The surprising photochemistry of sultams related to saccharin

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ABSTRACT. The known light induced reactions of sulfonamides and sultams are in most (but not all) cases initiated by S – N homolysis. Sulfur dioxide release may be a consequence of this primary process. In the author's laboratory three hitherto unexplored photoreactions of saccharin-derived sultams have been investigated: (i) a novel formal oxygen shift from sulfur to nitrogen generating up to now unknown cyclic N-hydroxysulfinamides; (ii) a condensative dimerization of 2,3-dihydro-1,2- benzoisothiazole 1,1-dioxide generating a new cleft molecule, and (iii) a facile allylic skeletal rearrangement of a pyrrolo-anellated dihydro-1,2-benzoisothiazole. At least in the latter two cases an initial S – N-homolysis seems to be vital for the processes observed, whereas in the first case some ambiguity remains with respect to the first step. Scope and limitations are discussed and rationales for the conversions observed are presented, with special emphasis on structure proof by X-ray crystal structure determinations. All reactions discussed have to be treated within the wider context of current sulfonamide and sultam photochemistry.

1. INTRODUCTION

Some twenty years ago we studied the photodecarbonylation of 3,3-dimethyl-2,3-dihydro-indol-2(1H)-one [1] and wanted to have an independent access to 2,2-dimethyl-1,2-dihydrobenzazetes. Since it had been found that 1,3-dihydrobenz[c]-2,1-isothiazoles **1a,b** underwent sulfur dioxide extrusion upon 254 nm irradiation in solution [2] forming the benzazetine **3** (presumably via the *O*-quinonoid imine **2**) if $R^1 = R^2 = H$, while with **1b** ($R^1 = H$, $R^2 = R^3 = CH_3$) the 2-vinylaniline **4a** was formed, it became clear that a net hydrogen atom transfer from CH_3 to the nitrogen atom took place more efficiently than ring closure. So it was not surprising that electrocyclic ring closure to the desired benzazetine failed also for **2c**, the sulfur dioxide extrusion product of **1c** [3] (Scheme 1).

Electronically excited N-propylsaccharin (**5**) on the other hand, is known to undergo (albeit more slowly than the sultams of type **1**) a probably stepwise sulfur dioxide extrusion as well with formation of N-propylbenzamide (**6**) in hydrogen donating solvents and N-propyl-2-phenylbenzamide (**7**) in benzene [4, 5] (Scheme 2).

We therefore tried sulfur dioxide extrusion from 2,3-dihydro-3,3-dimethylbenzo-1,2-isothiazole 1,1-dioxide (**8a**), based on the reasonable assumption that S – N homolysis, being the preferred mode of primary reaction in electronically excited open chain sulfonamides [6–9], was also operating in this case generating biradical **9** and (hopefully) therefrom the desired benzazetine **10** (Scheme 3). In this way the hydrogen shift problem associated with intermediates like **2b,c** should be circumvented.

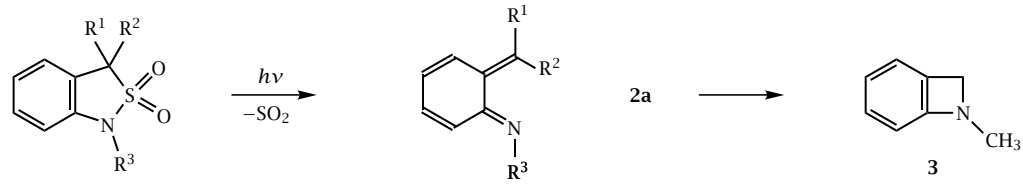
2. FORMAL OXYGEN MIGRATION

Since the UV-spectrum of **8a** in methanol displayed a slightly structured absorption around 263 nm ($\log \varepsilon = 2.90$) with a very weak tail to longer wavelengths, an irradiation with the 254 nm emission of the low pressure mercury arc seemed most appropriate, since irradiation with the Duran-filtered ($\lambda \geq 280$ nm) light of the high pressure mercury arc had failed to bring about any reaction.

To our surprise, however, no sulfur dioxide extrusion at all occurred. Instead, an efficient and probably stepwise rearrangement to the isomeric cyclic N-hydroxysulfinamide **11a** took place [10]. Analogous observations were made later upon photolysis of compounds **8b–g** [11, 12] (Scheme 4). Product quantum yields for two efficient transformations have been determined at 254 nm irradiation, **8a** → **11a** : $\Phi_P = 0.51$; **8b** → **11b** : $\Phi_P = 0.36$ [12].

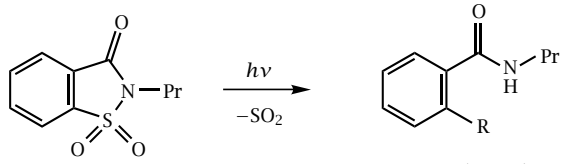
Yields may be smaller in cases where the products happen to be oils or do not precipitate easily from the photolysis mixture so that sequential dark reactions (e.g. dehydrations) or secondary photolyses generate more complex mixtures requiring chromatographic work-up.

When the photolysis of **8a** is monitored by UV spectroscopy, the overall absorbancy of the solution increases but this does not prevent complete conversion of the starting material. A less structured absorption of the product **11a** is built up, and by the routine method developed by Mauser [13] linear $\Delta A(\lambda_1)$ vs. $\Delta A(\lambda_2)$ diagrams are obtained for four different wavelengths indicating that no intermediate would be built up which were accessible to stationary UV spectroscopic detection. Thus, if the photolysis **8a** → **11a** would involve



4a: $R^1 = H$, $R^3 = CH_3$
4b: $R^1 = CH_3$, $R^3 = H$

Scheme 1.



in EtOH or PrOH: **6** (R = H)
in benzene: **7** (R = Ph)

Scheme 2.

formation of an intermediate the latter would be short lived [14].

Some general remarks regarding the scope of this reaction seem to be appropriate at this stage.

1. So far, transformations like **8** → **11** have been observed only with 2,3-dihydro-1,2-benzoisothiazole 1,1-dioxides.

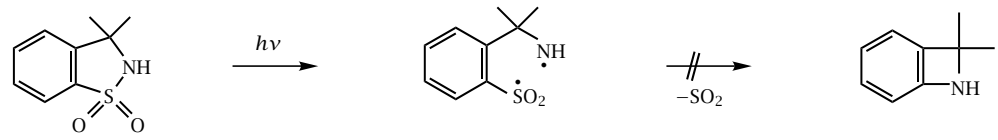
2. Among these, C-3 has to be substituted with at least one alkyl or aryl group, compound **8j** ($R^1 = R^2 = X = H$) does show another type of reaction [11] which will be treated further below.

3. The N – H proton may not be substituted by alkyl groups like methyl (as in **8h**, this compound on 254 nm irradiation gives an intractable complex mixture of products but no **11**-type product [14]) but with such groups capable of forming stable carbocations, as alkoxmethyl [12] or benzyl [15] (as in **8e–g**). In the case of **8g**, the isomer **11g** is only a by-product besides the main ring-enlarged product 4,4-dimethyl-2-phenyl-3,4-dihydro-2H-benzo-1,3-thiazine 1,1-dioxide [15], and this case deserves further study. Substitution by trimethylsilyl (**8i**) [16] does not contribute more insight since rapid desilylation occurs coupled to a build-up of turbidity when this compound is irradiated in acetonitrile [12] (in methanol, a desilylation takes place in the dark [15]).

The structures of all new compounds **11** were supported by spectroscopic data [12] and an X-ray single crystal structural analysis of **11a** [10]. Later, another X-ray structural analysis of the photoproduct of enantiopure (R)-**8c** became available (see below) which lend further support to structures **11a–e,g.** While there is no doubt about the correctness of the structural assignment it is suitable to briefly discuss the nature and properties of the photoproducts **11**.

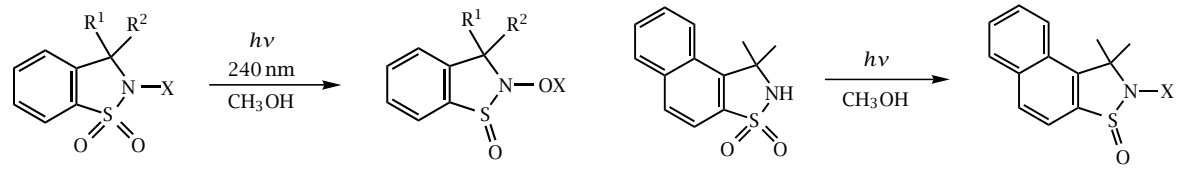
These are cyclic N-hydroxysulfinamides and thereby the first representatives of a new and hitherto inaccessible functional group, namely the sulfine hydroxamic acid (albeit in a cyclic version). All attempts to prepare this functionality by reacting a sulfinyl chloride or ester with a hydroxylamine have failed so far [17, 18]. On the other hand, *O*-alkylated sulfinyl hydroxylamines have become known but are of limited thermal stability [19]. Limited stability has also been observed for compounds **11**: While the solid samples have an infinite shelf life at room temperature, they slowly but markedly revert to starting materials **8** in solution [12]. This is also true for **11e** [12, 14]. The nature of this exothermic back reaction has not been elucidated yet, but depending on the acidity of the medium very likely more than one mechanism may be operating [14]. The back reaction may be monitored by ^1H NMR spectroscopy [14]. If an intermediate of whatever nature were involved in the back reaction it cannot be detected by this method, however.

The formal oxygen transfer from sulfur to nitrogen creates a situation in which both heteroatoms deviate in their oxidation stage from the most comfortable stage accessible: Compared to the starting materials **8**, the sulfur atom in **11** has become reduced while the nitrogen atom has become oxidized, and the backward reaction by whatever mechanism tends to restore the



8a **9** **10**

Scheme 3.

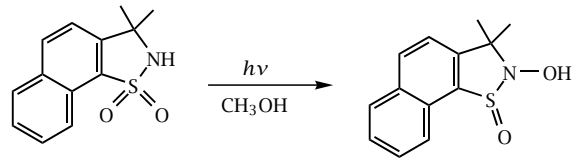


8 **11** **12**

13a: X = OH, 23%
13b: X = H, 6%

	R^1	R^2	X	
8a	Me	Me	H	(72%)
8b	Ph	Ph	H	**11b** (16%)
8c	Me	H	H	**11c** (Scheme 8)
8d	Ph	H	H	**11d** (Scheme 8)
8e	Me	Me	CH_2OMe	**11a** (51%)
8f	Me	Me	$CH_2O-i-Pr$	(see text)
8g	Me	Me	CH_2Ph	**11g** (10%, see text)
8h	Me	Me	Me	(see text)
8i	Me	Me	$SiMe_3$	(see text)
8j	H	H	H	(see text)

Scheme 4.



14 **15**

Scheme 5.

thermodynamically more stable sulfonic acid amide situation characteristical of **8**.

The photochemical processes involved may be envisaged as follows: Including the results obtained with the naphthoanellated starting materials **12** and **14** (Scheme 5), which behaved completely analogously to compounds **8** still requiring 254 nm excitation for the formation of **13** and **15**, and since no quenching has ever been observed in the presence of oxygen, the reaction may well start from an upper excited singlet state.

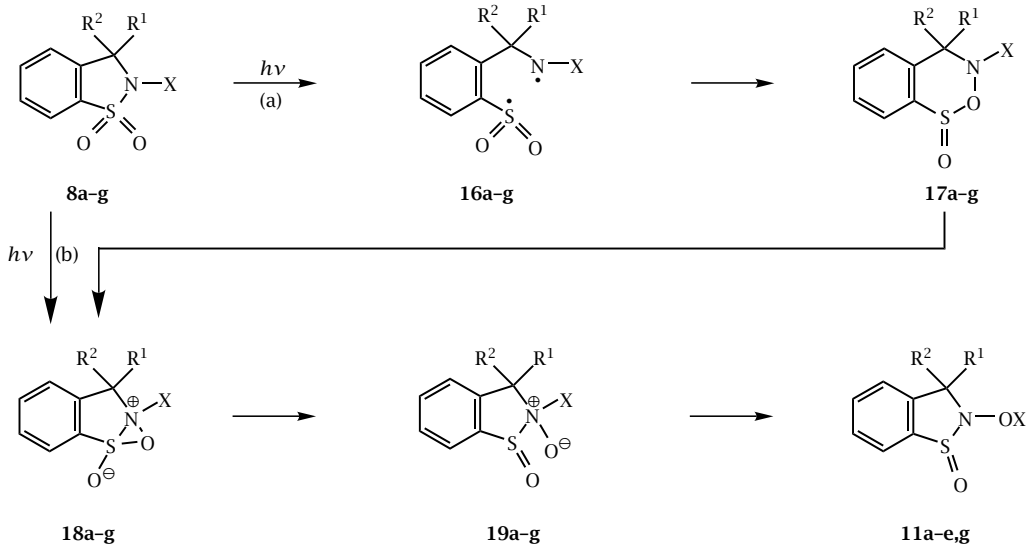
The first events following excitation may be either (a) S − N homolysis generating biradical **16** followed by N − O ring closure giving **17** (of hitherto unknown connectivity!) which finally rearranges to **18**, or (b) direct transformation of **8** into **18**, which in turn forms **19**. If X = H, a proton shift forming **11a–d** is most plausible (Scheme 6). In the case of starting materials **8e–g**, the alkyl group on N would have to be taken over by the migrated oxygen atom as well.

Photolysis of starting material **8f** (X = 2 − O−*i*−Pr) in methanol is associated with an exchange of the isopropoxy group against methoxy resulting in formation of **11e** instead of **11f**. A dark reaction exchanging the alkoxy group in methanol cannot be responsible for this result, as had been tested independently [14], so the exchange has to be coupled to the photorearrangement. A rationale has been suggested in Scheme 7.

It is assumed that 2-propoxide is released from **19f** while the N-oxide oxygen attacks the methylene carbon forming intermediate **20** which undergoes CH_2 − N heterolysis by solvent attack forming **11e**. An analogous process in **19e** would, of course, remain undetected under the conditions used.

The photoisomerizations of **8c,d** to **11c,d** show a moderate stereoselectivity. By ^{1}H NMR integration the ratio of the two diastereomers (*anti*- and *syn*-) formed upon photolysis of **8c** (**8d**) is 72:28 (69:31). In both cases the major (and thermodynamically more stable) isomer is the one with the sulfoxide O-atom *anti*-oriented to the substituent (Me, Ph) on C-3. This is both made likely by inspection of models and firmly corroborated by the single crystal X-ray structure analysis of the product (1*R*, 2*R*, 3*R*)-**11c** from (*R*)-**8c** [20] under the usual conditions. The same orientation and (relative) configuration of *anti*- and *syn*-**11d** is proposed by analogy (Scheme 8).

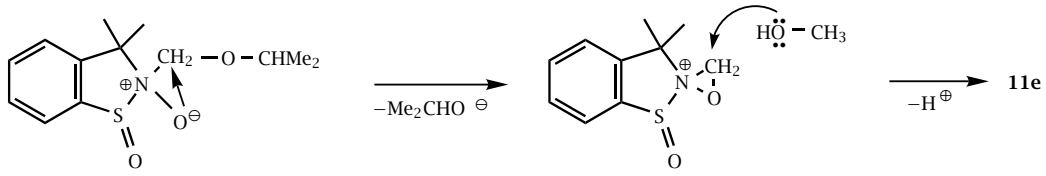
Pyramidalization at sulfur and (at least in the solid state) also on nitrogen is reflected in the ^{1}H NMR data of the products. A pyramidal array around the N-atom may well be prevailing also in solution since there is strong indication that electron attracting atoms or groups being not conjugated to the N lone pair stabilize



8a–g **16a–g** **17a–g**

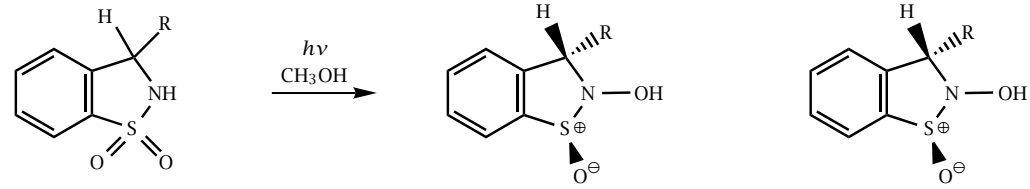
18a–g **19a–g** **11a–e,g**

Scheme 6.



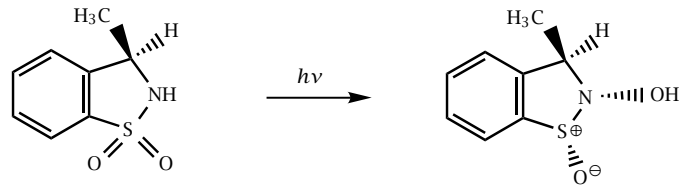
19f **20** **11e**

Scheme 7.



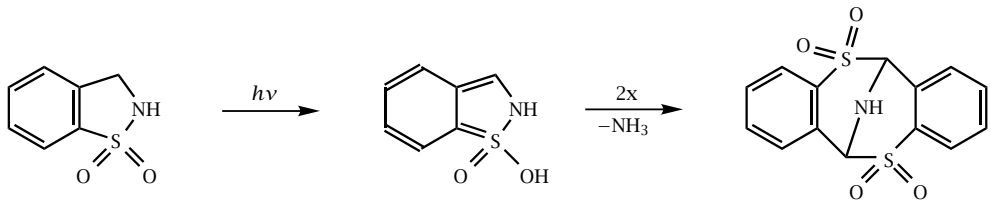
R = Me: **8c** *anti*-**11c** (> 14%) *syn*-**11c**

R = Ph: **8d** *anti*-**11d** (> 16%) *syn*-**11d**



(*R*)-**8c** (1*R*, 2*R*, 3*R*)-**11c**

Scheme 8.



8j **21** **22**

Scheme 9.

a pyramidal configuration at the N atom in heterocycles [21–23].

At present, the following problems are being tackled in our group:

1. *Secondary photolysis.* Preliminary results indicate that at least in alcoholic solvents overirradiation of starting materials **8** or irradiation of single isolated products **11** result in deoxygenation of the latter (see formation of product **13b** in Scheme 5 and other examples [14, 24]). Either one of the oxygen atoms in **11** may be lost initially [25], the final stable product always is a cyclic sulfinamide like **13b**. This problem is closely related to conventional reduction of compounds **11**.

2. *Mechanism of the backward reaction.* Upon treatment of an acetonitrile solution of **11a** with acid ($10^{-3}-10^{-4}$ M) quickly produces a brown colouring which slowly fades giving way to the formation of **8a** [14]. Another possibility of monitoring the back reaction **11** → **8** is following the change in rotation of (1*R*, 2*R*, 3*R*)-**11c**, the initial value of which (extrapolated to zero time in solution) is $[\alpha]_D^{20} = -2,3°$ (c = 0.76, methanol) [12] to $[\alpha]_D^{20} = +28°$ (c = 1.15, chloroform) which is the reported [20] specific rotation of (*R*)-**8c**.

3. A NEW CLEFT MOLECULE

As already mentioned, compound **8j** does not show any oxygen atom transfer as do **8a–g**. Instead, also under 254 nm irradiation in methanol, **8j** gave a crystalline material representing a compound formed from two molecules of starting material with loss of one molecule of ammonia [11, 26]. Since upon excitation the deuterium label of [3,3-d_2]-**8j** was exchanged quickly against hydrogen atoms [27] it seemed justified to assume that a process close to a photoenolization led to intermediate **21** which could dimerize and release ammonia to form **22** [26]. The latter compound has been fully characterized by spectroscopic data and by a single crystal X-ray structural analysis [28] showing (aside of the N – H bond) a symmetry close to C_2 and the two benzo rings folded towards each other and forming a cleft. The gross structure is somewhat reminiscent to Tröger's base (Scheme 9).

It should be clearly emphasized that

1. the course of the reaction ultimately leading to **22** so far is entirely speculative and awaits further clarification, and

2. dimerizations of diene-type compounds leading to eight-membered rings are not unusual and have been observed with various precursors [29].

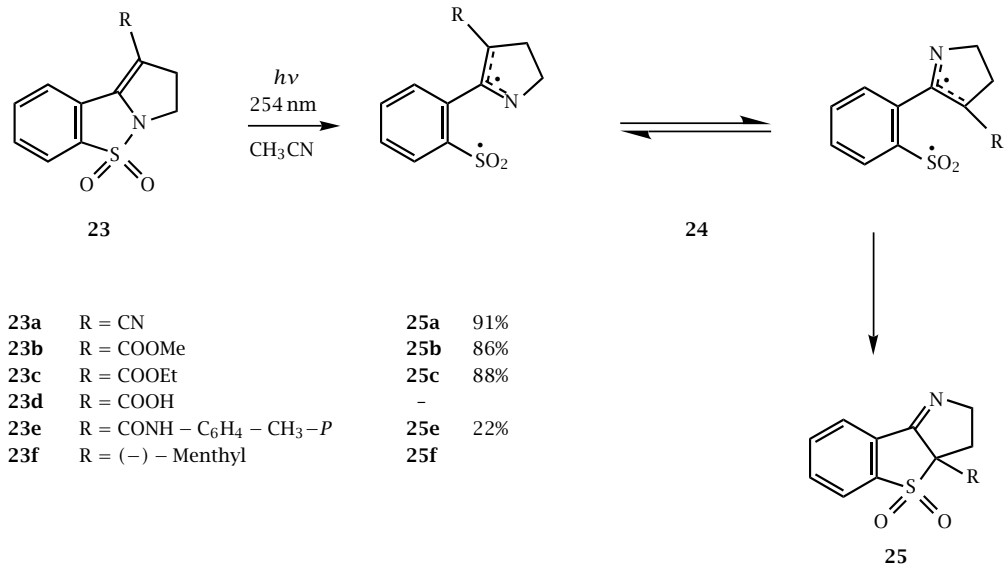
4. AN ALLYLIC SKELETAL REARRANGEMENT

Dihydropyrrolo[1,2-b][1,2]benzoisothiazole 5,5-dioxides **23a–c** [30] and **23d,e** [31] may be easily prepared from saccharin. Photolysis (254 nm) of **23a–d,e** in acetonitrile results in a clean rearrangement into the isomeric 2,3-dihydro[1]benzothieno[3,2-b]pyrrole 4,4-dioxides **25a–c,e** [31]. Again, the structures of the new products have been delineated from their spectral data (especially the consequences of build-up of a stereogenic center at C3a should be mentioned) and firmly corroborated by an X-ray single crystal structural analysis for compound **24b** [31].

The following rationale for the conversion **23** → **25** has been proposed: Light induced S – N homolysis generates the resonance-stabilized biradical **24** which uses its option to recyclize via C – S bond formation. In this way, a C = N double bond and a new C – S single bond are erected at the expense of a S – N and C = C bond. The UV-spectrum of **23c** (being representative for **23a–f**) in acetonitrile displays two distinct but structureless bands at λ_{max} = 324 nm ($\log \varepsilon$ = 4.0, with a tail to about 400 nm) and λ_{max} = 250 nm ($\log \varepsilon$ = 3.9). It had been found that irradiation into the short wavelength band of starting materials **23** most efficiently caused reaction and oxygen showed no effect, thus a start from an upper singlet state seems most plausible (Scheme 10).

Two details are especially noteworthy:

1. The comparatively long time of irradiation required to effect a 22% yield of **25e** may be rationalized not only by the reduced electron-withdrawing effect of the toluamide group but also by steric constraints compared to the more



Scheme 10.

electron demanding properties and smaller size of the acceptors present in **23a–c**.

2. When the ester **23f** formed with (–)-menthol is subjected to irradiation under otherwise the same conditions, the rearrangement shows high diastereoselectivity: Only one of the two diastereomers (with respect to absolute configuration at C-3a) of **25f** is formed [15], and a single-crystal X-ray structural analysis will allow to unravel the sense of chirality at C-3a.

A ring transformation which at first glance looks related to that reported above is seen in the rearrangement of a benzo-1,2-isothiazolo-[2,3-a]-8bH-azete into a 2a,7b-dihydro-benzothieno[3,2-b]azete as a consequence of the [2+2]-photocycloaddition of ethyl 2-butynoate to a 1,2-benzoisothiazole [32] which, however, has been interpreted by the authors in a different way. A related S – N homolysis is encountered in the photolysis of 2-sulfon-amidocyclohexen-2-ones [9] where a sulfonyl/cyclohexenaminyl radical pair is formed. In this case, however, release of sulfur dioxide is faster than recombination at the 1-azaallylic carbon atom C-3.

5. CONTEXTUAL AND CONCLUDING REMARKS

In this account coverage has been largely restricted to light induced conversions of fivemembered benzoanellated sultams studied in the author's laboratory. These cases, however, have to be seen in a wider context. A good deal of inspiration did come from the pioneering work on the photoextrusion of sulfur dioxide from sufones [33, 34] and the elucidation of the role of singlet and triplet excited states and biradicals therein. Of relevance and certainly in future also of influence on the work reported will be the aspect of electron-transfer mediation of light induced S – N homolysis in sulfonamides [35]. Intramolecular electron transfer may be responsible for the N – C mode of ring cleavage in sulforhodamines [36] adding to the various modes of reactivity to be encountered in sultam photochemistry.

Attention should also to be drawn to related work, as the classical studies on sulfur dioxide extrusion in N-propyl saccharin as already mentioned [4, 5], and the photoinduced homolyses of the O-alkyl bonds in pseudosaccharin ethers [37, 38]. It should be pointed out also that S – N homolysis, albeit a central issue in sultam photochemistry, is not restricted to the SO_2 – N moiety and may be found in non-dioxide systems as well, opening a way to interesting ring enlargements [39].

The photoreactivity of six-membered sultams is likewise attractive, as is demonstrated by the interest in the photochemistry of piroxicam [40] but also of other sixmembered sultams with various biological activities [41].

Since also many other five- and six-membered benzoanellated sultams have biological activity [42, 43], there is a natural interest in their photochemistry, and the availability of synthetic procedures [42, 44] will be helpful in preparing model substances.

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