Tetrahedron Letters No. 1, pp 91 - 94, 1974. Pergamon Press. Printed in Great Britain.

THIONE PHOTOCHEMISTRY: CYCLOADDITION TO THE NITRILE FUNCTION[1,2]

D.S.L. Blackwell, P. de Mayo* and R. Suau[3]
Photochemistry Unit, Department of Chemistry
University of Western Ontario, London, Canada

(Received in USA 23 October 1973; received in UK for publication 26 November 1973)

The photocycloaddition of excited species to multiple linkages has formed an important part of photochemical studies. Of these, addition to the triple bond has formed but a very minor part, and, has been restricted to the acetylene function.[4,5] We report here that the nitrile function is susceptible to addition by the excited thione group. The reaction appears to be general.

Irradiation of (1)[6] in acetonitrile at 254nm gave (2) [18%[7]; $\lambda_{max}^{C_6H_{12}}$ 268,431nm (ε 7900,92) ν_{max}^{CCl} 1640,1240 cm^{-1}]. The structure of 2 was proven chemically by reduction with $NaBH_4$ in methanol to give (3)[6] [64%; m.p. 123-4°, $\nu_{max}^{CCl_4}$ 3410,3305 cm^{-1}] and (4)[6] [36% m.p. 113-114°, $\nu_{max}^{CCl_4}$ 3390,3270 cm^{-1}]. Authentic samples were prepared by reduction of the ketone oxime, reduction and acetylation followed by P_2S_5 . The structure of 2 was confirmed by hydrolysis to the bicyclooctanone and thioacetamide.

The formation of 2 appears to be the first instance of the preparation of an N-thioacylketimine function. We presume that it arises by the electrocyclic opening of the first formed 5.[4a,5]

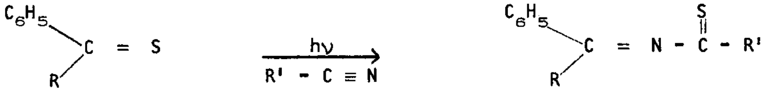
In a similar way thiofenchone (6), thiocamphor (7) and (8)[6] gave the corresponding N-thioacylketimine derivatives[6] in yields of 15%, 19% and 20% respectively.

Mixed arylalkylthiones[6] (9) underwent this reaction (see Table).[9] The products were obtained as yellow oils[6] [10a, $\lambda_{max}^{C_6H_{12}}$ 267,433nm (ε 7600,72), $\nu_{max}^{CCl_4}$ 1660,1590,1250 cm^{-1}]. The structure was proven (for 10a) by reduction to the thioamide[6] and the synthesis of the latter from the amine[10]. Hydrolysis gave the ketone and thioacetamide.

No absorbing intermediate could be detected during the irradiation of 9a and an isosbestic point at 472nm was observed. To demonstrate the intermediacy of substances of type (5) the irradiation was also conducted at -42° but (5) could not be detected.

One single example of a diarylthione (9e) was studied: the product was too unstable for isolation, and was reduced immediately to the thioamide.[11]

TABLE



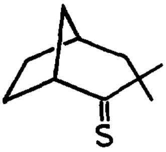
9 10

a)	R= $-C(CH_3)_2-CH_2-CH_3$	;	R' = $-CH_3$	(88%)
b)	R= "	;	R' = $-CH(CH_3)(CH_2-CH_3)$	(64%)
c)	R= $-C(CH_3)_2-(CH_2)_2-CH_3$	;	R' = CH_3	(10%)
d)	R= $-C(CH_3)_2-(CH_2)_2-C(CH_3)_3$	;	R' = CH_3	(77%)
e)	R= $-C_6H_5$	;	R' = CH_3	(33%)

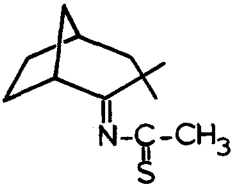
Irradiation of 9a in the n,π* absorption band (λ> 470nm) resulted in the slow disappearance of the starting material. After 35% conversion no absorption at 415nm (for 10a) could be observed, nor could 9a be detected by chromatographic separation. Irradiation of 6 (λ> 420nm) in its n,π* absorption band also yielded no trace of the thioacetylimine, but in this case, because of the slowness of reaction conversion was very small. The reaction may derive from S_2 (π,π*) state, the lifetime of S_2 in thiobenzophenone, at least, being long enough to permit intermolecular reaction;[12] the reaction may derive from the lowest triplet state, but in this case the triplet must be generated more efficiently from S_2 than S_1;[12] or the reaction may occur by direct excitation of molecules associated in the ground state. We are attempting to resolve this problem.

REFERENCES

1. Photochemical Synthesis. Part 54. This is the 14th in a series on Thione Photochemistry.
2. Publication No. 90 from the Photochemistry Unit, University of Western Ontario, London, Canada.
3. Holder of a "Fundacion Juan March" Fellowship (Spain) 1972-3.
4. a) Carbonyl addition: J.G. Atkinson, D.E. Ayer, G. Büchi and E.W. Robb, *J. Amer. Chem. Soc.*, **85**, 2257 (1963); b) Nitro addition: M.L. Scheinbaum, *J. Org. Chem.*, **29**, 2200 (1964); c) αβ-unsaturated carbonyl: P.E. Eaton, *Tetrahedron Letters*, 3695 (1964); P. de Mayo and M.C. Usselman, *Anales de Quimica*, **68**, 779 (1972); d) Thione: A. Ohno, T. Koizumi, Y. Ohnishi and G. Tsuchihachi, *Tetrahedron Letters*, 2025 (1970).
5. Very recently the addition of excited benzonitrile to olefines has been reported. This takes place on the nitrile function as well as on the aromatic nucleus: T.S. Cantrell, *J. Amer. Chem. Soc.*, **94**, 5929 (1972).
6. Proper analytical or precise mass determination were obtained for all new compounds characterised. The nmr and mass spectral data were in accord with the structures allocated.
7. In a typical experiment 250 mg of (**1**) on irradiation (Rayonet Preparative Photochemical Reactor with RUL 2537A° lamp) for 12 hours gave 100 mg of recovered **1**, 35 mg **2** and 90 mg of a mixture of cyclopropyl thiol, disulphide and saturated thiols.[8]
8. D.S.L. Blackwell and P. de Mayo, *J. Chem. Soc., Chem. Comm.*, 131 (1973).
9. The intermolecular reaction was in competition with intramolecular and other intermolecular processes which will be discussed elsewhere.
10. P. Billon, *Ann. Chim.*, [10], **7**, 349 (1927).
11. Prepared also from the corresponding amide: H.L. Wheeler, *Amer. Chem. J.*, **26**, 345 (1901).
12. P. de Mayo and H. Shizuka, *J. Amer. Chem. Soc.*, **95**, 3942 (1973).
13. A.H. Lawrence and P. de Mayo, *J. Amer. Chem. Soc.*, **95**, 4084 (1973).

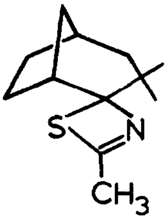


1

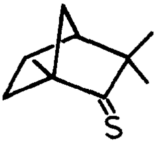


2

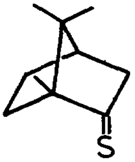
3 endo
4 exo



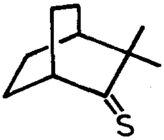
5



6



7



8