Menthyl *N*-[1-(phenyl)-2,2,2-trifluoroethyl]carbamate (9c) and 9d as a 1:9 diastereomeric mixure is a colorless solid: mp 93–105 °C.

After separation of the carbamate diastereomers **9c** and **9d**, NMR, IR, and elemental analysis of each are consistent with the assigned structure.

9c: NMR ($CDCl_3$) δ 0.80–1.00 [multiplet, $C(CH_3)_2$ and $-CHCH_3$], 1.19–2.20 (multiplet, C_6H_8), 2.25 [heptet of doublets, $(CH_3)_2CH$], 4.69 (triplet of doublets, OCH), 7.38 ppm (broad s, C_6H_5); IR ($CDCl_3$) 1705 cm^{-1} (C=O).

Anal. Calcd for $C_{19}H_{26}F_3NO_2$: C, 63.85; H, 7.33; N, 3.92. Found: C, 63.92; H, 7.19; N, 3.85.

9d: NMR ($CDCl_3$) δ 0.80–1.00 [multiplet, $C(CH_3)_2$ and $-CHCH_3$], 1.19–2.20 (multiplet, C_6H_8), 2.25 [heptet of doublets, $(CH_3)_2CH$], 4.69 (triplet of doublets, OCH), 7.38 ppm (broad s, C_6H_5); IR ($CDCl_3$) 1715 cm^{-1} (C=O).

Anal. Calcd for $C_{19}H_{26}F_3NO_2$: C, 63.85; H, 7.33; N, 3.92. Found: C, 63.81; H, 7.24; N, 3.88.

2-Octyl *N*-[1-(phenyl)-2,2,2-trifluoroethyl]carbamate (10c) and 10d as a 1:9 diastereomeric mixture is a colorless solid: mp 105–106 °C.

After separation of **10c** and **10d**, NMR, IR, and elemental analysis of each were consistent with the assigned structure.

10c: NMR ($CDCl_3$) δ 0.91 [t, $(CH_2)_5CH_3$], 1.20–1.83 [multiplet, $CH_3C(CH_2)_5$], 4.85 (sextet, OCH), 5.40 (quintet, NCH), 5.53 (broad doublet, NH), 7.35 ppm (broad s, C_6H_5); IR ($CDCl_3$) 1705 cm^{-1} (C=O).

Anal. Calcd for $C_{17}H_{24}F_3NO_2$: C, 61.62; H, 7.30; N, 4.23. Found: C, 61.55; H, 7.24; N, 4.18.

10d: NMR ($CDCl_3$) δ 0.91 [t, $(CH_2)_5CH_3$], 1.20–1.83 [multiplet, $CH_3C(CH_2)_5$], 4.85 (sextet, OCH), 5.40 (quintet, NCH), 5.53 (broad doublet, NH), 7.35 ppm (broad s, C_6H_5); IR ($CDCl_3$) 1715 cm^{-1} (C=O).

Anal. Calcd for $C_{17}H_{24}F_3NO_2$: C, 61.62; H, 7.30; N, 4.23. Found: C, 61.82; H, 7.34; N, 4.28

Acknowledgment. This work has been partially supported by grants from the National Science Foundation and the National Institutes of Health.

Registry No.—**2**, 62197-94-8; **3**, 2627-86-3; **4**, 434-45-7; **5**, 62197-91-5; **6** isomer 1, 62197-92-6; **6** isomer 2, 62197-93-7; **9a**, 17397-46-5; **9b**, 17397-45-4; **9c**, 62197-95-9; **9d**, 62197-96-0; **10a**, 62197-97-1; **10b**, 62197-98-2; **10c**, 62197-99-3; **10d**, 62198-00-9; **11**, 62198-01-0; **12**, 62198-02-1; **14** isomer 1, 62198-03-2; **14** isomer 2, 62198-04-3; **15** isomer 1, 62198-05-4; **15** isomer 2, 62198-06-5; benzyl trifluorometrhyl ketone, 350-92-5; 1,1,2,2,3,3,3-heptafluoropropyl phenyl ketone, 559-91-1.

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Photolysis and Thermolysis of 2,4,4-Trisubstituted Δ^2-Oxazolin-5-ones. Activation and Control by a Trifluoromethyl Group

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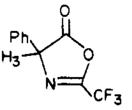
The photochemical and thermal reactivity of 4-methyl-4-phenyl-2-trifluoromethyl-Δ^2-oxazolin-5-one (1) and 2,4-dimethyl-4-phenyl-Δ^2-oxazolin-5-one (2) have been investigated. Photolysis of 1 in the presence of dipolarophiles gives Δ^1-pyrrolines presumably via carbon dioxide expulsion from 1 to give trappable nitrile ylides. However, photolysis of 2 (with or without dipolarophiles) gives *N*-(1-methylbenzylidene)acetamide (6) presumably via carbon monoxide expulsion. Thermally (refluxing xylene), 1 loses carbon monoxide to form *N*-(1-phenylvinyl)trifluoroacetamide (10); however, 2 is unreactive. A rationalization of the trifluoromethyl group's effect on the thermolysis of 1 is presented, and some points in possible photochemical reaction sequences at which a trifluoromethyl group may control photoreactivity are discussed.

One of the most troublesome aspects of synthetic photochemistry is the capriciousness of many photorearrangements. Therefore, the investigation and development of possible photodirecting, photoactivating, or photoprotecting groups which may make photoreactions more predictable or even controllable are worthwhile, if difficult, goals.

A substituent which may show promise at directing the course of photoreactions is the trifluoromethyl group. For example, Wexler and Swenton[1] have recently reported that the acetone sensitized cycloaddition of 5-trifluoromethyluracil to isobutylene occurs with greater than 95% regioselectivity.

In connection with work to photochemically synthesize β-lactam systems,[2] we have synthesized 4-methyl-4-phenyl-2-trifluoromethyl-Δ^2-oxazolin-5-one (1).[3] Because the photochemistry of Δ^2-oxazolin-5-ones has been studied only to a limited extent[4] (see below), and because a comparison of the photoreactivity of 1 with that of 2,4-dimethyl-4-phenyl-Δ^2-oxazolin-5-one (2)[5] would test the effect of the trifluoromethyl group, we have explored the photolytic and thermal behavior of 1 and 2. The results of the study will follow a brief discussion of pertinent published work.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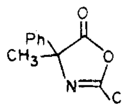
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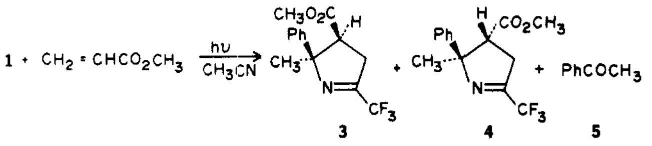
There are two reports of Δ^2-oxazolin-5-one photolysis.[4a,b] Padwa and Wetmore[4a] report that no Δ^1-pyrroline product is formed when a Δ^2-oxazolin-5-one is photolyzed in the presence of electron-deficient olefin dipolarophiles, but the products formed, if any, are not described.[6] The photolysis of one 2,4,4-trialkyl-Δ^2-oxazolin-5-one followed by acidic hydrolysis is reported by Slates et al.[4b] to yield a ketone derived from carbon 4 and its substituents. Carbon monoxide loss to give an *N*-(dialkylmethylidene)acetamide which is subsequently hydrolyzed to the product ketone was postulated but not demonstrated. This behavior contrasts with that of Δ^3-oxazolin-5-ones which usually give Δ^1-pyrrolines in synthetically useful yields when photolyzed in the presence of appropriate dipolarophiles.[4a,c] Trappable nitrile ylide intermediates are evidently generated[4a] by carbon dioxide expulsion from the Δ^3-oxazolin-5-ones. However, photolysis of a 2-trifluoromethyl-Δ^3-oxazolin-5-one gives products derived from an *N*-acylimine which is presumably formed by carbon monoxide expulsion.[7] Photolysis of a trifluoromethyl derivative of Δ^2-oxazolin-5-one has not been reported.

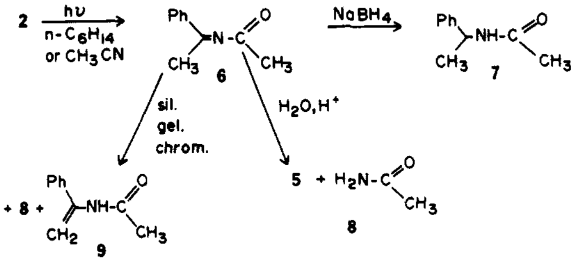
Attempted thermolysis of 2,4,4-trisubstituted Δ^2-oxazolin-5-ones in refluxing xylene is reported to cause no reaction.[8] Huisgen and co-workers[8] have studied the reaction of 2,4-disubstituted Δ^2-oxazolin-5-ones with dipolarophiles and have found that oxazolium ion intermediates are formed and that subsequent carbon dioxide loss gives pyrrolines. Nitrile ylide intermediates are not involved in this case. Steglich and co-workers[9] and Schmid et al.[4c] have observed that higher temperatures and proper substituents allow the thermolysis of trisubstituted Δ^2-oxazolin-5-ones to give carbon dioxide loss and products expected from nitrile ylide intermediates. Carbon monoxide loss to give an enamide has also been observed,[10] but only when both a 2-trifluoromethyl and a 4-thiophenoxy group are present in a 2,4,4-trisubstituted Δ^2-oxazolin-5-one system. Compound 1 has been reported to be stable at 200 °C (but see below).[11] For comparison, trisubstituted Δ^3-oxazolin-5-ones studied by Steglich[9] lose carbon dioxide thermally and form products expected from nitrile ylide intermediates. Padwa reports[4a] that several 2,4-disubstituted Δ^3-oxazolin-5-ones are stable to thermolysis.

Results

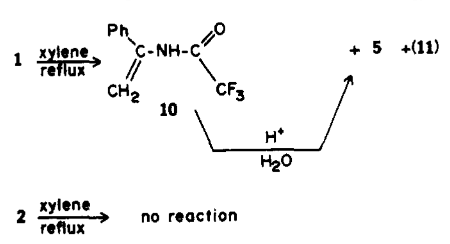
Photolysis of 1 and 2. Photolysis of 1 and methyl acrylate in acetonitrile gives reasonable yields (26 to 17%, respectively) of *cis*- and *trans*-2-trifluoromethyl-4-carbomethoxy-5-methyl-5-phenyl-Δ^1-pyrrolines (3 and 4 respectively), along with 7% acetophenone (5). Spectral and elemental analysis support the structures proposed. The stereochemical assignments are based on ^{1}H NMR spectra. Pyrroline 3 is assigned as the structure with phenyl and the carboxymethyl groups cis since the ester methyl group is more shielded in 3 as compared to 4.[12] Also, the chemical shift of the C-5 methyl in 3 is at lower field than that of 4 as would be expected if 3 has the 5-methyl and 4-carbomethoxy group trans.[13] The reaction is evidently highly regioselective since there is no higher field multiplet which would have been evident in a C-4 unsubstituted Δ^1-pyrroline.[12] Starting material (1) was isolated unchanged from a dark control sample worked up by the procedure applied to the photolyzed solution; therefore, acetophenone is the result of photolysis.



Photolysis of 2 in acetonitrile or hexane gives a good yield of the relatively unstable *N*-(1-methylbenzylidene)acetamide (6). The assignment of the structure of 6 is based on its ^{1}H NMR spectrum (singlets at δ 2.1 and 2.3 and the aromatic signals expected for an imine *C*-phenyl) and on the observation that sodium borohydride reduction of 6 gives *N*-(1-phenylethyl)acetamide (7). Acid-catalyzed hydrolysis of 6 immediately gives acetophenone (5) and acetamide (8), and silica gel chromatography of 6, which is not contaminated by 5, 8, or *N*-(1-phenylvinyl)acetamide (9), gives 5, 8, and 9 but no 6. Compound 9 was identified by its ^{1}H NMR spectrum and by comparison to a sample independently synthesized using the enamide synthesis of Padwa et al.[14] Since enamide 9 is easily hydrolyzed to 5 and 8, it is possible but not necessary that 5 and 8 are formed from 6 via 9. Irradiation of 2 in acetonitrile with methyl acrylate gives polymethyl acrylate as the only product in addition to those described above. The photoreactions of 1 and 2 are not quenched by piperylene added in concentrations such that excited states living for 10^{-7} s would have been 90% trapped.

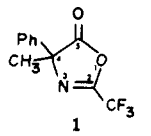


Thermolysis of 1 and 2. When 1 is refluxed in dry xylenes a good yield (66%) of *N*-(1-phenylvinyl)trifluoroacetamide (10) is obtained along with a small amount of 5 [presumably trifluoroacetamide (11) is also formed]. The identification of 10 is based on its spectral data. The ^{1}H NMR indicated the presence of an exo methylene, an amide hydrogen, and a phenyl group. The mass spectrum is most helpful since it shows the correct parent and parent plus one peaks for $C_{10}H_8NOF_3$ and shows a loss of trifluoromethyl and also trifluoroacetamide fragments. Compound 10 is hydrolyzed readily to 5 and presumably 11. Though 10 may have formed via an *N*-(1-methylbenzylidene)trifluoroacetamide (12) no evidence for it was found in the reaction mixture. When 2 was refluxed in xylenes with or without methyl acrylate for periods up to 15 h, it was recovered completely unchanged.



Discussion

Thermolysis. The most important feature of the results is the profound effect of the substitution of a trifluoromethyl group in place of a methyl group on the thermal and photochemical reactivity of a trisubstituted Δ^2-oxazolin-5-one. Considering the thermal reactivity first, the trifluoromethyl group greatly activates the Δ^2-oxazolin-5-one toward carbon monoxide loss when compared to a methyl group. The activation is selective and different from that of a 2-phenyl substituent which has been shown by Steglich and co-workers[9,10] to accelerate thermal carbon dioxide expulsion from trisubstituted Δ^2-oxazolin-5-ones. The trifluoromethyl group evidently encourages cleavage of the 4,5 bond, and possibly the 1,5 bond, while failing to activate or perhaps deactivating the system toward 1,2 bond breakage.



1

A consideration of the stability of diradicals which might be generated as intermediates, or which may resemble species on a concerted reaction pathway, helps rationalize the thermal results. Cleavage of the 1,2 bond in 1 would produce an iminoyl

σ radical[15] at carbon 2. Trifluoromethyl groups are known[16] to destabilize acyl radicals relative to methyl and phenyl groups. However, cleavage of the 4,5 bond would produce a π-type allyllike radical, with odd-electron density at centers 4 and 2, which would be more stabilized by a trifluoromethyl group than by a methyl group. Fluorine p–π interactions have been postulated to rationalize π-electron donation by trifluoromethyl groups to aromatic systems,[17] and these "interactions" have been invoked to rationalize the greatly enhanced stability of bis(trifluoromethyl) nitroxide as compared to dimethyl nitroxide.[18] Our experimental results do not indicate whether cleavage of the 1,5 bond is affected by the presence of a trifluoromethyl group.[19]

It is not possible to comment on the report[11] that 1 is stable to thermolysis because the conditions were not described. Contrary to an earlier hypothesis,[10] the presence of a 4-thiophenoxy group as well as a 2-trifluoromethyl group is not required for thermal carbon monoxide expulsion from Δ^2-oxazolin-5-ones. However, the extent to which substitution at C-4 can be varied without suppressing carbon monoxide expulsion is not known.

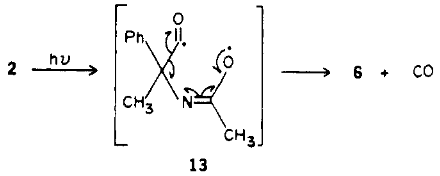
Photolysis. The very different photochemical behavior of 1 and 2 shows that the trifluoromethyl group can also strongly influence excited state behavior. The light-induced expulsion of carbon monoxide from a 2,4,4-trisubstituted Δ^2-oxazolin-5-one as observed for 2 apparently has precedent in the work of Slates et al.[4b,20] However, this is the first instance in which the postulated *N*-(methylidene)acetamide photoproduct (e.g., 6) has been observed before hydrolysis. The substitution of a trifluoromethyl group for a methyl group (compound 1) leads to the photoinduced loss of carbon dioxide to presumably give a nitrile ylide which is trapped by a dipolarophile. Such a reaction had not been observed for Δ^2-oxazolin-5-ones.[4a] Reactions of 1 and 2 probably involve singlet or very short-lived triplet states since the reactions were not quenched by piperylene.

The high regioselectivity in the reaction of the postulated nitrile ylide intermediate from 1 with electron-deficient dipolarophiles can be rationalized by the work of Houk and Caramella.[21] They attribute the greater nucleophilicity of the divalent carbon of the nitrile ylide (15) to the larger size of its HOMO coefficient.

The reaction pathways followed by 1 and 2 may not be completely exclusive, since the acetophenone (5) among the photolysis products of 1 could have come from hydrolysis of 10 derived by carbon monoxide expulsion. However, 5 could also have arisen via rearrangement of untrapped nitrile ylide to give an enamine which subsequently hydrolyzed. Carbon dioxide loss from 2 to give trappable nitrile ylides does not occur since photolysis of 2 in the presence of large amounts of dipolarophile failed to give Δ^1-pyrroline.

The Effect of a Trifluoromethyl Group. The means by which the trifluoromethyl group in 1 influences the reaction pathway is not clear. However, it is useful to consider stages in possible concerted or stepwise reaction sequences at which substitution of trifluoromethyl for methyl may alter the reaction course. The first potential point of control in photochemical processes involves the absorption of light. Compounds 1 and 2 may be considered to have one, two, or three chromophores, depending on the interaction of the phenyl, carbonyl, and imine systems. Though trifluoromethyl groups are known to red shift the n–π^* and π–π^* absorptions of ketones[22] (and presumably imines), the UV spectra of 1 and 2 have the same maxima. Both resemble the spectrum of toluene, but both have higher extinction coefficients than toluene in the 225–250-nm region as if absorption from the "ketone" and/or "imine" chromophores were tailing into that region. In the 250–280-nm region the extinction coefficient of 1 is approximately twice that of 2. Absorption maxima do not shift as solvent polarity is changed, so the presence of n–π^* bands with energies lower than that of 250 nm light cannot be substantiated (or ruled out). The trifluoromethyl-induced changes in absorption seem to small to explain the difference in reactivity of 1 and 2.

A second perhaps more likely point of control is the intramolecular energy transfer which may be necessary from phenyl to either the ester (anhydride)-like carbonyl or the imine. α-Phenyl to ester carbonyl energy transfer has been reported in studies of ester photochemistry by Morrison[23] et al. With methyl present as in 2, energy transfer to the carbonyl may dominate and α-cleavage to give a diradical (13) like that postulated for the photo-Fries[24] reaction may lead to carbon monoxide loss and the observed product 6 (Note that 2 is an analogue of a vinyl ester). The substitution of a trifluoromethyl for methyl as in 1 should lower the energy of the π–π^* and n–π^* levels of the imine,[22] and energy transfer to the imine followed by α-cleavage as postulated for azirines[4a] could lead to 14. Loss of carbon dioxide would give nitrile ylide 15,



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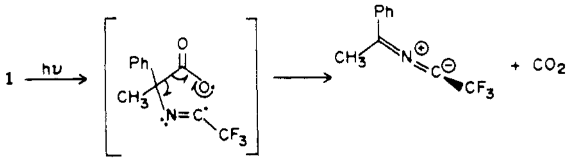
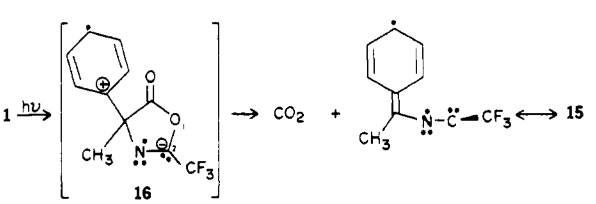


14 15

which, when trapped by a dipolarophile, would give the observed Δ^1-pyrrolines. If the "imine" and "carbonyl" form a single excited state, the trifluoromethyl group could increase the importance of the "imine" description (by changing orbital weighting coefficients) and thus aid carbon dioxide expulsion.

A third possible point of control presupposes a different reaction mechanism: electron transfer from the photoexcited phenyl group to either the carbonyl or the imine group.[25] In the case of 2 a rational mechanism involving carbon monoxide loss leads from a species with phenyl radical cation and carbonyl radical anion character to 6. When a trifluoromethyl replaces methyl as in 1, electron transfer to the imine may lead to a species like 16. A 1,2-bond fragmentation of 16 may be viewed as an analogue of α-elimination reactions which generate carbenes.[26] The carbene generated by carbon dioxide loss can be a resonance contributor for nitrile ylide 15.[21] The importance of electron transfer in the photoreactions of 1 and 2 is not now known, and it is possible that electron transfer competes with energy transfer. Electron transfer may, for example, be important only for 1.



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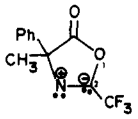
In the points of possible control discussed thus far the trifluoromethyl and methyl groups are envisioned to influence major changes (energy or electron transfer) in excited state geometry and electron density. A consideration of surfaces[27] in regions related to specific "chromophore" excited states may also be useful. For example, trifluoromethyl perturbation (as in 1) of the "imine" region of the surface might lower activation barriers[28] and minima to favor 1,2-bond lengthening, and eventually 1,2-bond cleavage, by making a $\pi-\pi^*$ or $n-\pi^*$ excited state more zwitterionic (see **17** and note its relationship to **16**).



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The trifluoromethyl group at carbon 2 should have much less effect on the "carbonyl" region of the excited surface. Changes in the "imine" excited surface could control the reactivity of **1** as long as energy can be transferred to that "chromophore" (the transfer does not have to be irreversible or exclusive). If the "imine" and "carbonyl" form a single potential well in the excited state surface, the trifluoromethyl group may decrease barrier heights involving carbon dioxide loss.

A different potential point of control involves decay to the ground state surface in a region near the geometry of the primary photoproduct. This decay process is aided by a close approach of the ground and excited state surfaces.[27] Closer approach can be accomplished by decreasing excited state energy as discussed above, or by increasing the ground state energy near the desired product geometry. If carbon dioxide is lost from **1** or **2** a primary product may have radical character at carbon 2. The trifluoromethyl destabilization of σ radicals, which may explain the thermal stability of the 1,2 bond in **1**, may help make a ground state σ-radical-like species photochemically accessible for **1** by raising the ground state energy surface and facilitating decay near a σ-radical-like geometry. The σ-radical stabilizing methyl group in **2** may not force the ground state surface to be as high at geometries involving carbon dioxide loss, as compared to **1**, and the excited state decays at geometries related to carbon monoxide loss instead.

At each of the possible points of control mentioned above the trifluoromethyl group seems to favor photochemical loss of carbon dioxide (at least by hindsight). This makes a determination of the actual control mechanism(s) difficult. However, the concurrence of several control points may rationalize the very sharp difference in reactivity of **1** and **2**.

Experimental Section

General. All solutions for photolysis were purged with argon for at least 15 min before and during the entire photolysis. NMR spectra were recorded on a Varian T-60 spectrometer with tetramethylsilane as internal standard. Infrared spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer. UV spectra were recorded on a Cary 17 spectrophotometer. Mass spectra were taken on a Hitachi Perkin-Elmer RMV-6D spectrometer. Microanalyses were performed by Instranal Laboratory, Rensselaer, N.Y. Melting points are uncorrected.

Absorption Spectra of 1 and 2. UV absorption spectra of **1** and **2** were recorded in both hexane and acetonitrile, and are summarized here: [λ (ϵ) (an asterisk indicates maximum, λ in nm)], **1** (hexane), 268* (243), 263* (429), 261* (484), 257* (629), 251* (828), 245 (1036), 240 (1172), 230 (1930), 220 (3502), 210 (8183); **1** (acetonitrile), 268* (209), 263 (359), 261 (443), 257* (585), 251* (802), 245 (969), 240 (1130), 230 (1595), 220 (3174), 210 (7643); **2** (hexane), 268* (137), 263* (269), 261 (288), 257* (428), 251* (607), 245 (786), 240 (866), 230 (995), 220 (3731), 210 (8407); **2** (acetonitrile), 268* (98), 263* (197), 261 (208), 257* (384), 251 (519), 245 (711), 240 (909), 230 (1081), 220 (3091), 210 (8547).

Synthesis of 2,4-Dimethyl-4-phenyl-Δ^2-oxazolin-5-one (2).[5] A solution of 2.0 g (12.1 mmol) of α-phenylalanine in 15 mL of acetic anhydride was heated at reflux under a nitrogen atmosphere for 1 h. The solution was allowed to cool and excess acetic anhydride removed under reduced pressure. The residue was distilled under reduced pressure to yield 1.62 g (71%) of 2,4-dimethyl-4-phenyl-Δ^2-oxazolin-5-one (**2**): bp 62 °C (0.12 mm); NMR ($CDCl_3$) δ 1.7 (3 H, s), 2.2 (3 H, s), 7.1–7.6 (5 H, m).

Photolysis of 2,4-Dimethyl-4-phenyl-Δ^2-oxazolin-5-one (2). A solution of 205 mg (1.08 mmol) of 2,4-dimethyl-4-phenyl-Δ^2-oxazolin-5-one (**2**) in 330 mL of dry hexane was irradiated (Hanovia 450-W) through a Vycor filter for a period of 2.5 h. Solvent removal under reduced pressure gave a yellow liquid [presumably *N*-(1-methylbenzylidene)acetamide], which had an NMR spectrum containing singlets at δ 2.1 (3 H), and multiplets at δ 7.0–7.4 (4.5 H) and 7.6–7.8 (2 H), in addition to broad high-field signals attributed to polymeric material. No acetophenone or *N*-(1-phenylvinyl)acetamide were observed.[29] Treatment of an NMR sample of this material with slightly wet trifluoroacetic acid resulted in immediate formation of acetophenone and acetamide, identified by addition of authentic samples. Chromatography of 182 mg of the initial photolysis product on silica gel (Mallinckrodt CC-7), with methylene chloride elution, yielded a mixture containing 63 mg (54%) of acetophenone and 23 mg (15%) of *N*-(1-phenylvinyl)acetamide which had the following spectral data: NMR ($CDCl_3$) δ 2.1 (3 H, s), 5.1 (1 H, br s), 5.8 (1 H, br s), 6.8–7.2 (1 H, br s), 7.0–7.2 (5 H, m). Irradiation of 2,4-dimethyl-4-phenyl-Δ^2-oxazolin-5-one in the presence of methyl acrylate gives, as the only additional product, polymethyl acrylate.

Similar irradiation of 167 mg of **2** in the presence of 86.6 mg (1.28 mmol) of *trans*-piperylene for 2.5 h followed by the same workup showed no starting material to be present. The combined yield of acetophenone and **9** was 53%. The concentration of piperylene was sufficient to reduce the quantum yield to 10% of its original value for a reactive lifetime of 10^{-7} s, assuming $k_{dif} = 2.7 \times 10^{10}$ for hexane.

Photolysis of 2,4-Dimethyl-4-phenyl-Δ^2-oxazolin-5-one and Reduction of Products. A solution of 192 mg (1.015 mmol) of 2,4-dimethyl-4-phenyl-Δ^2-oxazolin-5-one (**2**) in 320 mL of dry hexane was irradiated (Hanovia 450-W) through a Vycor filter for a period of 2 h. Solvent removal under reduced pressure gave 196 mg of a yellow oil. The oil was dissolved in 50 mL of dry tetrahydrofuran, 110 mg (2.9 mmol) of sodium borohydride was added, and the solution was heated at reflux temperature for 18 h. The solution was allowed to cool and quenched with water, and then methylene chloride and more water were added. The organic layer was removed, washed once with 0.1 M HCl, dried over sodium sulfate, and filtered, and the solvent was removed to yield 165 mg of a yellow oil. The oil was chromatographed on a silica gel column (Mallinckrodt CC-7) using 2% methanol/methylene chloride elution. One band came off, which consisted a mixture of *N*-(1-phenylethyl)acetamide (identified by its NMR spectrum[30]) and polymeric material. NMR analysis of the mixture using dioxane as an internal standard indicated a yield of 41% of *N*-(1-phenylethyl)acetamide, which had the following NMR spectrum ($CDCl_3$): δ 1.5 (3 H, d), 1.9 (3 H, s), 4.95 (1 H, quintet), 6.5–7.0 (1 H, br s), 7.1 (5 H, m).

Synthesis of *N*-Trifluoroacetyl-α-phenylalanine. In a slightly modified literature[3] procedure, a solution of 11.1 g (67.3 mmol) of α-phenylalanine and 10 mL (68 mmol) of trifluoroacetic anhydride in 30 mL of trifluoroacetic acid was stirred at room temperature for 8 h under a nitrogen atmosphere. The trifluoroacetic acid and anhydride used were previouly dried by distillation from phosphorus pentoxide. Solvent was removed under reduced pressure to yield a brown solid which was purified by filtration through a short silica gel column (Mallinckrodt CC-7), eluting with methylene chloride. Solvent removal yielded 14.6 g (83%) of *N*-trifluoroacetyl-α-phenylalanine: mp 131.5–132.5 °C (lit.[3] 126–128 °C); NMR ($CDCl_3$) δ 2.0 (3 H, s), 6.5 (2 H, br s), 7.3 (5 H, m); IR (Nujol) 1710 (vs), 1550 cm^{-1} (s).

Preparation of 4-Methyl-4-phenyl-2-trifluoromethyl-Δ^2-oxazolin-5-one (1). In a modified literature[3] procedure a solution of 14.6 g (60 mmol) of *N*-trifluoroacetyl-α-phenylalanine in 30 mL of thionyl chloride (purified by distillation from triethyl phosphite) was heated to 60 °C and maintained at that temperatue for 1 h. Excess thionyl chloride was removed at room temperature using aspirator vacuum, and the residue distilled at reduced pressure to yield 12.6 g (92%) of 2-trifluoromethyl-4-methyl-4-phenyl-Δ^2-oxazolin-5-one: bp 52 °C (0.5 mm) [lit.[3] 53–57 °C (0.6 mm)]; NMR ($CDCl_3$) δ 1.9 (3 H, s), 7.2–7.6 (5 H, m); IR (neat) 1850 (vs), 1680 (s), 1370 cm^{-1} (vs).

Thermolysis of 4-Methyl-4-phenyl-2-trifluoromethyl-Δ^2-oxazolin-5-one (1). A solution of 143 mg (0.588 mmol) of 4-methyl-4-phenyl-2-trifluoromethyl-Δ^2-oxazolin-5-one (**1**) in 5 mL of dry xylenes was heated at reflux temperature for a period of 20 h under a nitrogen atmosphere. Solvent removal under reduced pressure yielded a mixture containing, by NMR analysis, 6.7 mg (9.6%) of acetophenone, 21 mg (15%) of starting material, and 83 mg (66%) of *N*-(1-phenylvinyl)trifluoroacetamide, which had the following spectral data: NMR ($CDCl_3$) δ 5.3 (1 H, br s), 5.8 (1 H, br s), 6.8–7.6 (1 H, br s), 7.2 (5 H, s) (signals assigned to acetophenone and starting material were also present); mass spectrum (70 eV) *m/e* (rel intensity)[31] 216, (11.5), 215 (100), 146 (75), 120, 118 (13), 105, 104 (38), 103

(96), 91 (58), 77, 69 (52), 51; IR (neat) 3300 (s), 3050 (m), 1720 (vs), 1310 (vs), 1160 cm^{-1} (vs). On standing for several weeks, the enamide hydrolyzed completely to acetophenone.

Photolysis of 4-Methyl-4-phenyl-2-trifluoromethyl-Δ^2-oxazolin-5-one (1). A solution of 205 mg (0.843 mmol) of 4-methyl-4-phenyl-2-trifluoromethyl-Δ^2-oxazolin-5-one (1) and 2 mL of methyl acrylate in 230 mL of dry acetonitrile was irradiated for 8 h through a Vycor filter with a Hanovia 450-W medium pressure lamp. Solvent removal at reduced pressure followed by silica gel chromatography (Mallinckrodt Silicar CC-7) with methylene chloride elution gave 105 mg of a mixture containing, by NMR analysis, 52 and 34% of the *cis*- and *trans*-2-trifluoromethyl-4-carbomethoxy-5-methyl-5-phenyl-Δ^1-pyrrolines, respectively. The remainder of the material, 14%, was acetophenone. By repeated silica gel chromatography, eluting with methylene chloride, a pure sample of the cis pyrroline was obtained, having the following spectral data: NMR ($CDCl_3$) δ 1.85 (3 H, s), 3.1 (3 H, s), 2.9–3.7 (3 H, m), 7.0–7.2 (5 H, m); IR (neat) 1740 (vs), 1440 (m), 1200 (vs), 1150 cm^{-1} (vs); mass spectrum (70 eV) *m/e* (rel intensity) 285 (28), 270 (11), 266 (6), 254 (6), 226 (42), 199 (57), 198 (25), 104 (100), 103 (88), 91 (15), 77 (57).

Anal. Calcd for $C_{14}H_{14}F_3NO_2$: C, 58.95; H, 4.95; N, 4.91. Found: C, 58.92; H, 5.07; N, 4.98.

By the same method a small portion of the pure trans isomer was also obtained, having the following spectral data: NMR ($CDCl_3$) δ 1.48 (3 H, s), 2.8–3.6 (3 H, m), 3.7 (3 H, s), 7.0–7.2 (5 H, m); mass spectrum (70 eV) *m/e* (rel intensity) 285 (50), 270 (18), 266 (11) 254 (16), 226 (76), 199 (100), 198 (46), 179 (21), 104 (92), 103 (82), 91 (17), 77 (58).

Photolysis of 177.5 mg of 1 in the presence of 152.5 mg (2.24 mmol) of *trans*-piperylene in 230 mL of acetonitrile for 6.25 h followed by the same workup gave the same products in essentially identical yields. The concentration of quencher was sufficient to reduce the quantum yield to 10% of its original value if the reactive lifetime were 10^{-7} s, assuming $k_{\mathrm{diff}} = 1 \times 10^{10}$ for acetonitrile.

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Registry No.—1, 62263-54-1; **2**, 4855-22-5; **3**, 62263-55-2; **4**, 62263-56-3; **6**, 52762-80-8; **7**, 6284-14-6; **9**, 57957-24-1; **10**, 62288-65-7; α-phenylalanine, 565-07-1; *N*-trifluoroacetyl-α-phenylalanine, 62318-98-3; trifluoroacetic anhydride, 407-25-0; methyl acrylate, 96-33-3.

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Reaction of Organic Azides with Ethoxycarbonylnitrene

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The reaction of *n*-hexyl azide with ethoxycarbonylnitrene generated by α-elimination from *N*-(*p*-nitrobenzenesulfonoxy)urethane in nitromethane generates *n*-hexaldehyde ethoxycarbonylhydrazone, which arises from the initial formation and rearrangement of ethyl *n*-hexylazocarboxylate. Ethyl phenylazocarboxylate is produced and isolated from a similar reaction with phenyl azide. Studies employing various organic azides, solvents, reaction conditions, and additives indicate *n*-hexyl azide to be reactive toward singlet ethoxycarbonylnitrene with a major competing reaction being the crossover of ethoxycarbonylnitrene from its singlet to its triplet state.

As part of a research program designed to explore the interaction of organic azides and reactive intermediates,[1-3] we have examined the reactions of organic azides with ethoxycarbonylnitrene. Azide–nitrene reactions have been observed in studies of the photolysis of alkyl[4] and aryl[5] azides, and the thermolysis of carbamoyl,[6] aryl,[7-11] and sulfonyl[12] azides. In each of these studies the focus of interest was the chemistry of the azide or the resulting nitrene rather than the reaction