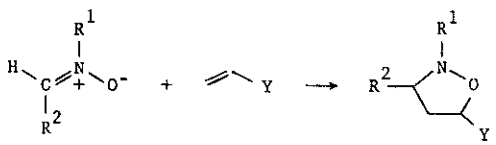
CYCLOADDITION REACTIONS OF ETHENESULFONIC ACID DERIVATIVES WITH NITRONES

Josette Chanet-Ray, Roger Vessière*, and Abdellah Zéroual
Laboratoire de Chimie Organique 2, Ecole Nationale Supérieure de Chimie de Clermont-Ferrand, Université de Clermont II, B.P. 45, 63170 Aubière, France

Abstract - The reaction of several derivatives of ethenesulfonic acid (CH_2=CX-SO_2R ; X = H, Br ; R = F, NEt_2) with different nitrones have been investigated. Regiospecific cycloadditions are observed, the reactions lead to 4-substituted isoxazolidines whatever is the nitrone involved. These results confirm Houk's predictions, according to which the amount of 4-substituted adduct increases with the electrophilic character of the substituted alkenes.

The regioselectivity concerning the cycloaddition of nitrones to monosubstituted olefins has been reported in many reviews[1,2].

When the dipolarophile shows a pronounced nucleophilic character, on account of the presence of a electrodonor group, the reaction is regiospecific and affords exclusively the 5-substituted adduct :



Y = electron supplying group

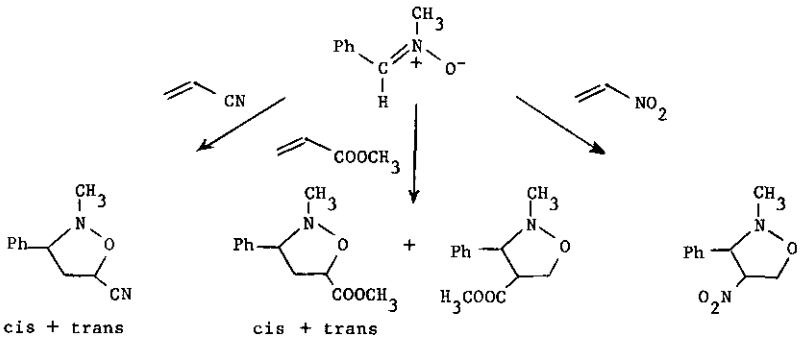
However, with monosubstituted olefins containing electron-withdrawing groups the reaction evolves preferentially or exclusively towards 4-substituted isoxazolidine.

The regioselectivity of the reaction is then considerably affected by the electron-withdrawing ability of the substituent.

It has been proved that the greater electron deficient dipolarophile is, the greater the quantity of 4-substituted adduct[3].

For example, the reaction of N-methyl-C-phenylnitrone with acrylonitrile produced a mixture of two 5-substituted isoxazolidines stereoisomers.

The reaction of this nitrone with methyl acrylate leads to the formation of two adducts resulting in a bidirectional orientation, while the nitroethene leads exclusively to the 4-substituted isoxazolidine[1,2].

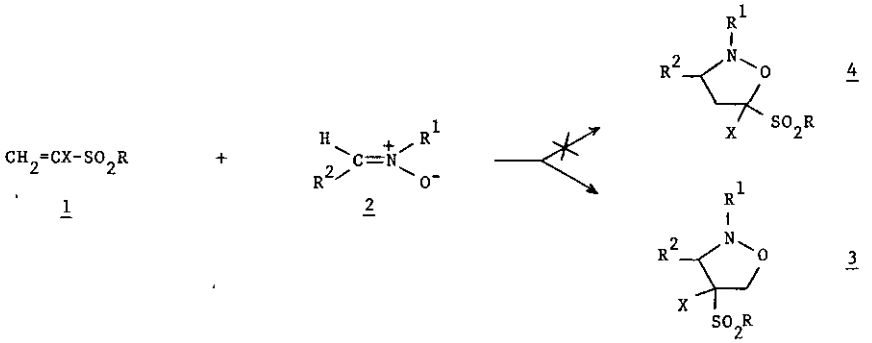


The formation of a single 4-substituted adduxt has also been observed when α,β-ethylenic sulfones reacted with several nitrones[3-5].

Our investigations concerning the use of derivatives of ethenesulfonic acids in organic synthesis[6,7] led us to examine their behaviour in 1,3-cycloaddition reactions.

In this paper we describe the results observed in the reaction of the three nitrones 2a-c on the ethenesulfonic acid fluorides and α-bromoethenesulfonic acid fluorides 1a, 1b as well as on the corresponding N-diethylsulfonamides 1c, 1d.

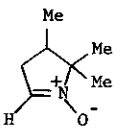
Theoretically, the greater electron-withdrawing ability of the fluorosulfonyl and aminosulfonyl group should increase the regioselectivity of the reaction.



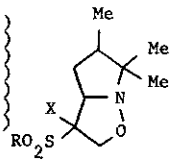
a : R = F ; X = H
b : R = F ; X = Br
c : R = NEt_2 ; X = H
d : R = NEt_2 ; X = Br

a : $R^1 = R^2$ = Ph
b : R^1 = Ph ; R^2 = Me

2c :



a : R = F ; $R^1 = R^2$ = Ph ; X = H
b : " " " X = Br
c : R = NEt_2 ; $R^1 = R^2$ = Ph ; X = H
d : " " " X = Br
e : R = F ; R^1 = Me ; R^2 = Ph ; X = H
f : " " " " X = Br
g : R = NEt_2 ; R^1 = Me ; R^2 = Ph ; X = H
h : " " " " X = Br
i : R = F ; X = H
j : R = F ; X = Br
k : R = NEt_2 ; X = H
l : R = NEt_2 ; X = Br



The treatment of C,N-diphenylnitrone 2a by refluxing a benzene solution of α-bromoethenesulfonic acid fluoride 1b affords the two 4-substituted isoxazolidine stereoisomers 3b.

The structural proofs are based on the spectroscopic ^{1}H nmr (200 MHz) results. The presence of one singlet (5.04 ppm, 1H) characterizes a type 3 structure and is incompatible with a 5-substituted isoxazolidine 4. This peak was attributed to C-3 proton of 3b. The four doublets near 5 ppm (2H) due to the C-5 protons show the presence of two stereoisomers of 3b ; we are however unable to supply further details as to their configurations.

The ^{13}C magnetic resonance spectrum exhibited two peaks at 125.20 and 118.70 ppm characterizing the quaternary carbons of the two stereoisomers. The absence of resonance at 25-30 ppm excludes the formation of 5-substituted isoxazolidine, indeed the methylene carbon of a 5-substituted isoxazolidine with both vicinal carbons would produce a resonance at a higher field, probably at about 30 ppm.

The spectrum of ^{1}H nmr of the product resulting from the addition of the nitrone 2a with fluoride 1a at room temperature reveals the presence of a doublet at 4.91 ppm (1H, J = 5 Hz) and two multiplets at 4.52 ppm (2H) and 4.20 ppm (1H) characterizing an isoxazolidine 3a and are attributed respectively to H-C-3, H-C-5 and H-C-4. The formation of a single isoxazolidine is confirmed by the ^{13}C nmr spectrum, however it is not possible to indicate its configuration.

The same conclusions were drawn after examining ^{1}H nmr spectrum (200 MHz) and ^{13}C nmr spectrum formed when the nitrone 2a reacts on the N-diethylsulfonamide 1c : one single 4-substituted isoxazolidine 3c is obtained ; its configuration is not given.

The nitrone 2a reacts with the sulfonamide 1d less easily than with its non bromic analogous 1c, the reaction will be carried out by refluxing a benzene solution and leads to the single isoxazolidine 3d characterized by its ^{1}H nmr spectrum.

N-Methyl-C-phenylnitrone 2b :

The reaction of nitrone 2b with the fluoride acid 1b at room temperature leads to the formation of two isoxazolidine stereoisomers 3f.

The ^{1}H nmr spectrum (200 MHz) of the resulting crystals shows two singlets at 4.19 and 4.25 ppm characterizing the H-C-3 of the two stereoismers. The methylene protons (H-C-5) form two doublets for each of the two isomers situated respectively at 4.92 and 4.47 ppm for the one and at 4.91 and 4.48 ppm for the other.

The N-methyls are characterized by two singlets at 2.71 and 2.72 ppm. The relative intensities of both groups of signals show that the two stereoisomers are in the ratio of 70/30.

The ^{13}C nmr spectrum confirms the formation of the two isoxazolidines.

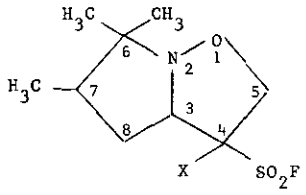
As in the case of the reaction described above concerning 1a and 2a, only one isomer of isoxalidine 3e is obtained when the nitrone 2b reacts with fluoride 1a ; in the ^{1}H nmr spectrum, a single doublet is observed at 3.90 ppm for H-C-3 and one singlet only at 2.57 ppm ($N-CH_3$). The formation of a single isoxazolidine is confirmed by the ^{13}C nmr spectrum.

A single isoxazolidine 3g is also obtained when the sulfonamide 1c reacts with nitrone 2b at room temperature ; the isoxazolidine 3g is characterized among other things by the presence of a single doublet at 3.83 ppm (H-C-3) and a single singlet at 2.62 ppm ($N-CH_3$) in the ^{1}H nmr spectrum at 200 MHz.

It is the same when the bromosulfonamide 1d reacts with the nitrone 2b, however, as we have already pointed out 1d is less reactive than 1c and a higher temperature is required (by refluxing benzene solution). The isoxazolidine 3h which has been isolated appears in one of the two possible forms of the stereoisomers, indeed we can observe a single singlet for the proton H-C-3 (4.20 ppm) and a single signal $N-CH_3$ (2.70 ppm).

4,5,5-Trimethylpyrroline Oxide :

The nitrone 2c reacts, at room temperature, with an ether solution of fluoride 1b to produce a solid to which we gave the structure of the 4-substituted isoxazolidine 3j. This assignment is based on the ^{1}H and ^{13}C nmr spectrum ; there again, the ^{1}H nmr spectrum does not allow us to characterize the configuration of the isoxazolidine produced. The fluoride 1a reacts in the same conditions as 1b with the nitrone 2c to form a product whose ^{1}H nmr spectrum (200 MHz) is more complex, but nevertheless is characteristic of a 3i type structure.



3i X = H

3j X = Br

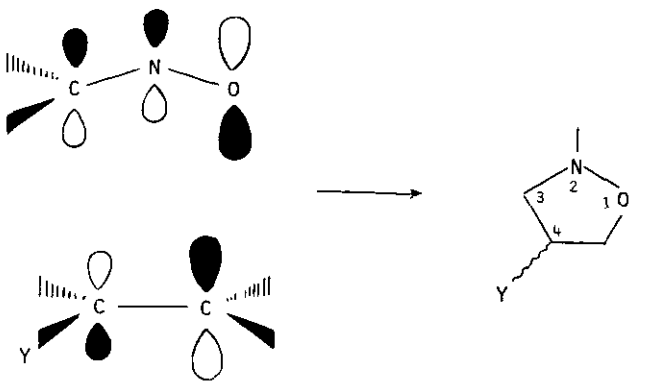
In examining the spectrum in the resonance zone of methyl groups, we can presume that two stereoisomers of 3i have been formed ; indeed, the presence of two doublets situated at 0.97 ppm (J = 6.96 Hz) and 1.13 ppm (J = 7.20 Hz) characterizes the methyl groups on carbon C-7 for the both stereoisomers. Moreover, we can observe the presence of four singlets ; two of those situated at 1.09 and 1.17 ppm are assigned to the methyl groups on the carbon C-6 belonging to the first isomer, the other two situated at 0.91 and 1.29 ppm characterizing the second isomer. The relative intensity of these signals shows that both isomers are in a 3/1 ratio ; the presence of the two isomers is confirmed by the number of signals in the ^{13}C nmr spectrum.

Treatment of nitrone 2c with 1c in benzene solution affords the corresponding cycloadduct 3k ; the ^{1}H nmr spectrum is complex but it is possible to assign the structure of 4-substituted isoxazolidine to compound 3k. The presence of two quartets (4H) at 3.0-3.4 ppm shows that we are in presence of two stereoisomers of 3k ; this result is confirmed by the ^{13}C nmr data ; the two stereoisomers have never been separated.

The compound 1d reacts in the same conditions as 1c with the nitrone 2c to produce a single 4-substituted isoxazolidine 3l ; its ^{1}H nmr spectrum is complex but is characteristic of a 3l type structure.

Orientation of the Reaction :

The results we have observed confirm HOUK's previsions[3]; the regioselectivity of the reaction is controlled by the nitrone LUMO until the nitrone does not become too electron-rich, or the dipolarophile becomes too electron-deficient. The reaction then leads to 5-substituted isoxazolidine. When the ionization potential of the nitrone decreases or when the electronic affinity of the olefin increases, we can observe the predominance formation of 4-substituted adduct ; this corresponds to an increase in nitrone HOMO energy or decrease in olefin LUMO energy. The reaction is then controlled by the nitrone HOMO - olefin LUMO interaction. For the nitrone HOMO level the coefficient of the atomic orbital is to be larger at oxygen than at carbon ; in the LUMO of the olefin the larger coefficient is associated with the β-carbon. Thus, the formation of 4-substituted isoxazolidine is in accord with the theory :



Conclusion :

The results of this work confirm the lines generally accepted to describe the regioselectivity of the 1,3-cycloaddition reactions of nitrones with olefins.

The regioselectivity of the reaction is controlled by the nitrone LUMO energy and dipolarophile HOMO energy in as much as the nitrone is not too electron-rich and the dipolarophile is not too electron-deficient. The reaction then leads to 5-substituted isoxazolidines.

The electron-withdrawing character of fluorosulfonyl and aminosulfonyl groups within some derivatives of ethenesulfonic acids we have examined leads to a considerable decrease in the olefin LUMO energy, the reaction is then controlled by nitrone HOMO - dipolarophile LUMO. The reaction then leads to 4-substituted isoxazolidines.

EXPERIMENTAL

The ^{1}H nmr spectrum were obtained on a VARIAN T 60 (60 MHz) and a BRUCKER 1200 SY (200 MHz) ; ^{13}C nmr spectrum were recorded on a JEOL FX (60 MHz) ; chemical shifts are in parts per million (δ) relative to tetramethylsilane ; coupling constants (J values) are in Hertz.

Preparation of Compounds 1 :

CH_2=CH-SO_2F 1a is prepared according to ref.[9]

CH_2=CBr-SO_2F 1b : bromination-dehydrobromination of 1a gives 1b, ref.[7]

CH_2=CH-SO_2NEt_2 1c is prepared according to ref.[6] by a modification of ref.[10]

CH_2=CBr-SO_2NEt_2 1d is prepared according to ref.[6]

Preparation of Nitrones 2 :

Nitrones are known compounds and were prepared following the standard procedures :

C,N-diphenylnitrone 2a : ref.[11]

C-phenyl N-methylnitrone 2b : ref.[12]

4,5,5-trimethylpyrroline oxide 2c : ref.[13]

Preparation of Isoxazolidine Cycloadducts 3. General Procedure :

A solution of the nitrone 2 (0.01 mol.) and the olefin 1 (0.01 mol.) in benzene (10 ml) was stirred at room temperature or was heated at reflux for the requisite time. The solvent was evaporated and the crude product was purified by chromatography on silica gel with hexane / ethyl

acetate to give 3.

Reaction of C,N-Diphenylnitrone 2a with Ethenesulfonic Acid Fluoride 1a : 3a

The reaction mixture was stirred at room temperature for 24 h, oil (2.1 g, 68% yield) ; ir (ν, cm^{-1}) : 1420 and 1210 (SO_2) ; ^1H nmr ($CDCl_3$, 60 MHz) : 7.6-7.8 (m, 10H), 4.9 (d, J = 5, 1H), 4.7-4.3 (m, 2H), 4.3-4.2 (m, 1H) ; ^{13}C nmr ($CDCl_3$) : 70.62 (C-3), 73.22 (C-4), 66.33 (C-5). Anal. calcd. for $C_{15}H_{14}NSO_3F$: C, 58.92 ; H, 4.52 ; N, 4.53 ; S, 10.66 ; F, 6.01. Found : C, 58.61 ; H, 4.59 ; N, 4.55 ; S, 10.43 ; F, 6.18.

Reaction of C,N-Diphenylnitrone 2a with 1-Bromoethenesulfonic Acid Fluoride 1b : 3b

The reaction mixture was heated at reflux for 24 h, white solid, mp 82-83°C (2.8 g, 72% yield) ; ir (ν, cm^{-1}) : 1420 and 1220 (SO_2) ; ^1H nmr ($CDCl_3$, 200 MHz) : 7.65-7.10 (m, 10H), 5.07, 4.71, 5.07, 4.69 (4d, J = 11.22, 2H), 5.04 (s, 1H) ; ^{13}C nmr ($CDCl_3$) : 76.66 (C-3), 81.67 (C-4), 80.76 (C-4), 74.65 (C-5). Anal. calcd. for $C_{15}H_{13}BrSO_3F$: C, 46.64 ; H, 3.39 ; Br, 20.68 ; N, 3.62 ; S, 8.30. Found : C, 46.64 ; H, 3.30 ; Br, 20.66 ; N, 3.60 ; S, 8.33.

Reaction of C,N-Diphenylnitrone 2a with N,N-Diethylamino-1-sulfonylethene 1c : 3c

The reaction mixture was heated at reflux for 24 h, white solid, mp 130-131°C (2.4 g, 67% yield) ; ir (ν, cm^{-1}) : 1340 and 1150 (SO_2) ; ^1H nmr ($CDCl_3$, 200 MHz) : 7.75-6.90 (m, 10H), 4.89 (d, J = 5.40, 1H), 4.42 and 4.43 (2d, J = 6.70, 2H), 4.20-4.05 (m, 1H), 3.21 and 3.20 (2q, J = 7, 4H), 1.05 (t, J = 7, 6H) ; ^{13}C nmr ($CDCl_3$) : 71.01 (C-3), 74.65 (C-4), 67.44 (C-5). Anal. calcd. for $C_{19}H_{24}N_2SO_3$: C, 63.60 ; H, 6.66 ; N, 7.77 ; S, 8.88. Found : C, 62.99 ; H, 6.60 ; N, 7.78 ; S, 8.83.

Reaction of C,N-Diphenylnitrone 2a with 1-Bromo-N,N-diethylamino-1-sulfonylethene 1d : 3d

The reaction mixture was heated at reflux for 4 days, white solid, mp 115-116°C (2.0 g ; 45% yield) ; ir (ν, cm^{-1}) : 1340 and 1150 (SO_2) ; ^1H nmr ($CDCl_3$, 200 MHz) : 7.80-6.90 (m, 10H), 5.27 (s, 1H), 4.95 and 4.57 (2d, J = 10.5, 2H), 3.7-3.1 (2q, J = 7, 4H), 1.08 (t, J = 7, 6H) ; ^{13}C nmr ($CDCl_3$) : 77.70 (C-3), 87.90 (C-4), 75.30 (C-5). Anal. calcd. for $C_{19}H_{23}BrN_2SO_3$: C, 51.93 ; H, 5.27 ; Br, 18.18 ; N, 6.37 ; S, 7.29 ; O, 10.92. Found : C, 51.05 ; H, 5.15 ; Br, 18.11 ; N, 6.18 ; S, 7.37 ; O, 9.89.

Reaction of C-Phenyl-N-methylnitrone 2b with Ethenesulfonic Acid Fluoride 1a : 3e

The reaction mixture was stirred at room temperature for 48 h, oil (1.7 g 69% yield) ; ir (ν, cm^{-1}) : 1410 and 1210 (SO_2) ; ^1H nmr ($CDCl_3$), 60 MHz) : 7.6-7.2 (m, 5H), 4.50-4.30 (m, 2H), 4.30-4.20 (m, 1H), 3.9 (d, J = 6.15, 1H), 2.57 (s, 3H) ; ^{13}C nmr ($CDCl_3$) : 72.77 (C-3), 74.00 (C-4), 66.40 (C-5). Anal. calcd. for $C_{10}H_{12}NSO_3F$: C, 48.97 ; H, 4.93 ; N, 5.71 ; S, 13.07. Found : C, 48.63 ; H, 4.96 ; N, 5.57 ; S, 12.95.

Reaction of C-Phenyl-N-methylnitrone 2b with 1-Bromoethenesulfonic Acid Fluoride 1b : 3f

The reaction mixture was stirred at room temperature for 24 h, solid, mp 52-53°C (2.6 g ; 81% yield) ; ir (ν, cm^{-1}) : 1420 and 1210 (SO_2) ; ^1H nmr ($CDCl_3$, 200 MHz) : 7.5 (s, 5H), 4.92, 4.91, 4.48, 4.47 (4d, J = 11,40, 2H), 4.25, 4.19 (2s, 1H), 2.72-2.71 (2s, 3H) ; ^{13}C nmr ($CDCl_3$) : 80.69, 81.60 (C-3), 85.69 (C-4), 77.57, 77.18 (C-5). Anal. calcd. for $C_{10}H_{11}BrNSO_3F$: C, 37.06 ; H, 3.42 ; Br, 24.65 ; N, 4.32 ; S, 9.89 ; F, 5.86. Found : C, 36.97 ; H, 3.45 ; Br, 24.46 ; N, 4.29 ; S, 9.92 ; F, 5.90.

Reaction of C-Phenyl-N-methylnitrone 2b with N,N-Diethylamino-1-sulfonylethene 1c : 3g
The reaction mixture was stirred for 24 h at room temperature, white solid, mp 92-93°C (2.3 g ; 77% yield) ; ir (ν, cm^{-1}) : 1340 and 1150 (SO_2) ; ^1H nmr ($CDCl_3$, 200 MHz) : 7.5-7.3 (m, 5H), 4.40-4.20 (2dd, J = 4.5, J = 8, J = 9.5, 2H), 4.15-4.00 (m, 1H), 3.83 (d, J = 7.5), 3.22-3.07 (2q, J = 7, 4H), 2.62 (s, 3H), 0.99 (t, J = 7, 6H) ; ^{13}C nmr ($CDCl_3$) : 72.96 (C-3), 74.26 (C-4), 66.85 (C-5). Anal. calcd. for $C_{14}H_{22}N_2SO_3$: C, 56.34 ; H, 7.43 ; N, 9.38 ; S, 10.08. Found : C, 56.31 ; H, 7.46 ; N, 9.42 ; S, 10.86.

Reaction of C-Phenyl-N-methylnitrone 2b with 1-Bromo-N,N-diethylamino-1-sulfonylethene 1d : 3h
The reaction mixture was heated at reflux for 4 days, white solid, mp 88-90°C (1.5 g ; 40% yield) ; ir (ν, cm^{-1}) : 1330 and 1150 (SO_2) ; ^1H nmr ($CDCl_3$, 200 MHz) : 7.6-7.3 (m, 5H), 4.8, 4.4 (2d, J = 10.66, 2H), 4.20 (s, 1H), 3.7-3.3 (2q, J = 7, 4H), 2.70 (s, 3H), 1.20 (t, J = 7, 6H) ; ^{13}C nmr ($CDCl_3$) : 78.09 (C-3), 87.32 (C-4), 77.12 (C-5). Anal. calcd. for $C_{14}H_{21}BrN_2SO_3$: C, 44.56 ; H, 5.61 ; Br, 21.17 ; N, 7.42 ; S 8.49 ; O, 12.72. Found : C, 44.47 ; H, 5.74 ; Br, 20.87 ; N, 7.47 ; S, 8.52 ; O, 12.80.

Reaction of 4,5,5-Trimethyloxide Pyrroline 2c with Ethenesulfonic Acid Fluoride 1a : 3i
The reaction mixture was heated at reflux for 4 days, white solid, mp 41-42°C (1.6 g ; 67% yield ; ir (ν, cm^{-1}) : 1410 and 1210 (SO_2) ; ^1H nmr ($CDCl_3$, 200 MHz) : 4.50-4.00 (m, 4H), 2.60-2.20 (m, 1H), 2.20-1.90 (m, 1H), 1.70-1.30 (m, 1H), 1.13 and 0.97 (2d, 3H), 1.29 and 0.91, 1.17 and 1.09 (4s, 6H) ; ^{13}C nmr ($CDCl_3$) : 68.41 (C-3), 68.22 (C-3), 69.84 (C-4), 70.75 (C-4), 65.88 (C-5), 63.93 (C-5). Anal. Calcd. for $C_9H_{16}NSO_3F$: C, 45.55 ; H, 6.79 ; N, 5.90 ; S, 13.51 ; F, 8.00. Found : C, 45.11 ; H, 6.71 ; N, 5.87 ; S, 13.40 ; F, 7.72.

Reaction of 4,5,5-Trimethyloxide Pyrroline 2c with 1-Bromoethenesulfonic Acid Fluoride 1b : 3j
The reaction mixture was heated at reflux for 24 h, solid, mp 112-114°C (1.6 g ; 50% yield) ; ir (ν, cm^{-1}) : 1410 and 1210 (SO_2) ; ^1H nmr ($CDCl_3$, 200 MHz) : 4.58 and 4.35 (2d, J = 10.26, 2H), 4.26 (dd, J = 9.55, J = 2.73, 1H), 2.70-2.20 (m, 2H), 2.10-1.80 (m, 1H), 1.30 (s, 3H), 0.99 (d, J = 6.73, 3H), 0.96 (s, 3H) ; ^{13}C nmr ($CDCl_3$) : 76.13 (C-3), 82.38 (C-4), 68.15 (C-5). Anal. calcd. for $C_9H_{15}BrNSO_3F$: C, 34.18 ; H, 4.78 ; Br, 25.27 ; N, 4.42 ; S, 10.14 ; F, 6.00. Found : C, 34.28 ; H, 4.79 ; Br, 24.72 ; N, 4.33 ; S, 9.42 ; F, 5.20.

Reaction of 4,5,5-Trimethyloxide Pyrroline 2c with N,N-Diethylamino-1-sulfonylethene 1c : 3k
The reaction mixture was heated at reflux for 24 h, oil (1.8 g ; 62% yield); ir (ν, cm^{-1}) : 1340 and 1150 (SO_2) ; ^1H nmr ($CDCl_3$, 200 MHz) : 4.40-3.55 (m, 4H), 3.40-3.02 (2q, J = 7, 4H), 2.45-1.30 (3m, 3H), 1.30-0.80 (m, 15H) ; ^{13}C nmr ($CDCl_3$) : 69.45 (C-3), 72.57 (C-4), 72.25 (C-4), 63.60 (C-5), 63.41 (C-5). Anal. calcd. for $C_{13}H_{26}N_2SO_3$: C, 53.70 ; H, 9.00 ; N, 9.52 ; S, 10.97 ; O, 17.03. Found : C, 53.74 ; H, 9.02 ; N, 9.64 ; S, 11.03 ; O, 16.52.

Reaction of 4,5,5-Trimethyloxide Pyrroline 2c with 1-Bromo-N,N-diethylamino-1-sulfonylethene 1d : 3l
The reaction mixture was heated at reflux for 4 days, solid, mp 120-121°C (1.5 g ; 41% yield) ; ir (ν, cm^{-1}) : 1340 and 1150 (SO_2) ; ^1H nmr ($CDCl_3$, 200 MHz) : 4.65 and 4.35 (2d, J = 10.35, 2H), 4.21 (dd, J = 10.35, J = 1.6, 1H), 3.59 and 3.35 (2q, J = 7.1, 4H), 2.90-2.80 (m, 1H), 2.40-2.20 (m, 1H), 1.80-1.60 (m, 1H), 1.31-1.20 (m, 9H), 0.95 (s, 3H), 0.90 (d, 3H) ; ^{13}C nmr ($CDCl_3$) : 76.79 (C-3), 85.89 (C-4), 75.69 (C-5). Anal. calcd. for $C_{13}H_{25}BrN_2SO_3$: C, 42.27 ; H, 6.82 ; Br, 21.63 ; N, 7.58 ; S, 8.68 ; O, 12.99. Found : C, 42.20 ; H, 6.88 ; Br, 22.05 ; N, 7.53 ; S, 8.62 ; O, 12.90.

REFERENCES

1. A. Padwa, L. Fisera, K.F. Koehler, A. Rodriguez and G.S.K. Wong, J.Org. Chem., 1984, **49**, 276.
2. J. Sims and K.N. Houk, J. Am. Chem. Soc., 1973, **95**, 5798.
3. A.Z. Bimanand and K.N. Houk, Tetrahedron Lett., 1983, **24**, 435.
4. P. Dallacroce, C. La Rosa and R. Stadi, J. Heterocyclic Chem., 1983, **20**, 519.
5. M. Barzaghi, P. Beltrame, P. Dallacroce, P. Del Buttero, L. Licandro, S. Mai Orana and G. Zecchi, J. Org. Chem., 1983, **48**, 3807.
6. G. Aumaitre, J. Chanet-Ray, J. Durand, R. Vessière and G. Lonchambon, Synthesis, 1983, **10**, 816.
7. A. Champseix, J. Chanet, A. Etienne, A. Le Berre, J. Masson, C. Napierala and R. Vessière, Bull. Soc. Chim., 1985, 463.
8. J.B. Hendrickson and D.A. Person, Tetrahedron Lett., 1983, **24**, 4657.
9. J.J. Krutak, R.D. Burpitt, W.H. Moore and J.A. Hyatt, J. Org. Chem., 1979, **44**, 3847.
10. C.S. Rondesvedt, J. Am. Chem. Soc., 1954, **76**, 1926.
11. I. Brüning, R. Grashey, H. Hauck, R. Huisgen and H. Seidl, Org. Syntheses, 1966, **46**, 127.
12. O.L. Brady, F.P. Dunn and R.F. Goldstein, J. Chem. Soc., 1926, 2386.
13. R. Bonnet, R.F.C. Brown, V.M. Clark, I.O. Sutherland and A. Tood, J. Chem. Soc., 1959, 2094.

Received, 28th July, 1986