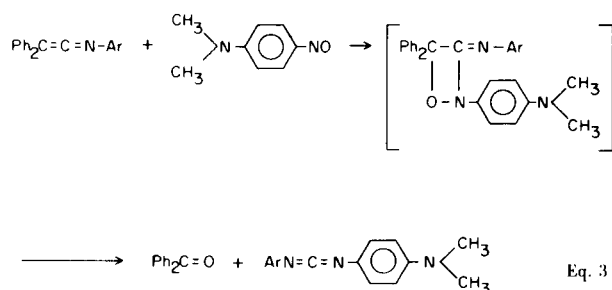




dimethylaminonitrosobenzene except the 3-iminosubstituted oxazetidine could not be isolated. The only products observed were a carbodiimide and benzophenone. These products can only be accounted for from a 3-iminosubstituted oxazetidine intermediate (Eq. 3).



The foregoing experimental results and deductions seem to rule out the possible ground state structures of nitrosobenzene for the reactive species. Either a mixture of products is predicted or the reaction can be shown to occur when the various ground state species are known to be absent. Thus, our attention was turned to the consideration of excited state species for this reaction of nitrosoarenes with ketenimines. Calculations show that orbital overlap consistent with the observed product (III) occurs with ketenimine in the ground state and nitrosobenzene in the first excited state or with nitrosobenzene in the ground state and ketenimine in the first excited state. Jaffé (11) predicts an energy gap of 1.5 electron volts between the ground state and first excited state of nitrosobenzene and this value agrees with the accepted  $n \rightarrow \pi^*$  transition for nitrosobenzene of 38.2 kcal/mole (7800 Å). We predict a value of approximately 100 kcal/mole for the energy difference between the ground state and the first excited state for ketenimine. Thus, the reaction could be occurring through ground state ketenimine and first excited state nitrosobenzene (the lower energy process) through the  $n \rightarrow \pi^*$  transition of nitrosobenzene.

To discern if an  $n \rightarrow \pi^*$  excitation process is important in the observed cyclization, rate studies on the cycloaddi-

TABLE I

Rate Constants (a) for the Dark and the Photolytic 1,2-Cycloaddition of  $p$ -X-C<sub>6</sub>H<sub>4</sub>-NO to Diphenylketene  $N$ -( $p$ -tolyl)imine in carbon tetrachloride, 0° (b).

X	K Dark (1/mole-sec)	K Photolytic (1/mole-sec)
H	$1.8 \pm .2 \times 10^{-3}$	$2.4 \pm .3 \times 10^{-3}$
NO <sub>2</sub>	$2.8 \pm .1 \times 10^{-2}$	$2.8 \pm .1 \times 10^{-2}$

(a) Average values for three determinations. (b) All reaction mixtures were initially 0.01 *M* in both reactants.

tion of nitrosobenzene and  $p$ -nitronitrosobenzene to diphenylketene  $N$ -( $p$ -tolyl)imine (III, Ar =  $p$ -tolyl) under dark and photolysis conditions were conducted. Both the cycloaddition of nitrosobenzene and  $p$ -nitronitrosobenzene to this ketenimine proved to be second order for the runs under dark and photolysis conditions. The rate constants are recorded in Table I. From this data it is obvious that simple illumination of the reaction components does not increase the rate of reaction.

In 1953 Orgel (12) proposed that the  $n \rightarrow \pi^*$  transition for nitrosobenzene is singlet-singlet and involves the promotion of one electron from the lone pair on nitrogen to an antibonding  $\pi$  orbital. We have been unable to locate any literature citations to the effectiveness of the  $S_1 \rightarrow T_1$  transition for nitrosobenzene. If this transition is ineffective and if the actual cycloaddition observed (Eq. 2) occurs only through a triplet nitrosobenzene, then sensitization of the photolyzed reaction mixture should result in an increase in rate. To test this hypothesis, rates for the loss of ketenimine for the reaction illustrated by Equation 2 (Ar =  $p$ -tolyl) were determined with several substituted nitrosobenzenes with and without an added sensitizer. The results summarized in Table II show a definite increase in the rate of loss of ketenimine for the sensitized reactions. Rate constants have not been compared because of insufficient data on the zero order sensitized reactions.

TABLE II

Rate (a) of Loss of Keteneimine (mole/l-min) with X-C<sub>6</sub>H<sub>5</sub>-NO Under Photolytic Conditions (b,c)

X	Unsensitized	Sensitized (d)
H	$1.4 \pm .4 \times 10^{-5}$	$2.9 \pm .2 \times 10^{-5}$
CH <sub>3</sub>	$8.3 \pm .1 \times 10^{-6}$	$3.0 \pm .2 \times 10^{-5}$
Cl	$1.2 \pm .2 \times 10^{-5}$	$2.8 \pm .2 \times 10^{-5}$
Br	$1.2 \pm .1 \times 10^{-5}$	$3.4 \pm .2 \times 10^{-5}$

(a) All results are the average of three runs. (b) Each component was initially 0.01 *M*. (c) All runs were at 0° in carbon tetrachloride. (d) Anthracene (0.01 *M*) was used as the sensitizer because of its triplet energy of 42 kcal/mole (13), its quantum yield for intersystem crossing at 0.75 (14), and its lack of reaction with either of the starting materials.

It is interesting to note that the unsensitized reactions (Table II) approach a common rate value of  $1 \times 10^{-5}$  mole/l-min while the sensitized reactions approach a common rate value of  $3 \times 10^{-5}$  mole/l-min. We interpret this data to mean that the reaction is occurring through the triplet state of excited nitrosobenzene. Since photolysis without sensitization does not enhance the rate of

reaction, the non-sensitized reactions must be occurring through a thermally achieved triplet multiplicity.

#### EXPERIMENTAL

Melting points were determined on Fisher-Johns and Mel-Temp apparatuses and are corrected. Infrared spectra were determined in carbon tetrachloride and potassium bromide on Perkin-Elmer Model 137 and 137G Infracords. The gas chromatography measurements were made on the Aerograph Auto-Prep Instrument and analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Calculations were performed on a UNIVAC 1106 computer with programs obtained from the Quantum Chemistry Program Exchange at the University of Indiana. The calculations were performed using the Extended Hückel Method (EHM), CNDO, CNDO/2, CNDO-C1, and INDO. The EHM illustrated exaggerated charge distributions which is common with the more electronegative atoms. The other methods were consistent in the predictions relevant to this work.

#### 4,4-Diphenyl-2-(*p*-iodophenyl)-3-*N*-(*p*-tolyl)imino-1,2-oxazetidine.

To a solution of 0.40 g. (0.0017 mole) of *p*-iodonitrosobenzene in 5.0 ml. of carbon tetrachloride was added a solution of 0.50 g. (0.0018 mole) of diphenylketene-*N*-(*p*-tolyl)imine in 5 ml. of carbon tetrachloride. The two solutions were mixed and the reaction mixture was allowed to stand at room temperature. When the infrared spectrum showed complete disappearance of the 2000  $\text{cm}^{-1}$  ketenimine absorption band, the solvent was evaporated under reduced pressure (aspirator) without the application of heat. The resulting red oil was dissolved in a minimum amount of hexane and allowed to stand at 0°. After several hours, 0.03 g. (33%) of the crude oxazetidine precipitated (m.p. 89-98°). Recrystallization of the sample from hexane gave an analytically pure sample of the material, m.p. 93.5-94°.

*Anal.* Calcd. for  $\text{C}_{27}\text{H}_{21}\text{N}_2\text{O}$ : C, 62.80; H, 4.10; N, 5.42. Found: C, 63.06; H, 4.13; N, 5.67.

#### Addition of *p*-Nitroso-*N,N*-dimethylaniline to Diphenylketene-*N*-(*p*-tolyl)imine.

To a solution of 1.0 g. (0.0035 mole) of diphenylketene-*N*-(*p*-tolyl)imine in 50 ml. of carbon tetrachloride was added a solution of 0.7 g. (0.0046 mole) of *p*-nitroso-*N,N*-dimethylaniline in 50 ml. of carbon tetrachloride. The reaction mixture was allowed to stand for four hours at room temperature. The infrared spectrum showed strong absorptions at 2130  $\text{cm}^{-1}$  (carbodiimide), 2000  $\text{cm}^{-1}$  (C=C=N), and 1670  $\text{cm}^{-1}$  (C=O). No absorption was seen at 1710  $\text{cm}^{-1}$ . No products were isolated.

#### Rate Measurements.

The rate studies were run at 0° since photolysis of the reaction mixtures at room temperature resulted in decomposition of the products to benzophenone and a carbodiimide. Oxygen was excluded from the reaction by saturating all solvents with nitrogen and operating under a nitrogen atmosphere.

The ketenimine (with or without sensitizer) and the nitrosoarene were each weighed directly into a tared 50 ml. volumetric flask. The flasks were flushed with nitrogen, and deoxygenated

solvent was added to the mark. The two solutions were placed in an ice bath and cooled to 0°. The two solutions were quickly added, under a stream of nitrogen, to a jacketed reaction vessel in a Srinivasan-Griffin Photochemical Reactor equipped with sixteen 3500 Å low pressure mercury lamps. The reaction vessel had been thermostated at 0° and flushed with nitrogen. The cold solution was quickly mixed by bubbling a stream of nitrogen through it. Irradiation was begun and the concentration of the ketenimine as a function of time was determined by recording the 2000  $\text{cm}^{-1}$  absorbances at regular intervals and comparing these absorbances to the standard curve. The usual irradiation period was 7200 seconds, carrying the reaction to 25-50% completion.

#### Kinetic Results.

The data resulting in Table I would fit a second order plot only. Both zero and first order plots were definitely nonlinear.

#### Rate Studies with a Sensitizer.

Rates for the sensitized reactions were determined as previously described using carbon tetrachloride solutions which were 0.01 *M* with respect to ketenimines, nitrosoarene, and anthracene. All reactions proved to be zero order.

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