

STUDY OF THE GEOMETRICAL STRUCTURES OF SUBSTITUTED N-TRIMETHYLSILYLOXYISOXAZOLIDINES

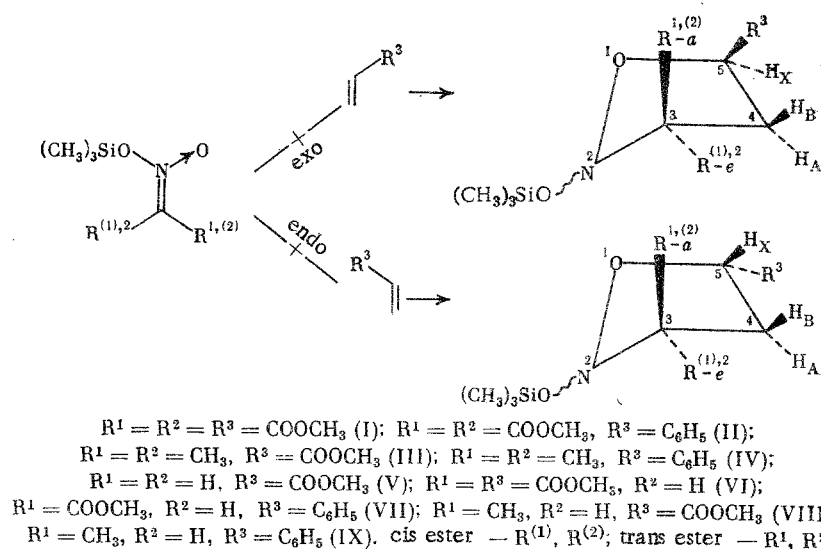
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Establishment of the geometrical structures of the N-alkoxyisoxazolidines is a matter of interest [1-8] since a knowledge of the stereochemistry of their conformationally stable adducts would yield information concerning the transition state geometry for the 1,3-cycloaddition reaction leading to their formation. X-ray structural analysis [3] suggests that the isoxazolidine ring exists in an envelope conformation with the nitrogen atom displaced out of the plane of the other four atoms (N^E).

The present work was a study of the geometrical structures of the cycloadducts of the nitronic acid silyl esters (NASE) with styrene and methyl acrylate (MA).

Scheme



Various numbers of isomers (α , β and γ), differing, in principle, in the configurations of the ring carbon and nitrogen atoms, can be formed here, depending on the NASE and olefin involved in the reaction. In order to determine the type of olefin approach (exo or endo) to the 1,3-dipole (cf. scheme), it is necessary to know the relative orientations of the R^3 and N relative to the ring plane. The C^3 configuration is determined by the geometry of the ester, an axial arrangement of R^1 (with $R^2 = \text{H}$) indicating a trans structure, and an equatorial arrangement a cis structure, in the ester precursor. The cycloadducts undergo spatial isomerization under certain conditions, and the nature of this reaction can be deduced by comparing the configurations of the kinetic and thermodynamic cycloaddition products.

EXPERIMENTAL

The cycloadducts of NASE with styrene and MA were prepared by well-known methods: (Ia) and (IIa) by the procedures of [9] and (VI) and (VII) by the procedures of [10].

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General Methods for Synthesizing the Cycloadducts (IIIa), (IVa), (Va), (VIII), and (IX). Mixtures of the nitroparaffin and bis(trimethylsilyl)acetamide (BSA) were held at 20°C for the time indicated in the table. At the end of this period the olefin was added,* and the mixture pumped off to 12 mm at 20°C. The precipitate was filtered off, dissolved in ether, and washed with water to remove the acetamide. The ether layer was dried over CaCl_2 , and the cycloadduct purified, by fractionation in the case of (Va) and by recrystallization in the case of (IX). The cycloadduct structure was determined by chemical reaction [9-11] and by study of the PMR spectra. The conditions of synthesis, and the properties of the cycloadducts, are indicated in Table 1.

Isomerization of the NASE Adducts. Isomerization of (Ia) and (IIa) was carried out by the method of [9]. A solution of 0.5 g of (Va) in 1 ml toluene was heated to 100-108°C for 30 min. Study of the PMR spectra indicated a 96% yield of invertomer (Vb) which passed over to 5-carbomethoxyisoxazolidine on vaporization of the solvent. The cycloadduct (IIIa) was either held for several days at 20°C, or dried in ether over MgSO_4 immediately after preparation. Each treatment led to a 5.5:1 mixture of isomers (IIIa) and (IIIb) whose composition which remained constant with the passage of time. This last point was confirmed in a special series of experiments.

Synthesis of NASE Cycloadducts Containing the ^{15}N Isotope. Some $(2-4) \cdot 10^{-2}$ mole of the respective nitroparaffins were obtained by reacting $\text{Na } ^{15}\text{NO}_3$ (enrichment in excess of 90%) with CH_3I [12], $\text{C}_2\text{H}_5\text{I}$, and $(\text{CH}_3)_2\text{CHBr}$ [13] in DMSO, following standard procedures. The reaction products were separated by distillation at 1 mm, the bath temperature being allowed to go no higher than 30°C. The distillate was washed with a small amount of water, the organic layer dried over MgSO_4 and distilled. The yields obtained were: $\text{CH}_3^{15}\text{NO}_2$ - 40%, $\text{CH}_3\text{CH}_2^{15}\text{NO}_2$ - 55%, $(\text{CH}_3)_2\text{CH}^{15}\text{NO}_2$ - 38%. The ^{15}N -methyl nitroacetate [14] and ^{15}N -dimethyl nitromalonate [15] were prepared by well-known methods.

The ^{15}N -NASE cycloadduct was prepared by the method described above.†

Determination of the Spectral Parameters of the NASE Cycloadducts. The PMR spectra of (I)-(IX) and NASE were obtained with Perkin-Elmer R-12, Varian DA-60, HA-100, and Bruker HX-90 spectrometers, working at 35°C in 10-15% solutions. Homonuclear double resonance and IN-DOR were used for line assignment in some cases. The parameter values are for the first-order spectrum approximation. The accuracy of determination was 0.03 ppm for the chemical shifts, and 0.2 Hz for the SSC constants (Table 2).

DISCUSSION OF RESULTS

The stereochemical variation of $J_{\text{H},\text{H}}^{\text{vic}}$ has been used to determine the configurations of the N-methoxyisoxazolidines [4-8, 16]. A similar approach was not open in the present case where there was a complete lack of information concerning the configuration of the ring carbons. Here it was necessary to measure $J_{\text{H}^3,\text{H}^4}^{\text{vic}}$ and $J_{\text{H}^4,\text{H}^5}^{\text{vic}}$, determine the stereochemical variation of $^4J_{\text{CH}_3,\text{H}}$ [17], $^2J_{^{15}\text{N},\text{H}}$, and $^3J_{^{15}\text{N},\text{H}}$ [18], and obtain the PMR spectra of the cycloadducts in the presence of the paramagnetic lanthanide complexes (PLC) [19]. The procedure adopted in establishing the geometrical structures of the N-trimethylsilyloxyisoxazolidines will be illustrated for (IIIa, b). The stereochemical variation of $^3J_{^{15}\text{N},\text{H}}^\ddagger$ was first drawn on to obtain the configurations of the C^4 and C^5 atoms in these compounds [18]. Double resonance measurements showed that the widening of the CH_3 group signal observed in these PMR spectra (1.10 ppm for (IIIa) and 1.07 ppm for (IIIb)) resulted from long-range SSC with the H_A proton. Coupling of this kind is possible only between the CH_3^q group and a trans-oriented H_A proton [17, 20].**

*The cycloadduct of the trimethylsilyl ester of methylnitronic acid with MA (Va) was obtained by adding the olefin directly to the BSA-nitromethane mixture.

†Although only one ^{15}N geometrical isomer (VIa) separated out here, the formation of two isomeric isoxazolidines from (VI) has been reported in [10].

‡We have found [14] that either $^3J_{^{15}\text{N},\text{H}^4}$ or $^3J_{^{15}\text{N},\text{H}^5}$ is equal to 1-2 Hz for ring-plane trans-orientation, and equal to approximately zero for ring-plane cis-orientation, of the H^4 or H^5 with respect to the N atom.

**Thus, in the case of (IIIa), an H_A proton assignment based on $^4J_{\text{CH}_3,\text{H}_\text{A}}$ values is identical with that based on $^3J_{^{15}\text{N},\text{H}_\text{A}}$.

TABLE 1. Properties, and Conditions of Synthesis, of the Cycloadducts (III), (IV), (V), (VIII), and (IX)

| Nitroparaffin | Nitroparaffin:BSA mole ratio | Reaction time, h (T, °C) | $R=\overset{\text{O}}{\text{N}}-\text{OSi}(\text{CH}_3)_3$ where R is | Olefin | NASE:olefin mole ratio | Reaction time | Cycloadduct | Yield, % |
|-----------------------------------|------------------------------|--------------------------|--|---------|------------------------|---------------|-------------|----------|
| CH_3NO_2 | 1:5.9 | — | CH_2 | MA | 1:3 | 10 hr | (Va)† | 90 |
| $\text{C}_2\text{H}_5\text{NO}_2$ | 1:1.3 | 2(60-70) | CH_2CH | MA | 1:2 | 2 hr | (VIIIa-c) | 97 |
| $\text{C}_2\text{H}_5\text{NO}_2$ | 1:1.3 | 2(60-70) | CH_2CH | Styrene | 1:2 | 5 day | (IXa,b) | 97 |
| $(\text{CH}_3)_2\text{CHNO}_2$ | 1:1.2 | 3(100-110) | $(\text{CH}_3)_2\text{C}$ | MA | 1:2.5 | 40 hr | (IIIa) | 90 |
| $(\text{CH}_3)_2\text{CHNO}_2$ | 1:1.2 | 3(100-110) | $(\text{CH}_3)_2\text{C}$ | Styrene | 1:2 | 14 day | (IVa)** | 63 |

*On a nitroparaffin-consumed basis

†bp 50°C (0.3 mm). Found: C 43.84; H 7.76; N 6.58; Si 12.69%.

$\text{C}_8\text{H}_{17}\text{NO}_4\text{Si}$. Calculated: C 43.84; H 7.77; N 6.40; Si 12.79%.

‡Determined by PMR methods, using an internal standard.

**mp 61-62°C (from styrene). Found: C 63.32; H 8.92; N 5.54;

Si 9.88%. $\text{C}_{14}\text{H}_{23}\text{NO}_2\text{Si}$. Calculated: C 63.40; H 8.70; N 5.29;

Si 10.52%.

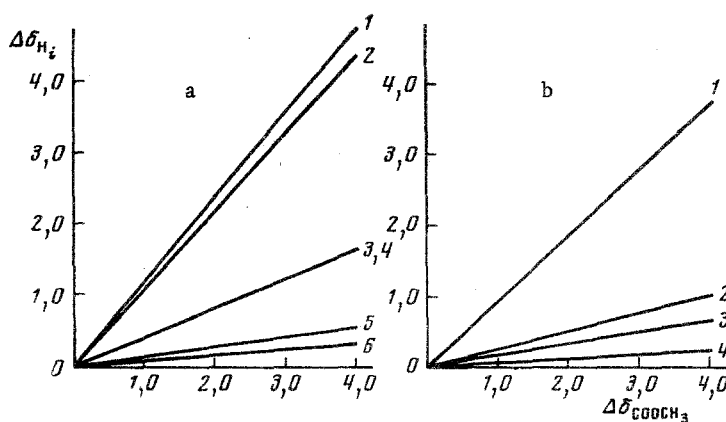


Fig. 1. Relative change in the proton chemical shifts in the presence of $\text{Eu}(\text{dpm})_3$. a. For (IIIa): 1) $\Delta\delta_{\text{H}_X}$; 2) $\Delta\delta_{\text{H}_B}$; 3) $\Delta\delta_{\text{H}_A}$; 4) $\Delta\delta_{\text{CH}_3-\alpha}$; 5) $\Delta\delta_{\text{CH}_3-\epsilon}$; 6) $\Delta\delta_{\text{Si}(\text{CH}_3)_3}$. b. For (IIIb): 1) $\Delta\delta_{\text{H}_X}$; 2) $\Delta\delta_{\text{SH}(\text{CH}_3)_3}$; 3) $\Delta\delta_{\text{CH}_3-\epsilon}$; 4) $\Delta\delta_{\text{CH}_3-\alpha}$.

It is necessary to consider $^3J_{15\text{N},\text{CH}_3}$ values in deducing the nitrogen atom configuration. Comparison of dihedral angles for the isoxazolidine molecules [3] and $^3J_{15\text{N},\text{CH}_3}$ values for the various conformations of the fragment containing the coupled nuclei [18], shows the nitrogen atom configuration to be determined by the following inequalities

$$^3J_{15\text{N},\text{CH}_3-e} \gg ^3J_{15\text{N},\text{CH}_3-a} \text{ (nitrogen free electron pair (NFEP) axial)}$$

$$^3J_{15\text{N},\text{CH}_3-a} \gg ^3J_{15\text{N},\text{CH}_3-e} \text{ (NFEP equatorial)}$$

The data of Table 2 indicate that the NFEP is equatorially oriented and thus the complete configuration of (IIIa) and (IIIb) can be deduced from $^3J_{15\text{N},\text{H}}$ and $^4J_{\text{CH}_3,\text{H}}$. Use was

made of this fact in determining the relation between the COOCH_3 group orientation and the relative alteration of the chemical shifts of the various groups of protons in the presence of PLC.* Study of the concentrational variation of the $\Delta\delta_{\text{H}_1}$, that is the change in the chemical shifts of the H_1 protons of (IIIa) and (IIIb) relative to $\Delta\delta_{\text{COOCH}_3}$ [21] (Fig. 1), showed

*The fact that there was no change in the PMR spectrum of (IX) at maximum $\text{Eu}(\text{dpm})_3$ concentration suggested that the PLC form complexes only through the COOCH_3 group, while $\text{Eu}(\text{fod})_3$ bonds to the cycloadducts in various ways.

TABLE 2. Proton Chemical Shifts and Coupling Constants for (I)-(IX)

| Compound | δ , ppm (relative to HMDS) | | | | | | J, Hz | | | | | | Isomer ratio, % | | |
|-----------|-----------------------------------|----------------|----------------|----------------|-----------------------------|----------------------------------|-----------------|-----------------|---------------------------------|---------------------------------|---------------------------------|----------------------------------|-----------------|-----------------|-----------------|
| | Si(CH ₃) ₃ | H _A | H _B | H _X | ³ H _M | CH ₃ | J _{AX} | J _{BX} | J _{15N, H_A} | J _{15N, H_B} | J _{15N, H_X} | J _{15N, CH₃} | | J _{AM} | J _{BM} |
| (I) a* | 0.24 | 3.46 | 2.88 | 4.91 | | | 10.1 | 4.3 | <0.1 | 1.1 | <0.1 | | | | 55 |
| b | 0.20 | 3.34 | 3.00 | 4.68 | | | 6.2 | 9.1 | <0.1 | 1.0 | 2.4 | | | | 45 |
| (II) a* | 0.15 | 3.69 | 2.46 | 5.62 | | | 9.0 | 6.4 | <0.1 | 0.5 | <0.1 | | | | 70 |
| b | 0.12 | 3.06 | 2.96 | 5.05 | | | 10.0 | 7.6 | <0.1 | 1.3 | 1.3 | | | | 30 |
| (III) a* | 0.1 | 2.31 | 1.93 | 4.63 | | | 10.6 | 4.2 | <0.1 | 1.2 | <0.1 | 2.0 | | | 85 |
| b | 0.06 | 2.41 | 1.96 | 4.43 | | 1.18 1.10 † 1.18 1.07 † | 6.9 | 9.0 | | | 2.3 | 3.6 † 2.1 3.4 † | | | 15 |
| (IV) a* | 0.15 | 2.52 | 1.78 | 5.48 | | 1.22 1.13 † | 9.5 | 5.0 | | | | | | | 100 |
| (V) a* | 0.10 | 2.77 | 2.28 | 4.68 | | | 9.6 | 3.8 | | | <0.1 | | | | |
| b | 0.02 | | 4.27 | 4.27 | | | 7.0 | 11.0 | | | <0.1 | | | | |
| (VI) a* | 0.15 | 2.91 | 2.68 | 4.88 | 4.01 | | 10.0 | 5.5 | | | <0.1 | | 8.0 | 2.5 | 50 |
| b*, † | 0.1 | 3.10 | 2.39 | 4.89 | 4.09 | | 10.5 | 3.5 | | | <0.1 | | 10.0 | 8.0 | 50 |
| (VII) a* | | 3.83 | 2.40 | 5.40 | 4.11 | | 8.5 | 8.5 | | | <0.1 | | 9.0 | 4.5 | 60 |
| b* | | 3.25 | 2.03 | 5.48 | 4.18 | | 9.5 | 5.0 | | | <0.1 | | 9.5 | 9.0 | 40 |
| (VIII) a* | 0.1 | | 4.68 | | | 1.14 0.98 | 9.5 | 3.7 | | | <0.1 | 2.6 3.9 † 2.7 | | | 73 |
| b* | 0.1 | | | | | ~1.14 | ~10.0 | ~5.0 | | | | | | | 15 |
| c* | ~0.1 | | | | | | | | | | | | | | 12 |
| (IX) a* | 0.13 | | 5.32 | | | 1.10 1.02 | 10.6 | 4.3 | | | | | | | 85 |
| b* | 0.13 | | | | | | | | | | | | | | 15 |

*Formed in the cycloaddition reaction.

†Axial CH₃ group (signal in the PMR spectrum widened because of ⁴J_{CH₃,H_A}).#J_{15N,H_M}³ = 4.6 Hz.

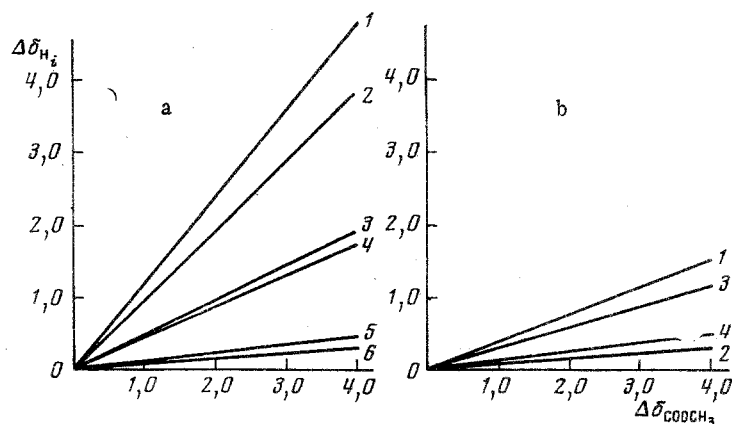
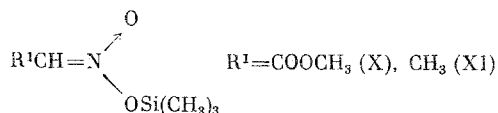


Fig. 2. Relative change in the proton chemical shifts in the presence of $\text{Eu}(\text{dpm})_3$. a. For (VIIIa): 1) $\Delta\delta_{\text{H}_X}$; 2) $\Delta\delta_{\text{H}_B}$; 3) $\Delta\delta_{\text{H}_A}$; 4) $\Delta\delta_{\text{H}_M}$; 5) $\Delta\delta_{\text{Si}(\text{CH}_3)_3}$; 6) $\Delta\delta_{\text{CH}_3}$. b. For (VIIIc): 1) $\Delta\delta_{\text{CH}_3}$; 2) $\Delta\delta_{\text{Si}(\text{CH}_3)_3}$; for (VIIIc): 3) $\Delta\delta_{\text{Si}(\text{CH}_3)_3}$; 4) $\Delta\delta_{\text{CH}_3}$.

that the former values could be used as a basis for deducing the mutual orientations of the H_i and the COOCH_3 groups.

The x-ray data [3] suggest that NASE occupies a pseudo-equatorial position in all of the N-alkoxyisoxazolidines. We have shown such to actually be the case for solutions of the N-methoxy-3-carbomethoxy-4,5-dicyanoisoxazolidines [14]. On the other hand, it is possible that attaching the more bulky $\text{OSi}(\text{CH}_3)_3$ group to the N atom alters the configuration of the molecule. The fact that NASE occupies a pseudo-equatorial position in (IIIa) and (IIIb) has already been pointed out. The configuration of the N atom in (VI) and (VII) was determined from $^2J_{15\text{N},\text{H}^3}$.* It can be seen from Table 2 that $^2J_{15\text{N},\text{H}^3} < 0.1$ Hz for isomer VIIa, in which H^3 is axial, and $^2J_{15\text{N},\text{H}^3}$ values for (VIb) and (VIIb) were 4.6 and -3.6 Hz. In view of the conformational characteristics of the $^2J_{15\text{N},\text{H}}$ values for the isoxazolidines [14], this would indicate that NASE must occupy an pseudo-equatorial position in the cycloadducts (VI) and (VII). From the N configurations in (III), (VI), and (VII), it was concluded that the FPNE occupies a pseudo-equatorial position in the NASE cycloadducts of (I)-(IX).

It is a well-known fact that there is a rapid intramolecular exchange of NASE $\text{Si}(\text{CH}_3)_3$ groups between the oxygen atoms of the O-N-O fragment [22], the result being that NASE with nonequivalent R^1 and R^2 substituents exist in the thermodynamically favored form. The fact that the $^2J_{15\text{N},\text{CH}}$ values for ^{15}N compounds of the type were less than 0.1 Hz [14] suggests that the trans isomers are preferred forms in (X) and (XI).



It was not possible to detect the presence of the cis isomers in these products by physico-chemical methods. The geometrical structures of (X) and (XI) were established by determining the configurations of their cycloadducts (VI)-(VIII).

The reaction scheme shows the NASE trans isomers (X) and (XI) reacting with the olefin to give a cycloadduct with an $\text{H}^3\text{-e}$, and the corresponding cis isomers reacting to give cycloadducts with an $\text{H}^3\text{-}\alpha$. Only the adducts with an $\text{H}^3\text{-e}$ should have low $J_{\text{H}^3,\text{H}^4}^{\text{vic}}$ values [5-7, 23]. On this basis, the data of Table 2 would indicate that (VIa) and (VIIa) are addition products of the trans ester (X), while isomers (VIb) and (XIb), with both $J_{\text{H}^3,\text{H}^4}^{\text{vic}}$ of considerable magnitude, come from the cis ester (X). The C^3 configuration of (VIIIa-c) was determined from

*See below for the procedure followed in fixing the C^3 configuration in (VI) and (VII).

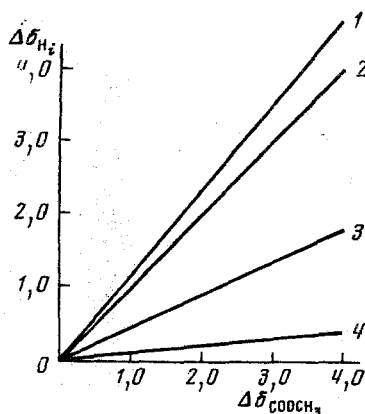
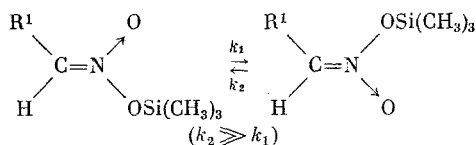


Fig. 3. Relative change in the proton chemical shift in the presence of Eu(dpm)_3 , for (Va): 1) $\Delta\delta_{\text{H}_X}$; 2) $\Delta\delta_{\text{H}_B}$; 3) $\Delta\delta_{\text{H}_A}$; 4) $\Delta\delta_{\text{Si}(\text{CH}_3)_3}$.

the CH_3 group orientation. Figure 2 shows $\Delta\delta_{\text{H}_i}$ values for (VIII) in the presence of Eu(dpm)_3 . Comparison of $\Delta\delta_{\text{Si}(\text{CH}_3)_3}$ values in (IIIa, b) with similar values for (VIIIa-c) shows that there is a trans arrangement of COOCH_3 group and N atom in (VIIIa, b), just as in (IIIa), and a cis arrangement of COOCH_3 group and N atom in (VIIIc), just as in (IIIb). Comparison of $\Delta\delta_{\text{CH}_3}$ values suggested that the CH_3 group is equatorial in (VIIIa) and axial in (VIIIb).

This conclusion was confirmed by study of the $^4\text{J}_{\text{CH}_3, \text{H}_A}$ values and comparison of $^3\text{J}_{1,5\text{N}, \text{CH}_3}$ with the corresponding coupling constants for (IIIa, b). It is seen from Fig. 1 that the values of $\Delta\delta_{\text{CH}_3-\alpha}$ and $\Delta\delta_{\text{CH}_3-\epsilon}$ were approximately the same for (IIIb) with cis arrangement of COOCH_3 group and nitrogen. The configuration of the C^3 atom in (VIIIc) was therefore established from the $^3\text{J}_{1,5\text{N}, \text{CH}_3}$ value and the fact that there was no widening of the CH_3 group signal in the spectrum of this compound ($^4\text{J}_{\text{CH}_3, \text{H}_A} < 0.1 \text{ Hz}$). On this basis, the CH_3 group was assigned an equatorial orientation in (VIIIc). Summing, it can be said at this point that (VIIIa, c) corresponds to the cis ester (XI) and (VIIIb) to the trans ester (XI).

Thus, it has for the first time, been shown that the unsymmetrical NASE's exist as equilibrium mixtures



in which the trans isomer predominates. The fact that the reaction products contain considerable quantities of the cycloadducts of the cis esters (X) and (XI) could be due to the high rate of cycloaddition of the nitronic acid cis esters to olefins [7]. Passage from $\text{R}^1\text{-COOCH}_3$ to $\text{R}^1\text{-CH}_3$ increases the fraction of the isomeric cycloadducts of the cis esters (VIb) and (VIIIa, c). This may be due to a shift in the point of equilibrium toward the NASE cis isomer as the size of the R^1 substituent is reduced.

The type of olefin (styrene or MA) approach to the NASE was established for the cycloadducts (I)-(VIII) (cf. Table 2 and Figs. 1-3). The most general approach here is through $^3\text{J}_{1,5\text{N}, \text{H}^3}$ values just as in determination of the C^3 configuration of (I)-(III) and (V)-(VIII). In the case of (III), (V) and (VIII), use was also made of PLC [$\Delta\delta_{\text{Si}(\text{CH}_3)_3}$] values, and, in the case of (IV) and (VI) of $^4\text{J}_{\text{CH}_3, \text{H}_A}$ and $\text{J}_{\text{H}^4, \text{H}^5}^{\text{vic}}$ values. With MA and styrene it is, apparent-

ly, the exo approach of olefin to NASE which is realized in every case. An exception here may be that of the cis isomer (XI) for which an MA endo approach is observed (~12%).*

The NASE cycloadducts show lower thermal stability than the isoxazolidines reported on earlier [1, 2, 4, 5-7], and study of their isomerization is not only difficult, but actually impossible in some cases. On the otherhand, (I) and (II) do undergo an inversion process which is clearly analogous to the isomerization of the corresponding N-methoxyisoxazolidines [1, 2, 9]. Since passage from (Ia) to (Ib), and from (IIa) to (IIb), involves an alteration in the relative positions of the R⁴ substituent and the N atom (cf. ³J_{1,5}N,H values in Table 2), isomerization of (I) and (II) must proceed through a so-called inversion-with-buckling scheme (2, 5-7, 14]. A different type of non-first-order isomerization results in (IIIa) from introduction of MgSO₄ and in (Va) from heating in toluene. The products, (IIIa) + (IIIb) and (Vb), are obviously the thermodynamically favored forms the value of the (IIIa)/(IIIb) ratio and 100% (Va)-to-(Vb) conversion being repeatedly confirmed in various experiments. The values of ³J_{1,5}N,H and ⁴J_{CH₃H}, and the results from the PLC experiments, show that (IIIa) and (IIIb) differ in relative orientations of the COOCH₃ group and N atom with respect to the ring plane, the (IIIa) ⇌ (IIIb) conversion corresponding formally to an inversion-with-buckling reaction scheme. From what has been said it can be seen that this process might follow some other mechanism, for example, epimerization through the C⁵ atom. The geometry of (Vb) has not been studied since the compound is thermally unstable, breaking down on addition of Eu(dpm)₃ and passing over completely to 5-carbmethoxyisoxazolidine-2,3 on evaporation of the solvent. It is possible that the chemical behavior of (Vb) reflects a distorted ring geometry, since the PMR spectrum fails to show a ¹⁵N-H⁵ SSC constant of the expected value (cf. Table 2).

By using several methods to determine the configurations of the cycloadducts (I)-(VIII) (cf. Table 2, and Figs. 1-3) it was possible, in some cases, to independently fix the H_A and H_B protons at the C⁴ atom. In most cases identical results were obtained. A contradiction of assignments based on J^{vic}_{N⁴,H⁵} and ³J_{1,5}N,H values was observed in the case of (IIb).[†] This indicates that a J^{vic}_{H⁴,H⁵} assignment of isoxazolidine configurations must be viewed with caution because of the slight difference in J^{cis}_{H⁴,H⁵} and J^{trans}_{H⁴,H⁵} values, a point made earlier by various authors. It is interesting to note that the results of x-ray analyses of analogous heterocyclic systems suggest that the spatial hindrances resulting from a cis arrangement of the C⁵ C₆H₅ group and the N atom must give rise to pronounced changes in the five-membered ring geometry [24].

CONCLUSIONS

1. Three methods have been proposed for determining the geometrical structures of the N-trimethylsilyloxy-3,5-substituted isoxazolidines, these involving study of the stereochemical variation of J_{1,5}N,H and ⁴J_{CH₃H} and analysis of the PMR spectra obtained in the presence of paramagnetic lanthanide complexes.

2. As a rule, it is the exo approach of the olefin to the 1,3-dipole which is realized in the cycloaddition of nitronic acid silyl esters to styrene and methylacrylate.

3. The free electron pair of the nitrogen in N-trimethylsilylisoxazolidines is pseudo-equatorially oriented.

4. Isomerization of the cycloadducts of the nitronic acid silyl esters can be described as an inversion-with-buckling process.

5. The nitronic acid silyl esters with nonequivalent substituents at the carbon atom exist as equilibrium mixtures of cis and trans isomers with the latter predominant.

*It has been reported in [7] that MA approach to the cis ester $\text{H}_3\text{COOCC}(\text{H})=\text{N} \begin{array}{c} \nearrow \text{O} \\ \searrow \text{OCH}_3 \end{array}$, is also

of the endo type, rather than the exo type as with the trans isomer.

[†]Assignment of H_A and H_B in (IIb) was made on the basis of ³J_{1,5}N,H values, since this seemed to us to be the most general approach.

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