke,[†] and Christopher J. Michejda*[†]

LBI-Basic Research Program and PRI, Inc., Chemical Carcinogenesis Program, NCI-Frederick Cancer Research Facility, Frederick, Maryland 21701

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^{15}N and ^{13}C NMR spectra of *N*-nitroso-*N*-methylaniline and 15 meta and para ring-substituted derivatives have been measured. Complete assignments of all the atoms have been made. Correlations of the ring carbon-1, the amino nitrogen, the nitroso nitrogen, and the methyl carbon chemical shifts with substituent constants have been obtained. It is shown that the ring carbon shift is primarily influenced by π electron density at that position. The chemical shifts of the exocyclic atoms are explained in terms of the substituent effects on the resonance structure of the nitrosamino moiety. It is shown that the amino nitrogen is relatively invariant with substitution because its net hybridization (percent s character) remains relatively constant. The nitroso nitrogen shift correlates with Hammett σ constants with a positive slope, while the methyl carbon exhibits a small but negative correlation. This is explained in terms of increasing double bond character of the N–N bond as the substituents become more electron donating.

Introduction

NMR spectroscopy of heteroatoms has become a very important adjunct to more conventional proton and ^{13}C spectroscopy. The reason for this outburst of activity has been the development of pulsed high field multinuclear spectrometers which allow the observation of low sensitivity nuclei in natural abundance. The development of ^{15}N NMR spectroscopy as a widely used tool was pioneered by Roberts and his co-workers.[1] Most classes of nitrogen compounds have been examined during the past decade,

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[†] LBI-Basic Research Program.

[‡] PRI, Inc.

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Table I. Chemical Shifts of Substituted *N*-Nitroso-*N*-methylanilines

substituent	C-1	C-2	C-3	C-4	C-5	C-6	C_N	N-1	N-2
4-OCH_3[a]	135.6	121.0	114.5	158.7	114.5	121.0	31.99	−129.9	161.3
4-CH_3[b]	139.7	119.1	129.7	137.1	129.7	119.1	31.64	−129.1	163.5
4-$CH(CH_3)_2$[c]	140.0	119.2	127.2	148.0	127.2	119.2	31.61	−129.0	164.0
3-CH_3[d]	142.2	116.2	139.4	127.9	129.2	119.8	31.26	−128.6	164.9
H	142.0	118.9	129.2	127.0	129.2	118.9	31.20	−128.5	165.4
4-F[h]	138.5	121.0	116.1	161.4	116.1	121.0	31.64	−130.1	165.0
3-OCH_3[e]	143.4	105.0	160.4	112.7	130.1	111.0	31.20	−128.7	165.9
4-Cl	140.6	119.9	129.4	132.6	129.4	119.9	31.10	−130.1	166.1
4-Br	141.1	120.1	132.3	120.4	132.3	120.1	30.97	−130.0	166.1
3-F[i]	143.4	106.3	162.8	113.7	130.6	114.1	30.76	−129.2	167.8
3-Cl	143.1	118.8	135.0	126.8	130.3	116.6	30.77	−129.5	167.5
3-Br	143.1	121.5	122.8	129.7	130.5	117.0	30.80	−129.8	167.5
3-CF_3[f,j]	143.0	115.6	132.0	123.7	130.3	122.0	30.86	−129.8	168.4
4-CF_3[g,k]	145.1	118.4	126.5	128.8	126.5	118.4	30.45	−129.2	169.9
3-NO_2	143.1	113.1	148.6	121.2	130.4	123.9	30.61	−129.8	169.6
4-NO_2	147.1	117.9	125.2	145.9	125.2	117.9	30.06	−128.5	173.6

[a] OCH_3 55.42 ppm. [b] $-CH_3$, 20.64. [c] $-CH(CH_3)_2$, 33.65, 23.88. [d] CH_3, 21.39. [e] OCH_3, 55.4. [f] CF_3, 123.9 [g] CF_3, 124.2. [h] $J_{^{19}F-^{13}C}$ (Hz), $C_1 = 3$, $C_2 = C_6 = 8$, $C_3 = C_5 = 23$, $C_4 = 247$. [i] $J_{^{19}F-^{13}C}$ (Hz), $C_8 = 9$, $C_2 = 20$, $C_3 = 245$, $C_4 = 25$, $C_5 = 10$, $C_6 = 0$. [j] $J_{^{19}F-^{13}C}$ (Hz), $C_1 = 0$, $C_2 = 4$, $C_3 = 33$, $C_4 = 4$, $C_6 = 0$, $CF_3 = 273$. [k] $J_{^{19}F-^{13}C}$ (Hz), $C_3 = C_5 = 4$, $C_4 = 32$, $CF_3 = 272$.

and the spectra of aromatic amines and related substances have been determined by several groups. The natural abundance ^{15}N spectra of aniline and various substituted derivatives were obtained in 1974 by Lichter and Roberts,[2] who utilized time averaging techniques to obtain spectra with usuable signal-to-noise. Axenrod and co-workers examined the ^{15}N spectra of enriched anilines[3] in 1971 and anilinium ions[4] in 1976. Anet and Ghiaci[5] measured the aromatic C–N rotation barriers in *N*-methylaniline and *p*-nitro-*N*-methylaniline and compared them to the values predicted from the position of the ^{15}N chemical shift in those compounds. The latter is possible because the chemical shift of ^{15}N is known to be dominated by the paramagnetic term in the expression for the chemical shift of a nucleus in a molecule. This term, in turn, is dominated by the amount of π bonding at the nitrogen.[6] Barriers to rotation in *N*,*N*-dimethylanilines and anilines were determined from the chemical shifts of ^{15}N by Dorie, Mechin, and Martin.[7] Recently, Gouesnard and Martin[8] determined the ^{15}N and ^{13}C spectra of a number of nitrosamines, including *N*-nitroso-*N*-methylaniline, and compared these with the spectra of hydrazones, triazenes, and protonated nitrosamines.

The present paper discusses the ^{15}N and ^{13}C NMR spectra of a variety of substituted *N*-nitroso-*N*-methylanilines (NMA's) and attempts to correlate the chemical shifts with the unique characteristics of the nitrosamino function.

Experimental Section

Chemicals. The preparation and characterization of various substituted *N*-nitroso-*N*-methylanilines and their proton NMR spectra have been described by us previously.[9] All of these substances exist as the *E* rotamers, with no evidence for the *Z* form (<1%).

NMR Spectroscopy. The ^{15}N spectra were obtained at 30.4 MHz on an Nicolet NT-300 wide-bore spectrometer. The 3-mL samples (33% by volume in $CDCl_3$) were contained in 12-mm tubes. The reference signal was obtained from neat deuterated nitromethane, contained in a 5-mm concentric tube. All of the ^{15}N spectra were obtained with the decoupler (1 watt) gated off during the delay times to suppress the variable NOE's. The acquisition time was 1.2 s, the recycle time was 4 s, and the pulse angle was 18°. Depending on the sample, 1000–40 000 transients were collected. No significant chemical shift variation was found in the ^{15}N spectra of 1.25%, 25%, 33%, and 50% solutions of *N*-nitroso-*N*-methylaniline. The ^{13}C spectra were obtained on a Varian XL-100 spectrometer with continuous broad band proton decoupling (10 W of decoupler power). The samples, 33% by volume in $CDCl_3$, were contained in 5- or 12-mm sample tubes.

Results and Discussion

Chemical Shift Assignment. The ^{13}C shifts were assigned readily on the basis of group shift effects on substituted benzenes.[10] The calculated chemical shifts usually fell within a few tenths of a part per million from the experimentally determined values. The assignments of the fluorine-containing substituents (*m*-F, *p*-F, *m*-CF_3, and *p*-CF_3) were aided further by the signatures of ^{19}F–^{13}C coupling constants, which are listed as footnotes in Table I for the relevant substituents. Thus, all of the ^{13}C lines could be assigned without ambiguity, as listed in the Table I.

The assignment of the nitrogen resonances was also straightforward. The aniline nitrogen was always upfield from the external nitromethane reference, while the nitroso nitrogen was far downfield.[8] All of the NMA's examined were predominantly in the *E* conformation (nitroso group oxygen syn to the methyl), hence no complications of doubling of the resonance lines due to the presence of the *Z* conformer were encountered.

Effect of Substituents on Chemical Shifts. The chemical shift correlations of the ring C-1, the *N*-methyl C(C_N), the amine nitrogen (N-1), and the nitroso nitrogen (N-2) with various substituent constants were examined. The ring carbon, C-1, shift failed to correlated in any regular pattern when the shifts of the meta- and para-substituted NMA's were plotted against a variety of substituent constants. A good correlation, however, was obtained when the difference between the shifts of the para substituent and the same meta substituent were plotted vs. σ_R, the "resonance substituent constant"[11] (Figure 1).

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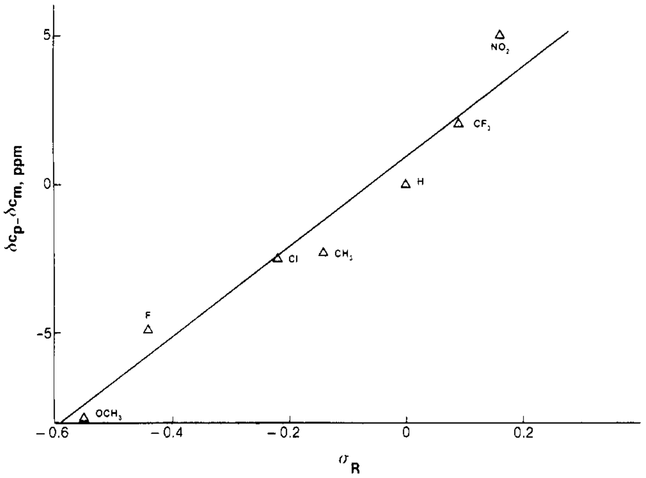
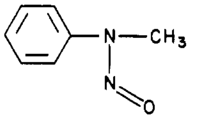


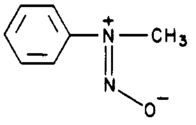
Figure 1. Correlation between the difference in the chemical shift of the C-1 carbon of para- and meta-substituted NMA's and the resonance constant, σ_R; correlation coefficient = 0.974.

A similar effect in substituted fluorobenzenes was observed by Maciel and Natterstad[12] who concluded that the corrected shift, $\delta c_p - \delta c_m$, was linearly related to the para π electron density as a result of resonance interaction with the substituent. It is interesting to note that the correlation is good over the range of substituents used in this study.

The shift correlations of the amino nitrogen (N-1), the nitroso nitrogen (N-2), and the methyl carbon (C_N) with the various substituents were very instructive. Reference to the table indicates that the chemical shift of N-1 is constant within 2 ppm over the whole range of substituents. This lack of a pronounced substituent effect contrasts sharply with the substituent effects observed in the ^{15}N spectra of anilines.[2,3] A likely reason for the lack of sensitivity to substituents in the NMA derivatives is connected with the electronic structure of the nitrosamines. It is well-known that nitrosamines can be represented, at least in zeroth-order approximation, as a combination of the resonance forms A and B, and calculations indicate that dipolar forms are a significant component of the hybrid.[13] Electron attracting substituents on the aromatic ring will tend to enhance the importance of the canonical form A at the expense of B. For example, in the extreme, the *p*-NO_2 group will withdraw electron density from the amino nitrogen, since one of the canonical forms will put a formal positive charge on that atom. In fact, all electron-attracting substituents will tend to destabilize B, even if valence bond structures such as C cannot be drawn, as is the case for the meta substituents. Conversely, all electron-donating substituents will tend to stabilize the canonical form B. Again, in the extreme, the *p*-OMe substituent will tend to place a negative charge on C-1.



A



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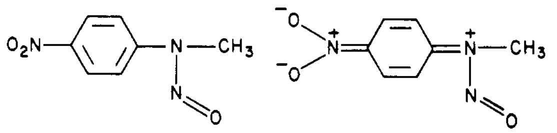

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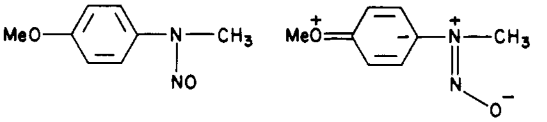

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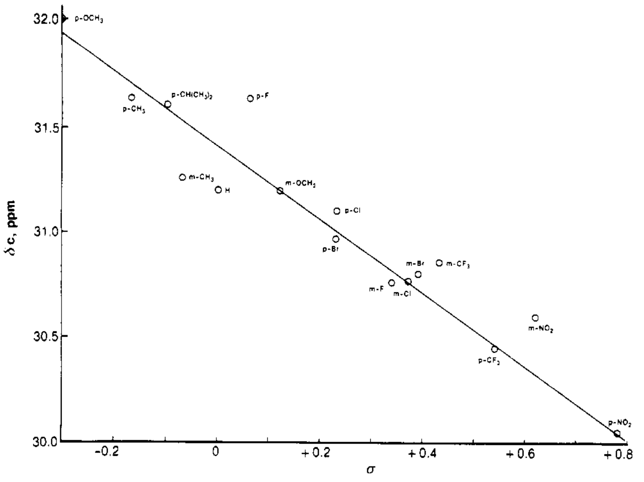

Figure 2. Correlation of the chemical shift of N-2, the nitroso nitrogen, of NMA's with the Hammett constants, σ; correlation coefficient = 0.969.

This simple analysis suggests that the electronic environment of the amino nitrogen of NMA will not change dramatically with substantial changes in the substituents. This is due to the fact that structures such as C and D will cause the net hybridization, and, therefore, the percent s character of that atom, to remain relatively constant. This means that the paramagnetic contribution to the total screening constant of N-1 does not change appreciably with the changes in the ring substituents.

This analysis also helps to explain the substituent effects on N-2 and on C_N. Reference to the table and to Figure 2 shows that the nitroso nitrogen chemical shifts are fairly well correlated by simple Hammett substituent constants. The only substituents which fall off the line are the strongly resonating *p*-NO_2 and *p*-OMe. In general, electron-attracting substituents cause a downfield shift and electron-donating substituents cause an upfield shift. Since electron-donating substituents stabilize the canonical form B, this situation causes the nitroso nitrogen to experience a net shielding environment in contrast to the electron-attracting substituents, which tend to stabilize form A. It is interesting to note in this regard that the principal substituent effect appears to be an inductive one, except for the *p*-MeO and *p*-NO_2 substituents, which exert their influence principally by resonance.

The effect on the methyl carbon (C_N) is in the opposite direction to that observed for the nitroso nitrogen. Figure 3 shows that the slope of the correlation is negative, indicating that the electron-attracting substituents produced upfield shifts. It should be noted that the range of shifts of that carbon are relatively small (>2 ppm). Since the electronic environment of the amino nitrogen, N-1, remains relatively constant over a wide change in substituents, its effect on the chemical shift of the methyl carbon will be negligible. We believe that the primary effect on the chemical shift of C_N is similar to that which causes the opposite correlation for the N-2 nitrogen. Consequently, substituents which enhance the importance of form B will tend to cause a downfield shift in C_N and electron-attracting substituents will tend to stabilize form A and

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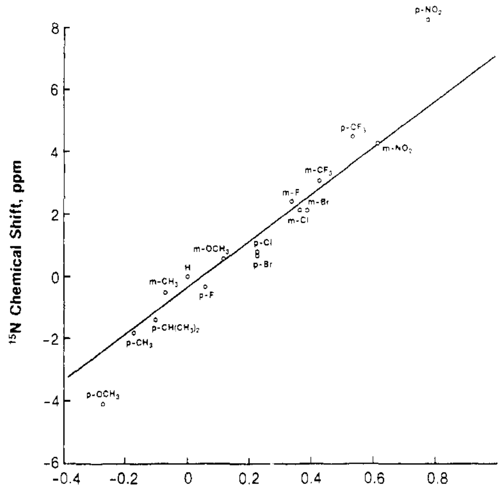

Figure 3. Correlation of the chemical shift of the methyl carbon of NMA's with the Hammett constant, σ; correlation coefficient = 0.954.

produce an upfield shift for that carbon. Alternatively, these small shift differences can be attributed to substituent field effects, as has been proposed to explain the anomalous shift effects in the proton spectra of benzal imines.[14]

The foregoing discussion of the chemical shifts suggests that the NMR properties of the nitrosamine moiety are largely dictated by the unique features of that functional group. These data also suggest that while nitrosamines have to be considered as resonance hybrids, the importance of the two principal canonical forms can be manipulated by appropriate substitution. Various chemical properties, such as the acidity of the α-hydrogens,[15,16] and various biological reactions, such as enzymatic N-demethylation,[9] ought to be influenced by that effect.

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Registry No. 4-Methoxy-*N*-nitroso-*N*-methylaniline, 940-11-4; 4-methyl-*N*-nitroso-*N*-methylaniline, 937-24-6; 4-isopropyl-*N*-nitroso-*N*-methylaniline, 79073-95-3; 3-methyl-*N*-nitroso-*N*-methylaniline, 17485-25-5; *N*-nitroso-*N*-methylaniline, 614-00-6; 4-fluoro-*N*-nitroso-*N*-methylaniline, 937-25-7; 3-methoxy-*N*-nitroso-*N*-methylaniline, 18559-18-7; 4-chloro-*N*-nitroso-*N*-methylaniline, 1007-19-8; 4-bromo-*N*-nitroso-*N*-methylaniline, 937-23-5; 3-fluoro-*N*-nitroso-*N*-methylaniline, 1978-26-3; 3-chloro-*N*-nitroso-*N*-methylaniline, 4243-20-3; 3-bromo-*N*-nitroso-*N*-methylaniline, 17405-06-0; 3-(trifluoromethyl)-*N*-nitroso-*N*-methylaniline, 79073-93-1; 4-(trifluoromethyl)-*N*-nitroso-*N*-methylaniline, 91385-14-7; 3-nitro-*N*-nitroso-*N*-methylaniline, 18600-50-5; 4-nitro-*N*-nitroso-*N*-methylaniline, 943-41-9.

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High Diastereoface Selection in an Ester Enolate Addition to α-Alkoxy Aldehydes: Stereoselective Synthesis of α-Methylene-β-hydroxy-γ-alkoxy Esters[1]

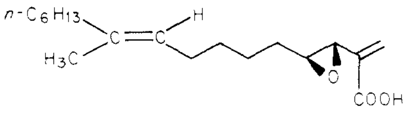
Luca Banfi, Anna Bernardi, Lino Colombo, Cesare Gennari, and Carlo Scolastico*

Istituto di Chimica Organica dell'Università e Centro C.N.R. per le sostanze organiche naturali,
via Venezian 21, 20133 Milano, Italy

Received November 30 1983

The aldol-type condensation of β-(dimethylamino)propionates 3 and 4 with a series of α-alkoxy aldehydes proceeds with unprecedented high stereoselectivity (up to 24:1) to give anti α-methylene-β-hydroxy-γ-alkoxy esters. The best results were obtained when the reaction was carried out in diethyl ether and the ester enolate was allowed to equilibrate to the thermodynamically more stable geometric isomer.

During the course of our studies directed toward the total synthesis of the antibiotic conocandin (1),[2] we became interested in developing a method for the stereoselective synthesis of anti[3] (threo)[4] esters of general formula 2.[5] We thought that the most straightforward way to achieve this goal was an aldol-type condensation between a chiral α-alkoxy aldehyde and a synthetic equivalent of acrylate α-anion (Scheme I).



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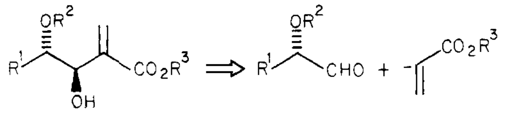
Scheme I



2

Actually optically pure α-alkoxy aldehydes are easily available in a multigram scale by stereoselective reduction of optically active α-(p-tolylsulfinyl)-α-(p-tolylthio) ketones.[6] Moreover, condensation of simple metal enolates

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[5] In this paper we use the nomenclature proposed by Masamune:[3] drawing the carbon backbone in a "zig-zag" fashion, the isomer projecting the two substituents either toward or away from the viewer has been defined syn and anti the other one.

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