Photochemical Behavior of Aromatic 1,2-Diazine *N*-Oxides[1]

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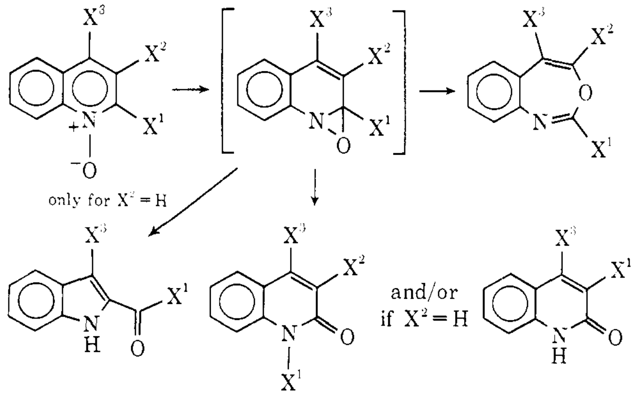
London WIX 4BS, England. *Received January 27, 1973*

Abstract: The ultraviolet irradiation of 3,6-diphenylpyridazine *N*-oxide results mainly in formation of 3-benzoyl-5-phenylpyrazole and 2,5-diphenylfuran. By varying the temperature or the intensity of the light one of these two products could be formed preferentially. The irradiation of 1,4-diphenylphthalazine *N*-oxide in various solvents results in the formation of 1,3-diphenylisobenzofuran. In each case transient intermediates were detected and characterized by their uv and ir spectra. These intermediates are identified as diazo ketones and the results of the irradiation of 3,6-diphenylpyridazine *N*-oxide are interpreted on the basis of competing thermal and photochemical pathways for the decomposition of the intermediate diazo ketone. The formation and disappearance of this diazo ketone were studied with conventional as well as nanosecond flash photolysis; from these results we conclude that it is generated from a singlet excited state, and most likely directly from the excited state, without the formation of a transient oxaziridine, as previously believed.

The photochemistry of a variety of heteroaromatic *N*-oxides, in particular pyridine and quinoline *N*-oxides, has been extensively examined, and a large amount of data, especially about the latter two classes of compounds, has been documented in the literature.[4] Most of these compounds undergo very efficient photochemical reactions, and the mechanisms of these reactions have been the subject of debate in many of the previous papers.[5]

In most of the more recent papers, in order to explain the rearrangements, oxaziridines have been proposed as the first ground-state species[6] after excitation, and it has been attempted to correlate the large majority of results by postulating three different pathways leading from oxaziridines to isolable products, *e.g.*, Scheme I, where this is shown for quinoline *N*-oxides.[5a] Furthermore, it has been proposed in several papers,[7,8] based on various experimental evidence, that the rearrangements originated from a singlet excited state, presumably the lowest one, whereas the other general reaction, deoxygenation, takes place from the lowest triplet state.

Scheme I



In no case, however, were oxaziridines observed, and it thus is of considerable interest to search for these intermediates,[5a,8] as well as to attempt to clarify from which excited states the reactions take place.

Only a few reports on the light-induced reactions of 1,2-diazine *N*-oxides have been published, and the results were partially misinterpreted. Thus the reported hydroxymethylation of some pyridazine *N*-oxides[9] with concomitant loss of oxygen is most probably due to secondary reaction of the parent pyridazine.[10] Igeta, *et al.*,[11] reported the photochemistry of several pyridazine *N*-oxides which resulted mainly in deoxygenation.

We have reported preliminary results from a study of the light-induced reactions of 3,6-diphenylpyridazine *N*-oxide and 1,4-diphenylphthalazine *N*-oxide.[12,13]

From these results, it appeared that in particular 1,4-diphenylpyridazine *N*-oxide was well suited for a further mechanistic study. This paper reports the experimental details of the previous work as well as some new observations and interpretations.

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[1] Photochemical Studies. XX. For the previous paper, see O. Buchardt, K. B. Tomer, and V. Madsen, *Tetrahedron Lett.*, 1311 (1971).

[2] Danish National Science Foundation Postdoctoral Fellow, 1970–1971.

[3] (a) University of Copenhagen; (b) Saginaw Valley College; (c) Davy Faraday Laboratory of the Royal Institution.

[4] Visiting professor from The Weizmann Institute of Science, Rehovot, Israel.

[5] (a) G. G. Spence, E. C. Taylor, and O. Buchardt, *Chem. Rev.*, **70**, 231 (1970). (b) Some of the most recent papers are on cinnoline *N*-oxides [W. H. Horspool, J. R. Kershaw, and A. W. Murray, *J. Chem. Soc., Chem. Commun.*, 345 (1973)] and benzotriazine *N*-oxides: W. M. Horspool, J. R. Kershaw, A. W. Murray, and G. M. Stevenson, *J. Amer. Chem. Soc.*, **95**, 2390 (1973).

[6] Although this was never stated explicitly.

[7] See, *e.g.*, O. Buchardt, C. L. Pedersen, and N. Harrit, *J. Org. Chem.*, **37**, 3592 (1972).

[8] Recently an argument against oxaziridines as intermediates in the photochemistry of isoquinolines was put forward: C. L. Lohse, *J. Chem. Soc., Perkin Trans. 2*, 229 (1972).

[9] M. Ogata and K. Kano, *Chem. Commun.*, 1176 (1967).

[10] T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Lett.*, 3839 (1970).

[11] H. Igeta, T. Tsuchiya, M. Yamada, and H. Arai, *Chem. Pharm. Bull.*, **16**, 767 (1968); T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Lett.*, 2747 (1969); 2213 (1970).

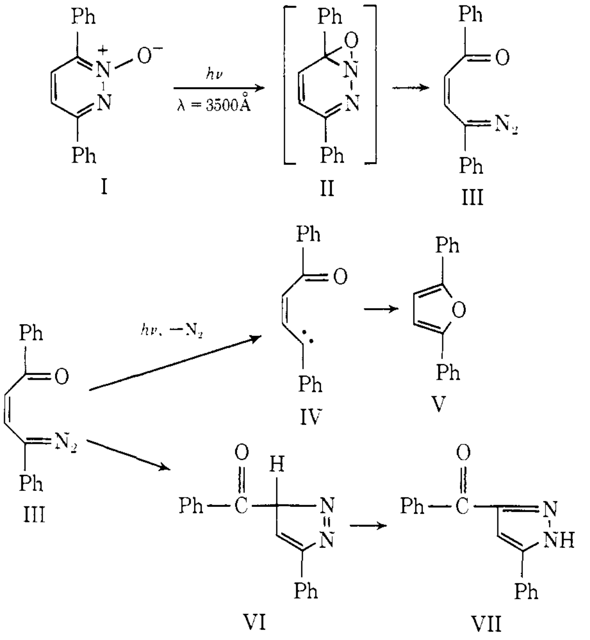
[12] O. Buchardt, *Tetrahedron Lett.*, 1911 (1968); P. L. Kumler and O. Buchardt, *J. Amer. Chem. Soc.*, **90**, 5940 (1968).

[13] It has very recently been reported that irradiation of tetraphenylpyridazine *N*-oxide results in the formation of a mixture of tetraphenylfuran, 1,2-diphenyl-1,2-dibenzoylethylene (*cis*- and *trans*-), 1-(1,2,3-triphenylcyclopropenyl)bicyclo[3.2.0]-3,6-heptadien-2-one, and tetraphenylpyridazine: T. Tsuchiya, H. Arai, and H. Igeta, *Tetrahedron Lett.*, 2579 (1971); T. Tsuchiya, H. Arai, T. Tonami, and H. Igeta, *Chem. Pharm. Bull.*, **20**, 300 (1972). See also T. Tsuchiya, H. Arai, and H. Igeta, *J. Chem. Soc., Chem. Commun.*, 550 (1972).

Results and Discussion

3,6-Diphenylpyridazine N-Oxide. Photolysis of 3,5-diphenylpyridazine *N*-oxide (I) with 3500-Å light resulted in a high-yield conversion to 3-benzoyl-5-phenylpyrazole, 2,5-diphenylfuran, and molecular nitrogen. Previously a mechanism to account for the formation of these products was proposed, which is repeated in Scheme II.

Scheme II



This mechanistic proposal involved the formation of an oxaziridine (II) as the first ground-state molecule, which is subsequently converted in a thermal process to the diazo compound III. Conversion of the oxaziridine to the diazo compound is analogous to the formation of phenylnitrene from 2,3,3-triphenyloxaziridine observed by Splitter and Calvin.[14] The formation of the diazo ketone III during the ultraviolet irradiation of 3,5-diphenylpyridazine *N*-oxide could be detected by both infrared and ultraviolet spectroscopy. Thus, dilute solutions of the *N*-oxide I were irradiated in an appropriate spectroscopic cell at room temperature, and the infrared and ultraviolet spectra were monitored periodically. During the irradiation an intense yellow color developed, and this solution also showed the presence of a sharp absorption band in the infrared at 2070 cm^{-1}. This band, which disappeared along with the yellow color when the solution was kept in the dark, is in the region characteristic of the diazo linkage.[15] To examine the thermal stability of the diazo ketone III the absorption spectrum of this intermediate was recorded at −70° in ethanol. The absorption spectrum is structured and exhibits maxima at 423, 345, and 303 nm. The absorption at 423 nm was monitored at −70° for 30 min during which time the intensity did not change.

The intermediacy of diazo ketones in these photolyses is similar to that proposed by Dolbier and Williams in the photolyses of some nonaromatic azine *N*-oxides.[16]

To obtain additional supporting evidence for the intervention of the diazo intermediate III, it was attempted to synthesize this compound by oxidation of the corresponding monohydrazone of *cis*-1,2-dibenzoylethylene, but this compound could not be prepared. However, the monohydrazone of *trans*-1,2-dibenzoylethylene could be prepared in high yield by the reaction of equimolar amounts of the diketone and hydrazine. The monohydrazine was relatively stable in the solid state but some decomposition (as evidenced by a significant color change from light yellow to deep orange) occurred after a period of months at room temperature. In contrast, the decomposition was rapid in solution, particularly in chloroform or dimethyl sulfoxide. The mercuric oxide oxidation of this monohydrazone in benzene solution resulted in the isolation of 3-benzoyl-5-phenylpyrazole (VII) in good yield. Again in this case a transient diazo compound indistinguishable from III could be detected by infrared spectroscopy.

The intermediate diazo ketone III has two competitive pathways open to it. One pathway is the intramolecular 1,3-dipolar cycloaddition resulting in the formation of 3-benzoyl-5-phenylpyrazole (VII) *via* the tautomeric [3H]pyrazole VI; this thermal isomerization is expected to be even faster than the known isomerization of vinyldiazomethane to pyrazole.[17] The other competing reaction pathway involves a photodecomposition of the diazo ketone to a carbene which reacts intramolecularly to yield 2,5-diphenylfuran.[18] Since there are competing thermal and photochemical reactions it would be expected that irradiating with a more intense light source or lowering the temperature during irradiation would increase the photochemical reaction, *i.e.*, the conversion to 2,5-diphenylfuran (V).

Experimentally both assumptions proved to be correct. When different light sources were used for irradiation of a solution of 3,5-diphenylpyridazine *N*-oxide at room temperature the product distribution changed from 75% 3-benzoyl-5-phenylpyrazole and 3% 2,5-diphenylfuran (external irradiation in a Rayonet reactor, 350-nm lamps) to 27% of the pyrazole and 67% of the furan (Pyrex filter, Hanau 700-W immersion lamp).[19] Furthermore, when a similar solution was irradiated in the Rayonet reactor at −65° the major product was 2,5-diphenylfuran (45%).[20]

Conventional Flash Photolysis. The disappearance of the diazo ketone III could conveniently be followed by measuring the decay rate of the absorption at 420 nm after flashing (Table I).

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(14) G. S. Splitter and M. Calvin, *Tetrahedron Lett.*, 1445 (1968).

(15) A. Foffoni, C. Pecite, and S. Ghersetti, *Tetrahedron*, **11**, 285 (1960).

(16) N. H. Williams and W. R. Dolbier, Jr., *J. Amer. Chem. Soc.*, **94**, 3955 (1972).

(17) D. C. Hurd and S. C. Lui, *J. Amer. Chem. Soc.*, **57**, 2656 (1935); D. W. Adamson and J. Kenner, *ibid.*, **57**, 286 (1935).

(18) Since the reaction of the *trans*-diazo ketone to give 2,5-diphenylfuran (V) is unlikely, the cis isomer is most probably involved. However, it cannot be excluded that the carbene IV is generated as the trans form, and that succeeding cis–trans isomerization takes place in the photochemical process. The intramolecular 1,3-dipolar cycloaddition to give 3-benzoyl-5-phenylpyrazole is not sterically restricted in the same manner but can take place from the *cis*- as well as the *trans*-diazo ketone.

(19) In an attempt to trap any carbene product during the irradiation conditions which led to loss of nitrogen, the irradiation of the *N*-oxide I was carried out in cyclohexene–acetone (1:1) solution. No identifiable cyclohexene adduct was observed.

(20) Since our evidence indicates that a diazo ketone intermediate can lead to either a pyrazole or a furan product depending upon conditions, the formation of a 1,2,3-oxadiazepine (proposed by Tsuchiya, *et al.*, as an intermediate in one of two possible mechanisms for furan formation[11,13]) is not necessary. Their results are consistent with their alternate mechanism involving a diazo ketone.

Table I. Rate Constants for the Disappearance of Diazo Ketone III at 25°

Solvent	EtOH (96%)	C_6H_6	$CHCl_3$	CH_3COCH_3	C_6H_{12}
Rate constant, sec^{-1}	1.5×10^{-2}	6.2×10^{-3}	8.0×10^{-3}	1.4×10^{-3}	4.1×10^{-3}

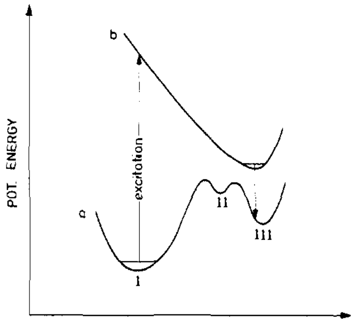


Figure 1. Cross-section of (a) hypothetical hypersurface illustrating the thermal rearrangement of I, *via* II to III; and (b) excited state leading to reaction.

The results show only a slight, and irregular, dependence of rate on solvent polarity. This seems to be in good correspondence with the 1,3-dipolar addition reaction by which it disappears.[21] As could be expected, the decay rate was dependent on the intensity of the monitoring light beam. Accordingly the intensity was kept at such a low level that further decrease showed no effect on the decay rates.

By using low flash energies, *i.e.*, high time resolution, it was shown that the diazo ketone had reached maximum concentration after 20 μsec.

Since very careful deoxygenation of the ethanol and the cyclohexane solution by the freeze–thaw method did not lead to the appearance of any new species, it was attempted to produce the triplet state of the *N*-oxide by sensitization with triphenylene. By flashing a deoxygenated solution of triphenylene, its triplet could be observed.[22] Addition of 3,6-diphenylpyridazine *N*-oxide caused almost complete quenching of the triphenylene triplet without the appearance of any new absorptions. It was not possible to avoid some direct excitation of the *N*-oxide, and very small amounts of the diazo ketone III were formed. But since this amount was the same with or without deoxygenation, and since the *N*-oxide caused quenching of the triphenylene triplet it is concluded that the diazo ketone originates from the excited singlet state of the *N*-oxide.

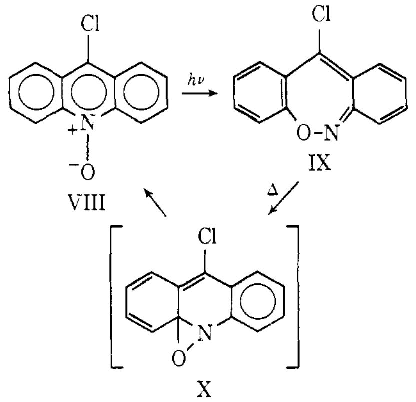
Nanosecond Flash Photolysis. The upper time limit for the formation of the diazo ketone III estimated by conventional flash methods was diminished further by nanosecond flash photolysis experiments. The grow-in of the absorption of the diazo intermediate measured at 420 nm in ethanol or cyclohexane, either aerated or outgassed, followed the profile of the exciting laser pulse. Therefore the diazo ketone III must originate from a species of a lifetime shorter than the pulse width, which is 20 nsec. No other transient absorptions were detected in the range 400–600 nm.

On the basis of these results as well as the related ones for quinoline *N*-oxide by Lohse,[8] the existence of the oxaziridine II as precursor to the diazo ketone III is highly questionable in view of the fact that oxaziridines as a rule are either stable at room temperature, or have half-lives >1 sec.[5a,23] We now wish to propose that the oxaziridine III may not be formed at all, but that the geometry of the excited-state hypersurface is such that there is no minimum or "well"[24] corresponding to the stable ground-state oxaziridine. This is illustrated in Figure 1, which shows cross-sections of the hypothetical ground-state (thermal) reaction leading from I, through II to III, and of the excited state leading to reaction.

Since the geometry of an excited state can be very different from that of the corresponding ground state,[24] it appears likely that the geometry of the excited state compared to that of the ground state is such that the excited state in its vibrational relaxation bypasses the geometry corresponding to oxaziridines and crosses over from excited state to ground-state hypersurface with a geometry corresponding to the diazo ketone III.[25]

Since there are now two classes of *N*-oxides, *cf.*[8] where a search for the previously postulated oxaziridine intermediates with nanosecond flash spectroscopy failed to observe any, it may be a common feature for *N*-oxide photochemistry. Thus the recently published work by Kaneko, *et al.*,[26] where it is shown that one of the products (IX) in the light-induced reaction of 9-chloroacridine *N*-oxide (VIII) (Scheme III) thermally reverted to *N*-oxide, which seems only possible *via* the corresponding oxaziridine (X), is just an example to show that light-induced reactions and thermal reactions, connecting the same substances, may use different pathways.

Scheme III



Quantum yields for the disappearance of 3,5-diphenylpyridazine *N*-oxide (I) were determined by irradiation of a 9.5×10^{-5} *M* solution of I in ethanol in a 1-cm cell with monochromatic light of λ 3500 Å (SP-200 high-pressure mercury lamp equipped with a

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[21] E. M. Kosower, "Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, pp 211–214.

[22] G. Porter and F. Wilkinson, *Proc. Roy. Soc., Ser. A*, **264**, 1 (1961).

[23] E. Schmitz, "Dreiringe mit zwei Heteroatomen," Springer-Verlag, West Berlin, 1967, ff.

[24] For a discussion of photochemistry in these terms, see J. Michl, *Mol. Photochem.*, **4**, 243, 257, 287 (1972).

[25] The possibility that the oxaziridine III is generated in an electronically excited state is not ruled out, but appears highly unlikely in view of the spectroscopic characteristics of oxaziridines *vs.* *N*-oxides; see ref 23; and A. R. Katritzky and J. M. Lagowski, "Chemistry of the Heterocyclic N-Oxides," Academic Press, London, 1971, p 12.

[26] S. Yamada, M. Ishikawa, and C. Kaneko, *J. Chem. Soc., Chem. Commun.*, 1093 (1972).

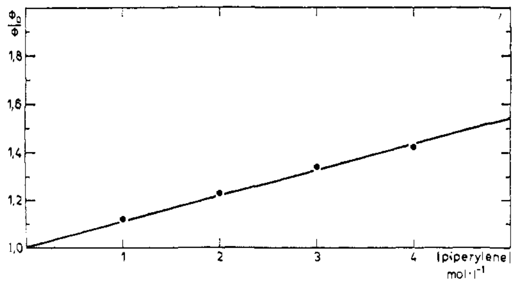


Figure 2. Stern–Volmer plot for the quenching of photorearrangement of 3,6-diphenylpyridazine *N*-oxide by piperylene (mixture of cis and trans isomers) in benzene solution.

Bausch and Lomb monochromator). The progress of the reaction was followed by measuring the decrease in the absorption at this wavelength where none of the final products absorb. An incident light intensity of 7.69 × 10^{14} quanta/sec was employed for this determination. Actinometric measurements with ferrioxalate[27] were made before and after every run. The average value of the quantum yield obtained in three experiments was 0.20 ± 0.01.

A straight line Stern–Volmer plot was obtained, using piperylene in high concentrations as quencher (Figure 2). The linearity indicates that the photoreaction takes place from only one excited state,[28] most probably the singlet, as inferred by the conventional flash experiments (*vide supra*).

No wavelength dependence was observed for the quantum yield.

Emission Spectroscopy. The fluorescence spectrum of 3,6-diphenylpyridazine *N*-oxide is shown in Figure 3. Upon irradiation in the cell the fluorescence with maximum at 408 nm was gradually replaced by the superimposed fluorescence spectra of the photoproducts V and VII, the fluorescence spectra of which are also shown in Figure 3.

Single photon counting experiments indicated that the fluorescence lifetimes of the *N*-oxide I in both aerated and outgassed ethanol and cyclohexane are less than 1 nsec.

No phosphorescence from the *N*-oxide I was detected in ether–isopentane–ethanol glass at 77°K.

1,4-Diphenylphthalazine *N*-Oxide. Irradiation of 1,4-diphenylphthalazine *N*-oxide (XI) with 3500-Å light in the absence of oxygen resulted in the formation of 1,3-diphenylisobenzofuran (XII) (chemical yield up to 65%) with concomitant expulsion of nitrogen (identified by mass spectroscopy) and small amounts of the parent amine.

A reaction sequence leading to the isobenzofuran by way of the diazo compound XII and the carbene XIII is shown in Scheme IV.

It is reasonable to expect loss of nitrogen from the diazo compound XII to be highly favored over a possible thermal cyclization (analogous to the process III → VI). The latter process is energetically very unlikely since the double bond which would have to participate is part of an aromatic system and considerable resonance stabilization would necessarily be lost.

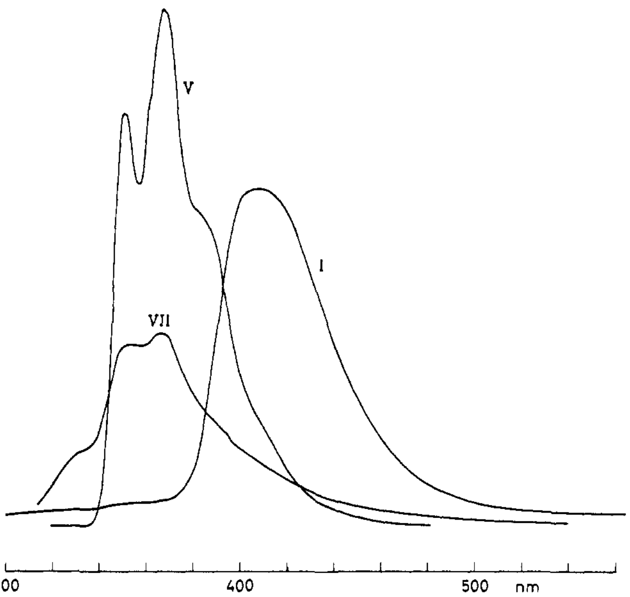
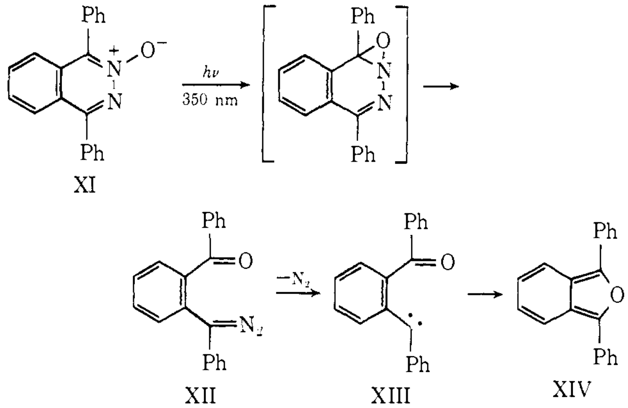


Figure 3. Uncorrected fluorescence spectra of 3,6-diphenylpyridazine *N*-oxide (I) in ether–isopentane–ethanol (5:5:2), 2,5-diphenylfuran (V) in ethanol, and 3-benzoyl-5-phenylpyrazole in ethanol. Fluorescence intensity scales are arbitrary.

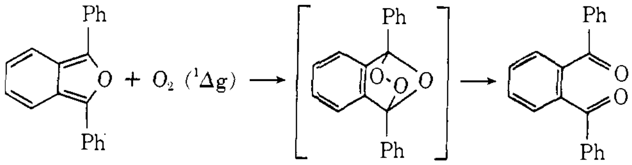
Scheme IV



The transient species XII developed during the irradiation of XI could also be detected in the infrared spectrum by the sharp absorption band at 2040 cm^{-1}. The half-life of this species was 115 min at 26°.

When the irradiation of XI in solution was carried out in the presence of oxygen the main product isolated was 1,2-dibenzoylbenzene. The 1,2-dibenzoylbenzene most probably arises from the 1,4-cycloaddition of singlet oxygen generated *in situ* to the furan skeleton of 1,3-diphenylisobenzofuran[29] (Scheme V).

Scheme V



Experimental Section

The irradiations were performed in a Rayonet reactor (Type RPR-208) using RUL-3500 lamps or in an immersion apparatus equipped with a Hanovia 700-W high-pressure mercury vapor lamp cooled internally with running water. Pyrex filters were employed.

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[27] C. G. Hatchard and C. A. Parker, *Proc. Roy. Soc., Ser. A*, **235**, 518 (1956).

[28] A. A. Lamola and N. J. Turro in "Technique of Organic Chemistry," P. A. Leermakers and A. Weisberger, Ed., Interscience, New York, N. Y., 1969, p 338.

[29] T. Wilson, *J. Amer. Chem. Soc.*, **88**, 2898 (1966).

Preparative layer chromatography (plc) was performed on silica gel (Merck PF 259); petroleum ether–benzene–acetone, 7:7:1, was used as eluent.

Infrared spectra were recorded on Beckman IR 20 A or Perkin-Elmer 337 spectrophotometers; ultraviolet spectra were recorded on Beckman DB or Unicam SP 800 spectrophotometers. Nmr spectra were determined with a Varian A-60 instrument. Samples were dissolved in $CDCl_3$ with TMS as an internal reference. Mass spectra were recorded with an Atlas CH-4 instrument. Fluorescence spectra were recorded on a Perkin-Elmer-Hitachi, Model MPF-3, instrument. Elemental analyses were carried out in the microanalytical laboratory of this laboratory, directed by Mr. P. Hansen.

Preparation of 3,6-Diphenylpyridazine. A solution of semicarbazide hydrochloride (5.6 g) and 1,2-dibenzoylethane (11.8 g), in methanol (200 ml), was refluxed on a steam bath for 45 min. The solution was cooled and sodium acetate solution added; the resultant precipitate was filtered and recrystallized from glacial acetic acid to give 5.7 g (50%), mp 222–224° (lit. mp 221°).[30]

Preparation of 3,6-Diphenylpyridazine *N*-Oxide. A sample of 3,6-diphenylpyridazine (4.0 g) was dissolved in chloroform (400 ml), 3-chloroperbenzoic acid (4.4 g *ca.* 80% purity) was added, and the resulting solution was allowed to stand at room temperature for 3 days. Dilute sodium hydroxide solution (10%) was then added, and the organic layer was separated, washed with water, and dried over $MgSO_4$. Removal of the solvent gave the *N*-oxide VI, 3.7 g (87%); mp 198–199°. *Anal.* Calcd for $C_{16}H_{12}N_2O$: C, 77.40; H, 4.87; N, 11.29. Found: C, 77.30; H, 4.96; N, 11.18.

Preparation of 1,4-Diphenylphthalazine. A solution of 1,2-dibenzoylbenzene (613 mg) and hydrazine hydrate (1.5 ml) in 90% ethanol (20 ml) was refluxed 7 hr. The solution was cooled to *ca.* −20° and filtered to yield 1,4-diphenylphthalazine (500 mg), mp 195–196° (lit.[31] mp 194°).

Preparation of 1,4-Diphenylphthalazine *N*-Oxide. 1,4-Diphenylphthalazine (7.5 g) and 3-chloroperbenzoic acid (7.5 g *ca.* 80% purity) were dissolved in chloroform (200 ml) and kept at room temperature for 4 days. The solution was washed well with dilute base and water and dried over magnesium sulfate. The solvent was removed at reduced pressure and the product recrystallized from benzene–petroleum ether, yield 6.4 g, mp 193–194°. *Anal.* Calcd for $C_{20}H_{14}N_2O$: C, 80.51; H, 4.73; N, 9.39. Found: C, 80.55; H, 4.79; N, 9.44.

Typical irradiations are described for 3,6-diphenylpyridazine *N*-oxide and 1,4-diphenylphthalazine *N*-oxide.

Irradiation of 3,6-Diphenylpyridazine *N*-Oxide. **a.** A solution of I (1.00 g) in acetone (850 ml) was irradiated in a Rayonet reactor with 3500-Å light for 1.5 hr. The solvent was evaporated and the residue was recrystallized from chloroform–hexane to yield 463 mg of 3-benzoyl-5-phenylpyrazole, mp 168–170° (lit.[32] mp 170.5–171°). A second crop, 250 mg, was also obtained; plc of the remainder yielded 2,5-diphenylfuran (25 mg, 6%), 35 mg of 3-benzoyl-5-phenylpyrazole, and 19 mg of a nitrogen-containing compound; in addition low yields of three other compounds (<20 mg) were obtained.

b. Compound I (1.00 g) in 350 ml of 1:1 acetone–cyclohexane was irradiated under purified nitrogen for 0.5 hr with a Hanovia 700-W immersion lamp. The solution was filtered to yield VI (210 mg, 27%). 2,5-Diphenylfuran (600 mg, 67%), mp 91–92°, was isolated by plc (lit.[33] mp 91°).

c. A solution of compound I (250 mg) in ethanol (400 ml) containing Dry Ice in a Pyrex dewar vessel was irradiated at 3500 Å for 4 hr. Plc of the product yielded 2,5-diphenylfuran (95 mg, 43%) and an unidentified material containing no nitrogen (55 mg).

Irradiation of 1,4-Diphenylphthalazine *N*-Oxide. 1,4-Diphenylphthalazine *N*-oxide in acetone was irradiated for 2 hr with a Pyrex-filtered 700-W immersion lamp while purging with purified nitrogen. Removal of the solvent led to a crude material which was identified as 1,3-diphenylisobenzofuran by ir and tlc comparison with an authentic material. This material was rapidly oxidized on a plc plate to yield 1,2-dibenzoylbenzene as the main product. When the same reaction was carried out in the presence of oxygen, 1,4-diphenylphthalazine and 1,2-dibenzoylbenzene were the major products isolated by plc.

Preparation of Monohydrazone of *trans*-1,2-Dibenzoylethylene. A sample of *trans*-1,2-dibenzoylethylene (7.08 g, 0.03 mol) was suspended in absolute ethanol (200 ml) and 85% hydrazine hydrate (1.5 g, 0.03 mol) was added dropwise at room temperature. During the addition the suspension almost completely went into solution and a precipitate began to form. After approximately 10 min all starting material had disappeared (tlc); the solution was cooled in an ice bath and the pale yellow solid was isolated (4.55 g, 61%), mp 140–144° (color change to red at 135°). An additional crop of less pure orange gummy crystals (2.55 g), mp 136–142°, was obtained by concentration of the mother liquors from above. The material melting at 140–144° was recrystallized from 200 ml of 95% ethanol to give the monohydrazone as bright yellow needles (3.78 g): mp 149–151° (lit.[34] 146–147°); ir (KBr) 3600–3100 (br, bonded NH), 3330 (s, free NH), 3060 (vinyl CH), and 1685 cm^{-1} (C═O). *Anal.* Calcd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64; N, 11.19. Found: C, 76.56; H, 6.52; N, 11.04.

Oxidation of Monohydrazone of 1,2-Dibenzoylethylene. Dibenzoylethylene monohydrazone (1.787 g) was dissolved in 200 ml of reagent grade benzene and yellow mercuric oxide (Alfa Inorganics, 1.728 g) was added. The suspension was stirred at room temperature for 4 days, and the resultant gray suspension (Hg) was filtered through three thicknesses of filter paper. Evaporation of the solvent gave a gummy yellow solid which was purified by preparative layer chromatography on silica gel. The major product was removed from the plate by extraction of the zone with benzene. Removal of the solvent gave crude 3-benzoyl-5-phenylpyrazole VII, which was recrystallized from cyclohexane–benzene to give VII (1.188 g, 67%), mp 169–170°, identical (melting point, mixture melting point, infrared spectrum) with an authentic sample.

Flash Photolysis. The flash spectrograph is of conventional design (furnished by the Northern Precision Co., Ltd., England). For the experiments in which the disappearance of the diazo ketone was followed, the 20-cm long, vertical cell was filled with 9.6×10^{-6}–2.5×10^{-5} *M* solutions of 3,6-diphenylpyridazine *N*-oxide. The condenser was 10.5 μF, charged to 8 kV, and fired across one 20-cm long lamp consisting of two tungsten electrodes in a sealed quartz tube containing a few centimeters of Hg or xenon. The monitoring light was filtered to prevent decomposition of the *N*-oxide and the intermediate diazo ketone, using either an interference filter or a Corning 3–74 filter having a cut-off at 4100 Å. The flash lamp was surrounded by a Pyrex filter and by a jacket of 2 cm of acetone when the latter was used as solvent.

In the experiments with high-time resolution a condenser of 0.5 μF was used. This was charged to 16 kV when a 20-cm lamp was used and to 10 kV for a lamp having the electrodes at a distance of 5 cm and using a cell of the same dimensions. The half-width of the flash profile of the latter lamp was measured as less than 10 μsec. With a 1.2×10^{-4} *M* *N*-oxide solution reliable determination of the optical density was possible after *ca.* 20 μsec. The oscilloscope (Tektronix 549) was triggered by means of a photocell.

All solvents for flash photolysis were Spectroscopic grade or analytical grade and used without further purification except for the cyclohexane used in the triplet-seeking experiments. This was purified by shaking with concentrated sulfuric acid and passing through a column with basic Al_2O_3. The 3,6-diphenylpyridazine *N*-oxide was purified by four recrystallizations from cyclohexane–benzene (both analytical grade). The triphenylene was purified by three recrystallizations from Spectroscopic grade ethanol. The purity of triphenylene and cyclohexane was checked by uv and fluorescence spectroscopy.

Deoxygenation was done by the usual freeze–pump–melt–shake–freeze cycles, the last two evacuations being to a pressure of at least 2×10^{-5} mm. The absorption spectra of all solutions investigated were measured before flashing.

The nanosecond kinetic flash photolysis apparatus utilized single 347-nm pulses from a frequency doubled, Q-switched ruby laser for photolysis, as described by Porter and Topp,[35] and a pulsed xenon arc as the monitoring source as described by Porter and West.[36] Solutions for nanosecond flash photolysis were made up in a 1-cm photolysis cell to optical densities of about 0.3 at 347 nm, corresponding to concentrations of 3,6-diphenylpyridazine *N*-oxide of about 4×10^{-5} mol $l.^{-1}$.

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