

The Photochemistry of Imines

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1 Introduction

During the past two decades organic photochemistry has developed into a major branch of organic chemistry. Considerable advances have been made in understanding the mechanisms of light-induced reactions, particularly those of olefins¹ and carbonyl compounds,² and in exploiting these for synthetic purposes.³ Under photochemical conditions, a reacting molecule in the excited state has considerably more energy than in the ground state. This, allied to the alteration in electron density distribution which accompanies electronic excitation, typically causes it to undergo chemical reactions which are quite different from those encountered for ground-state reactions under thermal conditions.

This review is aimed at surveying the major photochemical reactions associated with the C=N group in imines. In general, attention has been confined to compounds which have alkyl, aryl, or acyl substituents at nitrogen. The photochemistry of hydrazones, azines, oximes and other classes of compounds containing the C=N—X grouping (where X represents a heteroatom) has been excluded, as has that of molecules containing the C=N group as part of an aromatic heterocycle. Mechanistic details are discussed where appropriate.

Nitrogen lies between carbon and oxygen in the Periodic Table and it might be expected that the photochemistry of the C=N chromophore would be intermediate between that of C=C and C=O. However, though some resemblances do exist, imine photochemistry differs in many respects from that of olefins and carbonyl compounds. For reasons of greater stability and ease of handling, most work in this area has been with C-aryl or N-aryl imines.

2 Excitation

Alkyl imines exhibit two major absorption bands in the u.v. region of the spectrum. The short-wavelength absorption at 170–180 nm is of high intensity and is believed to involve a $\pi \rightarrow \pi^*$ transition.⁴ The less intense band at 230–260 nm is considered to result from an $n \rightarrow \pi^*$ transition.⁴ The latter wavelength

¹ For a review of olefin photochemistry see J. D. Coyle, *Chem. Soc. Rev.*, 1974, 3, 329.

² For reviews of carbonyl photochemistry see (a) J. D. Coyle and H. A. J. Carless, *Chem. Soc. Rev.*, 1972, 1, 465; (b) N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, M. Niemczyk, and N. Schore, *Accounts Chem. Res.*, 1972, 5, 92.

³ For reviews of photochemical reactions in synthesis see (a) P. G. Sammes, *Quart. Rev.*, 1970, 24, 37; (b) T. Kametani and K. Fukumoto, *Accounts Chem. Res.*, 1972, 5, 212; (c) N. J. Turro and G. Schuster, *Science*, 1975, 187, 303.

⁴ G. Wettermark in 'The Chemistry of the Carbon-Nitrogen Double Bond', ed. S. Patai, Interscience, New York, 1970, p. 566.

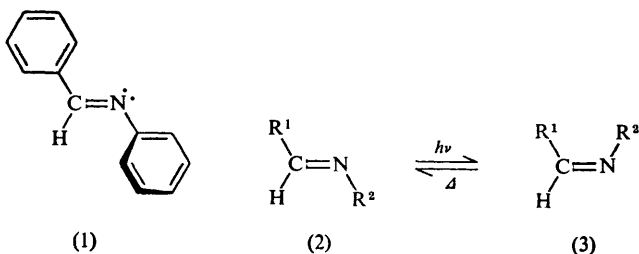
region is much more commonly used in photochemistry and the n, π^* excited state is the most readily accessible one.

Aryl substituted imines absorb at longer wavelengths.⁴ They exhibit complex spectroscopic behaviour, the number of bands observed and their positions depending on the aromatic substituents present. These bands have been interpreted as being of the $\pi \rightarrow \pi^*$ and charge-transfer type.⁵ Benzylideneaniline (1) exhibits an intense maximum at 252 nm and a shoulder at 315 nm. The expected $n \rightarrow \pi^*$ transition has not been unambiguously assigned and may be concealed by more intense absorption bands.⁵

The lack of similarity between the absorption spectra of benzylideneaniline and stilbene is quite marked. There is general agreement that this is because benzylideneaniline exists in the E-form in a conformation (1) in which the PhC=N moiety is planar, whilst the plane of the N-phenyl ring makes an angle of approximately 60° with the remainder of the molecule. This allows conjugation with the lone pair electrons on the nitrogen atom but considerably reduces stilbene-like conjugation between the phenyl rings through the C=N linkage.

3 Geometrical Isomerisation

Disubstituted imines exist in the more stable E-form (2).^{6,7} Irradiation can be used to effect equilibration with the Z-form (3) in a reaction analogous to olefin photoisomerisation.¹ However, the barrier to interconversion is normally so small for imines that at ambient temperatures very rapid complete thermal reversion to the more stable E-form (2) occurs.⁶



Spectroscopic observation of imine photoisomerisation was first noted 20 years ago.⁸ Irradiation of some diarylimines in solution at -100°C induced initial dramatic changes in the u.v. spectra of such solutions. Extended irradiation led to a photoequilibrium. The spectrum of the E-isomer (2) was restored

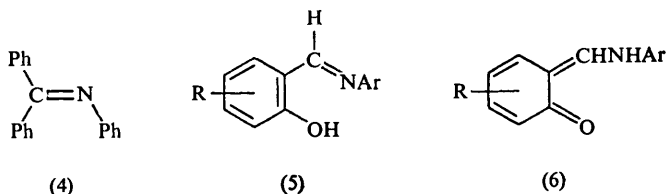
⁴ (a) M. A. El-Bayoumi, M. El-Aasser, and F. Abdel-Halim, *J. Amer. Chem. Soc.*, 1971, **93**, 586; (b) M. El-Aasser, F. Abdel-Halim and M. A. El-Bayoumi, *ibid.*, 1971, **93**, 590.

⁵ G. Wettermark, *Svensk Kem. Tidskr.*, 1967, **79**, 249.

⁷ G. G. McCarthy in ref. 4, p. 363.

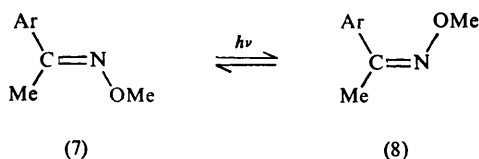
⁸ (a) E. Fischer and Y. Frei, *J. Chem. Phys.*, 1957, **27**, 808; (b) A recent n.m.r. investigation supports the assignment of the Z-configuration to the photoisomers produced from p-dimethylamino-benzylideneanilines below -70°C : M. Kobayashi, M. Yoshida and H. Minato, *J. Org. Chem.*, 1976, **41**, 3323.

on allowing the solutions to warm up. No changes occurred for benzhydrylideneaniline (4), for which only a single isomeric form can exist.⁸ Flash photolysis techniques have been used at room temperature to observe geometrical isomerisation of benzylideneanilines and salicylideneanilines and to follow the rapid thermal reformation of the more stable E-isomers.⁹ The photochemistry of salicylideneaniline derivatives (5) is complicated by competing reversible photoreactions involving transfer of the phenolic proton to the imino nitrogen with formation of the corresponding *o*-quinoid forms (6).



Photochemical techniques have been used as a practical method for obtaining solutions rich in the less favoured Z-isomer of aryl-*N*-alkylimines (3; R¹ = aryl, R² = alkyl).¹⁰

The fact that the configurational stability of oxime ethers is in marked contrast to that of *N*-aryl and *N*-alkyl imines, the rate for the thermal Z → E interconversion being very slow, has proved useful in studies of C=N geometrical isomerisation.¹¹ It has been shown from quenching studies with the oxime ethers (7) and (8) that photoequilibration occurred from the singlet excited state on direct irradiation. A triplet-initiated equilibrium could be achieved by sensitization.



Ar = Ph,β-naphthyl

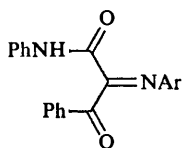
The question of whether photoisomerization occurs by a torsion mechanism, involving rotation about the carbon–nitrogen double bond, or by an inversion mechanism, which involves transfer of the substituent at nitrogen from one side

⁹ (a) D. G. Anderson and G. Wettermark, *J. Amer. Chem. Soc.*, 1965, **87**, 1433; (b) G. Wettermark, J. Weinstein, J. Sousa, and L. Dogliotti, *J. Phys. Chem.*, 1965, **69**, 1584; (c) G. Wettermark, *Ark. Kemi*, 1967, **27**, 159; (d) N. Kanamaru and K. Kimura, *Mol. Photochem.*, 1973, **5**, 427; (e) R. Potashnik and M. Ottolenghi, *J. Chem. Phys.*, 1969, **51**, 3671; (f) T. Rosenfeld, M. Ottolenghi, and A. Y. Meyer, *Mol. Photochem.*, 1973, **5**, 39.

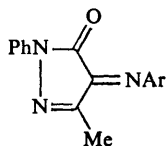
¹⁰ H. J. C. Yeh, H. Ziffer, D. M. Jerina, and D. R. Boyd, *J. Amer. Chem. Soc.*, 1973, **95**, 2741.

¹¹ (a) A. Padwa and F. Albrecht, *J. Amer. Chem. Soc.*, 1974, **96**, 4849; (b) A. Padwa and F. Albrecht, *J. Org. Chem.*, 1974, **39**, 2361.

of the molecule to the other *via* a linear transition state which retains the carbon-nitrogen double bond intact, is difficult to resolve. It has been proposed¹² that the torsion mechanism is facilitated by electron-donating substituents and the inversion mechanism by electron-withdrawing substituents in the aryl ring attached to the imino nitrogen of the azomethine dyes (9) and (10).



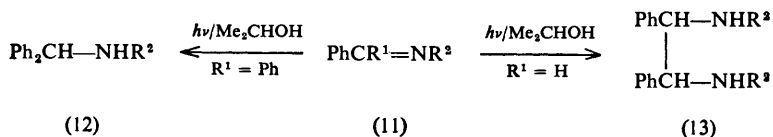
(9)



(10)

4 Photoreduction and Hydrogen Abstraction

The photoreduction commonly observed for ketones is initiated by the carbonyl n, π^* triplet excited state.² Aryl-*N*-alkylimines are also readily photoreduced in hydrogen-donating solvents, *e.g.* propan-2-ol and ethanol, though imine excited states are not intermediates. Benzophenone imines (11; $R^1 = \text{Ph}$) are converted to the corresponding amines (12), whereas benzaldehyde imines (11; $R^1 = \text{H}$) yield reductive dimerization products (13).¹³



A 'chemical sensitization' mechanism, involving ground-state reaction of the imines with ketyl radicals, is believed to operate for these photoreductions.¹³ Carbonyl compounds present in the reaction mixture as impurity (*e.g.* from hydrolysis), an added sensitizer, or as a species produced by photo-oxidation, generate the ketyl radicals. Scheme 1 outlines the mechanism for benzophenone-sensitized reductions in propan-2-ol.

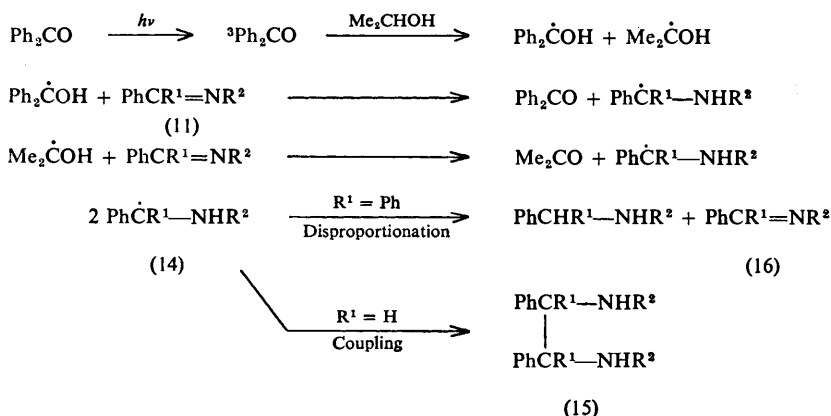
Triplet excited imine could be excluded as a hydrogen abstracting species in the photoreduction of benzophenone-*N*-methylimine (11; $R^1 = \text{Ph}$, $R^2 = \text{Me}$) since, when generated by benzonitrile sensitization, reduction did not occur.^{13c} In the photoreduction of benzaldehyde-*N*-benzylimine (11; $R^1 = \text{H}$, $R^2 = \text{CH}_2\text{Ph}$) using benzophenone sensitization in propan-2-ol, the imine quenched benzophenone photoreduction but did not quench benzophenone phosphorescence.

¹² W. G. Herkstroeter, *J. Amer. Chem. Soc.*, 1976, **98**, 330.

¹³ (a) M. Fischer, *Chem. Ber.*, 1967, **100**, 3599; (b) A. Padwa, W. Bergmark, and D. Pashayan, *J. Amer. Chem. Soc.*, 1968, **90**, 4458; (c) A. Padwa, W. Bergmark, and D. Pashayan, *ibid.*, 1969, **91**, 2653.

This implies that an intermediate of benzophenone photoreduction ($\text{Ph}_2\dot{\text{C}}\text{OH}$), rather than a triplet excited state of the imine, initiates the reduction.^{13c} Thermally generated free radical initiators could also effect reduction, verifying that the hydrogen abstracting species need not be an excited state of the imine.^{13c}

Two opposing factors determine whether coupling or disproportionation is observed.^{13c} Coupling introduces steric strain as the trigonal carbon atom in (14) becomes tetrahedral during formation of (15), an effect which increases in severity with increasing steric bulk of the group R^1 at the imino carbon atom. Disproportionation, on the other hand, has a high activation energy owing to the extensive electron reorganisation which has to occur as the hydrogen atom is transferred from the radical (14), which is stabilised by overlap of the singly-occupied orbital at carbon with the 'non-bonding' orbital at nitrogen, to form the carbon-nitrogen double bond in (16). This activation energy should be largely



Scheme 1

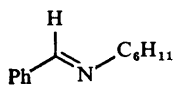
independent of the size of the substituent R^1 . For the hindered diphenylamino-methyl radicals (14; $\text{R}^1 = \text{Ph}$) strain due to coupling would be severe, so the disproportionation pathway is followed. With the much less hindered phenyl-aminomethyl radicals (14; $\text{R}^1 = \text{H}$) there is negligible coupling strain, so coupling is observed.

To explain the low reactivity of excited imines in hydrogen abstraction, Fischer suggested that the rate of the hydrogen abstraction reaction was very slow.^{13a} Padwa and co-workers have suggested, as an alternative explanation, that excited imines undergo very rapid radiationless decay to ground state, possibly because of ready E-Z isomerism about the carbon-nitrogen double bond, with the result that hydrogen abstraction is prevented.¹⁴

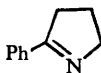
Incorporation of the imino-group into a ring system should prevent deactivation of the imine excited state by twisting. Hornback and co-workers compared

¹⁴ A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, *Pure Appl. Chem.*, 1973, 33, 269.

the photoreduction of the acyclic imine (17) with that of the cyclic compound (18) and showed that both imines underwent very inefficient excited state reductive



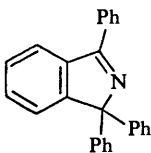
(17)



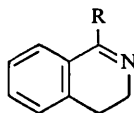
(18)

dimerization at essentially equal rates under conditions designed to exclude a 'chemical sensitization' mechanism. This suggests that the low reactivity of these imines is not due to rapid radiationless decay involving twisting about the carbon-nitrogen double bond but is more likely a consequence of low rates for the hydrogen abstraction reaction.¹⁵

Phosphorescence studies have suggested¹⁶ that the cyclic imines (19) and (20), which do not undergo excited state hydrogen abstraction, have π, π^* lowest



(19)



(20) R = CH₂Ph, Ph, Me

triplet excited states. It has been proposed that possession of a π, π^* lowest triplet excited state may account for the low reactivity of excited imines in hydrogen abstraction reactions.¹⁶

Inefficient intramolecular γ -hydrogen abstraction may occur for the substituted cyclic imine (21). Low yields of 1-methyl-3,4-dihydroisoquinoline (22) were suggested¹⁷ to arise by a process (Scheme 2) analogous to the Norrish Type II photocleavage of carbonyl compounds.²

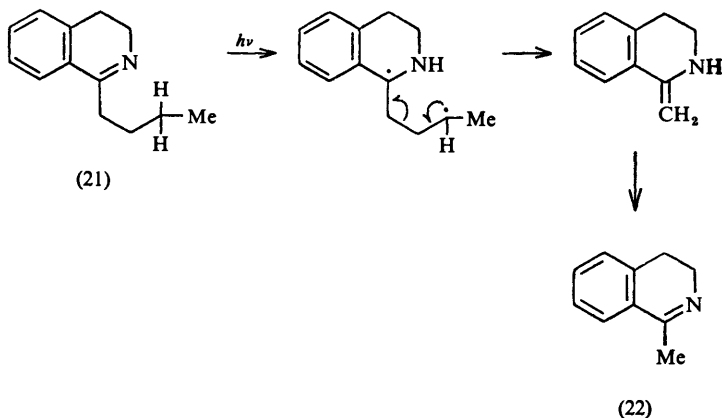
In an inert solvent in the presence of a sensitizer, an imine may act as the hydrogen donor.¹⁸ Benzonitrile and tert-butylbenzene were obtained when imine (23) was irradiated in benzene in the presence of benzophenone.^{18a} They were proposed to result from cleavage of the radical (24) produced by abstraction of the imino hydrogen by triplet excited benzophenone. In a related reaction, Baum and Karnischky have isolated oxazolidines (25) from irradiation of aryl ketones and isopropylidene isopropylamine (26) in benzene. Initial abstraction of the tertiary hydrogen atom of (26) produced the stabilized radical (27). Coupling of

¹⁵ J. M. Hornback, G. S. Proehl, and I. J. Starner, *J. Org. Chem.*, 1975, **40**, 1077.

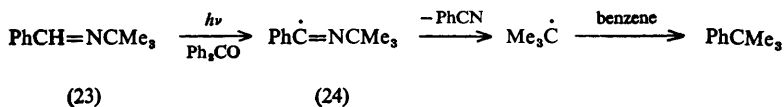
¹⁶ H. Ohta and K. Tokumaru, *Tetrahedron Letters*, 1974, 2965.

¹⁷ Y. Ogata and K. Takagi, *Tetrahedron*, 1971, **27**, 2785.

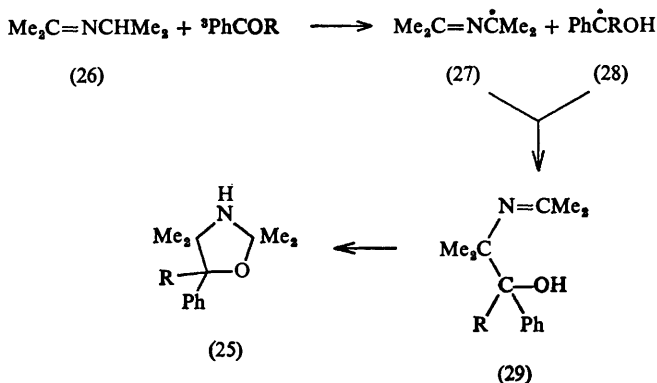
¹⁸ (a) H. Ohta and K. Tokumaru, *Chem. and Ind. (London)*, 1971, 1301; (b) A. A. Baum and L. A. Karnischky, *J. Amer. Chem. Soc.*, 1973, **95**, 3072.



Scheme 2



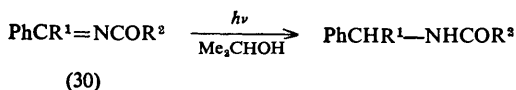
(27) with the ketyl radical (28), followed by cyclization of imino alcohol (29) produced the observed oxazolidines (25).^{18b}



N-Acylimines contain the C=N—C=O chromophore and are aza analogues of α,β -unsaturated carbonyl compounds whose photochemistry has been extensively investigated.¹⁹ *N*-Acyphenylketimines (30) undergo saturation of the carbon–nitrogen double bond when irradiated in propan-2-ol.²⁰

¹⁹ P. E. Eaton, *Accounts Chem. Res.*, 1968, **1**, 50.

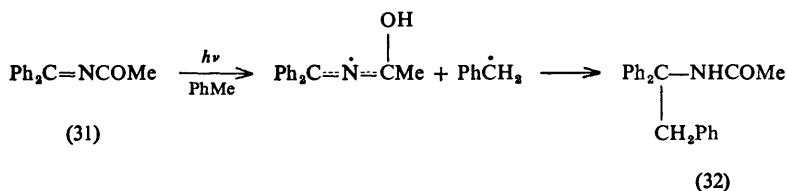
²⁰ (a) T. Okada, K. Saeki, M. Kawanisi and H. Nozaki, *Tetrahedron*, 1970, **26**, 3661; (b) A. Padwa and W. P. Koehn, *J. Org. Chem.*, 1975, **40**, 1896.



The mechanism operating in the case of *N*-aroylphenylketimines of the type (30; R² = aryl) appears to depend on the identity of the group R¹ at the imino carbon atom. Thus, Padwa and co-workers^{20b} demonstrated a 'chemical sensitization' mechanism (*cf.* Scheme 1) for compounds with a phenyl substituent at this position, whereas with alkyl substitution the acylimine n,π^* triplet excited state was believed^{20b} to be responsible for initiating the observed photo-reduction, with transfer of hydrogen from the solvent to the carbonyl oxygen initially rather than to the imino nitrogen.

The low quantum yields observed for these imine excited state reactions were shown to be due to small bimolecular hydrogen-abstraction rates (*ca.* 100 times less than that of benzophenone) operating in conjunction with very rapid triplet decay rates (*ca.* 50 times greater than that of benzophenone).^{20b} This situation is similar to that found for α,β -unsaturated ketones.¹⁹ Those *N*-acylimines which are photoreduced by a 'chemical sensitization' mechanism may possibly have lowest π,π^* triplet excited states or a negligible intersystem crossing efficiency from the singlet excited state.

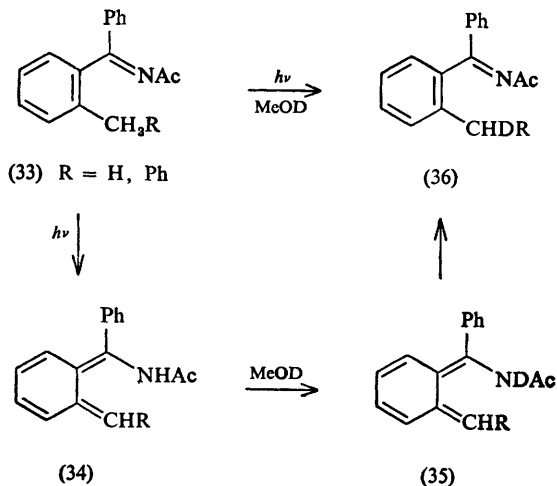
In solutions of hydrocarbons containing allylic or benzylic hydrogens, *e.g.* cyclohexene or toluene, *N*-acetyldiphenylketimine (31) underwent photoaddition of the hydrocarbon to the carbon-nitrogen double bond.²¹ In toluene, the adduct (32) was obtained. An intramolecular version of this hydrogen abstraction



reaction has been reported. Irradiation of *o*-methyl or *o*-benzyl compounds (33) in [*O*-²H]methanol led to incorporation of deuterium.²² A mechanism similar to that known to operate for the photoenolization reactions of *o*-alkyl-substituted aromatic carbonyl compounds² has been proposed (Scheme 3). γ -Hydrogen abstraction transfers a hydrogen from the *o*-alkyl substituent to the imino nitrogen with formation of the *o*-quinodimethane (34). Subsequent exchange

²¹ (a) N. Toshima, S. Asao, K. Takada and H. Hirai, *Tetrahedron Letters*, 1970, 5123; (b) H. Hirai, N. Toshima, S. Asao, and K. Takada, *Chem. Abs.*, 1973, 78, 124309; (c) H. Hirai, N. Toshima and S. Asao, *ibid.*, 1973, 79, 5145; (d) H. Hirai, N. Kojima, and S. Asao, *ibid.*, 1974, 81, 13247; (e) S. Asao, N. Toshima and H. Hirai, *Bull. Chem. Soc., Japan*, 1976, 49, 224 report that a triplet excited state of (31) is involved in the photoaddition of toluene.

²² M. Saeki, N. Toshima, and H. Hirai, *Bull. Chem. Soc., Japan*, 1975, 48, 478.



Scheme 3

of the mobile amino hydrogen for deuterium forms the species (35) which, by rapid thermal 1,5-transfer of deuterium, generates (36) differing from imine (33) only by the presence of deuterium at the benzylic position of the *o*-alkyl group.²²

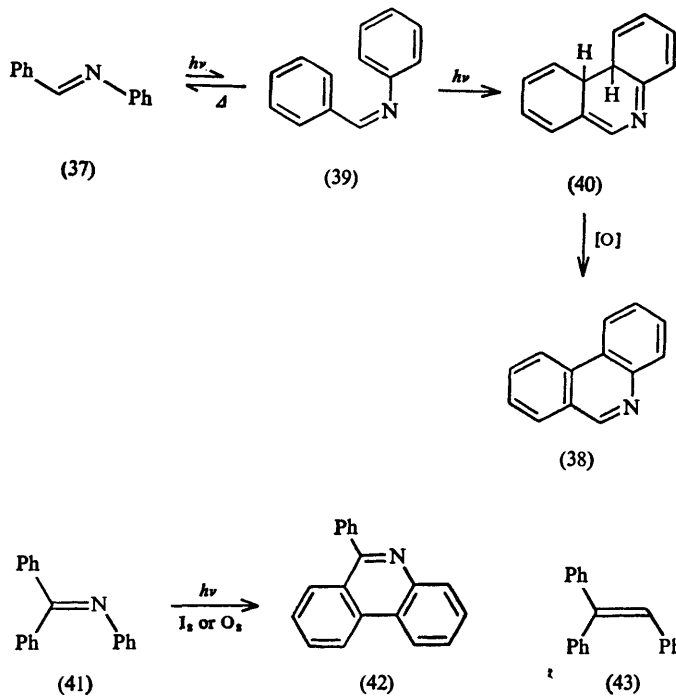
5 Photocyclization of *N*-Benzylideneanilines

In olefin photochemistry the singlet π, π^* excited state cyclization of stilbenes to dihydrophenanthrenes is well known, and under oxidative conditions provides a useful synthetic route to phenanthrenes.¹ Early efforts to achieve a similar oxidative photoconversion of *N*-benzylideneaniline (37) to phenanthridine (38) in conventional organic solvents were unsuccessful.²³ *N*-Benzylideneaniline (37) exists as the *E*-isomer, and the concentration of *Z*-isomer (39) necessary to capture sufficient light for successful cyclization to the dihydro-compound (40) could not be achieved by room temperature photoequilibration. At lower temperatures the rate of the thermal *Z* \rightarrow *E* reaction is decreased and the steady-state concentration of the *Z*-isomer is increased. Irradiation at -10°C , in the presence of dissolved oxygen or iodine as oxidizing agent, achieved a 2% yield of phenanthridine (38).²⁴ *N*-Benzhydrylideneaniline (41), which does not need to isomerize prior to cyclization, cyclized successfully²⁴ to yield the expected 2-phenylbenzo[3,4]quinoline (42). The quantum yield for this conversion was, however, merely 10^{-2} times that for oxidative photocyclization of the related triphenylethylene (43), which must, of necessity, undergo cyclization from a π, π^* excited state. It was suggested²⁴ that, by analogy with *N*-benzylideneaniline (37) whose lowest singlet excited state is probably n, π^* in character,²⁵ the imine (41)

²² (a) E. V. Blackburn and C. J. Timmons, *Quart. Rev.*, 1969, 23, 482; (b) P. Hugelshofer, J. Kalvoda, and K. Schaffner, *Helv. Chim. Acta*, 1960, 43, 1322.

²³ F. B. Mallory and C. S. Wood, *Tetrahedron Letters*, 1965, 2643.

²⁴ (a) H. H. Jaffé, S. J. Yeh, and R. W. Gardner, *J. Mol. Spectroscopy*, 1958, 2, 120; (b) K. H. Grellmann and E. Tauer, *J. Amer. Chem. Soc.*, 1973, 95, 3104.



has a lowest ${}^1n,\pi^*$ excited state and that cyclization from the ${}^1\pi,\pi^*$ state has to compete with rapid internal conversion to the lower energy inactive ${}^1n,\pi^*$ state. This suggestion has received support from the reports that *N*-benzylideneaniline (37)²⁶ and many substituted *N*-benzylideneanilines²⁷ cyclize readily to the corresponding benzo[3,4]quinoline derivatives in strongly acidic media in which the protonated imine (44) is undergoing cyclisation. Since the nitrogen lone-pair electrons are occupied in bonding to the proton, cation (44) must have a lowest ${}^1\pi,\pi^*$ excited state.

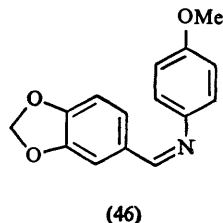
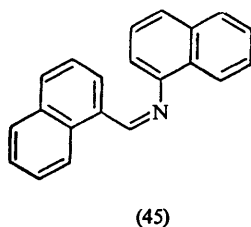
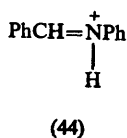
Not all substituted *N*-benzylideneanilines, however, require acidic media for successful cyclization. Thus *N*-(1-naphthylidene)-1-naphthylamine (45) and the trialkoxy-compound (46) readily form the expected oxidative ring closure products in aerated ethanol and diethyl ether, respectively.²⁸ These compounds may possibly possess lowest ${}^1\pi,\pi^*$ excited states.

A related photocyclization which yields the 1,2-dihydrobenzo[3,4]quinoline (47) has been reported for *N*-(2-propylidene)-2-aminobiphenyl (48). The isolated

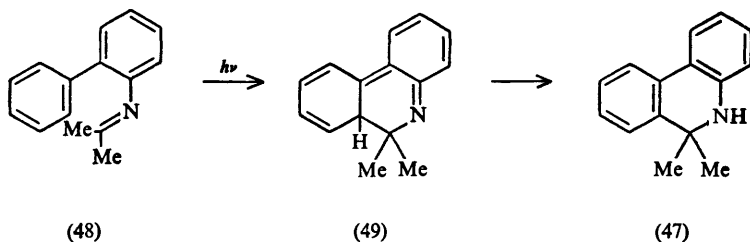
²⁶ G. M. Badger, C. P. Joshua, and G. E. Lewis, *Tetrahedron Letters*, 1964, 3711.

²⁷ (a) M. Scholz, F. Dietz, and M. Mühlstädt, *Tetrahedron Letters*, 1970, 2835; (b) H. H. Perkampus and B. Behjati, *J. Heterocyclic Chem.*, 1974, **11**, 511.

²⁸ (a) M. P. Cava and R. H. Schlessinger, *Tetrahedron Letters*, 1964, 2109; (b) T. Onaka, Y. Kanda and M. Natsume, *ibid.*, 1974, 1179.

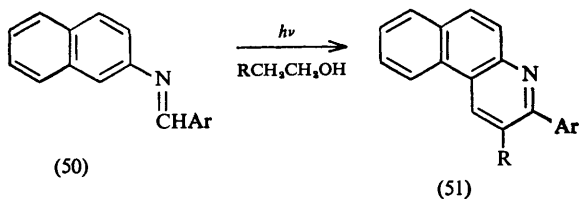


product (47) may be formed by a thermally-allowed 1,5-hydrogen shift from (49), the initial cyclisation product.²⁹



6 Alkylative Photocyclizations of Imines

When *N*-arylidene-2-naphthylamines (50) are irradiated in alcohols of the type $\text{RCH}_2\text{CH}_2\text{OH}$ under oxidative conditions, formation of 2-arylbenzo[5,6]-quinolines (51) occurs with incorporation of the alkyl group of the solvent and

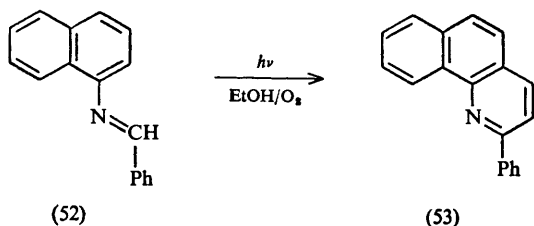


cyclization on to the *N*-substituted ring exclusively in the α -position.³⁰ Where the α -position is blocked, reaction occurs at the β -position, *e.g.* (52) \rightarrow (53).^{30a} Incorporation and cyclization on to a phenyl ring, rather than naphthyl, may be achieved by using an aniline-derived imine, *e.g.* (54) \rightarrow (55).^{30d}

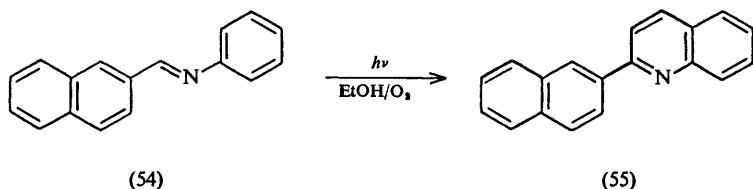
The two-carbon fragment incorporated as part of the new six-membered ring

²⁹ J. S. Swenton, T. J. Ikeler, and G. L. Smyser, *J. Org. Chem.*, 1973, **38**, 1157.

³⁰ (a) J. S. Shannon, H. Silberman, and S. Sternhell, *Tetrahedron Letters*, 1964, 659; (b) P. J. Collin, H. Silberman, S. Sternhell, and G. Sugowdz, *ibid.*, 1965, 2063; (c) P. J. Collin, J. S. Shannon, H. Silberman, S. Sternhell, and G. Sugowdz, *Tetrahedron*, 1968, **24**, 3069; (d) M. Scholz, H. Herzsuh, and M. Mühlstädt, *Tetrahedron Letters*, 1968, 3685.



in these alkylative cyclizations is probably derived from the aldehyde RCH_2CHO formed by photo-oxidation of the solvent $\text{RCH}_2\text{CH}_2\text{OH}$.³⁰ A detailed mechanism involving an initial 'chemical sensitization' step has been proposed³¹ for these reactions.



7 (2 + 2) Photocycloadditions to Imines

In contrast to the situation found for olefins¹ and carbonyl compounds,² which readily undergo (2 + 2) photocycloaddition reactions to form cyclobutanes and oxetans respectively, there appears to be no undisputed example of four-membered ring formation by intermolecular photocycloaddition to a simple alkyl or aryl substituted imine.³² It has been suggested³⁶ that the presence of a conjugated electron-withdrawing group may be necessary for successful photocycloaddition to the carbon-nitrogen double bond.

N-Acylimines, aza-analogues of α,β -unsaturated ketones, have been shown to undergo (2 + 2) photoaddition to olefins, a reaction typical of enone photochemistry.¹⁹ For example, the keto-imine (56) undergoes triplet excited-state addition to olefins,³⁷ 1,1-dimethoxyethylene adding to form the azetidine (57). A similar reaction with olefins is observed for (58),³⁸ in the absence of added olefin an α -cleavage reaction (see Section 8) occurs with formation of epoxyisocyanate (59).³⁸

³¹ F. R. Stermitz, R. P. Seiber, and D. E. Nicodem, *J. Org. Chem.*, 1968, **33**, 1136.

³² A claim³³ that a 1,3-diazetidene was formed by (2 + 2) photodimerisation of benzaldehyde-*N*-cyclohexylimine has been disproved,^{13b} and the intermediacy of a 1,2-diazetidene in the photofragmentation of *N*-(4-dimethylaminobenzylidene)-aniline³⁴ is in doubt since an attempt to repeat the reaction met with failure.³⁵

³³ R. O. Kan and R. L. Furey, *J. Amer. Chem. Soc.*, 1968, **90**, 1666.

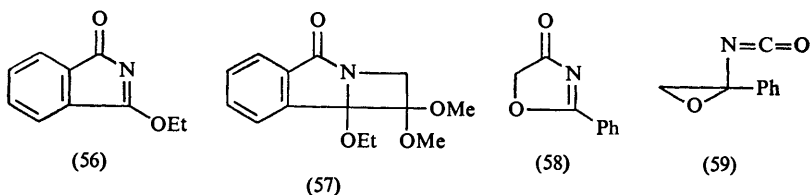
³⁴ S. Searles and R. A. Clasen, *Tetrahedron Letters*, 1965, 1627.

³⁵ D. R. Arnold, V. Y. Abraitys, and D. McLeod, *Canad. J. Chem.*, 1971, **49**, 923.

³⁶ J. S. Swenton, and J. A. Hyatt, *J. Amer. Chem. Soc.*, 1974, **96**, 4879.

³⁷ K. A. Howard and T. H. Koch, *J. Amer. Chem. Soc.*, 1975, **97**, 7288.

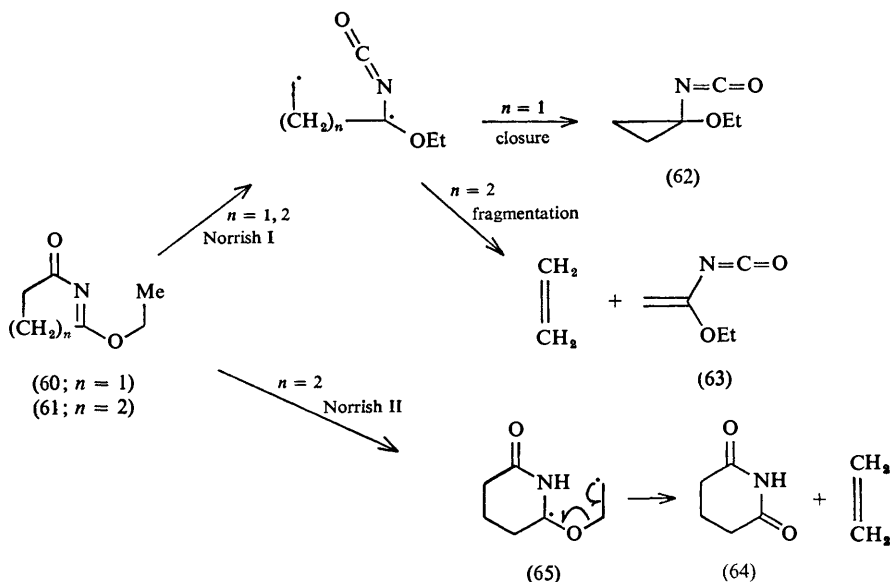
³⁸ R. M. Rodenhorst and T. H. Koch, *J. Amer. Chem. Soc.*, 1975, **97**, 7298.



It has been suggested that *N*-acylimines which undergo (2 + 2) photocycloaddition do so from reactive π, π^* excited states.³⁸

8 α -Cleavage of *N*-Acylimines

In contrast to the acylimines (56) and (58), imines (60) and (61) (Scheme 4) do



Scheme 4

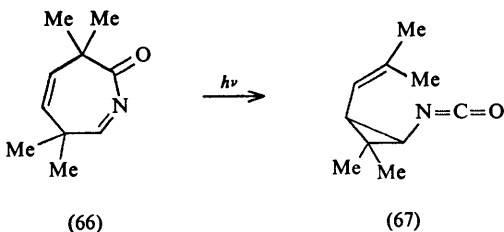
not undergo photoaddition reactions. Instead, α -cleavage reactions occur from the singlet n, π^* excited state.³⁹ The $n \rightarrow \pi^*$ transition for *N*-acylimines is in the 265–285 nm region and hence sufficient energy is available for cleavage of the carbon–carbon single bond adjacent to the carbonyl group in (60) and (61).³⁹ α, β -Unsaturated ketones have lower ${}^1n, \pi^*$ excited state energies and do not normally exhibit α -cleavage.¹⁹

The acylimine (60) is converted to the cyclopropyl isocyanate (62) and imine (61) yields an unsaturated isocyanate (63) on irradiation.³⁹ The first step in each

³⁹ T. H. Koch, R. J. Sluski, and R. H. Moseley, *J. Amer. Chem. Soc.*, 1973, **95**, 3957.

of these reactions (Scheme 4) is analogous to the Norrish Type I reaction often observed in the photochemistry of non-conjugated carbonyl compounds² and typically initiated from an n, π^* excited state. In the case of (61) a competing reaction, which yields glutarimide (64), is also observed.³⁹ This is initiated by γ -hydrogen abstraction from the alkyl side chain, followed by cleavage of the 1,4-biradical (65) so formed, in a manner analogous to the Norrish Type II reaction² of n, π^* excited carbonyl compounds.

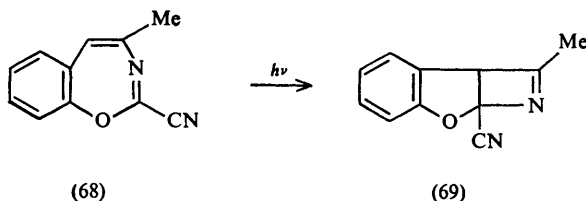
The aroylimine (56), because of aryl conjugation with the carbonyl group, has a strong α -bond and does not exhibit α -cleavage reactions.³⁷ However, imine (58) does undergo α -cleavage to form epoxyisocyanate (59),³⁸ though the reaction, analogous to the conversion of (60) \rightarrow (62) in Scheme 4, cannot compete with the much faster (2 + 2) photoaddition which is observed in the presence of added 1,1-dimethoxyethylene.³⁸ The *N*-acylimine (66) undergoes an analogous α -cleavage reaction with formation of (67).⁴⁰



9 Electrocyclic Reactions of Conjugated Imines

Conjugated imines may be considered as aza-analogues of butadiene and hexatriene. Theory predicts⁴¹ that the electrocyclic reactions of 2-azabutadiene and of aza- and diaza-hexatrienes should proceed along pathways similar to those found for the corresponding hydrocarbons.

The conjugated cyclic imine (68) has been reported⁴² to undergo photocyclization to the 1-azetine (69). In a related reaction, the imine (70) was postulated⁴³ to undergo triplet excited state ring closure to yield (71). The 1-azetine (71) was



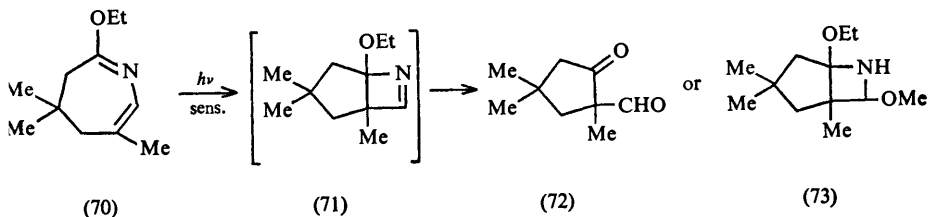
⁴⁰ T. Sasaki, S. Eguchi, and M. Ohno, *J. Amer. Chem. Soc.*, 1970, **92**, 3192.

⁴¹ Z. Neiman, *J.C.S. Perkin II*, 1972, 1746.

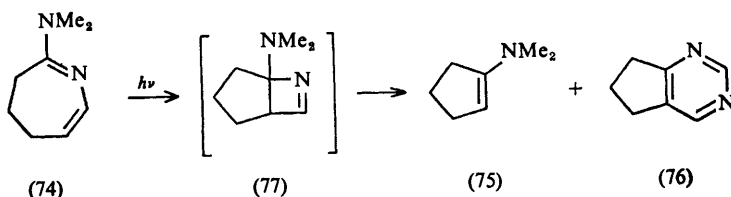
⁴² C. Lohse, *Tetrahedron Letters*, 1968, 5625.

⁴³ T. H. Koch and D. A. Brown, *J. Org. Chem.*, 1971, **36**, 1934.

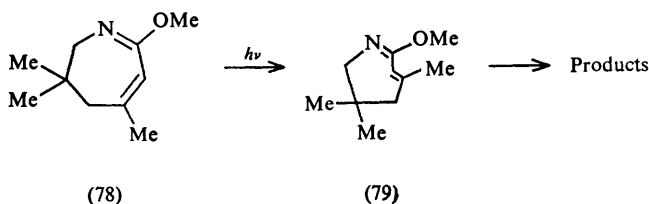
not isolated but was converted to the products (72) or (73) under acidic conditions or when formed in the presence of methoxide ion, respectively.⁴³ The



imine (74), which is closely related to (70), undergoes singlet excited state conversion to the products (75) and (76). These compounds were believed⁴⁴ to be formed from the bicyclic intermediate (77).



The 1-azabutadiene (78) does not give products of electrocyclic ring closure. Rather, on irradiation in the presence of a sensitizer, geometrical isomerization about the carbon-carbon double bond is believed to occur and the products obtained arise from ground-state reactions of the severely strained, and consequently highly reactive, isomer (79).⁴⁵



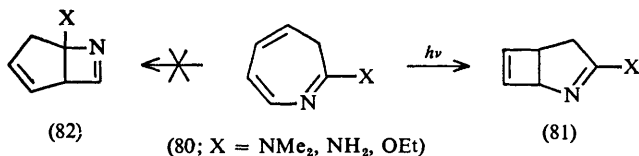
In the case of the 3*H*-azepines (80), two modes of closure are possible. On irradiation, the cyclobutene (81) was the sole product isolated.⁴⁶ The retention of the N=C—X resonance energy in the formation of (81) may have been the decisive factor in determining the observed selectivity.⁴⁶ Formation of the

⁴⁴ E. Lerner, R. A. Odum, and B. Schmall, *J.C.S. Chem. Comm.*, 1973, 327.

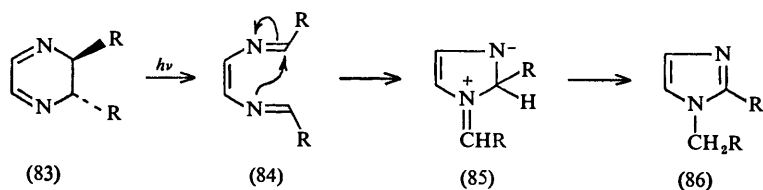
⁴⁵ T. H. Koch, M. A. Geigel, and C. Tsai, *J. Org. Chem.*, 1973, **38**, 1090.

⁴⁶ R. A. Odum and B. Schmall, *J.C.S. Chem. Comm.*, 1969, 1299.

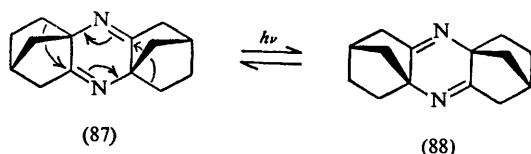
alternative product (82) would have necessitated loss of such resonance energy.



Irradiation of cyclohexa-1,3-dienes commonly results in electrocyclic ring opening to form linear hexatrienes.¹ A similar conversion occurred in the excited state reactions of 2,3-dihydropyrazines (83).^{35,47} Photochemically-allowed conrotatory ring-opening formed the corresponding enedi-imines (84) in benzene solution. In methanol or ethanol, rapid cyclization of the enedi-imines (84) occurred with formation of ylide intermediates (85). A proton transfer subsequently completed formation of imidazoles (86), the isolated products. Cyclization of the enedi-imines (84) was facilitated by the ability of the hydroxylic solvents to stabilize the developing charge centres by solvation.



The optically active 2,5-dihydropyrazine (87) underwent photoracemization in methanol.⁴⁸ A concerted (2 + 2 + 2 + 2) reaction may be involved in the conversion of (87) to its enantiomer (88).



10 1,3-Dipole Formation by 2*H*-Azirines

The photochemistry of 2*H*-azirines (89) has been extensively studied by the schools of Padwa¹⁴ and Schmid.⁴⁹ The bulk of the work reported has been with

⁴⁷ (a) P. Beak and J. L. Miesel, *J. Amer. Chem. Soc.*, 1967, **89**, 2375; (b) A. Padwa, S. Clough, and E. Glazer, *ibid.*, 1970, **92**, 1778; (c) A. Padwa and E. Glazer, *ibid.*, 1972, **94**, 7788.

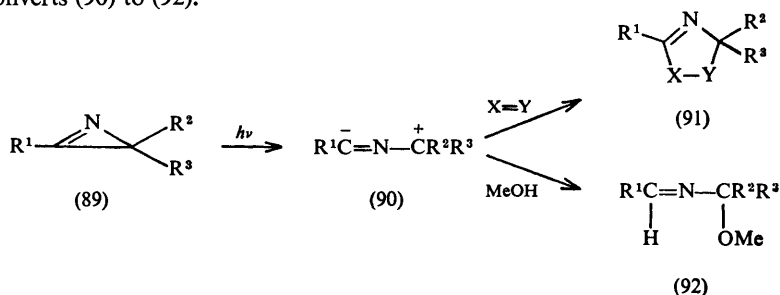
⁴⁸ D. G. Farnum and G. R. Carlson, *J. Amer. Chem. Soc.*, 1970, **92**, 6700.

⁴⁹ P. Claus, Th. Doppler, N. Gaskis, M. Georganakis, H. Giezendanner, P. Gilgen, H. Heimgartner, B. Jackson, M. Märky, N. S. Narasimhan, H. P. Rosenkranz, A. Wunderli, H.-J. Hansen, and H. Schmid, *Pure Appl. Chem.*, 1973, **33**, 339.

2-substituted-3-phenyl-2*H*-azirines (89; $R^1 = \text{Ph}$), though the photochemistry appears to be largely independent of the presence or absence of aryl or alkyl substitution on the three-membered ring.

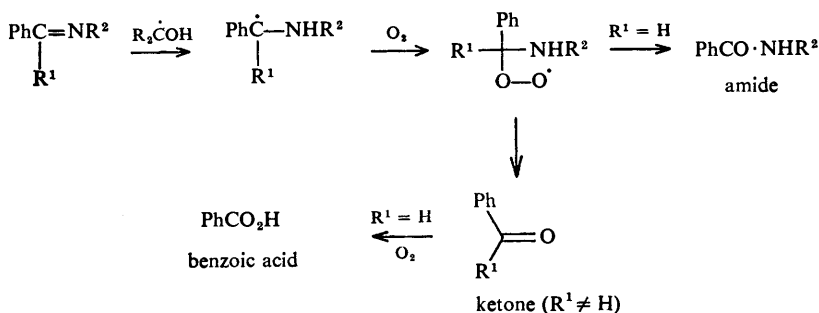
Cleavage of the carbon-carbon bond in the electronically excited 2*H*-azirine ring forms a nitrile ylide, (89) \rightarrow (90).^{14,49} The reaction is initiated from the 2*H*-azirine singlet excited state⁵⁰ and the 1,3-dipolar species (90) has been observed spectroscopically at low temperatures in a hydrocarbon matrix.⁵¹

The 1,2-dipole (90) may be intercepted by a wide variety of dipolarophiles,⁵² $X=Y$, present during irradiation of the 2*H*-azirine (89). Formation of numerous five-membered nitrogen heterocycles (91) has been achieved in this manner.⁵³ Alternatively, a protic solvent may be used to trap the 1,3-dipole; *e.g.* methanol converts (90) to (92).⁵⁴



11 Photo-oxidation

Ketones, amides, and benzoic acid have been isolated from the products of irradiation of *C*-arylimines in oxygenated propan-2-ol.⁵⁵ A chemical sensitization mechanism (Scheme 5), related to that proposed for imine photoreduction, has



Scheme 5

⁵⁰ A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, *J. Amer. Chem. Soc.*, 1973, **95**, 1945.

⁵¹ W. Sieber, P. Gilgen, S. Chaloupka, H.-J. Hansen, and H. Schmid, *Helv. Chim. Acta*, 1973, **56**, 1679.

⁵² R. Huisgen, *Helv. Chim. Acta*, 1967, **50**, 2421.

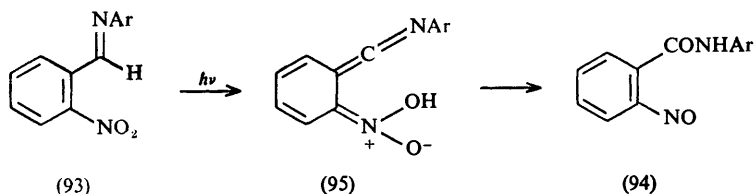
⁵³ For leading references see (a) W. Stegmann, P. Gilgen, H. Heimgartner and H. Schmid, *Helv. Chim. Acta*, 1976, **59**, 1018 and (b) A. Padwa, A. Ku, A. Mazzu, and S. I. Wetmore, *J. Amer. Chem. Soc.*, 1976, **98**, 1048.

⁵⁴ A. Padwa, J. K. Rasmussen, and A. Tremper, *J. Amer. Chem. Soc.*, 1976, **98**, 2605.

⁵⁵ N. Toshima and H. Hirai, *Tetrahedron Letters*, 1970, 433.

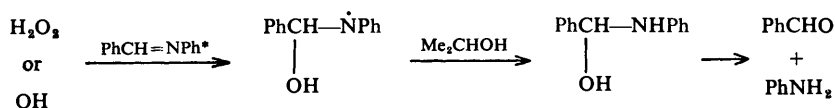
been proposed. The observation that acetophenone, which possesses a hydrogen-abstracting triplet excited state, sensitizes the oxidations whereas 1-acetylnaphthalene, which is inactive in hydrogen-abstracting reactions, fails to act as a sensitizer is consistent with this mechanism.

The intramolecular oxidation of the carbon–nitrogen double bond of 2-nitrobenzylideneanilines (93) is one of the earliest photochemical reactions reported for imines.⁵⁶ Formation of the corresponding 2-nitrosobenzanilide (94) is believed to involve the intermediacy of a short-lived *o*-quinone imine derivative (95).⁵⁷



12 Photohydrolysis

Benzylideneaniline yields benzaldehyde and aniline when irradiated in the presence of benzophenone in oxygenated ethanol or propan-2-ol.⁵⁸ Hydrogen peroxide is produced under these conditions and it, or hydroxyl radicals derived from it, was believed to be the agent responsible for the hydrolysis (Scheme 6).



Scheme 6

13 Vision

In vision, one of the key steps in the conversion of a light signal received at the photoreceptors in the retina to an electrical pulse to be transmitted to the brain by the optic nerve, involves photoisomerization of the protonated imine (96) to the geometrical isomer (97). The imine (96) is formed following condensation of 11-*cis*-retinal with the visual protein opsin.⁵⁹

⁵⁶ (a) F. Sachs and R. Kempf, *Ber.*, 1902, **35**, 2704; (b) A. Senier and R. Clarke, *J. Chem. Soc.*, 1914, **105**, 1917.

⁵⁷ E. Hadjoudis and E. Hayon, *J. Phys. Chem.*, 1970, **74**, 2225.

⁵⁸ R. L. Furey and R. O. Kan, *Tetrahedron*, 1968, **24**, 3085.

⁵⁹ Aspects of the chemistry of vision are discussed in a series of five review articles in *Accounts Chem. Res.*, 1975, **8**, 81–112.

