THE PHOTOCHEMICAL REACTIONS OF AZOXY COMPOUNDS, NITRONES, AND AROMATIC AMINE N-OXIDES

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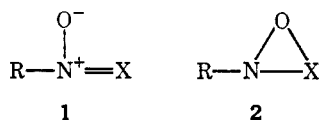*The H. C. Orsted Institute, 2100 Copenhagen, Denmark*

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I. Introduction

This review deals with the photochemical reactions of compounds containing structural unit 1, where X is either nitrogen or carbon. The R group may be either an alkyl or an aryl sub-

1   2

stituent, or R and X can be linked together to form an aromatic nucleus.

The majority of the known photochemical reactions of systems with the general formula 1 involve the nitrogen–oxygen bond, and lead either to rearrangements or to deoxygenation. Cyclization to products of type 2 may sometimes actually be observed, but in most cases such three-membered rings are formed only as intermediates which undergo further reactions. Besides three-membered rings, five-membered rings have in some instances been suggested as transient intermediates.

The photochemistry of system 1 has not previously been the subject of a systematic review, although photochemical rearrangements of compounds containing system 1 have received brief discussion.[2–7] The photochemistry of aromatic amine N-oxides was the subject of an M. I. T. seminar.[8] A review of the mechanism of the isomerization of azoxy compounds has appeared,[9] but this last article deals mainly with the Wallach rearrangement, a nonphotochemical reaction. The photochemistry of nitrones is treated briefly in two reviews of the chemistry of nitrones.[10,11]

II. Azoxy Compounds

A. SCOPE AND NOMENCLATURE

This section deals with the photochemical reactions of compounds containing function 1 in which X is nitrogen. Most of the reported work in this field deals with diaryl azoxy compounds, although two reactions of dialkyl azoxy compounds have been reported. The photochemical reactions of nitroso dimers are included in this section.

In naming azoxy compounds, especially unsymmetrical

(2) O. L. Chapman, *Advan. Photochem.*, 1, 410 (1963).
(3) A. Mustafa, *ibid.*, 2, 87 (1964).
(4) P. de Mayo, *Advan. Org. Chem.*, 2, 411 (1960).
(5) P. de Mayo and S. T. Reid, *Quart. Rev.* (London), 15, 416 (1961).
(6) A. Schönberg, G. O. Schenck, and O.-A. Neumüller, "Preparative Organic Photochemistry," 2nd ed, Springer-Verlag, New York, N. Y., 1968, pp 48–53.
(7) R. O. Kan, "Organic Photochemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, pp 147–150.
(8) J. A. DeFeo, "Massachusetts Institute of Technology Seminars," 2nd semester, 1966–1967, p 390.
(9) M. M. Shemyakin and V. I. Maimind in "Recent Progress in the Chemistry of Natural and Synthetic Colouring Matters and Related Fields," T. S. Gore, B. S. Joshi, S. V. Sunthankar, and B. D. Tilak, Ed., Academic Press, New York, N. Y., 1962, p 441.
(10) J. Hamer and A. Macaluso, *Chem. Rev.*, 64, 473 (1964).
(11) G. R. Delpierre and M. Lamchen, *Quart. Rev.* (London), 19, 329 (1965).

(1) (a) Princeton University; (b) University of Copenhagen.

derivatives, the following system will be used. Substituents on the ring adjacent to the N-O function are given primed numbers, while substituents on the ring more distant from the N-O function are given unprimed numbers. Thus **3** is 4'-bromoazoxybenzene, and **4** is 4-bromoazoxybenzene. This system can be ambiguous if the aryl groups are of different size (*e.g.*, phenyl and naphthyl). In order to avoid confusion,

3   **4**
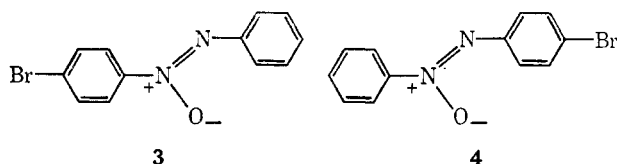
much of the literature has used an α,β system in which the α compound is the one with the N-O function adjacent to the smaller or less highly substituted aryl group. The former system will be used in this section because it is simpler and unambiguous for the compounds mentioned.

B. REARRANGEMENTS TO HYDROXYAZO COMPOUNDS

The first observation of the instability to light of azoxy compounds was made in 1901 by Wacker,[12] who found that paper impregnated with 1,1'-azoxynaphthalene turned red on exposure to sunlight. It was proposed that the red color was due to the formation of an "oxy-azo" compound. In the following year Knipscheer[13,14] found that azoxybenzene (**5**), impregnated in paper, rearranged to 2-hydroxyazobenzene (**6**) on exposure to sunlight. In the same year Bamberger[15] found that

**5**   **6**
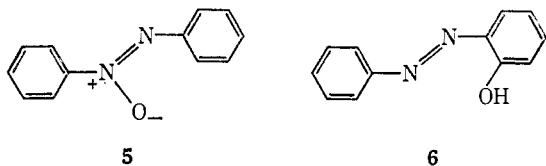
5 and **6** and several other compounds were formed when a solution of nitrosobenzene in benzene was exposed to sunlight for 4 months. Compound **6** was probably formed by a photochemical reaction of **5**.[14,16] Similarly, Ciamician and Silber[17] isolated **5** and **6** as products of the photolysis of a mixture of nitrobenzene and benzaldehyde. The rearrangement of **5** to **6** was also observed when solutions of **5** in various solvents were irradiated with ultraviolet light.[18]

An analogous reaction was proposed by Baudisch[19,20] to explain the formation of a red color when fabric impregnated with the ammonium salt of N-nitroso-N-(1-naphthyl)hydroxylamine (**7**) was exposed to light. The reaction was

7   **8**

9
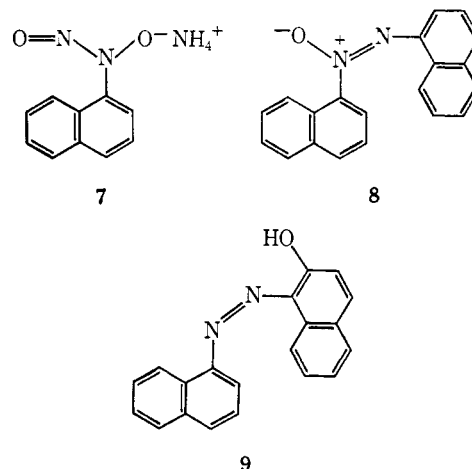
thought to involve initial formation of 1,1'-azoxynaphthalene (**8**) and photochemical rearrangement of **8** to 2-hydroxy-1,1'-azonaphthalene (**9**). The latter reaction was confirmed when it was found that **8** rearranges photochemically to **9**,[21-23] and that 2,2'-azoxynaphthalene rearranges to 1-hydroxy-2,2'-azonaphthalene.[23,24]

It was reported that **8** rearranged to a "red isomeride" of identical melting point and analysis on exposure to light.[21] The red compound was thought to be N,N'-bis(1-naphthyl)oxadiaziridine (**10**). It was later shown that the red compound is actually a mixture of **8** and **9**.[23] The red compound reported

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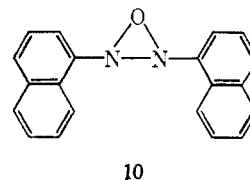
by Bellaart[25] to be formed by irradiation of 2,2'-azoxynaphthalene is probably a similar mixture of starting material and 1-hydroxy-2,2'-azonaphthalene.

In the early part of this century, several other papers[26] reporting that azoxy compounds are unstable to light appeared. The nature of the photochemical reaction was not further studied, and the products were not fully identified. As late as 1931, the author of a review on azoxy compounds stated that available evidence did not support the hypothesis that the rearrangement of azoxy compounds to hydroxyazo compounds could be caused by the action of light.[27]

In 1954 Badger and Buttery[23] made a careful study of the photochemical rearrangement of azoxy compounds and proposed a mechanism. By studying the rearrangements of unsymmetrical azoxy compounds, they found that the oxygen atom always migrates to the *ortho* position of the aryl group

(12) L. Wacker, *Ann. Chem.*, **317**, 375 (1901).

(13) H. M. Knipscheer, *Proc. Koninkl. Ned. Akad. Wetenschap.*, **5**, 51 (1902).

(14) H. M. Knipscheer, *Rec. Trav. Chim. Pays-Bas*, **22**, 1 (1903).

(15) E. Bamberger, *Chem. Ber.*, **35**, 1606 (1902).

(16) H. Mauser and H. Heitzer, *Z. Naturforsch., B*, **20**, 200 (1965).

(17) G. Ciamician and P. Silber, *Chem. Ber.*, **38**, 1176 (1905).

(18) W. M. Cumming and G. S. Ferrier, *J. Chem. Soc.*, **127**, 2374 (1925).

(19) O. Baudisch, *Chemiker-Ztg.*, **35**, 1141 (1911).

(20) O. Baudisch and R. Fürst, *Chem. Ber.*, **45**, 3426 (1912).

(21) W. M. Cumming and J. K. Steel, *J. Chem. Soc.*, **123**, 2464 (1923).

(22) W. M. Cumming and G. Howie, *ibid.*, 3181 (1931).

(23) G. M. Badger and R. G. Buttery, *ibid.*, 2243 (1954).

(24) W. M. Cumming and G. S. Ferrier, *ibid.*, **125**, 1108 (1924).

(25) A. C. Bellaart, *Tetrahedron*, **21**, 3285 (1965).

(26) T. Rotarski, *Chem. Ber.*, **41**, 865 (1908); A. Angeli and L. Alessandri, *Atti Accad. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat.*, [II] **20**, 170 (1911); *Chem. Abstr.*, **5**, 3808 (1911); A. Angeli and B. Valori, *Atti Accad. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat.*, [I] **21**, 729 (1912); *Chem. Abstr.*, **6**, 2747 (1912); A. Angeli, *Gazz. Chim. Ital.*, [II] **46**, 67 (1916); A. Pieroni and G. Giannini, *ibid.*, **54**, 162 (1924); D. Bigiavi and V. Sabatelli, *ibid.*, **57**, 557 (1927); D. Bigiavi and C. Albanese, *ibid.*, **64**, 897 (1934).

(27) H. E. Bigelow, *Chem. Rev.*, **9**, 117 (1931).

more distant from the N–O function. Thus **3** rearranges exclusively to 4-bromo-2'-hydroxyazobenzene (**11**), and **4** rearranges exclusively to 4-bromo-2-hydroxyazobenzene (**12**).

11   **12**
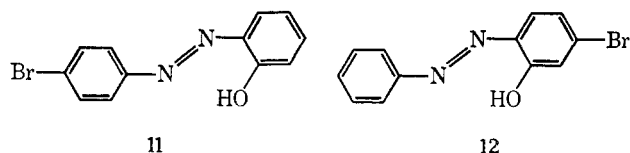
They explained the results with an intramolecular mechanism

Scheme I

5

13   **6**
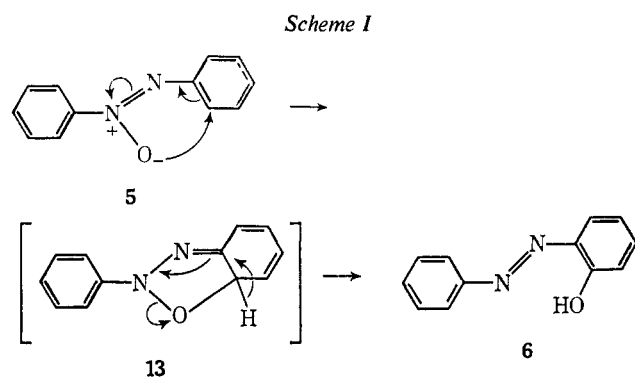
involving nucleophilic attack by oxygen on the *ortho* position of the more distant aryl substituent; a reformulation of their proposed mechanism is given in Scheme I. This mechanism is favored by the N=N—O angle of approximately 120° which places the oxygen atom very close to the *ortho* position of the more distant ring. Thus cyclization of the charge-separated species **5** leads to an intermediate **13** that can readily tautomerize to an aromatic compound **6**.
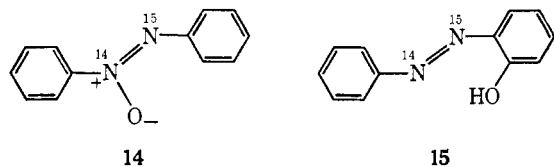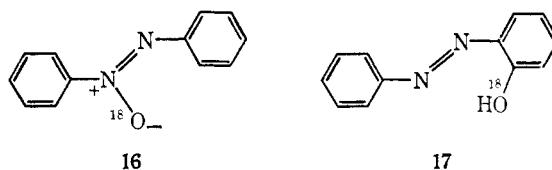
Evidence to support the mechanism of Scheme I was presented by Shemyakin, Maimind, and Vaichunaite,[28] who showed that the oxygen atom in azoxybenzene itself migrates to the more distant ring. Azoxybenzene labeled with ^{15}N was used to prove this point. Thus **14** rearranged exclusively to **15**.


14   **15**

The reaction has been shown to be intramolecular by the use of [18]O labeled materials.[29–31] Thus **16** rearranges to **17** with complete retention of the label.[29] When **5** is irradiated in an ethanol solution containing 15% of water enriched with

(28) M. M. Shemyakin, V. I. Maimind, and B. K. Vaichunaite, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 866 (1960); *Bull. Acad. Sci., USSR, Div. Chem. Sci.*, 808 (1960); *Chem. Abstr.*, **54**, 24474g (1960); *Zh. Obshch. Khim.*, **28**, 1708 (1958); *J. Gen. Chem. USSR*, **28**, 1756 (1958); *Chem. Abstr.*, **53**, 1201f (1959); *Chem. Ind.* (London), 755 (1958).

(29) M. M. Shemyakin, Ts. E. Agadzhanyan, V. I. Maimind, R. V. Kudryavtsev, and D. N. Kursanov, *Dokl. Akad. Nauk SSSR*, **135**, 346 (1960); *Proc. Acad. Sci. USSR, Chem. Sect.*, **135**, 1295 (1960); *Chem. Abstr.*, **55**, 11337d (1961).

(30) S. Oae, T. Fukumoto, and M. Yamagami, *Bull. Chem. Soc. Jap.*, **36**, 601 (1963).

(31) S. Oae, T. Fukumoto, and M. Yamagami, *ibid.*, **34**, 1873 (1961).

16   **17**

$H_2{}^{18}O$, there is almost no incorporation of the label into the product (**6**).[30]

The mechanism of Scheme I is further supported by the fact that irradiation of 2,4,6-trimethylazoxybenzene (**18**) in

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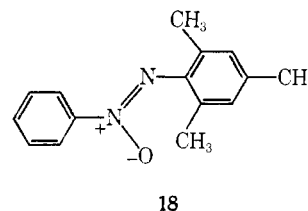
ethanol causes no change in its ultraviolet spectrum.[32] Thus a free *ortho* position in the ring more distant from the N–O function is necessary for the rearrangement to occur.

Scheme II

19   **20**

21   **22**

23

+

24
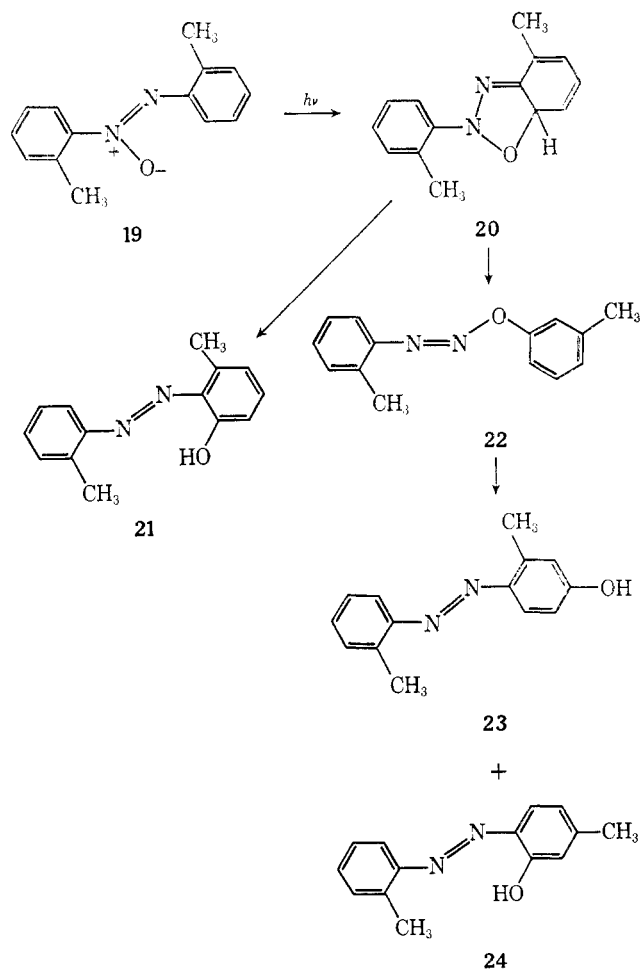
The photochemical rearrangement of azoxy compounds to hydroxyazo compounds appears to involve a π–π^* singlet

(32) G. E. Lewis and J. A. Reiss, *Aust. J. Chem.*, **19**, 1887 (1966).

excited state of the azoxy compound.[33-35] Deliberate excitation to the triplet state by the use of benzophenone as sensitizer causes a change in the course of the reaction. The yield of hydroxyazo compound is drastically reduced, and the major product is an azo compound, the product of simple deoxygenation. When oxygen is added as a quencher during the photosensitized reaction, the hydroxyazo compound again becomes the major product, and the yield of azo compound decreases almost to zero.

Lewis and Reiss have shown that irradiation of 2,2'-dimethylazoxybenzene (19) in ethanol leads to the formation of 4-hydroxy-2,2'-dimethylazobenzene (23) and 2-hydroxy-4,2'-dimethylazobenzene (24) as well as to the expected product, 2-hydroxy-6,2'-dimethylazobenzene (21).[32] To explain the formation of the unexpected products, the authors proposed that the initial oxadiazoline intermediate 20 rearranged to the azo ether 22 (see Scheme II). The known thermal conversion of O-(4-chlorophenylazo)-4-chlorophenol to 2-hydroxy-5,4'-dichloroazobenzene (25), as well as to other

25
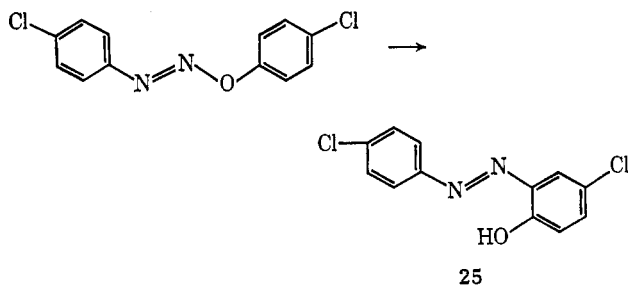
products,[36] was then cited as precedent for the proposed subsequent rearrangement of 22 to 23 and 24. However, the mechanism advanced for the formation of the azo ether 22 from 20 is untenable, and the reaction deserves further study.

Interpretation of the mass spectra of some azoxy compounds has led to the proposal that rearrangements analogous to those proposed by Lewis and Reiss may occur upon electron impact.[37,38]

The photolytic conversion of azoxybenzene derivatives to o-hydroxyazobenzene derivatives requires long irradiation times. The process is inefficient, possibly due to competitive light absorption by the products. It is possible to observe other photochemical processes when shorter irradiation times are used. Thus it was reported in 1932 that "isoazoxybenzene" (mp 81°) is converted to "normal" azoxybenzene (mp 36°) when irradiated at 0°.[39] No structures are given for the two isomers, but the reaction is probably a cis–trans isomerization. Webb and Jaffé[40] have shown that irradiation of trans-4,4'-dimethoxyazoxybenzene at low temperatures for 18 hr causes equilibration of the cis and trans forms. Badger, Buttery, and Lewis[41] found that oxidation of trans-azobenzene in the presence of sunlight brought about the forma-

tion of some cis-azoxybenzene. The latter reaction might be caused by prior photolytic equilibration of cis- and trans-azobenzene rather than by equilibration of the azoxybenzenes.[40] Recently Tanikaga[35] showed that trans-azoxybenzene, besides rearranging, also isomerized to the cis form from the singlet excited state. It has also been found that irradiation of 3,3'-dinitro-4,4'-bis(2-pyridylmethyl)azoxybenzene (26) causes simultaneous equilibration of the cis and trans forms and equilibration of the nitro and aci-nitro forms (see Scheme III).[42]

Scheme III
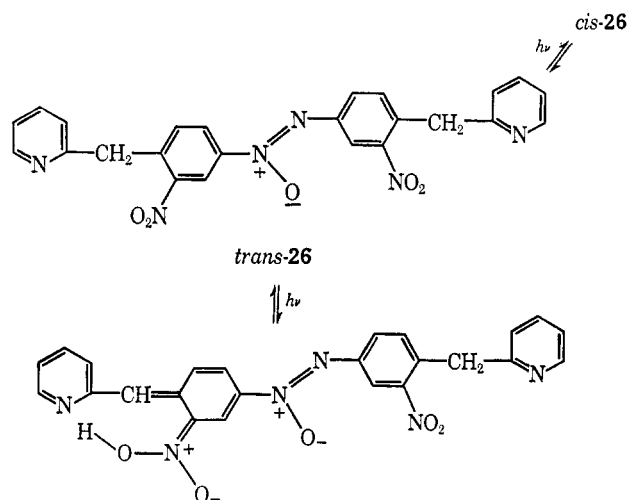
Irradiation of pure acrylonitrile does not cause polymerization; irradiation of acrylonitrile in the presence of azoxybenzene causes polymerization to occur.[43] No explanation has been given for this observation.

C. RELATION TO THE WALLACH REARRANGEMENT

The photochemical rearrangement of azoxy compounds appears at first sight to be very similar to the Wallach rearrangement,[44] by which azoxy compounds are converted to para-hydroxyazo compounds in strong acids. There are, however, major differences between the two rearrangements. While the photochemical reaction leads exclusively to ortho-hydroxyazo compounds, the Wallach rearrangement leads to almost exclusive formation of para-hydroxyazo compounds. When ortho-hydroxyazo compounds are formed in the Wallach rearrangement, they are usually formed in very low yield unless both para positions of the starting azoxy compound are blocked by the presence of a substituent.[45] The second major difference between the two rearrangements is in their mechanisms. A great deal of work has been done on the mechanism of the Wallach rearrangement,[9,46] and it has been shown that

(33) R. Tanikaga, K. Maruyama, R. Goto, and A. Kaji, *Tetrahedron Lett.*, 5925 (1966).

(34) R. Tanikaga, *Bull. Chem. Soc. Jap.*, 41, 1664 (1968).

(35) R. Tanikaga, *ibid.*, 41, 2151 (1968).

(36) T. Kauffmann, H. O. Friestad, and H. Henkler, *Ann. Chem.*, 634, 64 (1960).

(37) J. H. Bowie, G. E. Lewis, and R. G. Cooks, *Chem. Commun.*, 284 (1967).

(38) J. H. Bowie, R. G. Cooks, and G. E. Lewis, *Aust. J. Chem.*, 20, 1601 (1967).

(39) E. Müller, E. Hory, W. Krüger, and W. Kreutzmann, *Ann. Chem.*, 493, 166 (1932).

(40) D. Webb and H. H. Jaffé, *Tetrahedron Lett.*, 1875 (1964).

(41) G. M. Badger, R. G. Buttery, and G. E. Lewis, *J. Chem. Soc.*, 2143 (1953).

(42) J. Weinstein, J. A. Sousa, and A. L. Bluhm, *J. Org. Chem.*, 29, 1586 (1964).

(43) J. W. Breitenbach and H. Frittum, *J. Polym. Sci.*, 24, 300 (1957).

(44) O. Wallach and L. Belli, *Chem. Ber.*, 13, 525 (1880).

(45) M. M. Shemyakin, Ts. E. Agadzhanyan, V. I. Maimind, and R. V. Kudryavtsev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1339 (1963); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1216 (1963); *Chem. Abstr.*, 59, 12619b (1963).

(46) C. S. Hahn, K. W. Lee, and H. H. Jaffé, *J. Amer. Chem. Soc.*, 89, 4975 (1967).

the reaction is intermolecular and involves a symmetrical intermediate.[28-30,45,47]

Interestingly, the formation of *ortho*-hydroxyazo compounds *via* the Wallach rearrangement appears to involve an intramolecular process at least to some extent.[30,45] Since there is no mention of deliberate attempts to exclude light during the course of the Wallach rearrangement, it is intriguing to speculate that the intramolecular formation of *ortho*-hydroxyazo products might in fact occur *via* an independent photochemical reaction. Although the photochemical process is relatively inefficient, it might account for the small amount of intramolecular product formed.
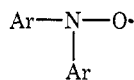
D. NITROSO DIMERS

Many nitroso compounds exist as dimers at room temperature. Recently it has been shown that nitroso dimers have a diazine dioxide structure (27),[48] and they are thus closely re-
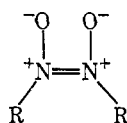
27

lated to azoxy compounds (1, X = N). In fact, nitroso dimers can be converted to azoxy compounds by reduction[49-52] or by deoxygenation with phosphorus compounds.[53,54] The photochemical reactions of nitroso dimers are not, however, similar to those of azoxy compounds.

Maruyama, Tanikaga, and Goto[55] have shown that aryl nitroso compounds form nitroxides (28) on irradiation. Mauser and Heitzer observed the same reaction while studying


28

the mechanism of photolysis of nitrosobenzene.[16] Theilacker, Knop, and Uffmann[56] observed that those nitroso compounds which exist as dimers exhibit esr spectra in solution. It was demonstrated[57] that the esr spectra become stronger on irradiation of the solutions. The esr spectra were attributed to the photochemical formation of nitroxides. Since, in the initial studies of the photochemical formation of nitroxides from nitroso compounds, only nitroso compounds that exist as dimers were found to undergo this reaction, it was assumed that the nitroxides were formed *via* a photochemical reaction of the nitroso dimers.

Recently it has been found that the species involved in the photochemical reaction is probably the monomeric nitroso

compound.[58] The reaction can be accomplished by irradiation in a wavelength region in which the monomers, but not the dimers, absorb. Also, mixed nitroxides can be formed by the irradiation of a mixture of nitroso compounds. Thus when a mixture of 2-methyl-2-nitrosopropane (29) and nitrosobenzene is irradiated at a wavelength at which only 29 absorbs, one of the products is *t*-butylphenylnitroxide (30). The yield of 30

29   30
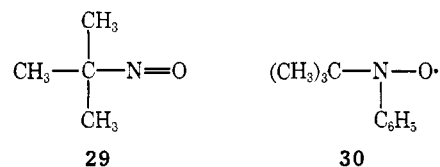
depends on the concentrations of the nitroso compounds in the mixture. It has also been shown that irradiation of nitroso dimers can cause dissociation into the monomers.[59] On the basis of this evidence a mechanism (Scheme IV)[58] has been

Scheme IV
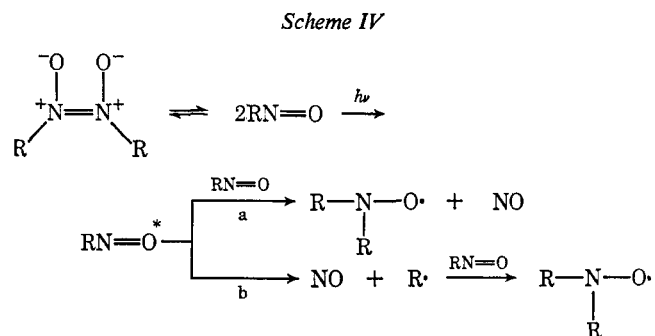
proposed in which the monomer, present in low concentration in the solution or formed by photodissociation of the dimer, is excited. The excited state molecule can then either attack a ground state molecule of the nitroso compound (path a), or it can break down to nitric oxide and a free radical which attacks a molecule of nitroso compound[58] (path b). Another possibility that was not mentioned is that the product could be formed by reaction of the excited state monomer with the ground state dimer.

The irradiation of nitroso compounds is now a common method of preparing nitroxides.[60-62]

E. DIALKYL AZOXY COMPOUNDS

Dialkyl azoxy compounds are not able to undergo the photochemical rearrangement that is characteristic of diaryl azoxy compounds. It has recently been reported, however, that low-temperature irradiation of azoxy-*t*-butane (31) leads to the formation of 1,3-di-*t*-butyloxadiaziridine (32).[63]

(47) L. C. Behr and E. C. Hendley, *J. Org. Chem.*, **31**, 2715 (1966).
(48) J. P. Freeman, *ibid.*, **28**, 2508 (1963).
(49) J. G. Aston, D. F. Menard, and M. G. Mayberry, *J. Amer. Chem. Soc.*, **54**, 1530 (1932).
(50) H. Meister, *Ann. Chem.*, **679**, 83 (1964).
(51) W. Lüttke and V. Schabacker, *ibid.*, **687**, 236 (1965).
(52) J. Beger, R. Holm, and W. Pritzkow, *Tetrahedron Lett.*, 2617 (1965).
(53) L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956).
(54) P. J. Bunyan and J. I. G. Cadogan, *J. Chem. Soc.*, 42 (1963).
(55) K. Maruyama, R. Tanikaga, and R. Goto, *Bull. Chem. Soc. Jap.*, **37**, 1893 (1964).
(56) W. Theilacker, A. Knop, and H. Uffmann, *Angew. Chem.*, **77**, 717 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 688 (1965).
(57) E. T. Strom and A. L. Bluhm, *Chem. Commun.*, 115 (1966).

(58) A. Mackor, T. A. J. W. Wajer, T. J. de Boer, and J. D. W. van Voorst, *Tetrahedron Lett.*, 2115 (1966).
(59) A. L. Bluhm and J. Weinstein, *Nature*, **215**, 1478 (1967).
(60) E. T. Strom, A. L. Bluhm, and J. Weinstein, *J. Org. Chem.*, **32**, 3853 (1967).
(61) T. A. J. W. Wajer, A. Mackor, T. J. de Boer, and J. D. W. van Voorst, *Tetrahedron*, **23**, 4021 (1967).
(62) A. Mackor, T. A. J. W. Wajer, and T. J. de Boer, *ibid.*, **24**, 1623 (1968).
(63) S. S. Hecht and F. D. Greene, *J. Amer. Chem. Soc.*, **89**, 6761 (1967).

O⁻
|+
N=N
(CH₃)₃C   C(CH₃)₃

31

O
N——N
(CH₃)₃C   C(CH₃)₃

32

Formation of an oxadiaziridine in the above example is favored because the *t*-butyl groups stabilize the three-membered ring. When azoxymethane (**33**) is irradiated the major products are nitrogen, nitrous oxide, methane, and ethane.[64] No oxadiaziridine was isolated, but the possibility that it might have been formed but was unstable under the conditions of the reaction was not discussed. The products were explained by two initial photochemical processes (Scheme V). Ethane is formed by dimerization of a methyl radical, while

Scheme V

O⁻
|+
N=N
CH₃   CH₃

hv ⟶ 2CH₃· + N₂O

⟶ CH₃· + N₂ + ·OCH₃

33

methane is formed by extraction of a hydrogen atom by a methyl radical.

III. Nitrones

A. SCOPE AND NOMENCLATURE

This section deals with the photochemical reactions of compounds containing the nitrone function **34**. In naming nitrones, the system used by *Chemical Abstracts*[65] has been employed; substituents on carbon are prefixed by α, and substituents on nitrogen are prefixed by N. Nitrones at one time were named

O⁻
|+
C=N—

34

O
C——N—

35

as N-substituted derivatives of oximes or as "N-ethers" of oximes. These names have not been completely abandoned even now. The first structure assigned to nitrones was that of a three-membered heterocycle (**35**). The structure was soon discarded; however, many reactions described in this section involve formation of this isomer, which was originally named isonitrone or oxazirane. Recently the name oxaziridine has gained general acceptance,[66] and it will be used in this section. Substituents on oxaziridines are numbered as shown in **35**.

B. REARRANGEMENTS TO AMIDES VIA OXAZIRIDINES

It has long been known that most nitrones are unstable to light. Many early reports of syntheses of nitrones noted that

the nitrones changed color on exposure to light.[67-79] In fact, this property was considered a characteristic of the nitrone system.

In 1910 Alessandri[70] found that when α,N-diphenylnitrone was exposed to sunlight, benzanilide was formed along with other products. He also found that N-phenyl-α-(β-styryl)-nitrone (**36**) was converted to cinnamaldehyde anil (**37**) by the action of light.

O⁻
|+
C₆H₅CH=CHCH=NC₆H₅

36

C₆H₅CH=CHCH=NC₆H₅

37

Before the mechanism of the rearrangement was elucidated, the major photoproducts of nitrones were recognized to be the corresponding amides. Thus it was reported that N-phenyl-α-(9-acridinyl)nitrone (**38**) rearranged to the anilide of acridine-9-carboxylic acid (**39**) on exposure to sunlight in acetone solution.[80] Similarly, the products of irradiation

O⁻
|+
CH=N—C₆H₅

38

O
||
C—NHC₆H₅

39

of a mixture of nitrosobenzene and 9-methylbenz[a]acridine were the benz[a] derivatives of **38** and **39**.[81] Benz[a]-**39** was probably formed in a photochemical reaction of benz[a]-**38**. The formation of benzanilide as one of several products of irradiation of a mixture of benzaldehyde and nitrobenzene[17] can probably also be explained by initial formation of α,N-diphenylnitrone followed by rearrangement to the amide.

In 1957 Kröhnke[82] reported that N-aryl-α-benzoylnitrones rearrange to N-aryl-N-formylbenzamides on irradiation. He proposed a mechanism (Scheme VI) involving initial formation of oxaziridine **40** and rapid rearrangement to the amide. Kamlet and Kaplan[83] also proposed formation of an oxaziridine to explain the change in the ultraviolet spectra of nitrones when solutions were exposed to light. At the time oxaziridines

(64) B. G. Gowenlock, *Can. J. Chem.*, **42**, 1936 (1964).

(65) *Chem. Abstr.*, **65**, 2317S (1966).

(66) E. Schmitz, "Dreiringe mit Zwei Heteroatomen," Springer-Verlag, Berlin, 1967, pp 6–66.

(67) G. Plancher and G. Piccinini, *Atti Accad. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat.*, [II] **14**, 36 (1905); *Chem. Zentr.*, [II] **76**, 764 (1905).

(68) M. O. Forster and H. Holmes, *J. Chem. Soc.*, **93**, 242 (1908).

(69) A. Angeli, L. Alessandri, and R. Pegna, *Atti Accad. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat.*, [I] **19**, 650 (1910); *Chem. Abstr.*, **4**, 2457 (1910).

(70) L. Alessandri, *Atti Accad. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat.*, [II] **19**, 122 (1910); *Chem. Abstr.*, **5**, 276 (1911).

(71) L. Alessandri, *Atti Accad. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat.*, [II] **23**, 129, 216, 347 (1914); *Chem. Abstr.*, **9**, 1045 (1915).

(72) L. Alessandri, *Atti Accad. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat.*, [I] **24**, 62 (1915); *Chem. Abstr.*, **9**, 2240 (1915).

(73) L. Alessandri, *Atti Accad. Naz. Lincei, Rend., Classe Sci. Fis. Mat. Nat.*, [II] **24**, 194 (1915); *Chem. Abstr.*, **10**, 1350 (1916).

(74) H. Staudinger and K. Miescher, *Helv. Chim. Acta*, **2**, 554 (1919).

(75) L. Alessandri, *Gazz. Chim. Ital.*, [I] **51**, 75 (1921).

(76) O. L. Brady and G. P. McHugh, *J. Chem. Soc.*, **125**, 547 (1924).

(77) L. Alessandri, *Gazz. Chim. Ital.*, **55**, 729 (1925).

(78) V. Bellavita, *ibid.*, **70**, 584 (1940).

(79) J. S. Splitter and M. Calvin, *J. Org. Chem.*, **20**, 1086 (1955).

(80) L. Chardonnens and P. Heinrich, *Helv. Chim. Acta*, **32**, 656 (1949).

(81) B. M. Mikhailov and G. S. Ter-Sarkisyan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 656 (1954); *Chem. Abstr.*, **49**, 10953c (1955).

(82) F. Kröhnke, *Ann. Chem.*, **604**, 203 (1957).

(83) M. J. Kamlet and L. A. Kaplan, *J. Org. Chem.*, **22**, 576 (1957).

Scheme VI

40

were a new class of heterocyclic compounds discovered by Krimm[84,85] and further studied by Emmons.[86,87] Emmons had shown that some oxaziridines rearrange thermally to amides.[87]

The above hypotheses were confirmed in 1958 when Splitter and Calvin showed that the same oxaziridine could be formed either by photolysis of a nitrone or by peracid oxidation of the corresponding imine.[88] Rearrangement of the oxaziridines to amides then occurred thermally (Scheme VII). It is interesting

Scheme VII

that oxaziridines can revert thermally to nitrones.[66] In this reversal of the ring closure of nitrones, elementary molecular orbital symmetry considerations predict that *cis*- and *trans*-oxaziridines should open to give the same ratio of stereoisomeric nitrones. In this connection it should be noted that Splitter and Calvin[89] found that the oxaziridine formed by photolysis of N-(*m*-nitrophenyl)-α-(*p*-dimethylaminophenyl)-nitrone upon thermolysis led to another nitrone which thermally reverted to starting material. Further experiments using *cis–trans* isomeric nitrones and oxaziridines are clearly indicated to elucidate the stereochemistry both of ring closure of nitrones and ring opening of oxaziridines.

It now seems that the initial photochemical reaction of most nitrones is isomerization to the corresponding oxaziridines. This fact was not recognized at first because many oxaziridines are highly unstable and rearrange to the corre-

sponding amides as soon as they are formed. In general, oxaziridines with aryl substituents in both the 2 and 3 positions are too unstable thermally to be isolated.[66,89] Thus, when α,α,N-triphenylnitrone is irradiated, N,N-diphenylbenzamide is isolated in almost quantitative yield.[90a] However, more recently it has been found that triphenyloxaziridine can in fact be isolated and is fairly stable.[90b] Another reason for failure to isolate the oxaziridines is that they are often also unstable to light and rearrange to amides or to other products on prolonged irradiation.[89,91–94]

Some unstable oxaziridines have been detected, but not isolated, during the photolysis of nitrones. When a KBr pellet containing α,N-diphenylnitrone was irradiated at 77°K, the ir spectrum showed bands which were attributed to 2,3-diphenyloxaziridine.[95,96] At higher temperatures, or after prolonged irradiation, only peaks attributable to decomposition products of the oxaziridine were observed.

In some cases, particularly when the substituent on nitrogen is alkyl, oxaziridines are the products isolated when nitrones are irradiated. The product of photolysis of N-methyl-α-(4-bromo-2,6-dimethylphenyl)nitrone **(41)** is the *trans* form of the oxaziridine **42**,[97] the structure of which has been proven by X-ray analysis.[98] Similarly, the structure of the photo-

41   **42**

product from the corresponding chloro compound was examined by X-ray analysis and thereby shown also to be the *trans* form of the expected oxaziridine.[99] Irradiation of N-(2-oxo-3-indolylidene)aniline N-oxides **(43)** leads to 3-phenyl-

43

44   **45**

(84) H. Krimm and K. Hamann (Farbenfabriken Bayer A.-G.), German Patent 952,895 (1956); *Chem. Abstr.,* **53,** 15977a (1959); German Patent 959,094 (1957); *Chem. Abstr.,* **53,** 3059i (1959); British Patent 743,940 (1956); *Chem. Abstr.,* **51,** 3656f (1957).
(85) H. Krimm, K. Hamann, and K. Bauer (Farbenfabriken Bayer A.-G.), U. S. Patent 2,784,182 (1957); *Chem. Abstr.,* **51,** 12146g (1957).
(86) W. D. Emmons, *J. Amer. Chem. Soc.,* **78,** 6208 (1956).
(87) W. D. Emmons, *ibid.,* **79,** 5739 (1957).
(88) J. S. Splitter and M. Calvin, *J. Org. Chem.,* **23,** 651 (1958).
(89) J. S. Splitter and M. Calvin, *ibid.,* **30,** 3427 (1965).

(90) (a) M. L. Scheinbaum, *ibid.,* **29,** 2200 (1964); (b) H. K. Ono and M. Calvin, private communication.
(91) G. F. Field and L. H. Sternbach, *J. Org. Chem.,* **33,** 4438 (1968).
(92) L. S. Kaminsky and M. Lamchen, *J. Chem. Soc.,* C, 2295 (1966).
(93) E. Meyer and G. W. Griffin, *Angew. Chem.,* **79,** 648 (1967); *Angew. Chem. Intern. Ed. Engl.,* **6,** 634 (1967).
(94) J. S. Splitter and M. Calvin, *Tetrahedron Lett.,* 1445 (1968).
(95) H. Shindo and B. Umezawa, *Chem. Pharm. Bull.* (Tokyo), **10,** 492 (1962).
(96) K. Shinzawa and I. Tanaka, *J. Phys. Chem.,* **68,** 1205 (1964).
(97) H. Hjeds, K. P. Hansen, and B. Jerslev, *Acta Chem. Scand.,* **19,** 2166 (1965).
(98) L. Brehm, K. G. Jensen, and B. Jerslev, *ibid.,* **20,** 915 (1966).
(99) B. Jerslev, *Acta Cryst.,* **23,** 645 (1967).

2,4-(1H,3H)quinazolinediones (45), presumably *via* oxaziridine (44) intermediates.[100] The photochemical conversion of 2-phenylisatogen to 2-phenyl-4H-3,1-benzoxazin-4-one has recently been reported.[101]

Table I lists some acyclic nitrones that have been converted photochemically to stable oxaziridines.

Table I

Some Acyclic Nitrones That Have Been Converted Photochemically to Stable Oxaziridines

Nitrone	*Oxaziridine*

	% yield	*Mp, °C*	*Ref*
$R^1 = p\text{-}NO_2C_6H_4;\ R^2 = H;$			
$R^3 = Et$	35	Oil	88, 89
$R^1 = p\text{-}NO_2C_6H_4;\ R^2 = H;$			
$R^3 = t\text{-}Bu$	40	58–60	88, 89
$R^1 = C_6H_5;\ R^2 = H;$			
$R^3 = t\text{-}Bu$	95	...^{a}	88, 89
Compound 41	...^{a}	88–89	97, 98

^{a} Not stated

Many cyclic nitrones have been converted to stable oxaziridines. 7-Chloro-4,5-epoxy-2-methylamino-5-phenyl-3H-1,4-benzodiazepine (47, R^1 = $NHCH_3$) is formed when 7-chloro-2-methylamino-5-phenyl-3H-1,4-benzodiazepine 4-oxide (46, R^1 = $NHCH_3$) is irradiated.[102] Similar reactions occur with 1 - formyl - 7-chloro-5-phenyl-2,3-dihydro-1H-1,4-benzodiazepine 4-oxide (1,2-dihydro-46, R^1 = H; R^2 = CHO) and with 1 - acetyl - 7 - chloro-5-phenyl-2,3-dihydro-1H-1,4-benzodiazepine 4-oxide (1,2-dihydro-46, R^1 = H; R^2 = $COCH_3$).[103]
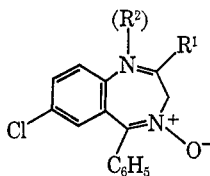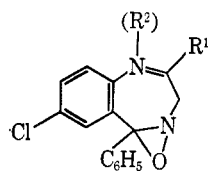
46   47

Similarly, nitrones 48 upon photolysis yield the expected oxaziridines 49.[104]

48   49

Oxaziridino[2,3-a]pyrrolidines (51) are the products of photolysis of Δ^1-pyrroline 1-oxides (50).[92,105–108]

50   51

Table II lists some cyclic nitrones that have been converted to stable oxaziridines by photolysis.

Table II

Some Cyclic Nitrones That Have Been Converted Photochemically to Stable Oxaziridines

Nitrone	*% yield*	*Oxaziridine Mp or bp (mm), °C*	*Ref*
46, R = $NHCH_3$	65	167–170	102
1,2-Dihydro-**46**, R^1 = H; R^2 = CHO	...^{a}	150–152	103
1,2-Dihydro-**46**, R^1 = H; R^2 = $COCH_3$	...^{a}	161–163	103
50, $R^1 = R^2 = R^3 = R^4 =$ H; $R^5 = R^6 = CH_3$	11	55–60 (25)	105
50, $R^2 = R^3 = R^4 =$ H; $R^1 = R^5 = R^6 = CH_3$	28	40 (20)	92, 106, 107
50, $R^2 = R^5 = R^6 =$ H; $R^1 = R^3 = R^4 = CH_3$	50	48 (15)	92, 107
50, $R^1 = R^3 = R^4 =$ H; $R^2 = R^5 = R^6 = CH_3$	50	60 (22)	92, 107
50, $R^1 = R^3 = C_6H_5$; $R^2 = R^4 =$ H; $R^5 = R^6 = CH_3$	75	155	108

^{a} Not stated

It has been shown that 5,5-dimethyl-2,4-diphenyl-Δ^1-pyrroline 1-oxide (50, R^1 = R^3 = C_6H_5; R^2 = R^4 = H; R^5 = R^6 = CH_3) is stereospecifically converted to the corresponding oxaziridine (51, R^1 = R^3 = C_6H_5; R^2 = R^4 = H; R^5 = R^6 = CH_3) on photolysis.[108] Only one isomer is formed, and it is different from the oxaziridine formed by peracid oxidation of the corresponding Δ^1-pyrroline. The isomer formed by photolysis is reported to have the phenyl groups *cis* to one another, while the one formed by oxidation has the phenyl groups *trans* to one another; similar results were obtained by generating steroid oxaziridines photochemically from the corresponding nitrones and by oxidation of the corresponding imines.[109] Photoisomerization of a monocyclic dinitrone to two stereoisomeric dioxaziridines has recently been reported.[110]

(100) T. Sasaki and M. Takahashi, *Bull. Chem. Soc. Jap.*, 41, 1967 (1968).

(101) D. R. Eckroth and R. H. Squire, *Chem. Commun.*, 312 (1969).

(102) L. H. Sternbach, B. A. Koechlin, and E. Reeder, *J. Org. Chem.*, 27, 4671 (1962).

(103) W. Metlesics, G. Silverman, and L. H. Sternbach, *ibid.*, 28, 2459 (1963).

(104) O. Hromatka, M. Knollmüller, and D. Binder, *Monatsh. Chem.*, 99, 1117 (1968).

(105) R. Bonnett, V. M. Clark, and A. Todd, *J. Chem. Soc.*, 2102 (1959).

(106) L. S. Kaminsky and M. Lamchen, *Chem. Commun.*, 130 (1965).

(107) L. S. Kaminsky and M. Lamchen, *J. Chem. Soc.*, C, 2128 (1967).

(108) J. B. Bapat and D. St. C. Black, *Chem. Commun.*, 73 (1967).

(109) J. Parello, R. Beugelmans, P. Milliet, and X. Lusinchi, *Tetrahedron Lett.*, 5087 (1968).

(110) M. Lamchen and T. W. Mittag, *J. Chem. Soc.*, C .1917 (1968).

Oxaziridino[2,3-*a*]pyrrolidines rearrange to the corresponding 2-pyrrolidones (**52**) either thermally[105,107] or photolytically.[92] The one exception is compound **51** (R[1] = R[3] =

R[3] R[2]
R[4]—⎯—H
R[5]
R[6]
N
R[1]
O

52

H₃C CH₃
N
C O
CH₃

53

H₃C CH₃
N
CH₃

54
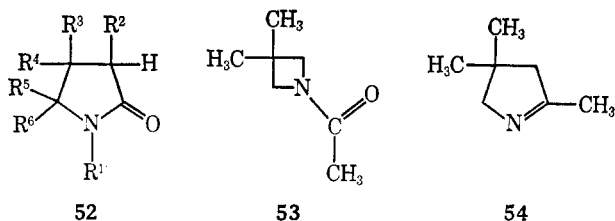
R[4] = CH₃; R[2] = R[5] = R[6] = H), which forms 1-acetyl-3,3-dimethylazetidine (**53**) and 2,4,4-trimethyl-Δ¹-pyrroline (**54**) on photolysis,[92] and **53** on heating.[107] To explain the formation of **53** the intermediacy of an unstabilized primary carbonium ion was proposed;[107] a mechanism such as shown in Scheme VIII, which avoids the formation of such an unstable ion, is preferable.

Scheme VIII

CH₃
H₃C—
N
O
CH₃

→

CH₃
·H₃C—
N
O
CH₃

→

CH₃
H₃C—
N
C=O
CH₃

53
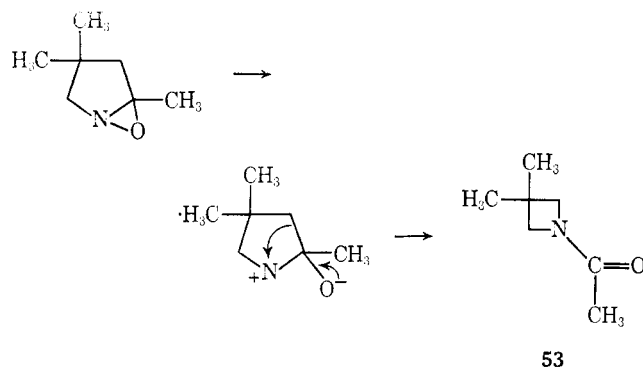
Oxaziridines with an acyl substituent at position 3 are unstable, and attempts to prepare them by irradiating the corresponding nitrones have been unsuccessful. The products of photolysis of α-acylnitrones are diacylamines (**56**),[82,111] not α-ketoamides, showing that the acyl group migrates preferentially. To explain the preferential migration, a mechanism (Scheme IX) involving nucleophilic attack of nitrogen on the

Scheme IX

C₆H₅
O
C—N
O=C
R
C₆H₅

→

C₆H₅—C
O
N
R
C
O C₆H₅

→

O R O
‖ | ‖
C₆H₅C—N—CC₆H₅

56

55

(111) A. Padwa, *J. Amer. Chem. Soc.*, 87, 4365 (1965).
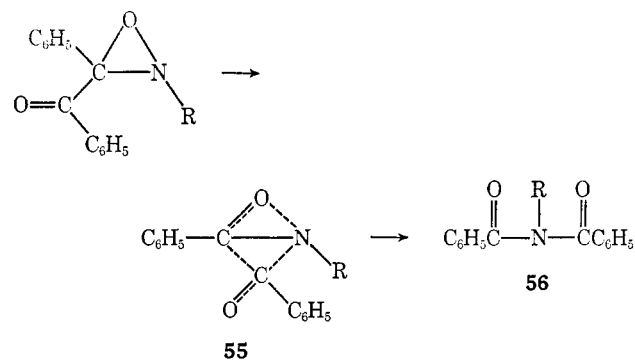
carbonyl group to form a bicyclobutane-like transition state (**55**) has been proposed.[111,112]

The formation of N,N-dibenzoylaniline (**56**, R = C₆H₅) by photolysis of the mono-anil of benzil (**57**) in the presence of

C₆H₅
C=NC₆H₅
C₆H₅C
‖
O

57

C₆H₅
O⁻
|+
C=NC₆H₅
C₆H₅C
‖
O

58
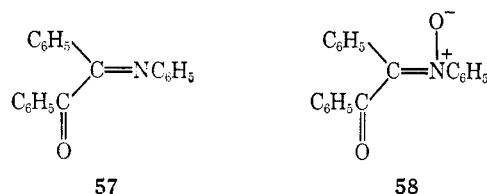
oxygen may involve initial formation of α,N-diphenyl-α-benzoylnitrone (**58**), followed by rearrangement of the diacylamine as in Scheme IX.[113]

Photolytic oxaziridine formation is a reaction of the singlet state of nitrones.[114] Deliberate excitation of either *cis*- or *trans*-α-cyano-α,N-diphenylnitrone to the triplet state by means of a sensitizer causes only *cis*–*trans* isomerization.[114] The photoequilibrium established is different from the thermal equilibrium, thus indicating that the photochemical isomerization is caused by triplet–triplet energy transfer. No oxaziridine is formed from the triplet state.

As in the case of azoxy compounds (section II) and aromatic N-oxides (section VI), the mass spectra of nitrones indicate that similar reactions may occur on photolysis and on electron impact. Thus it has been reported that the mass spectra of some nitrones indicate a rearrangement to oxaziridines on electron impact.[115–117]

C. MISCELLANEOUS REACTIONS

In some cases irradiation of nitrones causes simple deoxygenation to the corresponding imines.[70,95,118] The mechanism of the deoxygenation has not been elucidated, but it may be due to reduction of primarily formed oxaziridines.

Pedersen[119] has reported that dinitrone **59** forms mononitrone **60** and azobenzene on photolysis. The reaction may

O⁻ O⁻
| |
C₆H₅N⁺=⟨⟩=N⁺C₆H₅

59

O⁻
|
C₆H₅N⁺=⟨⟩=O

60

O⁻ O
| \ /
C₆H₅N⁺=⟨⟩—N—C₆H₅

61
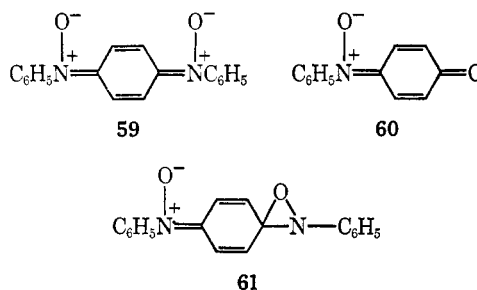
involve the elimination of phenylnitrene from oxaziridine **61**. No attempts to trap or otherwise identify phenylnitrene from this reaction were reported, but irradiation of unsymmetrical dinitrones led to formation of both symmetrical and unsym-

(112) A. Padwa, *Tetrahedron Lett.*, 2001 (1964).
(113) R. O. Kan and R. L. Furey, *ibid.*, 2573 (1966).
(114) K. Koyano and I. Tanaka, *J. Phys. Chem.*, **69**, 2545 (1965).
(115) L. A. Neiman, V. I. Maimind, M. M. Shemyakin, V. A. Puchkov, V. N. Bochkarev, Y. S. Nekrasov, and N. S. Vul'fson, *Zh. Obshch. Khim.*, **37**, 1600 (1967); *J. Gen. Chem. USSR*, **37**, 1517 (1967); *Chem. Abstr.*, **68**, 48863q (1968).
(116) T. H. Kinstle and J. G. Stam, *Chem. Commun.*, 185 (1968).
(117) B. S. Larsen, G. Schroll, S.-O. Lawesson, J. H. Bowie, and R. G. Cooks, *Tetrahedron*, **24**, 5193 (1968).
(118) M. Colonna, *Gazz. Chim. Ital.*, **91**, 34 (1961).
(119) C. J. Pedersen, *J. Amer. Chem. Soc.*, **79**, 5014 (1957).

metrical azobenzenes. Depending upon the wavelength of light employed, **60** reacts further to form *p*-quinone and azobenzene.

Two recent reports have shown that nitrene formation is in fact a photochemical reaction of oxaziridines. Thus when oxaziridine **62** is irradiated in the presence of diethylamine, one of the products is 2-(diethylamino)azepine (**63**).[93] It was proposed that **63** might be formed by reaction of phenylnitrene

62   63
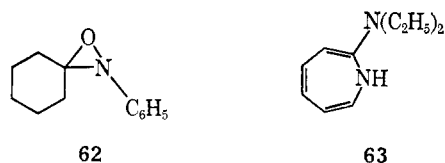
with diethylamine. When 3-(*p*-dimethylaminophenyl)-2-phenyloxaziridine is irradiated, the major reaction is fragmentation to *p*-dimethylaminobenzaldehyde and phenylnitrene.[94] Similarly, when 2,3,3-triphenyloxaziridine is irradiated, phenylnitrene is formed.[94] The presence of phenylnitrene was demonstrated by its esr spectrum, which was identical with that of phenylnitrene formed by irradiation of phenyl azide. The formation of phenylnitrene apparently involves a triplet state of the oxaziridine, for, in the presence of oxygen, a triplet scavenger, there is quenching of the photofragmentation reaction, but little quenching of the rearrangement to an amide.[94]

Nitrone **64** has been found to be stable to photolysis.[120a]

64
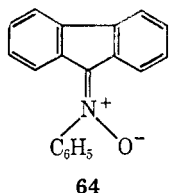
Azine N-oxides are also reported to be photoactive.[120b] Thus acetophenone azine N-oxide and benzophenone azine N-oxide both liberated nitrogen upon irradiation, thereby forming the parent ketones. In the case of benzophenone azine N-oxide tetraphenylethylene was also formed. It was inferred that the photochemical reaction first gave the parent ketone and a diazo compound (Scheme X); *cf.* section IV.H

Scheme X
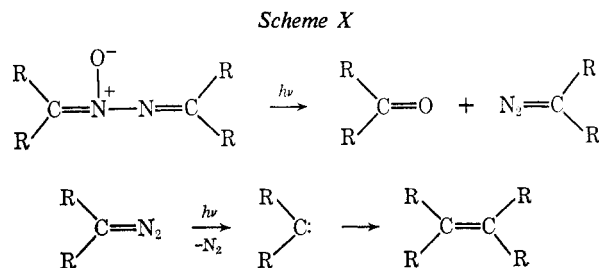
and section V. The diazo compound presumably was photolyzed to give a carbene, which then gave tetraphenylethylene upon dimerization.

Aldoximes and ketoximes have also been shown to undergo light-induced rearrangements.[121–125] The early reports[121,122] described the rearrangement to amides, and oxaziridines were suggested as intermediates. This was more recently demonstrated by Oine and Mukai[125] who succeeded in obtaining the oxaziridine **66** by photolysis of oxime **65**. The oxaziridine was stable in dilute solution but could not be isolated in the solid state. Similar results were obtained by Izawa, de Mayo, and Tabata[124] who observed that α-*p*-anisaldoxime upon irradia-

65   66
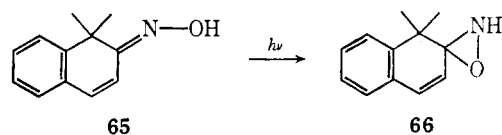
tion at −88° was transformed to a substance with a uv absorption spectrum which indicated oxaziridine formation. Furthermore, it was found that addition of iodide caused oxidation to iodine, but only at a very low temperature.

The most likely states leading to oxaziridine formation in the irradiation of oximes were inferred to be the π–π* triplet or singlet.[124] However, quenching experiments with piperylene or oxygen indicated that the reaction took place from a singlet state.[125] Labeling with ¹⁸O showed the overall oxygen rearrangement to be intramolecular.[124] The further secondary reactions of the initially formed oxaziridines, which can lead to a variety of products other than amides, can either be light-induced or thermal.[124]

The similarity of this photochemical oxaziridine formation to the one observed with nitrones can be rationalized by assuming that the immediate precursor of the oxaziridine **69** is the prototropic tautomer **68** rather than the oxime itself. This assumption is supported by the fact that quantum yields for

67   68   69
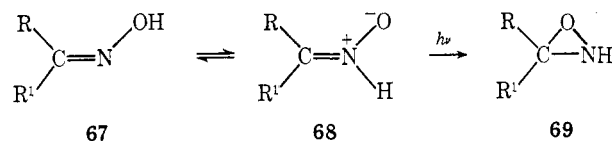
oxaziridine formation in the oxime series are much lower than in the nitrone series.[124]

Irradiation of isamic acid, a natural product previously thought to be the azomethine imine **70** with the functionality C=N⁺—N⁻,[126a] but recently shown to possess structure **71**,[126b] results in the formation of **72**.[127] A diaziridine inter-

70   71   72
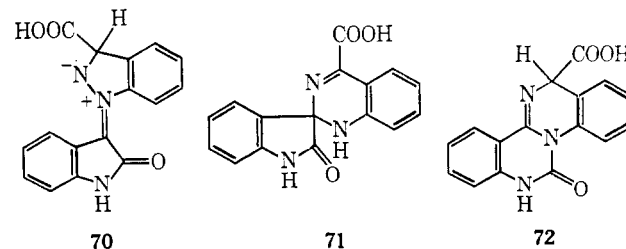
mediate was originally proposed for this conversion on the basis of the proposed (but incorrect) azomethine imine struc-

(120) (a) A. W. Johnson, *J. Org. Chem.*, **28**, 252 (1963); (b) L. Horner, W. Kirmse, and H. Fernekess, *Chem. Ber.*, **94**, 279 (1961).

(121) J. H. Amin and P. de Mayo, *Tetrahedron Lett.*, 1585, (1966).
(122) R. T. Taylor, M. Douek, and G. Just, *ibid.*, 4143 (1966).
(123) G. Just and L. S. Ng, *Can. J. Chem.*, **46**, 3381 (1968).
(124) H. Izawa, P. de Mayo, and T. Tabata, *ibid.*, **47**, 51 (1969).
(125) T. Oine and T. Mukai, *Tetrahedron Lett.*, 157 (1969).
(126) (a) P. de Mayo and J. J. Ryan, *Can. J. Chem.*, **45**, 2177 (1967); (b) G. F. Field, *Chem. Commun.*, 886 (1969).
(127) P. de Mayo and J. J. Ryan, *Tetrahedron Lett.*, 827 (1967).

ture for isamic acid.[127] However, a diaziridine has actually been isolated from the photolysis of a true azomethine imine.[128]

The sensitivity of nitrones to light has been put to use in the field of photography. Two patents[129,130] describe the preparation of photographic plates using a nitrone as one of the photosensitive elements.

IV. Aromatic Amine N-Oxides

A. SCOPE AND NOMENCLATURE

Aromatic amine N-oxides can formally be regarded as cyclic nitrones in which the nitrone function is incorporated into an aromatic system. This apparent close relationship in structure is reflected in the photolability of both types of systems. Furthermore, oxaziridine formation is now regarded to be the initial step in the light-induced rearrangements of aromatic amine N-oxides, although in these systems oxaziridines have not been isolated as yet. Besides rearrangements, deoxygenation is generally observed upon photolysis of aromatic amine N-oxides.

The results obtained from each type of aromatic amine N-oxide are treated in separate sections, arranged in the order of increasing complexity of the heterocyclic ring system, without detailed mechanistic discussion. A mechanistic discussion that attempts to generalize most of the results obtained from the light-induced reactions of aromatic amine N-oxides and some comments on the excited states initiating the reactions are presented separately in a following section.

In naming N-oxides, the position of the oxide function is often indicated by a numerical prefix. Thus pyridine N-oxide can be named pyridine 1-oxide. In most cases the use of the name N-oxide is unambiguous and sufficient. In the following sections this nomenclature will be used. Whenever necessary, numbers will be inserted in parentheses to avoid confusion.

B. GENERAL

The product distribution in the light-induced reactions of aromatic amine N-oxides at first glance seems rather confusing. However, by distinguishing between observed (or inferred) primary photoproducts and secondary thermal products derived from the former, a much simpler pattern appears, which accounts for the great majority of observed products. A detailed discussion of this is given in section V.

1. Observable Primary Products

a. Parent Amines

These are found in the pyridine, quinoline, isoquinoline, phenanthridine, acridine, pyridazine, benzo[c]cinnoline, phthalazine, quinazoline, quinoxaline, and purine series, e.g.

b. Lactam Formation

This type of rearrangement has been observed in the pyridine, quinoline, isoquinoline, phenanthridine, quinazoline, pyrazine, quinoxaline, and purine series, e.g.
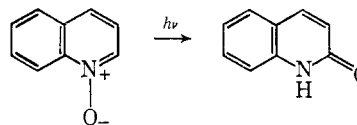
c. Ring Expansion to Seven-Membered Rings

This type of process is known to take place in the quinoline, isoquinoline, phenanthridine, quinoxaline, and quinazoline series, and has tentatively been suggested in one case in the pyridine series, and inferred in the pyrazine series, e.g.
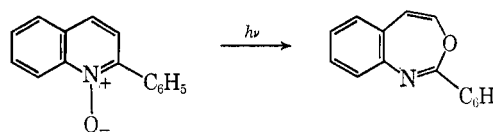
d. Apparent Direct Ring Contraction to Five-Membered Rings

This conversion has been observed in the pyridine, quinoline, phenanthridine, pyridazine, and pyrazine series. (In the pyridazine series, ring contraction was shown to take place via a transient acyclic diazo species), e.g.
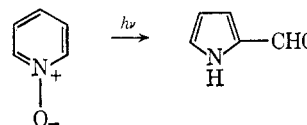
e. Rearrangement to 3-Hydroxy Derivatives

This has only been observed in the pyridine series. (Note, however, that some of the seven-membered ring compounds formed photochemically from 2-cyanoquinoline N-oxides have been observed to rearrange thermally to 2-cyano-3-hydroxyquinolines).

2. Secondary Thermal Products

All of these arise from seven-membered ring compounds, formed as primary photo-products.

a. Hydrolysis Products

Benz[d][1,3]oxazepines (from quinoline N-oxides), which in many instances are too unstable to isolate, hydrolyze as shown below to form the open-chain tautomers of N-acyl-2-indolinols

(128) M. G. Pleiss and J. A. Moore, *J. Amer. Chem. Soc.*, **90**, 4738 (1968).
(129) D. M. McQueen (E. I. Du Pont de Nemours & Co.), U. S. Patent 2,426,894 (1947); *Chem. Abstr.*, **41**, 7289e (1947).
(130) Kalle A.-G., Netherlands Application 6,407,189 (1965); *Chem. Abstr.*, **62**, 15636d (1965).
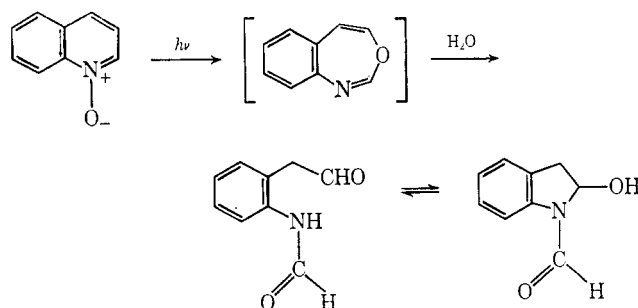
which, depending on the substituents, may close to the latter. Sometimes these products undergo further reactions. Similar hydrolyses, sometimes followed by ring closure, have been observed for all the other types of seven-membered ring compounds studied, with the single exception of the 1,3-oxazepine from 2,4,6-triphenylpyridine N-oxide.

b. Ring Contraction of Benz[d][1,3]oxazepines

As mentioned previously, the benz[d][1,3]oxazepines formed by irradiation of 2-cyanoquinoline N-oxides very easily form 2-cyano-3-hydroxyquinolines. In each case, however, it has been possible to isolate the seven-membered ring. The observed formation of 3-acylindole derivatives in the quinoline and acridine series presumably also has its origin in the intermediate formation of the corresponding seven-membered rings or their valence tautomers.
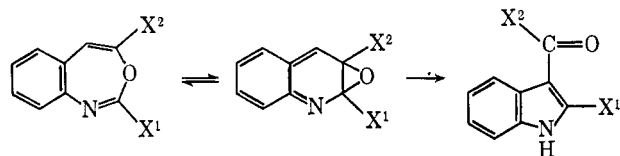
C. PYRIDINE N-OXIDES

Hata and Tanaka[131] studied the light-induced reaction of pyridine N-oxide (73a) in the gas phase, using either 3261- or 2537-Å light. In each case the main product was pyridine (74a). Similarly, vapor-phase photolysis of 3-methylpyridine N-oxide (73c) was reported to give mainly the parent 3-methylpyridine (74c).[132] A unique result is the finding by Hata[133] that irradiation of 2-methylpyridine N-oxide (73b) in the vapor phase with 3261-Å light resulted in the formation of 2-hydroxymethylpyridine (75), whereas irradiation with 2537-Å light resulted in deoxygenation.

75
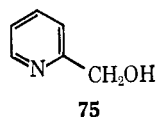
The light-induced reactions of pyridine N-oxides (73) in solution have been examined by several groups. Pyridine N-oxide (73a) and some of its methyl derivatives rearrange to 2-acylpyrroles (76) when irradiated in inert solvents.[134,135] In the photolysis of 2-methylpyridine N-oxide (73b), there was formed in addition a small amount of 6-methyl-2-pyridone (77b). In a more recent communication[136] a reinvestigation of the photolysis of methylpyridine N-oxides led to the observation that 2-methylpyridine N-oxide (73b) and 2,6-dimethylpyridine N-oxide (73e) rearranged to the corresponding 3-hydroxypyridines (78 and/or 79), accompanied by deoxygenation to the parent amines (74) and formation of the 2-acylpyrroles (76) which were previously reported.[134,135] Interestingly, the light-induced deoxygenation of pyridine N-oxides in benzene resulted in the formation of phenol. It was suggested that the first step is liberation of atomic oxygen, which reacts

with the solvent to form oxepine; the latter compound, presumably under catalysis by pyridine, then rearranges to phenol. Irradiation of methanol or ethanol solutions of pyri-

dine N-oxide resulted in the generation of 74a, 76a, traces of N-formylpyrrole (80), and the respective acetals of N-formylpyrrole (81).[137] Simultaneous oxidation of the solvents accounts for the oxygen lost in the deoxygenation. It was suggested that the loss of oxygen took place from a transient oxaziridine species.
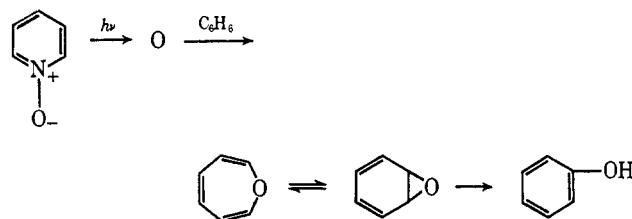
One of the characteristics of all the previously mentioned photolyses of pyridine N-oxides is the poor material balance (Table III). However, by irradiating 2,4,6-triphenylpyridine N-oxide (73g) a high material balance was obtained.[138] This compound, when irradiated in acetone, formed a mixture from which there was isolated 2-benzoyl-3,5-diphenylpyrrole (76g) as the main product, with minor amounts of 2,4,6-triphenyl-3-hydroxypyridine (78g), the parent amine (74g), and a substance which is thought to be 2,4,6-triphenyl-1,3-oxazepine (82).

It is interesting that photolysis of the dipolar species 83 results in a series of reactions that are at least formally analogous to some of the reactions found for pyridine N-oxides,[139] and that dipolar compounds of type 86, upon photolysis, rearrange to 87.[140,141]
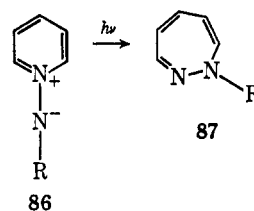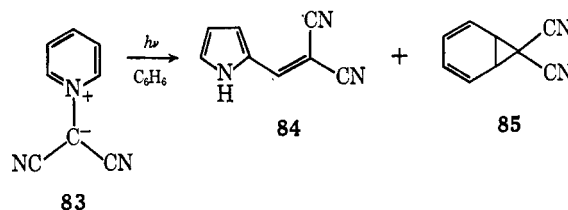
The irradiation of a series of 4-nitropyridine N-oxides (73h–l) in absolute ethanol with exclusion of oxygen was reported[142] to result in high yields of the corresponding 4-hydroxylaminopyridine N-oxides (88a,i–l). If the photolysis of 4-nitropyridine N-oxide (73h) in ethanol or 2-propanol was carried out in the presence of an excess of oxygen, 4-hydroxypyridine N-oxide (89a), as its salt with HNO_3, was obtained

(131) N. Hata and I. Tanaka, *J. Chem. Phys.*, **36**, 2072 (1962).

(132) N. Hata, *Bull. Chem. Soc. Jap.*, **34**, 1444 (1961).

(133) N. Hata, *ibid.*, **34**, 1440 (1961).

(134) J. Streith and C. Sigwalt, *Tetrahedron Lett.*, 1347 (1966).

(135) J. Streith, H. K. Darrah, and M. Weil, *ibid.*, 5555 (1966).

(136) J. Streith, B. Danner, and C. Sigwalt, *Chem. Commun.*, 979 (1967).

(137) A. Alkaitis and M. Calvin, *ibid.*, 292 (1968).

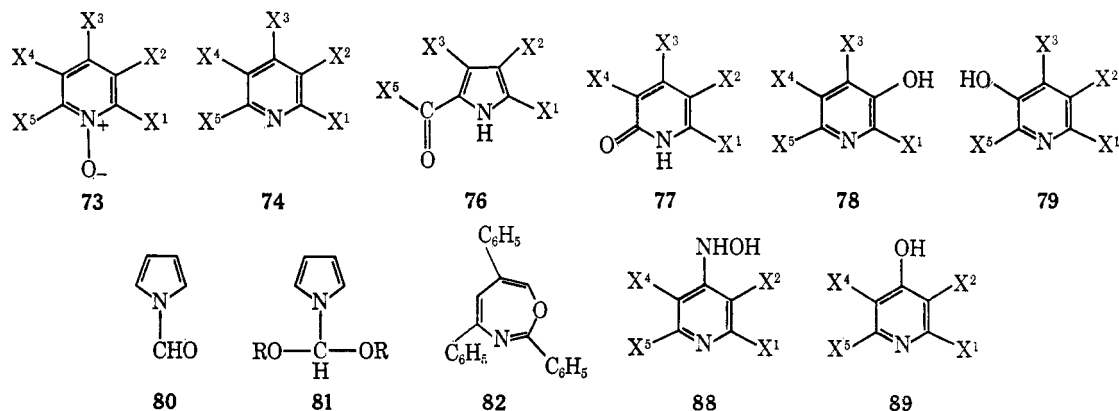(138) P. L. Kumler and O. Buchardt, *ibid.*, 1321 (1968).

(139) J. Streith and J.-M. Cassal, *C. R. Acad. Sci., Paris, Ser. C*, **264**, 1307 (1967).

(140) J. Streith and J.-M. Cassal, *Angew. Chem.*, **80**, 117 (1968).

(141) J. Streith and J.-M. Cassal, *Tetrahedron Lett.*, 4541 (1968).

(142) C. Kaneko, S. Yamada, I. Yokoe, N. Hata, and Y. Ubukata, *ibid.*, 4729 (1966).

Table III

Photolysis Products of Pyridine N-Oxides

73 74 76 77 78 79

80 81 82 88 89

73	X¹	X²	X³	X⁴	X⁵	Amount	Solvent	Products[b]	Ref
			Pyridine N-oxide[a]						
a						10 mmol	Inert	76a (10)	134
							MeOH	74a (6.8), 76a (1.3), 81a, R = Me or Et	137
							EtOH	(2.7), 80(trace)	
b	CH₃						Inert	76b (8), 77b	134
							Et₂O	74b, 76b, 78b, 79b (5)	136
c		CH₃						76c	135
d	CH₃	CH₃						76d	135
e	CH₃			CH₃				76e	135
f	C₆H₅					2 g	Acetone	74f, 76f (25)	186
g	C₆H₅		C₆H₅		C₆H₅	1 g	Acetone	74g (12), 76g (56), 78g (10), 82 (8)	138
h[c]			NO₂			1 g	EtOH	88h (high)	142
h[d]			NO₂				EtOH	89h, as HNO₃ salt (60–65)	143
i[c]	CH₃		NO₂				EtOH	88i (high)	142
j[c]	CH₃		NO₂		CH₃		EtOH	88j (high)	142
k[c]		CH₃	NO₂				EtOH	88k (high)	142
l[c,d]		CH₃	NO₂	CH₃		1.0 g	EtOH	89l (30)	144
m[d]			NO				EtOH	73h	143
			NHOH				EtOH	73h	143
n[c]	N₃					400 mg	Acetone	4,4'-Azopyridine N-oxide (90) (37)	145

ᵃ When X = H, no substituent is entered in the table. ᵇ Yields (%) are given in parentheses. ᶜ Flushed with nitrogen during irradiation. ᵈ Flushed with oxygen during irradiation.

in good yield.[143] With the sterically crowded 3,5-dimethyl-4-nitropyridine N-oxide (73l), photolysis in ethanolic or aqueous solution in the presence or absence of oxygen results in the formation of 3,5-dimethyl-4-hydroxypyridine N-oxide (89l).[144] It was furthermore found[143] that 4-hydroxylaminopyridine N-oxide (89a), which is not photolabile in the absence of oxygen, can be photooxidized to 4-nitropyridine N-oxide (73h) in the presence of oxygen. On the contrary, 4-nitrosopyridine N-oxide (73m) is reduced to 4-hydroxylaminopyridine N-oxide (88a) upon photolysis in the presence as well as in the absence of oxygen.[143]

The apparent lack of photoreactivity of the N-oxide function under these circumstances implies that light-induced reactions take place first at the substituents. The resulting 4-hydroxylamino- as well as 4-hydroxypyridine N-oxides have no uv absorption maxima at wavelengths longer than ca. 280 nm, and the employment of Pyrex filters thus prevents further reactions.

Photolysis of 4-azidopyridine N-oxide (73n) in acetone with sunlight has been reported[145] to result in the formation of 4,4'-azopyridine N-oxide (90).

73n 90
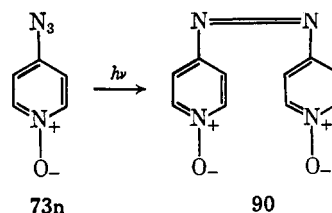
D. QUINOLINE N-OXIDES

Photochemical reactions of quinoline N-oxides have received much attention. Product distribution is highly dependent on the solvent employed and upon the nature of the substituents, particularly in the nitrogen-containing ring. We have thus subdivided our description of quinoline N-oxide photochemistry according to the substituents in the nitrogen-con-

(143) C. Kaneko, S. Yamada, and I. Yokoe, *Chem. Pharm. Bull.* (Tokyo), **15**, 356 (1967).

(144) C. Kaneko, I. Yokoe, and S. Yamada, *Tetrahedron Lett.*, 775 (1967).

(145) S. Kamiya, *Chem. Pharm. Bull.* (Tokyo), **10**, 471 (1963).

Table IV

Photolysis Products of Quinoline N-Oxides with Hydrogen in the 2 Position

			Quinoline N-oxide[a]				Solvent	Amount	Products[b,c]	Ref
91	X^1	X^2	X^3	X^4	X^5	X^6				
a							H_2O	0.5 g	**92a** (91), **93a** (tlc)	146, 149
							EtOH	1 g	**92a** (49), **96a** (13)	146
							MeOH	2 g	**92a** (60–70), **93a** (5–6), **94a** (2.5)	148
							Et_2O	1 g	**92a** (30), **93a** (tlc), **108a** (50)	148, 149
							Acetone		**92a** (15), **93a** (7), **94a** (3), **108a** (41)	135
b	CH_3						H_2O	0.1–1 g	**92b** (90)	147
c	C_2H_5						H_2O	1 g	**92c** (90), **93c** (tlc)	149
							Acetone	1 g	**92c** (17), **107c** (68)	149
d		CH_3					H_2O	0.1–1 g	**92d** (80)	147
							MeOH	2 g	**92d** (70–75), **93d**, (1–2), **95d** (5)	148
							Benzene	1 g	**92d** (42), **93d** (tlc), **108d**[d] (4), **95d** (10), 2-formamidoacetophenone (4)	149
							Et_2O	1 g	**92d** (25), **93d** (tlc), **108d**[d] (25), **95d** (tlc)	149
e			CH_3				H_2O	0.1–1 g	**92e** (88)	147
f				CH_3			H_2O	0.1–1 g	**92f** (80)	147
							EtOH	1 g	**96f** (90)	149
							Et_2O	1 g	**92f** (30), **93f** (tlc), **108f** (33), 2-formamido-5-methylbenzaldehyde (5)[e]	149, 155
g					CH_3		H_2O	0.1–1 g	**92g** (98)	147
							EtOH	0.1 g	**96g** (70)	149
h						CH_3	H_2O	0.1–1 g	**92h** (80)	147
							Acetone	1 g	**92h** (41), **108h** (23), 2-formamido-3-methylbenzaldehyde (9)[e]	149
i	C_6H_5						EtOH	270 mg	**92i** (98)	163
							Acetone	523 mg	**92i** (20), **111i** (80)	163
j		C_6H_5					EtOH	1 g	**92j** (90)	163
k	Br						EtOH	1 g	**92k** (50), **93k** (tlc)	149
							Acetone	1 g	**92k** (57), **93k** (tlc), 5 unidentified compounds (tlc)	149
l		Cl					MeOH	2 g	**92** (75–80), **93** (2–3)	148
							Acetone	1 g	**92** (50–70), **93** (5), **108**[f] (0–20), 5 unidentified compounds (tlc)	149
m		Br					H_2O	1 g	**92m** (50)	149
							EtOH	1 g	**92m** (50)	149
n				F			H_2O	1 g	**92n** (70)	149
							Acetone	1 g	**92n** (29), **93n** (4), **96n** (4), **108n** (45), 2 unidentified compounds (tlc)	149
o				Cl			H_2O	1 g	**92o** (95)	149
							EtOH	1 g	**96o** (70)	149
p				Br			H_2O	1 g	**92p** (80)	149
							Acetone	1 g	**92p** (39), **93p** (tlc), **108p** (33), 3 unidentified compounds (tlc)	149

Table IV (Continued)

91			Quinoline N-oxide^a				Solvent	Amount	Products^{b,c}	Ref
	X^1	X^2	X^3	X^4	X^5	X^6				
q					Cl		Acetone	1 g	92q (31), 93q (6), 108q (50)	149
r		OCH₃					MeOH	2 g	92r (60–70), 93r (4–5)	148
s				OCH₃			MeOH	2 g	92s (50–55), 93s (5)	148
							MeOH	1 g	96s (63)	148
							EtOH	1 g	96s (50)	148
							Benzene	1 g	92s (45), 108s (11), 2-formamido-5-methoxybenzaldehyde (0.5)^e	149, 155
t		CH₃		OCH₃			H₂O	1 g	92t (85)	149
							EtOH	1 g	92t (90)	149
							Benzene	1 g	92t (30), 93t (tlc), 7 other compounds (tlc)	149
u						OCH₃	H₂O	1 g	96u (50)	149
v		NO₂					ROH		4-Hydroxycarbostyril (127) (7)	144
x	CH₃	NO₂							4-Hydroxy-3-methylcarbostyril (30)	144
y		p-CH₃C₆H₄-S					EtOH	1 g	92y (90)	186
z		N₃					Various	1 g	4,4'-Azoquinoline N-oxide (70)	145

^{a} When X = H, no substituent is entered in the table. ^{b} Yields (%) are given in parentheses. ^{c} Tlc means detected by tlc. ^{d} Too unstable for complete characterization, but identified by ir spectroscopy. ^{e} Identified by ir and nmr spectroscopy. ^{f} Too unstable for complete characterization, but identified by uv and ir spectroscopy.

taining ring, the type of solvent employed, and the added nucleophiles.

1. Quinoline N-Oxides with Hydrogen in the 2 Position (91), and No Aromatic Substituents, in Protic Solvents (Table IV)

In aqueous, ethanolic, or methanolic media, N-oxides of type 91 or their hydrates are converted principally to the corresponding carbostyrils (92) upon irradiation.[146–149] In some of these irradiations, minor amounts of the parent quinolines (93) and of indole derivatives (94 and 95) were observed (see Table IV). Upon prolonged irradiation of type 91 quinoline N-oxides (X^1 and X^2 = H) high yields of carbostyril dimers (96) were observed. The structure of the dimers obtained from carbostyril (92a) and N-methylcarbostyril have unambiguously been demonstrated[150] to be cyclobutane derivatives (97). In some instances[151] it appears possible to deduce the stereo-
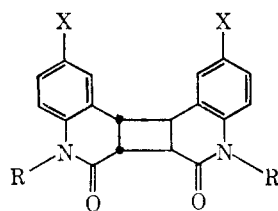
97a, R = H; X = H
b, R = CH₃; X = H
c, R = H; X = CH₃
d, R = H; X = Cl

chemistry of these photodimers by nuclear magnetic resonance

spectroscopy, and it was inferred that the dimers of 6-methyl- and 6-chlorocarbostyril possess the same structure (*i.e.*, 97). It seems reasonable to conclude that the other dimers isolated upon prolonged irradiation of quinoline N-oxides have the same structure and stereochemistry.

2. Quinoline N-Oxides with Methyl Substituents (98) in the 2 Position, and No Aromatic Substituents, in Protic Solvents

Carbostyril formation upon photolysis of N-oxides with hydrogen in the 2 position made it of obvious interest to examine derivatives where this position was blocked. Buchardt, Becher, and Lohse[147] found that irradiation of 2-methylquinoline N-oxide hydrate (98a) in aqueous or 96% ethanolic solution led to the formation of 3-methylcarbostyril (99a) in rather poor yield, whereas Ishikawa, Yamada, and Kaneko[152] found that irradiation of the same compound in dry methanol led to the formation of a mixture of 3-methylcarbostyril (99a), N-methylcarbostyril (100a), 2-methylquinoline (101a), and N-acetylindole (102a).[148] In the paper last cited it was reported that 2,4-dimethylquinoline N-oxide undergoes essentially the same type of rearrangement upon photolysis (Table V). Most of the simple quinoline N-oxides readily form hydrates, and in all instances where irradiations were performed in aqueous or 96% ethanol media, the N-oxides are probably totally or partially hydrated. An interesting observation was made by Kaneko, *et al.*,[148] who found that deoxygenation of the solutions to be irradiated led to a decrease in the amount of deoxygenation of the N-oxides taking place during irradiation.

3. Quinoline N-Oxides without Aromatic Substituents, with Methyl or Hydrogen in the 2 Position, in Aprotic Solvents

By altering the character of the solvent, a striking change in product distribution is seen. Thus, irradiation of a series of

(146) O. Buchardt, *Acta Chem. Scand.*, 17, 1461 (1963).

(147) O. Buchardt, J. Becher, and C. Lohse, *ibid.*, 19, 1120 (1965).

(148) M. Ishikawa, S. Yamada, H. Hotta, and C. Kaneko, *Chem. Pharm. Bull.* (Tokyo), 14, 1102 (1966).

(149) O. Buchardt, P. L. Kumler, and C. Lohse, *Acta Chem. Scand.*, 23, 159 (1969).

(150) O. Buchardt, *ibid.*, 18, 1389 (1964).

(151) L. Paolillo, H. Ziffer, and O. Buchardt, *J. Org. Chem.*, 35, 38 (1970).

(152) M. Ishikawa, S. Yamada, and C. Kaneko, *Chem. Pharm. Bull.* (Tokyo), 13, 747 (1965).

Table V

Photolysis Products from 2-Methylquinoline N-Oxides

Structures 98, 99, 100, 101, 102, 103, 104, 105, 106

98	X¹	X²	X³	Amount, g	Solvent	Products[b,c]	Ref
a				0.1	H₂O	99a (10)	147
				0.1	EtOH	99a (10)	147
				2	MeOH	99a (22), 100a (16), 101a, 102 (10)	148
				5	Benzene	99a, 101a, 102a, 104a (66), 105a	153, 154
b	CH₃			0.6	Benzene	101b, 103b (71), 105b (15)	154
c		CH₃		2	MeOH	99c (15), 100c (20), 101c (8), 106c (7)	148
				7	Benzene	99c (5), 101c (tlc), 102c, 104c (50), 105c (20), 106c (7)	154
d	CH₃	CH₃		2	Benzene	101d (tlc), 103d (65), 105d (1)	154
e			OCH₃	0.7	Benzene	101e (40), 104e (34)	154

The header of the table reads "——Starting material[a]——" spanning columns 98, X¹, X², X³.

[a] When X = H, no substituent is entered in the table.   [b] Yields (%) are given in parentheses.   [c] Tlc means detected by tlc, but not isolated.

2-methylquinoline N-oxides or their hydrates in benzene or ether, containing some water, led to formation of rather complicated reaction mixtures from which N-acetyl-2-indolinols (104) or their open-chain tautomers (103) were isolated as the major products.[149,153,154] Minor components were the parent quinolines (101) (from 2-methyl-6-methoxyquinoline N-oxide (98e); however, the parent quinoline was the major product), and in some cases varying amounts of compounds 99, 102, 105, and 106 (Table V). In ref 154 it was indicated that some of the products isolated from the above irradiations resulted from thermally unstable, poorly characterized intermediates. Although mechanistic details will be discussed in a later section, it seems nevertheless necessary to mention here that there is ample evidence that the N-acyl-2-indolinols (104) or their open-chain tautomers (103) are formed by hydrolysis of benzoxazepines, the poorly characterized intermediates just mentioned, and that the N-acylindoles (102) are formed by dehydration of the N-acyl-2-indolinols (104). In some cases the N-acylindoles (102) are easily hydrolyzed to indoles (106). The formation of compounds of type 105 is believed to be due to a photooxidation of N-acylindoles.[154]

Extension of studies of solvent effects to quinoline N-oxides with hydrogen in the 2 position (91) revealed that these N-oxides on irradiation in aprotic solvents yielded N-formyl-2-

indolinols (108) (or their open-chain tautomers (107)) and carbostyrils (92) as major products.[135,155]

Exceptions to the above photolytic behavior were found for 3-bromo-, 4-chloro-, 4-bromo-, and 6-methoxy-4-methyl-quinoline N-oxides, from which no N-acyl-2-indolinols were isolated upon irradiation in aprotic nonpolar solvents.[149]

4. Aryl-Substituted Quinoline N-Oxides

The irradiation of 2-phenylquinoline N-oxide (109a) in dry methanol was reported by Kaneko and Yamada[156] to result in the formation, in high yield, of only one product, which was

109a

110a   111a
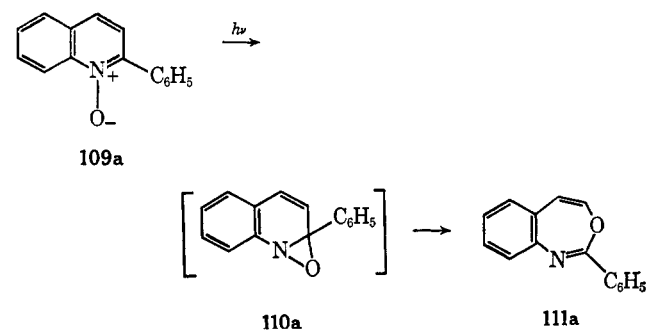
(153) O. Buchardt, J. Becher, C. Lohse, and J. Møller, *Acta Chem. Scand.*, 20, 262 (1966).
(154) O. Buchardt, J. Becher, and C. Lohse, *ibid.*, 20, 2467 (1966).
(155) O. Buchardt and C. Lohse, *Tetrahedron Lett.*, 4355 (1966).
(156) C. Kaneko and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), 14, 555 (1966).

assigned the oxaziridine structure **110a** (*cf*. ref 157–159). However, shortly afterwards Buchardt[160] investigated the photochemical behavior of a series of 2-phenylquinoline N-oxides in various solvents. This study resulted in the isolation of a series of the presumed oxaziridines in high yield when benzene was used as solvent; a very minor amount (0.5%) of 3-phenylcarbostyril (**112a**) was also isolated upon irradiation of 2-phenylquinoline N-oxide. If 96% ethanol was employed as solvent, a decrease in the yield of presumed oxaziridines, some formation of N-benzoyl-2-indolinols (**114**), and an increase in the yield of carbostyrils were observed; it was shown that the N-aroyl-2-indolinols arose by hydrolysis of the presumed oxaziridines (**110**), but that irradiation of the latter compounds did not result in carbostyril formation under conditions where this process took place from the quinoline N-oxides. These and other observations on the chemistry and spectroscopic properties of the main products from the photolysis of 2-aryl-substituted quinoline N-oxides led Buchardt to assign benz[*d*][1,3]oxazepine structures (**111**) to these compounds. This structural assignment was later confirmed by an X-ray study,[161] and Kaneko, *et al.*,[162] have agreed with the assignment. On the basis of these results, it seems certain that the N-aroylindolinols (**114**) or their open-chain tautomers (**113**) encountered in the photolysis of quinoline N-oxides arise

113   **114**
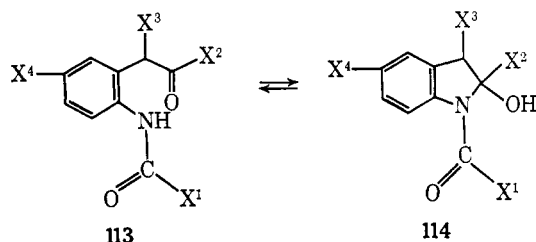
from a secondary thermal hydrolysis of the benz[*d*][1,3]-oxazepines (**111**), which can be regarded as cyclic imido esters of enols, and that the "unstable intermediates" mentioned on p 246 have this structure.

An excellent example of the remarkable effect of solvent on the course of the light-induced reactions of quinoline N-oxides is provided by the photolysis of 3-phenylquinoline N-oxides (**109i**) in acetone, which yields *ca*. 80% of 4-phenyl-benz[*d*][1,3]oxazepine (**111i**) and *ca*. 20% of 3-phenylcarbo-styril (**112a**); however, if the photolysis is conducted in 96% ethanol a 98% yield of 3-phenylcarbostyril results.[163] A similar pronounced solvent effect is found for 4-phenyl-quinoline N-oxide (**109j**), which upon photolysis in ethanol rearranges in high yield to 4-phenylcarbostyril (**112j**). Irradiation of 4-phenylquinoline N-oxide (**109j**) in cyclohexane resulted in the formation of a complicated mixture, which was separated into 4-phenylcarbostyril (**112j**), N-formyl-3-phenyl-2-indolinol (**114j**), and, as the major fraction, 3-phenyl-2-indolecarboxaldehyde (**115**).[163] The formation of the latter

109j   **110j**

114j   **115**
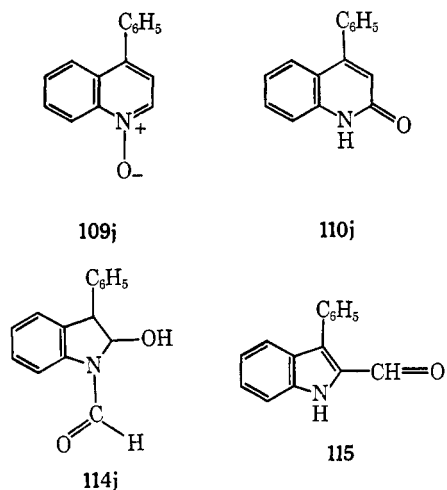
compound is interesting because it emphasizes the close relationship between the quinoline and pyridine series.

Nuclear magnetic resonance data indicate that the N-aroyl-2-indolinols (**114**) are in equilibrium with their open-chain tautomers (**113**).[154,161] When X^2 = H, the ring form **114** is preferred, whereas when $X^2 \neq$ H, the open-chain tautomer **113** is the more stable in solution as well as in the solid state. The N-formyl-2-indolinols (**108**), besides exhibiting the above-mentioned tautomerism, have been shown[164] to exist as two torsional single bond isomers because of restricted rotation about the amide bond. Mass spectrometric data indicate that the open-chain form is prevalent in the gas phase.[165]

5. 2-Cyanoquinoline N-Oxides (116)

The main photolysis products from 2-cyanoquinoline N-oxides (**116**) in aprotic solvents are the corresponding benz-[*d*][1,3]oxazepines (**117**),[161] first believed to be oxaziridines.[156–159] In the case of 2-cyano-4-methoxyquinoline N-oxide (**116f**) the irradiation led to 2-cyano-3-hydroxy-4-methoxyquinoline (**118f**).[158,159] This product was later shown to arise *via* 2-cyano-5-methoxybenz[*d*][1,3]oxazepine (**117f**).[166]

116f   **117f**   **118f**
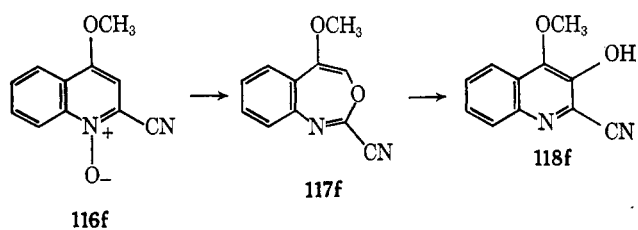
An interesting type of reaction is found in the recent report by Kaneko, Yokoe, and Ishikawa[167] that irradiation of 2-cyano-4-methylquinoline N-oxide (**116c**) in the presence of primary or secondary aliphatic amines resulted in the formation of compounds identified as N-aminocarbostyrils (**119**) (Table VII) (*cf*. ref 168).

(157) C. Kaneko, S. Yamada, and I. Yokoe, *Tetrahedron Lett.*, 4701 (1966).
(158) C. Kaneko and S. Yamada, *Rept. Res. Inst. Dental Mater., Tokyo Medico-Dental Univ.*, 2, 804 (1966).
(159) C. Kaneko, S. Yamada, and M. Ishikawa, *Tetrahedron Lett.*, 2145 (1966).
(160) O. Buchardt, *ibid.*, 6221 (1966).
(161) O. Buchardt, B. Jensen, and I. K. Larsen, *Acta Chem. Scand.*, 21, 1841 (1967).
(162) C. Kaneko, S. Yamada, I. Yokoe, and M. Ishikawa, *Tetrahedron Lett.*, 1873 (1967).
(163) O. Buchardt, P. L. Kumler, and C. Lohse, *Acta Chem. Scand.*, 23, 2149 (1969).

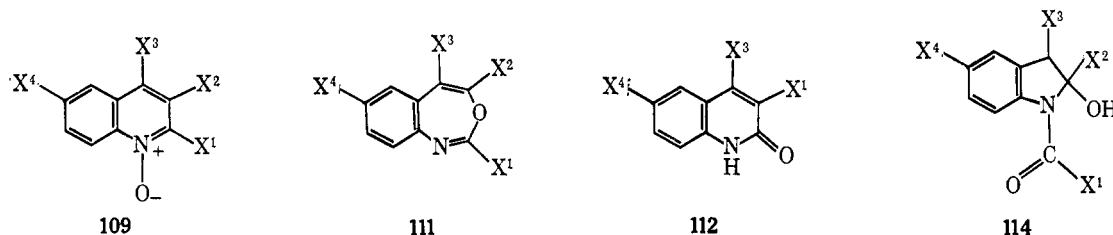(164) O. Buchardt, P. L. Kumler, and C. Lohse, *ibid.*, 23, 1155 (1969).
(165) O. Buchardt, A. M. Duffield, and C. Djerassi, *ibid.*, 22, 2329 (1968).
(166) C. Kaneko and S. Yamada, *Chem. Pharm. Bull.* (Tokyo), 15, 663 (1967).
(167) C. Kaneko, I. Yokoe, and M. Ishikawa, *Tetrahedron Lett.*, 5237 (1967).
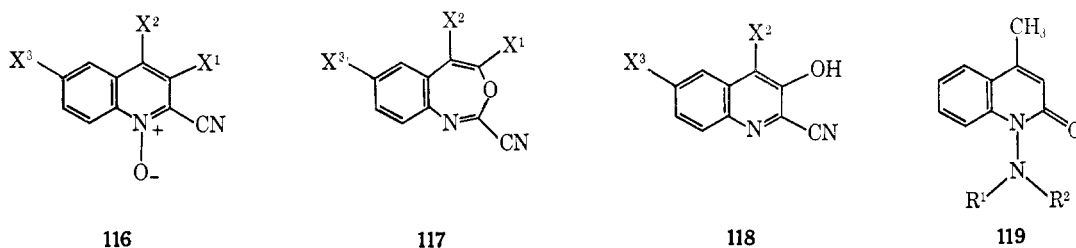(168) C. Kaneko and I. Yokoe, *ibid.*, 5355 (1967).

Table VI

Photolysis Products of Aryl-Substituted Quinoline N-Oxides

109   111   112   114

109	X^1	X^2	X^3	X^4	Amount	Solvent	Products[b]	Re_
a	C_6H_5				2 g	EtOH	**112a** (8), **111a** (80), **114a**	161, 156, 160
					10 g	Acetone	**111a**	161
b	C_6H_5	CH_3			10 g	Acetone	**111b** (90)	161, 160
c	C_6H_5		CH_3		1 g	EtOH	**112c** (12), **114c** (14)	161, 160
					1 g	Acetone	**111c** (90)	161, 160
d	C_6H_5			CH_3	1 g	EtOH	**112d** (9), **111d** (56)	161, 160
					1 g	Acetone	**111d** (90)	161
e	C_6H_5			Br	1 g	Acetone	**111e** (65)	161
f	p-BrC_6H_4				1 g	Acetone	**111f** (85)	161
g	p-BrC_6H_4			Br	1 g	Acetone	**111g** (80)	161
h	p-ClC_6H_4				1 g	Acetone	**111h** (70)	165
i		C_6H_5			270 mg	EtOH	**112a** (98)	163
					523 mg	Acetone	**111i** (80), **112a** (20)	163
j			C_6H_5		600 mg	Ethyl acetate	**112j** (83), 4-phenylquinoline (9)	163
					900 mg	Cyclo-hexane	**112j** (135 mg), **114j** (133 mg), 3-phenyl-2-indolecarboxalde-hyde (401 mg)	163

ᵃ When X = H, no substituent is entered in the table. ᵇ Yields (%) are given in parentheses.

Table VII

Photolysis Products of 2-Cyanoquinoline N-Oxides in Various Solvents, with or without Added Amines

116   117   118   119

116	X^1	X^2	X^3	Amount	Solvent	Added amine R^1	R^2	Products[b]	Ref
a				1 g	Acetone			**117a** (90)	164, 156
b	CH_3			1 g	Acetone			**117b** (70)	161
c		CH_3		1 g	Acetone			**117c** (90)	161, 156
d			CH_3	1 g	Acetone			**117d** (95)	161
e	Cl				CH_2Cl_2			**117e** (80)	159
f	OCH_3				CH_2Cl_2			**118f** (80)	159, 166
					CH_2Cl_2			**117f** (100)	166, 159
g			OCH_3	1 g	Acetone			**117g** (90)	161
h		CH_3	OCH_3	1 g	Acetone			**117h** (65)	161
c		CH_3		1 g	CH_2Cl_2	H	CH_3ᶜ	**119i** (0.4 g)	167
		CH_3		1 g	CH_2Cl_2	CH_3	CH_3ᶜ	**119j** (1 g)	167
		CH_3		1 g	CH_2Cl_2	H	C_2H_5ᶜ	**119k** (0.29 g)	167
		CH_3		1 g	CH_2Cl_2	C_2H_5	C_2H_5	**119l** (0.7 g)	167

ᵃ When X = H, no substituent is entered in the table. ᵇ Yields (%) are given in parentheses. If amounts rather than percentage yields are given in the original article, they are reported as, *e. g.*, (0.4 g). ᶜ Aqueous solution.

116c

119

91v

127

91z

128
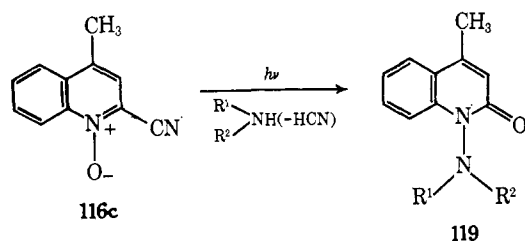
6. Miscellaneous Quinoline N-Oxides

An intriguing difference was found in the photolysis of the two quinoline N-oxides 120 and 122.[162] 2,3-Cyclopentenoquinoline N-oxide (120) gave, in addition to the parent quinoline, an excellent yield of 1,2,3,4-tetrahydrocarbazole-4-one (121), whereas 1,2,3,4-tetrahydroacridine N-oxide (122) is reported to yield 123 as a primary product; compound 123, however, is apparently too reactive to be isolated in a pure state, and reacts further to give 124 and 125, which were isolated and characterized. Note that the thermolysis of a series of stable

120   121

122

123

124

125
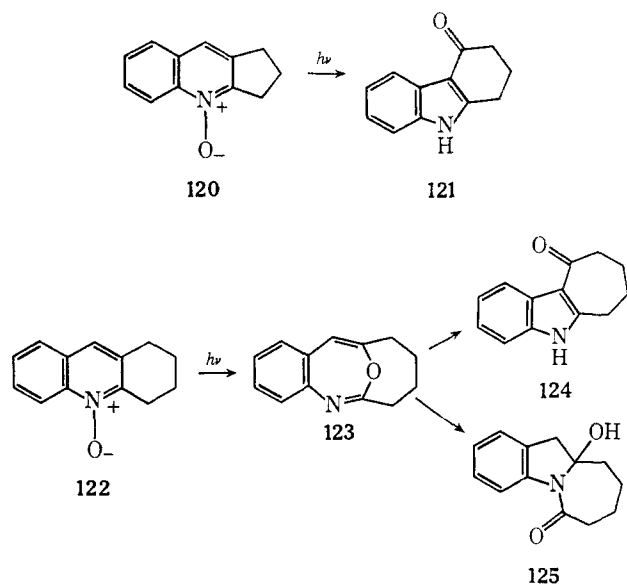
benz[d][1,3]oxazepines (111) to 3-acylindoles (126) was recently demonstrated.[163] The formation of 125 is remarkable because in all other reported instances[135,149,153,154,157,160,164] where N-acyl-2-indolinols have been isolated as the preferred tautomer, hydrogen has been present in the 2 position.

111   126
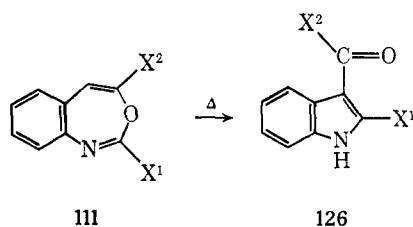
In connection with the previously mentioned work on 4-nitropyridine N-oxides, irradiation of 4-nitroquinoline N-oxide (91v) and 3-methyl-4-nitroquinoline N-oxide (91x) in ethanol or 2-propanol was shown to give the corresponding 4-hydroxycarbostyrils (127) (Table IV).[144]

The irradiation of 4-azidoquinoline N-oxide (91z) proceeds in a fashion analogous to the previously described photolysis of 4-azidopyridine N-oxide and results in the formation of 128.[145]
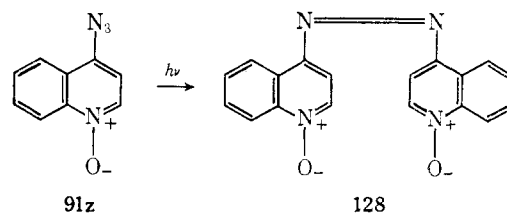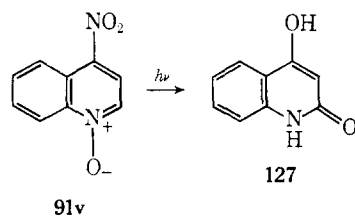
An unusual reaction has been observed with 2-chloroquinoline N-oxide (129a), which upon irradiation rearranged in high yield to 3-chlorocarbostyril (130a).[169] Preliminary experiments have shown that irradiation of 2-(4-methylphenyl-thio)quinoline N-oxide (129b) leads in part to 130b via a similar rearrangement.[169]

Irradiation of 2-carboxyquinoline N-oxide is reported[168] to yield carbostyril or its photodimer in high yield.

129

130

a, X = Cl

b, X = S—〈 〉—CH₃
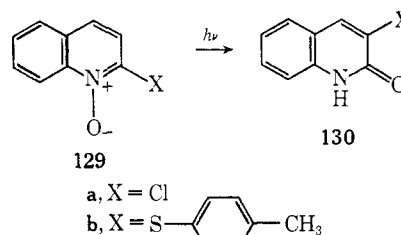
7. Irradiation of Quinoline N-Oxides in the Solid State

The photolysis of a series of 2-unsubstituted quinoline N-oxides (91a–g) in potassium bromide disks resulted in the formation of the corresponding carbostyrils (92a–g), whereas 2-methylquinoline N-oxide (98a) was converted to N-acetyl-2-indolinol (104a).[147] An attempt to utilize solid-phase photolysis preparatively met with very limited success.[154]

8. Addendum

Some esr measurements on nitroquinoline N-oxides and 4-hydroxylaminoquinoline N-oxide have been reported in a series of papers.[170,171] Only for 4-nitroquinoline N-oxides were esr signals found during photolysis, and these apparently have no direct bearing on the general course of photoprocesses occurring at the N-oxide group. It has, however, been found that irradiation of quinoline N-oxide at liquid nitrogen temperature produces a faint signal due to a triplet excited state.[172]

E. ISOQUINOLINE N-OXIDES

The light-induced reactions of isoquinoline N-oxides (131) are very similar to those of quinoline N-oxides. Thus, 1-

(169) O. Buchardt and P. L. Kumler, unpublished results.

(170) N. Kataoka, A. Imamura, Y. Kawazoe, G. Chihara, and C. Nagata, Chem. Pharm. Bull. (Tokyo), 14, 1171 (1966).

(171) N. Kataoka, A. Imamura, Y. Kawazoe, G. Chihara, and C. Nagata, ibid., 14, 897 (1966).

(172) J. Paxton and O. Buchardt, unpublished results.

Table VIII

Photolysis Products of Miscellaneous Quinoline N-Oxides, Acridine N-Oxides, and Phenanthridine N-Oxides

120, a = 2; b = 3
122, a = 2; b = 4
144, a = 1; b = 4

121, a = 2; b = 3 .
124, a = 2; b = 4
145, a = 1; b = 4

138

140

141

125

146a, R = CH₃
b, R = C₂H₅

142

143
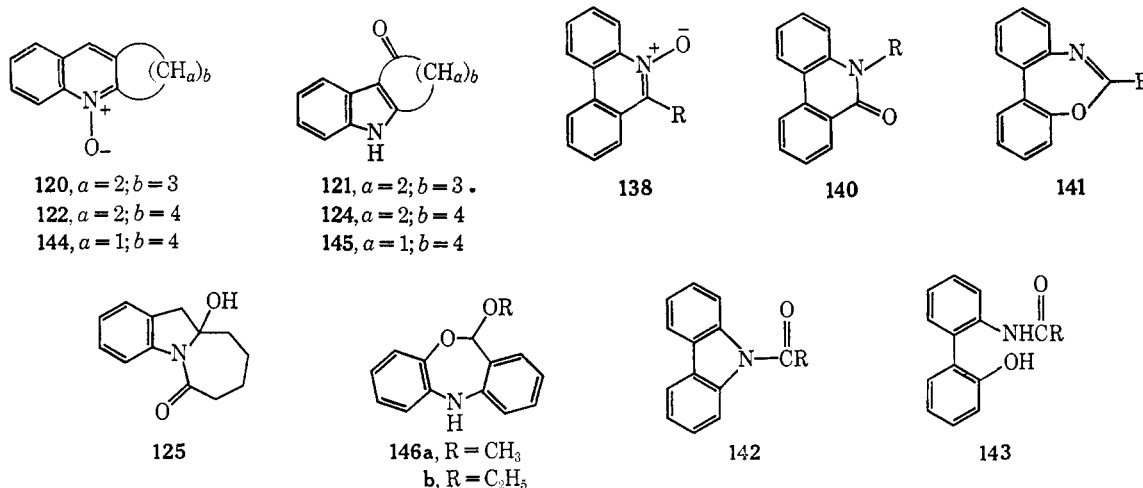
Starting material	Amount	Solvent	Products[a]	Ref
2-Chloroquinoline N-oxide (129a)	1 g	Acetone	3-Chlorocarbostyril (130a) (70)	186
2-(4-Methylphenylthio)-quinoline N-oxide (129b)	1 g	Acetone	3-(4-Methylphenylthio)carbostyril (130b) (50)	186
120		ClCH₂CH₂Cl	121 (80), parent amine (10)	162
122		ClCH₂CH₂Cl	124 (10), 125 (70), parent amine (8)	162
144	500 mg	CH₂Cl₂	145 (390 mg), acridine (13 mg)	182
		MeOH	146a	183
		EtOH	146b	183
138, R = H	2 g	MeOH	140a (85), parent amine (8)	148 (180, 181)
138b, R = CH₃	2 g	MeOH	140b (80), parent amine (2)	148 (180)
138c, R = C₆H₅		EtOH	140c (93)	180 (178)
		Benzene	140c (17), 141c (3), 142c (1) 143c (35), parent amine (11)	178
138d, R = CH(C₆H₅)CH₂CH₃ [α]²²D 7.85°		EtOH Benzene	140d, racemic	178
138e, R = CH(C₆H₅)₂		Benzene	140a (17), 140e (40), 1,1,2,2-tetraphenylethane (16)	178

[a] Yields (%) are given in parentheses.

phenyl- and 1-cyanoisoquinoline N-oxides upon irradiation rearrange to benz[f][1,3]oxazepines (132).[173,174] The benz-[f][1,3]oxazepines (132) were first obtained by Kaneko, Yamada, and Ishikawa,[157-159] who assigned the oxaziridine structure 133 to the products obtained from 1-cyanoiso-

131   132   133
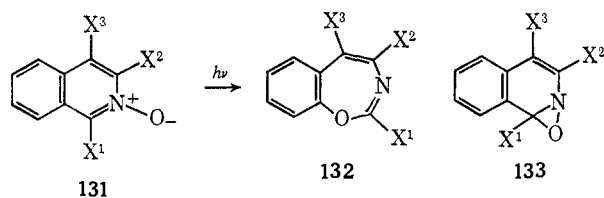
quinoline N-oxide (131g) and its 3-methyl derivative (131h). However, on the basis of spectroscopic and chemical properties of the photolysis products from 1-phenylisoquinoline N-oxide (131e) and its 3-methyl derivative (131f), Buchardt, Lohse, Duffield, and Djerassi[173] concluded that the photo-

products had the benz[f][1,3]oxazepine structure 132, not structure 133. The same conclusion was later reached independently by the Japanese group.[175] The benz[f][1,3]-oxazepine structure was recently conclusively confirmed by an X-ray study of the photoproduct from 1-cyano-4-bromo-isoquinoline N-oxide (131i), which was unambiguously shown to be 2-cyano-5-bromobenz[f][1,3]oxazepine (132i).[174]

The photolysis of isoquinoline N-oxide (131a) and its 3-methyl (131c) and 4-bromo derivatives (131d) in protic solvents leads to the corresponding isocarbostyrils (134) and minor amounts of the deoxygenated products (135).[176]

1-Methylisoquinoline N-oxide (131b) reacts analogously to 2-methylquinoline N-oxide on photolysis, with formation of N-methylisocarbostyril (134b) and a small amount of the parent quinoline 135b.[176]

In this series as well a remarkable solvent effect is observed. Thus, the photolysis of 1-methyl- (131b) and 3-methyliso-quinoline N-oxide (131c) in acetone containing small amounts

(173) O. Buchardt, C. Lohse, A. M. Duffield, and C. Djerassi, *Tetrahedron Lett.*, 2741 (1967).
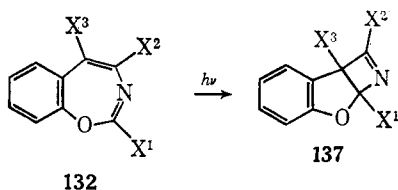(174) C. Lohse, O. Simonsen, and O. Buchardt, *Acta Chem. Scand.*, in press.

(175) C. Kaneko, S. Yamada, and I. Yokoe, *Rept. Res. Inst. Medical Eng., Tokyo Medico-Dental Univ.*, 1 (1967).
(176) C. Lohse, private communication.

of water gave compounds **136b,c**, in addition to the expected isocarbostyrils **134b,c** and isoquinolines **135b,c**.[176,177]


131

132   136
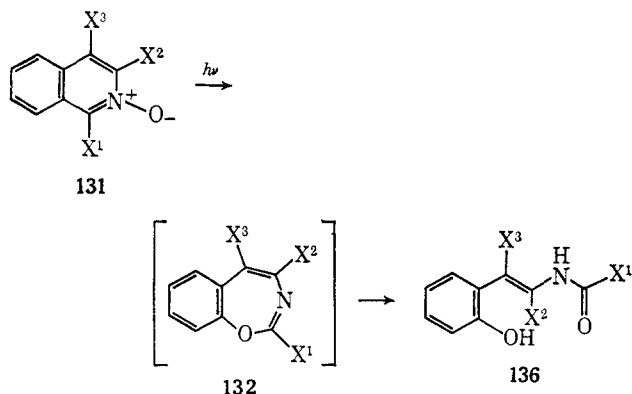
The benz[f][1,3]oxazepines (**132**) are undoubtedly intermediates in this reaction since it has been shown[178] that solvolysis of stable benz[f][1,3]oxazepines (**132**) leads to compounds of type **136**. The photolysis of 1-carboxy- and 1-carboxamidoisoquinoline N-oxides in acetone or ethanol results in very complex reaction mixtures, as does the photolysis of **131c** and **131d** in ethanol, and no attempts were made to separate the mixtures.[176] Contrary to what was found in the quinoline and quinoxaline series, the seven-membered ring compounds from isoquinoline N-oxides were quite reactive in Pyrex-filtered light. In two cases it has been shown that photolysis leads to the benzofuro[2,3-b]azete derivatives **137**.[177]

132   137

F. PHENANTHRIDINE N-OXIDES

Phenanthridine N-oxides (**138**) undergo the characteristic photochemical reactions of aromatic amine N-oxides—deoxygenation (to phenanthridines (**139**)[148,178,179]), rearrangement (to phenanthridin-6(5H)-ones (**140**)[148,178–181]), and
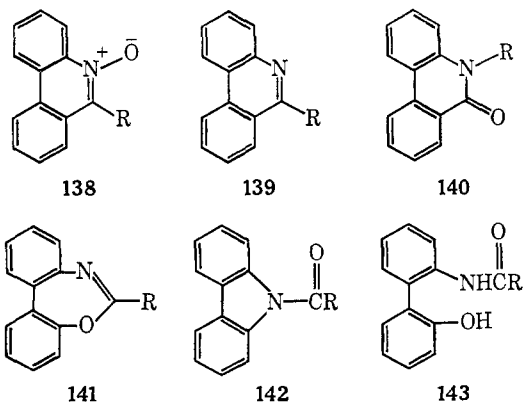
138   139   140

141   142   143

ring enlargement (to dibenz[d,f][1,3]oxazepines (**141**)[178,179]). As expected, the reaction is solvent dependent, formation of **140** being favored when the photolysis is carried out in protic solvents,[148,178–181] while formation of **141** is favored when the solvent is benzene.[178,179]

When 6-phenylphenanthridine N-oxide (**138c**) is irradiated in benzene solution, one of the minor products is 9-benzoylcarbazole (**142c**).[178] Compound **142** cannot be formed by hydrolysis of **141**, for the hydrolysis product of **141** is compound **143**, which cannot close to a carbazole by a dehydration process.[178,179]

When partially resolved 6-(1-phenylpropyl)phenanthridine N-oxide (**138d**) is irradiated, the 5-(1-phenylpropyl)phenanthridin-6(5H)-one (**140d**) isolated is totally racemic.

When 6-benzhydrylphenanthridine N-oxide (**138e**) is subjected to photolysis, two of the isolated products are 1,1,2,2-tetraphenylethane (15.8%) and phenanthridin-6(5H)-one (**140a**, 17.2%). The quantum yields for these photoreactions are quite high,[180] and it seems reasonable to assume that similarly high quantum yields exist for many of the other aromatic amine N-oxides, as is also evident from the necessary irradiation times.

G. ACRIDINE N-OXIDES

The light-induced transformations of acridine N-oxides (**144**) show a dramatic solvent dependence. When acridine N-oxide was irradiated in benzene or dichloromethane, rearrangement to **145** took place in high yield. As a minor product, acridine was isolated.[182] However, when acridine N-oxide was irradiated in methanol or ethanol, one molecule of solvent was added, leading to compounds assigned 11-alkoxy-5,11-dihydrodibenz[b,e][1,4]oxazepine structures (**146**).[183a] These compounds were previously believed to be 9-alkoxy-N-hydroxyacridines[183b] (cf. ref 184).

145   144   146
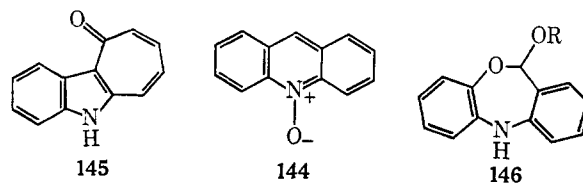
H. PYRIDAZINE N-OXIDES

The main product of photolysis of 3,6-diphenylpyridazine N-oxide (**147f**) in either acetone or methanol was 3-benzoyl-5-phenylpyrazole (**149f**); minor amounts of the parent amine (**148f**) and an unidentified crystalline compound were also formed.[185] Besides these isolated products, a transient yellow intermediate was observed in the photolysis of **147f**, which has been assigned the structure **150** on the basis of its spectroscopic properties and its thermal transformation to **149f**.[185] In order to examine the possibility that the above-mentioned unidenti-

(177) C. Lohse, *Tetrahedron Lett.*, 5625 (1968).

(178) E. C. Taylor and G. G. Spence, *Chem. Commun.*, 1037 (1968).

(179) G. G. Spence, Ph.D. Thesis, Princeton University, 1968.

(180) E. C. Taylor and G. G. Spence, *Chem. Commun.*, 767 (1966).

(181) E. C. Taylor, B. Furth ,and M. Pfau, *J. Amer. Chem. Soc.*, 87, 1400 (1965).

(182) M. Ishikawa, C. Kaneko, and S. Yamada, *Tetrahedron Lett.*, 4519 (1968).

(183) (a) H. Mantsch, V. Zanker, and G. Prell, *Ann. Chem.*, 723, 95 (1969); (b) H. Mantsch and V. Zanker, *Tetrahedron Lett.*, 4211 (1966).

(184) J. H. Markgraf and M. K. Ahn, *J. Amer. Chem. Soc.*, 86, 2699 (1964).

(185) P. L. Kumler and O. Buchardt, *ibid.*, 90, 5640 (1968).

Table IX

Photolysis Products of Isoquinoline N-Oxides

| 131 | 132 | 134 | 135 | 136 |

┌─────Starting material[a]─────┐						
131	*X¹*	*X²*	*X³*	*Amount, g*	*Solvent*	*Products[b]*	*Ref*
a				2	MeOH	**134a** (70), **135a** (5)	148
				0.5	EtOH	**134a** (60)	176
				0.5	Acetone	**138a, 136a**	176
b	CH₃			2	MeOH	**134b** (45), **135b** (10)	148
				0.5	EtOH	**134b** (48)	176
				0.5	Acetone	**136b** (52)	176
c		CH₃		2	MeOH	**134c** (75), **135c** (5)	148
				0.5	EtOH	**134c** (80)	176
				0.5	Acetone	**134c** (28), **136c** (34)	176
d			Br	0.5	EtOH	**134d** (100)	176
e	C₆H₅			1	Acetone	**132e** (50)	173, 174
f	C₆H₅	CH₃		1	Acetone	**132f** (50)	173, 174
g	CN			1	Acetone	**132g** (20)	173, 158, 174
h	CN	CH₃		1	Acetone	**132h** (20)	173, 174
i	CN		Br	0.5	Acetone	**132i** (25)	174

[a] When X = H, no substituent is entered in the table. [b] Yields (%) are given in parentheses.

150
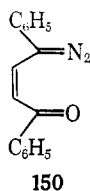
fied crystalline compound might have been the product of a secondary photoprocess from **149f**, this latter compound was photolyzed with and without benzophenone as sensitizer. However, under conditions where all **147f** was photolyzed, no formation of the unknown compound was observed from **149f**, with or without sensitizer.[186]

Photolysis of a series of pyridazine N-oxides (**147a–e**) in various solvents was recently reported[187,188] to result mainly in deoxygenation. It is interesting that deoxygenation took place even though the irradiations were performed in the absence of oxygen (*cf.* discussion on p 245). Besides deoxygenation, which was found for all five pyridazine N-oxides, the hydroxymethyl compounds **151** were isolated in small yields in four cases, and in two cases 0.2% of the ring-contracted isomers **149**, analogous to products from pyridine N-oxides, were observed when methanol was employed as solvent.[187] By comparison with the results obtained for 1,4-diphenylphthalazine N-oxide, it could have been expected that furan derivatives would be formed. However, only small fractions of the total starting material were accounted for in the latter work; the possibility of furan formation was not disproved.

I. CINNOLINE N-OXIDES

Apparently only one report on the photolysis of cinnoline N-oxides has appeared; irradiation of benzo[c]cinnoline N-oxide has been reported to result only in deoxygenation.[34] From the reported data it is apparent that the quantum yield for this reaction is very small. This is in good correspondence with some preliminary results with benzo[c]cinnoline N-oxide and both possible N-oxides of 3,4-diphenylcinnoline, and indicates that these compounds are only slightly affected, even upon very prolonged irradiation, by Pyrex-filtered light.[186]

J. PHTHALAZINE N-OXIDES

The results obtained upon photolysis of 1,4-diphenylphthalazine N-oxide (**152**) in various solvents[189] are totally different from those reported for monocyclic derivatives, as well as different from those observed for the rest of the aromatic amine N-oxide series. 1,4-Diphenylphthalazine N-oxide (**152**) upon photolysis gives rise to 1,3-diphenylisobenzofuran (**153**) as the primary product with concomitant nitrogen expulsion. When oxygen was present during irradiation, some deoxygenation to 1,3-diphenylphthalazine (**154**) and oxidation of the initially formed 1,3-diphenylisobenzofuran (**153**) to 1,2-dibenzoylbenzene (**155**) was observed; exclusion of oxygen
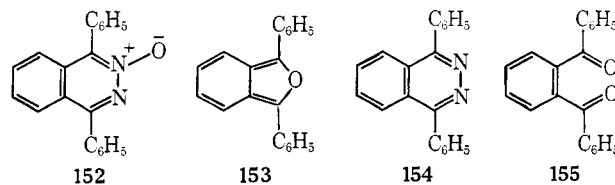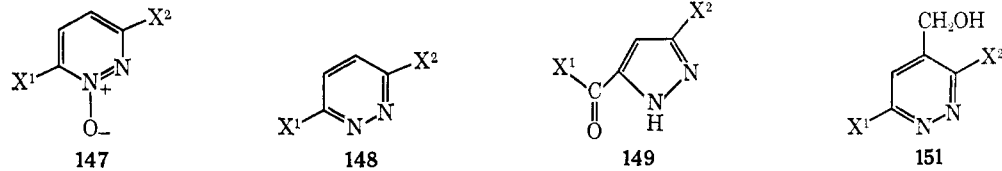
(186) O. Buchardt and P. L. Kumler, unpublished results.
(187) M. Ogata and K. Kano, *Chem. Commun.*, 1176 (1967).
(188) H. Igeta, T. Tsuchiya, M. Yamada, and H. Arai, *Chem. Pharm. Bull.* (Tokyo), 16, 767 (1968).

| 152 | 153 | 154 | 155 |

(189) O. Buchardt, *Tetrahedron Lett.*, 1911 (1968).

Table X

Photolysis Products of Pyridazine and Phthalazine N-Oxides

	Starting material[a]					
147	X^1	X^2	Amount	Solvent	Products[b]	Ref
a				MeOH	**148a** (25), **149a** (0.2), **151a** (7)	187
b	CH_3			MeOH	**148b** (6)	187
c	CH_3	CH_3		MeOH	**148c** (11), **151c** (0.5)	187
d	CH_3	Cl		MeOH	**148d** (19), **151d** (0.02)	187
e	CH_3	OCH_3		MeOH	**148e** (9), **149e** (0.2), **151e** (1)	187
f	C_6H_5	C_6H_5	1 g	Acetone	**149f** (75), unknown (10)	185
152, 1,4-diphenylphthalazine N-oxide				Acetone	1,3-Diphenylisobenzofuran (5), 1,2-dibenzoylbenzene (40–60), 1,4-diphenylphthalazine (0–15)	189

[a] When X = H, no substituent is entered in the table. [b] Yields (%) are given in parentheses.

resulted in a very high conversion of **152** to **153**. After prolonged irradiation, however, several new spots were observed by thin layer chromatography, indicating the photolability of **153** and **155**.[190] The small yield of 1,3-diphenylisobenzofuran (**153**) isolated is undoubtedly due to decomposition during the preparative thin layer chromatographic separation employed.

K. PYRIMIDINE N-OXIDES

In the pyrimidine N-oxide series no photolysis results have been reported thus far. Some preliminary experiments with 4,6-diphenylpyrimidine N-oxide indicate that this compound upon photolysis in acetone yields a complicated mixture of products.[186]

L. QUINAZOLINE N-OXIDES

Kaneko and Yamada[191] reported that irradiation of 4-phenylquinazoline N(3)-oxide (**156**) and its 2-methyl derivative **157** in benzene resulted in the formation of the benz[f][1,3,5]-oxadiazepines **158** and **159** as the major products. From **157** a small amount of 4-phenyl-2-methylquinazoline was isolated. It was also reported that quinazoline N(3)-oxide (**160**) on irradiation gave a mixture of 4-quinazolone (**161**) and quinazoline. The benz[f][1,3,5]oxadiazepines **158** and **159** were identi-

fied by the similarity of their spectra with those of the previously described benz[f][1,3]oxazepines, and by their facile solvolysis to benzoxazole derivatives among other products.
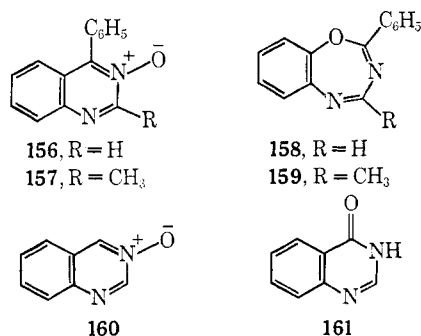
Shortly afterwards Field and Sternbach[91] reported similar results with some other quinazoline N(3)-oxides. These authors also reported that photolysis of the quinazoline N(1)-oxide **162** resulted in formation of the indazole derivative **163**.
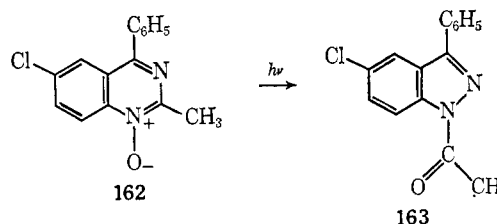
M. PYRAZINE N-OXIDES

An interesting series of reactions has been reported by Ikekawa, Honma, and Kenkyusho[192] for 2,5-dimethylpyrazine N-oxide (**164a**) and 2,5-diphenylpyrazine N-oxide (**164b**). It was found that the photolysis of 2,5-dimethylpyrazine N-oxide (**164a**) in benzene flushed with nitrogen resulted in the formation of 2-acetyl-4-methylimidazole (**165a**) and 2,4-dimethylimidazole
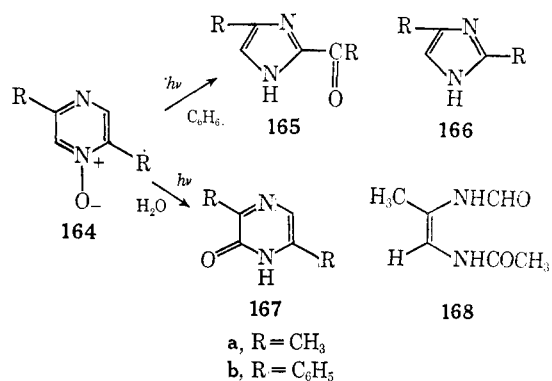
(190) P. Courtot and D. H. Sachs, *Bull. Soc. Chim. Fr.*, 2259 (1965).
(191) C. Kaneko and S. Yamada, *Tetrahedron Lett.*, 5233 (1967).
(192) N. Ikekawa, Y. Honma, and R. Kenkyusho, *ibid.*, 1197 (1967).

(166a) in rather low yields. If the irradiation of 164a was performed in aqueous solution, 3,6-dimethyl-2-pyrazinone (167a) and 1-acetamido-2-formamido-1-propene (168) were isolated, again in rather low yields. The irradiation of 2,5-diphenyl-pyrazine N-oxide (164b) in benzene resulted in a high yield of deoxygenated product along with small amounts of 3,6-diphenyl-2-pyrazinone (167b) and 2,4-diphenylimidazole (166b).
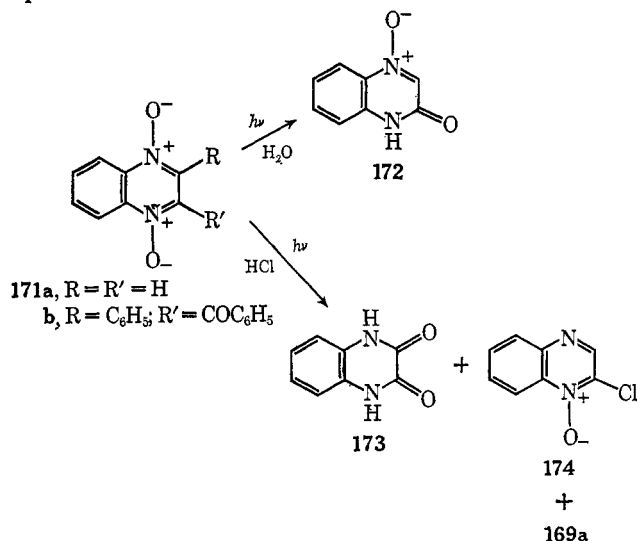
N. QUINOXALINE N-OXIDES

Landquist[193] in 1953 examined the light-induced reactions of quinoxaline N-oxide (169a) and quinoxaline N,N'-dioxide (171a); these were the first aromatic amine N-oxides to be examined in this way. More recent studies have been concerned primari y with the photoreactions of the mono-N-oxides of phenyl-substituted quinoxalines.

Landquist[193] showed that quinoxaline N-oxide (169a) upon photolysis in aqueous solution rearranged to quinoxalone (170a), and that quinoxaline N,N'-dioxide (171a) rearranged to 2-quinoxalone N(4)-oxide (172). Irradiation of 171a in

169a, R = R' = H
b, R = H; R' = C₆H₅
c, R = C₆H₅; R' = H
d, R = R' = C₆H₅
e, R = R' = p-BrC₆H₄

170a, R = H
b, R = C₆H₅
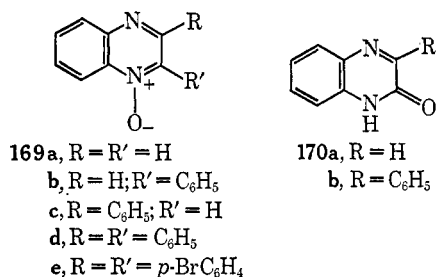
hydrochloric acid, on the other hand, resulted in the formation of a chloroquinoxaline mono-N-oxide and a very small amount of 2,3-quinoxalinedione (173). Irradiation of the di-N-oxide 171a in hydrochloric acid was later reinvestigated by Cheeseman and Törzs,[194] and it was shown that the chloro-quinoxaline N-oxide had the chlorine atom in the 2 position (174), and that some deoxygenation to quinoxaline mono-N-oxide (169a) also took place. Photolysis of quinoxaline N,N'-dioxide (171a) in aqueous alkali or in chloroform was reported[193] to result in complex reaction mixtures that were not separated.

Studies on a series of phenyl-substituted quinoxaline N-oxides (169b–d) were reported by Kaneko, Yokoe, Yamada, and Ishikawa.[195] It was found that 2-phenylquinoxaline N(1)-oxide (169b) upon irradiation in benzene rearranged to a very reactive compound which on treatment with water yielded N-benzoyl-N'-formyl-o-phenylenediamine (176). The reactive compound was originally believed to be the oxaziridine 177a. Similarly, 2,3-diphenylquinoxaline N-oxide (169d) was reported to give 177b, whereas 3-phenylquinoxaline N(1)-oxide (169c) upon irradiation in benzene was transformed into a

175   176   177

a, R = H; R' = C₆H₅
b, R = R' = C₆H₅
c, R = R' = p-BrC₆H₄
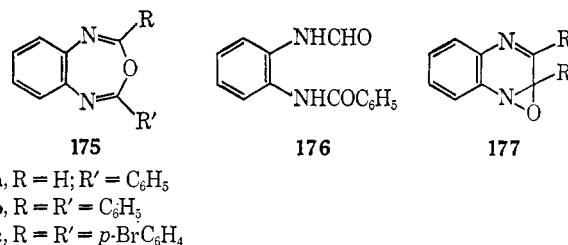
mixture of N-benzoyl-N'-formyl-o-phenylenediamine (176) and 3-phenyl-2-quinoxalone (170b). More recently Kaneko, et al.,[162] corrected their original structural assignment of the presumed oxaziridines 177. By analogy with results obtained with quinoline N-oxides, seven-membered ring structures (i.e., benz[d][1,3,6]oxadiazepines, (175)) were put forward instead.[162,196] Final proof for the benz[d][1,3,6]oxadiazepine structure was recently obtained by Buchardt and Jensen[197] in an X-ray study of the photoproduct from 2,3-bis(4-bromo-phenyl)quinoxaline N-oxide (169e), which unambiguously demonstrated the structure of the product as 2,4-bis(4-bromo-phenyl)benz[d][1,3,6]oxadiazepine (175c).

The photolysis of 2-benzoyl-3-phenylquinoxaline N,N'-dioxide (171b) in methanol was reported[198] to result in the formation of 1,3-dibenzoylbenzimidazolone (178) in high yield. In contrast, some preliminary studies of the photolysis of 2,3-diphenylquinoxaline N,N'-dioxide in various solvents showed that a very complex reaction mixture was formed, from which no products have been identified.[186] Finally, it should

171a, R = R' = H
b, R = C₆H₅; R' = COC₆H₅

173

174

+

169a

171b

178
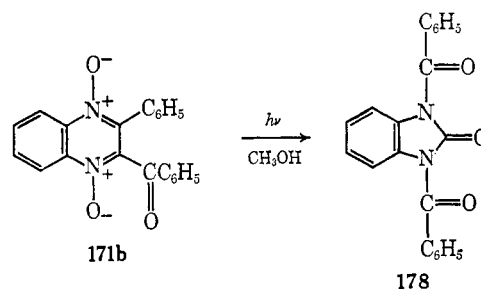
be mentioned that phenazine N,N'-dioxide upon photolysis was reported to give the monoxide, which in turn could be deoxygenated photolytically to the parent amine.[199]

(193) J. K. Landquist, J. Chem. Soc., 2830 (1953).
(194) G. W. H. Cheeseman and E. S. G. Törzs, J. Chem. Soc., C, 157 (1966).

(195) C. Kaneko, I. Yokoe, S. Yamada, and M. Ishikawa, Chem. Pharm. Bull. (Tokyo), 14, 1316 (1966).
(196) O. Buchardt and J. Feeney, Acta Chem. Scand., 21, 1399 (1967).
(197) O. Buchardt and B. Jensen, ibid., 22, 877 (1968).
(198) M. J. Haddadin and C. H. Issidorides, Tetrahedron Lett., 753 (1967).
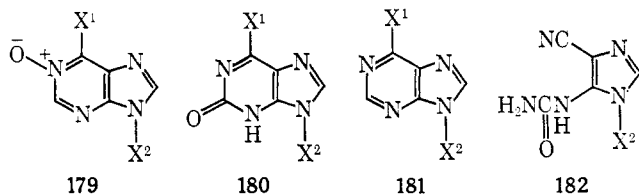(199) C. W. Rees and J. H. Waite, Annu. Rept. Brit. Empire Cancer Campaign, 626 (1961).

O. PURINE N-OXIDES

Purine bases that are N-oxidized in the 1 position (179) show some remarkable photochemical reactions.[200-202] Upon photolysis in water they rearrange to the 2-oxo isomers (180), probably *via* the open-chain tautomer 182 in the case

when X^1 = NH_2.[202] Furthermore, some deoxygenation takes place with formation of the parent purine bases 181. Extrapolation of results obtained with isoquinoline N-oxides and quinazoline N(3)-oxides would have predicted migration of oxygen to the 6 position rather than the 2 position.

V. Mechanistic Explanations of the Photochemistry of Aromatic Amine N-Oxides

Very little is known about the excited states leading to photochemical reactions in the aromatic amine N-oxide series. The long wavelength absorption of these compounds was classified as $n-\pi^*$ by Ito and Hata[203] as well as by Dal Monte, Mangini, and Montanari.[204] The assignment was justified by the hypsochromic shift of this absorption band when the polarity of the solvent was increased. However, it has been pointed out by Sidman[205] that the high extinction coefficients found for these bands (log ϵ $\sim$4, with the exception of isoquinoline N-oxide which had log ϵ $\sim$3) suggest rather that these are due to $\pi-\pi^*$ transitions. In a more recent investigation Ziolkowsky and Dörr[206] concluded that no definite indications of a long wavelength $\pi-\pi^*$ transition could be found in the ultraviolet spectra of a series of aromatic amine N-oxides, but that the effect of the N^+-O^- group on the spectra, by comparison with the spectra of the parent amines and other compounds, resembles that of a substituent with π-donor action. In a very recent paper[207] it is, however, inferred that the long wavelength absorption band in pyridine N-oxide is $n-\pi^*$.

At present no conclusive evidence exists concerning singlet *vs.* triplet states in the photochemical reactions of aromatic amine N-oxides. The possibility that some of the reactions, although light-induced, take place from vibrationally excited ("hot") ground states cannot be entirely excluded. Thus much work remains to be done in this area.

Some preliminary experiments aimed at clarification of this problem have been undertaken (*vide infra*).

Although the previously summarized light-induced reactions of the aromatic amine N-oxides represent a wide variety of types of isolated products, it is possible to unify most of

these results (only liquid-phase photolyses are taken into account) in a general mechanistic interpretation.

It is found in most cases that deoxygenation to the parent amines takes place, in addition to more complex reactions. The fact that decreasing the oxygen concentration present during irradiation of quinoline N-oxides,[148,149,158] isoquinoline N-oxides,[176] and 1,4-diphenylphthalazine N-oxide[189] results in a decrease in deoxygenation points toward the possibility that the deoxygenation takes place from a singlet state, since the triplet quenching efficiency of oxygen is high (*cf.* ref 208, p 598). However, as pointed out in the last reference, great care must be taken in interpreting oxygen quenching results. It seems of considerable interest that some preliminary electron spin resonance measurements on irradiated glasses of quinoline N-oxides at liquid nitrogen temperature have resulted in the observation of weak triplet signals.[172] Even if the deoxygenation should take place from singlet excited states in the types of N-oxides just discussed, any generalizations are distorted by some preliminary photolysis experiments with carefully deoxygenated solutions of 2,4,6-triphenylpyridine N-oxide (73g) in ethanol.[138] Photolysis under these conditions yielded mainly 2-benzoyl-3,5-diphenylpyrrole (76g, Table III), with minor amounts of the parent amine (74g) and other products. When benzophenone was added as sensitizer (the concentration of benzophenone ensured that more than 90% of the light was absorbed by the sensitizer) in the photolysis, a dramatic increase in the yield of 74g and a decrease of 76g was observed.[138] Furthermore, when the photolysis was carried out in the presence of sensitizer, one of the minor components observed in the unsensitized reaction, tentatively believed to be the oxazepine 82, could not be observed. Considering that the approximate value for the long wavelength 0-0 band in the uv spectrum of 2,4,6-triphenylpyridine N-oxide (73g) in ethanol is 3100 Å, indicating an approximate S_1 energy level of 90 kcal,[186] and the triplet energy of benzophenone is 69 kcal (ref 208, p 297), there seems to be a reasonable basis for concluding that deoxygenation in this case takes place from a triplet excited state. Although the above experiments are very incomplete (the products in the sensitized experiments were only observed by tlc), it seems to be a reasonable working hypothesis that deoxygenation of the amine N-oxides takes place from one excited state and most of the other observed processes *via* another excited state.[209] As previously mentioned, vibrationally excited ground states cannot with certainty be excluded as the reactive species, at least in some cases. In the following discussion, deoxygenation will not be mentioned in each case that it has been observed, but it is assumed that it takes place from an excited state different from that leading to the rearrangements.

It has also been suggested that deoxygenation takes place *via* an intermediate oxaziridine.[137] It was argued that since oxaziridines are strong oxidizing agents they could oxidize the solvents. Photolysis of pyridine N-oxide (73a) in methanol or ethanol was shown to proceed with the formation of formaldehyde and acetaldehyde, respectively. It had previously been shown[136] that when benzene is used as solvent during the photolysis of pyridine N-oxide some phenol is formed. Similar results were obtained for pyridazine N-oxide.[188]

(200) G. B. Brown, G. Levin, and S. Murphy, *Biochemistry*, 3, 880 (1964).

(201) G. Levin, R. B. Setlow, and G. B. Brown, *ibid.*, 3, 883 (1964).

(202) F. Cramer and G. Schlingloff, *Tetrahedron Lett.*, 3201 (1964).

(203) M. Ito and N. Hata, *Bull. Chem. Soc. Jap.*, 28, 260 (1955).

(204) D. Dal Monte, A. Mangini, and F. Montanari, *Gazz. Chim. Ital.*, 88, 1035 (1958).

(205) J. W. Sidman, *Chem. Rev.*, 58, 689 (1958).

(206) B. Ziolkowsky and F. Dörr, *Ber. Bunsenges. Phys. Chem.*, 69, 448 (1965).

(207) E. M. Evleth, *Theor. Chim. Acta*, 11, 145 (1968).

(208) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, New York, N. Y., 1966.

(209) Recently it was shown that the deoxygenation of benzo[c]cinnoline N-oxide by photolysis presumably takes place from a triplet excited state.[34]

Table XI

Photolysis Products from Quinazoline, Pyrazine, Quinoxaline, and Purine N-Oxides

	Starting material	*Amount*	*Solvent*	*Products*[a]	*Ref*
160	Quinazoline N(3)-oxide		Benzene	Quinazoline (5), 4-quinazolone (161) (40)	191
156	4-Phenylquinazoline N(3)-oxide	1 g	Benzene	2-Phenylquinazoline, 2-phenylbenz-[*f*][1,3,5]oxadiazepine (158)	191
157	2-Methyl-4-phenylquinazoline N(3)-oxide	1 g	Benzene	2-Methyl-4-phenylquinazoline (~5), 2-phenyl-4-methylbenz-[*f*][1,3,6]oxadiazepine (~50)	191
	4-Phenyl-6-chloroquinazoline N(3)-oxide	10 g	Benzene	3-Phenyl-6-chloro-1,3-benzoxazole (2.3 g)	91
	2-Methyl-4-phenyl-6-chloroquinazoline N(3)-oxide	10 g	Benzene	2-Phenyl-4-methyl-8-chlorobenz-[*f*][1,3,5]oxadiazepine (8.3 g)	91
	2,4-Diphenylquinazoline N(3)-oxide	10 g	Benzene	2,4-Diphenylbenz[*f*][1,3,5]oxadiazepine (8.3 g)	91
162	2-Methyl-4-phenyl-6-chloroquinazoline N(1)-oxide	7 g	Benzene	1-Acetyl-3-phenyl-5-chloroindazole (163) (2.1 g)	91
164a	2,5-Dimethylpyrazine N-oxide		Benzene	2-Acetyl-4-methylimidazole (165a) (5), 2,4-dimethylimidazole (166a) (5)	192
			H_2O	3,6-Dimethyl-2-pyrazinone (167a) (10), 1-acetamido-2-formamido-1-propene (168) (20)	192
164b	2,5-Diphenylpyrazine N-oxide		Benzene	2,4-Diphenylimidazole (166b) (29), 2,5-diphenylpyrazine (50), 3,6-diphenyl-2-pyrazinone (167b) (3)	192
169a	Quinoxaline N-oxide	500 mg	H_2O	2-Quinoxalone (170a) (20)	193
169b	2-Phenylquinoxaline N(1)-oxide		Benzene	2-Phenylquinoxaline, 2-phenyl-benz[*d*][1,3,6]oxadiazepine (175a)[b]	162, 195
169c	3-Phenylquinoxaline N(1)-oxide		Benzene	2-Phenylquinoxaline, 3-phenyl-2-quinoxalone (170b) (40), N-formyl-N'-benzoyl-1,2-phenylenediamine (176) (20)	162, 195
169d	2,3-Diphenylquinoxaline N-oxide		Acetone	2,4-Diphenylbenz[*d*][1,3,6]oxadiazepine (175b) (70)	195
169e	2,3-Bis(4-bromophenyl)-quinoxaline N-oxide		Acetone	2,4-Bis(4-bromophenyl)benz[*d*]-[1,3,6]oxadiazepine (175c) (70)	197
171a	Quinoxaline N,N'-dioxide	7.5 g	H_2O	2-Quinoxalone N(4)-oxide (172) (3 g)	193
		4 g	HCl	2-Chloroquinoxaline N(1)-oxide (174) (34), 169a (10), 2,3-quinoxalinedione (173) (5)	133
171b	2-Phenyl-3-benzoylquinoxaline N,N'-dioxide		MeOH	1,3-Dibenzoylbenzimidazolone (178) (70)	198
179	Adenine N(1)-oxide (X_1 = NH₂; X_2 = H)		H_2O	Isoguanine (180, X_1 = NH₂; X_2 = H), adenine (181, X_1 = NH₂; X_2 = H) 182 (X_2 = H)	200 202
179	Adenosine N(1)-oxide (X_1 = NH₂; X_2 = β-D-ribofuranosyl)		H_2O pH ~6	A Crotonoside (180, X_1 = NH₂; X_2 = β-D-ribofuranosyl) (20) B Adenosine (181, X_1 = NH₂; X_2 = β-D-ribofuranosyl) (10) C 182 (X_2 = β-D-ribofuranosyl) (20)	202
			H_2O pH ~10	A (60)	202
			0.01 N H_2SO_4	A (7) B (25) C (5)	202
			H_2O	A, B	200
179	6-Methylpurine N(1)-oxide (X_1 = CH₃; X_2 = H)		H_2O	2-Hydroxy-6-methylpurine (180, X_1 = CH₃; X_2 = H), 6-methylpurine (181, X_1 = CH₃; X_2 = H)	200
180	Isoguanine N(1)-oxide (X_1 = NH₂; X_2 = H, N(1)-oxide)		H_2O	Isoguanine (180, X_1 = NH₂; X_2 = H)	200

[a] Yields (%) are given in parentheses. [b] Unstable.

As a starting point for the discussion of photochemical N-oxide rearrangements, the quinoline N-oxides will be chosen as sample substrates. These compounds are the most thoroughly examined group of N-oxides, and extensive series of various types of substituted quinoline N-oxides (Tables IV–VIII) show the very general character of most of the observed reactions.

With the background of the light-induced oxaziridine formation in the nitrone series, it was suggested in several papers (see, e.g., ref 147–149, 152) that the first step in the light-induced rearrangements of quinoline N-oxides (183), as well as of the other aromatic amine N-oxides,[91,134,158,174,180,187,189,191,-192,195,197,200] was the formation of an oxaziridine (e.g., 184). As will be shown below, most of the rearrangement products can be explained as arising from 184 by processes accepted in ground state mechanistic organic chemistry. The proposed oxaziridine formation, however, deserves further comment, since all attempts to observe oxaziridines in the photolysis of quinoline N-oxides, as well as other aromatic amine N-oxides, have been unsuccessful. This failure to isolate the oxaziridine intermediates can be explained in several ways.[163]

(1) The oxaziridines may be thermally too unstable to isolate, but are photochemically stable when Pyrex-filtered light (or the least energetic light able to bring about reaction with aromatic amine N-oxides) is employed. If this is the case, low-temperature photolysis combined with spectroscopy should be of great help in demonstrating intermediate oxaziridine formation.

(2) Excited atomic arrangements corresponding to oxaziridines may be on the reaction pathway, but only as transition states or species with a very short lifetime.

(3) Oxaziridines may be formed, but break down photochemically with a quantum yield equal to or greater than that for their formation.

(4) Oxaziridines are not formed as intermediates, and an entirely different mechanism is operating.

The proposed intermediate oxaziridines formed from quinoline N-oxides must of necessity possess a 2-phenyl (or aryl) substituent, with various other substituents in the 3 position. According to Emmons,[87] 2-phenyloxaziridines are rather unstable, although they can exist. From the work of Kaminsky and Lamchen,[92,107] it can be inferred that bicyclic oxaziridines are more stable than monocyclic ones. There is thus, a priori, no reason why some of the presumed oxaziridines (184) should be too unstable to be observed in solution at low temperature, and experiments to clarify this possibility are currently under way. Thus it was found, in some preliminary experiments,[210] that irradiation of 2-phenylquinoline N-oxide (109a) at −190° in an ethanol glass resulted in a change from colorless to reddish. The reaction mixture, upon heating, turned yellow (recooling did not influence this color) and a thin layer chromatographic analysis showed that the expected benz[d][1,3]oxazepine (111a) was formed. This experiment clearly indicates the existence of a thermally unstable species, perhaps the oxaziridine (110a). The formation of N-aminocarbostyrils by photolysis of 2-cyano-4-methylquinoline N-oxide in the presence of amines is also indicative of oxaziridines as primary products.[167]

If, however, the oxaziridines cannot be characterized even at low temperatures, this may indicate that they are formed, but with so much thermal energy that they immediately break down. The difference between this view and the possibility

that a transition state with an oxaziridine-like atomic arrangement occurs is, of course, rather subtle. However, such a mechanism is consistent with currently known facts.

There have recently been several reports[89,91–94] dealing with photolysis of oxaziridines. In two of these reports the formation of nitrenes was inferred[93,94] and products different from the thermolysis products were obtained. In a third paper[92] products analogous to those obtained by thermolysis were found, and it was shown that much longer irradiation times were necessary to convert the oxaziridines than to convert the corresponding nitrones to the oxaziridines. Furthermore, the oxaziridines examined in the latter paper were said to show absorption only in the vacuum uv range. The oxaziridines from quinoline N-oxides would be expected to exhibit uv maxima at much shorter wavelengths than the N-oxides; e.g., the oxaziridine that could be formed in the photolysis of quinoline N-oxide would be expected to exhibit a uv spectrum similar to that of styrene. However, the photolysis of quinoline N-oxide in ether proceeds in good yield when 3500-Å light is employed.[149] Since styrene itself has no uv maximum at a wavelength longer than ca. 2900 Å (ϵ 15, in isooctane, ref 208, p 505), it is quite unlikely that the hypothetical oxaziridine from quinoline N-oxide would be photolyzed at a rate equal to or greater than the rate of photolysis of quinoline N-oxide itself under these conditions. A mechanism of this sort is difficult to rule out completely, however, since quinoline N-oxide or quinoline formed during the photolysis, etc., could act as a triplet sensitizer for oxaziridine photolysis. Here also further experiments are indicated.

We will thus tentatively adopt the oxaziridine hypothesis and proceed to explain the formation of the various rearrangement products found in the photolysis of quinoline N-oxides. *From this discussion it will emerge that the large majority of these results can be explained by invoking four pathways from the oxaziridines, i.e. paths a–d.*[164] Similar pathways are proposed for the other series of aromatic amine N-oxides.

The two general rearrangements of quinoline N-oxides observed upon photolysis lead to carbostyrils (187, 189, or 190) and benz[d][1,3]oxazepines (192); the latter type of compound often leads to further products via subsequent thermal reactions. A reaction scheme which accounts for the observed carbostyrils is shown in Scheme XI.

Path a is believed to involve formation of the zwitterion 185–186. This ion can now rearrange by the indicated 1,2 shifts. The C,N shift has only been observed for two quinoline N-oxides, namely 2-methyl- (98a) and 2,4-dimethylquinoline N-oxide (98c) (Table V). Unfortunately, in each case, the solvent employed was absolute methanol, which casts some doubt on the origin of the N-methyl group.

The C,C shifts have been observed in 183 with X^1 = CH_3 (Table V), X^1 = C_6H_5 (Table VI), and X^1 = Cl or p-CH₃-C_6H_4S (Table VIII), with the highest yield of rearrangement product found for X^1 = Cl (70%).

Similarly, in the series with X^1 = H, both types of rearrangement may occur. The fate of the 2-hydrogen atom is uncertain in these cases, and it may be that another type of rearrangement is involved.[149]

Although it is known that 1,2-migration can take place during homolytic reactions, alkyl shifts are extremely unlikely under these conditions, whereas the types of shift observed are in good agreement with the ionic mechanism proposed.[211]

(210) O. Buchardt, N. Harrit, and V. H. Madsen, unpublished results.

(211) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, Inc., New York, N. Y., 1959, p 755.

Scheme XI

183 → 184

185 ↔ 186 ↔ 185 → path a

187 186 path b

188 X²=H → 189

188 X¹=H → 190
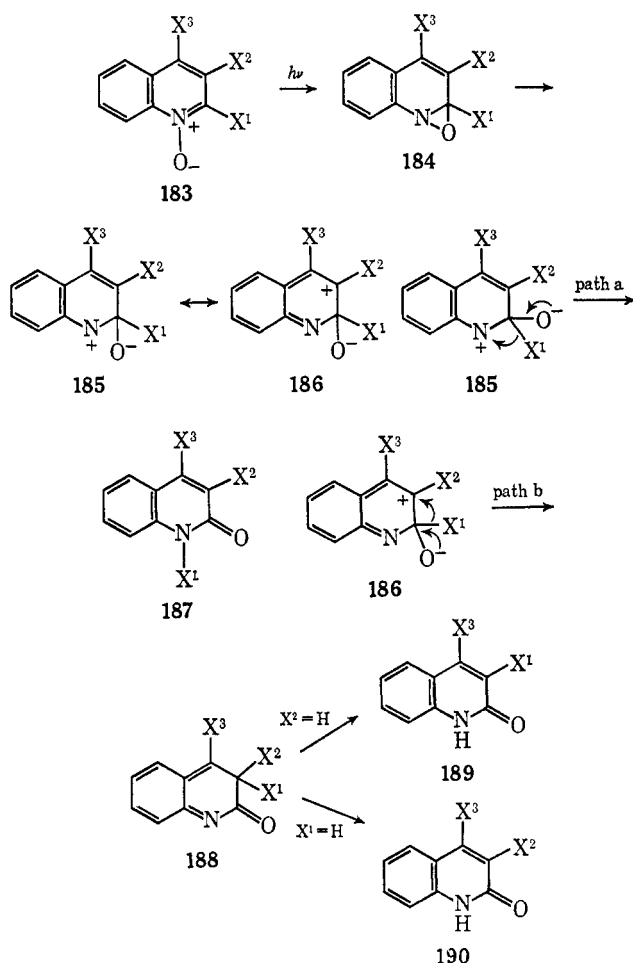
Very similar mechanisms have been suggested for the nitrone → oxaziridine → amide rearrangements.[89,107] It should be noted that protonation of the –O⁻ group may take place during these rearrangements.

Previously (*e.g.*, ref 161) the benz[*d*][1,3]oxazepines **192** were believed to arise as a result of attack by the –O⁻ group on the C-3 atom in the zwitterion **186**. Although it cannot be excluded with certainty that formation of the benz[*d*][1,3]-oxazepines (**192**) takes place *via* zwitterionic intermediates or *via* free radical species,[178] it seems attractive to formulate the reaction as a symmetry-allowed thermal [1,5]-sigmatropic shift[163,212] to **191** (Scheme XII). Analogies for the **184** → **191** rearrangement have recently been discussed in related sys-

Scheme XII

path c

184 → 191 ⇌ 192
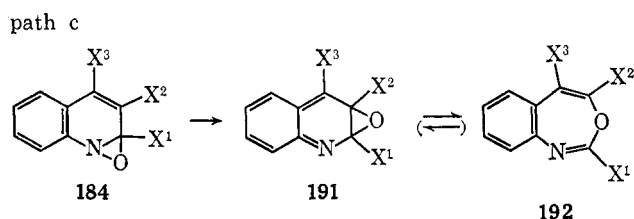
tems.[213] The similarly allowed thermal rearrangement of **191** to **192** has many precedents.[214,215]

From the spectra of the compounds **192** there is no indication that oxiranes (**191**) are present.[161] This fact is in good correspondence with observations on the closely related benz-[*d*]oxepines, where it can be inferred that the energy barrier between the two forms is appreciably higher than in the monocyclic benzene oxide–oxepine system, where a rapid valence-tautomerization has been well established.[214,215] However, at least in some of the 2-cyanobenz[*d*][1,3]oxazepines, the very easy transformation to 2-cyano-3-hydroxyquinolines[166] (Table VII) may take place *via* the oxirane isomers **191**. Only when the seven-membered ring is substituted with strongly electron-withdrawing substituents (Tables VI and VII) are the benz-[*d*][1,3]oxazepines stable enough to be isolated and characterized. However, the benz[*d*][1,3]oxazepines from 2-methyl-and 2,4-dimethylquinoline N-oxide have been observed as transient intermediates.[154,158] The less stable benz[*d*][1,3]-oxazepines are very reactive toward water, and their hydrolysis products have usually been isolated.

The very high reactivity of these compounds with water is reasonable, since the benz[*d*][1,3]oxazepines (**192**) can also be regarded as imido esters of enols, a class of compound which apparently has not previously been described. Attack of water presumably would result in ring opening to **193**, which can cyclize to the N-acyl-2-indolinols (**194**).[161]

192 → H₂O → 193 ⇌ 194
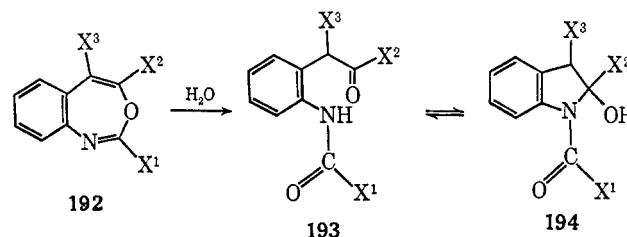
One of the more salient features in the photolysis of the quinoline N-oxide series is the solvent effect. By comparing Tables IV–VII it is seen that polar protic solvents favor carbostyril formation, whereas nonpolar aprotic solvents favor benz[*d*][1,3]oxazepine formation. The above mechanistic interpretation is in good agreement with this observed solvent effect. In polar protic media the zwitterionic species, and the transition states leading to these, are expected to be energetically more favored than in nonpolar protic media.

The formation of 3-phenyl-2-indolecarboxaldehyde (**118**) in the photolysis of 4-phenylquinoline N-oxide (**109j**) is depicted as taking place *via* the nitrene **195** (Scheme XIII, path d). This is the only example of such a reaction in the quinoline N-oxide series,[163] although it has ample precedent in some of the other series (see discussion below of the phthalazine, pyridine, and pyridazine series). It should be noted that this mechanism is analogous to the formation of phenylnitrene and oxo compounds in the photolysis of some oxaziridines.[94] This ring contraction could also be explained by assuming formation of the benzoxazepine **197** which presumably would be in equilibrium with **110j**. This benzoxazepine could then undergo a light-induced [1,3]-sigmatropic shift[213] to **196**, etc.

In the photolysis of the 2,3-cycloalkenoquinoline N-oxides (**120** and **122**) a new type of isolable product (**121**, **124**) was
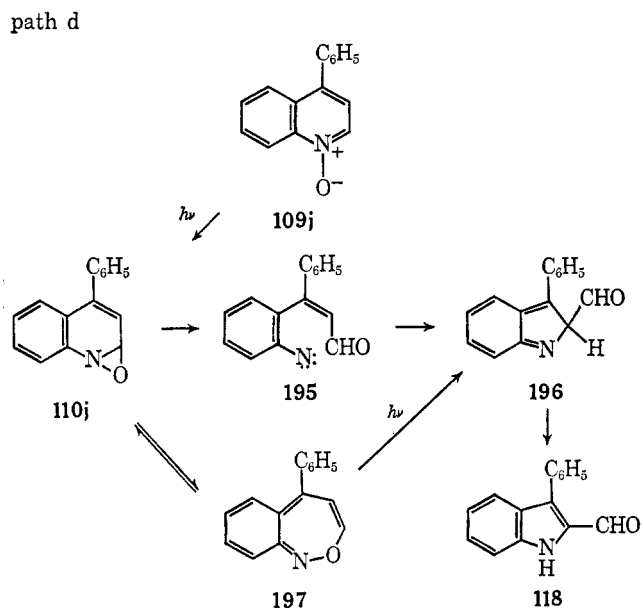
(212) See R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968), for a recent survey.

(213) J. A. Berson, *ibid.*, **1**, 152 (1968).
(214) E. Vogel and H. Günther, *Angew. Chem.*, **79**, 429 (1967).
(215) G. Maier, *ibid.*, **79**, 446 (1967).

Scheme XIII

path d

109j

110j → 195 → 196

197 → 118

encountered.[162] Since it has been shown[163] that the thermolysis of stable benz[*d*][1,3]oxazepines can lead to 3-acylindoles, the formation of compounds **121** and **124** presumably occurs *via* the indicated path (Scheme XIV).[162] Having thus accounted

Scheme XIV

120, *n* = 3
122, *n* = 4

121, *n* = 3
124, *n* = 4
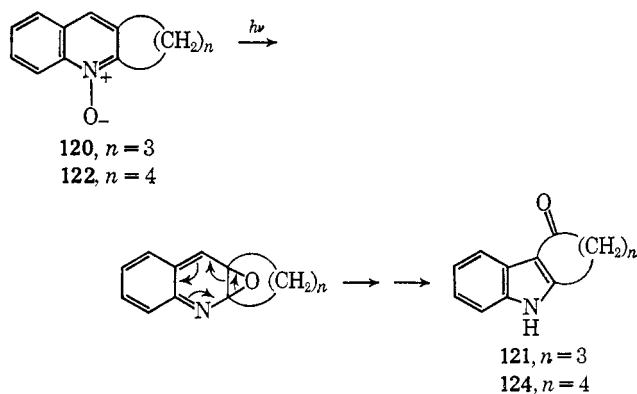
for most of the isolated major products in the photolysis of quinoline N-oxides, we will proceed to comment on some of the minor products (Scheme XV). In some cases (Tables IV and V) N-acylindoles (**198**), indoles (**199**), and 2-(N-acylamino)-benzaldehydes or related ketones (**200**) have been generated in the photolysis of quinoline N-oxides. The N-acylindoles undoubtedly are formed by dehydration of the N-acylindolinols (for another explanation see ref 148, 152); in some instances hydrolysis occurs accounting for the observed indoles (**199**). The 2-(N-acylamino)benzaldehydes or related ketones (**200**) are probably formed in a light-induced oxidation of the N-acylindoles (**198**).[154]

In a secondary photochemical process,[149,150] photodimers of carbostyrils with hydrogen in the 3 and 4 positions are often formed during the photolysis of the corresponding quinoline N-oxides. If the irradiation of a quinoline N-oxide is pro-

Scheme XV

194 → 198

200

199
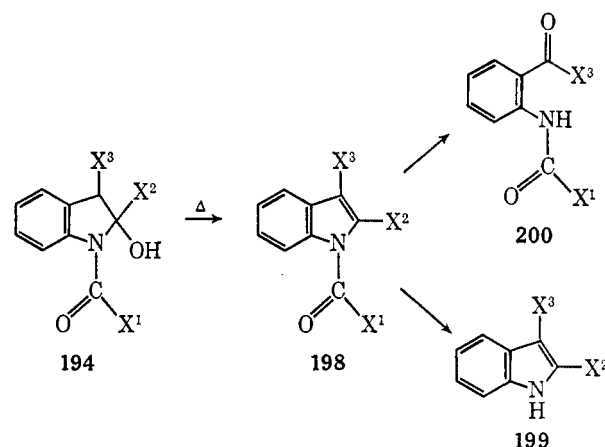
longed it is possible to isolate all of the initially formed carbostyril in the form of its photodimer (*cf.* Table IV).

The light-induced formation of N-aminocarbostyrils (**119**) from 2-cyano-4-methylquinoline N-oxide (**116c**) and amines (Table VII) was regarded as good evidence for an oxaziridine intermediate (**201**) by Kaneko, *et al.*[167] This very interesting reaction does look as though an intermediate has been intercepted, but this could formally be the zwitterion **202** (Scheme XVI).

Scheme XVI

116c → 201

202

119
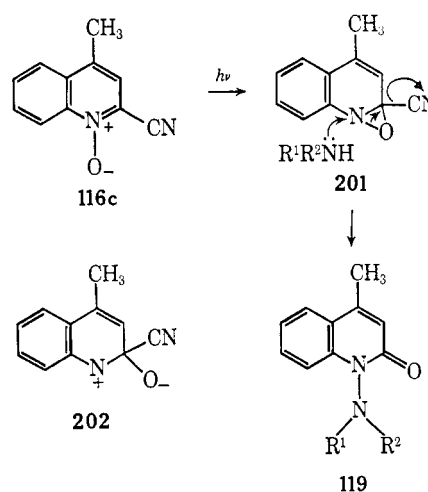
The present discussion is primarily concerned with reactions that alter the N$^+$-O$^-$ function, and therefore the mechanisms proposed for the light-induced reactions of 4-nitro-[144] and 4-azidoquinoline N-oxides[145] will not be reviewed here.

Comparison of the light-induced reactions of quinoxaline mono N-oxides (**169**) with those of quinoline N-oxides shows them to be very similar, and an analogous explanation accounts for the observed results (Scheme XVII).[197]

By analogy with the quinoline N-oxides, it is proposed that deoxygenation takes place from one excited state and that the other reactions observed take place from another excited state, possibly *via* an unstable oxaziridine (**177**). Quinoxalone (**170**) formation has only been observed with R′ = H. No evidence for valence tautomerization between the possible

Scheme XVII

Scheme XIX
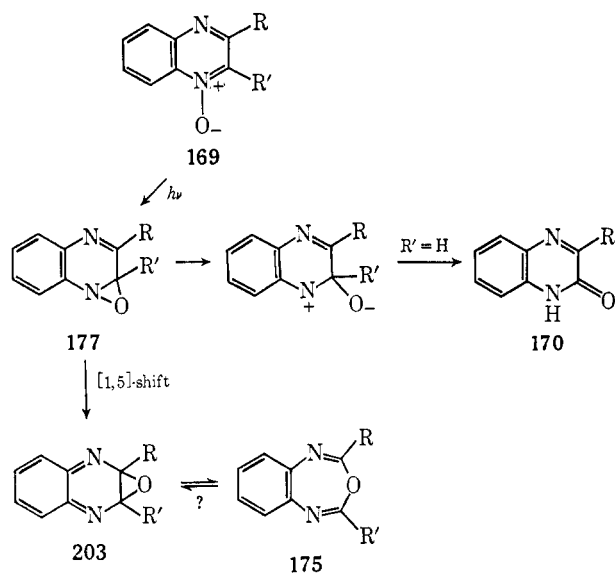
oxirane intermediate (203) and the benz[*d*][1,3,6]oxadiazepine (175) has been found. As with the quinoline N-oxides, the presence of strongly electron-withdrawing substituents was necessary for isolation and characterization of the seven-membered ring compounds (Table XI). The benz[*d*][1,3,6]-oxadiazepine (175b or c) obtained in the photolysis of either of the two phenylquinoxaline N-oxides (169b or c) was rather unstable, and hydrolyzed easily to N-benzoyl-N'-formyl-*o*-phenylenediamine (176).[162]

The results obtained with quinoxaline N,N'-dioxides are at present very limited (Table XI).

A free radical mechanism (Scheme XVIII) was proposed to

Scheme XVIII
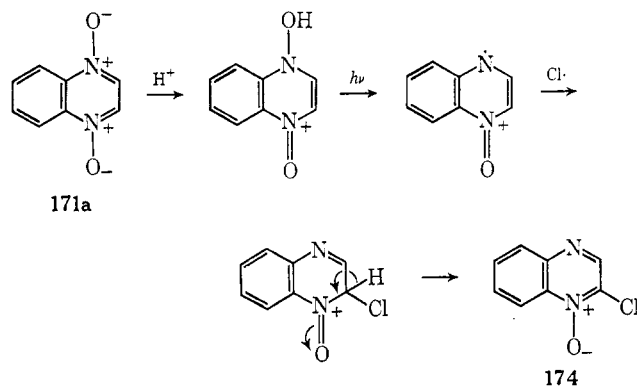
explain the formation of 2-chloroquinoxaline N-oxide (174) by photolysis of quinoxaline N,N'-dioxide (171a).[194]

The light-induced rearrangement of 2-benzoyl-3-phenyl-quinoxaline N,N'-dioxide (171b) to 1,3-dibenzoylbenzi-midazolone (178) was proposed to involve a double N-oxide → amide rearrangement *via* intermediate oxaziridines[198] (Scheme XIX). An alternative interpretation, which has the advantage of accommodating the observed exclusive rearrangement of the acyl groups, would involve attack by the
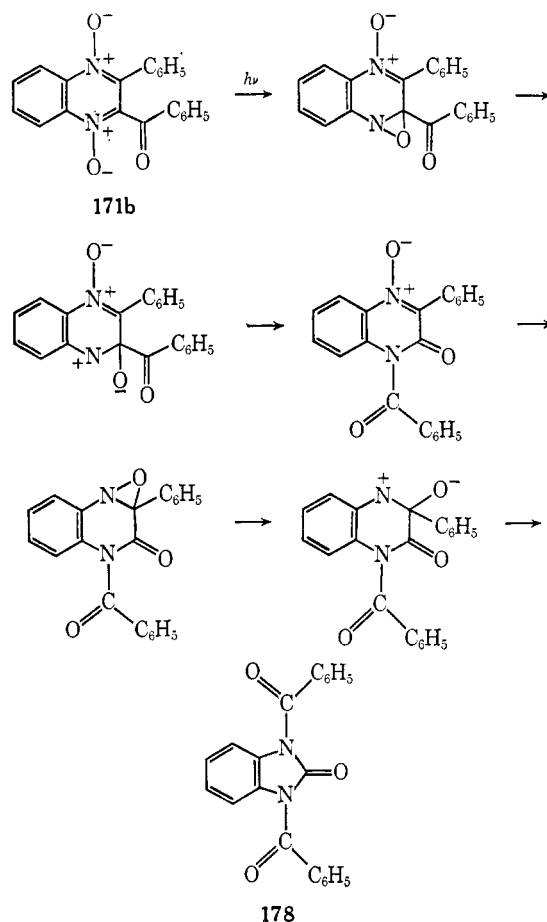
nitrogen atom of the intermediate oxaziridine upon the adjacent carbonyl (see Scheme IX).

The results obtained in the photolysis of isoquinoline N-oxides (131, Table IX) seem to be closely related to those from quinoline N-oxides. For these light-induced rearrangements the following reaction scheme (Scheme XX) is seen to account for the observed products. Only when X^1 = H or CH_3 has isocarbostyril (134) formation been observed.

The benz[*f*][1,3]oxazepines (132) were stable enough to isolate only when X^1 was strongly electron withdrawing (X^1 = C_6H_5 or CN). When the benz[*f*][1,3]oxazepines were unstable, either the hydrolysis products 136 or further degradation products (206) were observed (Table IX). The thermally stable benz[*f*][1,3]oxazepines (132) reacted similarly upon solvolysis in aqueous methanol.[173] Light-induced deoxygenation in this series is also supposed to take place from an excited state different from that leading to the rearrangements.[176] Solvent dependence is rather analogous to what was found for quinoline N-oxides,[176] and probably for similar reasons. Contrary to what was found for the benz[*d*][1,3]oxazepines (192) and the benz[*d*][1,3,6]oxadiazepines (175), which were stable to Pyrex-filtered light, it was found that a secondary light-induced reaction took place for the benz[*f*][1,3]oxazepines (132). The products in the latter reaction have been identified as benzofuro[2,3-*b*]azete derivatives (137) in two cases.[177]

The photolysis of quinazoline N(3)-oxides (see Table XI) proceeds analogously to the photolysis of isoquinoline N-oxides, and a similar mechanism is probably operative.

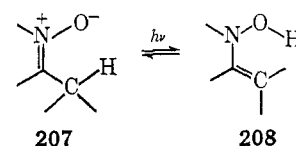Phenanthridine N-oxides (138) upon photolysis undergo

Scheme XX

Scheme XXI
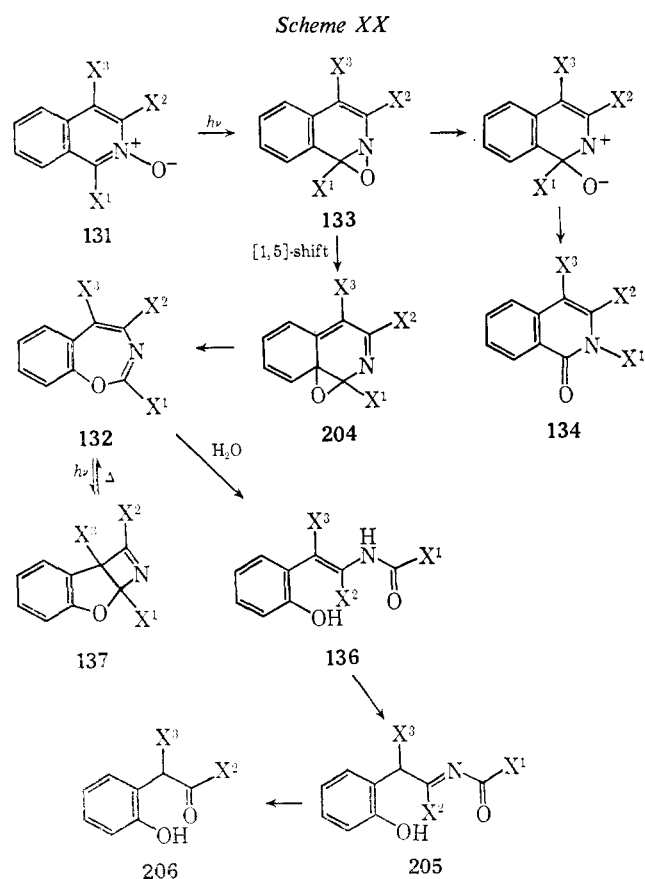
deoxygenation and rearrangement to phenanthridin-6 (5H)-ones (140) in alcoholic solution.[148, 178, 181] In benzene the usual solvent effect operated. Thus irradiation of 6-phenylphenanthridine N-oxide (138c) in benzene solution led to deoxygenation and rearrangement to 140c, 2-phenyldibenz-[d,f][1,3]oxazepine (141c), or its hydrolysis product (143c), and 9-benzoylcarbazole (142c).

Two photochemical experiments on phenanthridine N-oxides have led to the proposal of a free radical mechanism to explain the formation of compounds 140–142.[178] When partially resolved 6-(1-phenylpropyl)phenanthridine N-oxide (138d) is irradiated, the 5-(1-phenylpropyl)phenanthridin-6(5H)-one (140d) isolated is totally racemic. This seems to indicate that the migrating group R is either a planar species or a species that can rapidly invert about the α-carbon atom. When 6-benzhydrylphenanthridine N-oxide (138e) is irradiated, two of the isolated products are 1,1,2,2-tetraphenylethane (15.8%) and phenanthridin-6(5H)-one (140a, 17.2%). It was proposed that 1,1,2,2-tetraphenylethane is formed by dimerization of a benzhydryl radical and that phenanthridin-6(5H)-one (140a) is formed by extraction of a hydrogen from the solvent (slightly wet benzene) by a phenanthridin-6(5H)-onyl radical, formed by escape of the benzhydryl radical from the solvent cage. A mechanism was proposed to explain these results, involving oxaziridine formation, homolysis of the N–O bond, and rearrangement via three paths to compounds 140–142 (Scheme XXI).

These results can also be explained by the usual mechanism with the exception of the formation of 9-benzoylcarbazole (142c). The loss of optical activity in the rearrangement of 138d to 140d could also be explained by assuming the photo-

equilibrium 207 ⇌ 208.[216] It seems reasonable that formation of free radicals takes place upon irradiation of the 6-benzhydrylphenanthridine N-oxide (138e), owing to the stable character of the benzhydryl radical, thus rendering this N-oxide, and presumably similar types, i.e., benzyl derivatives,


etc., special cases. The quantum yields for phenanthridone formation have been found to vary between 0.06 and 0.37.[180]

The photolysis of acridine N-oxide (144) in methylene chloride results in the formation of 145.[182] This rearrangement is analogous to the formation of 3-acylindole derivatives in the photolysis of certain quinoline N-oxides (vide supra) and a similar reaction mechanism is proposed.

The photolysis of acridine N-oxide (144) in methanol or ethanol results in addition of solvent with formation of 146,[183a] previously described as 9-alkoxy-N-hydroxyacridines.[183b] The suggested mechanism is indicated in Scheme XXII. However, it should be noted that the intermediacy of 209 is not necessary for formation of 210. Compound 210 could be formed from the oxaziridine corresponding to 144 by two successive [1,5] shifts.

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(216) M. G. Ettlinger, personal communication.

Scheme XXII
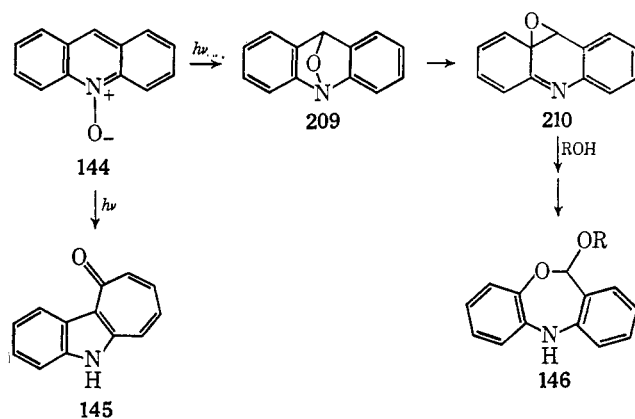

Only one compound has been examined in the phthalazine series. Photolysis of 1,4-diphenylphthalazine N-oxide (152) gave 1,3-diphenylisobenzofuran (153), 1,2-dibenzoylbenzene (155), the parent amine, an unidentified amorphous substance, and nitrogen.[189] From the proposed mechanism below (Scheme XXIII), it is seen that the first steps are consistent

Scheme XXIII
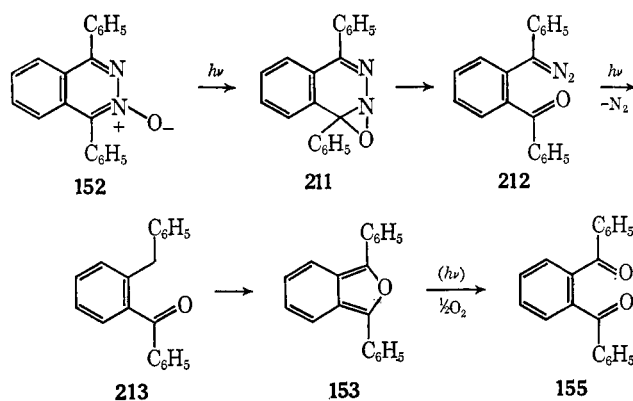
with the general mechanism (path d). This case also provides one of the best examples of the influence of oxygen. When oxygen is carefully excluded, no deoxygenation of the amine N-oxide (152) takes place, whereas appreciable amounts of the parent amine are formed in the presence of oxygen.[189] It was postulated by analogy with the previous discussion that the first step in the photolysis is oxaziridine (211) formation. The next step is rearrangement of 211 to the diazo compound 212, which in turn may react further under irradiation, giving the carbene 213. Ring closure of the carbene leads to 1,3-diphenylisobenzofuran (153). In acetone, some oxidation of 1,3-diphenylisobenzofuran takes place even after very careful deoxygenation by flushing with purified nitrogen. This oxidation may be due to residual traces of oxygen (very dilute solutions were irradiated), since it is known that 1,3-diphenyl-isobenzofuran (153) is easily photooxidized.[217] On the other hand, it is possible that acetone, in the presence of small amounts of water, may have functioned as the oxidizing agent

under the irradiation conditions. The very low yield of iso-benzofuran reported[189] was later shown to be due to the method of purification, *i.e.*, preparative thin layer chromatography. If the photolysis of 1,4-diphenylphthalazine N-oxide (152) was carried out in ether–pentane, an almost quantitative yield of 1,3-diphenylisobenzofuran (153) was
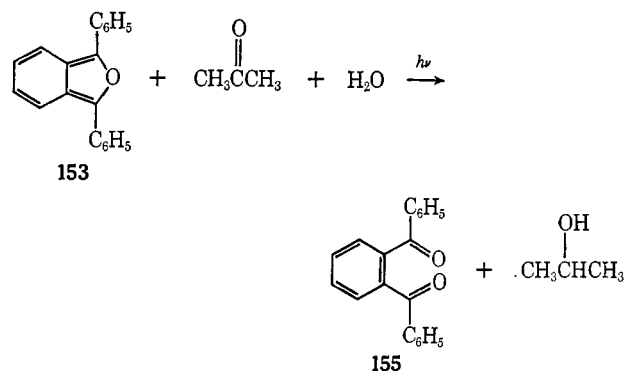
obtained.[186] In order to test for possible oxaziridine (211) formation in this case, low temperature photolysis ($\sim$77°K) was carried out in an ether–pentane matrix. The irradiation was continued twice as long as was necessary for total conversion under otherwise similar conditions at room temperature. A yellow color developed, which was similar to that formed in the room temperature photolysis of 1,4-diphenyl-phthalazine N-oxide (152). When the light was turned off, a green-yellow phosphorescence was observed. A similar phosphorescence was observed when a sample of 1,3-di-phenylisobenzofuran (153) was irradiated under similar conditions. Warming of the irradiated matrix of the N-oxide to room temperature produced no visible changes. Thin layer chromatography showed the presence of only starting material and 1,3-diphenylisobenzofuran (153). From these results it is concluded that either the hypothetical oxaziridine 211, if formed at all, reacts further photochemically (by comparison with benzophenone hydrazone ($\lambda_{max}^{Et_2O-pentane}$ 273 nm, log ϵ 4.01),[186] 211 would be expected to absorb in the 2800-Å region), or 211 is so unstable that the diazo compound 212 is formed thermally even at this very low temperature. The well-known photoreactivity of diazo compounds accounts for the postulated carbene 213, which again would be expected to be a highly energetic intermediate that would close to 1,3-diphenylisobenzofuran (153) in a fast reaction even at low temperature. Nitrogen evolution was shown to take place. The formation of the diazo compound 212 can also be explained as taking place from a zwitterion.[189] Shortly after these findings, the related diazo compound was detected in the photolysis of 3,6-diphenylpyridazine N-oxide, thus substantiating the proposed mechanism (*vide supra*) (*cf.* ref 120b).

The purine N-oxides (179) which have been subjected to photolysis represent an interesting change in reaction pathway. By comparison with isoquinoline N-oxides and quinazoline N(3)-oxides, it would be expected that rearrangement would proceed *via* attack of –O⁻ at the 6 position and not, as observed, by attack at the 2 position. No obvious explanation for this difference can be offered. Again an initial oxaziridine-zwitterion type mechanism will account for the rearrangement of 179 to 180. It is possible that at least when $X^1 = NH_2$, 180 is formed wholly or partially from 182, which can be converted to 180, and which in some cases has been

(217) A. Schönberg, "Präparative Organische Photochemie," Springer-Verlag, Berlin, 1958, p 67.

observed as a product in these photolyses under neutral or acidic conditions.[202]

The photochemistry of monocyclic aromatic amine N-oxides has not been studied as extensively as that of the fused ring systems. In most cases reported, however, deoxygenation to the parent amine has been observed, and in accordance with the previous discussion, it is assumed that deoxygenation takes place from one excited state and rearrangements from another. By analogy with the previously discussed light-induced rearrangements, it is believed that the first step is the formation of an intermediate oxaziridine. Because the light-induced reactions in the monocyclic series have not been very extensively studied, and because two oxaziridine intermediates are possible in many instances, it is more difficult to present a general mechanistic approach. Furthermore it appears that more pathways for reactions are operating in these series than in the ones previously discussed.

In the pyridine N-oxides (214) several rearranged products have been observed. Streith, et al.,[184] have proposed that the first step in these rearrangements is the formation of oxaziridines (215, 216). The oxaziridines were then depicted as undergoing valence-tautomerization to 1,2-oxazepines (217, 218), analogous to the benzene oxide–oxepine isomerization (Scheme XXIV).[214,215]

Scheme XXIV
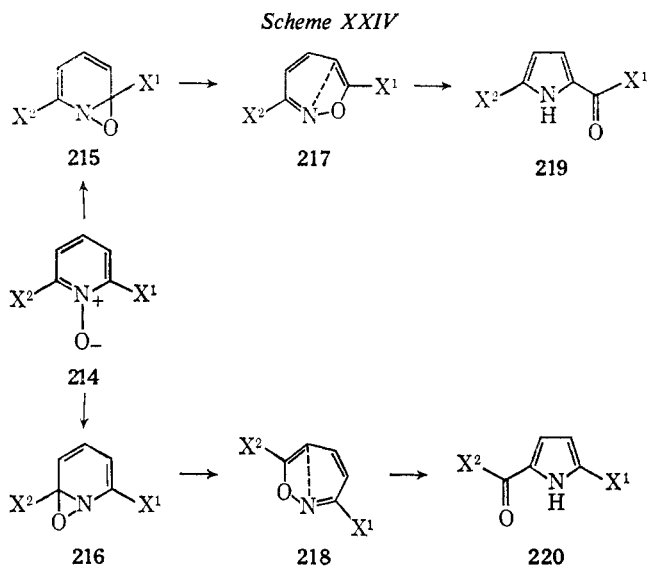
Further rearrangement involving "*l'hypothèse d'une deuxième tautomérie de valence de "l'oxazepine"* (217, 218 here) *aboutissant à un cycle à cinq chaînons, suivie d'une prototropie,"* would account for the formation of the pyrrole derivatives 219 and/or 220. This proposal is reasonable if the ring contraction (a [1,3]-sigmatropic shift[212]) is taken to be photochemical (217 and 218 should absorb at long enough wavelengths). Here, in contrast to the quinolines, etc., formation of the 1,2-oxazepines does not involve loss of aromaticity in a second ring (cf., however, footnote 4 in ref 212). The very recent results obtained in the pyridazine N-oxide series[185] (see below) indicate that another pathway may exist for the formation of 2-acylpyrroles (219, 220). This involves formation of an intermediate nitrene (222 from 215), which upon ring closure and tautomerization would give 219 (path d, Scheme XXV). The formation of nitrenes and ketones from oxa-

Scheme XXV
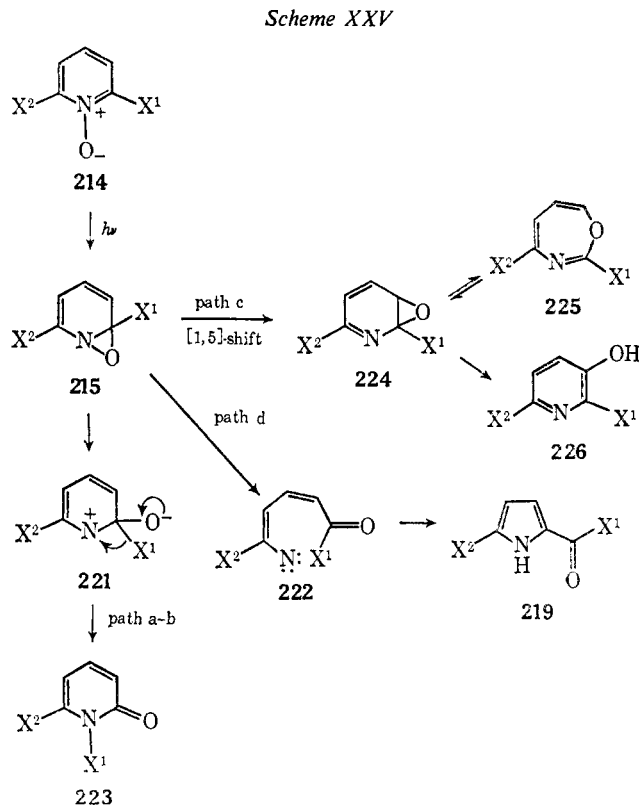
ziridines upon photolysis was recently reported.[94] However, by analogy with the previous discussion concerning quinoline N-oxides, a secondary photochemical process involving an intermediate oxaziridine seems unlikely. To account for the formation of various minor products, it can be assumed that a competing process involving the zwitterion 221 is operating (for simplicity only one of the possible oxaziridines, *i.e.*, 215, is discussed, but it is, of course, to be expected that all of these steps can take place analogously, starting with 216). The zwitterion can react further, analogously to what has been suggested previously for the fused ring systems (paths a–b), giving pyridones (223) (so far observed only for X[1] = H, X[2] = CH$_3$ in 214). The indicated [1,5]-sigmatropic shift (path c) would give the oxiranes 224, possibly in equilibrium with 1,3-oxazepines (225). Evidence for the intermediate existence of 224–225 is found in the recent observation[186,188] that 3-hydroxypyridines (*e.g.*, 226) are formed as minor products in the photolysis of pyridine N-oxides. In the photolysis of 2,4,6-triphenylpyridine N-oxide (73g) there was found, *inter alia*, a compound that may have the corresponding 1,3-oxazepine structure (82, Table III).[188] The observed formation of acetals of N-formylpyrrole (81) in the photolysis of pyridine N-oxide in methanol or ethanol[187] can also be regarded as confirmatory evidence for the intermediacy of 1,3-oxazepines (225), since it has previously been reported[156,163] that 2-phenylbenz[*d*][1,3]oxazepine, upon treatment with boiling alcohols, forms an analogous compound (227).
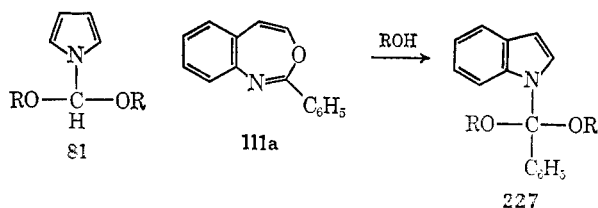
The formation of trace amounts of N-formylpyrrole (**80**) in the photolysis of pyridine N-oxide (**73a**) in methanol or ethanol was ascribed[187] to the hydrolysis of **81**. The formation of N-acylindoles from benz[d][1,3]oxazepines in the quinoline N-oxide series is well established,[161] however, and a similar mechanism cannot with certainty be excluded in the pyridine N-oxide series. It is well known[218] that N-acylpyrroles easily rearrange in thermal reactions to 2-acylpyrroles. It is interesting that in every case where either X^1 or X^2 = H, no 2-acylpyrroles other than 2-formylpyrroles have been isolated (Table III). The material balance was poor in these cases, and repetition of most of these photolyses will probably give more insight into the reactions involved.

The mechanism involved in the light-induced processes of 4-nitro-, 4-nitroso-, 4-hydroxylamino-, and 4-azidopyridine N-oxides will not be discussed here since this review is primarily concerned with changes involving the N^+-O^- function (for mechanistic interpretations, cf. ref 142–145).

The photolysis of 3,6-diphenylpyridazine N-oxide (**147f**) proceeds in a very interesting manner.[185] During irradiation of **147f**, an intense yellow color (bright even with 5×10^{-4} M N-oxide, λ_{max}^{MeOH} 410 nm) developed within a minute and persisted until no more starting material could be detected by thin layer chromatography. The color, which is ascribed to the diazo compound **150**, faded gradually when the photolysis was interrupted and the sample kept in the dark. The colored species, owing to its instability, has not been isolated. However, irradiation of a 10% chloroform solution of 3,6-diphenylpyridazine N-oxide (**147f**), followed by immediate recording of the infrared spectrum of the yellow solution, showed the appearance of a sharp absorption at 2070 cm^{-1}, in the specific region (2040–2120 cm^{-1}) where diazo compounds absorb. If this yellow solution was kept in the dark until it became colorless, the absorption at 2070 cm^{-1} disappeared. This observation is regarded as good evidence that photolysis of 3,6-diphenylpyridazine N-oxide produces the diazo compound **150**. A mechanism (Scheme XXVI), analo-

diphenylphthalazine N-oxide (Scheme XXIII) and of 3,6-diphenylpyridazine N-oxide (Scheme XXVI). Isomerization of the diazo compound **150** via the tautomeric 3H-pyrazole (**229**) to 3-benzoyl-5-phenylpyrazole (**149f**), the main product isolated upon completion of the photolysis of **147f**, is analogous to the well-known isomerization of vinyldiazomethane to pyrazole (see footnote 10 in ref 185).

It seems reasonable to assume that loss of nitrogen occurs from the diazo compound **212** because the thermal cyclization (analogous to the process **150** → **229**) is energetically unfavorable. It is possible that some of the minor products observed in the photolysis of 3,6-diphenylpyridazine N-oxide (**147f**) arise by loss of nitrogen from the diazo compound or the 3H-pyrazole derivative (cf. footnotes 12 and 13 in ref 185). In the light-induced reactions of five other pyridazine N-oxides (**147a–e**, Table X), only trace amounts of compounds **149** were found. However, a poor material balance was obtained (<35%). A free radical mechanism for the formation of the hydroxymethylated pyridazines (Table X) was suggested[187] (Scheme XXVII).

Two pyrazine N-oxides (**164a,b**) have been subjected to photolysis (Table XI). The results from these were explained[192] by mechanisms involving seven-membered ring tautomers of the initial oxaziridines, analogous to those suggested for pyridine N-oxides.[134] The mechanism suggested (Scheme XXVIII) for the reactions leading to 2-acylimidazoles (**165**) is consistent with mechanisms previously suggested for 2-acylpyrrole formation from pyridine N-oxides, and 3-acylpyrazole formation from pyridazine N-oxides. Decarbonylation of **234**, **165**, or **235** accounts for the formation of **166**.[192] To explain the rest of the rearrangement products, the usual intermediates are assumed, and reactions analogous to those for the quinoxaline N-oxide series are proposed (Scheme XXIX).

It has been reported that phenazine N-oxide and phenazine N,N'-dioxide show M–CO peaks in their mass spectra. No analogous photochemical reaction has yet been reported.

VI. Mass Spectroscopy and Aromatic Amine N-Oxide and Nitrone Photochemistry

Aromatic amine N-oxides have been the subject of several recent examinations[219–228] by mass spectrometry. The possibility that some of the reactions of the positive ions of the aromatic amine N-oxides formed by electron impact in the mass spectrometer, and of the electronically excited species formed by the action of light, could be correlated has been discussed.[224,227,228] From the currently known mass spectro-

Scheme XXVI
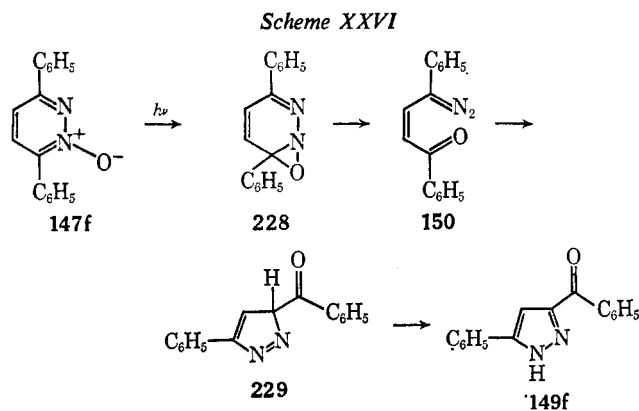
gous to the one via the hypothetical diazo compound **212** in the photolysis of 1,4-diphenylphthalazine N-oxide (**152**), is proposed; the actual observation of the transient intermediate in the pyridazine case is regarded as good evidence in favor of the mechanisms proposed for the photolysis both of 1,4-

(218) H. Fischer and H. Orth, "Die Chemie des Pyrrols," Vol. I, Akademische Verlagsgesellschaft M.B.H., Leipzig, 1934, p 31.

(219) T. A. Bryce and J. R. Maxwell, Chem. Commun., 206 (1965).
(220) R. Grigg and B. G. Odell, J. Chem. Soc., B, 218 (1966).
(221) Y. Morita, Chem. Pharm. Bull. (Tokyo), 14, 426 (1966).
(222) J. H. Bowie, R. G. Cooks, N. C. Jamieson, and G. E. Lewis, Aust. J. Chem., 20, 2545 (1967).
(223) S. M. Roberts and H. Suschitzky, Chem. Commun., 893 (1967).
(224) A. Kubo, S.-I. Sakai, S. Yamada, I. Yokoe, C. Kaneko, A. Tatematsu, H. Yoshizumi, E. Hayashi, and H. Nakata, Chem. Pharm. Bull. (Tokyo), 15, 1079 (1967).
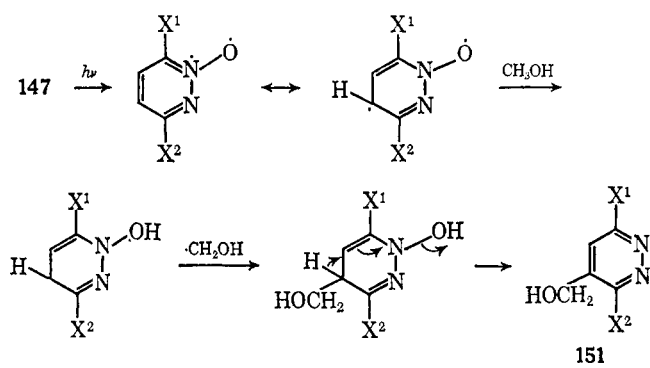(225) A. Tatematsu, H. Yoshizumi, E. Hayashi, and H. Nakata, Tetrahedron Lett., 2985 (1967).
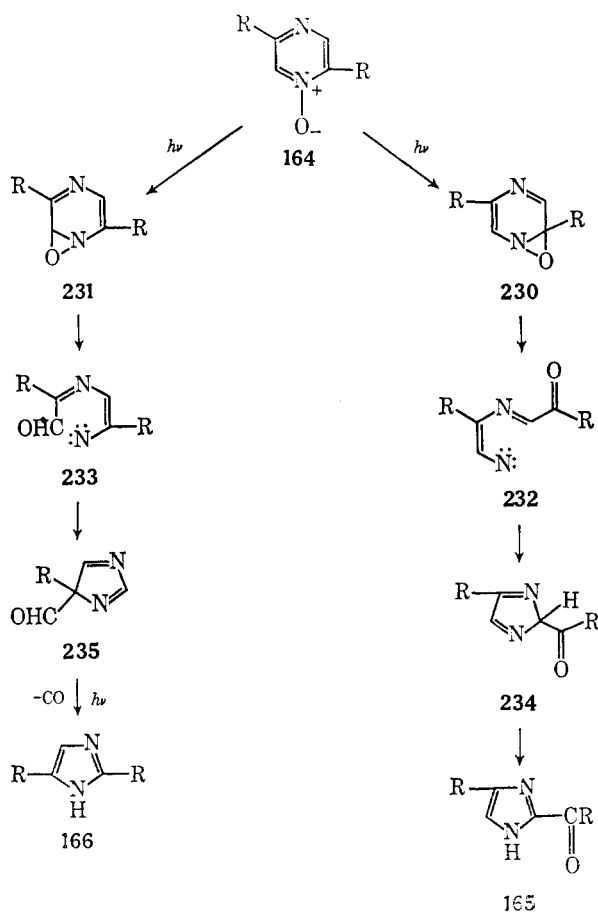(226) N. Bild and M. Hesse, Helv. Chim. Acta, 50, 1885 (1967).
(227) O. Buchardt, A. M. Duffield, and R. H. Shapiro, Tetrahedron, 24, 3139 (1968).
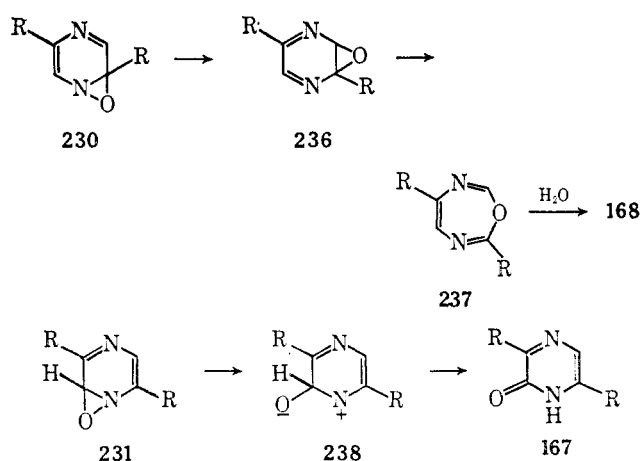(228) A. Kubo, S.-I. Sakai, S. Yamada, I. Yokoe, and C. Kaneko, Chem. Pharm. Bull. (Tokyo), 16, 1533 (1968).

Scheme XXVII

147 $\xrightarrow{h\nu}$ ⟷ $\xrightarrow{CH_3OH}$

$\xrightarrow{\cdot CH_2OH}$

151

Scheme XXVIII

164

$h\nu$ $h\nu$

231   230

233   232

235   234

166   165

$-CO \downarrow h\nu$

metric data it is apparent that the similarity between the reactions of the two types of excited states, if it is real at all,

Scheme XXIX

230   236

$\xrightarrow{H_2O}$ 168

237

231   238   167

exists only for the N-oxides without α-hydrogen-containing aliphatic substituents or phenyl substituents next to the N-oxide function. In some of these cases, however, striking similarities were observed. Thus quinoline N-oxide (**91a**) and isoquinoline N-oxide (**131a**) appear to follow the same fragmentation routes as their photoisomers, carbostyril (**92a**) and isocarbostyril (**134a**), respectively, upon electron impact.[227,228] This fact led to the postulation of oxaziridine ion formation in the electron impact induced fragmentation of these N-oxides.[206] It has been postulated,[224,228] on the basis of the similarity of the mass spectra of 2-cyanoquinoline N-oxide (**116a**) and 2-cyanobenz[d][1,3]oxazepine (**117a**), that the molecular ion of **116a** rearranges *via* an oxaziridine ion to the molecular ion of **117a**. In this case, as well as in all other reported mass spectra of aromatic amine N-oxides, loss of oxygen from the molecular ions was observed,[219–228] a process which also takes place in many instances on photolysis of these compounds. On the basis of the currently known facts, it may thus be concluded that some similarity seems to exist in the two types of processes for some of the N-oxides examined. Similar reactions were suggested in an attempt to correlate the electron impact induced reactions of nitrones with light-induced ones.[115–117] It should be remembered that the former take place in the gas phase, whereas the latter take place in solution. Thus it is doubtful whether there is more than a superficial analogy between the two types of processes.