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Photooxygenations of Sydnones and Azomethine Imines

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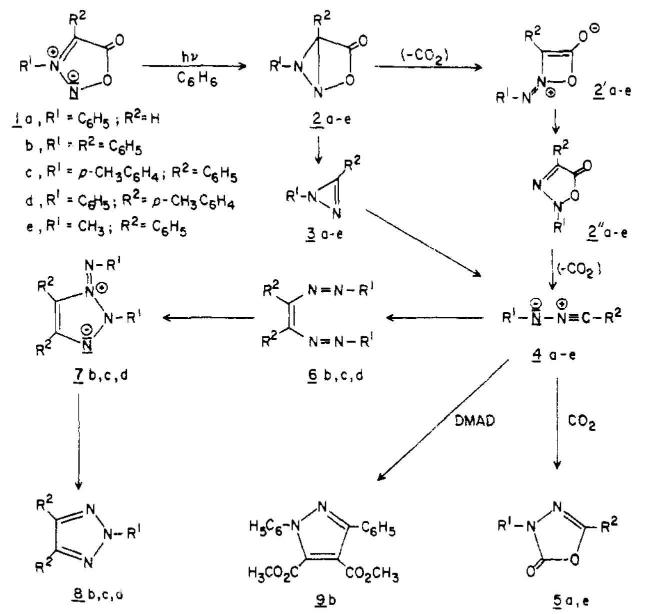
Sensitized photooxygenations of a few sydnones and azomethine imines have been studied. The photooxygenation of 3,4-diphenylsydnone (**1b**), for example, gave a 25% yield of α,β-dibenzoylphenylhydrazine (**16b**) as the only isolable product, whereas the photooxygenation of 4-phenyl-3-*p*-tolylsydnone (**1c**) resulted in the formation of a mixture of products containing α,β-dibenzoyl-*p*-tolylhydrazine (**16c**, 8%) and 4,5-diphenyl-2-*p*-tolyl-1,2,3-triazole (**8c**, 8%). Under analogous conditions, 3-phenyl-4-*p*-tolylsydnone (**1d**) gave a mixture of products consisting of α,β-di-*p*-toluylphenylhydrazine (**16d**, 10%) and 2-phenyl-4,5-di-*p*-tolyl-1,2,3-triazole (**8d**, 1%). Irradiation of **1d** in either benzene or methanol and in the absence of any oxygen gave the triazole **8d** as the only isolable product. Similarly, the photooxygenation of 3-methyl-4-phenylsydnone (**1e**) in methanol gave a mixture of benzoic acid (**12b**, 10%) and α,β-dibenzoylmethylhydrazine (**16e**, 5%), whereas irradiation of **1e** in benzene gave a 10% yield of 4-methyl-2-phenyl-Δ^2-1,3,4-oxadiazolin-5-one (**5e**). The photooxygenation of an azomethine imine, namely, *C*-biphenylene-N^α-(4-chlorophenyl)-N^β-cyanoazomethine imine (**19**), gave a 78% yield of 9-fluorenone (**21**). Reasonable mechanisms have been suggested for the formation of the various products in these reactions.

Scheme I



In recent years, different groups of investigators have examined the photochemical transformations of several sydnone derivatives.[3-9] As early as 1966, Krauch et al.[3] had shown that 3-phenylsydnone (**1a**), for example, when photolyzed in benzene gives rise to Δ^2-1,3,4-oxadiazolin-5-one (**5a**) as the only isolable product. These authors had suggested that *N*-phenylnitrilimine (**4a**) is formed as an intermediate in the photolysis of **1a**, which subsequently combines with carbon dioxide to give the oxadiazolinone **5a** as shown in Scheme I. Subsequent studies by different investigators[4-7] have essentially substantiated the salient features of the mechanistic suggestions advanced by Krauch et al. for the phototransformations of sydnones. The photolysis of 3,4-diphenylsydnone (**1b**) in benzene, for example, has been reported to give 2,4,5-triphenyl-1,2,3-triazole (**8b**) as the major product.[4-7] The formation of the triazole **8b** in this reaction has been rationalized in terms of the initial formation of *N*,*C*-diphenylnitrilimine (**4b**) which then is transformed to 1,2-bis(phenylazo)stilbene (**6b**) and ultimately to the triazole (**8b**), as shown in Scheme I. It has been suggested earlier[5] that the diazirine intermediate **3b** could be a precursor for the

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(1) (a) Department of Chemistry, Indian Institute of Technology; (b) Radiation Laboratory, University of Notre Dame.

(2) This is Document No. NDRL-1962 from the Notre Dame Radiation Laboratory.

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nitrilimine **4b** in these reactions. However, it is likely that **4b** may arise through an alternative pathway, involving intermediates like **2′b** and **2″b** as shown in Scheme I.[8b] The intermediacy of *N*,*C*-diphenylnitrilimine, **4b**, in the phototransformation of **1b** has been further substantiated through trapping experiments in the presence of dimethyl acetylenedicarboxylate (DMAD), which resulted in the formation of the pyrazole derivative **9** (Scheme I).

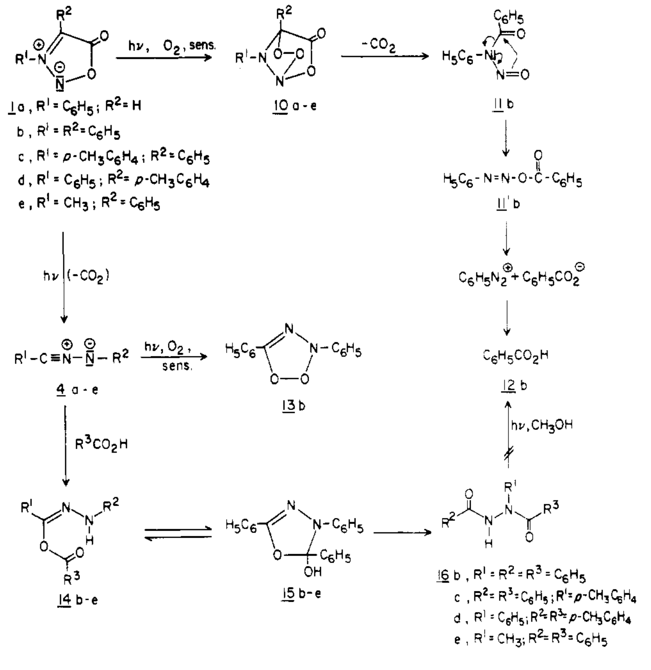
It has been shown that sydnones undergo photochemical addition reactions with several acetylenic and olefinic dipolarophiles and that these additions are essentially the addition reactions of the appropriate nitrilimines (**4**), formed under photochemical conditions from the starting sydnones, with different dipolarophiles, through a 1,3-dipolar mode. Some of the dipolarophiles which have been treated with sydnones under photochemical conditions include carbon dioxide,[3] dimethyl acetylenedicarboxylate,[5] dimethyl fumarate,[5] dimethyl maleate,[5] dicyclopentadiene,[4] indene,[6] and carbon disulfide.[7] Until now, there has been no report on the use of singlet oxygen as a dipolarophile in the photoreactions of sydnones. The object of the present investigation, therefore, has been to examine the photooxygenations of a few sydnones with a view to studying the nature of the products formed in these reactions.

Results and Discussion

The sydnones that we have studied include 3-phenylsydnone (**1a**), 3,4-diphenylsydnone (**1b**), 4-phenyl-3-*p*-tolylsydnone (**1c**), 3-phenyl-4-*p*-tolylsydnone (**1d**), and 3-methyl-4-phenylsydnone (**1e**). Photooxygenation of a solution of 3,4-diphenylsydnone (**1b**) in methanol and in the presence of Rose Bengal, for example, gave a 25% yield of a product melting at 177–178 °C and identified as α,β-dibenzoylphenylhydrazine (**16b**). The structure of **16b** was arrived at on the basis of analytical data, spectral information, and chemical evidence. Neat thermolysis of **16b** at 280 °C for 3 h, for example, gave rise to a mixture of products consisting of benzoic acid (**12b**, 32%) and benzoylphenylhydrazine (38%). Hydrolysis of **16b** employing a 5% solution of methanolic potassium hydroxide likewise gave a mixture of benzoic acid (39%) and benzoylphenylhydrazine (32%). Further confirmation of the structure of **16b** was derived by comparison of its spectral data with that of an authentic sample.[10] The mass spectrum of **16b**, for example, was in full agreement with the fragmentation modes reported for similar dibenzoylphenylhydrazines.[11,12]

A probable route to the formation of **16b** in the photooxygenation of the sydnone **1b** is shown in Scheme II. In this scheme, we assume that singlet oxygen adds on to 3,4-diphenylsydnone (**1b**) by a 1,3-dipolar mode to give the *N*-nitroso derivative **11b**. Rearrangement of **11b** will lead to the diazotate **11′b**, which will then decompose to give benzoic acid (**12b**). An independent mode of transformation of **1b** under photochemical conditions would be its conversion to *N*,*C*-diphenylnitrilimine (**4b**), as shown in Scheme I. It is quite likely that the reactions leading to the formation of *N*,*C*-diphenylnitrilimine (**4b**) and benzoic acid (**12b**) may be occurring side by side, under our experimental conditions. The formation of α,β-dibenzoylphenylhydrazine (**16b**), however, can be explained in terms of the reaction of nitrilimine **4b** with benzoic acid to give the imido ester **14b**, which can subsequently rearrange to give **16b**. It is quite likely that the rearrangement of **14b** to **16b** may be occurring under thermal conditions and may proceed through the cyclic intermediate **15b**, as shown in Scheme II.[13]

Scheme II



One of the possible modes of formation of benzoic acid in this reaction is through the further photolysis of **16b**. However, we have shown in a separate experiment that the photolysis of **16b** in methanol for 1 h does not give any benzoic acid, but most of the starting material is recovered unchanged under these conditions.

In support of the suggestion that **16b** in the photooxygenation of **1b** arises through the reaction of *N*,*C*-diphenylnitrilimine (**4b**) with benzoic acid, we have shown, in a separate experiment, that **4b**, generated in situ, through the reaction of α-chlorobenzaldehyde phenylhydrazone (**17**) with triethylamine,[12] reacts with benzoic acid to give a 44% yield of **16b**. Further, we have observed that the photolysis of **1b** when carried out in presence of 1 molar equivalent of benzoic acid will give **16b** in better yields (48%) than in the case where no benzoic acid has been added. It might be mentioned in this connection that Märky et al.[6b] have quite recently observed the formation of *N*-acyl-*N*-arylbenzohydrazides when sydnones like **1b** have been photolyzed in the presence of acetic and propionic acids.

It is reasonable to assume that the nitrilimine **4b** formed from **1b**, under photooxygenation conditions, could react with singlet oxygen to give the dioxadiazole derivative **13b** which may subsequently undergo further transformations. To examine this possibility, we have investigated the photooxygenation of 2,5-diphenyltetrazole (**18**), a substance which is known to give **4b** under photolytic conditions.[5,15] Irradiation of a methanol solution of **18** in the presence of oxygen and Rose Bengal gave a 31% yield of 2,4,5-triphenyl-1,2,3-triazole (**8b**) as the only product. The same triazole (**8b**) was formed in a 44% yield when the photolysis of **18** was carried out in methanol and in the absence

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[13] For a similar rearrangement of **14b** to **16b** see J. T. Howard and S. A. Samad, *Can. J. Chem.*, 41, 1638 (1963).

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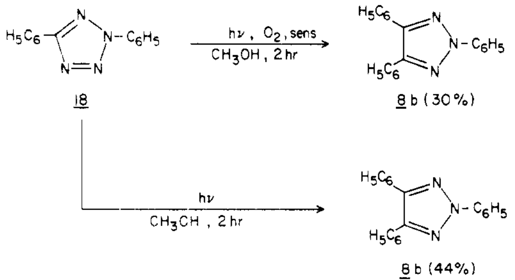
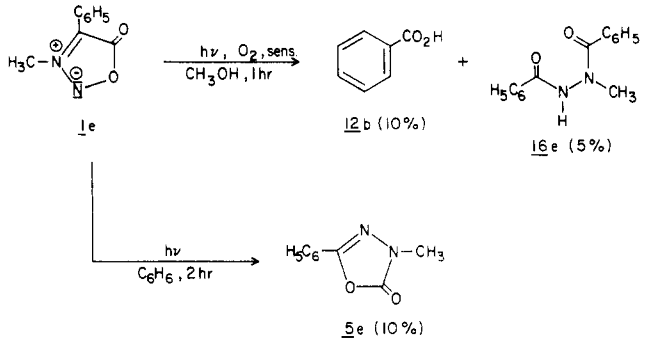
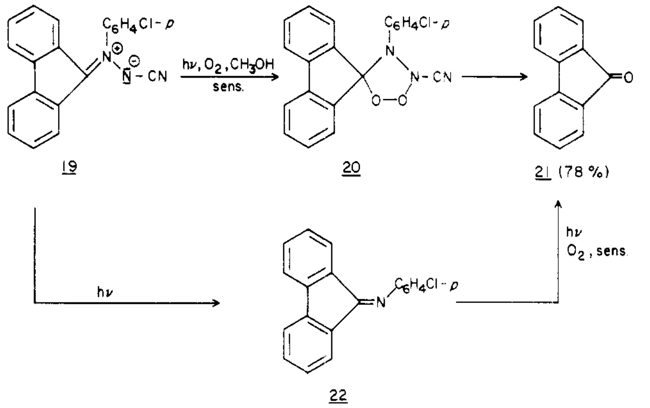
Scheme III



Scheme IV



Scheme V



of oxygen (Scheme III). The formation of the triazole **8b** as the only product in the attempted photooxygenation of **18** would suggest that the nitrilimine **4b** formed from **18** is not reacting with singlet oxygen to give the dioxadiazole **13b** but undergoes transformation through a different route, similar to the one shown in Scheme I and involving intermediate **6b** and **7b** to give **8b**.

Examination of Scheme II reveals that the initial step in the photooxygenation of **1b** involves the addition of singlet oxygen to give the endoperoxide **10b**. With a view to ascertaining whether singlet oxygen is actually involved as the reacting species in this case, we have examined the photolysis of **1b** in the presence of oxygen, but without any sensitizer. Irradiation of a methanol solution of **1b** in the presence of oxygen for 1 h using a Pyrex filter gave a 22% yield of the triazole **8b**. None of the photooxygenation product **16b** could be isolated from this reaction. The absence of any **16b** in this reaction would suggest that the key step in the photooxygenation of **1b** involves the addition of singlet oxygen to give the intermediate **10b** as shown in Scheme II.

Photooxygenation of 4-phenyl-3-*p*-tolylsydnone (**1c**) in methanol for 2 h gave a mixture of products consisting of 4,5-diphenyl-2-*p*-tolyl-1,2,3-triazole (**8c**, 8%) and α,β-dibenzoyl-*p*-tolylhydrazine (**16c**, 8%). Irradiation of **1c** in methanol and in the presence of 1 molar equivalent of benzoic acid, however, gave a 42% yield of **16c**, in addition to a 6% yield of the unchanged starting material, **1c**. Mention may be made in this connection that the direct photolysis of **1c** in dioxane solution is reported to give a 14% yield of the triazole **8c**.[6] Similarly, the photooxygenation of 3-phenyl-4-*p*-tolylsydnone (**1d**) in methanol gave a mixture of products consisting of 2-phenyl-4,5-di-*p*-tolyl-1,2,3-triazole (**8d**, 1%) and α,β-di-*p*-toluylphenylhydrazine (**16d**, 10%). Irradiation of **1d** in methanol and in the presence of 1 molar equivalent of *p*-toluic acid, however, gave a 9% yield of the triazole **8d** and a 5% yield of **16d**. Direct photolysis of **1d** in methanol for 0.75 h and in the absence of any oxygen gave a 7% yield of the triazole **8d**, whereas the photolysis of **1d** in benzene for 2 h gave a 9% yield of the triazole **8d**.

In contrast to the reactions of the sydnones **1c**,**d**, the photooxygenation of 3-methyl-4-phenylsydnone (**1e**) in methanol gave a mixture of products consisting of benzoic acid (**12b**, 10%) and α,β-dibenzoylmethylhydrazine (**16e**, 5%) (Scheme IV). Direct photolysis of **1e** in benzene for 2 h in the absence of any oxygen, however, gave a 10% yield of 4-methyl-2-phenyl-Δ^2-1,3,4-oxadiazolin-5-one (**5e**) as the only isolable product. The structure of **5e**, for example, showed a strong absorption band around 1774 cm^{-1}, characteristic of the CO group present in oxazolinones. The NMR spectrum of **5e** showed a singlet at δ 3.45 (3 H) due to the *N*-methyl protons and a multiplet, centered around δ 7.60 (5 H), due to the aromatic protons.

The formation of products like α,β-dibenzoyl-*p*-tolylhydrazine (**16c**), α,β-di-*p*-toluylphenylhydrazine (**16d**), and α,β-dibenzoylmethylhydrazine (**16e**) in the photooxygenation of **1c**–**e**, respectively, can be rationalized by the same pathway as in the case of the formation of α,β-dibenzoylphenylhydrazine (**16b**), shown in Scheme II. Similarly, the triazoles **8c**,**d** from **1c**,**d**, respectively, can be accounted for in terms of the corresponding nitrilimines **4c**,**d**, which will undergo further transformations, analogous to those shown in Scheme I. The formation of the oxazolinone **5e** in the direct photolysis of **1e** is analogous to the formation of **5a** from **1a** observed earlier by Krauch et al.[3]

The formation of benzoic acid (**12b**) in the photooxygenation of **1e** is of interest in that it substantiates our earlier suggestion that the endoperoxides **10** formed from the reaction of sydnones with singlet oxygen may undergo cleavage to the corresponding *N*-nitroso compounds **11**, which may then be further oxidized to benzoic acid (Scheme II).

It is interesting to note that, in contrast to the different products obtained in the photooxygenations of sydnones like **1b**–**e**, the attempted photooxygenation of 3-phenylsydnone (**1a**) in methanol did not lead to any isolable product. It is likely that intractable fragmentation products are formed in this reaction.

In continuation of our studies, we have examined the photooxygenation of an azomethine imine, namely, *C*-biphenylene-N^{α}-(4-chlorophenyl)-N^{β}-cyanoazomethine imine (**19**). The photooxygenation of **19** in a mixture of benzene and methanol gave a 78% yield of 9-fluorenone (**21**) as the sole product. The formation of **21** in this reaction can be rationalized in terms of the addition of singlet oxygen to **19** to give the endoperoxide **20**, which in turn undergoes fragmentation to give **21**, as shown in Scheme V. It is also likely that the starting azomethine imine **19** undergo photofragmentation to give the corresponding Schiff base **22**, which could then be converted to fluorenone (**21**) through its reaction with singlet oxygen. We mentioned in this connection that the Schiff base **22** is reported to be formed in a 32% yield, when a benzene solution of **19** is photolyzed for 2 h.[16]

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 the internal standard. The mass spectra were recorded on either a Varian MAT CH7 mass spectrometer or a Hitachi RMU-6E single-focusing mass spectrometer at 70 eV. All irradiation experiments were carried out by using a Hanovia 450-W, medium-pressure mercury lamp in a water-cooled, quartz-jacketed immersion well.

Starting Materials. *N*-Phenylsydnone (**1a**),[17] mp 134 °C, 3,4-diphenylsydnone (**1b**),[18] mp 184–185 °C, 4-phenyl-3-*p*-tolylsydnone (**1d**),[19] mp 145–146 °C, 3-methyl-4-phenylsydnone (**1e**),[20] mp 131–132 °C, and *C*-biphenylene-N^{α}-(4-chlorophenyl)-N^{β}-cyanoazomethine imine (**19**),[21] mp 192–193 °C, were prepared by reported procedures. Petroleum ether, bp 60–80 °C, was used.

Photooxygenation of 3,4-Diphenylsydnone (1b). A methanolic solution of 3,4-diphenylsydnone (**1b**) (1.0 g, 4.2 mmol in 750 mL) containing a small amount (0.02 g) of Rose Bengal was flushed with oxygen gas for 15 min and then irradiated for 1 h, using a Pyrex filter, under oxygen bubbling. Removal of the solvent from the photolysate under reduced pressure left an oily residue which was chromatographed over silica gel. Elution of the column with a mixture (4:1) of benzene and ethyl acetate gave 0.34 g (25%) of α,β-dibenzoylphenylhydrazine (**16b**); mp 176–178 °C (mixture melting point).[10] No other product could be isolated from this run.

Thermolysis of α,β-Dibenzoylphenylhydrazine (16b). A sample of α,β-dibenzoylphenylhydrazine (**16b**, 0.1 g, 0.317 mmol), obtained from the photooxygenation of 3,4-diphenylsydnone (**1b**), was heated in a sealed tube at 280 °C for 3 h. The thermolyzed product was dissolved in methylene chloride (50 mL) and then extracted with a saturated solution of sodium bicarbonate (30 mL). The aqueous layer on acidification gave 0.01 g (32%) of benzoic acid (**12b**); mp 120–121 °C (mixture melting point).

The methylene chloride solution was dried over anhydrous sodium sulfate and the solvent was removed under vacuum to give a residue which was chromatographed over alumina (neutral). Elution with benzene gave 0.02 g (20%) of the unchanged starting material **16b**; mp 176–177 °C (mixture melting point).

Attempted Photolysis of α,β-Dibenzoylphenylhydrazine (16b). A solution of **16b** (0.632 g, 2 mmol) in absolute methanol (450 mL) was irradiated for 1 h. Evaporation of the solvent from the photolyzed mixture gave an oily residue, which on fractional crystallization from ethanol gave 0.61 g (96%) of the unchanged starting material, **16b**; mp 176–177 °C (mixture melting point).

Attempted Photooxygenation of 3,4-Diphenylsydnone without Any Sensitizer. A solution of 3,4-diphenylsydnone (**1b**, 0.5 g, 2.1 mmol) in methanol (175 mL) was irradiated for 1 h, using a Pyrex filter, while a slow stream of oxygen gas was being bubbled through it. After removal of the solvent under vacuum, the resultant residue was chromatographed over silica gel. Elution with petroleum ether gave 0.18 g (22%) of 2,4,5-triphenyl-1,2,3-triazole (**8b**); mp 123–124 °C (mixture melting point).[23]

Subsequent elution of the column with benzene gave 0.08 g (16%) of the starting sydnone, **1b**; mp 185–186 °C (mixture melting point).

Reaction of *N*,*C*-Diphenylnitrilimine with Benzoic Acid. Triethylamine (3 mL) was added dropwise to a stirred mixture of α-chlorobenzaldehyde phenylhydrazone (**17**, 0.46 g, 2 mmol) and benzoic acid (0.366 g, 3 mmol) in dry benzene (20 mL). The reaction mixture was stirred at room temperature for 5 h and the precipitated triethylamine hydrochloride was separated by filtration. Removal of the solvent under vacuum from the organic filtrate gave a viscous mass which was triturated with ethanol to give a solid product. Recrystallization of this product from ethyl alcohol gave 0.32 g (44%) of α,β-dibenzoylphenylhydrazine (**16b**); mp 177–178 °C (mixture melting point).

Irradiation of 3,4-Diphenylsydnone with Benzoic Acid. A mixture of 3,4-diphenylsydnone (0.12 g, 0.5 mmol) and benzoic acid (0.091 g, 0.75 mmol) dissolved in methanol (220 mL) was irradiated for 1 h. Removal of the solvent under vacuum gave a residual product, which was chromatographed over silica gel. Elution with a mixture (19:1) of benzene and ethyl acetate gave 0.075 g (48%) of α,β-dibenzoylphenylhydrazine, **16b**; mp 177–178 °C (mixture melting point).

Attempted Photooxygenation of 2,5-Diphenyltetrazole (18). A solution of 2,5-diphenyltetrazole (**18**) (1.8 g, 8.1 mmol) in methanol (1200 mL) containing a small amount (0.03 g) of Rose Bengal was irradiated under oxygen bubbling for 2 h. Removal of the solvent under vacuum gave a viscous product, which was triturated with methanol to give 1 g (31%) of 2,4,5-triphenyl-1,2,3-triazole (**8b**), mp 124–125 °C (mixture melting point), after recrystallization from petroleum ether.

Photolysis of 2,5-Diphenyltetrazole (18). A solution of 2,5-diphenyltetrazole (1.2 g, 5.4 mmol) in methanol (800 mL) was irradiated under oxygen-free nitrogen for 2 h. Removal of the solvent under vacuum gave an impure product, which was chromatographed over silica gel. Elution with petroleum ether gave 0.7 g (41%) of the triazole **8b**: 124–125 °C (mixture melting point).

Photooxygenation of 4-Phenyl-3-*p*-tolylsydnone (1c). A solution of 4-phenyl-3-*p*-tolylsydnone (**1c**) (1.008 g, 4 mmol) in methanol (800 mL), containing a small amount of Rose Bengal (0.03 g), was irradiated under oxygen bubbling for 2 h. Removal of the solvent under vacuum gave a product mixture, which was chromatographed over silica gel. Elution of the column with petroleum ether gave 4,5-diphenyl-2-*p*-tolyl-1,2,3-triazole (**8c**) (0.075 g, 8%); mp 109–110 °C (mixture melting point).[4]

Further elution of the column with benzene gave 0.105 g (8%) of α,β-dibenzoyl-*p*-tolylhydrazine (**16c**): mp 186–188 °C (mixture melting point).[24]

Irradiation of 4-Phenyl-3-*p*-tolylsydnone in the Presence of Benzoic Acid. A solution containing a mixture of 4-phenyl-3-*p*-tolylsydnone (0.5 g, 2 mmol) and benzoic acid (0.3 g, 2 mmol) in methanol (400 mL) was irradiated for 2 h, using a Pyrex filter. Removal of the solvent under vacuum gave a viscous residue, which was chromatographed over silica gel. Elution with a mixture (3:7) of benzene and petroleum ether gave 0.1 g (33%) of unchanged benzoic acid; mp 120–121 °C (mixture melting point).

Further elution of the column with benzene gave 0.03 g (6%) of the unchanged sydnone, **1c**; mp 162–163 °C (mixture melting point).

Continued elution of the column with a mixture (4:1) of benzene and ethyl acetate gave 0.275 g (42%) of α,β-dibenzoyl-*p*-tolylhydrazine, **16c**; mp 185–187 °C (mixture melting point).

Photooxygenation of 3-Phenyl-4-*p*-Tolylsydnone (1d). A solution of 3-phenyl-4-*p*-tolylsydnone (**1d**) (1.008 g, 4 mmol) in methanol (800 mL) containing a small amount (0.03 g) of Rose Bengal was irradiated under oxygen bubbling for 1 h. Removal of the solvent under vacuum gave a product mixture, which was chromatographed over silica gel. Elution with petroleum ether gave 13 mg (1%) of 2-phenyl-4,5-*p*-tolyl-1,2,3-triazole (**8d**), mp 145–146 °C (mixture melting point),[25] after recrystallization from petroleum ether.

Further elution of the column with benzene gave 0.12 g (10%) of α,β-di-*p*-toluylphenylhydrazine (**16d**); mp 187–188 °C (mixture melting point).

Irradiation of 3-Phenyl-4-*p*-tolylsydnone (1d). A. In Methanol. A solution of **1d** (1.01 g, 4 mmol) in methanol (650 mL) was irradiated under a nitrogen atmosphere for 0.75 h. After removal of the solvent, the resultant product mixture was chromatographed over silica gel. Elution with petroleum ether

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gave 95 mg (7%) of 2-phenyl-4,5-di-*p*-tolyl-1,2,3-triazole (**8d**); mp 144–145 °C (mixture melting point).

No other product could be isolated from this run.

B. In Benzene. A solution of **1d** (1.008 g, 4 mmol) in benzene (650 mL) was irradiated under nitrogen atmosphere for 0.5 h. Workup of the mixture, as in the earlier case, by chromatography over silica gel and elution with petroleum ether gave 0.12 g (9%) of the triazole **8d**; mp 144–145 °C (mixture melting point).

Irradiation of 3-Phenyl-4-*p*-tolylsydnone (1d) with *p*-Toluic Acid. A mixture of **1d** (0.51 g, 2 mmol) and *p*-toluic acid (0.3 g, 2.1 mmol) was dissolved in methanol (200 mL), and the solution was irradiated for 1 h under a nitrogen atmosphere. Removal of the solvent under vacuum gave a product mixture, which was chromatographed over silica gel. Elution with petroleum ether gave 3 mg (9%) of the triazole **8d**; mp 145–146 °C (mixture melting point).

Subsequent elution of the column with a mixture (1:1) of benzene and petroleum ether gave 25 mg (6%) of *α*,*β*-di-*p*-toluylphenylhydrazine (**16d**).

Photooxygenation of 3-Methyl-4-phenylsydnone (1e). A solution of 3-methyl-4-phenylsydnone (**1e**) (0.88 g, 4 mmol) in methanol (450 mL) containing a small amount (0.01 g) of Rose Bengal was irradiated for 1 h, under oxygen bubbling. Removal of the solvent under vacuum gave a viscous mass, which was dissolved in methylene chloride (100 mL) and subsequently extracted with sodium bicarbonate. The aqueous layer, on acidification with dilute hydrochloric acid, gave 0.11 g (10%) of benzoic acid (**12b**); mp 120–121 °C (mixture melting point).

The organic layer was dried over anhydrous magnesium sulfate, and the solvent was removed under vacuum to give a product which was subsequently recrystallized from a mixture (1:1) of benzene and petroleum ether to give 65 mg (5%) of *α*,*β*-dibenzoylhydrazine (**16e**); mp 144–146 °C (mixture melting point).[26]

Photolysis of 3-Methyl-4-phenylsydnone (1e). A benzene solution of 3-methyl-4-phenylsydnone (**1e**) (1.06 g, 6 mmol in 450 mL) was irradiated for 2 h, under a nitrogen atmosphere. Removal of the solvent under vacuum gave a product mixture which was subsequently chromatographed over silica gel. Elution of the column with a mixture (1:1) of benzene and petroleum ether gave 0.1 g (10%) of 4-methyl-2-phenyl-Δ^2-1,3,4-oxadiazolin-5-one (**5e**) after recrystallization from petroleum ether: mp 105–106 °C; IR spectrum (KBr) ν_{max} 3104 (ν_{C-H}, aromatic), 2924 (ν_{C-H}, aliphatic), 1774 ($\nu_{C=O}$), 1616, 1600, 1576, 1494, 1454, 1426, 1390, 1349, 1285, 1018, 1008, 988 cm^{-1}; NMR spectrum ($CDCl_3$) δ 3.45 (s, 3 H, CH_3 protons), 7.60 (m, 5 H, aromatic protons).

Anal. Calcd for $C_9H_8N_2O_2$: C, 61.35; H, 4.54; N, 15.93. Found: C, 61.44; H, 4.85; N, 15.9.

Attempted Photooxygenation of 3-Phenylsydnone (1a). A solution of 3-phenylsydnone (0.648 g, 4 mmol) in methanol (450 mL) was mixed with a small quantity (0.01 g) of Rose Bengal, and the resulting solution was irradiated under oxygen bubbling for 2 h. Removal of the solvent under vacuum gave a brown residue, which was chromatographed over silica gel. Elution with different solvents did not give rise to any identifiable product.

Photooxygenation of *C*-Biphenylene-*N*$^{\alpha}$-(4-Chlorophenyl)-*N*$^{\beta}$-cyanoazomethine Imine (19). To a benzene solution of *C*-biphenylene-*N*$^{\alpha}$-(4-chlorophenyl)-*N*$^{\beta}$-cyanoazomethine imine (**19**) (0.6 g, 1.8 mmol, in 700 mL) was added a methanol solution of Rose Bengal (0.03 g in 30 mL), and the resultant mixture was irradiated for 2 h, under oxygen bubbling. Removal of the solvent under vacuum gave a viscous residue, which was chromatographed over neutral alumina. Elution with petroleum ether gave 0.26 g (78%) of 9-fluorenone (**21**), mp 84–86 °C (mixture melting point), after recrystallization from ethyl alcohol.

No other product could be isolated from this run.

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Registry No. 1a, 120-06-9; **1b**, 3815-83-6; **1c**, 3815-77-8; **1d**, 70702-63-5; **1e**, 35431-71-1; **5e**, 879-60-7; **8b**, 27653-10-7; **8c**, 18411-23-9; **8d**, 10591-73-8; **12b**, 65-85-0; **16b**, 5455-22-1; **16c**, 70702-64-6; **16d**, 70749-44-9; **16e**, 21150-15-2; **17**, 15424-14-3; **18**, 18039-45-7; **19**, 5825-75-2; **21**, 486-25-9.

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Cycloadditions of Ketenes with *N*-Fluorenylidenealkylamine and -arylamine Oxides. Synthesis of Spirooxazolidinones and Spiroisoxazolidinones[1]

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The cycloadditions of several *N*-fluorenylidenearylamine and -alkylamine oxides (**1** and **2**) with cyclopentamethyleneketene, *tert*-butylcarbethoxyketene, and *tert*-butylcycanoketene were investigated. In general, the *N*-aryl derivatives afforded spirooxazolidinones (**3**) while the *N*-alkyl derivatives gave spiroisoxazolidinones (**4**). ^{1}H NMR and ^{13}C NMR studies of **3** and **4** were carried out to substantiate their structures. A mechanistic scheme which accounts for all of the observed cycloaddition products is proposed.

Our previous interest in the reactions of ketenes with *N*-aryl-[2a] and *N*-alkylimines,[2b] ketenimines,[2c] and azines[2d] led us to examine the cycloadditions of ketenes and nitrones. As we had developed a convenient method for the synthesis of *N*-methyl nitrones,[3] we initially studied the cycloaddition of *N*-fluorenylidenemethylamine oxide with *tert*-butylcyanoketene. We then extended these investigations to other N-substituted nitrones and other ketenes as well.

N-Aryl nitrones (**1a–c**) were prepared in 78–91% yields by the oxidation of the corresponding imines with *m*-chloroperbenzoic acid in methylene chloride. Nitrone **1d**

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