starting terminal acetylene which can be recovered by chromatography. We believe that it is important to employ an excess of the aluminum acetylide because the initial product of conjugate addition is an aluminum enolate which can react with additional unsaturated ketone to give the aldol adduct. In the presence of excess aluminum acetylide, the added unsaturated ketone in the presence of the nickel catalyst preferentially reacts with it. If less aluminum acetylide is employed, then the desired product and oligomers are observed. Specifically, we could isolate, in addition to the desired product, the compound formed by aldol condensation[11] of the aluminum enolate derived from conjugate addition to methyl vinyl ketone with another equivalent of methyl vinyl ketone.



$$(2)$$
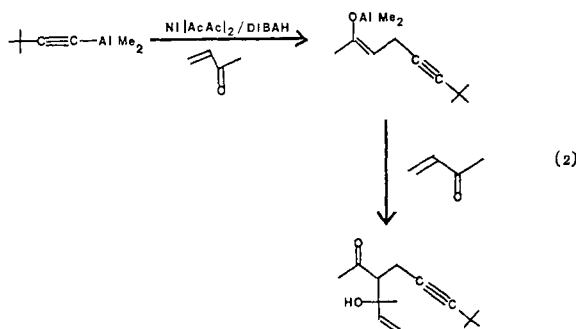
Lewis basic solvents such as THF are not effectively employed and reduced yields in this solvent are observed. Adding oxygen functionality to the unsaturated ketone also slows down the rate of conjugate addition. Thus cyclohexenone and cyclopentenone react more rapidly with this conjugate addition reagent system than does 4-cumyloxycyclopentenone.

We have examined the use of other acetylides in this conjugate addition procedure. However, we find that lithium, magnesium, zinc, and bis(cyclopentadienyl)zirconium acetylides give rise to no or only trace amounts of desired conjugate adduct. We have observed that Ni(acac)$_2$ in the absence of added Dibah will catalyze conjugate addition of dialkylaluminum acetylides to $\alpha,\beta$-enones;[8] however, here, a yield approximating an equimolar amount (based on nickel) of coupled diacetylene is obtained. An investigation into the use of other nickel species as possible catalysts revealed that NiCl$_2$(PEt$_3$)$_2$, Ni(PPh$_3$)$_4$, and Ni[P(OPh)$_3$]$_4$, in conjunction with aluminum acetylides, gave rise only to trace amounts of the desired conjugate adduct at best.

As shown in Chart I, we have observed that direct addition occurs of acetylide to $\alpha,\beta$-enones via dimethylaluminum acetylide.[12] Here yields were found to suffer from product destruction over a relatively short period of time in the presence of the catalytically reactive nickel species. We attribute this to side reactions involving the product, a terminal acetylene.[13] As indicated in Chart I, this difficulty can be easily circumvented by the use of the (trimethylsilyl)acetylide reagent shown.[14] Silylated products obtained could be cleanly and easily converted to terminal acetylenes through cleavage with KF.[15]

We are currently investigating the structure of the catalytically active species formed from Ni(acac)$_2$ and Dibah and are also investigating alkylation chemistry of the dialkylaluminum enolates[16] formed by these conjugate addition routes.

Raman spectra, and Professor B. B. Snider for helpful comments and suggestions.

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(9) A small amount of the diyne product of dimerization of RC≡CH is observed (<5%).
(10) NMR spectral data (CCl$_4$): $\delta$ 1.05 (s, 9, H-7), I.5 ("d", 6, H-2, 3.5-Hz separation), I.9–2.4 (m, 3, H-5 and H-6), 2.8 (m, 2, H-4), 3.85 ("q", 1, $J = 5.2$ Hz, H-3), 7.2 (m, 5, H-1).
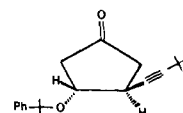


(11) It is possible that this condensation could be catalyzed by a Ni species.
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(14) HC≡CSiMe$_3$ was prepared by the method of U. Krüerke, *J. Organomet. Chem.*, **21**, 83 (1970). Me$_2$AlC≡CSiMe$_3$ was prepared from the acetylene by treatment with MeLi in ether at 0 °C, followed by reaction of the LiC≡CSiMe$_3$ with Me$_2$AlCl in ether at −6 °C for 1.5 h.
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(17) Alfred P. Sloan Fellow, 1976–.

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**Cyanoketenes. Mechanism of Cycloaddition of Chlorocyanoketene to Imidates**

*Sir:*

The most widely employed synthetic route to 2-azetidinones ($\beta$-lactams) involves the reaction of an acid halide with an imine in the presence of an amine base.[1] It is generally assumed that this transformation is actually a nonconcerted [2 + 2] cycloaddition of a ketene with the imine and that a dipolar zwitterionic intermediate is the penultimate precursor to the $\beta$-lactam. However, little unambiguous evidence has appeared to substantiate this mechanism. Evidence for the nonconcerted nature of the reaction comes primarily from the facts that the cycloadditions are often nonstereospecific when prochiral reagents are employed, and, in some cases, adducts are formed in which the ratio of ketene to imine is 2:1. Even though such data are consistent with a ketene precursor, a mechanism which is as reasonable would be an initial acylation of the imine by the acid halide followed by proton abstraction to give the zwitterion and its subsequent ring closure to the $\beta$-lactam.[2] That preformed ketenes do cycloadd to imines has been es-

tablished.[3] However, until recently, most of this work focussed upon symmetrical ketenes such as diphenyl and dimethyl, and thus, no stereochemical probe of the reaction was possible. Recently, studies of the cycloadditions of cyanoketenes (*tert*-butyl-, methyl-, chloro-, bromo-, and iodo-) to imines, formimidates, and thioformimidates have revealed that the resulting β-lactams are formed by a stereospecific route.[4] That is, the 2-azetidinones are those in which the C-3 cyano group and the C-4 proton are in a trans relationship. Such stereochemistry is counter to that expected for a concerted [$_\pi 2_s$ + $_\pi 2_a$] cycloaddition. However, the fact that the reactions are highly stereospecific is not the usual outcome of a stepwise process. *This mechanistic conflict has now been unambiguously resolved by a set of unique experiments reported herein which clearly establish the dipolar nonconcerted pathway. Specifically, and for the first time, the zwitterionic intermediate proposed in a cyanoketene/imidate cycloaddition has been independently generated, trapped, and shown to give the same product and stereochemistry as obtained in the cycloaddition itself.*

The genesis of the mechanistic probe described here stems from our earlier observation that 4-azido-3-halo-5-alkoxy-2-pyrrolinones give β-lactams upon thermolysis and that a source of chlorocyanoketene exists from the thermolysis of β-azido-α-chloro-γ-methoxy-$\Delta^{\alpha,\beta}$-crotonolactone.[5] Thus, our initial study was to compare the products obtained from the thermolysis of 4-azido-3-chloro-1-cyclohexyl-5-ethoxy-2-pyrrolinone (**1**)[5] with those resulting from the cycloaddition
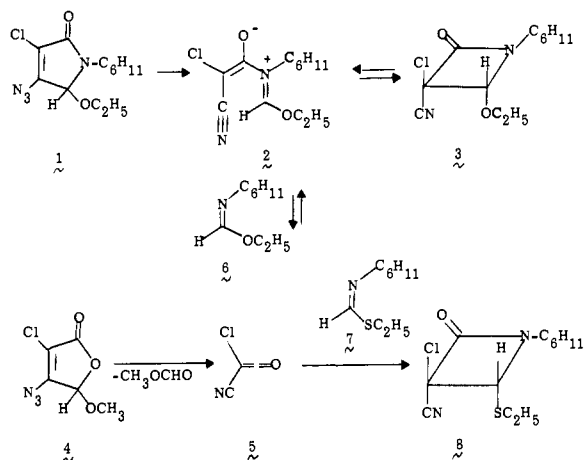


of chlorocyanoketene (**5**) to *N*-cyclohexyl-*O*-ethylformimidate (**6**). Thermolysis of **1** in refluxing benzene ($k$ = 0.24 h$^{-1}$)[6] gave only the β-lactam, **3** (94%).[4c] The same product was obtained in similar yield when **4** was decomposed in refluxing benzene containing a 10% molar excess of the imidate, **6**. In this latter experiment it was also shown that the rate of the decomposition of the chlorocyanoketene precursor, **4**, was independent of the imidate concentration, and thus any mechanism in which the imidate **6** interacts directly with the butenolide, **4**, prior to ketene formation is unlikely.[7] These results alone clearly do not establish a common intermediate to the β-lactam, **3**, from both the pyrrolinone and the ketene cycloaddition since the conversion of **1** to **3** could arise by at least three possible pathways, i.e., (1) a concerted ring contraction; (2) fragmentation of **1** to chlorocyanoketene, **5**, and the imidate, **6**, followed by their subsequent cycloaddition to give **3**; (3) cleavage of **1** to the zwitterion, **2**, and its subsequent ring closure to **3**.

In order to investigate the above possibilities the decomposition of **1** was accomplished as described above except that a 1.0 molar equiv of *N*-cyclohexyl-*S*-ethylthioformimidate (**7**) was added. Here, both β-lactams, **8** and **3**, were realized, and after 24% conversion (30 min) of the starting azide, **1**, the respective ratio of these products was 1.3:1.0. This ratio increased

to 1.9:1.0 after 96% conversion (5.0 h). Next, the thermolysis (refluxing benzene) of **4** in the presence of 1.0 molar equiv of each of the imidates **6** and **7** was investigated in order to obtain an estimate of the relative rates of the reaction of chlorocyanoketene with the respective imidates. Here again, both β-lactams **8** and **3** were formed, and after ~25% conversion of **4** (15 min), their respective ratio was 2.4:1.0 which increased to 3.3:1.0 after complete reaction (~4.5 h). The observed time dependence of the **8** to **3** product ratio in the above experiments is due to the fact that the β-lactams slowly revert to chlorocyanoketene and imidate in refluxing benzene. For example, when a benzene solution containing equivalent amounts of the β-lactam, **3**, and the thioimidate, **7**, was refluxed for 48 h an equilibrium mixture of the two β-lactams **8** (82%) and **3** (18%) was obtained.[8] During the early stages of this equilibration experiment the rate of disappearance of **3** follows pseudo-first-order kinetics[6] and a rate constant of $k$ = 0.045 h$^{-1}$ can be estimated. This is 5.3 times slower than the rate of decomposition of the pyrrolinone, **1** ($k$ = 0.24 h$^{-1}$). The salient points of these data are the following: (1) thermolysis of **1** in the presence of **7** gives both **8** and **3**; (2) chlorocyanoketene reacts with **7** faster than it does with **6**; (3) the β-lactam, **3**, reverts to chlorocyanoketene in refluxing benzene, but at a slower rate than the decomposition of **1**.

The most consistent interpretation of these results is as follows. A concerted ring contraction of **1** to **3** can be ruled out. This is eliminated on the fact that both β-lactams **8** and **3** are formed when **1** is decomposed in the presence of the thioimidate, and that very little of **8** could arise from the cleavage of **3** to chlorocyanoketene after only 30 min of reaction time. Also, a pure ketene mechanism is unreasonable since, if this were so, one would expect the ratio of **8** to **3** to be much greater than the observed 1.3:1.0 after 30 min. That is, since chlorocyanoketene reacts faster with the thioformimidate, **7**, than with its oxygen analogue, **6**, and since the concentration of **6** would be very much smaller relative to that of **7** during the early stages of the reaction, one can reasonably assume that all ketene formed during the early stages of the decomposition of **1** would be trapped by **7** to give **8**. Since after 30 min 43% of the product mixture is the β-lactam, **3**, and 57% is the β-lactam, **8**, a mechanism in which **1** exclusively fragments to chlorocyanoketene and *N*-cyclohexyl-*O*-ethylformimidate and that these then cycloadd to give **3** must be rejected. That leaves as the most reasonable alternative, a mechanism in which the pyrrolinone, **1**, cleaves to the zwitterion, **2**, and that this partitions between ring closure (43%) to β-lactam, **3**, and cleavage (57%) to chlorocyanoketene and imidate.

One would anticipate that a zwitterion such as **2** could be trapped with a protic solvent.[9] Therefore, the decomposition of **1** was carried out in refluxing anhydrous ethanol (11 h). This resulted in a mixture of products which has not yet been completely resolved. However, the results are exceptional in some regards. The four major products, as revealed by $^1$H NMR and $^{13}$C NMR analysis of the crude reaction mixture, are ethyl chlorocyanoacetate,[5] *N*-cyclohexyl-1-chloro-1-cyanoacetamide (**10**), *N*-cyclohexyl-*N*-(1,1-diethoxymethyl)-1-chloro-1-cyanoacetamide (**9**), and the β-lactam, **3**, and these are formed in a respective ratio of 4.0:3.0:2.3:1.0. The ester and β-lactam were identified by analysis of the $^{13}$C and $^1$H NMR spectra of the crude reaction mixture with and without authentic samples added. The amides, **9** and **10**, were isolated in pure form and identified by spectral (IR, NMR, $^{13}$C NMR, mass spectra) and analytical properties which are all in strict accord with their proposed formulations. In addition to the above products, several minor and as yet unidentified compounds were detected. However, the critical observation is that the amides **9** and **10** are formed in reasonable yields and that these are products that one would anticipate as arising from ethanolysis of the zwitterion **2**.

2         9         10
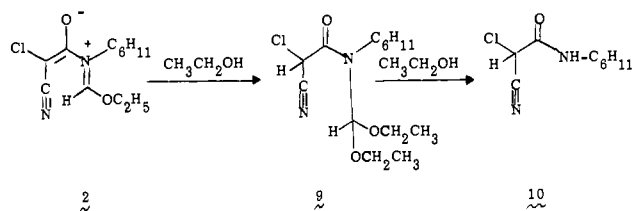
Finally, a brief comment on the stereospecificity of cyanoketene/imidate cycloadditions is in order. As mentioned,[4] a large variety of such cycloadditions have now been studied, and in all cases the reactions appear to be stereospecific, giving $\beta$-lactams having stereochemistry analogous to **3**. We suggest that such results from a conrotatory ring closure of the zwitterionic intermediates analogous to **2**. Thus, an endo preference for the cyano group and the iminium ion proton in these zwitterions must be invoked. Such structures are not completely obvious on steric grounds alone, particularly for chlorocyanoketene cycloadditions. However, an electrostatic attraction between the negative charge density on the cyano group in **2** and the positive charge of the iminium ion may dictate the suggested endo preference of the cyano group, while endo preference for the iminium ion proton can be made on the basis of steric arguments.

In conclusion we wish to summarize some significant points resulting from this investigation. (1) For the first time the zwitterion resulting from the interaction of a ketene with an imidate has been independently generated and shown to give the same products as the cycloadditions themselves. (2) The fact that a zwitterion is formed in the thermolysis of **1** establishes our earlier general proposal that such intermediates can result from appropriately substituted vinyl azides and thus a powerful predictive model is at hand.[5] (3) The results here provide a precedent that suggests a general mechanistic probe for the cycloadditions of cyanoketenes. That is, from appropriately substituted cyclic $\beta$-azidoenones one can envisage the generation of zwitterions that could result from the cycloaddition of cyanoketenes to ketenes, alkenes, allenes, etc. (4) From a purely synthetic perspective, the construction of $\beta$-lactams from the readily available azidopyrrolinones[5] may have clear advantages over simple cycloadditions of cyanoketenes to imines, particularly where the imines are difficult to prepare.

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(6) The rate of decomposition was followed by ¹H NMR analysis of the reaction solution as a function of time.
(7) It is, of course, possible that an intermediate in the thermolysis of **4** reacts with the imidate, **6**, to ultimately give **3**. However, we do not consider this to be a likely process.
(8) The equilibrium was also approached starting with equivalent amounts of **8** and **6**. Here, after 48 h in refluxing benzene, the respective concentrations of **8** and **3** were 89 and 11%.
(9) Such trapping exeriments are analogous to the elegant work of R. Huisgan

and his co-workers concerning the cycloaddition of TCNE to enol ethers. See, for example, R. Huisgen, *Acc. Chem. Res.*, **10**, 117 (1977); H. B. Kagan and J. L. Luche, *Tetrahedron Lett.*, 3093 (1968).
(10) Taken in part from the Ph.D. Dissertation of Louis Hernandez, Jr.

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## Preparation of $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$. The First Organometallic Thionitrosyl Complex[1]

*Sir:*

At the present time there is a striking paucity of thionitrosyl complexes, and the few such coordination compounds that are known[2] result from the reaction of elemental sulfur, propylene sulfide, or disulfur dichloride with coordinated nitrido ligands in the precursors. We now wish to report that trithiazyl trichloride, $S_3N_3Cl_3$, can be used to directly introduce the thionitrosyl functionality into an organometallic complex by the reaction

$$Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3] + \tfrac{1}{3}(S_3N_3Cl_3) \xrightarrow[-78\ °C]{THF}$$

$$(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS) + CO + NaCl$$
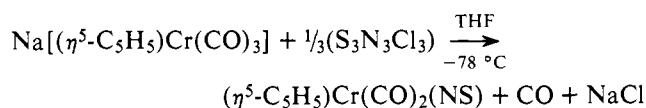
Furthermore, a comparison of the physical properties of the new thionitrosyl product (I) with those exhibited by its nitrosyl analogue (II)[3] enables us, for the first time, to contrast the bonding properties of NO and NS ligands.
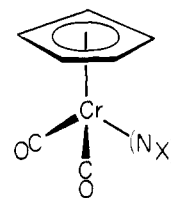


I, X = S;   II, X = O

In a typical experiment 4.50 g (20.1 mmol) of $Na[(\eta^5\text{-}C_5H_5)Cr(CO)_3]$[3] were dissolved in 100 mL of THF under $N_2$ and the resulting yellow solution was cooled to $-78\ °C$. To this rapidly stirred solution was added dropwise a bright green THF solution (40 mL) containing 1.55 g (6.34 mmol) of $S_3N_3Cl_3$.[4] Gas evolution occurred, a precipitate formed, and the reaction mixture developed a dark red-brown coloration. After the addition of the $S_3N_3Cl_3$ solution was complete, the mixture was stirred for 1 h at $-78\ °C$ and then was allowed to warm slowly to room temperature. Solvent was removed in vacuo and the residue was extracted with hexane (250 mL) and filtered. The filtrate was taken to dryness in vacuo and sublimation of the dried residue at $35\ °C$ ($5 \times 10^{-3}$ mm) onto a water-cooled probe produced 0.93 g (4.25 mmol, 21% yield) of crystalline $(\eta^5\text{-}C_5H_5)Cr(CO)_2(NS)$. Anal. Calcd for $C_7H_5CrO_2NS$: C, 38.36; H, 2.30; N, 6.39. Found:[5] C, 38.64; H, 2.20; N, 6.37.

Dicarbonyl $(\eta^5\text{-cyclopentadienyl})$thionitrosylchromium (I) is a dark red-violet, diamagnetic solid which dissolves in common organic solvents to give blood-red solutions that eventually deposit some decomposed matter when exposed to air for several hours; I itself is reasonably stable in air, but is best stored under $N_2$. Its IR spectrum in hexane (Table I) exhibits the expected three strong bands attributable to terminal CO and NS groups. The $\nu(NS)$ band occurs in the frequency range found[2] for other thionitrosyl complexes. The $\nu(CO)$ bands of I appear at slightly higher frequencies than

    