PHOTOCHEMICAL AND THERMAL REACTIONS OF HETEROCYCLES. IV.1, 2.
PHOTO-OXIDATION REACTIONS OF MESOIONIC DITHIOLIUMOLATE,
THIAZOLIUMOLATE, AND RELATED HETEROCYCLES. SOLVENT EFFECTS ON THE COURSE OF THE PHOTO-OXIDATION

Hiroshi Kato, Kazue Tanl, Haruki Kurumisawa, and Yoshiko Tamura
Department of Chemistry, Faculty of Science, Shinshu University,
Asahi, Matsumoto 390, Japan

Abstract — Photo-oxidation of mesoionic 1,3-dithiolum-4-olates (1) gave
diacyl disulfide (2), and that of a mesoionic thiazolium-4-olate (6) and
oxazolium-5-olate (9) gave diacylamides as the main products. The forma-
tion of these products was rationalized by a route involving fragmentation
of the corresponding endoperoxides, which are formed by cycloaddition of
singlet oxygen on the mesoionic rings. Photo-oxidation of 5(4H)-oxazolones
(12) and a 5(4H)-thiazolone (17) in dichloromethane gave the corresponding
dehydro-dimers, while that of the former in dimethylformamide gave mainly
diacylamides. The acylamides were considered to arise via the endoper-
oxides of the mesoionic tautomers.

Mesomorphic compounds, as the name implies, may be considered as resonance-stabilized cyclic ylide
systems, and, as a consequence of this structural feature, many mesomorphic systems undergo ready 1,3-
dipolar cycloaddition reactions with dipolarophiles with a variety of multiple bonds.3 Since singlet
oxygen is known as a potent dipolarophile,4 we initiated a survey of the photo-oxidation reactions of
several mesomorphic compounds as a part of our studies on photochemical and cycloaddition reactions on
these ring systems.5 Such reactions had not been reported at the time when we initiated this
study.2 During the course and after completion of these studies, several independent reports have
appeared which describe the photo-oxidation reactions of mesomorphic compounds.6–12 We report here
details of our preliminary report2 together with results of some additional works on these ring systems.
Results and Discussion

When a solution of the mesomorphic 2,5-diphenyl-1,3-dithiolium-4-olate (1a) in dichloromethane or benzene was irradiated with a tungsten-halogen lamp in the presence of oxygen, dibenzoyl disulfide (2) was isolated as the main product (76%) accompanied by a small amount (9.6%) of the dimer (3a). Oxygen does not participate in the dimer formation because the dimer was isolated in a higher yield (49%) by irradiation of the dithioliumolate (1a) in the absence of oxygen. It was found that the photo-oxidation of this highly colored compound (1a) proceeded both in the presence or absence of methylene blue, and the reaction was considerably retarded in the presence of diazabicyclo[2.2.2]octane. The solution of the dithioliumolate was stable to oxygen in the dark. These results thus support the view that singlet oxygen participates in the reaction and the dithioliumolate (1a) itself can act as the singlet oxygen sensitizer.

\[
\begin{align*}
\text{(1)} & \quad (1a), (3a): \quad R = \text{Ph} \\
(1b): & \quad R = \text{Me} \\
(1c), (3c): & \quad R = p-\text{MeC}_6\text{H}_4
\end{align*}
\]

The photo-oxidation of unsymmetrically substituted dithioliumolates was investigated next in order to see whether the disulfide resulted from an intramolecular or intermolecular process. Attempted photo-oxidation of the mesonic 5-methyl-2-phenyldithiollumolate (1b) gave a product of a quite different type. The structure of this product was unambiguously established as 4-methyl-1,6-diphenyl-6-endo-pyruvylthio-2,5,7-trithiabicyclo[2.2.1]heptan-3-one (3b) by the independent work of Gotthardt et al. The rapid consumption of the 5-methyl derivative (1b) either under irradiation or in the dark would support the view that (3b) is the auto-oxidation product rather than the photo-oxidation product. Photo-oxidation of 2-phenyl-5-p-tolyldithioliumolate (1c) gave the dimer (3c) (8%) and dibenzoyl disulfide (2) (39%) as the main product with only a trace amount of di-p-tolyldisulfide. Inspection of the crude reaction products by hplc showed another peak between the two peaks cor-
responding to the two disulfides described above. Although we suspected that this peak might correspond to benzoyl p-tolyl disulfide, attempts at its isolation were not successful. These results show that a considerable portion of the disulfide is mainly formed intermolecularly from the moiety constituting the 2- and 1- (or 3-) positions of the dithioliumolate.

The above results differ in two main points with the independent works of Gotthardt and his coworkers on photo-oxidation of mesionic dithioliumolates under somewhat different conditions (Na lamp; Rose Bengal sensitizer; methanol solvent). In their experiments, no dimer formation was observed, and the reaction did not occur in the absence of the sensitizer. Presumably, the light from a sodium lamp (λ = 589 nm) may not be absorbed effectively by the dithioliumolate (Ia) (λ_max (EtOH) 540 nm).

The formation of the disulfides has been explained by Gotthardt, et al., by a mechanism involving the methanol adduct (5) of the endoperoxide (4). However, other mechanism should also be considered to explain the formation of the disulfide in the aprotic benzene, and the products distribution from the unsymmetrically substituted dithioliumolate (Ic). However, the exact route to the disulfide in this case remains to be elucidated.

\[
\begin{align*}
\text{PhN}^+ & \quad \text{Ph} \quad \text{O}^- \\
\text{Ph} & \quad \text{S} \quad \text{Ph}
\end{align*}
\]

\[
\begin{align*}
\text{PhN}^+ & \quad \text{Ph} \quad \text{O}^- \\
\text{Ph} & \quad \text{S} \quad \text{Ph}
\end{align*}
\]

\[
\begin{align*}
\text{PhCONHPh} + \text{PhCOCONHPh} + \text{PhCO}_2\text{H} + \text{PhCO}_2\text{CO}_2\text{H}
\end{align*}
\]

Irradiation of the mesoionic 2,3,5-triphenylthiazolium-4-olate (6) under an atmosphere of argon resulted in the formation of complex reaction products, although several photo-products have been isolated from other mesoionic thiazolium-4-olates. When oxygen was present, the reaction took a quite different course. In the preliminary communication, it was reported that photo-oxidation of the thiazoliumolate (6) and chromatographic separation of the products afforded benzanilide as the main product (53%) accompanied by a small amount of phenylglyoxylanilide (3.1%). It was then suggested that they are probably the secondary products formed by hydrolysis of N-benzoylphenylglyoxylanilide (8) during chromatographic separation. Hplc evaluation of the crude photo-oxidation product indicated the presence of N-benzoylphenylglyoxylanilide (8) (54%) and benzamide (17%). This primary product (8) could be isolated (44%) by recrystallization of the reaction product. N-Benzoylphenylglyoxylanilide
was readily hydrolyzed by silica gel treatment to benzamide (81%) and phenylglyoxylanilide (4%). The photo-oxidation of this intensely red compounds (6) occurred both in the presence or absence of a dye sensitizer, and was retarded considerably on addition of diazabicyclo[2.2.2]octane. The thiazoliumolate (6) was stable to oxygen in the dark. The formation of the diacylanilide (8) will be rationalized by assuming the fragmentation of the endoperoxide (7), formed by cycloaddition of singlet oxygen to the thiazoliumolate (6).

Irradiation of the mesionic 3-methyl-2,4-diphenyloxazolium-5-olate (9) in dichloromethane in the presence of methylene blue and oxygen gave N-methyl dibenzamide (11) (29%), N-methylbenzamide (2%), and benzoic acid (4.1%). Although the oxazoliumolate (9) is known to undergo ready auto-oxidation in solution to give similar products15 a part of the products in this case might be formed by photo-oxidation through the endoperoxide intermediate (10).

\[
\text{Ph}-\text{N}^{+}\text{O}^{-}\text{Ph} \xrightarrow{\text{h}^+} \text{Ph}-\text{N}^{+}\text{O}^{-}\text{Ph} \rightarrow (\text{PhCO})_2\text{NMe} + \text{PhCONHMe} + \text{PhCO}_2\text{H}
\]

(9) \hspace{1cm} (10) \hspace{1cm} (11)

The photo-oxidation of 2,4-diphenyl-5(4H)-oxazolone (12a) was next tried. From a spectroscopic investigation, Gotthardt, et al., concluded that it exists in the keto form (12Aa) in nonpolar solvents, whereas in polar solvents, it exists mainly in the mesionic tautomeric form (12Ba).16 It appeared thus interesting to find out if the solvent may control the course of photo-oxidation. The photo-oxidation of the oxazolone (12a) in dichloromethane in the presence of a polymer-supported Rose Bengal gave, after treatment with methanol, the 4,4'-bisoxazolone (15a) (11%) and methyl 2-(benzoylamino)-2-phenylacetate (9%). This ester is probably the product of alcoholysis of the recovered oxazolone (12a). On the other hand, the same reaction in dimethylformamide gave dibenzamide (16a) (13%) with only a trace amount (0.6%) of the bisoxazolone (15a). Similarly, the photo-oxidation of the corresponding 2-p-tolyl derivative (12b) in benzene gave the dehydro-dimer (15b) (12%), while that in dimethylformamide gave N-p-tolylbenzamide (16b) (5.1%) and p-toluamide (9.5%). The oxazolone is susceptible also to auto-oxidation: when oxygen was bubbled through a solution of the oxazolone (12a) in dimethylformamide in the dark, the bisoxazolone (15a) (5.6%) and dibenzamide (16a) (13%) were formed. A considerable portion of dibenzamide (16a) which was formed in the irradiated experiment, should have resulted from photo-oxidation because the yield of the bisoxazolone (15a) was remarkably decreased. The formation of the diacylamide (16) by the above reaction will best be ex-
plained by decarboxylative fragmentation of the endoperoxide (13). The dehydro-dimers are probably formed via the radical (14) formed by dehydrogenation of the oxazolones (12) by triplet oxygen. These findings would support the view that dehydrogenation of the oxazolone (12A) to the dehydrodimer (15) is the main course in nonpolar solvents, whereas in dimethylformamide in which the mesonic form (12B) predominates, formation of the endoperoxide (13) by cycloaddition of singlet oxygen to (12B) becomes the main route; and that triplet oxygen competes with singlet oxygen in the latter solvent, to give the dehydro-dimer (15) and a part of the diacylamide (16). Dixit, et al. independently reached to a similar conclusion from photo-oxidation studies of a few 5(4H)-oxazolones under considerably different conditions (medium-pressure mercury lamp; quartz apparatus; methanol and benzene-methanol solvent).7 Under the conditions adopted by these authors, nonoxidative photochemical products were also formed. Gotthardt, et al.16 reported that the dehydro-dimer (15a) is formed as a by-product when the oxazolone (12a) was prepared in the presence of air. It was also reported recently that air oxidation of 5(4H)-oxazolones in dimethylsulfoxide in the presence of palladium-on-charcoal or bases gives good yields of diacylamides.17

In order to check the possibility that the dehydro-dimer formation of this type is a general phenomenon, the photo-oxidation of a structurally analogous 5(4H)-thiazolone was briefly investigated. The photo-oxidation of 4-methyl-2-phenyl-5(4H)-thiazolone (17) in dichloromethane in the presence of
methylene blue gave the corresponding bisthiazolone (18) (65%). It has been known that the thiazolone (17) exists entirely as the keto form in this solvent.\textsuperscript{18} It was reported recently that the photolysis of a related system, the mesonic 3-methyl-2-phenylthiazolium-5-olate, in the presence of air gave several products, one of which is probably formed by participation of singlet oxygen.\textsuperscript{3}

From the results of our studies on the photo-oxidation of several mesonic and related systems presented above, as well as the related works by other research groups, one may conclude that the photo-oxidation of mesonic heterocycles generally proceeds through the corresponding endoperoxides which are formed by cycloaddition of singlet oxygen on the mesonic rings.

**EXPERIMENTAL.**

Mps were determined on a Yanagimoto hot-stage apparatus. \textsuperscript{1}H- (100 and 90 MHz) and \textsuperscript{13}C- (22.5 MHz) nmr spectra were determined on a JEOL JNM-4H-100 and JNM-FX-90Q spectrometers for solutions in deuteriochloroform (tetramethylsilane internal standard). Mass spectra were measured with a JEOL 01 SG spectrometer. Hplc was run with a JASCO Trirotar-III, and tic separations were performed on Merck Kieselgel PF\textsubscript{254}. Yields are based on isolated products with sufficient purity.

**General Procedure of Photo-oxidation.** -- A solution of the substrate in a solvent (60--80 ml) was irradiated externally with an air-cooled 500-W tungsten-halogen lamp while a slow stream of oxygen was bubbled through the solution. The temperature of the solution was kept below 30 °C by cooling with running water.

**Photo-oxidation of the Mesonic 1,3-Dithiolium-4-olates (1).** -- 2,5-Diphenyl-1,3-dithiolium-4-olate (1a).

(a) A solution of the dithioliumolate (1a)\textsuperscript{19} (500 mg) in benzene was irradiated for 3 h in the presence of oxygen. The solution was concentrated and the residue was extracted with ethanol to give dibenzoyl disulfide\textsuperscript{20} (from acetone–ethanol) (192 mg, 76%), mp and mixed mp 129--130 °C (Anal. Calc. for C\textsubscript{14}H\textsubscript{10}O\textsubscript{2}S\textsubscript{2}: C, 61.29; H, 3.67; S, 23.37. Found: C, 61.53; H, 3.44; S, 23.15). The residue which remained after the ethanol extraction was recrystallized from dimethylformamide to give the dimer (3a)\textsuperscript{1} (48 mg, 9.6%), mp and mixed mp 190--191 °C (decomp.). (b) The dithioliumolate (1a) (100 mg) was completely consumed after similar irradiation of a dichloromethane solution for 40 min in the presence or absence of methylene blue. (c) When a solution of the dithioliumolate (1a) (100 mg) in benzene was similarly irradiated, the deep violet color of the dithiolumolate faded within 36 min. After irradiation of a solution of the same composition for 130 min in the presence of diazabiclo[2.2.2]octane, the violet color of the dithioliumolate still strongly persisted, and the main tic spot corresponded to the dithioliumolate (1a). (d) Oxygen was bubbled for 170 min through a solution of the dithioliumolate (100 mg) (1a) in dichloromethane in the dark. The
dithioliumolate (Ia) (96 mg) was recovered unchanged. 2-Phenyl-5-methyl-1,3-dithiolium-4-olate (lb). (a) A solution of the dithioliumolate (lb) (500 mg) in dichloromethane was irradiated in the presence of oxygen. The characteristic color of the dithioliumolate faded within 5 min. After 10 min irradiation, the mixture was concentrated and the residue was recrystallized from chloroform--cyclohexane to give 4-methyl-6-pyruvylthio-1,6-diphenyl-2,5,7-trithiabicyclo[2.2.1]heptan-3-one (3b) (58 mg, 11%) mp 168--170 °C, lit. 1171--173 °C. Spectral data agreed with the reported values. (b) Oxygen was bubbled through a solution of the dithioliumolate (lb) (100 mg) in dichloromethane in the dark. Work-up of the mixture by a similar procedure as described above gave the trithiabicyclonone (3b) (13 mg, 12%), identical with the sample isolated by procedure (a) above. 2-Phenyl-5-tert-butyl-1,3-dithiolium-4-olate (lc). A solution of the tolyldithioliumolate (lc) (100 mg) in dichloromethane was irradiated for 1 h in the presence of oxygen. Hplc assay of the crude mixture (Permaphase DOS; water : methanol, 60 : 40 → 40 : 60 v/v) showed three peaks in area ratio of 260 (A) : 150 (B) : 1 (C), of which the retention times of fraction A and C coincided with those of dibenzoyl disulfide and di-p-tolyl disulfide, respectively. The products from 300 mg of the dithioliumolate (lc) was extracted with acetone, the acetone extract was separated on a column (silica--dichloromethane) then on tlc (dichloromethane--cyclohexane), and the disulfide fraction was sublimed and recrystallized from ethanol to give dibenzoyl disulfide (56.3 mg, 39%). The residue from the acetone washings was recrystallized from acetonitrile--benzene to give the dimer (3c) (24.6 mg, 8%), mp 183--185 °C (decomp.). IR: 1685 cm⁻¹ (C=O); MS: m/z 284 (M/2 83%), 135 (MeC₆H₄, 44), and 121 (PhCS, 100). Anal. Calcd. for C₃₂H₂₄O₂S₄: C, 67.58; H, 4.25. Found: C, 67.32; H, 4.30.

Photo-oxidation of the Mesotropic 2,3,5,7-Triphenylthiazolium-4-olate (6). -- (a) A solution of the thiazollumolate (6) (500 mg) in dichloromethane was irradiated for 10.5 h in the presence of oxygen. Concentration of the reaction mixture and trituration of the residue with cold methanol followed by recrystallization from cyclohexane gave N-benzoylphenylglyoxylanilide (8) (233 mg, 44%), identical (mp and mixed mp 132-133 °C; ir, 1H- and 13C-nmr) with an authentic specimen. Hplc analysis of the product on hplc (Cosmosil; methanol : water = 80 : 20) showed that N-benzoylphenylglyoxylanilide and benzalanilide were formed in yields of 54 and 17% respectively. (b) When the photo-oxidation products from the thiazollumolate (6) (200 mg) was separated on preparative tlc (benzene, then dichloromethane), benzalanilide (63 mg, 53%) (from ethanol), mp and mixed mp 166--167 °C and phenylglyoxylanilide (4.3 mg, 3.1%) (from cyclohexane), mp and mixed mp 62--63 °C were isolated. (c) The thiazollumolate (6) (200 mg) was consumed completely when it was similarly irradiated in dichloromethane for 170 min both in the presence or absence of methylene blue. In the presence of diazabicyclo[2.2.2]octane (500 mg), the deep red color of the thiazollumolate still strongly persisted after irradiation for 5 h, and tlc showed that the solution still consisted mainly of...
the thiazoliumolate (6).

Mesolonic 3-Methyl-2,4-diphenyloxazolium-5-olate (9). — This was prepared by a modification of the reported method. \(^\text{15}\) N-benzoyl-ß-phenylsarcosine was cyclized with acetic anhydride and triethylamine (1:1), and the oxazoliumolate (9) which separated out was collected and recrystallized. Although the yield of the oxazoliumolate by this method is somewhat lower (50–60%) than the reported yield, this method can by-pass the rather critical vacuum distillation of acetic anhydride.

Photo-oxidation of the Mesolonic 3-Methyl-2,4-diphenyloxazolium-5-olate (9). — A solution of the oxazoliumolate (9) (300 or 400 mg) and methylene blue (10 mg) in dichloromethane was irradiated for 1 h in the presence of oxygen. The combined reaction products from 1.0 g of the oxazoliumolate was extracted with ether, ethanol, and then hexane. The extracts were sublimed under vacuum, and the sublimates and the residue were finally purified by preparative tlc (alumina—chloroform) and recrystallized to give the following components: N-methyl dibenzamide (11) \(^\text{25}\) (276 mg, 29%) (from ethanol), mp and mixed mp 99–100 °C; N-methyl benzoamide (11 mg, 2%) (from benzene), mp and mixed mp 79 °C; benzoic acid (20 mg, 4.1%) (from carbon tetrachloride), mp and mixed mp 122 °C.

4-Phenyl-2-p-tolyl-5(4H)-oxazolone (12b). — This was prepared in 47% yield by the general method of Gotthardt, et al. \(^\text{16}\) Colorless needles (from cyclohexane), mp 117 °C. IR: 1810 (C=O) and 1635 (C-N) cm\(^{-1}\); NMR: \(\delta_H\) 2.43 (3H, s), 5.47 (1H, s), 7.26 and 7.94 (each 2H, d, \(J = 8\) Hz), and 7.36 (5H, br s); MS: \(m/z\) 251 (M, 12%), 207 (M - CO\(_2\), 54) and 119 (MeC\(_6\)H\(_4\)CO, 100). Anal. Calcd. for C\(_{16}\)H\(_{13}\)NO\(_2\): C, 76.48; H, 5.21; N, 5.57. Found: C, 76.33; H, 5.01; N, 5.47.

Photo-oxidation of 5(4H)-oxazolones. — 2,4-Diphenyl-5(4H)-oxazolone (12a). (a) A solution of the oxazolone (12a) \(^\text{16}\) (500 mg) and methylene blue (5 mg) in dichloromethane was irradiated for 3 h in the presence of oxygen. The solvent was concentrated and the residue was washed with methanol to give 4,4'-bis[2,4-diphenyl-5(4H)-oxazolone] (15a) \(^\text{16}\) (from dichloromethane—acetone) (55 mg, 11%), mp and mixed mp 197–198 °C. The methanol washings were chromatographed (alumina—dichloromethane) to give methyl 2-(benzoylamino)phenylacetate \(^\text{26}\) (51 mg, 9%) (from cyclohexane), mp 115 °C. IR: 3280, 1750 and 1625 cm\(^{-1}\); NMR: \(\delta_H\) 3.81 (3H, s), 5.85 (1H, d, \(J = 7\) Hz), 7.22 (1H, br s), 7.35–7.6 (8H, m), and 7.8–8.0 (2H, m); MS: \(m/z\) 269 (M\(^+\)). Anal. Calcd. for C\(_{16}\)H\(_{15}\)NO\(_2\): C, 71.37; H, 5.61; N, 5.20. Found: C, 71.16; H, 5.55; N, 5.03. (b) A solution of the oxazolone (12a) (500 mg) in dimethylformamide was irradiated for 1 h in the presence of oxygen and Rose Bengal which was adsorbed on Amberlite IRA-400 \(^\text{27}\) (0.1 g). The mixture was filtered and concentrated. The residue was washed with cyclohexane and then with hot benzene to give the dehydro-dimer (15a) (from ethanol) (3 mg, 0.6%). Concentration of the benzene washings afforded dibenzamide \(^\text{28}\) (from ethanol) (60 mg, 13%), mp and mixed mp 148–150 °C. (c) Oxygen was bubbled for 4 h through a solution of the oxazolone (12a) (0.5 g) in dimethylformamide (60 ml) in the dark. Fractional recrystallization
from ethanol gave the dehydro-dimer (15a) (28 mg, 5.6%) and dibenzamide (16a) (61 mg, 13%). 4-
Phenyl-2-p-toly-5(4H)-oxazolone (12b). (a) A solution of the oxazolone (12b) (500 mg) in benzene
was irradiated for 9 h in the presence of Rose Bengal-on-Amberlite while oxygen was bubbled
through the mixture. Chromatography (silica—dichloromethane) and recrystallization (dichloromethane—
acetone) gave 4,4'-bis[4-phenyl-2-p-toly-5(4H)-oxazolone] (15b) (61 mg, 12%), mp 194 °C.
IR: 1810 (C=O) and 1645 (C-N) cm⁻¹; NMR: δH 2.35 (6H, s), 7.1–7.5 (14H, m), and 7.6–7.9 (4H, m); MS:
m/z 456 (M - CO₂, 1%), 412 (M - 2CO₂, 13), 250 (M/2, 86), and 207 (M/2 - CO₂, 100). Anal.
Calcd. for C₃₂H₂₄N₂O₄: C, 76.79; H, 4.83; N, 5.60. Found: C, 76.97; H, 4.60; N, 5.68. (b) A
solution of the oxazolone (12b) (510 mg) in dimethylformamide was irradiated for 7 h in the presence
of Rose Bengal-on-Amberlite and oxygen. Recrystallization (dichloromethane—cyclohexane, then ben-
zene—cyclohexane) and tlc (ethyl acetate) gave N-p-toluylbenzamide (16b) (25 mg, 5.1%), mp and mixed mp 114–115 °C, and p-toluamide (26 mg, 9.5%), mp and mixed mp 164–166 °C.

Photo-oxidation of 4-Methyl-2-phenyl-5(4H)-thiazolone (17). -- A solution of the thiazolone (17) (500
mg) and methylene blue (10 mg) in dichloromethane was irradiated for 3 h in the presence of
oxygen. The mixture was concentrated and recrystallized from ethanol to give 4,4'-bis[4-methyl-2-
phenyl-5(4H)-thiazolone] (18) (321 mg, 65%), mp 140 °C. IR: 1710 cm⁻¹ (C=O); NMR: δH 1.74 (6H, s)
and 7.35–7.75 (10H, m); MS: m/z 352 (M⁺ – CO, 0.2%), 190 (M/2, 17), and 121 (PhCS⁺, 100).

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