Crystals of the title compound are triclinic with space group $P\bar{1}$ and four molecules in a unit cell of the following dimensions: a = 10.032 (1) Å, b = 11.076 (1) Å, c = 11.993 (1) Å, α = 74.78 (1)°, β = 96.90 (1)°, γ = 94.58 (1)°. This means that two molecules (A and B) are present in the asymmetric unit. Figure 1 represents a projection of molecule A onto the plane of the imidazole ring. The two molecules A and B in the asymmetric unit are very similar, only small differences being observed in the angles between the rings. The rings are planar within the limits accuracy. In both molecules C(6) is tilted out of the plane of the imidazole ring (0.19 and 0.12 Å in molecules A and B, respectively). The formyl groups at C(4) are practically coplanar with the imidazole rings. Coplanarity of the benzene rings with the imidazole ring is sterically impossible. In both molecules the benzene rings adopt similar positions with a large angle (75° and 69° in molecules A and B, respectively) between the imidazole ring and the benzene ring attached to N(1) and a smaller angle (41° and 32° for molecules A and B, respectively) between the imidazole ring and the benzene ring attached to C(2).

Experimental Section

Melting points are uncorrected. The ^{1}H NMR spectra were recorded on a Hitachi Perkin-Elmer R-24B apparatus with Me_4Si as internal standard. Infrared spectra were taken on a Perkin-Elmer 237 spectrometer in KBr. The mass spectra were performed on AE MS 902 mass spectrometer.

(1) Reaction of 5-Aminopyrimidine (1) with *N*-Phenylbenzimidoyl Chloride (2a). To a boiling solution of 540 mg (2.5 mmol) of *N*-phenylbenzimidoyl chloride (**2a**) in 25 mL of tetrachloroethylene was added 475 mg (5 mmol) of **1**. After the mixture was refluxed for 6 h, the solvent was evaporated off. The solution was made alkaline with aqueous ammonia and then extracted with chloroform. After the extract was dried over anhydrous $MgSO_4$, the solvent was evaporated off, and the crude mixture was separated by column chromatography using petroleum ether/ethyl acetate (7:3) as eluent. For the yields of the products **3a** and **4a**, see Table I. The physical data of those compounds are collected in Tables I and II.

(2) Reaction of 5-Aminopyrimidine (1) with Imidoyl Chloride (2c). Compound **2c** was prepared by refluxing a solution of 2.5 mmol of *n*-propylbenzamidine in 25 mL of chloroform with 524 mg (2.5 mmol) of phosphorus pentachloride for 1.5 h. Then the solvent was evaporated, and the residue (crude **2c**) was dissolved in 25 mL of tetrachloroethylene. A 175-mg (5 mmol) sample of **1** was added. After this solution was refluxed for 1 h, a few drops of the phosphorus oxychloride were added, and refluxing was continued for another 5 h. The solvent was evaporated, and the residue was worked up as described in section 1. The yields and physical data of the compounds obtained are collected in Tables I and II.

(3) Reaction of 5-Aminopyrimidine (1) with Imidoyl Chloride (2b). This reaction was carried out in the same manner as described in section 2. *N*-Phenylacetamide was used as the starting material for preparing **2b**, and chloroform was used as solvent.

(4) Preparation of *N*-Phenyl-*N'*-(5-pyrimidinyl)formamidine (3d). A 745-mg (5 mmol) sample of ethyl *N*-phenylformimidate[11] was heated with 475 mg (5 mmole) of 5-aminopyrimidine (**1**) at 170 °C for 3 h. The solid obtained was purified by column chromatography using ethyl acetate/methanol (9:1) as solvent.

Acknowledgment. We are indebted to Dr. C. A. Landheer for the mass spectra and to Mr. H. Jongejan for the microanalyses.

Registry No. **1**, 591-55-9; **2a**, 4903-36-0; **2b**, 874-69-1; **2c**, 39887-75-7; **2d**, 60566-41-8; **3a**, 75378-57-3; **3b**, 75378-58-4; **3c**, 75378-59-5; **3d**, 75378-60-8; **4a**, 75378-61-9; **4b**, 75378-62-0; **4c**, 75378-63-1; *n*-propylbenzamidine, 22286-00-6; *N*-phenylacetamide, 103-84-4; ethyl *N*-phenylformimidate, 6780-49-0.

Is Oxygen Abstraction by Nucleophilic Reagents a Characteristic Reaction of Oxaziridines?[1]

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The reaction of oxaziridines with nucleophilic reagents was studied. The summarized results are as follows. (1) The nucleophilic reactions occur preferentially on the nitrogen atom and the oxaziridine decomposes into a carbonyl compound and an ylide. (2) The reaction site shifts from nitrogen toward oxygen as the bulk of the ring substituents increases. (3) Cis isomers show faster reaction than trans isomers. (4) The carbon atom of the oxaziridine ring is completely inert to nucleophilic reagents.

Oxaziridines are very unique three-membered heterocyclic compounds constructed of three kinds of atoms having different electronegativities in adjacent positions. The reactions of oxaziridines with amines or sulfides are probably very important for elucidating the characteristic biological properties of oxaziridines based on comparison with that of analogous compounds such as aziridines or oxiranes. Although electrophilic reactions of oxaziridines have been extensively studied and N-protonation has been suggested as the preferred reaction path according to experimental and computational data,[2] a more attractive problem involving the nucleophilic reactions of oxaziridines was obscure until recently. The reactions of brucine or triphenylphosphine with oxaziridines were reported by Emmons[3a] and Horner[4] as early examples of oxygen abstraction from oxaziridines. The former example has been reexamined recently[3b] and appears actually not to involve

(1) This is the 9th paper of a series on fragmentations of ylides. The 8th paper is: Hata, Y.; Watanabe, M. *J. Org. Chem.* **1980**, *45*, 1691.

(2) Bonaccorsi, R.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1970**, *52*, 5270. Ghio, C.; Tomasi, J. *Theor. Chim. Acta* **1973**, *30*, 151. Garvey, J. F.; Hashmall, J. A. *J. Org. Chem.* **1978**, *43*, 2380. Bonaccorsi, R.; Scrocco, E.; Tomasi, J. *Theor. Chim. Acta* **1971**, *21*, 17. Butler, A. R.; White, J. G.; Challis, B. C.; Lobo, A. M. *J. Chem. Soc., Perkin Trans. 2* **1979**, 1039.

(3) (a) Emmons, W. D. *J. Am. Chem. Soc.* **1957**, *79*, 5739. (b) Rastetter, W. H.; Frost, J. W. *Tetrahedron Lett.* **1979**, 3353.

(4) Horner, L.; Jürgens, E. *Chem. Ber.* **1957**, *90*, 2184.

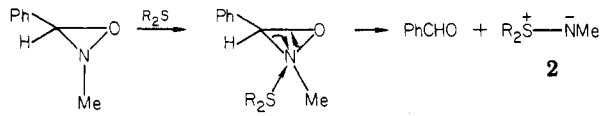
0022-3263/81/1946-0610$01.00/0

Table I. Reaction of Nucleophiles with 2-Methylspiro-[oxaziridine-3,2′-tricyclo[3.3.1.1^{3,7}]-decane] (3) (in $CDCl_3$)

nucleophilic reagents	reacn[a] conditions (temp, °C, time, h)	% N attack (% yield of 4)	% O attack (% yield of 6)	recovered starting material, %
Ph_3N	80, 70	0	0	99
Ph_3P	room temp, 50	24	85	0
Ph_3As	80, 4	39	24	c
Ph_2O	80, 70	0	0	95
Ph_2S	80, 70	19	0	86
Ph_2Se	80, 70	31	0	63
none	80, 70	3	0	96[b]

[a] 3, 27 mg (0.15 mmol), and nucleophilic reagents (2.5 mmol) were dissolved in $CDCl_3$ and heated in a constant-temperature bath. Diphenylmethane was used as an internal standard for NMR determination of 3. The yields of 4 and 6 were determined by IR. [b] Thermal decomposition of 3 will slightly raise the apparent yield of 4 from the nucleophilic reactions. [c] We did not study the recovery percentage.

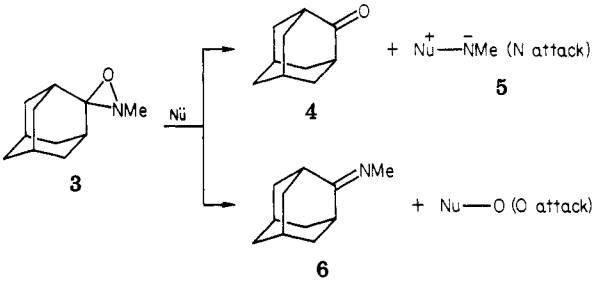
oxygen abstraction. Nonetheless, a study of the reactions with sulfur and phosphorus reagents reported recently[5] suggested to us that oxygen is the most electrophilic among the atoms of the oxaziridine ring and abstraction of oxygen is an essential characteristic of the reaction between oxiaziridines and nucleophilic reagents. However, in most of the oxaziridine derivatives used in these reports, the nitrogen atom, which is another possible reaction center, was occupied by a bulky substituent group such as *tert*-butyl and was seriously shielded from attack of the nucleophilic reagents. Thus, they were not the proper models with which to discuss the reactivity of oxaziridines. Last year, we observed that oxaziridines react easily with amines or sulfides.[6] The reaction occurs exclusively at the nitrogen atom of the oxaziridine ring with accompanying fragmentation and gives a carbonyl compound and ylide 2 derived from the reagent and nitrogen of the ring.



1 2

Here we discuss the inherent reactivity of several kinds of substituted oxaziridines with other examples of nucleophilic reagents.

(1) Nucleophilic Reaction of 2-Methylspiro[oxaziridine-3,2′-tricyclo[3.3.1.1^{3,7}]decane] (3).[7] In our study of the reactivity of oxaziridines, we first prepared 3 from adamantanone and methylamine followed by oxidation. The spiroadamantyl group completely shields the back side of the carbon atom of the oxaziridine ring, preventing any complicating reaction on the carbon atom. Six kinds of nucleophilic reagents were used as shown in Table I. The reaction was carried out in a sealed tube, using deuteriochloroform as a solvent. The mixture of 3 and 1.5 equiv of the reagent in the solvent was allowed to react at the appropriate temperature and the process was followed by IR and NMR spectroscopy and GC at suitable intervals. Too long a reaction time at too high a temperature caused decomposition of 3 and therefore the reaction was stopped before serious decomposition of the oxaziridine occurred. Among the products, adamantanone 4 was inert to ylide 5[8] and gave a reliable C=O absorption



band at 1701 cm^{-1} for calculation of the yield in the reaction mixture. The yield of imine 6[18] was also determined by the strong absorption band at 1665 cm^{-1} ($CDCl_3$) in the IR spectrum. Both yields are given in Table I as percent N attack and percent O attack, respectively. The amount of starting material (3) was measured by NMR spectroscopy, using diphenylmethane as an internal standard. Although we did not obtain an authentic sample nor isolate the ylide, ylide 5 (Nu^+ = As, Se, S) was identified by conversion into *N*-[*p*-nitrobenzylidene]methylamine by reaction with *p*-nitrobenzaldehyde which had been previously added to the reaction mixture.

In a previous study, we considered that the nucleophilic reactions of oxaziridines should proceed by either N attack or O attack followed by a fragmentation reaction. Actually, as shown in Table I, the reaction occurred on the nitrogen atom of the oxaziridine ring preferentially except in the case of triphenylphosphine. The order of reactivity of the reagents was $Ph_2O < Ph_2S < Ph_2Se$ for the 6th group and $Ph_3N < Ph_3As < Ph_3P$ for the 5th group of the periodic table. Triphenylphosphine characteristically favored attack on the oxygen of the oxaziridine ring.

(2) Nucleophilic Reactions of *cis*- and *trans*-2-Methyl-3-phenoxyoxaziridines (*cis*- and *trans*-7). Usually, inhibition of the pyramidal inversion of the nitrogen atom of oxaziridines gives cis and trans isomers in relation to the substituent on the carbon atom. Use of both isomers should give important information about the direction of attack of nucleophilic reagents. Here, we used *cis*- and *trans*-7 and studied the nucleophilic reactions.

The reaction was carried out by a procedure similar to that for 3, but *p*-nitrobenzaldehyde was added before the reaction to avoid possible confusion arising from reaction between benzaldehyde and ylide 5.[9] In the reaction, *p*-

(5) Davis, F. A.; Jenkins, R., Jr.; Yocklovich, S. G. *Tetrahedron Lett.* **1978**, 5171. Davis, F. A.; Jenkins, R., Jr.; Rizvi, S. Q. A.; Panunto, T. W. *J. Chem. Soc., Chem. Commun.* **1979**, 600. Davis, F. A.; Lamendola, J., Jr.; Nadir, U.; Kluger, E. W.; Sedergran, T. C.; Panunto, T. W.; Billmers, R.; Jenkins, R., Jr.; Turchi, I. J.; Watson, W. H.; Chen, J. S.; Kimura, M. *J. Am. Chem. Soc.* **1980**, *102*, 2000. Tamagaki, S.; Sakaki, K.; Oae, S. *Bull Chem. Soc. Jpn.* **1972**, *45*, 3179.

(6) Hata, Y.; Watanbe, M. *J. Am. Chem. Soc.* **1979**, *101*, 6671.

(7) 2-Methylspiro[oxaziridine-3,2′-tricyclo[3.3.1.1^{3,7}]decane] (3) was reported by O-Descherces et al. as a solid, mp 103 °C. Their NMR (C_6D_6) was δ 2.6 (s, 3 H), 1.7 (m, 14 H). According to the procedure they used to prepare 3, their compound should have been the same as ours and thus the melting point reported may be a mistake. O-Desherces, E.; Riviere, M.; Parello, J.; Lattes, A. *Synthesis* **1974**, 812.

(8) Triphenylarsinium methylide and diphenylselenium methylide were unknown prior to our study. We identified these intermediates by converting them into *N*-(*p*-nitrobenzylidene)methylamine in the reaction with *p*-nitrobenzaldehye in situ.

(9) The reaction of *p*-nitrobenzaldehyde with ylide 5 is much faster than that of benzaldehyde. Speziale, A. J.; Bissing, D. E. *J. Am. Chem. Soc.* **1963**, *85*, 3878.

(10) Eastes, J. W.; Aldridge, M. H.; Minesinger, R. R.; Kamlet, M. J. *J. Org. Chem.* **1971**, *36*, 3847. Osman, R.; Shvo, Y. *Tetrahedron.* **1978**, *34*, 2321.

(11) Jerslev, B. *Acta. Crystallogr.* **1967**, *23*, 645.

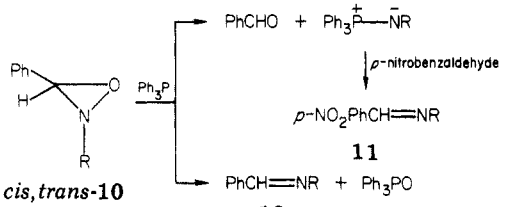
(12) Cannon, J. F.; Daly, J.; Silverton, J. V.; Boyd, D. R.; Jerina, D. M. *J. Chem. Soc., Perkin Trans. 2* **1972**, *1137*. Forni, A.; Garuti, G.; Moretti, I.; Torre, G.; Andreetti, G. D.; Bocelli, G.; Sgarabotto, P. *Ibid.* **1978**, 401.

Table II. Reaction[a] of *cis*- and *trans*-2-Methyl-3-phenyloxaziridine (7) with Nucleophilic Reagents (in $CDCl_3$)

config of 7	nucleophilic reagents	reacn conditions (temp, °C, time, min)	% N attack (% yield of 9)	% O attack (% yield of 8)	% starting material recovered
cis	PhSH	−20, 10	quantitative	0	0
trans	PhSH	−20, 30	38	0	60
cis	PhSeH	−20, 2	96	0	0
trans	PhSeH	−20, 2	69	24	0
cis	Ph_3P	room temp, 10	84	0	0
trans	Ph_3P	room temp, 30	58	39	0
cis	Ph_3As	room temp, 90	89	0[b]	0
trans	Ph_3As	room temp, 360	53	15[b]	30

[a] Reaction procedure was as described for 3. [b] See footnote 21.

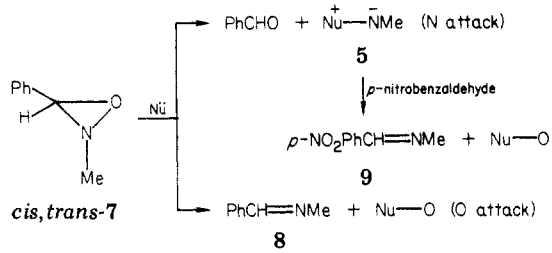
Table III. Reaction of 2-Alkyl-3-phenyloxaziridines (10) and Triphenylphosphine (in $CDCl_3$ at Room Temperature)[a]



R of 10 =	time, min	% N attack[b] (% yield of 11)	% O attack (% yield of 12)	N attack/O attack
cis-Me	10	84	0	only N attack
trans-Me	30	58	39	1.5
cis-Et	10	70	16	4.4
trans-Et	60	13	89	0.15
cis-*i*-Pr	60	2	97	0.02
trans-*i*-Pr	60	13	65	0.2
cis-cyclohexyl	60	10	75	0.13
trans-cyclohexyl	60	5	82	0.06
trans-*t*-Bu	180	0	91	only O attack

[a] Starting materials (10) were completely consumed after the indicated time. [b] % N attack corresponded to the yield of *N*-(*p*-nitrobenzylidene)alkylamine 11.

nitrobenzaldehyde had no effect on the reaction process of *cis*- or *trans*-7 and the reagents.[6]



The products were analyzed by GC and the yields of *N*-[*p*-nitrobenzylidene]methylamine (9) and *N*-[benzylidene]methylamine (8) are given in Table II as percent N attack and percent O attack, respectively. In separate experiments, the equilibrium reactions between benzaldehyde and 9 and between *p*-nitrobenzaldehyde and 8 could not be detected. The reaction solution of *cis*- or *trans*-7 with Ph_3As was allowed to stand for 24 h to observe the conversion of the product ratio. This ratio did not significantly differ from that given in Table II,[21] thus confirming that imine 8 or 9 remained for even longer reaction times.

As shown in Table II, the reactivity of *cis*-oxaziridine 7 toward nucleophilic reagents was much higher than that of the trans isomer and only the latter partially gave product 8 from O attack of the nucleophilic reagents. The relative reactivities, though qualitative, are clearly PhSH < PhSeH and Ph_3As < Ph_3P. This is the same tendency as that indicated in Table I.

For comparison, we attempted the reaction using Ph_3N as a nucleophile on *cis*- and *trans*-7, but only starting material was recovered. We also tried phenol and obtained a small amount of azomethane after very slow reaction.

(3) Nitrogen Substituent Effect in the Reactions with Triphenylphosphine. Next the bulk of the substituent on nitrogen of the oxaziridine was varied. The reactions of oxaziridine 10 (Table III), in which R = Me, Et, *i*-Pr, cyclohexyl, or *tert*-butyl, with Ph_3P were observed.

The reaction conditions and product analysis were the same as those described for 3 and *cis*- and *trans*-7 in Table

(13) Ingold, C. K. "Structure and Mechanism in Organic Chemistry", 2nd ed; Cornell University Press: Ithaca, NY, 1969; p 625. Krueger, J. H.; Sudbury, B. A.; Blanchet, P. F. *J. Am. Chem. Soc.* **1974**, *96*, 5733.
(14) Boyd, D. R.; Neill, D. C.; Watson, C. G.; Jennings, W. B. *J. Chem. Soc., Perkin Trans. 2* **1975**, 1813.
(15) Pews, R. G. *J. Org. Chem.* **1967**, *32*, 1628.
(16) Boyd, D. R.; Spratt, R.; Jerina, D. M. *J. Chem. Soc. C* **1969**, 2650.
(17) Klopman, G. "Chemical Reactivity and Reaction Paths"; Klopman, G., Ed.; John Wiley & Sons: New York, 1974, p 55.
(18) The product 6 was also inert under the reaction conditions and did not give the reverse-Wittig reaction product with diphenylselenium oxide in a separate experiment.
(19) Carbon attack was observed in the reaction of 2-butenoxide with *n*-Bu_3P. Boskin, M. J.; Denney, D. B. *Chem. Ind. (London)* **1959**, 330.
(20) Dermer, O. C.; Ham, G. E. "Ethylenimine and Other Aziridines"; Academic Press: New York, 1969; p 106 and references cited therein.

(21) The change of the product ratio of the reaction between *cis*- or *trans*-7 and Ph_3As was studied over longer times. Product 9 was stable and no trouble was encountered in the reaction of *cis*-7. However, *trans*-7 gave only 14% 8 at 1440 min after the reaction. This value was slightly less than the 16% which was estimated from 14% at 360 min and further comsumption of the *trans*-7 remaining in the reaction solution. Probably the discrepancy of the values occurred due to the degradation of 8.

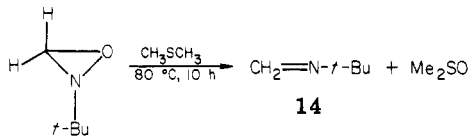
Table IV. Nucleophilic Reaction on 2-*tert*-Butyloxaziridine (13) (in $CDCl_3$)

nucleophilic reagent	reacn conditions[a] (temp, °C, time, h)	products[b]
Et_2NH	80, 6	no reaction (starting material recovered)
CH_3SCH_3	80, 10	CH_2=N-*t*-Bu, Me_2SO
Ph_3P	room temp, 0.5	CH_2=N-*t*-Bu, Ph_3PO (quantitative)

[a] Reaction was carried out as for *cis*-7. [b] Yield of *N*-methylenebutylamine was determined by NMR using diphenylmethane as an internal standard.

II. *p*-Nitrobenzaldehyde was also added to the reaction to obtain the percent N attack. After the end of the reaction, we confirmed complete consumption of starting material (*cis*- or *trans*-10). The results obtained are shown in Table III. The ratio N attack/O attack is generally larger for the *cis*-oxaziridines except for the isopropyl derivatives. Further, increasing the bulk of the nitrogen substituent of the oxaziridines favors product 12 formed by oxygen abstraction.

(4) Nucleophilic Reactions of Oxaziridines with no Substituent on the Ring Carbon Atom. The high reactivity of the nitrogen atom of oxaziridines and the gradual shift of the reaction site toward the oxygen atom by increasing the steric bulk of the *N*-alkyl group suggested very low reactivity of the carbon atom of the oxiaziridine ring. To confirm this, we prepared 2-*tert*-butyloxaziridine (13) from formaldehyde and *tert*-butylamine followed by oxidation and studied its nucleophilic reactions.



13 14

The reactions were carried out similarly to the case of *cis*- and *trans*-7 and product analysis was done by GC. Here the bulky substituent group on the nitrogen atom completely interrupted the attack of the reagent at nitrogen and we observed only the formation of oxygen-abstraction products in the reaction with dimethyl sulfide and triphenylphosphine as shown in Table IV.

When we used diethylamine, which was the reactive reagent on the nitrogen atom of *cis*-7 in a previous study,[6] only starting material was recovered. The carbon atom of oxaziridine 13 was completely inert to nucleophilic reagents under the conditions of Table IV.

Discussion

Our results are summarized as follows. (1) For oxaziridines without large steric hindrance of the ring nitrogen atom, the reaction with nucleophilic reagents occurs exclusively at the nitrogen atom followed by fragmentation of the oxaziridine ring, giving a carbonyl compound and ylide. (2) Soft reagents such as diphenylselenium or triphenylphosphine show higher reactivity and preferentially attack nitrogen. The reaction shifts toward oxygen abstraction with increasing bulk of the substituents on nitrogen or carbon of the oxaziridine ring. Oxaziridines are inert to alkoxide ion in alcohol. Thus, oxaziridines appear to have the characteristic of orbital-controlled reaction.[17] (3) The trans isomers (relative to the substituents on N and C) show a slower reaction rate than the cis isomers.[18] Attack of nucleophilic reagents on ring nitrogen in the trans isomers is probably retarded by steric interaction with the substituent on the oxaziridine carbon. Therefore the nucleophilic reaction at nitrogen appears to occur from the side opposite the substituent group on the nitrogen of the oxaziridine. (4) The carbon atom of the oxaziridine ring is inert to nucleophilic reagents even in the absence of steric hindrance from substituent groups.

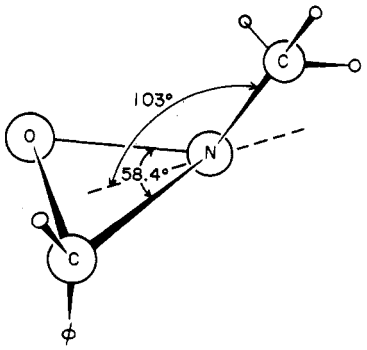


Figure 1. Bond angles of *trans*-2-methyl-3-(2,6-dimethyl-4-chlorophenyl)oxaziridine (calculated from the data of Jerslev[11]).

Intuitively, every atom of the oxaziridine ring is a possible site for nucleophilic reaction. Comparison of the reaction processes for aziridines[20] or oxiranes[19] led us to suppose initially that attack at carbon was the preferred course for nucleophilic reagents. The surprisingly high preference for attack at nitrogen probably is a result of several factors. (1) High angle strain of the three-membered ring of the oxaziridine causes rehybridization of the nitrogen atom reducing the basicity of its lone pair of electrons.[10] The tendency of lower basicity is accentuated by the oxygen atom in the adjacent position. The lone pair electrons of the nitrogen atom therefore do not seriously inhibit attack of nucleophilic reagents on the nitrogen atom. (2) The inner angle for nitrogen of the oxaziridine ring is significantly narrower than that of aziridines or oxiranes.[12] As shown in *trans*-2-methyl-3-(2,6-dimethyl-4-chlorophenyl)oxaziridine[11] (Figure 1), the O–N–C angle is only 58.4°. Consequently the angle between the plane of the oxaziridine ring and methyl group on nitrogen is reduced to 103°. These small angles provide ample space for the approach of nucleophilic reagents, thereby enhancing reactivity. (3) Introduction of heteroatoms in a small ring system causes strong localization of bonding electrons and results in a significant elongation of the O–N bond in the case of oxaziridines.[11,12] These factors should enhance the reactivity of nucleophilic reagents at nitrogen, the less electronegative terminal atom of the polarized O–N bond.[13] (4) The inertness of the carbon atom toward nucleophilic reagents remains poorly understood.

Experimental Section

cis- and *trans*-2-methyl-3-phenyloxaziridine (7),[14,6] *cis*- and *trans*-2-isopropyl-3-phenyloxaziridine,[6] *trans*-2-*tert*-butyl-3-phenyloxaziridine,[6] and 2-*tert*-butyloxaziridine[3] were prepared according to literature procedures. *cis*- and *trans*-2-ethyl-3-phenyloxaziridines were prepared according to the literature[15] and separated by column chromatography. The configuration was assigned according to Boyd.[16] Cis isomer: bp 45–46 °C (1 mmHg); NMR ($CDCl_3$) δ 7.4 (s, 5 H), 5.28 (s, 1 H), 2.5 (m, 2 H), 1.05 (t, 3 H). Trans isomer: bp 49–50 °C (1 mmHg); NMR ($CDCl_3$) δ 7.36 (s, 5 H), 4.5 (s, 1 H), 2.9 (m, 2 H), 1.3 (t, 3 H). *cis*- and *trans*-2-cyclohexyl-3-phenyloxaziridines were prepared according to the literature[4] and separated by column chromatography. The configuration was assigned as given above. Cis isomer: bp 103–105 °C (0.13 mmHg); NMR ($CDCl_3$) δ 7.4 (s, 5 H), 5.26 (s, 1 H), 1.5 (m, 11 H). Trans isomer: bp 105–107 °C (0.13 mmHg): NMR ($CDCl_3$) δ 7.31 (s, 5 H), 4.5 (s, 1 H), 1.6 (m, 11 H).

2-Methylspiro[oxaziridine-3,2′-tricyclo[3.3.1.1^{3,7}]decane] (3)[7] was prepared from adamantanone and methylamine followed by

oxidation with *m*-chloroperbenzoic acid according to the usual manner: bp 70–71 °C (1 mmHg); mp 18–19 °C; NMR ($CDCl_3$) δ 2.8 (s, 3 H), 1.9 (m, 14 H). Anal. Calcd for $C_{11}H_{17}NO$: C, 73.70; H, 9.56; N, 7.81. Found: C, 73.49; H, 9.74; N, 7.80.

Reaction of 2-Methylspiro[oxaziridine-3,2'-tricyclo-[3.3.1.1^{3,7}]decane] (3) with Nucleophilic Reagents. 3 (0.15 mmol) and 0.3 mmol of nucleophilic reagent were dissolved in 0.4 mL of freshly distilled deuteriochloroform and allowed to react at the appropriate temperature. Formation of products 4 and 6 in $CDCl_3$ solution was followed by monitoring IR absorptions at 1701 and 1665 cm^{-1}, respectively (the characteristic absorption bands of C=O and C=N). Starting material in the reaction solution was checked by NMR, using diphenylmethane as an internal standard.

Reaction of *cis*- and *trans*-2-Methyl-3-phenyloxaziridines (*cis*- and *trans*-7) with Nucleophilic Reagents. Reactions were carrried out as for 3. *p*-Nitrobenzaldehyde (0.4 mmol) was added before the reaction began and the products, *N*-(*p*-nitrobenzylidene)methylamine (9) and *N*-benzylidenemethylamine (6), were measured by GC analysis, using *n*-$C_{16}H_{34}$ and *n*-$C_{12}H_{26}$ as internal standards.

Reaction of *cis*- and *trans*-2-Alkyl-3-phenyloxaziridines (*cis*- and *trans*-10) with Triphenylphosphine. The reaction procedure and product analysis were similar to the above description. *n*-$C_{13}H_{28}$ was used as internal standard for GC analysis of *N*-benzylidenebutylamine.

Reaction of 2-*tert*-Butyloxaziridine (13) with Nucleophilic Reagents. The reaction procedure was similar to that described for the reactions of *cis*- or *trans*-7 with nucleophilic reagents. The yield of *N*-methylenebutylamine was determined by NMR, using diphenylmethane as internal standard.

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Registry No. 3, 54530-08-4; 4, 700-58-3; 6, 54530-06-2; *cis*-7, 39245-63-1; *trans*-7, 40264-03-7; 8, 622-29-7; 9, 877-80-5; *cis*-10 (R = Et), 57527-56-7; *trans*-10 (R = Et), 57527-57-8; *cis*-10 (R = *i*-Pr), 72257-44-4; *trans*-10 (R = I-Pr), 57527-58-9; *cis*-10 (R = cyclohexyl), 75780-72-2; *trans*-10 (R = cyclohexyl), 75768-08-0; *trans*-10 (R = *t*-Bu), 3585-81-7; 11 (R = Et), 25105-58-2; 11 (R = *i*-Pr), 25105-60-6; 11 (R = cyclohexyl), 42974-61-8; 12 (R = Et), 6852-54-6; 12 (R = *i*-Pr), 6852-56-8; 12 (R = cyclohexyl), 2211-66-7; 12 (R = *t*-Bu), 6852-58-0; 13, 16479-80-4; 14, 13987-61-6; *p*-nitrobenzaldehyde, 555-16-8; Ph_3N, 603-34-9; Ph_3P, 603-35-0; Ph_3As, 603-32-7; Ph_2O, 101-84-8; Ph_2S, 139-66-2; Ph_2Se, 1132-39-4; PhSH, 108-98-5; PhSeH, 645-96-5; Et_2NH, 109-89-7; CH_3SCH_3, 75-18-3.

Reactions of Allylsilanes with 4-Substituted 1,2,4-Triazoline-3,5-diones

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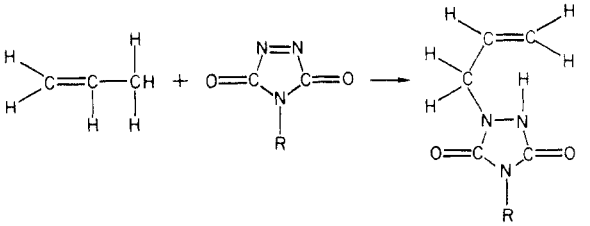
The reaction between allyltrimethylsilane (1) and 4-phenyl-1,2,4-triazoline-3,5-dione (2) was studied, and the structures of three products were determined by using ^1H NMR, ^{13}C NMR, and mass spectra. The effects of solvent and temperature on the relative yields of products were studied, and a reaction mechanism involving an ionic intermediate was suggested. The mechanism of the reaction between diallyldimethylsilane (3) with triazolinediones was found to be quite similar to that of 1.

We have previously reported that triazolinediones undergo a variety of interesting reactions with alkenes. For example, 4-phenyl-1,2,4-triazoline-3,5-dione (2) reacts rapidly with enol ethers to generate a dipolar species, the existence of which was proven by its interception with alkyl ketones.[1] Compound 2 also reacts rapidly at 0 °C with styrene on a 2:1 molar basis, the reaction sequence being an initial Diels–Alder reaction followed by an ene reaction.[2]

Enol esters undergo reaction with 2 to generate an intermediate dipolar species, which disappears rapidly via an unusual dipolar rearrangement.[3] The existence and participation of the dipole was confirmed via an extensive kinetic study.[4]

β-Dicarbonyl compounds undergo rapid reaction with 2, yielding both 1:1 and 1:2 adducts.[5] Kinetic studies support a reaction mechanism that involves a 1,4-dipolar intermediate, generated via reaction of 2 and the enol of the β-dicarbonyl compound.

Thus, the rapid reactions of 2 with a variety of structures opens up many potential uses of such compounds in synthesis. Kinetic investigations[6] have shown 2 to be one of the most powerful dienophiles known, being 10^3 times more reactive than tetracyanoethylene. It was first investigated as an enophile (eq 1) by Pasto and Chen.[7] More recent



(1)

investigations of the ene reaction of 2 have shown it to be 3×10^4 times more reactive than conventional azo dicarboxylates.[8] We have recently reported on the structure and properties[9] of the ene reaction of 2 with a variety of substituted alkenes, as well as a systematic kinetic study

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