

Interception of Photochemical Intermediates of Thiazole Derivatives. Formation and Isomerisation of Iminoazetine and Azetinone Intermediates

Hiroshi Kato,*^a Kozo Wakao,^a Akira Yamada,^a and Masanobu Kojima^b

^aDepartment of Chemistry, Faculty of Science, and ^b Faculty of Liberal Arts, Shinshu University, Asahi, Matsumoto 390, Japan

Irradiation of 4-aminothiazolium salts (**7**) in the presence of tributylphosphine gave enamionitriles (**9**) and benzoylacetone (**8**) by isomerisation and hydration of the iminoazetine intermediates (**11**), while a similar irradiation of the mesoionic triphenylthiazolium-4-olate (**1**) gave the quinolinol (**5**) by isomerisation of the azetinone intermediate (**3**).

It is generally accepted that one of the most common photochemical reactions of mesoionic ring systems is their initial valence isomerisation to bicyclic systems.¹ One such hypothetical bicyclic intermediate from a mesoionic 4-thiazolone was successfully trapped for the first time by Barton *et al.*²

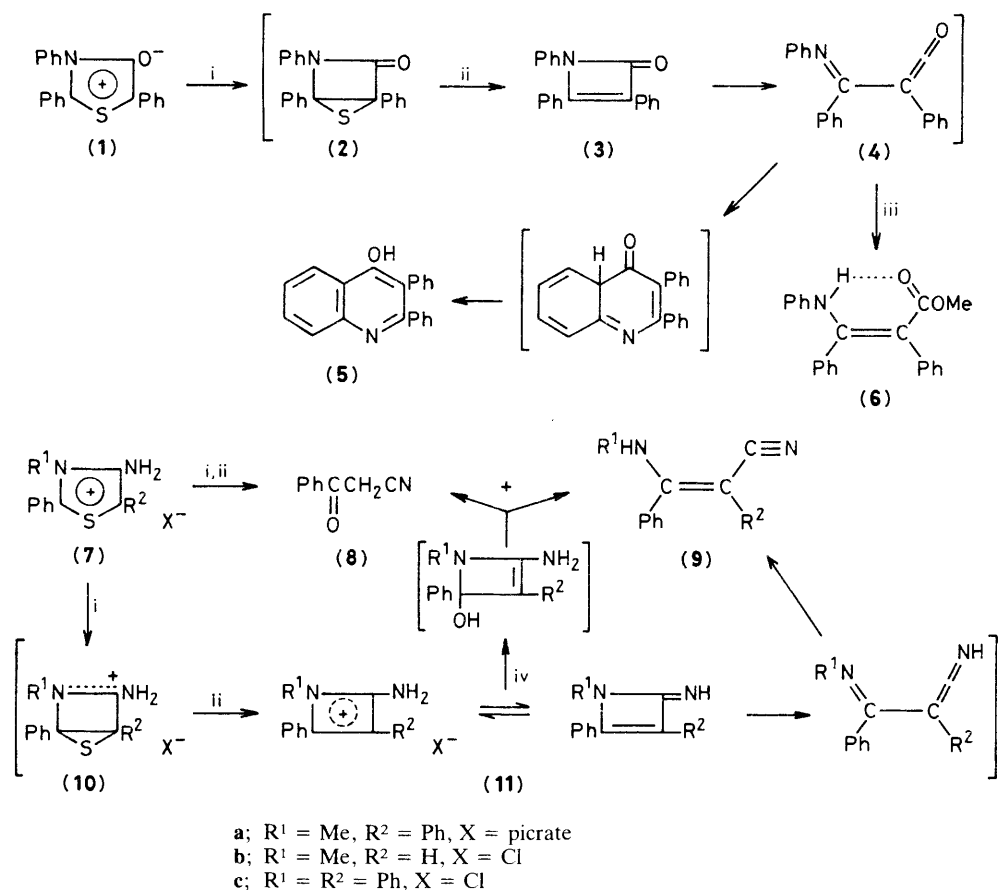
We report here another isomerisation mode of a similar azetinone intermediate and the formation and behaviour of a hitherto unknown iminoazetine intermediate.

It has been reported that irradiation of the triphenylthiazoliumolate (**1**) in methanol in the presence of tributylphosphine gave the aminoacrylate (**6**) in 50% yield as a result of the addition of methanol to the ketene (**4**), which is formed by desulphurisation and isomerisation of the bicyclic intermediate (**2**).³ When we performed the above reaction in benzene, 2,3-diphenylquinolin-4-ol (**5**), identical with an authentic

sample,⁴ was isolated in 34% yield after recrystallisation. The quinolinol (**5**) most probably arises from the internal trapping of the ketene intermediate (**4**). Thus this result further supports the intervention of the bicyclic (**2**) and the azetinone (**3**) intermediates in this reaction.

When a methanolic solution of the aminothiazolium picrate (**7a**) was irradiated (high-pressure mercury lamp; Pyrex filter) in the presence of tributylphosphine, a mixture of the *E*- and *Z*-isomers of the corresponding aminoacrylonitrile (**9a**) was formed in 55% yield.† In the case of the corresponding

† Products were isolated either by recrystallisation or by chromatography, and structure assignments are based on elemental and spectral analyses (i.r.; ¹H and ¹³C n.m.r.; mass).



Scheme 1. Reagents: *i*, *hv*; *ii*, Buⁿ₃P; *iii*, MeOH; *iv*, H₂O.

monophenyl chloride (**7b**), benzoylacetonitrile (**8**) (30%) was formed in addition to the expected enaminonitrile (**9b**) (15%). The products from the triphenyl derivative (**7c**) could be separated only with difficulty, and resulted in poor isolated yields of **(8)** (4%) and the enaminonitrile (**9c**) (4%). The formation of the enaminonitriles may readily be rationalised by a mechanism involving an initial photochemical valence isomerisation to the bicyclic system (**10**), its desulphurisation to the quasi-antiaromatic iminoazetidine (**11**), and, finally, its ring opening and prototropy as shown in Scheme 1. The hydration of the iminoazetidine intermediate may account for the formation of benzoylacetonitrile, though the possibility of hydrolysis of the enaminonitrile (**9**) during work-up cannot be excluded. These results thus show that the initial photochemical step of aminothiazolium salts (**7**) is their valence isomerisation to give the bicyclic system (**10**), and suggest that phosphines are effective reagents for trapping of a variety of bicyclic thiranes. Such systems are often suggested as likely short-lived intermediates in the photochemical reactions of

heterocyclic systems,⁵ and reactions of the present type may provide a new route to several small-ring heterocycles.

Received, 10th July 1984; Com. 991

References

- C. G. Newton and C. A. Ramsden, *Tetrahedron*, 1982, **38**, 2965; W. D. Ollis and C. A. Ramsden, *Adv. Heterocycl. Chem.*, 1976, **19**, 1; C. A. Ramsden, in 'Comprehensive Organic Chemistry,' eds. D. H. Barton and W. D. Ollis, Pergamon Press, Oxford, 1979, vol. 4, p. 1171.
- D. H. R. Barton, E. Buschmann, J. Hausler, C. W. Holzappel, T. Sheradsky, and D. A. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1107.
- K. Wakao, Y. Daikuhara, and H. Kato, Abstracts of Papers, 10th Annual Joint Meeting of The Chubu Chemical Societies, Hamamatsu, October 1979, p. 224; T. Sheradsky and D. Zbaida, *J. Heterocycl. Chem.*, 1983, **20**, 245.
- C. R. Hauser and J. G. Murray, *J. Am. Chem. Soc.*, 1955, **77**, 2851.
- E. g. A. Lablache-Combier, 'Photochemistry of Heterocyclic Compounds,' ed. O. Buchardt, Wiley, New York, 1976, p. 123.