# Photochemical and Thermal Reactions of Heterocycles. Part 5.[1,2] Products via Transient Quasiantiaromatic Azetine Intermediates Generated by Desulphurisation of Photochemical Intermediates from a Thiazolium-4-olate and 4-Aminothiazolium Salts

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Irradiation of the mesoionic triphenylthiazolium-4-olate (3) in the presence of tributylphosphine gave the quinolinone (7). This result was interpreted as arising via desulphurisation of the bicyclic intermediate (4) to the azetone (5), followed by its isomerisation to the ketene (6) and internal trapping. Similar irradiation of the 4-aminothiazolium salts (15) gave enamino nitriles (17) and benzoylacetonitrile (16). They are probably formed by isomerisation and hydration of the hitherto unknown quasiantiaromatic 2-imino-1,2-dihydroazete intermediates (20), which in turn are generated by desulphurisation of the bicyclic photochemical intermediates (19).

The photochemical behaviour of type-A mesoionic ring systems has attracted considerable attention.[3] Frequently, such reactions are believed to proceed through bicyclic intermediates which are formed by initial photochemical valence isomerisation. Barton and his co-workers were successful in generating an azet-2(1H)-one by desulphurisation of one such presumed intermediate (2) from a mesoionic 2-alkylthiothiazolium-4-olate (1), by performing the irradiation in the presence of a phosphine.[4]


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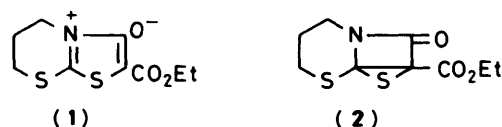
We report here the photochemical reactions of a mesoionic thiazolium-4-olate and 4-aminothiazolium salts in the presence of a phosphine, and propose that these reactions most probably proceed through an azetone and 2-imino-1,2-dihydroazete intermediates.

Results and Discussion

When the mesoionic 2,3,5-triphenylthiazolium-4-olate (3)[5] was irradiated in aprotic solvents in the presence of tributylphos-

phine, 2,3-diphenylquinolin-4(1H)-one (7) was isolated in good yield. Among several phosphines and phosphites, tributylphosphine was found to be the best desulphurisation reagent. Similar irradiation of the thiazoliumolate (3) in methanol is reported to give the anilinocinnamate (8) via a transient azetone (5) intermediate.[6] The formation of the quinolinone (7) can best be explained by initial valence isomerisation of the thiazoliumolate (3) to the bicyclic intermediate (4), desulphurisation to the azetone (5), isomerisation of the latter to the ketene (6), and finally its ring closure (Scheme 1). However, it was not possible to intercept the azetone or the ketene intermediate as their cycloadduct with furan. Similar quinolinones have been formed by the pyrolyses of oxopyrimidiniumolates (9)[7] and oxothiaziniumolates (10).[8] They were considered to be formed through azetone intermediates, formed by extrusion of phenyl isocyanate and carbonyl sulphide from (9) and (10) respectively. Isolation of monocyclic azet-2(1H)-ones has not been reported. However, photochemical generation of 1-methylazet-2(1H)-one and its ready isomerisation to (methyliminomethyl)ketene has been reported,[9] and intervention of monocyclic azetone intermediates has been suggested in the reactions of penicillins[10] and the photochemical reaction of a thiazoliumolate.[11]

We next turned our attention to the photochemistry of the related mesoionic N-(2,3-diphenylthiazolium-4-yl)benzamidate (11)[12] and 4-aminothiazolium salts (15).[13] If they undergo similar photochemical isomerisation to bicyclic systems, ex-

(7)   (8)
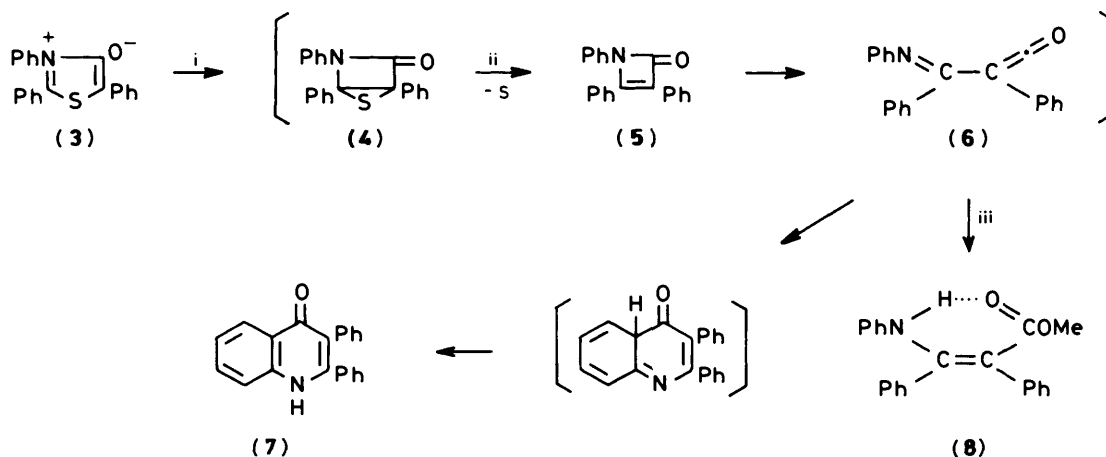
Scheme 1. *Reagents and conditions:* i, hv; ii, Bu₃P; iii, MeOH

trusion of sulphur from the intermediates will give the imino-dihydroazete intermediates (12) and (20) respectively. We thought it worthwhile to investigate the behaviour of such a quasiantiaromatic system. It appears that such systems have not been described although a related condensed system, 8-(phenylimino)-7-azabicyclo[4.2.0]octa-1,3,5-triene (13), has been suggested as a plausible intermediate in the thermolysis of 4-anilino-1,2,3-benzotriazine (14).[14]
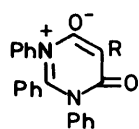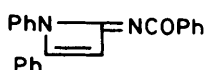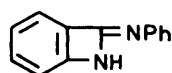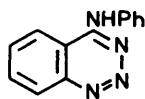

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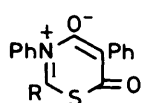
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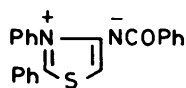
(11)

(12)

(13)

(14)

When the thiazoliumamidate (11) was irradiated in the presence of tributylphosphine, only an intractable mixture resulted. When a solution of 4-amino-3-methyl-2,5-diphenyl-thiazolium picrate (15a) in dichloromethane was irradiated (high-pressure mercury lamp; Pyrex filter) in the presence of tributylphosphine, a mixture of the E- and Z-isomer of β-(methylamino)-α-phenylcinnamonitrile (17a) (56%) was formed.

The E-configuration was assigned to the major isomer because a methylamino group on β-(methylamino)-α-phenyl(iso)crotono-nitrile is more deshielded by the adjacent cis-cyano group than by the cis-phenyl group.[15] The enamine (17a) was claimed to have been prepared.[15] However, the reported m.p. (88 °C) and spectral properties are considerably different from ours (see Experimental section): the i.r. absorption of the cyano group of the claimed sample falls to an abnormally low wavenumber (2 165 cm⁻¹), and n.m.r. signals of both the N-methyl and phenyl groups are reported to appear at exceptionally high magnetic fields (δ 2.22 and 6.2—6.8 respectively). The structure of the claimed sample should probably be modified.

Similar irradiation of 4-amino-3-methyl-2-phenylthiazolium chloride (15b) in dichloromethane gave a mixture of E- and Z-enamino nitrile (17b) in only moderate yield (15%), and the main product in this case was found to be benzoylacetonitrile (16) (29%). The enamino nitrile (17b) with a m.p. of 66 °C (E:Z = 7:1) was recently prepared in a straightforward manner.[16] Although our distilled sample failed to crystallise, it gave correct analytical values, and spectral data agreed well with the reported values. Irradiation of 4-amino-2,3-diphenyl-thiazolium chloride (15c) in the presence of tributylphosphine afforded only low yields of benzoylacetonitrile (16) (8%) and the enamino nitrile (17c) (7%). It is notable that the n.m.r. signals of both the α-carbon and α-hydrogen atoms of these enamino nitriles (17) appear at exceptionally high fields (δ 60.2—80.6 and 3.32—4.57 respectively) by the shielding effect of the α-cyano group and by the electron-donating β-amino substituent.

These thiazolium salts are stable in the dark under the experimental conditions used. The formation of the enamino nitriles (17) will be readily rationalised by a sequence of reactions (Scheme 2) involving the initial photochemical valence isomerisation to the bicyclic system (19), desulphuris-ation to the quasiantiaromatic 2-imino-1,2-dihydroazete or aminoazetium salt (20), and finally, ring opening and pro-

(15) (16) (17)

(18)

(19) (20A) (20B) (21)
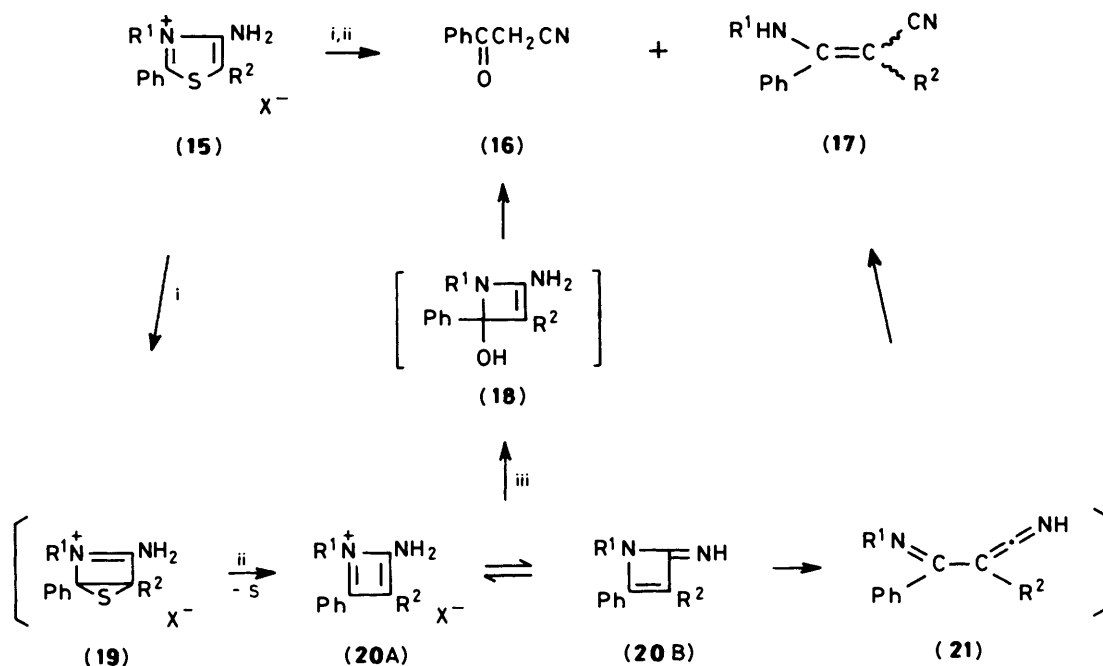
(15a), (17a) — (21a) R¹ = Me, R² = Ph, X = (NO₂)₃C₆H₂O

(15b), (17b) — (21b) R¹ = Me, R² = H, X = Cl

(15c), (17c) — (21c) R¹ = Ph, R² = H, X = Cl

Scheme 2. *Reagents and conditions:* i, *hv*; ii, Bu₃P; iii, water

totropy. Chinone *et al.* have suggested the bicyclic system (19c) as a plausible intermediate in a photochemical reaction of the aminothiazolium salt (15c).[17]

The formation of benzoylacetonitrile (16) in these reactions cannot be the result of secondary reactions of the enamino nitriles because it was found that the enamino nitrile (17c) was quantitatively recovered after chromatographic treatment on a silica gel column, and was stable to irradiation under the reaction conditions used for the desulphurisation. When the desulphurative irradiation of the 2,3-diphenyl derivative (15c) was repeated in dry and wet dichloromethane, the yield (h.p.l.c.) of benzoylacetonitrile (16) in the wet solvent was increased while that of the enamino nitrile (17c) was decreased. These findings would support the view that benzoylacetonitrile was formed through hydration of the aminoazetium (20A) or iminodihydroazete (20B) intermediate to (18) before isomerisation to the imino ketenimine (21).

The scope of the reactions of this type was investigated with several 2-(substituted amino)- and 2-(alkylthio)-thiazolium salts. In every case, the formation of enamino nitriles was suggested spectroscopically, but they could not be isolated in pure forms.

In summary, these results would suggest that the initial photochemical step of the thiazoliumolate (3) and 4-aminothiazolium salts (15) is valence isomerisation to the bicyclic system (4) and (19) respectively, and that these short-lived bicyclic thiiranes are effectively desulphurised by phosphines to give products *via* quasiantiaromatic azete intermediates (5) and (20). The above findings further suggest that reactions of this type may provide a new synthetic route to several unsaturated small-ring systems from condensed thiiranes. Such thiiranes are often suggested as likely intermediates in the photochemical reactions of some heterocyclic systems.[18]

Experimental

M.p.s were determined on a Yanagimoto hot-stage apparatus. I.r. spectra (KBr) were recorded with a Hitachi 345 spectrophotometer. ^{1}H (100 and 90 MHz) and ^{13}C (22.5 MHz) n.m.r. spectra were recorded with JEOL JNM-4H-100 and JNM-FX-90Q spectrometers, for solutions in deuteriochloroform (tetramethylsilane internal standard). Mass spectra were measured with a JEOL JMS-01SG-2 spectrometer. H.p.l.c. was performed on a JASCO Trirotar III. All irradiations were performed under argon. Unless otherwise stated, yields are based on isolated products with sufficient purity. The ratios of configurational isomers were calculated from ^{1}H n.m.r. integration.

Photolysis of 2,3,5-Triphenylthiazolium-4-olate (3) in the Presence of Tributylphosphine.—(*a*) A solution of the thiazoliumolate (3) (50 mg) and tributylphosphine (100 mg) in dichloromethane (60 ml) was irradiated for 4 h with a 500-W tungsten–halogen lamp. The solution was concentrated, and the residue was triturated with ethanol, and then recrystallised to give 2,3-diphenylquinolin-4(1*H*)-one (7) (35 mg, 78%), identical (i.r. and ^{1}H n.m.r.) with an authentic sample, [19] m.p. and mixed m.p. 337—338 °C (decomp.) (from AcOH) (Found: C, 84.6; H, 4.9; N, 4.65%; *M*$^+$, 297. Calc. for C$_{21}$H$_{15}$NO: C, 84.85; H, 5.1; N, 4.7%; *M*, 297). *O*-Acetate: m.p. and mixed m.p.[20] 153 °C.

(*b*) When a mixture of the thiazoliumolate (3) (664 mg) and tributylphosphine (1.2 g) in benzene (350 ml) was irradiated with a high-pressure mercury lamp through a Pyrex filter, the quinolinone (7) was isolated in 34% yield.

Photolysis of Aminothiazolium Salts in the Presence of Tributylphosphine.—(*a*) 4-*Amino*-3-*methyl*-2,5-*diphenylthiazolium picrate* (15a). A solution of the thiazolium salt (15a)

[λ$_{max.}$(MeOH)] 240 (log ε 4.34) and 355 nm (4.36)] (150 mg) and tributylphosphine (120 mg) in dichloromethane (300 ml) was irradiated for 3 h with a 100-W high-pressure mercury lamp through a Pyrex filter. The products from four such experiments were combined and concentrated. Filtration of crystals and chromatography (alumina; chloroform, then silica; benzene) of the mother liquor gave β-(methylamino)-α-phenylcinnamonitrile (17a) (*E*:*Z* = 59:41) (160 mg, 56%), m.p. 166—167 °C (from benzene–hexane) (lit.,[15] 88 °C) (Found: C, 81.85; H, 6.2; N, 12.1. C$_{16}$H$_{14}$N$_2$ requires C, 82.05; H, 6.0; N, 11.95%); ν$_{max.}$ 3 340 (NH) and 2 190 cm^{-1} (CN); δ$_H$ 2.58 (*E*) and 2.82 (*Z*) (3 H, d, *J* 5 Hz, Me), 5.1 (1 H, br s, NH), and 6.8—7.5 (10 H, m, Ph); δ$_C$(*E*-isomer) 32.4 (Me), 80.6 (C-α), 125.4 (CN), and 160 (NC=).

(*b*) 4-*Amino*-3-*methyl*-2-*phenylthiazolium chloride* (15b). A solution of the chloride (15b) [λ$_{max.}$(MeOH) 230 (log ε 3.96) and 350 nm (4.02)] (930 mg) and tributylphosphine (830 mg) in dichloromethane (600 ml) was similarly irradiated for 3.5 h with a 400-W high-pressure mercury lamp. The resulting solution was concentrated and the residue was extracted with methanol. Flash column chromatography (silica; dichloromethane) of the extract afforded benzoylacetonitrile (16) (176 mg, 29%), m.p. and mixed m.p.[21] 82—83 °C (from benzene–hexane); ν$_{max.}$ 2 250 (CN) and 1 685 cm^{-1} (C=O); δ$_H$ 4.10 (2 H, s) and 7.35—8.05 (5 H, Ph); δ$_C$ 29.4 (CH$_2$), 113.8 (CN), and 187.2 (C=O); and β-(methylamino)cinnamonitrile (17b) (*E*:*Z* = 87:13) (100 mg, 15%), b.p. 150 °C/5 Torr (bath temperature) (lit.,[16] m.p. 66 °C) (Found: C, 75.95; H, 6.25; N, 17.4%; *M*$^+$, 158. Calc. for C$_{10}$H$_{10}$N$_2$: C, 75.95; H, 6.35; N, 17.7%; *M*, 158); ν$_{max.}$(liquid film) 3 320 (NH) and 2 190 cm^{-1} (CN): δ$_H$ values virtually identical with the lit. values;[16] δ$_C$ 30.4 (q, NMe), 60.2 (d, C-α), 121.9 (s, CN), and 163.5 (s, NC=).

(*c*) 4-*Amino*-2,3-*diphenylthiazolium chloride* (15c). A solution of the chloride (15c) [λ$_{max.}$(MeOH) 227 (log ε 4.16) and 260 nm (3.88)] (400 mg) and tributylphosphine (280 mg) in dichloromethane (350 ml) was irradiated for 2.5 h with a 100-W high-pressure mercury lamp through a Pyrex filter. Chromatography (alumina; dichloromethane, then silica; dichloromethane) gave benzoylacetonitrile (16) (16 mg, 8%), m.p. and mixed m.p.[21] 82—83 °C, and β-anilinocinnamonitrile (17c) (*E*:*Z* = 52:48) (21 mg, 7%), m.p. and mixed m.p.[21] 138—141 °C (Found: C, 82.1; H, 5.75; N, 12.85%; *M*$^+$, 220. Calc. for C$_{15}$H$_{12}$N$_2$: C, 81.8; H, 5.5; N, 12.7%, *M*, 220); ν$_{max.}$ 3 270 (NH) and 2 190 cm^{-1} (CN); δ$_H$ values virtually identical with the lit. values;[16] δ$_C$ 66.6 (d, *J* 169 Hz) and 71.2 (d, *J* 177 Hz) (C-α), 118.3 (s) and 120.7 (s) (CN), and 159.6 (s) and 160.4 (s) (=CN).

(*d*) H.p.l.c. measurement showed that similar irradiation of compound (15c) in dry dichloromethane produced benzoylacetonitrile (16) (4.8%) and the enamine (17c) (6.1%) while that in dichloromethane in the presence of water (1 ml) produced benzoylacetonitrile (16) (7.5%) and the enamine (17c) (4.2%).

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