Registry No.—**3**, 57073-98-0; **4**, 61597-51-1; **5**, 29414-55-9; **6**, 56764-67-1; **7**, 61597-52-2; **8**, 511-02-4; **9**, 61597-53-3; **10a**, 61597-54-4; **11**, 10395-42-3; **12**, 61618-20-0; **13**, 61604-71-5; **14a**, 61597-55-5; myrcenol, 543-39-5; $FeSO_4$, 19468-88-3.

References and Notes

(1) Supported in part by a grant from the National Science Foundation (GP-12582).
(2) W. Herz, R. C. Ligon, J. A. Turner, and J. F. Blount, *J. Org. Chem.*, accompanying paper in this issue.
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(9) We wish to thank Dr. Matsumoto for supplying us with details on these reactions.
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(13) W. G. Dauben and V. F. German, *Tetrahedron*, **22**, 679 (1966).
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(15) J. W. Rowe, "The Common and Systematic Nomenclature for Cyclic Diterpenes", Forest Products Laboratory, U.S. Department of Agriculture, Madison, Wis., 1968.
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(22) K. Kondo and M. Matsumoto, *Chem. Lett.*, 701 (1974).
(23) Experimental details have been specified in ref 2.
(24) We wish to thank Dr. F. L. Pickard, Union Camp Corp., for a gift of β-myrcene and Dr. W. I. Taylor, International Flavors and Fragrances, Inc., for a gift of myrcenol.

Nitrones. 4.[1] Reactions of Δ^1-Pyrroline *N*-Oxides with Phosphonates. Alternative Formation of Aziridines and Enamines[2]

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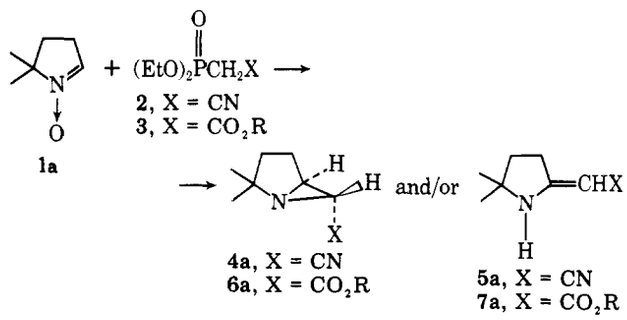
Variously methylated derivatives of Δ^1-pyrroline *N*-oxide (1) were reacted with diethyl cyanomethylphosphonate (2) and dialkyl alkoxycarbonylphosphonates 3 using sodium hydride in 1,2-dimethoxyethane or alkali metal alkoxides in alcoholic solvents. These reactions were shown to lead to 6-*exo*-cyano- and 6-*exo*-alkoxycarbonyl-1-azabicyclo[3.1.0]hexane derivatives 4 and 6, or alternatively 2-cyanomethylene- or 2-alkoxycarbonylmethylenepyrrolidine derivatives 5 and 7. This work describes the influence of substitution in the pyrroline *N*-oxide and of the variations in the reagents and solvents on the ratio of the products obtained in the reactions. It was found that when the reactions were carried out in 1,2-dimethoxyethane, the major product obtained was of aziridinic structure. However, using alcoholic solvents the yield of the enaminic products increased at the expense of the aziridinic products with increasing acidity of the solvent. The influence of the alkali metal cations on the course of the reaction was also studied, and it was found that lithium *tert*-butoxide promotes the formation of enaminic products as compared to sodium and potassium *tert*-butoxides.

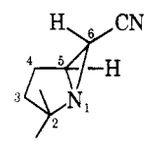
Previously we reported that the reactions of 5,5-dimethyl-Δ^1-pyrroline *N*-oxide (**1a**) with diethyl cyanomethylphosphonate (**2**) and triethyl phosphonoacetate (**3**, R = C_2H_5) may be directed to lead to aziridines or enamines.[3,4] In this paper we wish to describe in detail the influence of substitution in the substrate and the variations in the reagents and reaction conditions on the course of this novel reaction.



Results

The results from the reactions of a series of Δ^1-pyrroline *N*-oxides **1** with diethyl cyanomethylphosphonate (**2**) and dialkyl carbalkoxymethylphosphonate **3** are listed in Tables I–III. All reactions were monitored by thin layer chromatography and, when they resulted in the formation of more than one product, the mixtures were separated by chromatography. The identification of products is mainly based on their NMR spectra. Therefore it is of interest to present the significant features in the spectra of representative compounds.

The NMR spectrum of 6-*exo*-cyano-2,2-dimethyl-1-azabicylo[3.1.0]hexane (**4a**) shows the angular aziridinic hydrogen



4a

H-5 as a broad signal at δ 2.80 ppm and the second aziridinic hydrogen (H-6) as a doublet at higher field, namely at δ 1.94 ppm (J = 2.5 Hz).

We have previously suggested[5] that H-6 appears at higher field because of the shielding influence of the cis-related *N*-alkyl substituent. This assignment was subsequently confirmed by preparation of the 6-endo-deuterio derivative of **4a** using diethyl cyanomethylphosphonate-d_2. The coupling constant of H-6 indicates trans-aziridinic structure.[6]

Table I. Results from the Reactions of Diethyl Cyanomethylphosphonate (2) with Δ^1-Pyrroline *N*-Oxide Derivatives

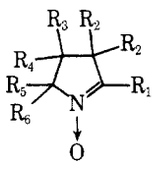
No.	Nitrone	Base	Solvent	Temp, °C	Time, h	Products: Aziridine	(yield, %)	Enamine	(yield, %)
1[a]	1a	NaH	DME	25	3	4a	(32)		(0)
2	1a	NaO-*t*-Bu	*t*-BuOH	40	3	4a	(59)	5a	(21)
3	1a	NaOEt	EtOH	25	21		(0)	5a	(95)
4	1a	NaOMe	Pentane	25	3	4a	(6)	5a	(80)
5[b]	1b	NaH	DME	25	24	4b + 4c	(20)	5b	(10)
6	1b	NaO-*t*-Bu	*t*-BuOH	Reflux	24	4b + 4c	(56)	5b	(25)
7	1b	NaOEt	EtOH	25	5		(0)	5b	(95)
8	1d	NaH	DME	Reflux	24	4d	(22)		(0)
9	1d	NaO-*t*-Bu	*t*-BuOH	Reflux	48	4d	(16)		(0)
10	1d	NaOEt	EtOH	Reflux	48		No reaction		
11	1d	NaOMe	MeOH	Reflux	48		No reaction		
12	1e	NaH	DME	25	48	4e	(18)	5e	(40)
13	1e	NaO-*t*-Bu	BuOH	40	24	4e	(26)	5e	(38)
14	1e	NaOEt	EtOH	25	24		(0)	5e	(40)
15	1f	NaH	DME	Reflux	48		No reaction		

[a] This experiment was first carried out by J. Pesso. [b] This experiment was first carried out by H. Sofer.

Table II. Results from the Reactions of Phosphonoacetates 3 with Δ^1-Pyrroline *N*-Oxides Derivatives[a]

No.	Nitrone	Base	Solvent	Time, h	Products: Aziridine	(yield, %)	Enamine	(yield, %)
1[b]	1a	NaH	DME	24	6a	(35)		(0)
2	1a	*t*-BuONa	*t*-BuOH	24	6a[c]	(75)		(0)
3	1a	EtONa	EtOH	24	6a	(15)	7a	(32)
4	1a	MeONa	MeOH	24	6a	(6)	7a	(36)
5	1b	NaH	DME	24	6b[d] + 6c[d]	(24)	7b	(11)
6	1b	*t*-BuONa	*t*-BuOH	24	6b[c] + 6c[c]	(38)	7b[e]	(46)
7	1b	EtONa	EtOH	24	6b + 6c	(27)	7b	(35)
8	1b	MeONa	MeOH	24		0	7b	(31)
9	1d	NaH	DME	120	6g + 6h	(30)		(0)
10	1d	*t*-BuONa	*t*-BuOH	96	6g[c] + 6h[c]	(40)		(0)
11	1d	EtONa	EtOH	48		No reaction		
12	1d	MeONa	MeOH	48		No reaction		
13	1e	NaH	DME	48	6e	(34)		(0)
14	1e	*t*-BuONa	*t*-BuOH	48	6e[f]	(35)		(0)
15	1e	EtONa	EtOH	48		No reaction		
16	1e	MeONa	MeOH	48		No reaction		

[a] All reactions were carried out in refluxing solvents. [b] This experiment was first carried out by S. Levi. [c] Contaminated by *tert*-butyl ester as evidenced by NMR. [d] The two isomers were present in the ratio of 45:55. [e] Separated by TLC to **7b**, R = Et (25%), and R = *t*-Bu (21%). [f] Separated by GLC to **6e**, R = Et and R = *t*-Bu (1:1).



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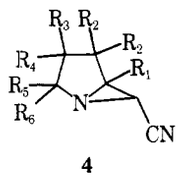

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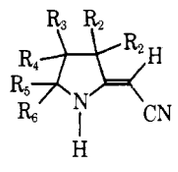

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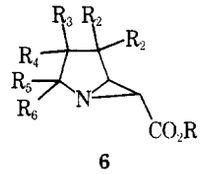

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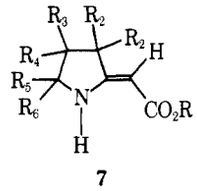
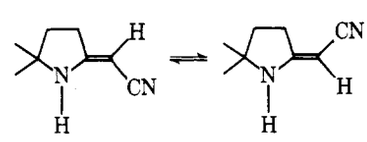


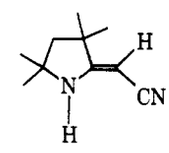
7

a, $R_1 = R_2 = R_3 = R_4 = H$; $R_5 = R_6 = CH_3$
b, $R_1 = R_2 = R_3 = H$; $R_4 = R_5 = R_6 = CH_3$
c, $R_1 = R_2 = R_4 = H$; $R_3 = R_5 = R_6 = CH_3$
d, $R_1 = R_3 = R_4 = CH_3$; $R_2 = R_5 = R_6 = H$
e, $R_1 = R_3 = R_4 = H$; $R_2 = R_5 = R_6 = CH_3$
f, $R_1 = R_5 = R_6 = CH_3$; $R_2 = R_3 = R_4 = H$
g, $R_1 = R_3 = R_4 = R_5 = H$; $R_2 = R_5 = CH_3$
h, $R_1 = R_3 = R_4 = R_6 = H$; $R_2 = R_6 = CH_3$

The enaminic derivatives also show characteristic NMR spectra. Enamino nitrile **5a** shows the NH signal at δ 5.80 ppm



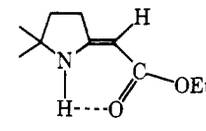
5a



5e

and two signals at δ 3.85 and 3.55 of ½ H each that may be assigned as belonging to the vinylic H, indicating the existence of equilibrium in solution.

In contrast, enamino ester **7a** shows the NH at a much lower field, namely at δ 7.70 ppm, presumably due to intramolecular hydrogen bonding with the ester oxygen, and the vinylic proton at δ 4.36 ppm as a singlet. These are in good agreement with the NMR data obtained by Eschenmoser and co-workers for 2-*tert*-butoxycarbonylmethylenepyrrolidine.[7] The vinylic protons as well as the NH protons of both types of enamines **5** and **7** exchange with D upon the addition of D_2O. Enamino



7a

Table III. Effect of Metal on the Reaction of Δ^1-5,5-Dimethylpyrroline *N*-Oxide (1a) with Phosphonates in *tert*-Butyl Alcohol

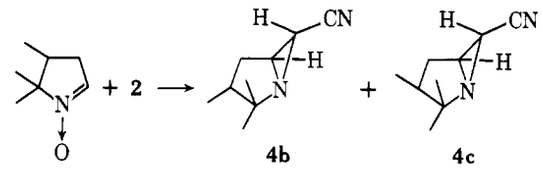
	M	Phosphonate	Temp, °C	Time, h	Products: Aziridine	Yield, %	Enamine	Yield, %
1	Li	2	40	3	**4a**	20	**5a**	80
2	Na	2	40	3	**4a**	59	**5a**	21
3	K	2	40	3	**4a**	41	**5a**	51
4	Li	3[a]	Reflux	24	**6a**[b]	61	**7a**[b]	34
5	Na	3[a]	Reflux	24	**6a**[b]	75	**7a**	0
6	K	3[a]	Reflux	24	**6a**[b]	75	**7a**	0

[a] R = C_2H_5. [b] These products were contaminated by the corresponding *tert*-butyl ester presumably resulting from transesterification during the reaction.

nitrile **5a** shows in the infrared spectrum an absorption band at 2180 cm^{-1}, also confirming the enamino nitrile structure.[8]

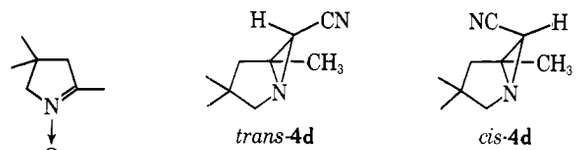
Examination of the results listed in Table I reveals that the reactions of pyrroline *N*-oxides with phosphonate **2** show marked dependence on the reaction conditions. By comparing reactions 1–3 in Table I, it is seen that while using NaH/DME only the formation of aziridine **4a** is observed, the use of *tert*-butyl alcohol already causes the formation of some enamine **5a,** and in ethanol only the latter is formed. Sodium methoxide in an inert solvent leads mainly but *not exclusively* to the formation of enamine. A similar trend is apparent on comparing reactions 5–7 and reactions 12–14 in Table I.

The reaction of 4,5,5-trimethylpyrroline *N*-oxide (**1b**) with **2** afforded the stereoisomeric aziridines **4b** and **4c** in approximately equal amounts as demonstrated by GLC.



1b **4b** **4c**

Reaction of keto nitrone **1d** with **2** cannot give enaminic product. The product obtained in these reactions (entries 8 and 9, Table I) showed in the NMR spectrum in $CDCl_3$ the aziridinic H as a singlet at 2.20 ppm. On the basis of this, it is impossible to distinguish between the two possible aziridines **4d.** We have attempted to do so by measuring aromatic solvent

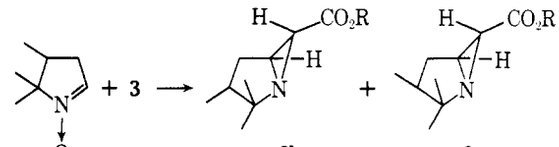


1d *trans*-**4d** *cis*-**4d**

induced shifts (ASIS) in the NMR spectra;[9] however, in contrast to other systems,[1,5,9] we found that all hydrogens of a representative compound of this series (see Experimental Section for the NMR spectra of **4a**) suffer an upfield shift upon passing from chloroform to benzene, rendering this approach unsuitable for the solution of such problems in this system. It should be emphasized that keto nitrone **1d** reacted with **2** only with NaH/DME and with NaO-*t*-Bu in *t*-BuOH but not with sodium alkoxides in ethanol and methanol (Table I, entries 10 and 11). In these reactions unreacted starting materials were recovered. In contrast to **1d,** keto nitrone **1f** did not react with **2** even with NaH/DME.

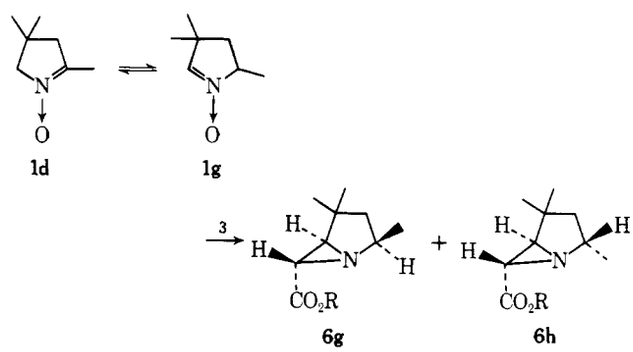
The results from the reaction of the nitrones **1** with phosphonoacetates **3** are listed in Table II. From the examination of this table, it is apparent that the reactions of the phosphonoacetates require more drastic conditions than those of the cyanomethylphosphonate. All the reactions of the phosphonoacetates were carried out in refluxing solvents for 24 h or more, in contrast to the cyanomethylphosphonate which reacted with the more reactive nitrones at room temperature within a few hours. Another general feature worthy of note is the decreased tendency of the phosphonoacetates, as compared to the cyanomethylphosphonates, to form enaminic products.

Similar to the reactions of cyanomethylphosphonate, we can see in the reactions listed in Table II variations in the product ratio with change of solvent. While the reaction of nitrone **1a** with phosphonate **3** (R = OEt) leads exclusively to aziridinic product **6a** when carried out with NaH in DME or with NaO-*t*-Bu in *t*-BuOH, increasing amounts of enamino ester **7a** are formed in ethanol and methanol (entries 1–4, Table II). Similar trends can be seen in the reactions of the trisubstituted nitrone **1b** (entries 5–8, Table II). Examination of the aziridinic fraction obtained from the reactions of **1b** and **3** by GLC revealed that, as in the reactions of **1b** and **2,** a mixture of stereoisomers **6b** and **6c** is obtained. The composition of the mixture is approximately 60:40. However, it is not known which isomer is in excess.



1b **6b** **6c**

The reaction of keto nitrone **1d** with phosphonoacetate **3** (R = Et) proceeds in a different way than that with cyanomethylphosphonate **2.** While the reaction of the latter afforded the expected aziridinic product **4d,** as evidenced by the appearance of the aziridinic hydrogen as a singlet, the NMR spectrum of the aziridinic product from this reaction showed two doublets at δ 2.55 and 1.88 ppm (J = 2.5 Hz) characteristic of trans-2,3-disubstituted aziridines. On the basis of this NMR spectrum and GLC analysis, we assume that the product of this reaction is a mixture of stereoisomers **6g** and **6h** that are formed from nitrone **1d** via its tautomer **1g.** Reactions of the

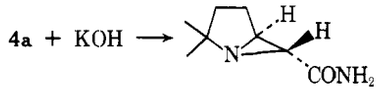


1d **1g** **6g** **6h**

tetrasubstituted aldonitrone **1e** with **3** led only to aziridine **6e**, and significantly, neither **1d** nor **1e** reacted with phosphonate **3** in ethanol or in methanol.

In Table III, there are listed a series of reactions of phosphonates **2** and **3** with a representative nitrone **1a** with three alkali metal *tert*-butoxides. Comparison of the first three entries in this table reveals that enamine formation is maximal when M = Li, decreases with M = Na, and increases again using K. From entries 4–6 it is again clear that the formation of enaminic product can be optimized using lithium.

In separate control experiments, we have ascertained that (1) nitrone **1a** can be recovered unchanged from a solution of sodium ethoxide in ethanol; (2) aziridinic ester **6a** is also stable in a solution of sodium ethoxide in ethanol; (3) treatment of cyanoaziridine **4a** with sodium ethoxide in ethanol results in the formation of **6a** but not **5a** or **7a**. Another example for the base stability of the 1-azabicyclo[3.1.0]hexane system is provided by the hydrolysis of **4a** to aziridinic amide **8** using potassium hydroxide in *tert*-butyl alcohol.

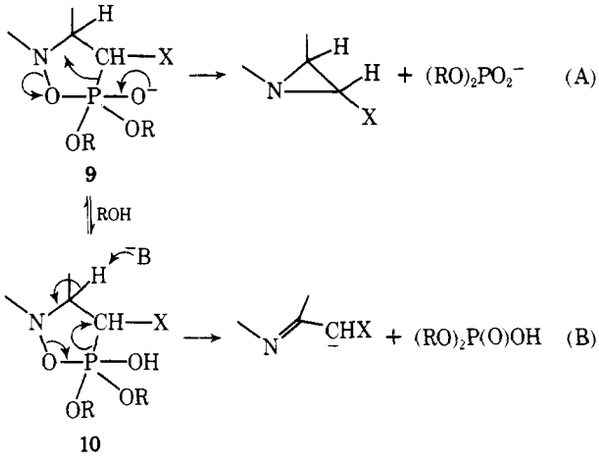


8

Discussion

The results of the control experiments described clearly indicate that the aziridinic and enaminic products formed in these reactions are not interconvertible under the reaction conditions. Therefore, it follows that the two types of products are formed by two different routes.

In our preliminary communication,[3] we have put forward the suggestion that the reaction between nitrones and phosphonates leads first to an oxazaphospholidine **9**, which may give rise to the aziridine by pathway A. Such fragmentation is presumably facilitated by back-donation from the negatively charged exocyclic oxygen.

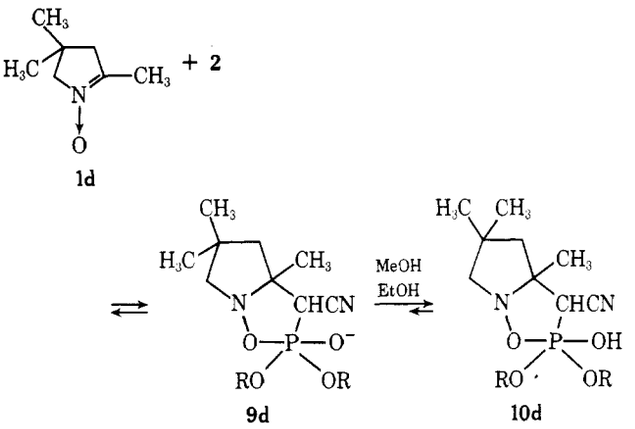


In the presence of protic solvents the negatively charged oxygen in **9** is protonated resulting in the formation of **10.** This intermediate may undergo a different type of base-catalyzed fragmentation to yield the corresponding enamine derivative (eq B). Therefore, it can be expected that the more acidic is the solvent the more will the formation of the aziridinic product be inhibited by protonation. These suggestions are supported by the experimental results.

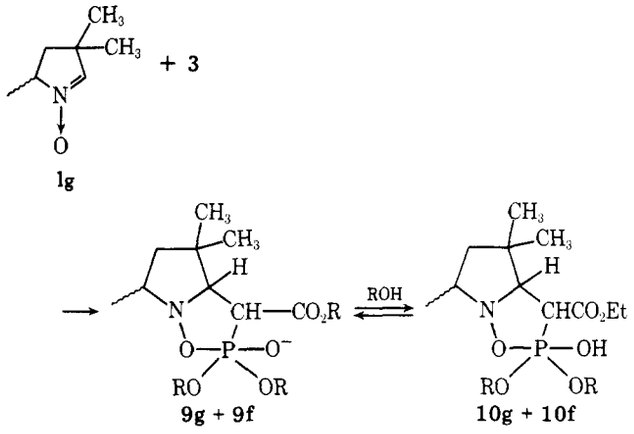
The proportion of the enaminic product increases in the order methanol > ethanol > *tert*-butyl alcohol, which is also the order of acidities of these alcohols[10] (see Table I, entries 2, 3; 6, 7; 13, 14; and Table II, entries 2–4, 6–8).

The inhibitory influence of the protic solvent upon the formation of aziridine can be seen in several examples. The reaction of keto nitrone **1d** cannot lead to enaminic product. This nitrone reacts with **2** to give aziridine **4d** in the presence of NaH/DME or NaO-*t*-Bu in *t*-BuOH. However, in the more acidic solvents, ethanol and methanol, no products are formed (Table I, 8–11).

This presumably indicates that in the more acidic solvent, the decomposition of **9d** is inhibited by its conversion to the protonated **10d.** Similar conclusions can be drawn from the



behavior of **1d** toward phosphonate **3** (Table II, 9–12). The behavior of this nitrone in its reactions with **3** could be rationalized by assuming the existence of the tautomeric equilibrium between **1d** ⇄ **1g.** We have previously observed[11] that the reaction of triethyl phosphonoacetate with a nitrone of low reactivity may lead to the formation of products via a less stable but more reactive tautomer.[12] Reaction of nitrone **1g** with **3** should lead to **9g** which may decompose to aziridines **6g** and **6f** by mechanism A. However, in the more acidic solvents, methanol and ethanol, the protonated **10g** and **10f** are obtained which cannot decompose to aziridines. Base-catalyzed fragmentation of **10g** + **10f** to enamine **7g** according to

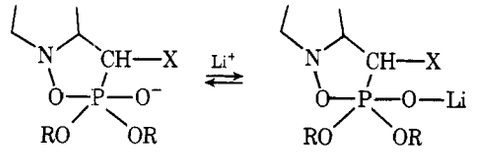


mechanism B is apparently inhibited by the two geminal methyl groups that hinder the approach of base to remove the proton from position 2. Similar behavior is exhibited by nitrone **1e** (Table II, 13–16).

The role played by base in the formation of enamines is demonstrated by experiment 4 in Table I. The high yield of enamine (80% as compared to aziridine 6%) in this experiment demonstrates the kinetic difference between the two modes of fragmentation. In the absence of protic solvent aziridine formation is not inhibited by protonation and both products result from intermediate **9.**

Another aspect is the effect of cation on the course of the reaction. The effect of cation, particularly lithium, upon the steric course of the Wittig reaction[13] and upon the Horner–Emmons[14] reactions has been demonstrated. We found that varying the cation has no effect on the stereochemistry of the products. However, we found, as indicated by the results in

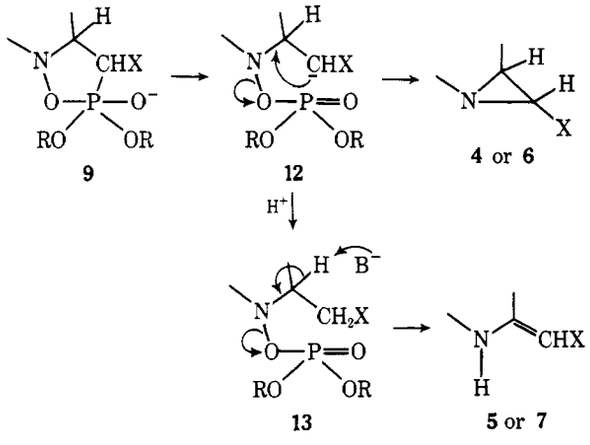
Table III, that change of the cation influences the aziridine: enamine ratio. The difference between the product ratio in reactions 2 and 3 in Table III can presumably be accounted for by the difference in basicities between sodium and potassium *tert*-butoxides. However, a different explanation is needed for the effect of lithium. It has been pointed out[15] that anomalous properties of lithium result mainly from the small size of the atom and of the ion. The polarization power of lithium cation is the greatest of all the alkali metal ions and leads to a singularly great tendency toward covalent bond formation. Consequently it is reasonable to assume that the formation of increased amounts of enaminic products in the presence of lithium is the result of inhibition of the decomposition of intermediate **9** to aziridine, by covalent bond formation between lithium and the negatively charged oxygen.



9 **11**

We have noted throughout this work (Tables I–III) and previously[1,3] the greater tendency to form enamines with the cyanophosphonate **2** than with phosphonoacetates **3.** It may be assumed that the stronger electron-withdrawing properties of the cyano group as compared to those of the carbethoxy group cause more P–C bond breaking in intermediate **9,** X = CN, then when X = CO_2Et, resulting in the formation of **12.**

This carbanion may undergo an S_Ni type reaction leading to aziridine, or protonation to **13,** followed by β-elimination to enamine. The effect of the nature of substituent X upon these two competing reactions of **12** has been discussed in terms of perturbation theory in our previous paper.[1]



9 **12**

Throughout this work and in our previous communications[1,3,11] we noted that the reactions of nitrones with phosphonates studied lead stereoselectively to trans aziridines. In this respect this reaction resembles the "modified Wittig" reaction[16] that leads preferentially to trans olefins. At the present, it seems reasonable to assume that, as in the case of the trans-olefin synthesis, the stereoselectivity of our reaction is a result of thermodynamic control upon the reversible formation and interconversion of the two possible diastereomeric erythro and threo reaction intermediates.

Experimental Section[17]

Starting Materials. Nitrones[18,19] and phosphonates[20] were prepared according to the literature. Diethyl cyanomethylphosphonate-d_2 was prepared by dissolving **2** in D_2O for 2 days and extracted with chloroform. This procedure was repeated four times.

General Procedure for Reactions in Dimethoxyethane. A 50% dispersion of sodium hydride in mineral oil (0.5 g, 0.01 mol) was washed with petroleum ether (bp 40–60 °C) (3 × 10 mL) in an inert atmosphere. After evaporation of the residual petroleum ether, 10 mL of DME (freshly distilled from lithium aluminum hydride) was injected, followed by 0.01 mol of diethyl cyanomethylphosphonate (**2**) or diethyl carboalkoxymethylphosphonate **3** dissolved in 5 mL of DME with cooling. After the liberation of hydrogen ceased 0.01 mol of the corresponding Δ^1-pyrroline *N*-oxide **1** dissolved in 5 mL of DME was introduced. The reaction mixture was stirred under the conditions (time and temperature) indicated in the tables. DME was evaporated in vacuo and the products were isolated as described below. The yields are given in tables.

General Procedure for the Reactions with Sodium Alkoxide in Alcohol. Sodium (0.23 g, 0.01 mol) was dissolved in 10 mL of dry alcohol ROH (R = *t*-Bu, Et, Me) in an inert atmosphere (in case of R = *t*-Bu about 9 h of reflux was needed). After the formation of the alkoxide, 0.01 mol of **2** or **3** dissolved in 5 mL of ROH was injected [the reactions in *tert*-butyl alcohol and ethanol were run using **3** (R = Et) while for those in methanol **3** (R = Me) was used], followed by a solution of 0.01 mol of the corresponding Δ^1-pyrroline *N*-oxide **1** in 5 mL of ROH. The reaction mixture was stirred under the conditions (time and temperature) indicated in tables. After evaporation of the alcohol in vacuo the products were isolated as indicated below. The yields are given in the tables.

Reactions of 1a with Phosphonates 2 and 3 with Potassium *tert*-Butoxide in *tert*-Butyl Alcohol. To a solution of 0.56 g (0.005 mol) of freshly sublimed potassium *tert*-butoxide in 10 mL of dry *tert*-butyl alcohol in an inert atmosphere was injected 0.585 g (0.005 mol) of **2** or 1.12 g (0.005 mol) of **3** (R = Et) dissolved in 2 mL of *tert*-butyl alcohol, followed by a solution of 0.565 g (0.005 mol) of 5,5-dimethyl-Δ^1-pyrroline *N*-oxide (**1a**) in 3 mL of *tert*-butyl alcohol. The reaction mixtures were stirred under the conditions (time and temperature) indicated in Table III. After evaporation of *tert*-butyl alcohol the isolation of the products was carried out in the usual way. The yields are given in Table III.

Reactions of 1a with Phosphonates 2 and 3 with Lithium *tert*-Butoxide in *tert*-Butyl Alcohol. To a solution of lithium *tert*-butoxide prepared by injection of 0.144 g (0.96 mL, 0.00225 mol) of 15% w/v *n*-butyllithium in hexane to 10 mL of dry *tert*-butyl alcohol was added a solution of 0.398 g (0.00225 mol) of **2** or 0.504 g (0.00225 mol) of **3** (R = Et) in 3 mL of *tert*-butyl alcohol followed by a solution of 0.254 g (0.00225 mol) of 5,5-dimethyl-Δ^1-pyrroline *N*-oxide (**1a**) in 2 mL of *tert*-butyl alcohol. The reaction mixtures were stirred under the conditions (time and temperature) indicated in Table III. After evaporation of the *tert*-butyl alcohol, the products were isolated, as indicated below. The yields are given in Table III.

Reaction of 1a with 2 with Sodium Methoxide in Pentane. To a solution of 0.27 g (0.005 mol) of sodium methoxide in 20 mL of dry pentane (freshly distilled from phosphorus pentoxide) in an inert atmosphere was added 0.885 g (0.005 mol) of **2** followed by 0.565 g (0.005 mol) of **1a,** and the reaction mixture was stirred under the conditions (time, temperature) indicated in Table I. After evaporation of pentane the products were isolated as usual. The yields are given in Table I.

Control Experiments. A. Nitrone **1a** (0.113 g, 0.001 mol) which was recovered after stirring in an inert atmosphere for 2 h at room temperature in a solution of sodium ethoxide prepared by dissolving 0.03 g (0.0013 mol) of sodium in dry ethanol (1.5 mL) was found to be identical with unreacted **1a.**

B. Aziridine **4a** (0.136 g, 0.001 mol) was kept in an inert atmosphere for 2 h at room temperature in a solution of sodium ethoxide prepared by dissolving 0.03 g (0.0013 mol) of sodium in dry ethanol (1.5 mL). Examination of the products by NMR and thin layer chromatography indicated the presence of starting material **4a** in addition to **6a,** and the complete absence of **5a** and **7a.**

C. Hydrolysis of 4a with Potassium Hydroxide. A solution of 0.136 g (0.001 mol) of **4a** and potassium hydroxide (0.066 g, 0.0013 mol) in 2 mL of *tert*-butyl alcohol was warmed on a water bath for a few seconds and left to stand overnight at room temperature. After evaporation of the solvent, the residue was taken up in chloroform–petroleum ether (3:2) and passed through a short alumina column. Recrystallization from chloroform–ether (1:1) gave 0.15 g of 2,2-dimethyl-1-azabicyclo[3.1.0]hexane-*exo*-6-carboxamide (**8**): mp 148–149 °C; IR (Nujol) 3300, 3140, 1730 cm^{-1}; NMR ($CDCl_3$) δ 6.45 2 H bs, 2.45 1 H m, 2.28–1.80 2 H m, 2.01 1 H d (J = 2.5 Hz), 1.50–0.98 8 H m; mol wt calcd, 154, found (MS) *m/e* 154, 110 (M − $CONH_2$).

Anal. Calcd for $C_8H_{14}N_2O$: C, 62.33; H, 9.09; N, 18.18. Found: C, 61.96; H, 9.12; N, 18.20.

Isolation of Products. Reactions were followed by thin layer

chromatographic analysis using plates of alumina G.F.$_{254}$ of 0.25-mm thickness. The residues obtained from the reactions after evaporation of the solvent were chromatographed on short columns of neutral alumina (70 g for a reaction on a 0.01 molar scale) to remove the diethylphosphate, followed by preparative thin layer chromatography (alumina G.F.$_{254}$, 1 mm) in those cases where both enaminic and aziridinic products were formed. The solvents used for elution of columns and development of plates ranged from chloroform to chloroform–petroleum ether (bp 40–60 °C) (1:3). In the ester series, the aziridines **6** were found to be more polar than the respectives enamines **7**, which contrasts to the nitrile series in which the aziridines **4** were less polar than the corresponding enamino nitriles **5**. Extraction of the compounds from the alumina in the preparative thin layer chromatographic separations was effected by boiling chloroform. We found that the recovery of the products from the alumina can be considerably improved by immersion of the suspension of alumina in chloroform in an "ultrasonic bath" for a few minutes.

***exo*-6-Cyano-2,2-dimethyl-1-azabicyclo[3.1.0]hexane (4a):** bp 77–90 °C (0.2 mm); mp (from petroleum ether) 77–78 °C; IR (Nujol) 2240 cm^{-1}; NMR ($CDCl_3$) δ 2.80 1 H m, 2.33–2.03 2 H m, 1.94 1 H d (J = 2.5 Hz), 1.45–1.00 2 H m, 1.26 3 H s, 1.17 3 H s; (C_6D_6) δ 2.27 1 H m, 1.70–1.35 2 H m, 1.46 1 H d (J = 2.5 Hz), 1.1–0.2 2 H m, 0.9 6 H s; mol wt calcd 136, found (MS) m/e 136, 108 (M − H_2CN).

Anal. Calcd for $C_8H_{12}N_2$: C, 70.58; H, 8.82; N, 20.58. Found: C, 70.60; H, 9.03; N, 20.19.

Deuterio-4a: IR (Nujol) 3000, 2240, 1480 cm^{-1}; NMR ($CDCl_3$) δ 2.80 1 H s, 2.33–2.03 2 H m, 1.45–1.00 2 H m, 1.26 3 H s, 1.17 3 H s.

5,5-Dimethyl-2-cyanomethylenepyrrolidine (5a): mp 85–87 °C (ether–petroleum ether); IR (Nujol) 3230, 2180, 1600 cm^{-1}; UV (EtOH) 267 nm (ϵ 23 200); NMR ($CDCl_3$) δ 5.80 1 H bs, 3.85 s and 3.55 s total 1 H, 2.69 2 H m, 1.82 2 H t (J = 7.5 Hz), 1.26 3 H s, 1.24 3 H s; mol wt calcd 136, found (MS) m/e 136, 121 (M − CH_3).

Anal. Calcd for $C_8H_{12}N_2$: C, 70.58; H, 8.82; N, 20.58. Found: C, 70.47; H, 9.10; N, 20.30.

***exo*-6-Cyano-2,2,3-trimethyl-1-azabicyclo[3.1.0]hexane (4b + 4c):** bp 84 °C (0.1 mm); IR (neat) 2250 cm^{-1}; NMR ($CDCl_3$) δ 2.75 1 H m, 2.15 1 H d (J = 2 Hz), 2.58–1.42 3 H m, 1.24–0.86 9 H m; mol wt calcd 150, found (MS) 150.

Anal. Calcd for $C_9H_{14}N_2$: C, 72.00; H, 9.33; N, 18.66. Found: C, 72.20; H, 9.39; N, 18.67.

The two diastereoisomers were separated on a glass column, 6 ft × 0.25 in., 10% Carbowax 20M on 60/80 Diatoport W, column temperature 115 °C, flow 20 mL He/min, in a ratio 48:52. Fraction I was contaminated with fraction II; fraction II was obtained in a pure state. Fraction I: NMR ($CDCl_3$) δ 2.75 1 H m, 2.15 1 H d (J = 2 Hz), 2.58–1.42 3 H m, 1.24 3 H s, 1.20 3 H s, 1.16 3 H s, 1.00 3 H s, 0.90 3 H d (J = 8 Hz), 0.86 3 H d (J = 7 Hz). Fraction II: NMR ($CDCl_3$) δ 2.71 1 H m, 2.58–1.42 3 H m, 2.13 1 H d (J = 2 Hz), 1.16 3 H s, 1.02 3 H s, 0.86 3 H d (J = 7 Hz).

4,5,5-Trimethyl-2-cyanomethylenepyrrolidine (5b): mp 87–89 °C (petroleum ether); IR (Nujol) 3290, 3200, 2190, 1610 cm^{-1}; UV (EtOH) 267 nm (ϵ 20 000); NMR ($CDCl_3$) δ 5.50 1 H bs, 3.85 t (J = 1 Hz), and 3.55 d (J = 1 Hz) total 1 H, 2.85–1.85 3 H m, 1.25 3 H s, 1.04 3 H s, 0.98 3 H d (J = 6 Hz); mol wt calcd 150, found (MS): m/e 150, 135 (M − CH_3), 120 (M − 2CH_3), 105 (M − 3CH_3), 108 (M − CH_3 − HCN).

Anal. Calcd for $C_9H_{14}N_2$: C, 72.00; H, 9.33; N, 18.66. Found: C, 71.87; H, 9.19; N, 18.64.

***exo*-6-Cyano-3,3,5-trimethyl-1-azabicyclo[3.1.0]hexane (4d):** bp 67–68 °C (0.3 mm); IR (neat) 2220 cm^{-1}; NMR ($CDCl_3$) δ 3.10 1 H d (J = 12.75 Hz), 2.46 1 H d (J = 12.75 Hz), 2.20 1 H s, 1.86 2 H m, 1.35 3 H s, 1.01 3 H s, 0.90 3 H s; (C_6D_6) δ 2.86 1 H d (J = 12.75 Hz), 2.05 1 H d (J = 12.75 Hz), 1.60 1 H s, 1.33 2 H m, 1.27 3 H s, 0.78 3 H s, 0.61 3 H s; mol wt calcd 150, found (MS): m/e 150, 135 (M − CH_3).

Anal. Calcd for $C_9H_{14}N_2$: C, 72.00; H, 9.33; N, 18.66. Found: C, 71.50; H, 9.84; N, 18.50.

***exo*-6-Cyano-2,2,4,4-tetramethyl-1-azabicyclo[3.1.0]hexane (4e):** bp 75 °C (0.5 mm); IR (neat) 2250 cm^{-1}; NMR ($CDCl_3$) δ 2.55 1 H d (J = 2.25 Hz), 1.90 1 H d (J = 2.25 Hz), 1.50–1.02 14 H m (includes CH_2 and four methyls at δ 1.31 s, 1.27 s, 1.16 s, 1.12 s); mol wt calcd 164, found (MS) m/e 164, 163, 149 (M − CH_3).

Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.17; H, 9.75; N, 17.04. Found: C, 73.07; H, 10.03; N, 17.35.

3,3,5,5-Tetramethyl-2-cyanomethylenepyrrolidine (5e): mp 185–187 °C (chloroform–petroleum ether); IR (Nujol) 3270, 2170, 1600 cm^{-1}; UV (CH_3OH) 268 nm (ϵ 18 600); NMR ($CDCl_3$) δ 5.52 1 H bs, 3.45 1 H s, 1.82 2 H s, 1.30 6 H s, 1.21 6 H s; mol wt calcd 164, found (MS) m/e 164, 149 (M − CH_3).

Anal. Calcd for $C_{10}H_{16}N_2$: C, 73.17; H, 9.75; N, 17.07. Found: C, 73.42; H, 9.85; N, 16.97.

***exo*-6-Carboalkoxy-2,2-dimethyl-1-azabicyclo[3.1.0]hexane. A. 6a, R = Et:** bp 80 °C (0.2 mm); IR (neat) 1725 cm^{-1}; NMR ($CDCl_3$) δ 4.16 2 H q (J = 7.25 Hz), 2.70 1 H m, 2.32–1.90 2 H m, 2.11 1 H d (J = 2.5 Hz), 1.50–1.13 11 H m; mol wt calcd 183, found (MS) 183.

Anal. Calcd. for $C_{10}H_{17}NO_2$: C, 65.57; H, 9.29. Found: C, 65.78; H, 9.48.

B. 6a, R = CH_3: oil; IR (neat) 1720 cm^{-1}; NMR ($CDCl_3$) δ 3.66 3 H s, 2.83–2.66 1 H m, 2.13 1 H d (J = 2.5 Hz), 2.30–1.50 2 H m, 1.50–1.17 8 H m; mol wt calcd 169, found (MS) 169.

5,5-Dimethyl-2-carboalkoxymethylenepyrrolidine. A. 7a, R = Et: bp 80 °C (0.1 mm); IR (neat) 3320, 1710, 1600 cm^{-1}; UV (EtOH) 279 nm (ϵ 18 700); NMR ($CDCl_3$) δ 7.70 1 H bs, 4.36 1 H bs, 4.25 2 H q (J = 6.75 Hz), 2.62 2 H t (J = 7.5 Hz), 1.77 2 H t (J = 7.5 Hz), 1.25 3 H t (J = 6.75 Hz), 1.27 6 H s: mol wt calcd 183, found (MS) 183.

B. 7a, R = CH_3: oil; IR (neat) 3320, 1710, 1600 cm^{-1}; NMR ($CDCl_3$) δ 7.87 1 H bs, 4.47 1 H s, 3.60 3 H s, 2.70 2 H t (J = 7.5 Hz), 1.80 2 H t (J = 7.5 Hz), 1.27 6 H s; mol wt calcd 169, found (MS) m/e 169, 154 (M − CH_3), 138 (M − OCH_3).

***exo*-6-Carboethoxy-2,2,3-trimethyl-1-azabicyclo[3.1.0]hexane (6b + 6c):** bp 87 °C (0.15 mm); IR (neat) 1740 cm^{-1}; NMR ($CDCl_3$) δ 3.97 2 H q (J = 7 Hz), 2.57–2.42 1 H m, 2.19 1 H d (J = 2.25 Hz), 2.13–1.32 3 H m, 1.32–0.67 12 H m; mol wt calcd 197, found (MS) m/e 197, 182 (M − CH_3), 168 (M − C_2H_5).

The two stereoisomers were separated on a glass column, 6 ft × 0.25 in., 10% Carbowax 20M on 60/80 Diatoport W, column temperature 160 °C, flow 40 mL He/min.

4,5,5-Trimethyl-2-carboalkoxymethylenepyrrolidine. A. 7b, R = Et: bp 88 °C (0.2 mm); IR (neat) 3330, 1730 cm^{-1}; UV (CH_3OH) 284 nm (ϵ 10 086); NMR ($CDCl_3$) δ 7.76 1 H bs, 4.34 1 H s, 4.02 2 H q (J = 7 Hz), 2.75–1.44 3 H m, 1.39–0.84 12 H m; mol wt calcd 197, found (MS) m/e 197, 182 (M − CH_3), 152 (M − OC_2H_5).

B. 7b, R = CH_3: oil; IR (neat) 3330, 1730, 1600 cm^{-1}; UV (CH_3OH) 282 nm (ϵ 9103); NMR ($CDCl_3$) δ 7.65 1 H bs, 4.28 1 H s, 3.48 3 H s, 2.85–1.35 3 H m, 1.25–0.75 9 H m; mol wt calcd 183, found (MS) m/e 183, 168 (M − CH_3).

C. 7b, R = *t*-Bu: solid; IR (Nujol) 3330, 1710, 1600 cm^{-1}; UV ($CHCl_3$) 284 nm (ϵ 9546); NMR ($CDCl_3$) δ 7.62 1 H bs, 4.32 1 H s, 2.97–1.57 3 H m, 1.44 9 H s, 1.34–0.67 9 H m; mol wt calcd 225, found (MS) m/e 225, 169 (M − C_4H_8).

***exo*-6-Carboethoxy-2,4,4-trimethyl-1-azabicyclo[3.1.0]hexane (6g + 6h):** oil; IR (neat) 1725 cm^{-1}; NMR ($CDCl_3$) δ 4.35–3.80 2 H q (J = 7.5 Hz), 2.55 1 H d (J = 2.5 Hz), 1.88 1 H d (J = 2.5 Hz), 2.45–1.60 1 H m, 1.55–1.00 14 H m; mol wt calcd 197, found (MS) m/e 197, 182 (M − CH_3), 152 (M − OC_2H_5). This mixture was found to contain two components that could not be separated for determination of their relative amount. Conditions: glass column, 6 ft × 0.25 in., 10% Carbowax 20M on 60/80 Diatoport W, column temperature 160 °C, flow 40 mL He/min.

***exo*-6-Carboalkoxymethyl-2,2,4,4-tetramethyl-1-azabicyclo[3.1.0]hexane. A. 6e, R = Et:** bp 78–79 °C (0.3 mm); IR (neat) 1730 cm^{-1}; NMR ($CDCl_3$) δ 4.25 2 H q (J = 7 Hz), 2.62 1 H d (J = 2 Hz), 2.20 1 H d (J = 2 Hz), 1.58–1.10 17 H m; mol wt calcd 211, found (MS) m/e 211, 196 (M − CH_3).

Anal. Calcd for $C_{12}H_{21}NO_2$: C, 68.24; H, 9.95; N, 6.63. Found: C, 68.58; H, 9.75; N, 6.61.

B. 6e, R = *t*-Bu: oil (purified by preparative gas chromatography); IR (neat) 1730 cm^{-1}; NMR ($CDCl_3$) δ 2.42 1 H d (J = 2.25 Hz), 1.99 1 H d (J = 2.25 Hz), 1.40 9 H s, 1.47–1.07 14 H m; mol wt calcd 239, found (MS): m/e 183 (M − C_4H_8).

Registry No.—1a, 3317-61-1; **1b,** 3146-84-7; **1d,** 6931-11-9; **1e,** 10135-38-3; **1f,** 4567-18-4; **2,** 2537-48-6; **3,** 867-13-0; **3** (R = Me), 1067-74-9; **4a,** 57740-50-8; deuterio-**4a,** 61649-96-5; **4b,** 61649-97-6; **4c,** 61740-03-2; **4d,** 61649-98-7; **4e,** 61649-99-8; *E*-**5a,** 57740-52-0; *Z*-**5a,** 57740-51-9; *E*-**5b,** 61650-00-8; *Z*-**5b,** 61650-12-2; **5e,** 61650-01-9; **6a** (R = Et), 57740-49-5; **6a** (R = Me), 61650-02-0; **6b** (R = Et), 61650-03-1; **6c** (R = Et), 61688-35-5; **6e** (R = *t*-Bu), 61650-04-2; **6e** (R = Et), 61650-05-3; **6g,** 61650-06-4; **6h,** 61688-36-6; **7a** (R = Et), 61650-07-5; **7b** (R = Et), 61650-08-6; **7b** (R = Me), 61650-09-7; **7b** (R = *t*-Bu), 61650-10-0; **8,** 61650-11-1.

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(21) **Note Added in Proof.** While this paper was processed, the full paper by Black and Davis appeared: D. St. C. Black and V. C. Davis, *Aust. J. Chem.*, **29**, 1735 (1976). In this paper full experimental data are given for reactions of Δ^1-pyrroline *N*-oxides **1a**, **1d**, and **1e** with **3** using sodium hydride in DME. The physical data given for the products of the reactions of **1a** and **1e** agree with those obtained in our work for **6a**, **6e**, and **7a** (R = C_2H_5). However, Black and Davis assigned structure **6d** (R = C_2H_5) for the product of the reaction of **1d** with **3**. In this reaction we obtained a mixture of products **6g** and **6h**.

Cycloaddition Reactions of Vinyl Sulfene Generated from Thiete 1,1-Dioxide[1]

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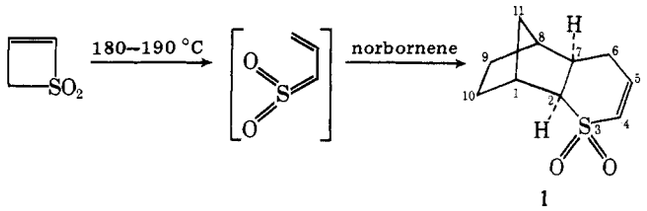
Thermolysis of thiete 1,1-dioxides in the presence of norbornenes gives cycloadducts of the Diels–Alder type resulting from the trapping of vinyl sulfene formed by ring opening of the thiete 1,1-dioxides. Other cyclic or acyclic alkenes gave little or no reaction.

Sulfenes ($R_2C{=}SO_2$) undergo [2 + 2] cycloadditions to activated olefins (e.g., enamines) to yield thietane 1,1-dioxides,[2] and sulfene itself ($CH_2{=}SO_2$) may serve as a dienophile in a [4 + 2] cycloaddition to enamino ketones.[3] Vinyl sulfenes (e.g., $R_2C{=}CHCH{=}SO_2$) have the capability of undergoing both [2 + 2] and [4 + 2] cycloadditions in which the vinyl sulfene may serve as either the two- or the four-electron reactant. These conjugated sulfenes have been proposed as intermediates in reactions of 1- or 2-propenesulfonyl chloride,[4] in the photolysis of cyclic unsaturated sultones and sulfones,[5] and in the thermal decomposition of thiete 1,1-dioxides.[6] The presence of vinyl sulfene intermediates has been supported by trapping experiments with phenol[6b,d] and by the formation of sultines[6a–d,g] and α,β-unsaturated carbonyl compounds.[6c,e,f] This report is about the trapping of vinyl sulfene intermediates acting as dienes in Diels–Alder or [4 + 2] cycloaddition reactions. Previously, Truce and Norell reported that vinyl sulfene obtained from 1- or 2-propenesulfonyl chloride gave a low yield (6.5–7.6%) of a [4 + 2] adduct with ketene diethyl acetal.[4a]

Results and Discussion

When thiete 1,1-dioxide is thermolyzed at 180–190 °C in the presence of norbornene in a sealed, degassed flask for 5 days, a 63–79% yield of an adduct, **1**, was obtained. The solvent was either *m*-xylene or benzene, the latter being preferred because of higher yields and the ease of workup of the reaction mixture. The thermolysis is quite clean, no tar being formed. At the end of the reaction period, a pale yellow solution remains which yields a crystalline adduct on removal of solvent.



1

The elemental analysis and mass spectrum are in agreement with the proposed structure, **1**, 3-thiatricyclo[6.2.1.$0^{2,7}$]undec-4-ene 3,3-dioxide. In addition to providing the molecular weight, the mass spectrum shows evidence for the retro-Diels–Alder reaction: intense ions at *m/e* 94 for norbornene and at *m/e* 104 for vinyl sulfene are observed. The presence of the sulfone group is indicated by strong absorption in the infrared at 1298 and 1120 cm^{-1}. A carbon–carbon double bond is indicated by the infrared spectrum (1620 cm^{-1})[7] and by the ^1H and ^{13}C NMR spectra.[8] The presence of the double bond excludes structure **2** and the ^1H NMR spectrum excludes structures **3** and **4**; the latter, a sulfene, would not be expected to be particularly stable. The double bond in **1** is conjugated with the sulfone group and undergoes, as expected, a Michael reaction with the anion of diethyl malonate to yield **5**.

The carbon chemical shifts of **1** are compared in Chart I with those of dihydrothiapyran 1,1-dioxide and with those calculated[9] for the strictly carbocyclic analogue (**6**) of **1**. The chemical shifts of the alkene carbons in **1** are assigned on the basis of the shifts observed in thiete 1,1-dioxide.[10] A partially proton-decoupled ^{13}C NMR spectrum of **1** shows a doublet for each alkene carbon atom which is caused by a one-bond coupling ($J_{\alpha CH}$ = 165; $J_{\beta CH}$ = 184 Hz). Each component of the