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PHOTOCHEMICAL REACTIONS OF N-BENZOYLFORMYL-N-(PHENYLTHIOCARBONYL)-AMINES. A NOVEL PHOTOCYCLIZATION INVOLVING 1,4-PHENYLTHIO MIGRATION

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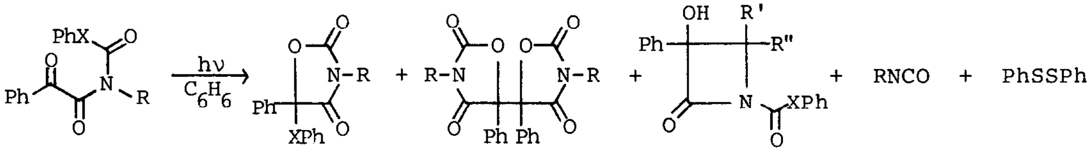
Summary: Photolysis of N-benzoylformyl-N-(phenylthiocarbonyl)amines gave 5-(phenylthio)oxazolidine-2,4-diones which were produced by cyclization involving 1,4-phenylthio migration, accompanied by dimeric products (3) and diphenyl disulfide.

In relation to our studies on photochemistry of α-oxoamides[1)] and α-oxoimides,[2)] we now wish to report the photochemical reactions of N-benzoylformyl-N-(phenylthiocarbonyl)amines (1a-1d) and an N-benzoylformylurethane (1e).



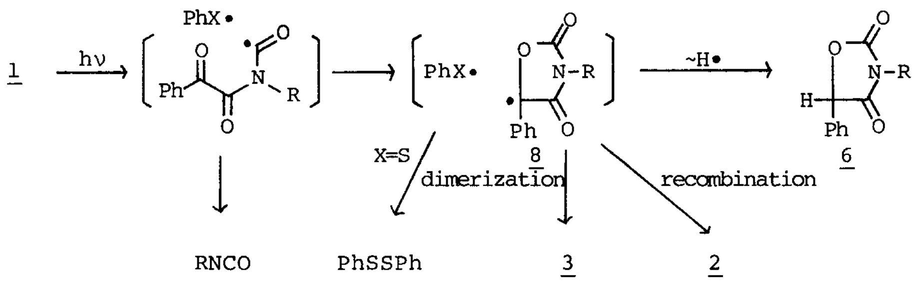
1 2 3 4 5

Table: Photoreaction of 1 (Yield %)

	2	3	4	5
a: X=S, R=Ph	53	0	0	40
b: X=S, R=p-tolyl	61	15	0	22
c: X=S, R=Pr^i	36	16	18	trace
d: X=S, R=CH_2Ph	3	0	27	5
e: X=O, R=Ph	20	20	0	0

When N-benzoylformyl-N-(phenylthiocarbonyl)aniline (1a) in benzene was irradiated with a high pressure mercury lamp under argon, 3,5-diphenyl-5-phenylthiooxazolidine-2,4-dione (2a) and phenyl isocyanate were obtained in 53% and 40% respectively. The structure of 2a was determined on the basis of elemental analysis and spectral data, in particular the close similarity of the IR spectrum to that of 3,5-diphenyloxazolidine-2,4-dione (6a).[3)] Irradiation of 1b under the same conditions gave 2b accompanied by bis-5,5'-(3,5-diphenyloxazolidine-2,4-dione) (3) and p-tolyl isocyanate. In the case of N-alkyl compounds (1c and 1d), β-lactams (4c and 4d) (type II cyclization products)[1)] were obtained in addition to 2 and isocyanates. In all cases described above, diphenyl disulfide was detected. Photolysis of a urethane (1e) also afforded the cyclization products (2e and 3e).

Scheme 2



It is well-known that thiol esters undergo the cleavage of the CO-S bonds on irradiation to produce acyl-thiyl radical pairs. The formation of 2 is reasonably explained in terms of the cleavage of the CO-S bond followed by cyclization of the acyl radical and recombination of the resulting cyclic radical (8) with the thiyl radical (Scheme 2). The formation of the dimeric products (3) and the disulfide is also consistent with the mechanism. Furthermore, when 1b was irradiated in benzene containing t-butyl mercaptan (a good hydrogen donor), 5-phenyl-3-p-tolyl-oxazolidine-2,4-dione (6b) was obtained in 15%. This fact strongly supports the intermediacy of the cyclic radical (8).

Photocyclization involving 1,4-shift of phenylthio or phenoxy group is quite rare.[4] Furthermore, many oxazolidine-2,4-dione derivatives are an important class as several members possess analgesic[5] and anti-epileptic[6] properties, and the synthesis of these compounds has been extensively investigated.[3] However, oxazolidine-2,4-diones possessing sulfur functions at the 5-position are hitherto unknown to our best knowledge. Since the starting materials (1) can be easily prepared by benzoylformylation of the corresponding N-(phenylthiocarbonyl)amines and urethanes, this photoreaction provides a useful synthetic method of some oxazolidine-2,4-diones.

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