PHOTOCHEMISTRY OF SOME HETEROCYCLIC SYSTEMS


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ABSTRACT

Whereas 2H-benztriazoles are photochemically stable, 1H-benztriazoles 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). 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 review and literature cited therein).
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)\. 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.

\[ \text{Scheme 2} \]

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 \( \sigma \)-type, and should thus behave as a free phenyl radical ('hard radical centre'). The radical centre on the nitrogen is of the \( \pi \)-type and the electron is thus partly delocalized through the benzene ring ('soft radical centre').

Since 5-chloro-1-methyl benztriazoie (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
Scheme 3

Scheme 4
biradical 16\((R = CH_3)\) attacked mainly the \(o-\) and \(p-\)positions of the aromatic ring of the solvent\(^\dagger\). 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 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 \((R = CH_3)\) 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.

![Scheme 5. Attack of reactive species formed by photolysis of 1-methyl benztriazole (4; \(c = 0.07-0.09\) M/l) on different aromatics.](image)

![Figure 1. Irradiation of 1-methyl benztriazole (4; \(c = 0.05\) M/l) in acetonitrile, in the presence of anisole.](image)

\(^\dagger\) 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.

342
Irradiation of 1-decyl benztriazole in a glass matrix composed of 2-methyl tetrahydrofuran and 3-methylpentane at 77°C, resulted in a product which showed the 7-line e.s.r. spectrum characteristic of a triplet radical. Given below are the spin densities obtained (by an approximation method) from the zero-field splittings ($D = 0.13 \pm 0.01 \text{ cm}^{-1}$; $E = 0.0040 \pm 0.0005 \text{ cm}^{-1}$) (see also ref. 11).

$R = (\text{CH}_2)_9 \text{CH}_3$

These findings support the analysis given above. Intramolecular variations of the reactions represented in scheme 2 are the photochemical conversions of 1-vinyl benztriazoles into indoles, 1-phenyl benztriazole into carbazole, and of 1-(2-pyridyl) benztriazole into mainly pyridino[1,2a]benzimidazole.

Photolysis of benztriazole (3) in methanolic solution yields aniline and $\sigma$-anisidine; in the presence of greater amounts of benzophenone, the Mannich condensation product, 1-anilinomethyl benztriazole, arises from the formaldehyde and aniline formed, along with the benztriazole (3). Finally, it should be mentioned that, in contrast to 2-alkylated indazoles, anthranils, and benzfurazan, both 2-alkylbenztriazoles 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).
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 rearrangements represent secondary photochemical conversions. Photocchemical 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 photocatalytic 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
31 into the quinolines 32 and 33 respectively can be formulated as shown in scheme 8†.

$$\begin{align*}
30: & \quad \text{Ar} \equiv \text{C}_6\text{H}_5 \\
31: & \quad \text{Ar} \equiv p-\text{CH}_3-\text{C}_6\text{H}_4
\end{align*}$$

**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).

$$\begin{align*}
37: & \quad \text{Ar} \equiv \text{C}_6\text{H}_5 \\
38: & \quad \text{Ar} \equiv p-\text{CH}_3-\text{C}_6\text{H}_4
\end{align*}$$

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.
The oxazolines 39 and 40 can arise only by cleavage of the starting materials into two fragments followed by recombination. Two hypotheses (pathways a and b) can be envisaged (scheme 10):

According to path a, the isoxazoline is cleaved by light to give benzaldehyde and the azirine 41, which is opened photochemically to the 1,3-dipole 42, the latter giving the oxazolines 39 or 40 with benzaldehyde. According to path b, styrene oxide and the aryl cyanide would appear as intermediates. But irradiation of both compounds together in benzene gives none of 39 or 40. On the other hand, if radioactively-labelled benzaldehyde is added to the irradiation solution of 24, then it is incorporated to a large extent in 39. These results, which had been observed as early as 1969, initiated an extensive investigation of the photochemistry of 3-phenyl-2H-azirines, which is reported in section 4. The photochemical isomerization of 24 or 25 to the chalcone oximes led to the investigation of the photolysis of protonated heterocyclic systems, which will be dealt with in section 6.

† See lecture of H. Schmid at the Deuxième Congrès International de Chimie Hétérocyclique, Montpellier, July 1969.
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-oxazolines. 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 benzonitrile methylene ylides of the type 42 (cf. the photochemical conversion of 3H-diazirine into diazomethane), 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 triethylamine.

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 mesoxalate (scheme 12), in which the C,O-double bonds are more strongly polarized (cf. ref. 28).

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-
According to Padwa and Smolanoff, regiospecific 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 13

According to Padwa and Smolanoff, regiospecific 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 regiospecifically, to give a stereo-isomeric mixture of the pyrrolines 52. On the other hand, the last-mentioned dipolarophile gives a 2:3-mixture of both pyrrole isomers 53 and 54 on reaction with 3-phenyl-2H-azirine (43), the reaction being no longer regiospecific.

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.
PHOTOCHEMISTRY OF SOME HETEROCYCLIC SYSTEMS

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 photoreaction\(^{30}\).

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)\(^{24}\).

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{H} & \\
\text{H}_3\text{COOC} & \quad \text{COOCH}_3 \\
\end{align*}
\]

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 photoreaction with carbon dioxide (scheme 15).

\[
\text{H}_5\text{C}_6 \quad \text{R}^1 \quad \text{N} \quad \text{R}^2 \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \text{hv, CO}_2 \\
\text{benzene} \\
\text{H}_5\text{C}_6 \quad \text{O} \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \text{N} \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \text{R}^1 \quad \text{R}^2
\]

43: R\(^1\) = R\(^2\) = H
44: R\(^1\) = H, R\(^2\) = CH\(_3\)
45: R\(^1\) = R\(^2\) = CH\(_3\)
46: R\(^1\) = H, R\(^2\) = Ph

YIELD: 30% 71% 84% 65%

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 Piek\(^{32}\), 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 (ε ~ 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†.

\[
\begin{align*}
&H_2C_6
\end{align*}
\]

\[
\begin{array}{c}
\text{H}_{\text{C}} \quad \text{R'} \\
\text{H}_5\text{C}_6\text{N} \quad \text{R}_3
\end{array}
\]

\[
\begin{array}{c}
\text{hv} \\
\text{benzene}
\end{array}
\]

\[
\begin{array}{c}
\text{R'} \\
\text{R}^3 \quad \text{N} \\
\text{N} \quad \text{R}^3
\end{array}
\]

\[
\begin{array}{c}
\text{hv} \\
\text{benzene}
\end{array}
\]

\[
\begin{array}{c}
\text{R}^1 \quad \text{R}^2 \quad \text{R}^3 \quad \text{X}
\end{array}
\]

\[
\begin{array}{c}
\text{R}^1 \quad \text{R}^2 \quad \text{R}^3 \quad \text{X}
\end{array}
\]

\[
\begin{array}{c}
\text{YIELD:} \quad \text{51}\% \\
\text{31}\% \\
\text{12}\% \\
\text{29}\% \\
\text{45}\% \\
\text{20}\%
\end{array}
\]

Scheme 16

German authors 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 obtained. 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. 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 photodimers of 3-phenyl-2H-azirines. 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) 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.
PHOTOCHEMISTRY OF SOME HETEROCYCLIC SYSTEMS

Scheme 17
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). Thermally, isomeric cycloaddition products are formed (see also refs 12, 40). On irradiation, 3-phenyl sydnone (69) appears not to react with 1,3-dipolarophiles, but forms 4-phenyl-Δ<sup>2</sup>-1,3,4-oxadiazolin-5-one (70) (scheme 20), 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.
The 2,4,5-triaryl-1,2,3-triazoles 71–73 were obtained in 25 to 32 per cent yield on irradiation of the sydnones 63–65 in the absence of dipolarophiles. The 1,2,3-triazoles are not obtained if there is a sufficient quantity of dipolarophile in the reaction mixture. On irradiation of an equimolar mixture of 64 and 65, then, as well as the triazoles 72 and 73, the cross-product, namely 2,4-di-p-tolyl-5-phenyl-1,2,3-triazole (74) is also obtained, in approximately the statistical ratio of 1:1:2 (scheme 21).

2,4,5-Triphenyl-1,2,3-triazole (71) is also formed in good yield, along with a little benzil osazone and traces of aniline (scheme 22), when 2,5-di-phenyl tetrazole (75) is irradiated. A similar photoreaction is also observed with 2-methyl-5-phenyl tetrazole.

There are several different explanations possible for the photochemical formation of the 1,2,3-triazoles from the sydnones. One of these, which is outlined briefly below (scheme 23), would be analogous to the conversion of the conversion of 2,3-diphenyl-2H-azirine (46) into 2,4,5-triphenyl imidazole (62) and would necessitate the formation of the anti-aromatic 1,3-diphenyl-1H-diazirine.

However, the phenyl rings at N(1) and C(3) may influence the stability of
the \(4\pi\)-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 photochemically\(^{47}\) (or even thermally\(^{48}\)) 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.
Japanese authors have made another suggestion\textsuperscript{49}. 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\textsuperscript{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 alcohols \(51\). The chemical yields of solvolysis
products, which were often isolated as the acetylated form, normally lay in
the range 20 to 75 per cent, based on reacted starting material \(51\). For the acid
concentrations given, the indazoles are completely protonated. The less basic
benzisoxazoles \(51\) and anthranils \(50, 51\) were irradiated in concentrated sul-
phuric 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-alkylamino-
acylbenzenes, substituted in the 5-position.

The simplest explanation for the formation of the observed photoproducts
is that arylazanium or aryloxenium 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 \(S^2N\)-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
proportions \(53\). If 2-azido acetophenone is dissolved in dioxan/water/sul-
PHOTOCHEMISTRY OF SOME HETEROCYCLIC SYSTEMS

\[
\text{H}_2\text{SO}_4 \quad \text{hv} \quad \text{H}_2\text{O} \quad \text{Ac}_2\text{O} \quad \text{HO}_3\text{SO} \quad \text{NH}_2
\]

2-Acetamino-5-acetoxy- and H\text{2}O
2-Acetamino-3-acetoxy-acetophenone
(14.5:1)

Scheme 25

phuric acid (3:3:1), then it is stable at room temperature, i.e. it is not yet protonated\(^5\). 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 aldime 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
Scheme 26

81 +

82 +

83 +

84

P. CLAUS, et al.
solvent to the azanium ions. On the contrary, we assume that the substitution products arise from the singlet state and the reduced products from the triplet state of the azanium ions (see ref. 56), which remove a hydrogen atom from the substrate—and/or the solvent molecules. The reduced products are indeed observed mainly when the rate of substitution is decreased either due to steric reasons or because of the low nucleophilicity of the solvent, so that a singlet → triplet conversion becomes possible. This aspect of the behaviour of aryl azanium ions is under current investigation.
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