Thioenamide Photochemistry

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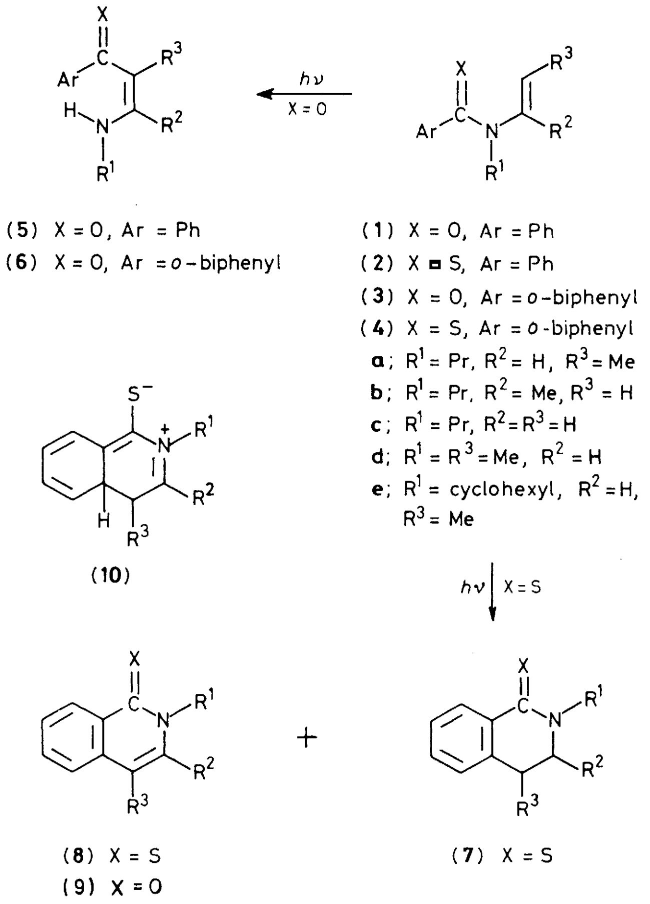
In contrast with their oxo-analogues, thioenamides undergo photochemical cyclization to yield isoquinolinethione derivatives which are easily converted into isoquinolones and tetrahydroisoquinolines by treatment with benzeneseleninic anhydride and EtO_3BF_4–$NaBH_4$, respectively.

Aromatic enamides are a class of conjugated systems possessing a marked degree of hexatrienic character. U.v. irradiation of these compounds usually results in stilbene–phenanthrene-like photo-conversion thus providing a general approach towards a wide variety of six-membered lactams.[1,2]

Curiously, the photochemical properties of aromatic thioenamides have been scarcely studied. Thus, we report an investigation of the photolytic reactions of some simple thioenamides (**2a**—**e**) and (**4a**, **d**) which illustrates an example of the dramatic difference in the photochemical behaviour of carbonyl and thiocarbonyl compounds.

Irradiation (quartz reactor, Rayonet RPR 3000 Å lamps, 2 h) of a degassed methanolic solution of the enamides[3] (**1a**—**e**) and (**3a**, **d**) results in almost complete conversion into the enaminoketones (**5a**—**e**) and (**6a**, **d**) (Scheme 1). This photo-migration of the acyl group has been already reported for a variety of *N*-acylenamines of aliphatic and aromatic systems[4] but was not observed for some enamides in which the double bond α to the nitrogen atom is exocyclic.[2,5]



Scheme 1

Assuming that the enaminoketones are probable products of a classical photo-Fries rearrangement we speculate that the use of the thio-analogues of (**1a**–**e**) and (**3a**, **d**) could induce a novel and different type of photoreaction. In fact, absence of photo-Fries rearrangement products has recently been observed in the photolysis of a variety of *o*-halogenothioacetanilides.[6]

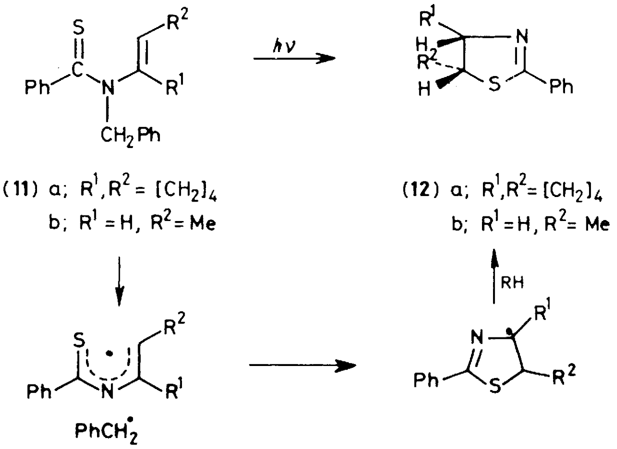
The thioenamides (**2a**—**e**) and (**4a**, **d**) are readily accessible by direct sulphuration of their oxygen analogues. The best sulphurating agent is undoubtedly the dimer of *p*-methoxyphenylthionophosphine sulphide (the commercial Lawesson reagent) in toluene (85—110 °C, 1 h) which gives conversions of up to 90%. Irradiation (quartz reactor, Rayonet RPR 2537 Å and 3000 Å lamps, 8 h) of a 0.02—0.03 M methanolic or hexane solution of the thioenamides (**2a**—**e**) afforded the isoquinolinethiones (**7a**—**e**) and (**8a**—**e**), easily separable by chromatography (Table 1). No traces of enaminothioketones (**5**) and (**6**) (X=S) could be detected in the photoreaction products.

The formation of the dihydroisoquinolinethiones (**7a**—**e**) can be attributed to a photochemical electrocyclic ring closure of a 6-electron system [leading to (**10**)] followed by a thermal [1,5]-hydrogen sigmatropic shift in compliance with the

Table 1

Reactant	Yield[a] of (**7**), %	Yield[a] of (**8**), %	Φ^bdis.
(**2a**)	35	18	0.09
(**2b**)	38	38	0.08
(**2c**)	37	25	0.08
(**2d**)	35	19	0.07
(**2e**)	40	25	0.10

[a] All new compounds gave satisfactory analytical results and had spectral properties (u.v., i.r., n.m.r., mass) consistent with the structures assigned. [b] Quantum yields of disappearance of (**2a**—**e**) estimated using 313 nm irradiation in hexane solution.



Scheme 2

Woodward–Hoffman rules. Although the solutions were thoroughly degassed before and during irradiation to exclude any photo-oxidation reaction of the thiocarbonyl group,[7] oxidized products (**8a**—**e**) were obtained. It is likely that partial desulphurization occurs during photolysis making the reaction medium slightly oxidizing. A similar phenomenon has been reported in the photolysis of *cis*-stilbene sulphide which is readily converted into phenanthrene even under anaerobic conditions.[8]

In addition to the cyclized products, irradiation of the *N*-benzylated thioenamide (**11a**) afforded the thiazoline (**12a**) whereas photolysis of the acyclic (**11b**) furnished exclusively the photochemically stable[9] thiazoline (**12b**). It is probable that the formation of these five-membered rings proceeds *via* homolysis of the *N*-benzyl bond followed by radical recombination and ultimate hydrogen abstraction as depicted in Scheme 2.

Under the conditions used in this study, the thioenamides (**4a**, **d**) were unaffected by irradiation.

The isoquinolinethiones (**8a**—**e**) can be converted into their oxo-analogues (**9a**—**e**) by treatment with benzeneseleninic anhydride[10] in tetrahydrofuran or by using sodium hydroxide with bromine under phase-transfer catalysis,[11] two viable new methods recently described. On the other hand, treatment of the dihydroisoquinolinethiones (**7a**—**e**) with triethyloxonium tetrafluoroborate followed by sodium borohydride afforded a variety of tetrahydroisoquinolines. The advantage of the utilization of thiocarbonyl compounds instead of their oxo-analogues in the reduction reaction has been recently demonstrated in the amide series.[12]

Thus, the results reported here demonstrate that the use of thio-analogues can extend the usefulness of the well documented photoelectrocyclization of aromatic enamides and can provide an alternative means of preparation of heterocyclic systems such as isoquinolone and isoquinoline derivatives.

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