

PHOTOCHEMISTRY OF SOME HETEROCYCLIC SYSTEMS

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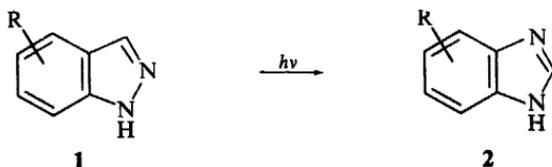
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ABSTRACT

Whereas 2H-benzotriazoles are photochemically stable, 1H-benzotriazoles yield biradicals after splitting off nitrogen. These biradicals attack aromatic substrates such as anisole, toluene, fluorobenzene or benzonitrile preferentially in the *o*- and *p*-positions with formation of the corresponding *o*-amino biphenyls (cf. schemes 2–5). With a deficiency of aromatic substrate, attack at the *o*-position is strongly favoured (cf. *Figures 1, 2*). Thereafter the very complex photochemistry of 3,5-diaryl-2-isoxazolines will be discussed (cf. schemes 7–9). This led to the discovery of the photochemical cycloaddition between 3-phenyl-2H-azirines and aldehydes, with formation of 3-oxazolines (cf. schemes 10, 11). The nitrile methylene ylides produced photochemically from azirines react, mainly in good yield, with substrates which contain cumulative (cf. schemes 15, 16) or activated (cf. schemes 12, 13) double bonds. Noteworthy, is the photochemical incorporation of carbon dioxide, leading to the little known isoazlactones (scheme 15). After a short discussion of the photochemistry of the sydnones (cf. schemes 19–23), which has been only briefly investigated so far, the photolysis of indazoles, benzisoxazoles, and anthranils in strongly acid solution will be discussed (cf. schemes 24–27). These photochemical reactions give rise to aryl azenium ions or aryl oxenium ions, which react with the solvent SH preferentially in the position para to the nitrogen or oxygen, respectively.

1. INTRODUCTION

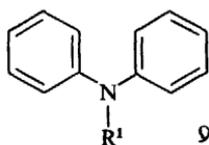
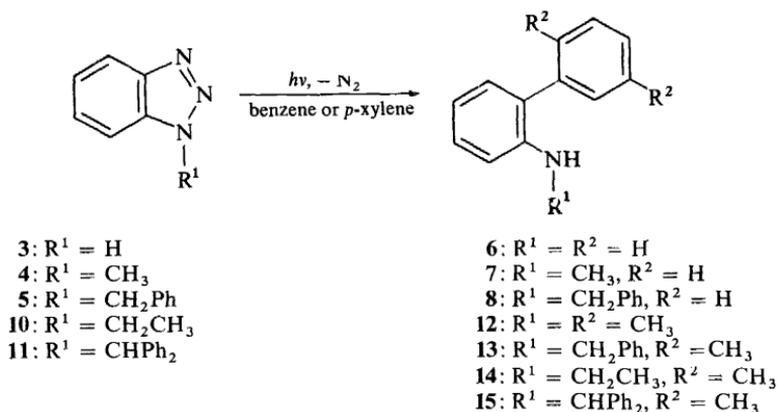
In the Chemical Laboratories of the University of Zürich, in 1964, the photo-isomerization of aromatic heterocycles, namely the conversion of indazoles **1** to benzimidazoles **2**, was observed for the first time (scheme 1)¹. Since then, various research groups have investigated similar isoelectronic systems; these also show, in many cases, an analogous bond-migration reaction on irradiation (see also a recent review² and literature cited therein).



Scheme 1

2. PHOTOLYSIS OF BENZTRIAZOLES

Irradiation of the benztriazoles 3–5 in benzene using a mercury high-pressure lamp with a nickel sulphate filter (transparent between 225 and 325 nm) at 15° to 17° under argon, leads to the *o*-amino biphenyls 6–8 (scheme 2)³. The photoreaction stops after ten to fifteen per cent conversion. Based on the amount of reacted benztriazole, the yields amount to 50 to 90 per cent. No isomeric diphenylamine derivatives of the type 9 are formed. The benztriazoles 4, 5, 10 and 11 give similar yields of the products 12–15 on irradiation in *p*-xylene.



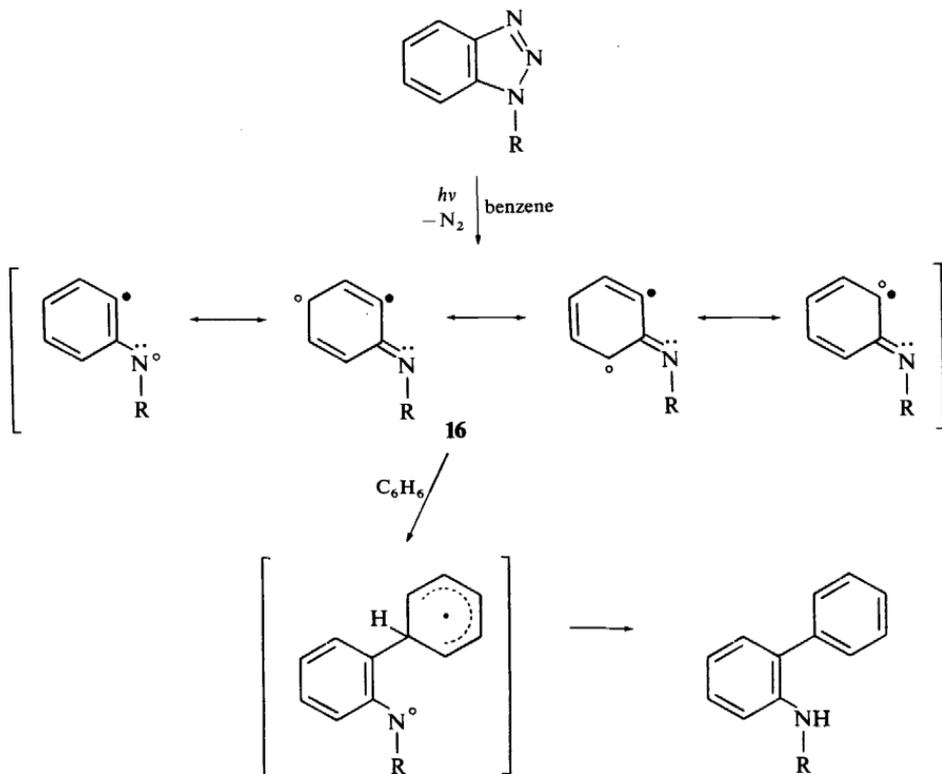
Scheme 2

The probable mechanism of the formation of the *o*-amino biphenyls is given in scheme 3. Loss of nitrogen from the excited benztriazoles results first of all in a diradical 16. The observation that only *o*-amino biphenyls (and no diphenylamines 9) are formed, can be explained as follows: the free radical centre at C(2) is of the σ -type, and should thus behave as a free phenyl radical ('hard radical centre'). The radical centre on the nitrogen is of the π -type and the electron is thus partly delocalized through the benzene ring ('soft radical centre').

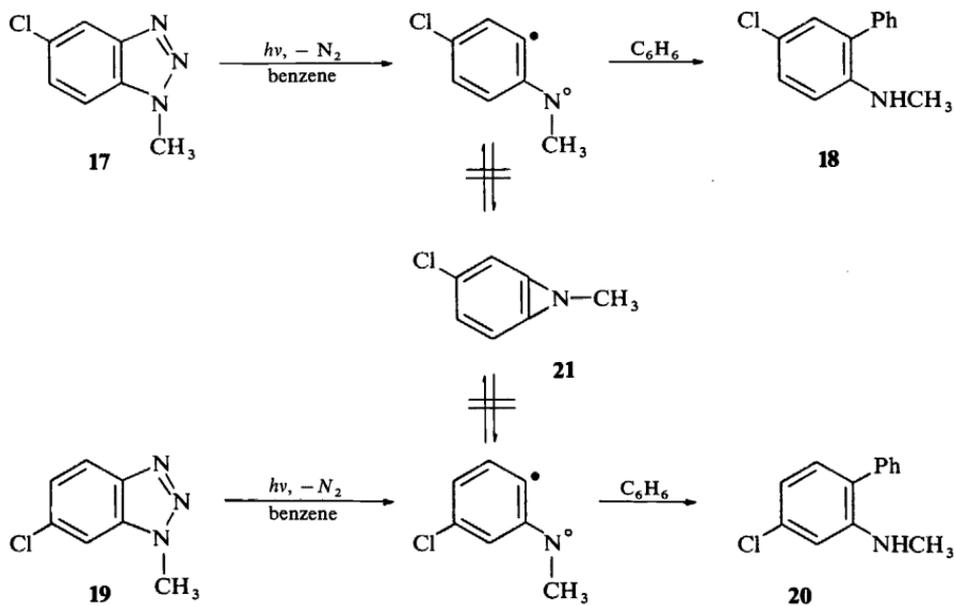
Since 5-chloro-1-methyl benztriazole (17), on irradiation in benzene, affords only a single *o*-amino biphenyl, namely 18, whereas 6-chloro-1-methyl benztriazole (19) gives only the *o*-amino biphenyl 20, it then follows that anti-aromatic benzazirines of the type 21 do not appear as intermediates (scheme 4).

Other workers have also postulated the formation of diradical intermediates in the photolysis of benztriazoles^{4–8}. In order to learn more about the properties of the postulated diradical, 1-methyl benztriazole (4) was irradiated neat in the aromatic solvents tabulated in scheme 5. The yields of photoproducts varied between 40 and 80 per cent based on reacted 4. The

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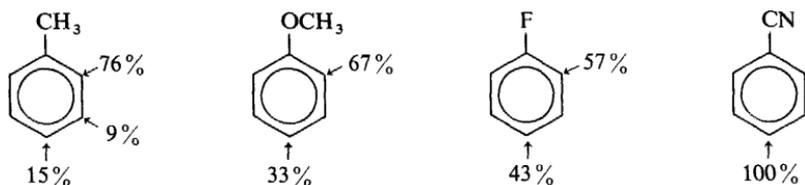


Scheme 3



Scheme 4

biradical **16** ($R = \text{CH}_3$) attacked mainly the *o*- and *p*-positions of the aromatic ring of the solvent[†]. The ratio of the *o*-/*p*-substitution changed strongly in favour of *o*-substitution with anisole and fluorobenzene, if the concentration of the anisole or fluorobenzene respectively was reduced when irradiating in



Scheme 5. Attack of reactive species formed by photolysis of 1-methyl benztriazole (**4**; $c = 0.07\text{--}0.09$ M/l) on different aromatics.

acetonitrile (Figures 1 and 2). With anisole for example, when the concentration of reaction partners is the same (0.05 M/l), then the *o*-/*p*-ratio is 2.4. This ratio rises to 11.7 on irradiation of a solution which is 0.05 molar in 1-methyl benztriazole (**4**) and 0.02 molar in anisole. These results indicate a change in the reaction mechanism. A simple explanation would be the following: at high concentrations of the aromatic substrates, the incoming light is almost completely absorbed by the latter. By singlet-singlet energy transfer, the biradical **16** could then exist in the singlet state which would immediately react with the surrounding aromatic substrate. At very low concentration of the aromatics, 1-methyl benztriazole absorbs the light and there is a reduction in the reaction rate between the biradical **16** ($R = \text{CH}_3$) and the aromatic species, so that there is the possibility of converting the former to the triplet state. According to this view, the qualitatively different substitution patterns are caused by the different multiplicities of the biradical **16**.

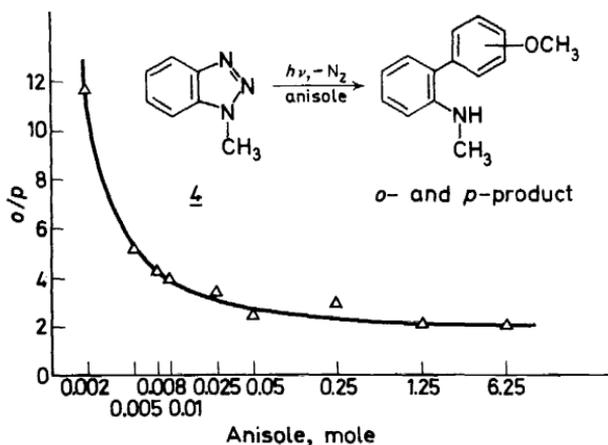


Figure 1. Irradiation of 1-methyl benztriazole (**4**; $c = 0.05$ M/l) in acetonitrile, in the presence of anisole.

[†] The same is true for chloro- and bromobenzene. Apart from the chloro- or bromo-substituted *o*-methylamino biphenyls, 9-methyl carbazole is also isolated. Methylbenzoate and nitrobenzene give no definite photoproducts.

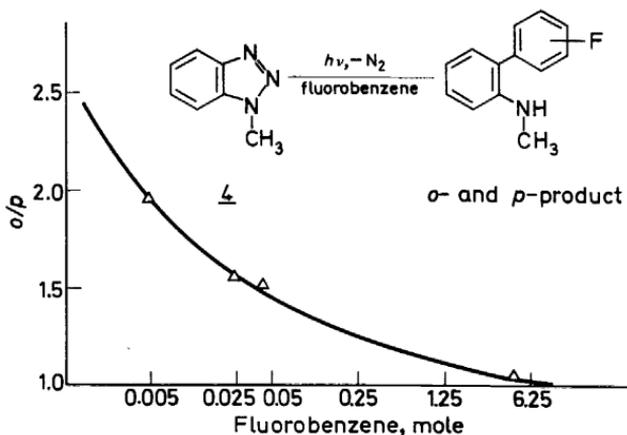
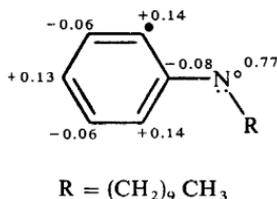


Figure 2. Irradiation of 1-methyl benzotriazole (4; $c = 0.05$ M/l) in acetonitrile, in the presence of fluorobenzene.

Irradiation of 1-decyl benzotriazole in a glass matrix composed of 2-methyl tetrahydrofuran and 3-methylpentane at 77°K, resulted in a product which showed the 7-line e.s.r. spectrum characteristic of a triplet radical⁹. Given below are the spin densities obtained (by an approximation method¹⁰) from the zero-field splittings ($D = 0.13 \pm 0.01$ cm⁻¹; $E = 0.0040 \pm 0.0005$ cm⁻¹) (see also ref. 11).

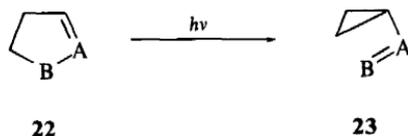


These findings support the analysis given above. Intramolecular variations of the reactions represented in scheme 2 are the photochemical conversions of 1-vinyl benzotriazoles into indoles^{3,12}, 1-phenyl benzotriazole into carbazole⁴, and of 1-(2-pyridyl) benzotriazole into mainly pyridino[1,2a]benzimidazole^{13,14}.

Photolysis of benzotriazole (3) in methanolic solution yields aniline and *o*-anisidine^{6, 8, 12}; in the presence of greater amounts of benzophenone, the Mannich condensation product, 1-anilinomethyl benzotriazole¹², arises from the formaldehyde and aniline formed, along with the benzotriazole (3). Finally, it should be mentioned that, in contrast to 2-alkylated indazoles¹⁵, anthranils^{16,17}, and benzfuran^{18,19}, both 2-alkylbenzotriazoles and 2-methyl isoindoles undergo no photoreactions.

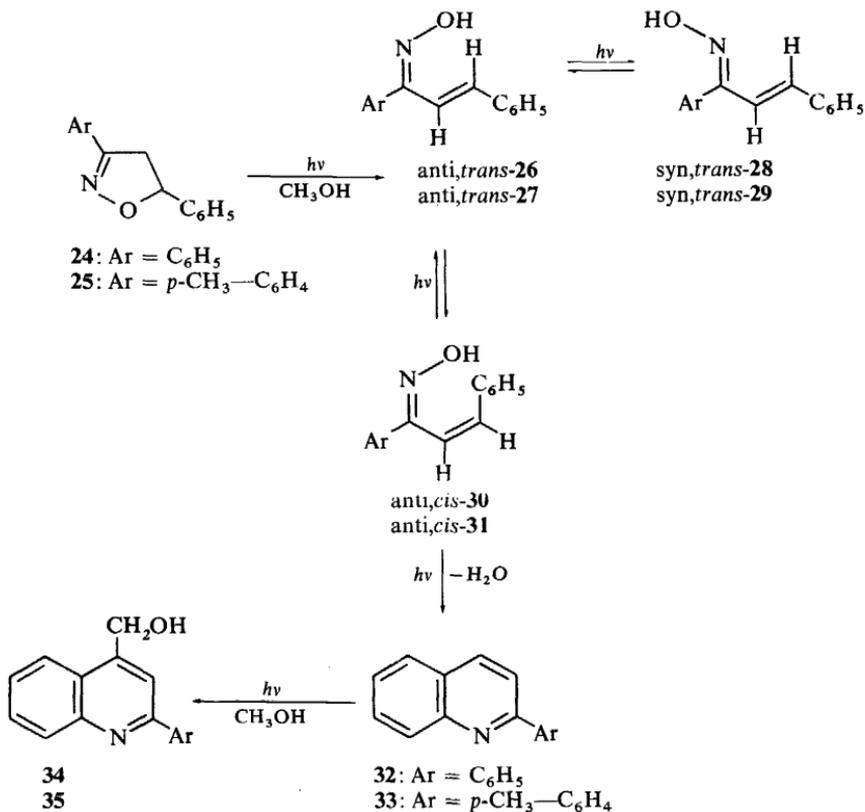
3. PHOTOCHEMISTRY OF 3,5-DIARYL-2-ISOXAZOLINES

It is known that a series of dihydro aromatic five-membered ring heterocycles of the type **22** can be isomerized photochemically to cyclopropane derivatives of the type **23** (scheme 6).



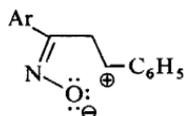
Scheme 6

In this connection, we investigated the photoreaction of 3,5-diphenyl- and 5-phenyl-3-(*p*-tolyl)-2-isoxazoline (**24** and **25**, respectively)²⁰. Two photoisomerizations were observed in methanol (scheme 7). In the first, a *syn*, *anti*- and *cis*, *trans*-mixture of chalcone oximes **26–31** is formed by cleavage of the O,C(5)-bond and shift of a hydrogen atom. The *syn* \rightleftharpoons *anti* and *cis* \rightleftharpoons *trans*



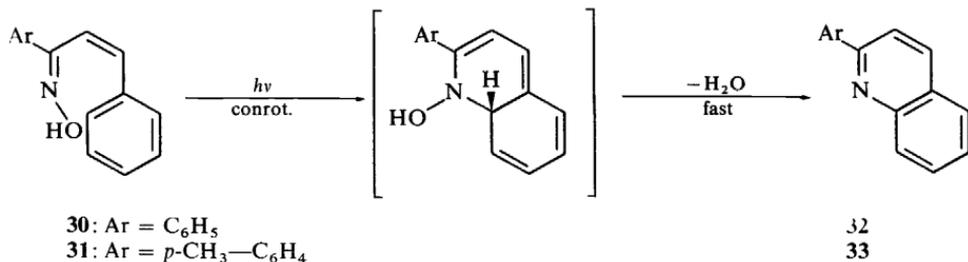
Scheme 7

rearrangements represent secondary photochemical conversions. Photochemical ring closure of the *anti*-*cis*-chalcone oximes **30** and **31** yielded the 2-aryl quinolines **32** and **33** respectively, which were hydroxymethylated to **34** and **35** respectively in a further photochemical reaction. All these products are present after 15 h irradiation of the isoxazoline. The conversion of isoxazoline \rightarrow chalcone oxime could be initiated in the excited substrate either by a homolytic fission of the O,C(5)-bond or by a heterolytic splitting to the zwitterion **36**. The conversion of the *anti*-*cis*-chalcone oximes **30** and



36

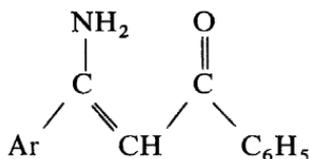
31 into the quinolines **32** and **33** respectively can be formulated as shown in scheme 8†.



Scheme 8

The ring closure has a parallel in the first step of the photochemical conversion of stilbenes into phenanthrenes (cf. ref. 21). Also related to the conversion **30**, **31** → **32**, **33**, is the thermal cyclization of pentadienal oximes into pyridines²². Reference 23 may be mentioned concerning the mechanism of the hydroxymethylation, which is sensitized by carbonyl compounds.

The second photoreaction (established in detail only for the isoxazoline **25**) yields the amino chalcone derivative **38** in low yield, the product arising by fission of the N,O-bond followed by a hydrogen shift. The product is not converted photochemically into 2-(*p*-tolyl)-quinoline (**33**).


37: Ar = C₆H₅
38: Ar = *p*-CH₃-C₆H₄

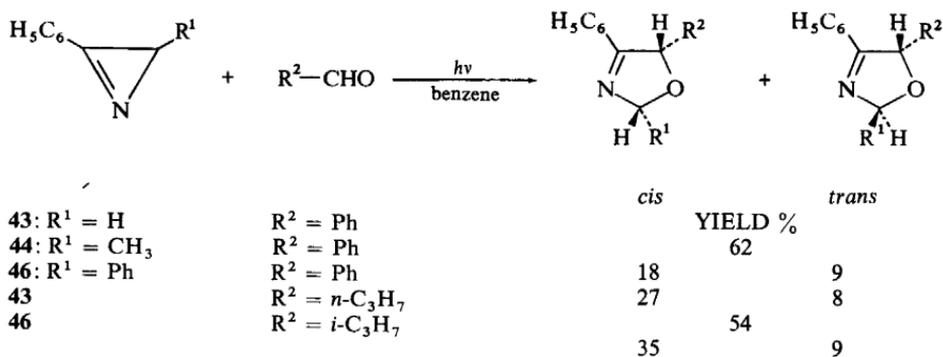
Small amounts of benzaldehyde, benzonitrile and *p*-methyl benzonitrile are also formed during the irradiation of the isoxazolines **24** and **25** respectively, in methanol.

If the first type of photoreaction of the isoxazolines in methanol is initiated by a heterolytic cleavage of the O,C(5)-bond, then one would expect that this would be suppressed by irradiation in non-polar solvents. Irradiation of **24** or **25** in benzene does in fact give, as the products of the photo-isomerization, the amino chalcones **37** and **38** respectively as well as the oxazoline derivatives **39** and **40** respectively (scheme 9), in addition to the above-mentioned cleavage products. However, chalcone oximes are no longer observed.

† Attempts to convert benzylidene acetone oxime or cinnamaldoxime into quinolines photochemically, have so far met with no success.

4. PHOTOCHEMISTRY OF 3-PHENYL-2H-AZIRINES

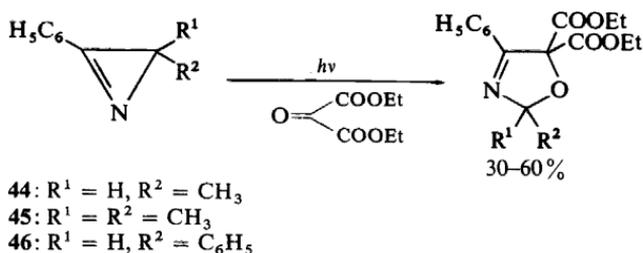
First of all, photochemical cycloadditions with 'activated' double and triple bonds may be described. This reaction of 3-phenyl-2H-azirine (**43**) is of a general nature. As well as **43**, the monomethyl derivative **44**, the dimethyl derivative **45**, and the phenyl derivative **46**, also react with aliphatic and aromatic aldehydes in preparative yields of 30 to 70 per cent, with formation of the corresponding 3-oxazolines²⁴. Reaction of azirines **44** and **46**, which are mono-substituted at C(2), results in a mixture of *cis* and *trans* isomers, in which there is normally a preponderance of the *cis* isomer. A few representative examples are given in scheme 11. In all cases, the azirines give initially



Scheme 11

benzoinitrile methylene ylides of the type **42** (cf. the photochemical conversion of 3H-diazirine into diazomethane²⁵), which then add to the aldehyde group in the same sense. The aldehyde group shows the same mode of addition with those benzonitrile methylene ylides which are generated from benzimidoyl chlorides with triethylamine²⁶.

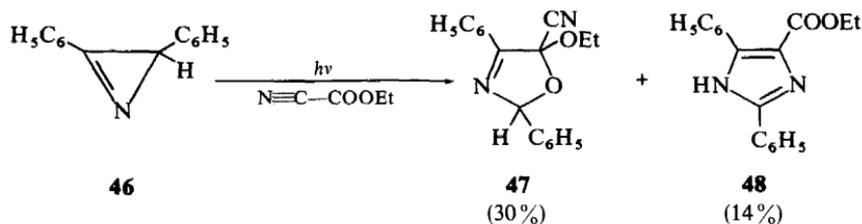
Upon irradiation the dimethyl phenylazirine **45** forms addition compounds with acetone, cyclohexanone or acetophenone in 80 to 90 per cent yield. **43** as well as **46**, however, do not react readily with acetone or acetophenone. That this non-reactivity is mainly due to electronic factors is shown from the irradiation of azirine **46** in the presence of phenyl trifluoromethyl ketone or diethyl mesoxalate²⁷ (scheme 12), in which the C,O-double bonds are more strongly polarized (cf. ref. 28).



Scheme 12

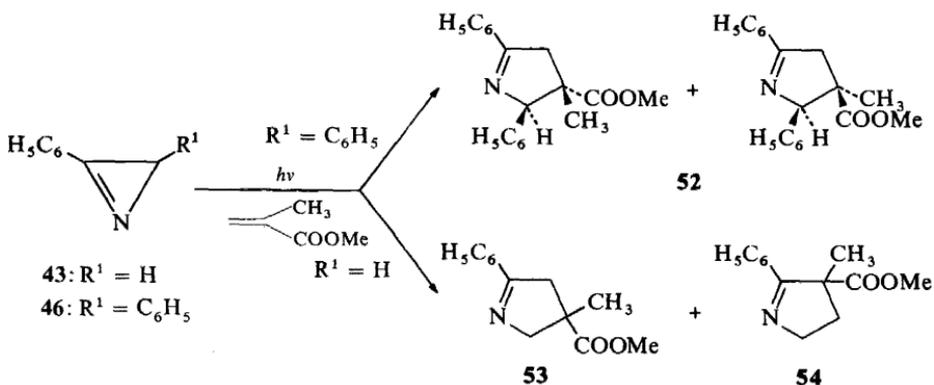
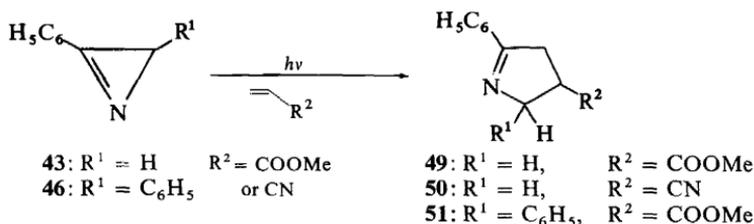
Even the C=O group in esters reacts if it is activated by a neighbouring electron acceptor. Thus, 2,3-diphenyl-2H-azirine (**46**) on irradiation in benzene with 1-cyano ethyl formate gives 5-cyano-2,4-diphenyl-5-ethoxy-3-

oxazoline (**47**), as a *cis,trans* mixture in 30 per cent yield. The $C\equiv N$ -addition product, namely 2,5-diphenyl-4-ethoxycarbonyl-imidazole (**48**), is also formed (scheme 13). 2,2-Dimethyl-3-phenyl-2H-azirine (**45**) reacts in an analogous manner.



Scheme 13

According to Padwa and Smolanoff²⁹, regioselective additions, which occur in the same sense as the additions to aldehydes, were also obtained on irradiation of 3-phenyl- and 2,3-diphenyl-2H-azirines (**43** or **46**) in methyl acrylate or acrylonitrile, in which cases the pyrrolines **49**, **50** or **51** arise (scheme 14).



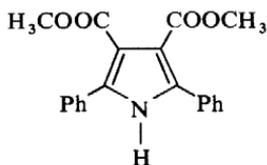
Scheme 14

The photoreaction of **46** and methyl methacrylate also proceeds in the same sense regioselectively, to give a stereo-isomeric mixture of the pyrroline **52**. On the other hand, the last-mentioned dipolarophile gives a 2:3-mixture of both pyrroline isomers **53** and **54** on reaction with 3-phenyl-2H-azirine (**43**), the reaction being no longer regioselective²⁹.

Since a mixture of **46**, a dipolarophile, and xanthone gives no photoproduct under conditions in which the latter absorbs all light, it can be concluded that the photoreaction with 313 nm light proceeds via the singlet state of **46**²⁹.

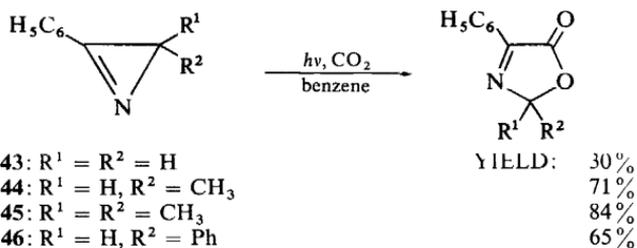
From the dependence of the quantum yield of the product on the concentration of the dipolarophile, the American authors concluded that nitrile methylene ylides are intermediates in the azirine photoreaction³⁰.

As well as the C,N-triple bond in 1-cyano ethyl formate, the C,C-triple bond in dimethoxycarbonyl acetylene can also serve as the dipolarophile for the benzonitrile methylene ylides produced photochemically from azirines. Thus, 2,3-diphenyl-2H-azirine (46) gives the 2,5-diphenyl-3,4-dimethoxycarbonyl-pyrrole (55)²⁴.



55

Especially interesting—also from a preparative point of view—are the photo-cycloadditions of phenyl azirines to cumulative double bonds^{24, 31}, which proceed mostly in good yield. Here the prime example is the photo-reaction with carbon dioxide (scheme 15).



Scheme 15

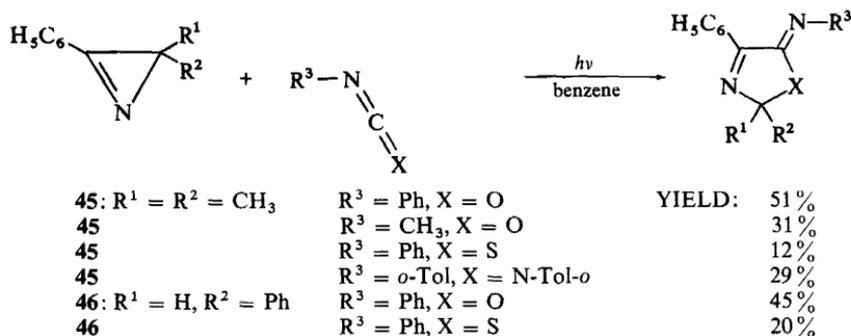
On vigorous bubbling of carbon dioxide through a benzene solution of the azirine and irradiation with a Pyrex filter, then 3-oxazolin-5-ones are formed in good to very good chemical yields. This class of compound was previously accessible only with difficulty. Some examples are listed in scheme 15. The heterocycles obtained can be regarded as isoazlactones†; if there is a H-atom on C(2), they can be isomerized with base to azlactones.

To the best of our knowledge, the above-mentioned photo-cycloaddition of carbon dioxide to a substrate represents the first reaction of its kind (see, however, the results of Krauch, Kuhls and Piek³², to be discussed later). Whereas in the natural assimilation of carbon dioxide, the oxidation number of the carbon is lowered to that in the sugars, in the incorporation of carbon dioxide into the phenyl azirine it is lowered by only one unit.

The phenyl azirines show a shoulder in the region 290 nm ($\epsilon \sim 1000$, alcohol), which we assign to the n, π^* -transition. Since the photoreaction is also observed in cyclohexane solution using a Pyrex filter, we assume that it is initiated by the n, π^* -excitation of the azirine (cf. p 348).

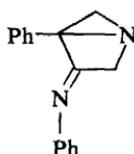
† The chemistry of these compounds is being studied more closely at the present time.

The photoreaction of phenyl azirines with substrates containing cumulative double bonds is of a general nature, as is evident from the further reactions given in scheme 16. With isocyanates and isothiocyanates it is not the C,N- but the C,O- or C,S-double bond respectively, which reacts†.



Scheme 16

German authors³³ have recently observed that irradiation of 3-phenyl-2H-azirine (**43**) in benzene solution yields a dimer, to which the structure given below was assigned. In the light of the following arguments, however, it is much more likely that this arises by a cycloaddition between **43** and the

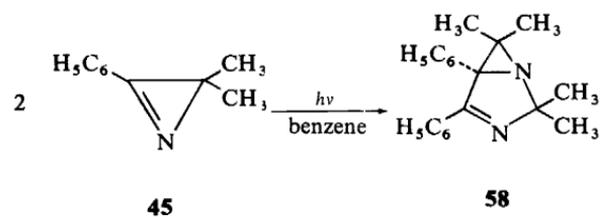
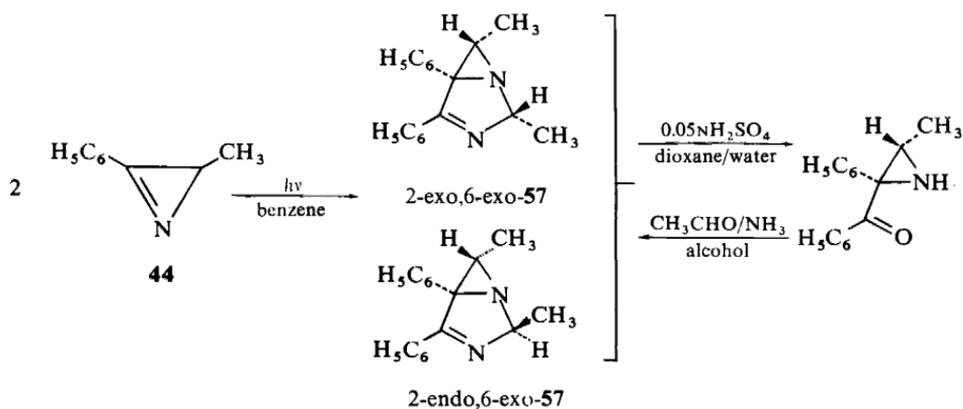
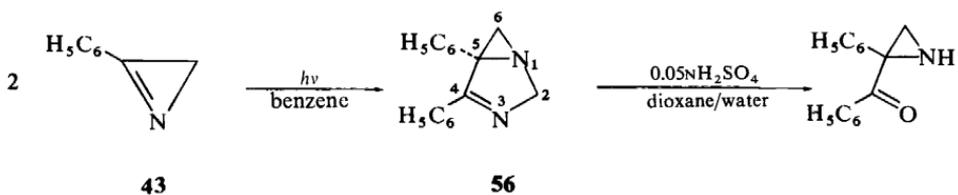


1,3-dipole **42**, produced photochemically from **43**. The dimer thus has the structure **56** (scheme 17)‡. On hydrolysis of **56**, the corresponding 2-benzoyl-2-phenyl aziridine is obtained³⁴. In analogous fashion, 2-methyl-3-phenyl-2H-azirine (**44**) and 2,2-dimethyl-3-phenyl-2H-azirine (**45**) gave on irradiation a mixture of 2-exo,6-exo and 2-endo,6-exo-**57**, and the tetramethyl bicyclic compound **58**, respectively^{12, 34}. In **57**, the methyl group on C(6) is in the exo-position in both isomers. Independently of us, Padwa, Clough, Dharan, Smolanoff and Wetmore have assigned the same structures to the photo-dimers of 3-phenyl-2H-azirines^{30, 35}. These authors also described the formation of the photo-dimers **59** from 2,3-diphenyl-2H-azirine (**46**) on irradiation of the azirine in cyclohexane.

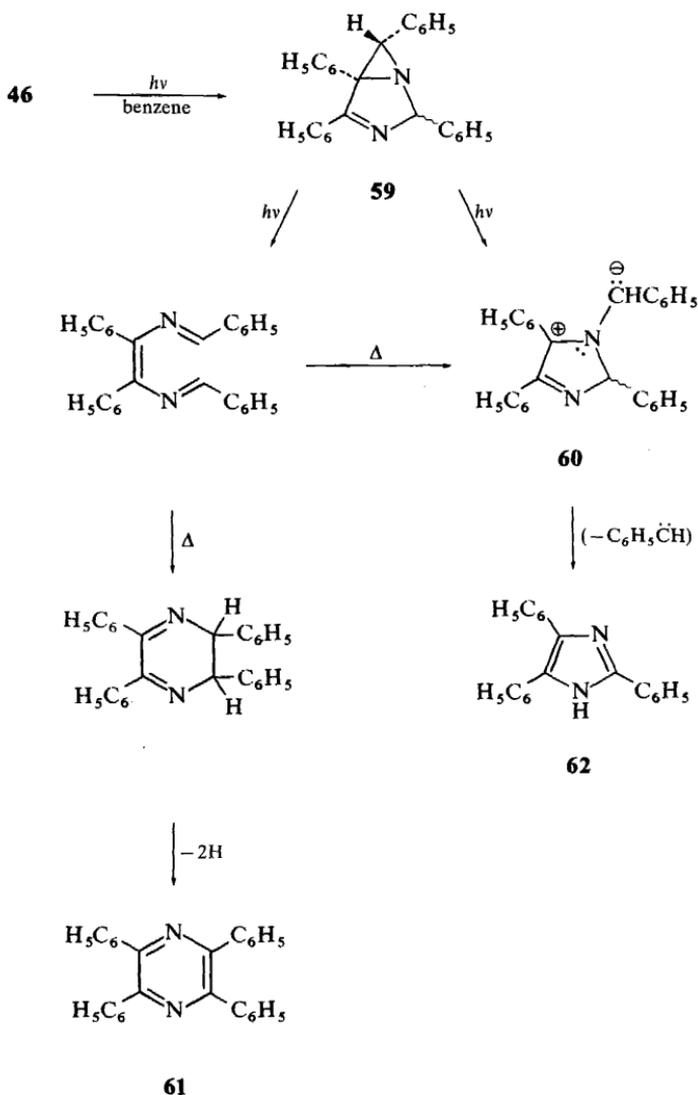
Irradiation of **46** in a benzene solution gives tetraphenylpyrazine (see refs. 30, 34) and 2,4,5-triphenyl imidazole (**62**) (scheme 18)³⁴ via **59**. Concerning the photochemical conversion of the 1,3-diazabicyclo[3,1,0]hex-3-enes into dihydropyrazines, see literature references 30, 36, and into dipoles of the type **60**, see references 37–39.

† Photo-cycloadditions with further cumulative double bond systems are in progress.

‡ Indeed, as we found, bicyclic compounds of the type **56** are also obtained, if benzonitrile methylene ylides are produced in the presence of azirines, from benzimidoyl chlorides with triethylamine.



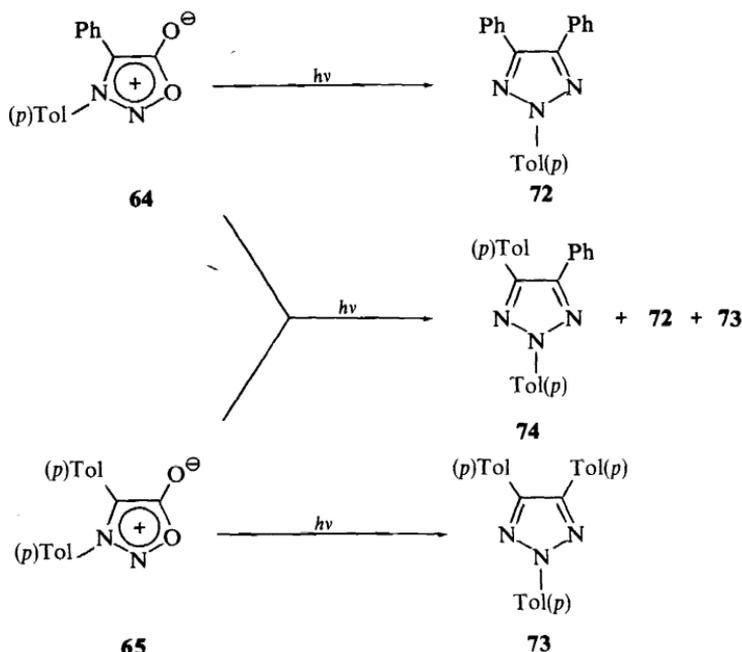
Scheme 17



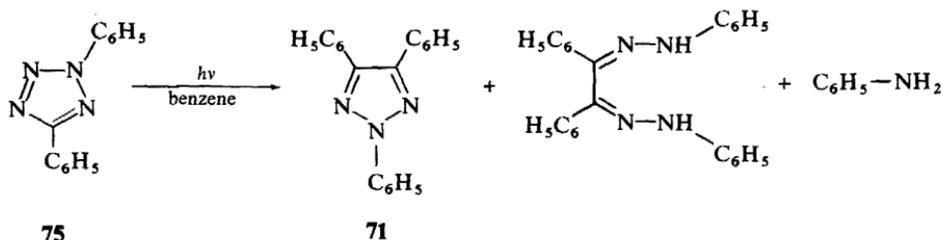
Scheme 18

5. PHOTOCHEMISTRY OF SYDNONES

Irradiation of 3,4-diaryl sydnones such as **63–65** in the presence of activated alkenes or alkynes, gives adducts whose formation can be thought of as arising by a 1,3-dipolar addition of the nitrile imines **66–68** (formed from the sydnones) to the substrates mentioned (scheme 19)^{40–43}. Thermally, isomeric cycloaddition products are formed⁴⁴ (see also refs 12, 40). On irradiation, 3-phenyl sydnone (**69**) appears not to react with 1,3-dipolarophiles, but forms 4-phenyl- Δ^2 -1,3,4-oxadiazolin-5-one (**70**) (scheme 20)³², by splitting off and then recombining with carbon dioxide. As precursors of the nitrile imines, the 1,3-diaryl-1H-diazirines, which are anti-aromatic 4π -systems, were suggested.

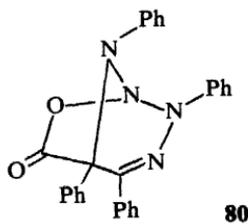


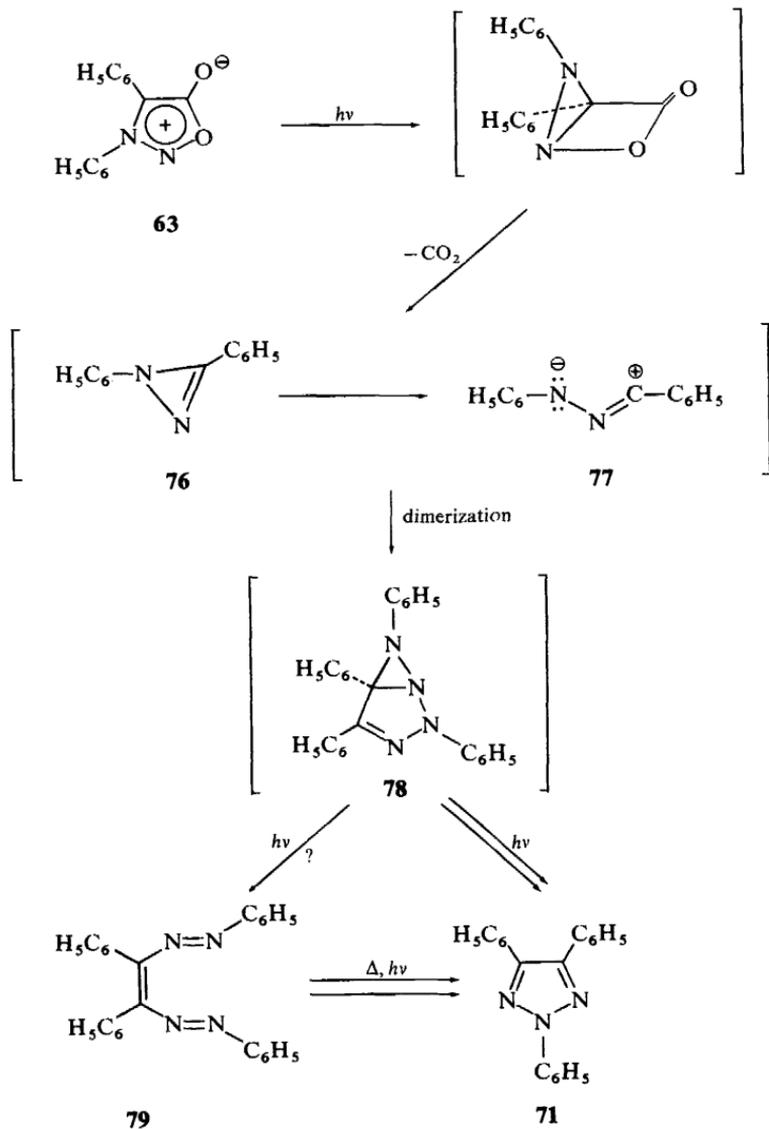
Scheme 21



Scheme 22

the 4π -systems by delocalization. Reaction of the latter with the 1,3-dipole formed from itself, could then give the dimeric bicyclic compound **78**. This could react in a manner analogous to the bicyclic compound **59** (scheme 18). It is possible that the reaction also proceeds in part via the bisazostilbene **79** (see ref. 45), about which it is known that it transforms photochemically⁴⁷ (or even thermally⁴⁸) into the 2,4,5-triphenyl-1,2,3-triazole (**71**). For the formation of **71**, one could also formulate an alternative pathway, starting with the addition of the nitrile imine **77** to the sydnone **63**, yielding an adduct **80**, which could give **78** on loss of carbon dioxide.





Scheme 23

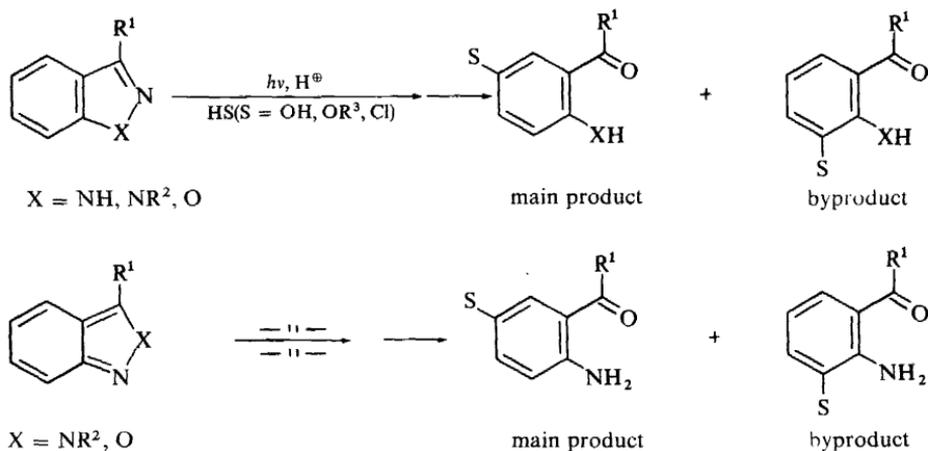
Japanese authors have made another suggestion⁴⁹. Possible formation of the 1,2,3-triazoles by dipolar addition of nitrile imines such as 77 to nitriles need not be considered, since no cross-products are formed when 63 is irradiated in the presence of an excess of *p*-toluonitrile or acetonitrile^{12, 41}.

6. PHOTOLYSIS OF INDAZOLES, BENZISOXAZOLES AND ANTHRANILS IN ACID SOLUTION

Whereas the above-mentioned ring systems undergo rearrangement reactions on photolysis in neutral solution, as was mentioned in the Intro-

duction, the reactions illustrated in scheme 24 are observed on irradiation of the protonated compounds^{50, 51} (see also ref. 52).

As a rule, the 1H- and 2H-indazoles were irradiated in 0.1–0.7 N sulphuric acid in water, methanol or other alcohols⁵¹. The chemical yields of solvolysis

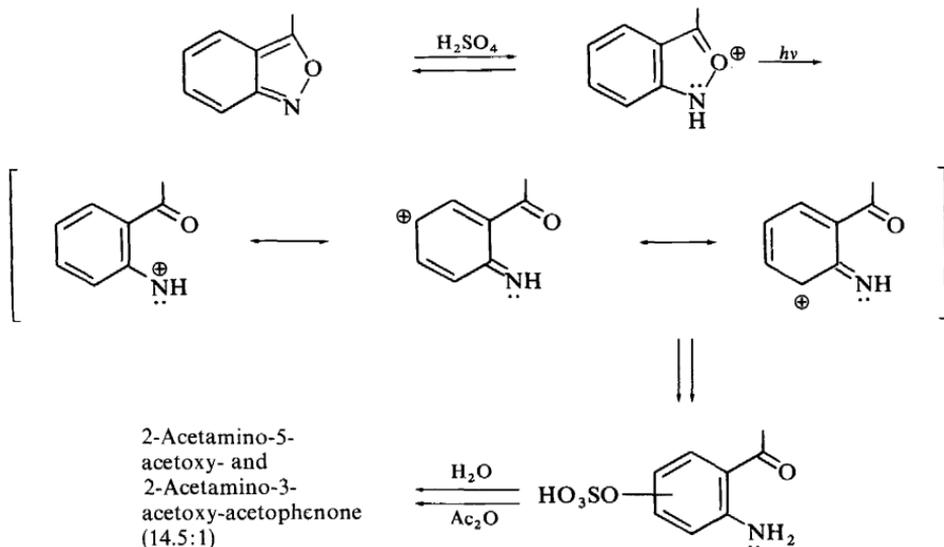


Scheme 24

products, which were often isolated as the acetylated form, normally lay in the range 20 to 75 per cent, based on reacted starting material⁵¹. For the acid concentrations given, the indazoles are completely protonated. The less basic benzisoxazoles⁵¹ and anthranils^{50, 51} were irradiated in concentrated sulphuric acid, concentrated hydrochloric acid, and also in 66 to 98 per cent sulphuric acid. The chemical yields of solvolysis products here were always significantly higher (as a rule, between 60 and 90 per cent). In all cases, it is the *p*-substitution product which predominates. The photo-induced reactions mentioned represent a preparative route to the 2-amino- or 2-alkylaminoacetylbenzenes, substituted in the 5-position.

The simplest explanation for the formation of the observed photoproducts is that arylazanium or aryloxonium ions arise by a heterolytic cleavage of the N,N- or O,N-bond in the excited, protonated starting material (presumably in the ¹S state). These ions would then react with the nucleophile SH, such that attack at the position para to the nitrogen or oxygen atoms is strongly favoured, the *o*-position being less favourable. The 2H-indazoles and the anthranils are protonated at N(1), the 1H-indazoles and benzisoxazoles at N(2), so that isoelectronic systems result. Because of the low nucleophilicity of SH (concentrated sulphuric acid!), we regard an S_N2'-type reaction of SH with the excited, protonated species as highly improbable (see later, also). On photolysis of indazoles and benzisoxazoles, the aldimine or ketimine function formed after the ring opening undergoes hydrolysis either in the reaction mixture or during work-up. The reaction path is illustrated in detail using 3-methyl anthranil as example in scheme 25.

The above-mentioned mechanism is supported by the observation that 2-azido acetophenone, on dissolving in concentrated sulphuric acid and working up under acetylating conditions, yields the same products in similar proportions⁵³. If 2-azido acetophenone is dissolved in dioxan/water/sul-



Scheme 25

phuric acid (3:3:1), then it is stable at room temperature, i.e. it is not yet protonated⁵³. On irradiation of the solution, the amino-hydroxy acetophenones are likewise formed. In this case, after splitting off nitrogen, the more basic azene is generated which is immediately protonated to the azenium ion (see ref. 55 and literature cited therein).

1H-Indazoles, methylated in the 5-position, and also 1,7-dimethyl indazole yield only reduced products of the type **81** (cf. scheme 26) on irradiation in aqueous acid solution. In methanolic acid solution, methyl ethers, in which the methoxy group is in the 6-position, are also formed, along with the reduced products. The methyl ethers certainly arise from the primarily formed dienimine intermediate **84** (or the equivalent intermediate with an aldimine group) which first of all adds methanol in an acid-catalysed reaction. Acid-catalysed elimination of methanol results in the 6-methoxy derivative (scheme 26).

5-Methyl-substituted anthranil behaves differently. Thus on photolysis in 98 per cent sulphuric acid followed by acetylating work-up, the latter compound forms the two substitution products **88** and **89**, along with the reduced product **87**. In the formation of **88**, the 5-methyl group has migrated to the 6-position, which is more electron deficient in the imine than the 4-position, the migration itself occurring by an acid-catalysed cyclohexadienimine \rightarrow aniline rearrangement. The formation of **89** involves the intermediate **86** (scheme 27). The same products, namely **87**, **88** and **89**, are also obtained when the corresponding azide **90** is dissolved in concentrated sulphuric acid (scheme 27).

The formation of the above-mentioned products requires further comment. Since they are mainly reduction products which are formed on irradiation of the indazoles in aqueous acid, and as such products were also observed on irradiation of the anthranils in concentrated sulphuric acid, then it is improbable that their formation is based upon hydride transfer from the

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