

ing the formation of $\text{Mo}(\text{CN})_8^{3-}$.¹⁴ The very high optical density of the solution prevented quantitative measurements. The quantum yield of proton uptake, $\Phi(\text{H}^+)$, increased with increasing $\text{Mo}(\text{CN})_8^{4-}$ concentration. The plot of $1/\Phi(\text{H}^+)$ vs. $1/[\text{Mo}(\text{CN})_8^{4-}]$ was linear with $\Phi(\text{H}^+)_{\text{lim}} = 0.05 \pm 0.01$ and $K_{\text{SV}} = 170 \pm 50 \text{ M}^{-1}$, in agreement with the value obtained from the quenching experiments (140 M^{-1} , Figure 1). The reaction was not suppressed by 0.1 M HCN, which prevented CN^- release from directly excited $\text{Mo}(\text{CN})_8^{4-}$ (see also ref 15). As the quantum yield of the direct $\text{Mo}(\text{CN})_8^{4-}$ aquation was 0.8 under our experimental conditions, the quenching of $^*\text{Ru}(\text{bpy})_3^{2+}$ cannot occur by energy transfer to a reactive $\text{Mo}(\text{CN})_8^{4-}$ level.¹⁶ For the $\text{Ru}(\text{bpy})_3^{2+}$ - $\text{Os}(\text{CN})_6^{4-}$ system, irradiation caused an increase in pH and the appearance of four bands at 306, 330, 405, and 414 nm, which are characteristic of $\text{Os}(\text{CN})_6^{3-}$.¹⁸ For short irradiation periods, the apparent quantum yield of $\text{Os}(\text{CN})_6^{3-}$ formation was of the order of 0.005. After long irradiation periods, both the pH and spectrum reached constant values. No spectral change was ever observed in the 450-nm region where $\text{Ru}(\text{bpy})_3^{2+}$ exhibits a very intense absorption band. The final $\text{Os}(\text{CN})_6^{3-}$ concentration was $\sim 1 \times 10^{-4} \text{ M}$, i.e., $\sim 2.5\%$ of the initial $\text{Os}(\text{CN})_6^{4-}$ concentration and $\sim 150\%$ of the $\text{Ru}(\text{bpy})_3^{2+}$ concentration. For the $\text{Ru}(\text{bpy})_3^{2+}$ - $\text{Ni}(\text{CN})_4^{2-}$ system, neither the pH nor the spectrum showed any change upon irradiation.

The results obtained with $\text{Mo}(\text{CN})_8^{4-}$ and $\text{Os}(\text{CN})_6^{4-}$ show that a reductive quenching (reaction 2) takes place and that a fraction of $\text{Mo}(\text{CN})_8^{3-}$ and $\text{Os}(\text{CN})_6^{3-}$ escapes the back-reduction by $\text{Ru}(\text{bpy})_3^+$. The quantum yield values show that this fraction is very small. As no $\text{Ru}(\text{bpy})_3^{2+}$ is lost, an alternative reoxidation path for $\text{Ru}(\text{bpy})_3^+$ must be present. The most probable is the reaction with O_2 , whose rate constant is reported to be $1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.¹⁹ The observed H^+ uptake is presumably due to a subsequent reaction of O_2^- with H^+ ,²⁰ although direct oxidation of $\text{Ru}(\text{bpy})_3^+$ by H^+ cannot be ruled out. For both $\text{Mo}(\text{CN})_8^{4-}$ and $\text{Os}(\text{CN})_6^{4-}$, quenching by energy transfer is not thermodynamically favorable (Table I) and oxidative quenching is rather implausible, so that the only important quenching mechanism is presumably reaction 2.²² For the same reasons, there is little doubt that the only quenching mechanism for $\text{Fe}(\text{CN})_6^{4-}$ is reaction 2 (see also ref 4).

The data gathered in Table I merit some further comments. With $\text{Cr}(\text{CN})_6^{3-}$, oxidative quenching is not thermodynamically favorable, while reductive quenching is presumably even less favorable since it should lead to a Cr(IV) cyanide complex. Energy transfer appears thus to be the only possible quenching mechanism, as already shown by sensitized luminescence experiments.²⁴ With $\text{Fe}(\text{CN})_6^{3-}$, energy transfer is not allowed and reductive quenching is completely implausible, so that only oxidative quenching is expected to occur. The lack of quenching by $\text{Co}(\text{CN})_6^{3-}$ can be explained since (i) energy transfer is not allowed, (ii) reductive quenching is implausible because it would lead to a Co(IV) complex, and (iii) oxidative quenching, even if thermodynamically not unfavorable, is expected to involve a high intrinsic barrier.^{9,10} In the case of $\text{Ni}(\text{CN})_4^{2-}$, oxidative quenching does not seem thermodynamically favorable, whereas reductive quenching may be possible since the electroactivity up to +1.0 V could be due to "kinetic" factors. On the other hand, quenching by energy transfer to the lowest $\text{Ni}(\text{CN})_4^{2-}$ triplet cannot be ruled out since the lowest energy shoulder in the absorption spectrum ($\sim 23 \text{ kK}$) has been attributed to either the second¹⁴ or the third²⁵ excited triplet. The complex is photochemically inert²⁶ and thus the observed lack of sensitized aquation does not rule out ener-

gy transfer. The strong distortion²⁷ of the d-d excited states of this complex may be a further argument in favor of an energy transfer mechanism. Finally, the lack of quenching by $\text{Pd}(\text{CN})_4^{2-}$ and $\text{Pt}(\text{CN})_4^{2-}$, for which energy transfer can safely be ruled out, indicates that both reductive and oxidative quenching cannot take place because of unfavorable thermodynamic and/or intrinsic barriers.

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Intramolecular 1,1-Cycloaddition Reactions of Nitrile Ylides¹

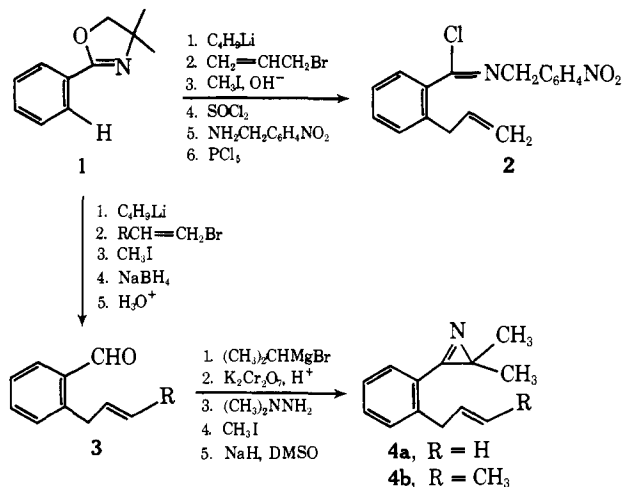
Sir:

Nitrile ylides are a long known and thoroughly investigated class of 1,3-dipoles.²⁻⁴ Access to this group of dipoles can be realized by (a) treatment of imido ylides with base,⁵ (b) thermal or photochemical elimination of phosphoric acid ester from 4,5-dihydro-1,3,5-oxazaphospholes,⁶ and (c) photolysis of 1-azirines.^{7,8} The greatest opportunity for structural variation is offered by the latter route. Among the possible resonance forms of a nitrile ylide, a car-

bene structure can be envisioned which makes conceivable a 1,1-cycloaddition of this 1,3-dipole.^{9,10} At this time we present evidence for the successful 1,1-trapping of a nitrile ylide generated from the base treatment of an imidoyl chloride. Taken with the formation of similar products from the irradiation of the related azirine system, this constitutes good evidence for the generality of 1,1-cycloadditions of nitrilium betaines.

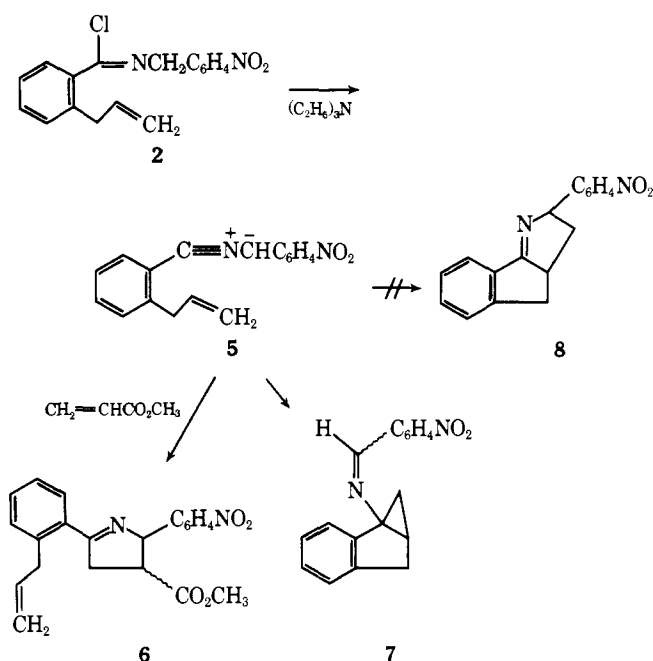
o-Allyl substituted imidoyl chloride **2** was conveniently prepared by the series of reactions outlined in Scheme I. *o*-

Scheme I



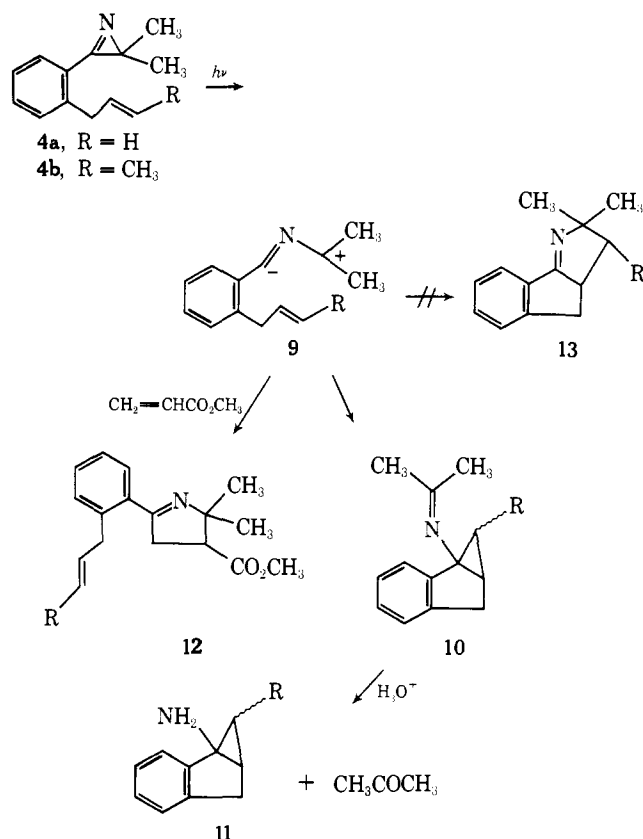
Allylbenzoic acid was synthesized from 2-phenyl-4,4-dimethyl-2-oxazoline (**1**) according to the general procedure of Meyers¹¹ and Gschwend.¹² This carboxylic acid was converted to **2** in high yield by successive treatment with thionyl chloride, *p*-nitrobenzyl amine, and phosphorus pentachloride. Scheme I also outlines the synthesis of the related azirine systems **4a** and **4b**.

Reaction of triethylamine with a benzene solution of **2** at room temperature produces triethylammonium chloride and an orange-red solution, which presumably contains the unstable nitrile ylide **5**. This reactive species undergoes facile 1,3-dipolar cycloaddition with methyl acrylate and affords a mixture of two diastereomeric Δ^1 -pyrrolines (**6**) in



high yield. In the absence of a dipolarophile, the only product isolated was benzobicyclo[3.1.0]hex-2-ene (**7**).¹³ No detectable quantities of the 1,3-dipolar adduct **8** could be observed in the crude reaction mixture. The identity of **7** was determined by its straightforward spectral properties (ir (neat) 6.20, 7.40, 9.01, and 10.90 μ ; uv (cyclohexane) 306 nm (ϵ 9700); NMR (60 MHz, CDCl_3) τ 9.08 (t, 1 H, J = 5.0 Hz), 8.12 (dd, 1 H, J = 8.0 and 5.0 Hz), 7.62 (m, 1 H), 7.12 (d, 1 H, J = 17.0 Hz), 6.60 (dd, 1 H, J = 17.0 and 6.0 Hz), 2.2–2.9 (m, 4 H), 2.10 (d, 2 H, J = 8.0 Hz), 1.80 (d, 2 H, J = 8.0 Hz) and 1.42 (s, 1 H)).

A similar 1,1-cycloaddition reaction occurred when azirines **4a** and **4b** were subjected to electronic excitation. Irradiation of a solution of **4a** in benzene with light of wavelength >250 nm gave a single photoproduct ($>95\%$) which showed all the properties expected for benzobicyclo[3.1.0]hex-2-ene (**10a**). This material was readily hydrolyzed to acetone and the corresponding amine (**11a**) on thick layer chromatography. The NMR spectrum of **11a** (benzene sulfonamide derivative, mp 138–139 $^\circ\text{C}$) showed a triplet at τ 9.64 (1 H, J = 5.0 Hz), a doublet of doublets at τ 8.63 (1 H, J = 8.0 and 5.0 Hz), a multiplet at τ 8.20 (1 H), a singlet for the amine protons at τ 7.80 (exchanged with D_2O), a doublet at τ 7.26 (1 H, J = 17.0 Hz), a doublet of doublets at τ 6.76 (1 H, J = 17.0 and 6.0 Hz), and a multiplet centered at τ 2.80 (4 H). Treatment of **11a** with *p*-nitrobenzaldehyde gave imine **7** in quantitative yield. Photolysis of **4a** (or **4b**) in the presence of excess methyl acrylate afforded cycloadduct **12** in high yield. Under these conditions, the formation of **10**, which is produced in quan-



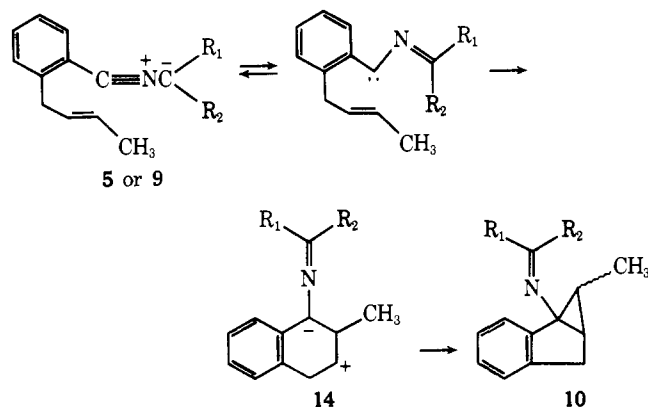
titative yield in the absence of a trapping reagent, is entirely suppressed. Irradiation of the closely related methyl substituted azirine system (**4b**) afforded a quantitative yield of bicyclohexene **10b** as a mixture of *endo* (20%) and *exo* (80%) isomers. Chromatography of the mixture over silica gel resulted in the separation of the corresponding amines (*exo*- and *endo*-**11b**).¹⁴ It should be pointed out that no detect-

able quantities of the isomeric 1,3-dipolar adduct **13** could be observed in the crude photolysate.

Concerted 1,3-dipolar additions are known to proceed via a "two-plane" orientation complex in which the dipole and dipolarophile approach each other in parallel planes.²⁻⁴ The cycloaddition of nitrile ylides **5** and **9** with added dipolarophiles proceeds in this fashion affording Δ^1 -pyrrolines as the primary cycloadducts (e.g., **6** and **12**). Inspection of molecular models of these *o*-allyl substituted nitrile ylides indicates that the normal "two-plane" orientation approach is possible only when the π -orbitals of the aromatic ring are orthogonal to the π -orbitals of the nitrile ylide. This approach is not followed since it involves disruption of phenyl conjugation with the 4π -allyl anion portion of the nitrile ylide. As a result, the normal 1,3-dipolar cycloadduct is not formed. Product formation is possible, however, if the linear nitrile ylide undergoes rehybridization to give a species of bent geometry (carbene form) which subsequently undergoes 1,1-cycloaddition with the neighboring double bond. In an earlier report, we suggested that the most favorable transition state for the 1,1-cycloaddition reaction is one in which the π -orbitals of the nitrile ylide and olefinic double bond are orthogonal.⁹ This orthogonality could permit the occurrence of an orbital symmetry-allowed [$\omega_s^2 + \pi_a^2$] cycloaddition. This unusual mode of addition was postulated in order to account for the complete inversion of stereochemistry that occurred about the π -system.⁹ Irradiation of azirine **4b**, however, was found to produce a mixture of stereoisomers. In this case the structure of the major product obtained (80%) corresponds to retention of stereochemistry about the double bond. From this work it is clear that the stereochemistry about the bicyclohexene system is not that predicted by a concerted [$\omega_s^2 + \pi_a^2$] carbene addition, and, consequently, an alternate explanation for the previous stereochemical results must be sought.¹⁵

The carbene (bent geometry) form of the nitrile ylide still possesses dipolar character. Attack of the carbene carbon on the terminal position of the neighboring double bond will generate a six-membered ring dipole (i.e., **14**) which contains a secondary carbonium ion as well as an azaallyl anion portion. Collapse of this new 1,3-dipole will result in the formation of the benzobicyclo[3.1.0]hex-2-ene system. In this case, **14** collapses to produce a mixture of the *exo* and *endo* substituted bicyclohexenes. The major product obtained corresponds to the thermodynamically more favored *exo* isomer.¹⁵

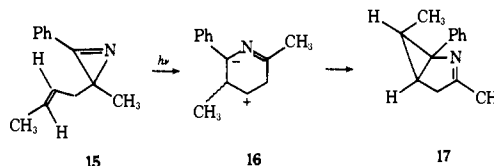
We are continuing to explore the scope and mechanistic details of this novel 1,1-cycloaddition reaction and look forward to determining whether other nitrilium betaines undergo this type of behavior.



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- (14) The *endo* bicyclohexene amine **11b** showed the following spectral properties: (60 MHz) τ 9.50 (d, 3 H, $J = 6.0$ Hz), 8.1-8.7 (m, 2 H), 7.60 (s, 2 H, exchanged with D_2O), 7.26 (d, 1 H, $J = 17.0$ Hz), 6.90 (dd, 1 H, $J = 17.0$ and 6.0 Hz), 2.6-2.8 (m, 4 H); benzene sulfonamide derivative mp 116-118 °C; *exo* bicyclohexene amine **11a** (60 MHz) τ 9.42 (dq, 1 H, $J = 6.0$ and 4.0 Hz), 8.76 (d, 3 H, $J = 6.0$ Hz), 8.30 (m, 1 H), 7.95 (s, 2 H, exchanged with D_2O), 7.26 (d, 1 H, $J = 17.0$ Hz), 6.82 (dd, 1 H, $J = 17.0$ and 6.0 Hz), 2.6-2.8 (m, 4 H); benzene sulfonamide derivative, mp 165-166 °C.
- (15) We previously reported that 2-phenyl-3-methyl-3-crotylazirine (**15**) produced 1-phenyl-3-methyl-6-*endo*-methyl-2-azabicyclo[3.1.0]hex-2-ene (**17**) on irradiation.⁹ The formation of this product is the result of a complete inversion of stereochemistry about the double bond. The stereochemical results can now be rationalized by assuming that collapse of the initial 1,3 dipole (i.e., **16**) to the thermodynamically more favored



exo isomer will result in a severe torsional barrier on closure. Collapse of **16** to the thermodynamically less favored *endo* isomer (i.e., **17**) moves the phenyl and methyl groups increasingly further apart and accounts for the formation of the less stable product. This type of eclipsing interaction is not present with dipole **14** and consequently closure will favor the thermodynamically more stable isomer (i.e., *exo*-**11b**).

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Photochemistry of Methyl 1-Methylbicyclo[3.3.1]nonan-9-one-3-carboxylates

Sir:

Photolysis¹ of a dioxane solution of methyl 1-methylbicyclo[3.3.1]nonan-9-one-3-*endo*-carboxylate (**1**) affords a single volatile product identified as the *cis*-methyl bicyclo[3.3.0]octane ester **5** while irradiation of the epimeric bicyclononanone *exo* ester **2** gives a single volatile product identified as *cis* fused *endo* ester **6**.² Significantly, there is no product crossover in either experiment.³ Though decarbonylation has been previously documented for other cyclic and bicyclic ketones,⁴ these examples provide the first dem-