

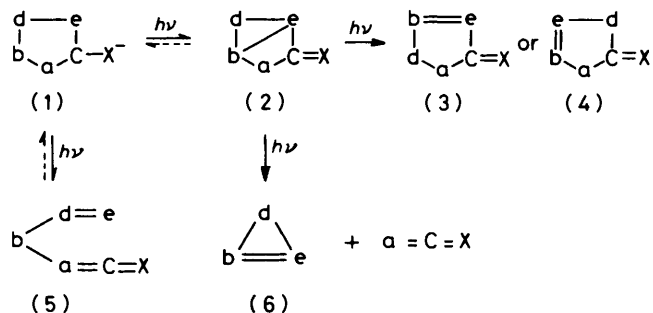
Photochemical and Thermal Reactions of Heterocycles. Part 3.1.2 Photoisomerisation, Photofragmentation, and Photodimerisation of Mesoionic 1,3-Dithiol-4-one and -4-imine Derivatives

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Photolysis of the mesoionic 2,5-diphenyl-1,3-dithiol-4-one (7) gave tetraphenyl-1,4-dithiin, tetraphenylthiophen, diphenylacetylene, and sulphur *via* the corresponding dimer (11) and 4,5-diphenyl-1,2-dithiol-3-one (12) which were isolable under appropriate conditions. Photolysis of the mesoionic *N*-benzoyl-2-phenyl-1,3-dithiol-4-imines (14) afforded the corresponding 1,2-dithiol-3-imines (15). The photochemical paths of the mesoionic dithiole systems are discussed in the light of the experimental results.

THE photochemical behaviour of mesoionic ring systems has attracted considerable attention.³ It is generally agreed that the photolysis of five-membered 'type A'^{3a} mesoionic compound (1) undergoes two types of reactions depending on the ring system and photolysis conditions. One (type I) is isomerisation to a bicyclic system (2) and its further isomerisation and/or fragmentation, while the other (type II) is ring-opening to a heterocumulene system (5).

Our interest in the photochemistry of mesoionic ring systems arose from the possibility that fragmentation of the bicyclic intermediate (2) from many type A mesoionic compounds would give fully conjugated anti-aromatic three-membered heterocycles (6), of which very little was then known.^{2a} Later, however, we modified our proposal in favour of another route (type I') consisting of a transposition reaction of a mesoionic ring *via* the bicyclic intermediate (2) to another five-membered heterocycle (3) or (4), and its final fragmentation.⁴



SCHEME 1

Here, we report the details of the photochemical reactions of mesoionic 1,3-dithiol-4-one (7) and -4-imine (14) derivatives, which were partly reported as preliminary communications.²

RESULTS AND DISCUSSION

Photochemistry of Dithiolone (7).—The irradiation of a benzene solution of the mesoionic 2,5-diphenyl-1,3-dithiol-4-one (anhydro-2,5-diphenyl-4-hydroxy-1,3-dithiol-1-ium hydroxide) (7) with a high-pressure mercury lamp through a Pyrex filter gave tetraphenyl-1,4-

dithiin (8) (18%), tetraphenylthiophen (9) (15%), diphenylacetylene (10) (31%), and sulphur (17%).

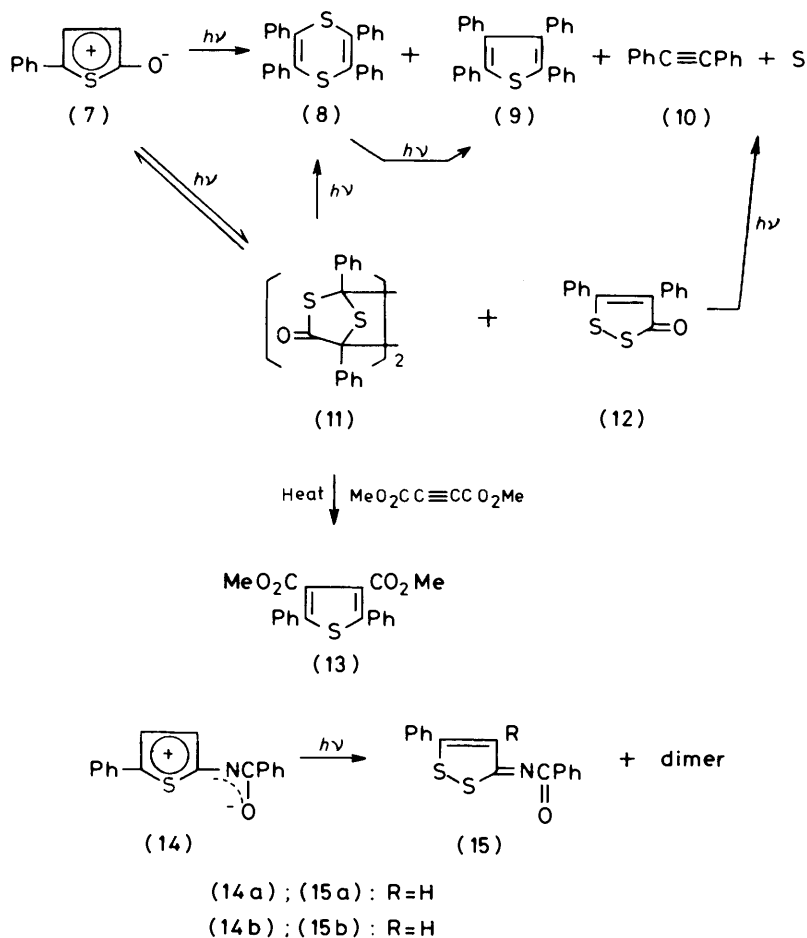
When the irradiation of the dithiolone (7) was stopped before the reaction was complete, a new product was formed besides the dithiin (8) (7%), the thiophen (9) (3%), and the acetylene (10) (18%). The new product, isolated in 7% yield, was an isomer of the 1,3-dithiolone (7), and was identified as 4,5-diphenyl-3*H*-1,2-dithiol-3-one (12) by comparison with an authentic sample. Gotthardt, *et al.*⁵ briefly referred to the formation of a 1,2-dithiol-3-one from a mesoionic dithiolone as unpublished work of Weischuhn.

The irradiation of the longest wave absorption band of the dithiolone (7) with a tungsten-halogen lamp afforded the 1,2-dithiolone (12) (13%), and another new main product. The latter product (49% yield) was assigned as the dimer (11) based on the considerations described below. The dimer had a correct elemental analysis and showed a carbonyl absorption at 1690 cm^{-1} suggestive of the presence of a strained thiolactone group. The field-desorption mass spectrum of this compound consisted of two peaks, corresponding respectively to the molecular ion of the dimer and to the monomer (7). Its electron-impact mass spectrum, while lacking the molecular ion peak, showed a strong peak corresponding to (7)⁺, and was almost identical with the mass spectrum of the dithiolone (7) excepting a new peak at m/e 178 corresponding to PhC:CPh^{+} , which is not observable in the mass spectrum of the dithiolone (7). This means that the compound still retains the dithiolone framework while an intermolecular carbon-to-carbon bond is formed.

In harmony with the lack of the molecular ion peak on electron impact, the compound appeared to dissociate readily to the monomer, because it regenerates the characteristic deep violet colour of the dithiolone, when heated or set aside in solvents. This possibility was supported by the isolation of the addition-extrusion product (13) (68%) between the dithiolone (7) and dimethyl acetylenedicarboxylate, by heating the dimer in the presence of the acetylene. After the completion of this work, Gotthardt, *et al.*⁶ recently reported the isolation of several similar dimers by treatment of mesoionic dithiolones with dicyclohexylcarbodi-imide,

and established their structures by *X*-ray single-crystal analysis.

Visible-light irradiation of the dithiolone (7) in the presence of anthracene reduced the yield of the dimer (11) to 16% while the yield of the 1,2-dithiolone (12) was slightly increased (24%).



SCHEME 2

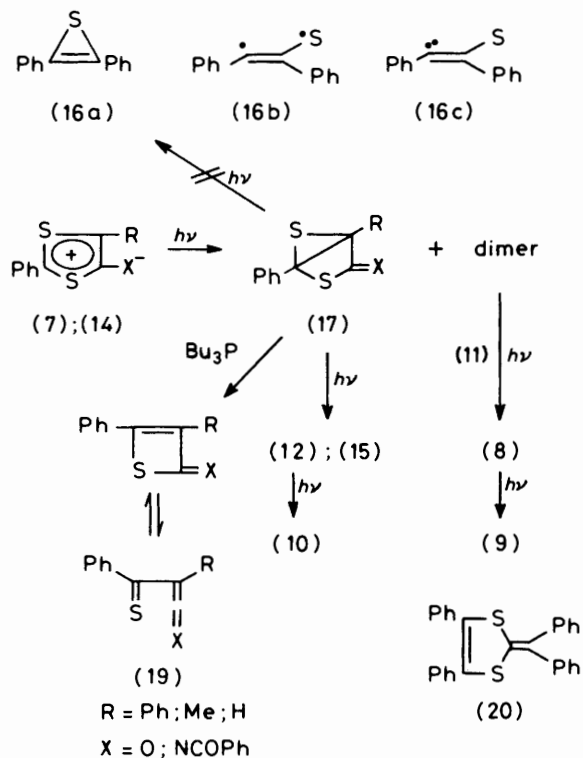
The 1,2-dithiol-3-one (12) underwent further photolysis by irradiation with a high-pressure mercury lamp in benzene to give diphenylacetylene (10) (64%). It has been reported that 4-phenyl-3*H*-1,2-dithiol-3-one is unaffected by an attempted photolysis.⁷ The dimer (11) readily gave the dithiin (8) (57%) and the thiophen (9) (6%) by irradiation with a high-pressure mercury lamp. These results suggest that the dithiin (8) and the thiophen are secondary photo-products of the dimer.

Photo-rearrangement of Dithiolimines (14).—As described in our preliminary report,^{2b} the photolysis of a benzene solution of the mesoionic *N*-benzoyl-2-phenyl-1,3-dithiol-4-imine (anhydro-4-benzoylamino-2-phenyl-1,3-dithiol-1-ium hydroxide) (14a) with a high-pressure mercury lamp gave *N*-benzoyl-5-phenyl-3*H*-1,2-dithiol-3-imine (15a) (80%), accompanied by a small amount of

a high-melting substance. The structure of the latter was tentatively assigned as the dimer based mainly on a field-desorption mass spectrum (*m/e* 594, *M*⁺, 100%), and a fair agreement of elemental analyses. Similar results were obtained when the 1,3-dithiolimine (14a) in acetonitrile, chloroform, acetic acid, or acetone was irradiated

with a high-pressure mercury lamp or a fluorescent lamp. Extensive decomposition occurred when the 1,3-dithiolimine (14a) was irradiated with a low-pressure mercury lamp, and no 1,2-isomer (15a) could be isolated. Further irradiation with a high-pressure mercury lamp of the 1,2-dithiolimine (15a) caused no photochemical reaction. That the photolysis of the mesoionic dithiolimine in acetic acid followed the same course as in other solvents suggested that the photolysis takes place even as the protonated form. The photolysis of the mesoionic 1,3-dithiolimine hydrochloride (14a)·HCl in ethanol was indeed found to give the 1,2-dithiol-3-imine (15a). Photolysis of the mesoionic *N*-benzoyl-5-methyl-2-phenyl-1,3-dithiol-4-imine (14b) likewise gave the corresponding 1,2-dithiol-3-imine (15b). The 5-methyl derivative (14b) was prepared by a modification of a conventional method (see Experimental section).⁸

Photochemical Paths of the Mesoionic Dithiole System.—Our initial concern regarding the photolysis of the mesoionic 1,3-dithiol-4-one system was to see whether or not the reaction proceeds *via* an anti-aromatic thiiren intermediate. From the results presented above, it may now be concluded that the mesoionic 1,3-dithiole ring system undergoes two competing photochemical transformations. One is the transposition reaction *via* the photochemically allowed disrotatory ring closure to the bicyclic intermediate (17), and the other is dimerisation.



SCHEME 3

The reaction stops at these stages with the dithiolimine system (14). The quenching experiment with anthracene ($E_T = 42.7$ kcal) suggests that the dimer originates mainly from the triplet excited state. In the case of the dithiolone (7), further photolysis of the primary products (11) and (12) gives the dithiin (8) and the acetylene (10) respectively as the final products.

Although the results presented above do not rigorously exclude the thiiren intermediate (16a), the possibility of the partial formation of the acetylene (10) by the fragmentation of the thiiren (16a) will be ruled out, because a thiiren intermediate rearranges to a thioketen rather than undergoing fragmentation.⁹

As to the formation of the thiophen (9), diphenylacetylene did not undergo cycloaddition with the dithiolone (7) under the reaction conditions in the dark. In order to check the possibility of the formation of the thiophen (9) by the cycloaddition of diphenylacetylene and the thiiren intermediate (16), the photochemical reaction between dimethyl acetylenedicarboxylate and

the dithiolone was tried. A consistently higher yield of dimethyl 2,5-diphenylthiophen-3,4-dicarboxylate (13) was isolated when the mixture was irradiated, than when the mixture was kept in the dark. This result, however, should probably be interpreted as a photochemical cycloaddition of the acetylene rather than interception of the thiiren intermediate (16) by the acetylene, because, in the latter case, the formation of the 2,3-dicarboxylate isomer would be expected.¹⁰ The formation of the thiophen (9) as a by-product of photolysis of the dimer (11) shows that it is formed as a secondary photoproduct of the dithiin (8) as recently reported by Lahiri, *et al.*¹¹ A part of the thiophen (9) may be formed by the photochemical cycloaddition-extrusion reaction between diphenylacetylene and the dithiolone (7).

The absence of tetraphenyl-1,4-dithiafulvene (20) among the products of the dithiolone photolysis also casts doubt about the possible intermediacy of the thiiren and related species (16). The photolysis of diphenyl-1,2,3-thiadiazole, which was interpreted as proceeding through the related biradical (16b,16c), gives both the dithiin (8) and the dithiafulvene (20).¹²

Attempts to intercept the proposed bicyclic intermediate (17) from either the dithiolone (7) or the dithiolimine (14a), by desulphurisation with tri-*n*-butylphosphine,¹³ and to trap the thiet (18) or its open-ring valence isomer (19) with furan, acetylenedicarboxylate, or 1,1-dimethylhydrazine were unsuccessful, and always resulted in the formation of intractable complex product mixture. However, the fact that the reaction takes a different course in the presence of the phosphine should probably be regarded as an indication that the photochemical reaction proceeds through the bicyclic intermediate (17).

In summary, the present work shows that the photolysis of five-membered mesoionic ring system *via* a transposition reaction is quite general, and further supports our view that many fragmentation reactions of mesoionic rings which have been interpreted as proceeding through anti-aromatic three-membered heterocycles,^{2b,14} may actually proceed through this indirect (type I') route, although with a mesoionic 1,3,2-oxathiazol-5-one, the formation of such anti-aromatic intermediate has been inferred spectroscopically.¹⁵

EXPERIMENTAL

M.p.s were determined with a Yanagimoto hot-stage apparatus. U.v. spectra were recorded with a Hitachi EPS-3T, and i.r. (KBr) spectra with a Hitachi 345 spectrophotometer. N.m.r. spectra were obtained on a JEOL JNM-4H-100 spectrometer for solutions in deuteriochloroform (tetramethylsilane internal standard). E.-I. and F.-D. mass spectra were measured respectively with a Hitachi RMU-6 and JEOL JMS-D300, JMA-2000 spectrometers. The F.-D. mass spectra were measured with an emission current of 16–17 mA, acceleration voltage of 3.0 kV, and a cathode voltage of –6.0 kV with dimethylformamide as solvent. G.l.c. were run with a Shimadzu GC-4BPF model, and t.l.c. separation was performed on Merck Kieselgel 60 PF₂₅₄. Compounds stated to be

identical were so with respect to m.p., mixed m.p., and i.r., and in most cases, n.m.r. determinations. Unless otherwise stated, yields are based on isolated products with sufficient purity.

Photolysis of the Mesoionic 2,5-Diphenyl-1,3-dithiol-4-one (7).—(a) A deaerated solution of the dithiolone (7) (1.00 g) [λ_{max} (EtOH) 245 (log ϵ 4.059), 275 (4.148), and 540 nm (4.123); λ_{max} (PhH) 285 (log ϵ 4.063) and 565 nm (4.141)] in benzene (500 ml) was irradiated under an atmosphere of argon with an immersion-type 400-W high-pressure mercury lamp through a Pyrex filter at 25–28 °C. After 8 h, the mixture was separated on preparative t.l.c. with carbon tetrachloride and recrystallised from appropriate solvents to give the following compounds: tetraphenyl-1,4-dithiin (8) (from chloroform–ethanol) (136 mg, 18%), m.p. 186–187 °C (lit.,^{12a} 184 °C) (Found: C, 79.6; H, 4.8. Calc. for C₂₈H₂₀S₂: C, 79.95; H, 4.8%), tetraphenylthiophen (9) (from benzene–hexane) (106 mg, 15%), m.p. 186–188 °C (lit.,¹⁶ 184 °C) (Found: C, 86.75; H, 5.2. Calc. for C₂₈H₂₀S: C, 86.55; H, 5.2%), diphenylacetylene (10) (from aqueous ethanol) (205 mg, 31% based on g.l.c. evaluation), m.p. 58–61 °C, and sulphur (40 mg, 17%). They were all identical with authentic specimens. The authentic thiophen (9) was prepared by pyrolysis of the dithiin (8) as described by Kirmse, *et al.*^{12a}

(b) A benzene solution of the dithiolone (7) (1.00 g) was similarly irradiated with a 100-W high-pressure mercury lamp for 6.9 h, and the products were separated on t.l.c. (benzene) to give 4,5-diphenyl-3*H*-1,2-dithiol-3-one (12) (66 mg, 7%), m.p. 116 °C (lit.,¹⁷ 116 °C), tetraphenyldithiin (8) (57 mg, 7%), tetraphenylthiophen (9) (23 mg, 3%), and diphenylacetylene (10) (119 mg, 18% based on v.p.c. evaluation), all identical with authentic specimens.

(c) A solution of the dithiolone (7) (200 mg) in benzene (70 ml) was irradiated with a 450-W tungsten-halogen lamp at 24–26 °C under an atmosphere of argon. After 6 h, the solution was concentrated, the residue was washed with acetonitrile, and recrystallised from dimethylformamide to give the dimer (11) (97 mg, 49%), m.p. 186–188 °C (decomp.) (Found: C, 66.45; H, 3.9. C₃₀H₂₀O₂S₄ requires C, 66.65; H, 3.75%), ν_{CO} 1 690 cm⁻¹; F.-D. mass spec. *m/e* 540 (52, M⁺) and 270 (100%, 7⁺); E.-I. mass spec. *m/e* 388 (1.3, 9⁺), 270 (100, 7⁺), 242 (7.6, 7⁺ – CO), and 178 (9.5, PhC:Ph⁺). The acetonitrile washings were concentrated and the residue was purified on preparative t.l.c. (benzene) followed by recrystallisation from benzene–hexane to give 4,5-diphenyl-3*H*-1,2-dithiol-3-one (12) (25 mg, 13%), identical with an authentic sample.

(d) A solution of the dithiolone (7) (203 mg) and anthracene (395 mg) in benzene (70 ml) was similarly irradiated with a 450-W tungsten-halogen lamp. Similar work-up as described above gave the dimer (11) (32 mg, 16%) and the 1,2-dithiolone (12) (48 mg, 24%).

(e) A solution of the dithiolone (7) (0.5 g) and dimethyl acetylenedicarboxylate (1.3 g) in benzene (250 ml) was similarly irradiated with a 100-W high-pressure mercury lamp for 18 h. The solution was concentrated and separated by column chromatography (silica–hexane, then benzene) to give the dithiin (8) (60 mg, 15%) and dimethyl 2,5-diphenylthiophen-3,4-dicarboxylate (13) (113 mg, 17%), m.p. 167 °C (lit.,¹⁸ 166–167 °C), identical with an authentic sample. When the two compounds were kept in the dark, and treated under otherwise identical conditions, the dithiolone (6) (0.4 g, 80%) was recovered, and the thiophen-dicarboxylate (13) could not be isolated.

Reaction of the Dimer (11) with Dimethyl Acetylenedicarboxylate.—A mixture of the dimer (11) (17 mg), dimethyl acetylenedicarboxylate (50 μ l), and xylene (1 ml) was heated under reflux for 50 min. The resulting solution was concentrated, and methanol was added to the residue. The crystals which separated out were recrystallised from methanol to give dimethyl 2,5-diphenylthiophen-3,4-dicarboxylate (13) (15 mg, 68%), identical with an authentic sample.

Photolysis of 4,5-Diphenyl-1,2-dithiol-3-one (12).—A solution of the 1,2-dithiolone (12) (201 mg) in benzene (430 ml) was irradiated with a 400-W high-pressure mercury lamp through a Pyrex filter for 1.6 h. The reaction mixture was purified on preparative t.l.c. (cyclohexane) to give diphenylacetylene (64%; g.l.c. evaluation), m.p. 58 °C, identical with an authentic sample.

Photolysis of the Dimer (11).—A suspension of the dimer (11) (172 mg) in benzene (450 ml) was similarly irradiated (400-W high-pressure mercury lamp; Pyrex filter) for 15 min. The reaction mixture was concentrated and the precipitate was filtered off to give the recovered dimer (11) (32 mg). The filtrate was concentrated further and the residue was recrystallised from chloroform–ethanol to give the dithiin (8) (62 mg, 57%). Separation on preparative t.l.c. (benzene) of the mother-liquor of recrystallisation gave the thiophen (9) (6 mg, 6%). Both products were identical with authentic samples.

Photolysis of the Mesoionic N-Benzoyl-2,5-diphenyl-1,3-dithiol-4-imine (14a).—A suspension of the 1,3-dithiolimine (14a) (500 mg) [λ_{max} (EtOH) 240 (log ϵ 4.367), 317 (4.228), and 475 (4.131)] in benzene (250 ml) was irradiated with a 100-W high-pressure mercury lamp through a Pyrex filter. After 5 h, the solution was concentrated to a volume of 50 ml, and a small amount of white precipitate which separated out was filtered off. The filtrate was concentrated further and the residue was recrystallised from benzene to give yellow needles of *N*-benzoyl-5-phenyl-3*H*-1,2-dithiol-3-imine (15a) (400 mg, 80%), m.p. 156–157 °C (lit.,¹⁹ 156 °C), identical with an authentic sample (Found: N, 4.35. Calc. for C₁₈H₁₁NOS₂: N, 4.7%).

Similar irradiation of the 1,3-dithiolimine (14a) in various solvents gave the 1,2-dithiolimine (15a) in yields listed below: acetonitrile (70%), acetone (52%), acetonitrile–acetic acid (63%). Irradiation of a benzene solution of the 1,3-dithiolimine (14a) with 'white' fluorescent lamps (10-W \times 4) for 15 h gave the 1,2-isomer (15a) in 43% yield.

The by-product of the above experiments which was soluble only with difficulty was combined and recrystallised from dimethylformamide to give fine needles of the dimer, m.p. 277–278 °C (Found: C, 63.85; H, 3.4; N, 4.7. C₃₂H₂₂N₂O₂S₄ requires C, 64.6; H, 3.75; N, 4.7%). ν_{CO} 1 645 cm⁻¹; F.-D. mass spec. *m/e* 594 (100, M⁺) and 297 (55%, 14a⁺); E.-I. mass spec. *m/e* 369 (7), 297 (4, 14a⁺), 121 (25, PhCS⁺), and 77 (100%, Ph⁺).

The irradiation of the 1,3-dithiolimine (14a) in acetonitrile or acetone with a 30-W low-pressure mercury lamp gave only intractable tar, and no 1,2-isomer (15a) could be isolated.

Photo-rearrangement of 4-Benzoylamino-2-phenyl-1,3-dithiol-1-ium Chloride (14a)·HCl.—A suspension of the 1,3-dithiolium chloride (14a)·HCl (390 mg) in ethanol (200 ml) was irradiated through a Pyrex filter for 4 h with a 100-W high-pressure mercury lamp. The resulting solution was concentrated, acetone was added, and the resulting precipitate was treated with aqueous sodium hydrogen carbon-

ate to give the 1,2-dithioimine (15a) (80 mg, 23%), identical with an authentic sample.

Mesoionic N-Benzoyl-5-methyl-2-phenyl-1,3-dithiol-4-imine (14b).—An ethanolic solution of potassium dithio-benzoate prepared from $\alpha\alpha$ -trichlorotoluene (13.8 g)²⁰ was concentrated, the residue was taken up in water and the solution washed with benzene; the aqueous solution was then concentrated to dryness under reduced pressure. To an ethanolic solution of the residue, 2-chloropropionitrile (3.17 g) was added, and the mixture was set aside overnight. The mixture was filtered, the filtrate was concentrated, and the residue was dissolved in dichloromethane. The solution was washed with water, dried over Drierite, concentrated, and the dark red residual oil was warmed with benzoyl chloride (2.63 g) for 1 h at 70 °C. The crystals which separated out were recrystallised from ethanol to give reddish brown crystals of 4-benzoylamino-5-methyl-2-phenyl-1,3-dithiol-1-ium chloride (14b)·HCl (1.3 g), m.p. 206—207 °C (Found: C, 58.55; H, 4.0; N, 3.95. $C_{17}H_{14}ClNOS_2$ requires C, 58.7; H, 4.05; N, 4.05%), ν_{CO} 1 645 cm^{-1} . An aqueous solution of the dithiolium chloride (500 mg) was treated with sodium hydrogen carbonate, and the free base was extracted with dichloromethane. Concentration of the extract and recrystallisation gave deep red needles of the mesoionic *N-benzoyl-5-methyl-2-phenyl-1,3-dithiol-4-imine* (14b) (430 mg), m.p. 210—211 °C (decomp.) (Found: C, 65.2; H, 4.25; N, 4.25. $C_{17}H_{13}NOS_2$ requires C, 65.55; H, 4.2; N, 4.5%), ν_{max} 1 355 cm^{-1} ; δ 8.50—8.38 (2 H, m, ArH), 7.90—7.70 (3 H, m, ArH), 7.60—7.42 (5 H, m, ArH), and 2.88 (3 H, s, Me).

Photo-rearrangement of the Mesoionic N-Benzoyl-5-methyl-2-phenyl-1,3-dithiol-4-imine (14b).—A suspension of the dithiolimine (14b) (400 mg) in benzene (290 ml) was irradiated through a Pyrex filter with a 100-W high-pressure mercury lamp for 7.5 h. The solution was concentrated and the residue was extracted with benzene and the extract was separated on column chromatography (silica-dichloromethane) and recrystallised from acetone to give yellow needles of *N-benzoyl-4-methyl-3-phenyl-3H-1,2-dithiol-3-imine* (15b) (96 mg, 24%), m.p. 123—125 °C (Found: C, 65.45; H, 4.1; N, 4.4. $C_{17}H_{13}NOS_2$ requires C, 65.55; H, 4.2; N, 4.5%), ν_{max} 1 315 cm^{-1} ; δ 8.52—8.35 (2 H, m, ArH), 7.58—7.35 (8 H, m, ArH), and 2.45 (3 H, s, Me); *m/e* 311 (28, M^+) and 105 (100%, $PhCO^+$).

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