treated dropwise with acetyl chloride (1.78 mL, 0.025 mol). The precipitate was stirred for 30 min and the solvent was removed via a filter stick and washed several times with dry Et_2O. The residue was suspended in dry DMF (50 mL) and treated with **1** (3.09 g, 0.01 mol). This mixture was stirred at ambient temperature for 1 h and 50 min, cooled in an ice bath, and treated with triethylamine (1.39 mL, 0.01 mol). The mixture was kept at ambient temperature for 4 h, poured into cold, dilute $NaHCO_3$, and extracted with $CHCl_3$. The extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was chromatographed on silica gel (200 g) with MeOH. The first material eluted from the column corresponded to recovered **1** by TLC and amounted to 1.4 g (crude weight). The second material eluted from the column was recrystallized from EtOAc to give 0.438 g (mp 187–188 °C) and 0.191 g (mp 187–188 °C) of **16**. The third compound eluted from the column was treated with 1 equiv of *p*-toluenesulfonic acid and crystallized from EtOH–EtOAc to give 1.03 g of **2**, mp 196–197 °C.

Reaction of 8-Chloro-1-methyl-6-phenyl-4*H*-*s*-triazolo[4,3-*a*][1,4]benzodiazepine (1) with Dimethyl(methylene)ammonium Chloride and Acetyl Chloride. Procedure D. A stirred solution of 1 (3.09 g, 0.01 mol) in dry DMF (50 mL) was cooled in an ice bath, under nitrogen, and treated successively with *N,N,N',N'*-tetramethyldiaminomethane (1.23 g, 0.012 mol) and then dropwise with acetyl chloride (0.923 mL, 0.013 mol). The cloudy mixture was kept in the ice bath for 1 h and 55 min and poured into a mixture of ice and saturated $NaHCO_3$. The solution was saturated with NaCl and extracted five times with $CHCl_3$. The extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. A solution of the resulting oil in absolute ethanol was acidified to pH 3.5–4 with a solution of *p*-toluenesulfonic acid (1 equiv) in absolute ethanol. The salt was crystallized to give 3.69 g (mp 196–197 °C), 0.612 g (mp 197–198 °C), and 0.022 g (mp 198.5–199 °C) (79.9%) of **2**.

8-Chloro-1-isopropyl-6-phenyl-4*H*-*s*-triazolo[4,3-*a*][1,4]benzodiazepine (11). A stirred mixture of 7-chloro-2-hydrazino-5-phenyl-3*H*-1,4-benzodiazepine[21] (7.13 g, 0.025 mol) in dry THF (60 mL) was cooled in an ice bath and treated during 4 min with a solution of isobutyryl chloride (2.65 g, 0.025 mol) in THF (12 mL). The resulting dark red solution was kept in the ice bath for 20 min and at ambient temperature for 2 h. It was then poured into a stirred mixture of crushed ice and saturated $NaHCO_3$. The solid was collected by filtration, washed with water, and dried in vacuo. A solution of the solid in AcOH (60 mL) was placed in an oil bath that had been preheated to 130 °C, refluxed for 30 min, cooled, and concentrated in vacuo. The residue was mixed with ice and dilute $NaHCO_3$ and extracted with CH_2Cl_2. The extract was washed with brine, dried (Na_2SO_4), and concentrated. The residue was crystallized from EtOAc to give 4.32 g (mp 202–202.5 °C) and 1.63 g (mp 200–202 °C) (70.7% yield) of **11**.

8-Chloro-1-(methoxymethyl)-6-phenyl-4*H*-*s*-triazolo[4,3-*a*][1,4]benzodiazepine (8). Compound **8** was prepared from 7-chloro-2-hydrazino-5-phenyl-3*H*-1,4-benzodiazepine[21] and methoxyacetyl chloride in a manner similar to that described for compound **11**. The yield was 66%.

Acknowledgment. The authors are indebted to Dr. E. C. Olson and his associates for physical and analytical data, to Dr. R. P. Holysz and his associates for the preparation of chemical intermediates, and to Mr. Alfred Koning for technical assistance. The author is also indebted to Ms. Brenda Simmons for preparing the manuscript for publication.

Registry No. **1**, 28981-97-7; **2**, 60218-33-9; **2** free base, 53257-71-9; **3**, 37115-32-5; **3** methanesulfonate salt, 57938-82-6; **4**, 71616-85-8; **5**, 28910-96-5; **6**, 71616-86-9; **7**, 71616-87-0; **8**, 37952-16-2; **9**, 71616-88-1; **10**, 71616-89-2; **11**, 28910-94-3; **13**, 28910-97-6; **14**, 66490-98-0; **15**, 66490-97-9; **16**, 71616-90-5; **17**, 71616-91-6; **18**, 71616-92-7; 8-chloro-4-[(dimethylamino)methyl]-1-isopropyl-6-phenyl-4*H*-*s*-triazolo[4,3-*a*][1,4]benzodiazepine *p*-toluenesulfonate, 71616-94-9; 7-chloro-2-hydrazino-5-phenyl-3*H*-1,4-benzodiazepine, 18091-89-9; *N,N,N',N'*-tetramethyldiaminomethane, 51-80-9; isobutyryl chloride, 79-30-1; methoxyacetyl chloride, 38870-89-2.

Supplementary Material Available: Complete physical and analytical data for compounds in Table I (3 pages). Ordering information is given on any current masthead page.

(20) This compound was prepared in these laboratories by Dr. Martin Gall, unpublished results.

(21) K. Meguro and Y. Kuwada, *Tetrahedron Lett.*, 4039 (1970).

Sensitized Photooxygenations of Δ^2-Oxazolin-5-ones and Related Studies[1]

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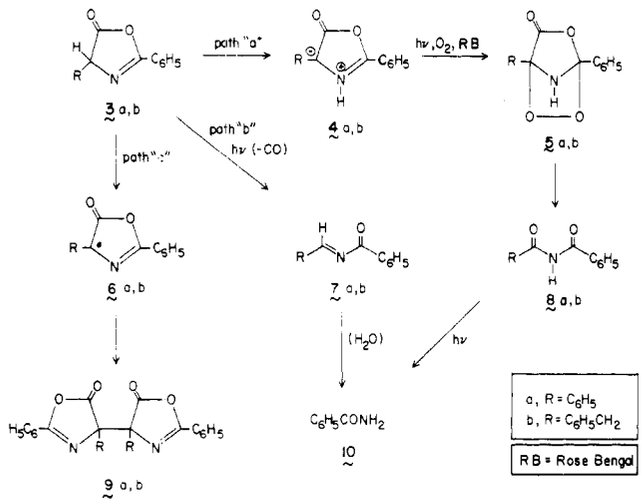
Received May 29, 1979

Sensitized photooxygenations of a few Δ^2-oxazolin-5-ones such as 2,4-diphenyl-Δ^2-oxazolin-5-one (**3a**), 4-benzyl-2-phenyl-Δ^2-oxazolin-5-one (**3b**), and 4-benzylidene-2-phenyl-Δ^2-oxazolin-5-one (**17**) have been studied, using Rose Bengal as a sensitizer. The photooxygenation of **3a** in a mixture of benzene and methanol for 0.25 h gave a mixture of bi-4,4'-(2,4-diphenyl-Δ^2-oxazolin-5-one) (**9a**, 44%) and benzamide (28%), whereas the photooxygenation of **3a** in methanol for 0.5 h gave a mixture of dibenzamide (**8a**, 40%) and benzamide (49%). In contrast, the irradiation of **3a** in either benzene or cyclohexane gave only benzamide. Nickel peroxide oxidation of **3a** gave a 38% yield of the bioxazolinone **9a**. Direct irradiation of **9a** in either benzene or acetone gave benzamide, whereas the thermolysis of **9a** in refluxing *o*-dichlorobenzene gave a 3% yield of 2,3,5,6-tetraphenylpyrazine (**16**). Photooxygenation of **3b** gave a 42% yield of *N*-benzoylphenylacetamide (**8b**), whereas the direct irradiation of **3b** gave only benzamide. Nickel peroxide oxidation of **3b** gave bi-4,4'-(4-benzyl-2-phenyl-Δ^2-oxazolin-5-one) (**9b**, 40%). Direct irradiation of **9b** gave exclusively benzamide. The photooxygenation of **17** in methanol gave a mixture of the α-benzamidocinnamate **18** (53%) and benzamide (29%), whereas the direct irradiation of **17** gave a mixture of α-benzamidocinnamic acid (**20**) (31%) and benzamide (52%). Resonable mechanisms have been suggested for the formation of the different products in these reactions.

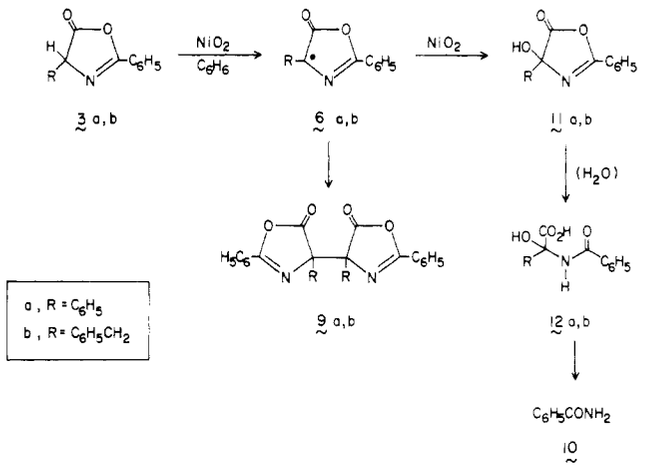
Although the chemistry of Δ^2-oxazolin-5-ones has been fairly well studied,[3] only very few reports concerning the photochemistry of these ring systems are available in the literature.[4-8] Recently, Johnson and Sousa,[8] for example,

0022-3263/79/1944-4169$01.00/0

Scheme I



Scheme II



have examined the photochemical transformations of both 4-methyl-4-phenyl-2-(trifluoromethyl)-Δ^2-oxazolin-5-one (**1**) and 2,4-dimethyl-4-phenyl-Δ^2-oxazolin-5-one (**2**) and have shown that these two oxazolinones behave quite differently under photochemical conditions. The photolysis of **1**, for example, proceeds with extrusion of carbon dioxide to give the corresponding nitrile ylide intermediate, which can be trapped in the presence of dipolarophiles. In contrast, the photolysis of **2** has been found to give *N*-(1-methylbenzylidene)acetamide, presumably formed through the loss of carbon monoxide.[8] The difference in the photochemical behavior of the two Δ^2-oxazolin-5-ones **1** and **2** has been attributed to the electronic effects of the trifluoromethyl substituent in **1**.

We have shown recently that sydnones, which contain an azomethine linkage, undergo cycloaddition with singlet oxygen, under sensitized photooxygenation conditions, leading to a mixture of products.[9] Although Δ^2-oxazolin-5-ones are reported to undergo cycloadditions with different dipolarophiles,[10-12] there has been no report so far on the use of singlet oxygen as a dipolarophile in these addition reactions. The object of the present investigation, therefore, has been to examine the photooxygenations of a few Δ^2-oxazolin-5-ones with a view to studying the nature of products formed in these reactions.

Results and Discussion

The Δ^2-oxazolin-5-ones that we have examined include 2,4-diphenyl-Δ^2-oxazolin-5-one (**3a**), 4-benzyl-2-phenyl-Δ^2-oxazolin-5-one (**3b**), and 4-benzylidene-2-phenyl-Δ^2-oxazolin-5-one (**17**).

Photooxygenation of 2,4-diphenyl-Δ^2-oxazolin-5-one (**3a**) in methanol and in the presence of Rose Bengal (0.5 h) gave a mixture of dibenzamide (**8a**, 40%) and benzamide (**10**, 49%), whereas in benzene–methanol (0.25 h) the main product was bi-4,4′-(2,4-diphenyl-Δ^2-oxazolin-5-one) (**9a**, 44%). The formation of products such as dibenzamide (**8a**), benzamide, and the bioxazolinone **9a** in the photooxygenation of **3a** can be rationalized in terms of the pathways shown in Scheme I. It has been assumed that one of the possible transformations of **3a** will be its initial conversion to the tautomeric oxazolium 5-oxide **4a**,[10-12] which in turn reacts with singlet oxygen to give the *endo*-peroxide **5a**, as per path a in Scheme I. Subsequent loss of carbon dioxide from **5a** will result in the formation of dibenzamide (**8a**). An alternative pathway (path b) for the transformation of **3a** would be through the initial loss of carbon monoxide to give *N*-benzylidenebenzamide (**7a**) which undergoes hydrolysis under the reaction conditions to give benzamide. Benzamide in this reaction may also arise through the further photolysis of **8a** under the reaction conditions. In order to distinguish between the two possible pathways for the formation of benzamide, we have examined the direct photolysis of **3a** in the absence of oxygen. Irradiation of a cyclohexane solution of **3a** (1.5 h) resulted in the formation of a 73% yield of benzamide (**10**), whereas irradiation in benzene (4 h) gave a 68% yield of **10**. It may be mentioned here that mere refluxing of **3a** in either cyclohexane or methanol (2 h) did not give any benzamide. In both of these cases, most of the starting material has been recovered unchanged. The formation of benzamide in the direct photolysis of **3a** would clearly indicate that under photochemical conditions **3a** undergoes facile loss of carbon monoxide to give *N*-benzylidenebenzamide (**7a**), which then gives rise to **10**, as per path b, shown in Scheme I.

The formation of the bioxazolinone **9a** can be rationalized in terms of the radical intermediate **6a**, formed through the abstraction of a hydrogen atom from the C_4 position of **3a** by molecular oxygen. Subsequent dimerization of **6a** will lead to **9a** as shown in Scheme I (path c). It may be pointed out here that Huisgen and co-workers[12] have observed the formation of the bioxazolinone **9a** when air was not excluded in the preparation of **3a**.

If a radical intermediate such as **6a** is produced through hydrogen abstraction, then we reasoned that the formation of the oxidative dimer **9a** should be facilitated by reagents which are known to bring about facile oxidations. In this context we have examined the reaction of **3a** with nickel

(1) This is Document No. NDRL-2014 from the Notre Dame Radiation Laboratory.

(2) (a) Indian Institute of Technology. (b) Radiation Laboratory.

(3) For some reviews on the chemistry of oxazolones, see: (a) Filler, R.; Rao, Y. S. *Adv. Hetercycl. Chem.* **1977**, *21*, 175. (b) Steglich, W. *Fortschr. Chem. Forsch.* **1969**, *12*, 77. (c) Filler, R. *Adv. Heterocycl. Chem.* **1965**, *4*, 75. (d) Carter, H. E. *Org. React.* **1946**, *3*, 198. (e) Conforth, J. W. *Heterocycl. Compd.* **1957**, *5*, 336–77. (f) Baltazzi, E. *Q. Rev., Chem. Soc.* **1955**, *9*, 150.

(4) Padwa, A.; Wetmore, S. I., Jr., *J. Am. Chem. Soc.* **1974**, *96*, 2414.

(5) Slates, H. L.; Tanb, D.; Kuo, C. H.; Wendler, N. L. *J. Org. Chem.* **1964**, *29*, 1424.

(6) Gakis, N.; Märky, M.; Hansen, H.-J.; Heimgartner, H.; Schmid, H.; Oberhanski, W. E. *Helv. Chim. Acta* **1976**, *59*, 2149.

(7) Steglich, W.; Wellenstein, K. A., unpublished work cited in ref 3b.

(8) Johnson, M. R.; Sousa, L. R. *J. Org. Chem.* **1977**, *42*, 2439.

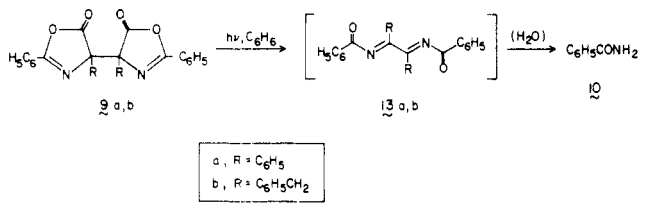
(9) Bhat, V.; Dixit, V. M.; Ugarkar, B. G.; Trozzolo, A. M.; George, M. V. *J. Org. Chem.* **1979**, *44*, 000.

(10) Huisgen, R.; Gotthardt, H.; Bayer, H. O. *Tetrahedron Lett.* **1974**, 481.

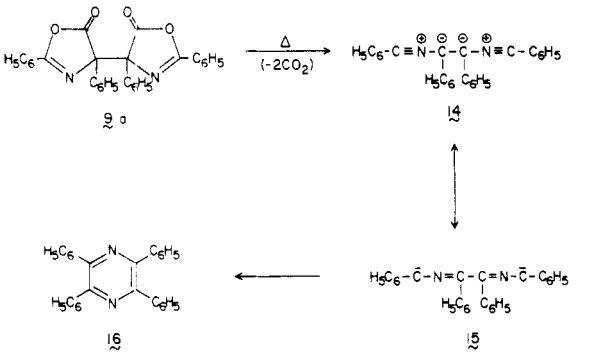
(11) Gotthardt, H.; Huisgen, R.; Schaefer, F. C. *Tetrahedron Lett.* **1964**, 487.

(12) Gotthardt, H.; Huisgen, R.; Bayer, H. O. *J. Am. Chem. Soc.* **1970**, *92*, 4340.

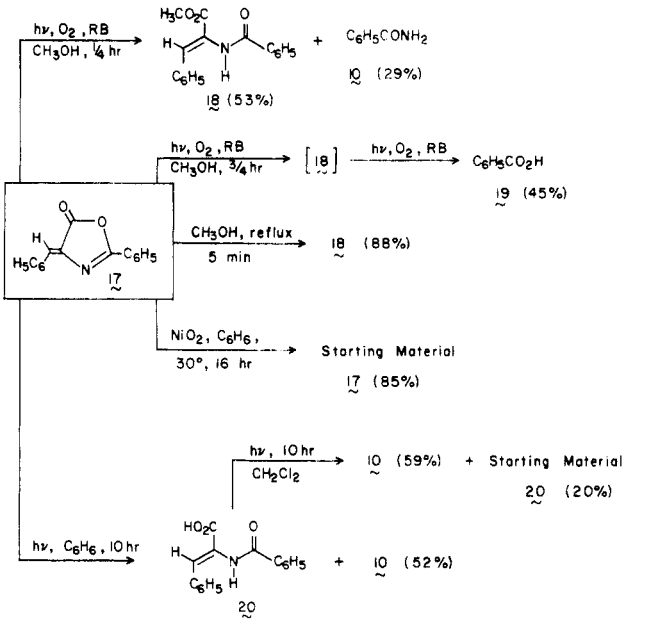
Scheme III



Scheme IV



Scheme V



peroxide. Treatment of **3a** with nickel peroxide in benzene at room temperature (0.5 h) gave a mixture of **9a** (38%) and benzamide (**10**, 25%). The formation of **10** in this reaction may be explained in terms of the hydroxylation of the radical intermediate **6a** in the presence of nickel peroxide to give the hydroxy derivative **11a**, which can undergo further hydrolysis to **12a** and subsequent fragmentation to give **10**, as shown in Scheme II. Such hydroxylations of organic substrates in the presence of nickel peroxide have been reported in the literature.[13]

For comparing the photochemical behavior of the oxazolinone **3a** with that of its oxidative dimer, we have examined the photolysis of **9a**. Irradiation of a benzene solution of **9a** (1.75 h) gave a 73% yield of benzamide (**10**). The photolysis of **9a** in acetone (2.5 h), on the other hand, gave a 49% yield of **10**. The formation of **10** in the photolysis of **9a** may be understood in terms of the intermediate **13a**, formed through the loss of 2 mol of carbon monoxide and the subsequent hydrolysis of **13a** under the reaction conditions (Scheme III). The thermal transformation of **9a**, however, has been reported to give poor yields of 2,3,5,6-tetraphenylpyrazine (**16**).[12,6] In the present studies we have observed that refluxing of **9a** in *o*-dichlorobenzene (~179 °C) gives a 3% yield of **16**, along with a 42% of the unchanged starting material. A reasonable pathway for the formation of **16** would involve the initial loss of 2 mol of carbon dioxide from **9a** to give the bis nitrile ylide **14**, which can also be represented as the carbene intermediate **15**. Intramolecular cyclization of **15** will result in the formation of **16**, as shown in Scheme IV.

In continuation of our studies, we have examined the photooxygenation of 4-benzyl-2-phenyl-Δ^2-oxazolin-5-one (**3b**). Photooxygenation of **3b** in benzene–methanol, using Rose Bengal, (1.75 h) gave benzamide (**10**, 50%), along with some unchanged starting material (**3b**, 50%). The formation of **8b** in the photooxygenation of **3b** may be rationalized in terms of the intermediate **5b**, as shown in Scheme I. The formation of benzamide in the photolysis of **3b**, likewise, can be explained in terms of the initial formation of **7b**, which then suffers hydrolysis in the presence of moisture. In contrast to the photoreaction of **3b**, it was observed that refluxing of **3b** in benzene for 7h, in a blank experiment, resulted in the recovery of the unchanged starting material (**3b**, 90%).

To ascertain whether the oxazolinone **3b** undergoes oxidative dimerization in a manner similar to the reaction of **3a**, we have examined the nickel peroxide oxidation of **3b**. Treatment of **3b** with nickel peroxide in benzene solution at room temperature (12 h) gave a mixture of the bioxazoline **9b** (40%) and benzamide (**10**, 29%). The IR spectrum of **9b** showed absorptions at 1839 (C=O) and 1646 (C=N) cm^{-1}. The mass spectrum (70 eV) of **9b** showed the most intense peak at m/e 250, attributed to the fragment $C_{16}H_{12}NO_2$, formed by the cleavage of the molecular ion. The various fragments observed in the mass spectrum of **9b** are in tune with the assigned structure for this compound. The formation of **9b** and benzamide in the oxidation of **3b** may arise through the initially formed radical intermediate **6b**, as shown in Scheme II.

Photolysis of **9b** in benzene (1.5 h) resulted in a 29% yield of benzamide; 40% of **9b** was recovered unchanged. The formation of benzamide from **9b** may be explained by fragmentation and hydrolysis of the intermediate **13b** (Scheme III).

The photooxygenation of 4-benzylidene-2-phenyl-Δ^2-oxazolin-5-one (**17**) in methanol for 0.25 h gave a mixture of products consisting of methyl α-benzamidocinnamate (**18**, 53%) and benzamide (**10**, 29%). When the photooxygenation of **17** in methanol, however, was carried out for 0.75 h, the only product that could be isolated was a 45% yield of benzoic acid (**19**) (Scheme V). The formation of **18** from **17** could be understood in terms of a simple addition of methanol to **17**, whereas products such as benzamide and benzoic acid could arise through the further transformation of **18**, as shown in Scheme V. In support of the suggestion concerning the formation of **18** from **17**, we have observed that treatment of **17** with refluxing methanol for 5 min gave an 88% yield of the methyl ester **18**.

Direct irradiation of the oxazolinone **17** in benzene for 10 h gave a mixture of α-benzamidocinnamic acid (**20**, 31%) and benzamide (52%) (Scheme V). The formation of **20** from **17** may be explained in terms of the addition of moisture to **17** under the reaction conditions, whereas benzamide can result from the photofragmentation of **20**. In support of this assumption, it has been observed that the photolysis of **20** in methylene chloride for 10 h gave

(13) George, M. V.; Balachandran, K. S. *Chem. Rev.* **1975**, *75*, 491.

a 59% yield of benzamide, along with a 20% recovery of **20**. In contrast to the photoreaction of **17**, it was observed that mere refluxing of **17** in cyclohexane for 10 h resulted in the recovery of an 87% yield of the unchanged starting material.

In contrast to the facile oxidative dimerizations of the oxazolinones **3a** and **3b** brought about by nickel peroxide, it has been observed that **17** is unaffected on treatment with nickel peroxide in benzene at room temperature for 16 h.

Experimental Section

All melting points are uncorrected and were determined on a Mel-Temp melting point apparatus. The IR spectra were recorded on Perkin-Elmer Model 137 and Model 521 infrared spectrometers. The electronic spectra were recorded on a Beckman DB spectrophotometer. NMR traces were recorded on a Varian A-60 NMR spectrometer, using tetramethylsilane as an internal standard. All irradiations were carried out with a Hanovia 450-W, medium-pressure mercury lamp in a quartz-jacketted immersion well.

Starting Materials. 2,4-Diphenyl-Δ^2-oxazolin-5-one (**3a**)[12] (mp 104–105 °C), 4-benzyl-2-phenyl-Δ^2-oxazolin-5-one (**3b**)[14] (mp 69–71 °C), and 4-benzylidene-2-phenyl-Δ^2-oxazolin-5-one (**17**)[15] (mp 165–166 °C) were prepared by reported procedures. Active nickel peroxide was prepared by a standard procedure.[13] The petroleum ether used was the fraction having a boiling point of 60–80 °C.

Photooxygenation of 2,4-Diphenyl-Δ^2-oxazolin-2-one (3a). A. In Methanol. A solution of **3a** (0.40 g, 1.7 mmol) in methanol (175 mL), containing a small amount of Rose Bengal (0.01 g), was irradiated under oxygen bubbling for 0.5 h. The residual solid obtained after the removal of the solvent under vacuum was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 0.15 g (40%) of dibenzamide (**8a**), mp 147–148 °C (mmp).[16]

Subsequent elution of the column with a mixture (1:1) of benzene and petroleum ether gave 0.1 g (49%) of benzamide, mp 126–128 °C (mmp).

B. In Benzene–Methanol. A solution of **3a** (0.80 g, 3.4 mmol) in benzene (450 mL) was mixed with a methanolic solution of Rose Bengal (0.03 g in 20 mL), and the resultant solution was irradiated for 0.5 h under oxygen bubbling. Workup of the mixture as in the earlier case gave a product mixture which was chromatographed over neutral alumina. Elution with petroleum ether gave 0.35 g (44%) of bi-4,4′-(2,4-diphenyl-Δ^2-oxazolin-5-one) (**9a**), mp 194 °C (mmp).[12]

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 0.1 g (28%) of benzamide, mp 126–128 °C (mmp).

Photolysis of 2,4-Diphenyl-Δ^2-oxazolin-5-one (3a). A. In Benzene. A solution of **3a** (0.80 g, 3.6 mmol) in benzene (450 mL) was irradiated under a nitrogen atmosphere for 4 h. Removal of the solvent gave a residual mass, which was chromatographed over neutral alumina. Elution of the column with a mixture (1:1) of petroleum ether and benzene resulted in 0.28 g (68%) of benzamide, mp 127–128 °C (mmp).

No other product would be isolated from this run.

B. In Cyclohexane. A solution of **3a** (0.40 g, 1.8 mmol) in cyclohexane (175 mL) was irradiated for 1.5 h, under a nitrogen atmosphere, and workup of the reaction mixture as in the earlier cases gave 0.15 g (73%) of benzamide, mp 126–128 °C (mmp).

Thermolysis of 2,4-Diphenyl-Δ^2-oxazolin-5-one (3a). A. In Refluxing Methanol. Refluxing of a solution of **3a** (0.20 g, 0.9 mmol) in methanol (50 mL) for 2 h and workup of the mixture in the usual manner gave 0.14 g (70%) of the unchanged starting material (**3a**), mp 104 °C (mmp), after recrystallization from petroleum ether.

B. In Refluxing Cyclohexane. A solution of the oxazolinone **3a** (0.20 g, 0.9 mmol) in cyclohexane (50 mL) was refluxed for 2 h and then the solvent was evaporated under reduced pressure. The resulting residual mass was triturated with petroleum ether to afford 0.18 g (90%) of the unchanged starting material, mp 104 °C (mmp).

Nickel Peroxide Oxidation of 2,4-Diphenyl-Δ^2-oxazolin-5-one (3a). A mixture of **3a** (0.40 g, 1.8 mmol) and nickel peroxide (4 g) in benzene (100 mL) was stirred at room temperature for 0.5 h. After removal of the unchanged nickel peroxide and solvent, the residual solid was fractionally crystallized from a mixture (1:1) of benzene and petroleum ether to give 0.15 g (38%) of the bioxazolinone **9a**, mp 194 °C (mmp).

The mother liquor left behind after the removal of **9a** was concentrated to give a product which on recrystallization gave 0.1 g (25%) of benzamide, mp 127–128 °C (mmp).

Irradiation of Bi-4,4′-(2,4-diphenyl-Δ^2-oxazolin-5-one) (9a). A. In Benzene. A solution of the bioxazolinone **9a** (0.80 g, 1.8 mmol) in benzene (800 mL) was irradiated under a nitrogen atmosphere for 1.75 h. Removal of the solvent under vacuum gave a product mixture which was chromatographed over alumina. Elution with a mixture (1:1) of benzene and petroleum ether gave *0.3 g (73%) of benzamide, mp 126–128 °C (mmp).*

B. In Acetone. Irradiation of a solution of the bioxazolinone **9a** (0.80 g, 1.8 mmol) in acetone (800 mL) for 2.5 h and workup as in the earlier case gave 0.2 g (49%) of benzamide, mp 126–127 °C (mmp).

Thermolysis of Bi-4,4′-(2,4-diphenyl-Δ^2-oxazolin-5-one) (9a). A. In Refluxing Cyclohexane. A solution of **9a** (0.80 g, 1.8 mmol) was refluxed in cyclohexane (50 mL) for 10 h under a nitrogen atmosphere. Removal of the solvent under vacuum gave 0.72 g (90%) of the unchanged starting material, mp *193–194* °C (mmp), after recrystallization from a mixture (1:1) of benzene and petroleum ether.

B. In Refluxing Acetone. A solution of **9a** (0.80 g, 1.8 mmol) in acetone (50 mL) was refluxed for 2.5 h under a nitrogen atmosphere and worked up as in the earlier case to give 0.72 g (90%) of the unchanged starting material, mp 194 °C (mmp).

C. In *o*-Dichlorobenzene. A solution of **9a** (0.47 g, 1 mmol) in *o*-dichlorobenzene (50 mL) was refluxed for 5 h. Removal of the solvent under vacuum gave a product which was chromatographed over alumina. Elution with petroleum ether gave 0.1 g (3%) of 2,3,5,6-tetraphenylpyrazine (**16**), mp 290 °C (mmp),[17] after recrystallization from ethanol.

Subsequent elution of the column with a mixture (1:3) of benzene and petroleum ether gave 0.2 g (42%) of the unchanged starting material (**9a**), mp 193–194 °C (mmp).

Photooxygenation of 4-Benzyl-2-phenyl-Δ^2-oxazolin-5-one (3b). A solution of **3b** (0.25 g, 1 mmol) in benzene (170 mL), containing a small amount of Rose Bengal (0.01 g in 10 mL of methanol), was irradiated under oxygen bubbling for 1.75 h. Removal of the solvent under vacuum gave a product mixture which was chromatographed over neutral alumina. Elution with methylene chloride gave 0.1 g (42%) of *N*-benzoylphenylacetamide (**8b**), mp 129–130 °C (mmp),[18] after recrystallization from petroleum ether.

Irradiation of 4-Benzyl-2-phenyl-Δ^2-oxazolin-5-one (3b). A benzene solution of **3b** (1.0 g, 4 mmol in 450 mL) was irradiated under a nitrogen atmosphere for 7 h. Removal of the solvent under reduced pressure gave a residue which was chromatographed over neutral alumina. Elution with petroleum ether gave 0.5 g (50%) of the unchanged starting material, mp 69–70 °C (mmp).

Further elution of the column with a mixture (1:1) of benzene and petroleum ether gave 0.12 g (50%) of benzamide, mp 126–127 °C (mmp).

Thermolysis of 4-Benzyl-2-phenyl-Δ^2-oxazolin-5-one (3b). A solution of **3b** (1.0 g, 4 mmol) in benzene (100 mL) was refluxed under a nitrogen atmosphere for 7 h. Removal of the solvent under vacuum gave 0.9 g (90%) of the unchanged starting material, mp 69–70 °C (mmp), after recrystallization from petroleum ether.

Nickel Peroxide Oxidation of 4-Benzyl-2-phenyl-Δ^2-oxazolin-5-one (3b). A solution of **3b** (0.25 g, 1 mmol) and nickel peroxide (2 g) in benzene (20 mL) was stirred at room temperature for 16 h. Removal of the unchanged nickel peroxide and solvent gave a product which was chromatographed over neutral alumina.

(14) Hohr, E.; Stroschein, F. *Ber. Dtsch. Chem. Ges.* **1909**, *42*, 2521.
(15) Gillespie, H. B.; Snyder, H. R. "Organic Syntheses", Collect. Vol. II; Wiley: New York, NY, 1943; p 489.
(16) Titherley, A. W. *J. Chem. Soc.* **1904**, *85*, 1673.
(17) Japp, F. R.; Davidson, W. B. *J. Chem. Soc.* **1895**, *67*, 32.
(18) Wenner, W. *J. Org. Chem.* **1950**, *15*, 548.

Elution with petroleum ether gave 0.1 g (40%) of bi-4,4'-(4-benzyl-2-phenyl-Δ^2-oxazolin-5-one) (**9b**), mp 210 °C, after recrystallization from a mixture (4:1) of petroleum ether and benzene. IR spectrum (KBr): ν_{max} 1839 ($\nu_{C=O}$), 1646 ($\nu_{C=N}$), 1437, 1302, 1276, 957, 862, 676 cm^{-1}.

Anal. Calcd for $C_{32}H_{24}N_2O_4$: C, 76.80; H, 4.80; N, 5.60. Found: C, 77.32; H, 4.49; N, 5.33.

Further elution of the column with a mixture (1:1) of petroleum ether and benzene gave 0.04 g (29%) of benzamide, mp 127–128 °C (mmp).

In a repeat run, a mixture of 0.25 g (1 mmol) of **3b** and 2 g of nickel peroxide in benzene (70 mL) was stirred at room temperature for 16 h. Workup of the mixture as in the earlier case gave 0.15 g (60%) of **9b**, mp 210 °C (mmp).

Irradiation of Bi-4,4'-(4-benzyl-2-phenyl-Δ^2-oxazolin-5-one) (9b). A solution of **9b** (0.50 g, 1 mmol) in benzene (450 mL) was irradiated for 1.5 h under a nitrogen atmosphere. Removal of the solvent under vacuum gave a product mixture which was chromatographed over neutral alumina. Elution with petroleum ether gave 0.2 g (40%) of the unchanged starting material, mp 210 °C (mmp), after recrystallization from a mixture (4:1) of petroleum ether and benzene.

Subsequent elution with a mixture (1:1) of benzene and petroleum ether gave 0.14 g (29%) of benzamide, mp 127–128 °C (mmp).

Sensitized Photooxygenation of 4-Benzylidene-2-phenyl-Δ^2-oxazolin-5-one (17). A solution of **17** (0.5 g, 2 mmol) in methanol (175 mL), containing a small amount of Rose Bengal (0.01 g), was irradiated under oxygen bubbling for 0.25 h. Removal of the solvent under vacuum gave a viscous material which was fractionally crystallized from a mixture (1:1) of benzene and petroleum ether to give 0.3 g (53%) of methyl α-benzamidocinnamate (**18**), mp 139–141 °C (mmp).[19]

The mother liquor after the removal of **18** was concentrated to give a product which was recrystallized from benzene to give 0.07 g (29%) of benzamide, mp 127–128 °C (mmp).

Thermolysis of 4-Benzylidene-2-phenyl-Δ^2-oxazolin-5-one (17). A. In Refluxing Methanol. A solution of **17** (0.2 g, 0.8 mmol) in methanol (10 mL) was refluxed for 5 min and the solvent was removed under vacuum. The residual solid that was left behind was triturated with a small amount of ethanol to give 0.2 g (88%) of methyl α-benzamidocinnamate (**18**), mp 140–141 °C (mmp), after recrystallization from a mixture (1:1) of petroleum ether and benzene.

B. In Refluxing Cyclohexane. Refluxing of a cyclohexane solution of **17** (0.15 g, 0.55 mmol in 50 mL) for 10 h and workup in the usual manner gave 0.13 g (87%) of the unchanged starting material, mp 165 °C (mmp).

Photooxygenation of Methyl α-Benzamidocinnamate (18). A solution of methyl α-benzamidocinnamate (**18**) (0.26, g, 1 mmol) in methanol (175 mL), containing a small amount of Rose Bengal (0.01 g), was irradiated under oxygen bubbling for 0.75 h. Removal of the solvent under vacuum gave a viscous product which was chromatographed over silica gel. Elution with a mixture (1:4) of benzene and petroleum ether gave 0.1 g (45%) of benzoic acid, mp 121–122 °C (mmp).

No other product could be isolated from this run.

Photolysis of 4-Benzylidene-2-phenyl-Δ^2-oxazolin-5-one (17). A solution of **17** (0.6 g, 2.4 mmol) in dry benzene (450 mL) was irradiated under nitrogen bubbling for 10 h. Removal of the solvent under vacuum gave a product which was chromatographed over neutral alumina. Elution of the column with petroleum ether gave 0.2 g (31%) of α-benzamidocinnamic acid (**20**), mp 233–235 °C (mmp).[19]

Further elution of the column with a mixture of (1:1) of petroleum ether and benzene gave 0.15 g (52%) of benzamide, mp 126–128 °C (mmp).

Attempted Nickel Peroxide Oxidation of 4-Benzylidene-2-phenyl-Δ^2-oxazolin-5-one (17). A mixture of **17** (0.3 g, 1 mmol) and nickel peroxide (2 g) in dry benzene (70 mL) was stirred at room temperature for 16 h. Removal of the unchanged nickel peroxide and solvent gave 0.25 g (85%) of the unchanged starting material (**17**), mp 165 °C (mmp), after recrystallization from a mixture (1:1) of benzene and petroleum ether.

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(19) Buckles, R. E.; Filler, R.; Hilfman, L. *J. Org. Chem.* **1952**, *17*, 233.

Iminium Salts from α-Amino Acid Decarbonylation. Application to the Synthesis of Some 1-Azabicyclo[*x.y.*0] Systems

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Proline, pipecolic acid, and hexahydroazepine-2-carboxylic acid have served as starting materials for the efficient synthesis of 1-azabicyclo[3.3.0]octanes (pyrrolizidines), 1-azabicyclo[4.3.0]nonanes (indolizidines), 1-azabicyclo[4.4.0]decanes (quinolizidines), and 1-azabicyclo[5.4.0]undecanes. For each ring system, the synthesis proceeded by alkylating the cyclic α-amino acid ester with a substituted malonic ester carrying a side chain of appropriate length. Iminium ion was then generated by decarbonylation of the α-(tertiaryamino) acid. Ring closure to the fused ring system resulted from attack of the nucleophilic malonate on the newly formed electrophilic carbon of the iminium ion.

Iminium salts have served as versatile reactive synthetic intermediates[3] by virtue of their ability to yield new carbon–carbon bonds via nucleophilic attack at the highly electrophilic masked carbonyl carbon and have been used in many syntheses involving fused-ring heterocycles. Although these reactive compounds have been used in the

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(3) H. Böhme and H. G. Viehe, Ed., "Iminium Salts in Organic Chemistry", Vol. 1 and 2, Wiley-Interscience, New York, 1976 and 1978.

0022-3263/79/1944-4173$01.00/0