Pergamon

Tetrahedron Letters, Vol. 35, No. 20, pp. 3235-3238, 1994
Elsevier Science Ltd
Printed in Great Britain
0040-4039/94 \$6.00+0.00

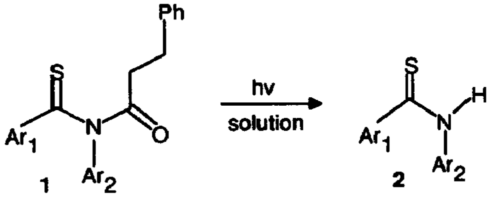
0040-4039(94)E0559-G

A NEW MECHANISM FOR THE PHOTOCLEAVAGE OF MONOTHIOIMIDES

Tai Y. Fu, John R. Scheffer* and James Trotter*
Department of Chemistry, University of British Columbia
Vancouver, British Columbia, Canada V6T 1Z1

Abstract. Based on solid state structure-reactivity correlation studies and on deuterium labeling experiments, it is concluded that the photochemical formation of thiobenzanilides **2a-d** from monothioimides **1a-d** does not involve initial γ-hydrogen atom abstraction as originally suggested in the literature. Alternative mechanistic possibilities are presented and discussed.

In a recent paper, Sakamoto and co-workers showed that acyclic monothioimides of general structure **1** form, among other products, substituted thiobenzanilides (**2**) when irradiated in solution.[1] Very reasonably, they suggested that the thiobenzanilides are formed through Norrish type II like γ-hydrogen abstraction and 1,4-biradical cleavage. In this communication we report experiments that establish that such a mechanism is not followed, either in the solid state or solution.



(**a**) $Ar_1 = Ar_2 = Ph$
(**b**) $Ar_1 = Ph, Ar_2 = p\text{-}BrPh$
(**c**) $Ar_1 = Ph, Ar_2 = 4\text{-}Br\text{-}2,6\text{-}diMePh$
(**d**) $Ar_1 = p\text{-}OMePh, Ar_2 = Ph$

Our interest in monothioimides stemmed from a desire to determine the geometric requirements for intramolecular hydrogen atom abstraction by sulfur through application of the solid state structure-reactivity correlation method. In this method, the chemical reactivity of a series of closely related compounds is determined in the crystalline state and correlated with structural data for the same compounds as measured by X-ray crystallography. Such studies have provided information on the geometric requirements for intermolecular [2+2] photocycloaddition[2] as well as for the process of intramolecular hydrogen atom abstraction by the oxygen atom of a photoexcited ketone.[3] Because they are crystalline, monothioimides appeared to be good candidates for parallel studies on the corresponding C=S···H abstraction process. Comparisons of the distance and angular requirements for C=O···H and C=S···H abstractions are of interest owing to the possibility in the latter case (but not the former) of abstraction by both n,π* and π,π* excited states, excited states that presumably utilize different (orthogonal) orbitals for abstraction.

To this end, we prepared the monothioimides **1a-d**; two of these (compounds **1a** and **1d**) had been studied previously by Sakamoto et al., who reported that upon irradiation in benzene using a 1000 W high pressure mercury lamp, they gave thiobenzanilides **2a** and **2d**, respectively along with substantial amounts of a δ-hydrogen abstraction photoproduct in each case.[1,4] Not having access to a 1000 W high pressure mercury lamp, we carried out our photolyses with a 450 W

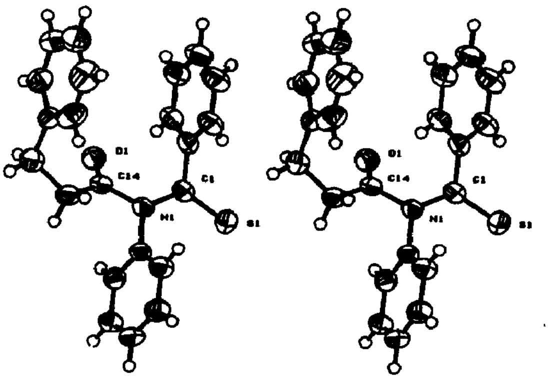
Havnovia lamp and Pyrex immersion well setup (Ace Glass). Under these conditions, in anhydrous benzene, no photoproducts of any type were formed from monothioimides **1a-d**. In benzene that had been allowed to equilibrate with the moisture in the atmosphere, however, photolysis afforded the corresponding thiobenzanilides **2a-d** and 3-phenylpropanoic acid (**5**). In a carefully controlled run with compound **1a**, photoproducts **2a** and **5** could each be isolated in 20% yield, and the only other components in the reaction mixture were unreacted starting material and a trace of benzanilide. Irradiations conducted in benzene containing 10% methanol afforded 85% isolated yields of methyl 3-phenylpropanoate and thiobenzanilide. The quantum yield under these conditions (313 nm, valerophenone actinometry) was 1.01 ± 0.09. The reaction in benzene/methanol is evidently a triplet state process, as it could be sensitized by Michler's ketone.

As in anhydrous benzene, photolysis of monothioimides **1a-d** in the solid state with rigorous exclusion of moisture led to no reaction. When no special attempts were made to exclude moisture, however, irradiation of compound **1a**, either as a powder or a single crystal, led exclusively to the same two photoproducts that were formed in benzene (**2a** and **5**), each in 9% isolated yield. Concomitant with the photochemical studies, the crystal and molecular structures of the monothioimides were determined by direct method, single crystal X-ray diffraction.[5] Surprisingly, the results of these investigations showed that compounds **1a-d** adopt conformations in the solid state for which γ or δ-hydrogen abstraction is most unlikely. All four monothioimides have essentially identical solid state conformations typified by that of **1a** shown in Figure 1. In this conformation, the shortest C=S...Hγ contact is 5.06 Å, considerably greater than the sum of the van der Waals radii for sulfur and hydrogen (3.00 Å).[6] The nearest δ hydrogen is even further away at 6.33 Å. Table 1 summarizes the shortest C=S···Hγ and C=S···Hδ distances for all four monothioimides. Based on previous research from our laboratory, which indicates that hydrogen atom abstraction by oxygen fails when the C=O···H contacts exceed the sum of the van der Waals radii by 0.3-0.4 Å,[3] we may safely conclude that the distances listed in Table 1 are too great to allow abstraction of either γ or δ hydrogen atoms.

Table 1. Crystallographic Contacts in Thioimides

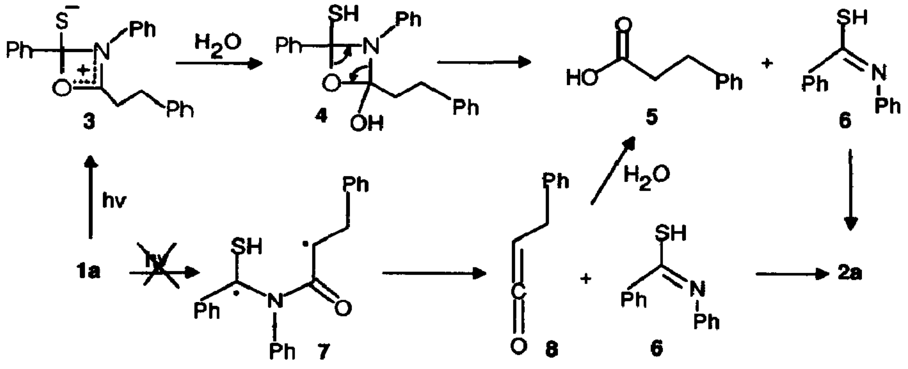
Imide	C=S···Hγ (Å)	C=S···Hδ (Å)	O···C=S (Å)
1a	5.06	6.33	2.86
1b	5.14	6.22	2.77
1c	5.06	6.55	2.82
1d	5.07	6.44	2.81

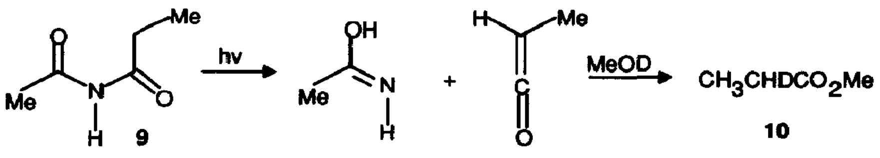
Figure 1. Stereodiagram of Thioimide **1a**



To verify the lack of hydrogen atom abstraction, we synthesized monothioimide **1a** containing two γ-deuterium atoms and subjected it to solid state photolysis under non-anhydrous conditions.[7] Detailed analysis by ^{1}H NMR and MS showed no detectable loss of deuterium label in the derived 3-phenylpropanoic acid. The alternative Norrish type II mechanism predicts the formation of monodeuterated 3-phenylpropanoic acid and is clearly inconsistent with the labeling results. Exactly the same result was obtained when compound **1a**-γ-d_2 was irradiated in moist benzene, indicating that γ-deuterium atom abstraction is absent in solution media as well. Further corroboration of this point was obtained by irradiating unlabeled **1a** in the presence of CH_3OD. Photolysis (450 W medium pressure mercury lamp) of monothioimide **1a** in a solvent system composed of 1:4 (v/v) CH_3OD:benzene gave undeuterated methyl 3-phenylpropanoate.

How are the thiobenzanilides and 3-phenylpropanoic acid formed in the solid state if not by initial γ-hydrogen abstraction? One possible mechanism involves direct attack of the nucleophile on the carbonyl carbon of the monothioimide in its excited state. Attempts to probe this mechanism by observing emission quenching by nucleophiles were foiled by the failure of monothioimide **1a** to fluoresce. A second mechanistic possibility is one in which the carbonyl carbon to nitrogen bond undergoes excited state heterolysis to form an acylium ion and the enolate anion of thiobenzanilide, species which could then react with water or methanol to give the observed photoproducts.





The clue to a third mechanistic possibility was found in the close contact that is evident in Figure 1 between the oxygen atom of the C=O group and the carbon atom of the C=S group. These contacts, which are given in Table 1, are well below the sum of the van der Waals radii for oxygen and carbon (3.22 Å).[6] Thus in the crystalline state, the oxygen atom is ideally positioned for excited state nucleophilic attack on the C=S double bond, and this process may be the first step of the mechanism by which thiobenzanilides are formed in this medium as well as in solution. This would lead reversibly to 1,3-oxazetidinium ion **3**, which could react with water present in the medium and then break down, *via* species **4**, to the enol of thiobenzanilide (**6**) and 3-phenylpropanoic acid (**5**). Attempts to trap intermediate **3** with methyl iodide were unsuccessful. In principle, intermediate **4** could also cleave to form thiobenzoic acid and the enol of N-phenyl-3-phenylpropanamide. Thiobenzoic acid and N-phenyl-3-phenylpropanamide were shown to be absent from the photolysis mixture by gas chromatography using authentic samples. The preference for breakdown of **4** to **5** and **6**, which has literature analogy,[8] may be related in part to the resonance stability of **6**.

Having established that photocleavage of compound **1a** (and presumably **1b**-**1d** as well) does not involve initial γ-hydrogen abstraction, we were curious to see whether fully oxygenated imides behave similarly. To this end, we photolyzed N-acetylpropanamide (**9**) in CH_3OD and found that one deuterium atom *is* incorporated into the major cleavage product, methyl propanoate (**10**).[9] Thus in this case, γ-hydrogen atom abstraction is occurring, a result that may be related to the fact that the preferred conformation of such imides in solution has the so-called E,Z geometry shown,[10] which brings the abstracting oxygen atom and the abstracted hydrogen atom into close proximity.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Financial support by the Natural Sciences and Engineering Research Council of Canada is also gratefully acknowledged.

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4. The fate of the oxygen-containing cleavage product in this reaction was not reported by Sakamoto et al.[1]
5. Compound **1a**: $P2_12_12_1$; a = 8.022(4), b = 38.685(4), c = 5.848(3) Å; Z = 4; R = 0.029. Compound **1b**: $P2_1/a$; a = 9.506(1), b = 17.643(2), c = 11.960(1) Å; β = 91.65(1)°; Z = 4; R = 0.042. Compound **1c**: $Pca2_1$; a = 38.032(3), b = 7.373(4), c = 7.725(4) Å; Z = 4; R = 0.031. Compound **1d**: Pbca; a = 26.345(6), b = 24.531(8), c = 6.07(1) Å; Z = 8; R = 0.045.
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7. The required deuterated starting material was prepared by treatment of methyl 3-phenylpropanoate with NaOMe/MeOD followed by hydrolysis in the presence of D_2O/OD^-, formation of the acid chloride by treatment with thionyl chloride and reaction of the acid chloride with thiobenzanilide according to the procedure of Sakamoto et al.[1] Proton NMR indicated > 96% deuterium incorporation.
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(*Received in USA* 13 *November* 1992; *revised* 15 *December* 1993; *accepted* 14 *March* 1994)