PHOTOCHEMISTRY OF QUATERNARY SALTS OF AROMATIC HETEROCYCLES AND SOME OF THEIR MESOIONIC DERIVATIVES (REVIEW)

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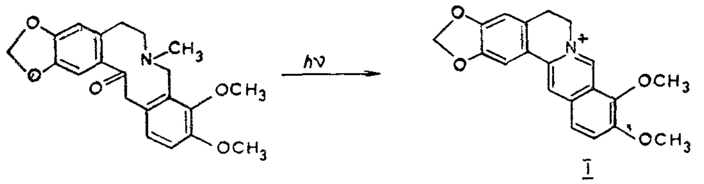
The photochemical methods for the synthesis of quaternary salts of aromatic heterocycles, their photochemical reduction reactions, photoreactions with water, some photochemical transformations that proceed without a change in the charged heterocycle, and photoreactions involving valence isomerization and fragmentation of the mesoionic derivatives are examined.

The photochemistry of quaternary salts of aromatic heterocycles and some of their mesoionic derivatives was not adequately reflected in a recent review on the photochemistry of heterocycles [1]. Considering the peculiarities of this class of compounds, we decided to fill this gap without, however, considering the formally related cyanine dyes and N-oxides. The properties of the former are associated to a considerable extent with the polymethine chain (see, for example, [2]), which is absent in the other systems, and the photochemistry of such dyes is therefore of independent interest. The principal directions of research on the photochemistry of N-oxides were presented in the review mentioned above [2], and the new research that has appeared since then (see [3]) has not fundamentally changed the situation.

Photochemical Methods for the Synthesis of Quaternary Salts of Aromatic Heterocycles

Several types of photoreactions that lead to quaternary aromatic heterocycles – construction of a properly charged heteroring, closing of new carbocycles or heterocycles to quaternary aromatic heterocyclic compounds, and alkylation (arylation) of heterocycles – have been described.

The reactions of the first type include the well-known (in the alkaloid series) photochemical closing of a quaternary heterocycle as a result of transannular interaction of the carbonyl and amino groups [4]. It leads to berberine (I) and its derivatives:



The photochemical intramolecular acylation of the benzene ring in II gives protoberberine derivatives III in good yield [5].

The photocyclization of the benzoyl analog of II proceeds differently under similar conditions to give IV [6]. (See equation on following page.)

Many quaternary and mesoionic aromatic heterocycles have been synthesized by photocyclodehydrogenation. Thus, irradiation of alcohol solutions of 1-styrylpyridinium salts and substituted 1-styrylpyrid-

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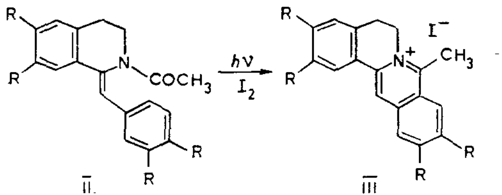
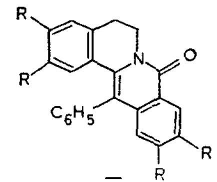
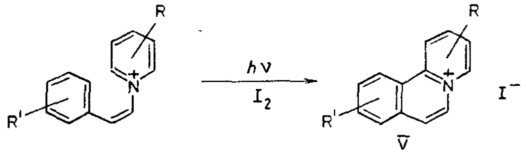


II III



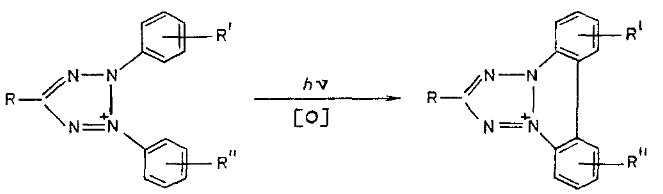
IV

inium salts in the presence of iodine makes it possible to obtain phenanthridizinium derivatives V in good yields (up to 60%) [7, 8]. Selective cyclization was not observed when the starting 3-methylpyridinium ring was unsymmetrically substituted [8] (both possible isomers are formed).



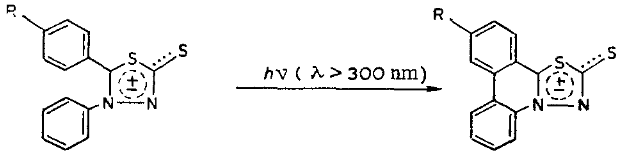
V

The photodehydrocyclization of 2,3-diaryltetrazolium salts (VI) has been studied for numerous examples [9-13]. As in the carbocyclic series, nitro compounds were not cyclized. In contrast to the β and γ isomers [13], cyclization did not occur if one of the aryl groups was α-pyridyl. Photocyclization often gives high yields (35-85%) and may be of preparative interest.

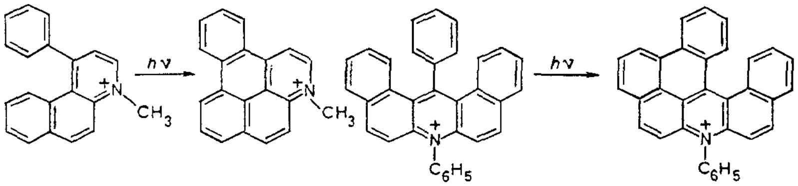


VI

Similar photocyclization was observed on irradiation of mesoionic diaryl-1,3,4-thiadiazoles VII (30% yield) [14, 15] and condensed pyridinium derivatives VII [16] and VIII [17].



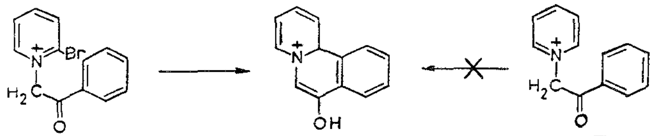
VII



VIII IX

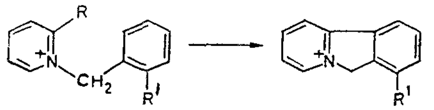
Although photodehydrocyclization of salts of aromatic heterocycles is, on the whole, extremely similar to the analogous reactions of carbocycles and heterocyclic bases, the differences in the reactivities of the salts and bases are sometimes extremely substantial. Thus, in contrast to quaternary salt VIII, the corresponding phenylbenzoquinoline is not cyclized under the same conditions but is capable of undergoing this sort of transformation in strongly acidic media [16]. 1,3-Diphenylbenzo[*f*]quinoline behaves similarly [18]. The reduced reactivity of the heterocyclic bases as compared with the salts is probably caused by the possibility of $\pi^* \leftarrow n$ transitions in the former. This same reason leads to loss of the ability to undergo cyclization in the case of some substituted stilbenes, which have low-lying n,π^* levels, inasmuch as the presence of the latter reinforces processes involving the deactivation of the excited $S_1(\pi^* \leftarrow \pi)$ state of the cis-stilbenes [19] that is responsible for the cyclization [20].

The photochemical dehydrocyclization of the 1-phenacylpyridinium ion (X) could not be realized, but the corresponding phenanthridizinium ion (XI) can be obtained by photocyclization of the 2-bromo-1-phenacylpyridinium ion (XII) [21].

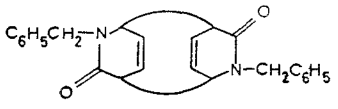


XII XI X

A related reaction, although it leads to closing of a nonaromatic ring, is photocyclization of 2-halo-1-benzylpyridinium ions (XIII, R = Cl, Br; R' = H), which makes it possible to obtain the previously unknown pyrido[2,1-a]isoindolium derivatives (XIV) in good yields [21, 22].



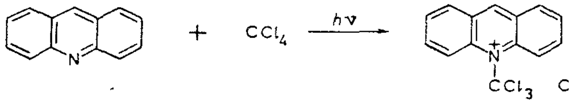
XIII XIV



XV

The isomer containing a halogen in the ortho position of the benzyl residue (XIII, R = H, R' = Hal) cyclizes much more slowly and gives a poorer yield; this indicates the lower reactivity of the halogen in the benzene ring. This is also indicated by the fact that the dibromo derivative (XIII, R = R' = Br) is cyclized only in one direction, corresponding to splitting out of a bromine atom from the pyridinium ring [22]. The fluoro derivative (XIII, R = F, R' = H) does not undergo photochemical cyclization but is converted to a 1-benyzl-2-pyridone dimer (XV). The primary reaction is apparently reaction with the solvent – water. The compound that does not contain a halogen atom (XIII, R = R' = H) photocyclizes very slowly [22].

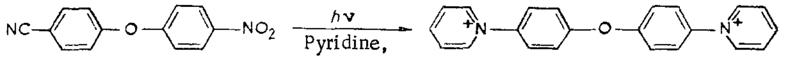
Examples of the photochemical quaternization of aromatic heterocycles are well known. Thus, UV irradiation of solutions of acridine [23, 24] and benzacridines [24] in CCl_4 and $CBrCl_3$ leads to N-trichloromethyl derivatives,



XVI

for example, to XVI. On the basis of a comparison of the quantum yields of the reaction with the calculated π-electron charges on the nitrogen atoms in the $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ excited states, Kellmann [24] proposes an ionic mechanism for the quaternization, but his conclusion seems inadequately substantiated.

The photochemical N-arylation of pyridine and 4-picoline occurs during nucleophilic substitution of the nitro group in the excited states of ethers and esters of p-nitrophenol [25-27]. p-Nitrophenol itself and m-nitroanisole, nitrobenzene, and p-dinitrobenzene do not react under these conditions [26]. On the other hand, the nitrile group in the other ring can be replaced simultaneously with replacement of the nitro group in diphenyl ether derivative XVII [27].



XVII

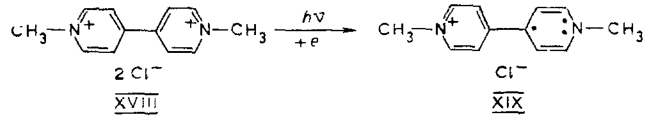
The N-arylation of pyridine gives good yields and is of preparative interest; this type of reaction has not been studied for other heterocycles.

Photochemical Reduction of Quaternary Aromatic Heterocycles

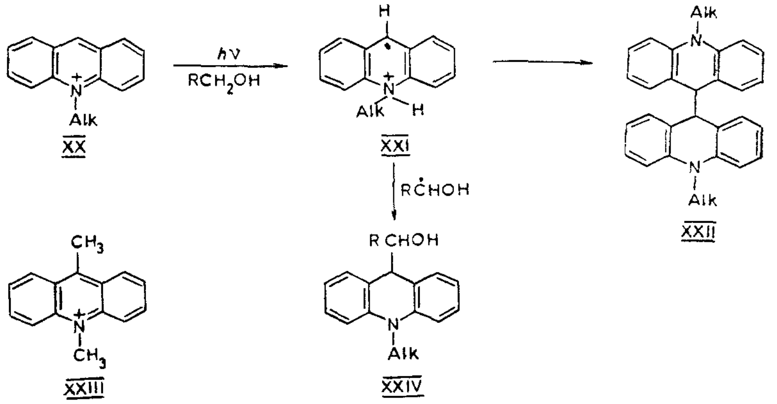
The appearance of anomalous long-wave absorption bands in the electronic spectra of the iodides or bromides of quaternary aromatic heterocycles has been explained as being the result of photoreduction of the cations to the corresponding radicals as a consequence of electron transfer from the halide ion to the positively charged heteroring in a solvated ion pair [28]. The $I_2^{-}\cdot$ and I_3^{-} ions were identified during flash photolysis of solutions of iodides of substituted N-alkylpyridinium and -quinolinium ions [29, 30]; this made it possible to consider the formation of $I^{\bullet}$ to be proved [30].

$$R + I^- \rightleftharpoons (R^{\cdot}I^{\cdot}) \rightleftharpoons R^{\cdot} + I^{\cdot}$$
$$I^{\cdot} + I^- \rightleftharpoons I_2^-$$
$$2I^{\cdot} \rightleftharpoons I_2$$
$$I^- + I_2 \rightleftharpoons I_3^-$$

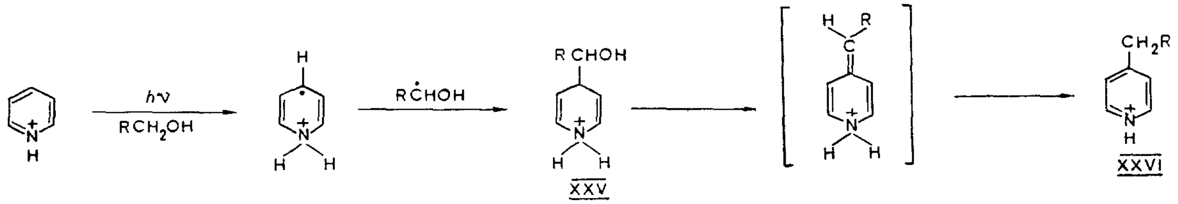
The same authors also observed absorption that was apparently related to the quinoline radical. The formation of $Cl^{\bullet}$ was similarly observed in the case of dichloride XVIII [31], i.e., the chloride ion also may act as a reducing agent of the most electrophilic quaternary salts of heterocycles during irradiation. Hopkins and co-workers [32] investigated the photoreduction of salts XVIII to cation radical XIX by primary and secondary alcohols. They assume that the rate-determining step is electron transfer from the alcohol molecule to the singlet excited state of dication XVIII. The alcohol radicals formed were detected by means of spin labeling.



The photoreduction of acridinium salts XX by alcohols proceeds via a different scheme. The principle products are 1,1'-dialkyl-9,9'-diacridanyls XXII [33, 34]. It is proposed [34] that the first triplet state of the acridinium ion strips a proton from the alcohol to give radical cation XXI, which dimerizes. Dimer XXII, although it can be isolated, is photochemically unstable and decomposes to 1-alkylacridinium ion and 1-alkylacridan [34]. Göth and co-workers [35] under similar conditions observed the formation of not only dimers XXII but also hydroxyalkyl derivatives XXIV, which correspond to the reaction of radical cations XXI with alcohol radicals. In the case of 9-substituted XXIII, in which dimerization is difficult, the yield of the product of reductive hydroxyalkylation increases to 40%.



Although there are no available data on similar photoreactions of quaternary pyridinium and quinolinium salts, the reaction of protonated pyridines [36] and quinolines [37] with alcohols, which occurs during irradiation, is well known.

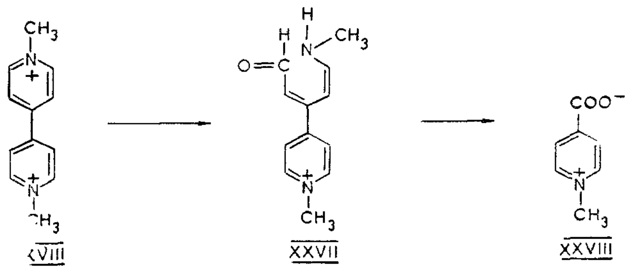


Its principle products are 1,2- and 1,4-dihydro derivatives (for example, XXV), which are readily dehydrated in acidic media to give 2- and 4-alkylquinolines and -pyridines (for example, XXVI).

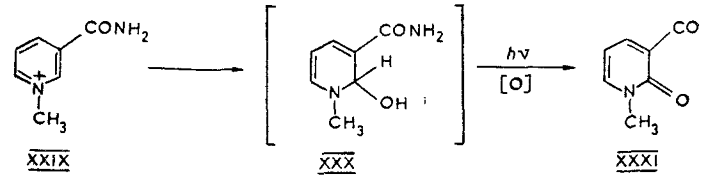
Biochemical investigations of photosynthesis processes in plants indicate that the photoreduction of a substituted pyridinium ion – nicotinamide adenine dinucleotide – possibly plays an important role in them (see, for example, [38]). However, an attempt to accomplish this transformation in vitro was unsuccessful [39].

Some Photoreactions of Quaternary Aromatic Heterocycles with Water

A number of pyridinium salts undergo complex transformations on irradiation in water. For example, the photodegradation of the herbicide paraquat (XVIII) leads to cleavage of the pyridinium ring to ultimately give an isonicotinic acid derivative (XXVIII) [31, 40]. Amino aldehyde XXVII is proposed [34-40] as the intermediate in the formation of the latter, but it remains unclear what relationship the paraquat radical cation, which is readily formed on irradiation, has to this process.



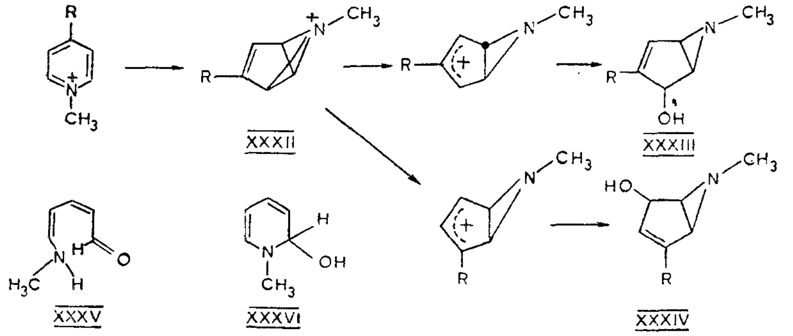
A quaternary derivative of nicotinamide (XXIX) undergoes photooxidation to a substituted α-pyridone (XXXI) on photolysis in aqueous solution [41]. It is supposed that the latter is formed from the product of the dark hydrolysis of the pyridinium ion – 1-methyl-2-hydroxy-1,2-dihydro derivative XXX – but this assertion has not been proved.



In addition, the photohydrolysis of pyridinium ions which includes a skeletal transformation is known [42]. In alkaline media, this reaction proceeds practically to completion and gives 6-azabicyclo[3.1.0]hex-3-en-2-ol derivatives XXXIII and XXXIV in good quantum yields (~0.1). To explain the 1,2-shift of substituents that is sometimes observed in the case of picolines and lutidines, it has been assumed that 1-(methylazonio) benzovalene (XXXII) is initially formed.

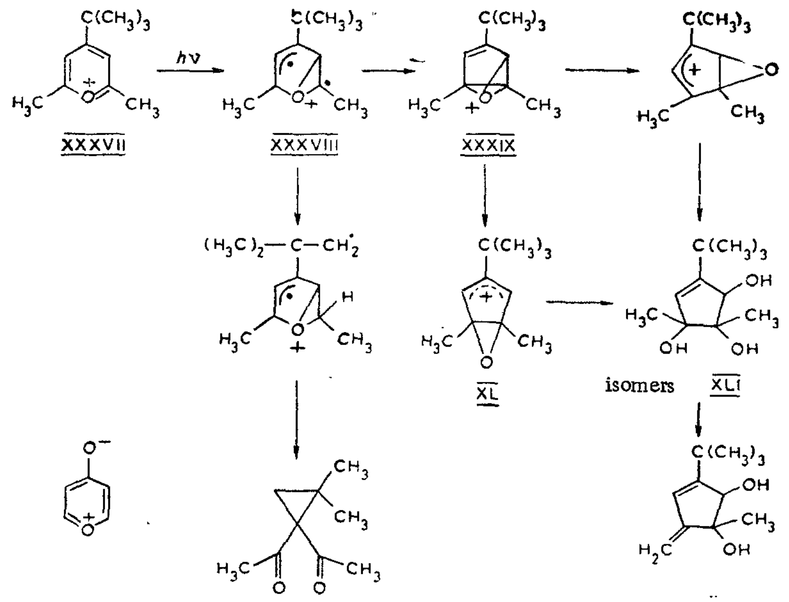
Thus, there is a similarity to the photohydration of benzene, which proceeds through benzovalene [43]. This similarity is apparently due to the $\pi^* \leftarrow \pi$ nature of the excitation of the quaternary heteroring. (Pyridine, in which $\pi^* \leftarrow n$ excitation is possible, is photohydrated differently to "Dewar pyridine" [44, 45].) In neutral or acidic media, bicyclic compounds (XXXIII) readily undergo reverse dark rearrangement to give pyridinium ions, and the intermediately observed UV absorption may be related in one case to chain amino aldehyde XXXV and in the other case to 1-methyl-2-hydroxy-1,2-dihydropyridine (XXXVI) [42].

In this connection, it can be assumed that bicyclic products of the XXXIII type are also initially formed in the above-described, more complex transformations of pyridinium ions [34, 40, 41], and the XXXIII then undergo transformations in analogy with XXXV or XXXVI.



In order to explain the origin of XLI-XLIII – products of the photolysis of pyrillium salt XXXVII in water – Barltrop and co-workers [46] successfully used the concept of the intermediate formation of oxoniobenzovalene XXXIX, (see equation on following page), the precursor of which is assumed to be cation diradical XXXVIII rather than cation XL, inasmuch as the transformations of the latter do not explain the development of diketone XLII.

The same authors propose a scheme with an oxoniobenzovalene intermediate to explain the data in [47] on the photolysis of α-pyrones. The prerequisite for the similarity between the latter and pyrillium salts is a sufficiently large contribution to their electronic structures of limiting structure XLIV.



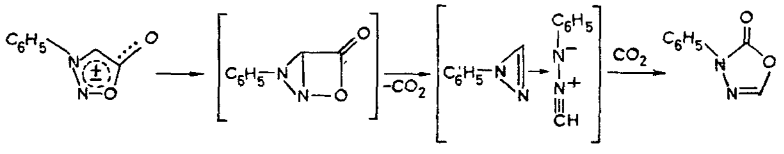
XXXVII XXXVIII XXXIX XL XLI XLII XLIII XLIV

Photochemistry of Mesoionic Compounds

Misoionic compounds can be considered to be aromatic quaternary heterocycles that have substituents with an integral negative charge in which the observed intramolecular compensation of charges can be transmitted only by valence structures of diradical character. The effective charges in mesoionic heterocycles are considerable, and this makes them closely resemble quaternary heterocycles.

The data presented below on the photochemical reactions of mesoionic compounds show that fragmentation and isomerization reactions are first and foremost characteristic for them, i.e., the excited states of the mesoionic heterocycles and quaternary heterocycles that are responsible for the photochemical transformations differ in their reactivities.

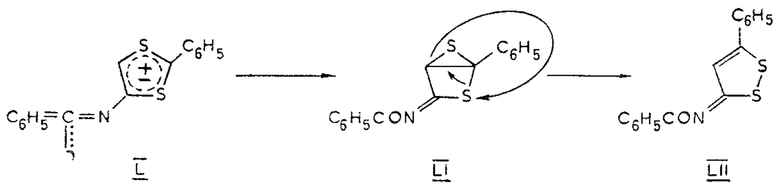
Several types of transformations during which, as it is assumed, intermediate [2.1.0] bicyclic compounds are formed, are known for five-membered mesoionic heterocycles. Thus, it has been found [48] that the photolysis of N-phenylsydnone (XLV) gives isomeric 4-phenyl-Δ^2-1,3,4-oxadiazolin-5-one (XLIX); experiments with $^{14}CO_2$ and a study of the dependence of the formation of oxadiazoline XLIX on the carbon dixoide pressure have shown that splitting out and subsequent addition of CO_2 in a different orientation apparently occur. It is assumed that either diazirine XLVII or nitrilimine XLVIII participate in the addition reaction. It should be noted that only the indicated photoisomerization was observed during an attempt to introduce sydnone XLV into photochemical cycloaddition with reagents containing multiple bonds.



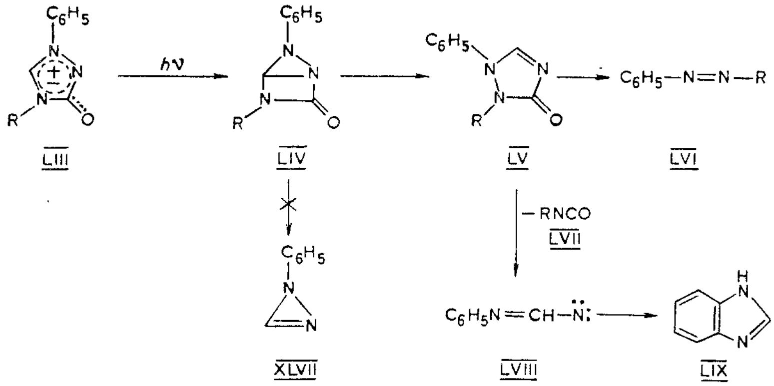
XLV XLVI XLVII XLVIII XLIX

This sort of isomerization was not noted in the photolysis of 3,4-diphenylsydnones. The formation of the chief photolysis products – 2,4,5-triphenyl-1,2,3-triazoles and some other substances – is explained [49-51] by a complex chain of transformations of C,N-diphenylnitrilimines or diphenyldiazirines that arise from the bicyclic compound, as in the case of XLVI. The structures of the adducts of the photochemical 1,3-dipolar cycloaddition of olefins and acetylenes, which gives yields up to 50-80% [50-52], also indicate that nitrilimines are formed intermediately during the photolysis [51].

However, the results of research on mesoionic 1,3-dithiolium [53] and 1,2,4-triazolium [54] derivatives provide evidence that valence isomerization to a new five-membered heterocycle that does not have formal charges may precede cleavage of the bicyclic intermediates. Thus, 1,3-dithiolium compound L is converted (in 80% yield) to 1,2-dithiol LII as a result, as assumed in [53], of sigmatropic rearrangement of bicycle LI.



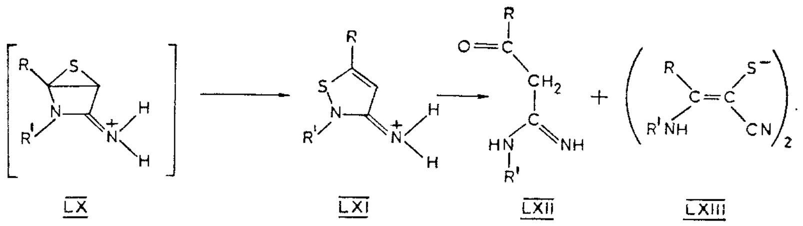
The principle products in the photolysis of LIII are arylazobenzene LVI, arylisocyanate LVII, and benzimidazole (LIX). The formation of benzimidazole in this case and its absence in the photolysis of N-phenylsydnone made it possible to conclude that these two phototransformations proceed without the formation of a common intermediate (diazirine XLVII might have been assumed to be such an intermediate). The isomerization of bicycle LIV to triazole LV with subsequent transformations of the latter explains the structures of the final products obtained.



The assumption of initial valence isomerization thus eliminates the necessity for resorting to an examination of the formation of unstable 4π-electron 1H-diazirines in the photofragmentation of mesoionic five-membered heterocycles.

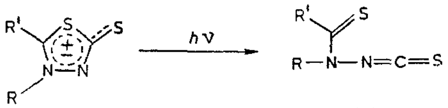
The two indicated schemes of the transformations (with the intermediate formation of a 4π-electron heterocycle and with valence isomerization) cannot be distinguished on the basis of other investigations, in which the individual photofragmentation products were identified. These investigations included, for example, the isolation of diphenylacetylene and sulfur during the photofragmentation of 2,4-diphenyl-1,3-dithiolium-5-olate [55] and the tying up of the benzonitrile sulfide formed during the photolysis of 4-phenyl-1,3,2-oxathiazolium-5-olate and its derivatives [56] as a result of reactions with acetylenedicarboxylic acid ester. It was apparently expedient to specially synthesize the proposed intermediate five-membered heterocycles and investigate their transformations in order to verify the assumption regarding the valence isomerization of the primary intermediate – a [2.1.0]bicycle.

The structures of the products of photolysis of 2,3-disubstituted 4-aminothiazolium salts in water enabled Chinone and co-workers [57] to also assume the formation of bicyclic compounds LX as intermediates. Although the scheme for the formation of the two chief final products of the reaction of LXII and LXIII is not completely clear, it seems probable that LXII arises as a result of valence isomerization of bicycle LX to isothiazole LXI and its subsequent cleavage.



Photolysis of sydnonimine salts in water gives α-keto acids [57]. The difference between these results and the above-indicated data on sydnones is apparently associated to a considerable extent with the pronounced change in the nature of the solvent.

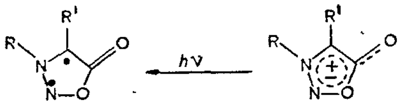
1,3,4-Thiadiazolium-2-thiolates (LXIV) undergo photofragmentation with the intermediate formation of unstable heterocumulenes LXV, which are detected from the IR spectra [58]. The formation of heterocumulenes LXV is not, however, a purely photochemical transformation, inasmuch as their bands are not observed in the IR spectrum during low-temperature photolysis.



LXIV LXV

In a recent study [59] it was found that the photolysis of 4-phenyl-1,3,2-oxathiazolium-5-olate apparently procedes simultaneously via two paths, one of which commences with the formation of a [2.1.0] bicycle, while the other begins with the formation of a heterocumulene.

Summarizing the above-indicated experimental data, which provide evidence for the ready formation of [2.1.0]bicyclic compounds from five-membered mesoionic heterocycles, it can be assumed that the bicyclic compounds arise directly from the excited states of the substrate molecules that have diradical character: the triplet states are more likely to have diradical character [60]. A calculation of sydnone, sydnonimine, and the sydnonimine cation by the MO method (within the Pople–Pariser–Parr approximation) [61] indicates the low energy of the first triplet state. Considerable charge transfer, which should occur during the $T_1 \leftarrow S_0$ transition (it can be thoroughly illustrated, with the well-known restriction [60], by valence structures LXVI and LXVII),

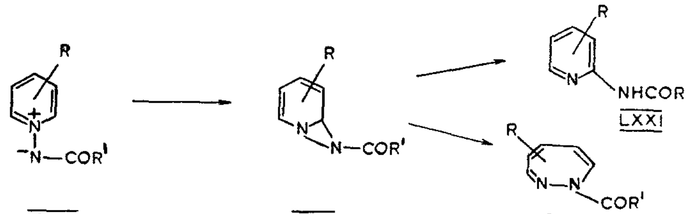


LXVI LXVII

can increase the probability of this transition.

It should be added that in the first triplet state of sydnone and its derivatives, the highest spin density values are precisely in the 2 and 4 positions, due to which a new σ bond should be formed (this is illustrated by structure LXVI). This allows us to assume that it is probable that the first triplet states participate in the examined photochemical transformations of sydnones and related compounds, but there is no direct experimental evidence for this, and there are no quantum-chemical calculations for derivatives other than those of sydnones.

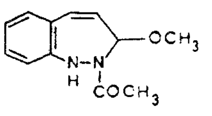
Of the six-membered mesoionic aromatic heterocycles, pyridinio-1-acylimides LXVIII, particularly 1-alkoxycarbonylimides [62-69] (in addition, 1-acetylimide [66], 1-benzoylimide, and 1-tosylimide [63, 66, 67, 69]) have been investigated almost exclusively. The chief photochemical reaction of these compounds is isomerization to 1-acyl-1H-1,2-diazepines (LXX). This photochemical synthesis seems of preparative interest, inasmuch as the yields reach 90-95% [62, 64, 67, 68]. The effect of substituents on this transformation has been investigated, although on a limited scale. Thus, it has been found that substitution of both of the α positions with methyl groups does not block the reaction, but incorporation of an ethoxycarbonylimino group in the mono-α-substituted compound occurs on the side of the unsubstituted α position [68]. A 4-ethoxycarbonyl group prevents photoisomerization (the substance is resistant to irradiation) [69]. It has been assumed [67-69] that the transformation proceeds through intermediate pyridodiazirine LXIX. The isolation of side products – 2-acylaminopyridines (LXXI) [69] and 2-aminopyridines [67] – is considered to be a confirmation of this scheme.



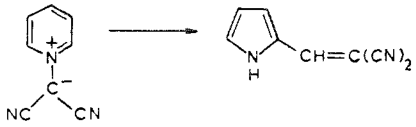
LXVIII LXIX LXXI LXX

Quinoliunio-1-acetylimide undergoes photolysis similarly to give, in low yields, 2-acetylaminoquinoline and benzodiazepine derivative LXXII, the methoxy group of which arises from the solvent (methanol) [70]. (See equation on following page.)

Inasmuch as the photoisomerization of pyridinio-1-alkoxycarbonylimide proceeds to give good yields in acetone, it has been assumed [68], that it occurs through a betaine triplet state, which is populated due to sensitization by acetone. However, it was later found [71] that the effect of the triplet sensitizer eosin



LXXII



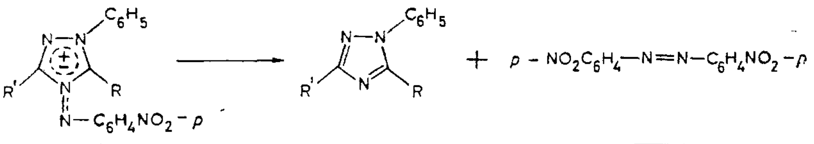
LXXIII LXXIV

reduces only to reinforcement of a side process (with respect to isomerization) – splitting out of a nitrene. When the irradiation was effected through a GWV filter in the presence of eosin, in which case the pyridiniumimide was not directly excited, cleavage predominated. In this connection, it has been concluded [71] a betaine triplet state participates in the cleavage of the nitrene. A quantum-chemical calculation [72] by the Pople–Pariser–Parr method indicates, on the other hand, an increase in the order of the bond between the exocyclic atom and the α-carbon atom of the heteroring of LXVIII in the S_1 state; this makes it possible to consider the participation of the later probable* in the formation of bicycle LXIX.

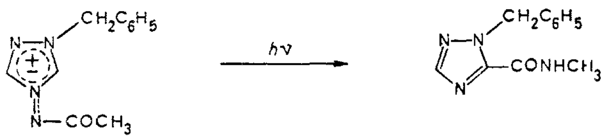
When the nature of the anionoid center of 1-pyridinium ylids there may be a pronounced change in the reactivities, which is demonstrated by the photochemical isomerization of 1-pyridinium dicyanomethylide (LXXIII) to 2-(2,2-dicyanovinyl)pyrrole (LXXIV) (the lower yield is associated with the simultaneous splitting out of a dicyanocarbene, which proceeds to a considerable degree) [64].

Side reactions (with respect to photoisomerization) of photocleavage of substituted nitrenes or carbenes were also observed in other cases [68, 70, 73, 74].

Triazolium imides LXXV have undergone only side cleavage, and the final product of the nitrene transformations was azo compound LXXVI [75]. Triazolium acetylimide LXXVII, in addition to similar cleavage, was simultaneously isomerized to triazolecarboxylic acid methylamide LXXVIII [76], but the mechanism of this reaction is not clear.



LXXV LXXVI



LXXVII LXXVIII

The reverse photochemical transformation of pyrylium 3-oxides, for example, LXXIX and its benzo derivative (LXXXI) [78, 79], to the corresponding oxides LXXX and LXXXII is well known [77]. In connection with the isolation of side products of the transformation LXXXI $\rightleftharpoons$ LXXXII in alcohol (cis- and trans-3-ethoxy-2-hydroxy-2,3-diphenylindanones), Ullmann and Henderson [79] assume that these photochromic transformations (forward and reverse) apparently proceed through vibrationally excited ground states of the tautomers, although the participation of the corresponding triplets is not excluded. To the latter one may add that the transformation of mesoionic pyrylium derivatives to bicyclic oxides could also occur via yet another mechanism – through oxoniobenzovalene derivatives LXXXIII. (See scheme on the following page.)

Photoreactions without Changes in the Quaternary Aromatic Heterocycle

The effect of a quaternary aromatic heterocycle is weakly manifested in a number of photochemical reactions of the side chain or adjacent ring. The cis-trans isomerization of quaternary salts of 1-aryl-2-hetarylethylenes [80-82], the dimerization of the same compounds to cyclobutane derivatives [80, 83, 84], and the dimerization of acridizinium salt LXXXIV [85] and its benzo derivatives [86] are among such trans-

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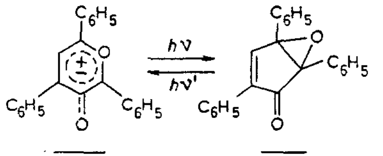
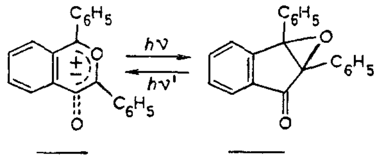
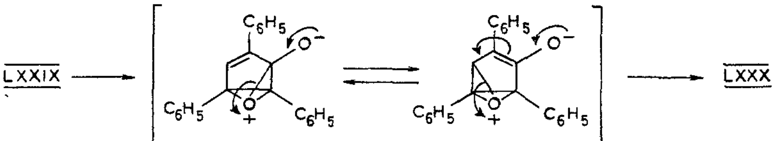
*A later study [92] showed that consideration of the orders of the bonds of the exocyclic nitrogen with the C_2 and C_6 atoms of the pyridine ring in the S_1 state is useful for the interpretation of the primary path of isomerization of substituted pyridinium imides. This path corresponds to a higher bond order, which is promoted by electron-donor substituents attached to the α-carbon atom and electron-acceptor substituents attached to the corresponding β-carbon atom.



LXXIX LXXX

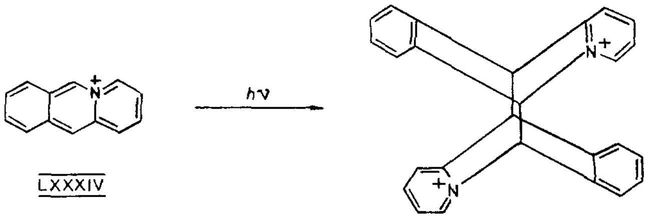


LXXXI LXXXII



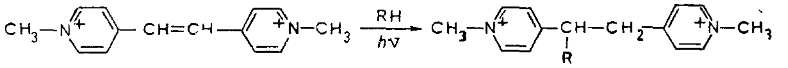
LXXXIII

formations, in which the principles established for carbocycles and uncharged heterocycles are basically retained.



LXXXIV

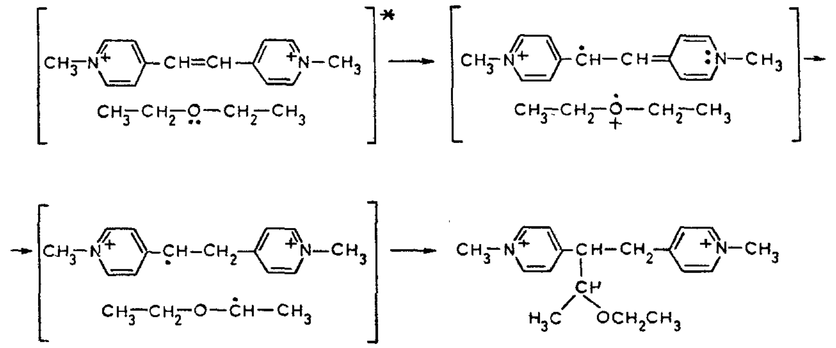
Examples of the few reactions in which the electron-acceptor effect of quaternary pyridinium rings is exerted are the photoreactions with nucleophiles of 1,2-bis(pyridinio)ethylene, for example, LXXXV [87]. The latter, like other olefins with electron-acceptor substituents [88], readily add water and alcohols on irradiation to give LXXXVI.



LXXXV LXXXVI R = OH , OR'

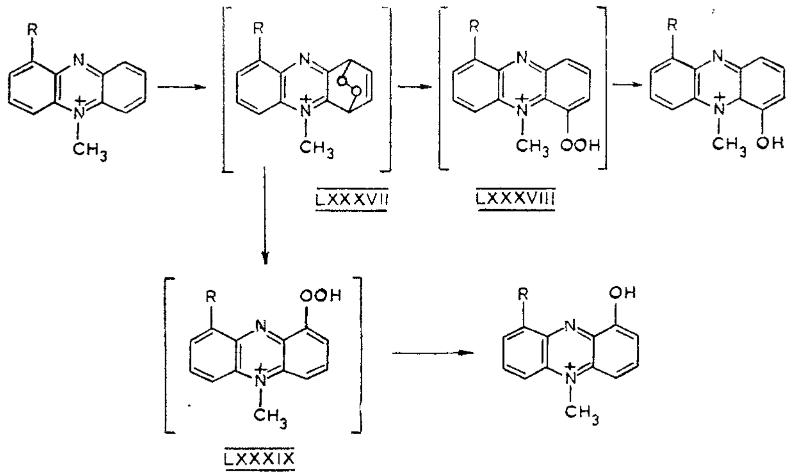
The quantum yields in the reaction of 3-pyridinio derivatives are considerably lower than in the reactions of the 2- and 4-isomers; this is explained by the weak acceptor properties of the 3-pyridinium residue.

It has been assumed [87] that the exiplexes of the LXXXV cation with water or alcohols are converted to adducts LXXXVI in the ground state (possibly with intermediate splitting out of a proton). Decomposition of the exiplex due to electron transfer to the olefin with subsequent proton transfer and addition of an ether radical is considered probable for the reaction with ethers:



The photolysis of (1-methyl-2-pyridinio)ferrocene does not involve the heterocycle and may serve as a method for the preparation of pyridinium cyclopentadienylides [89].

There are data available [90, 91] regarding the photooxidative hydroxylation of quaternary phenazine derivatives in the 6- and 9-positions.



McIlwain [90] proposes 6,9-endo-peroxide LXXXVII and the corresponding 6- and 9-hydroperoxides (LXXXVIII and LXXXIX) as intermediates.

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