Heterocycles by Cycloaddition. Part 6.[1] Cycloaddition–Double Fragmentation Reactions of Mesoionic Compounds with an Oxabicyclo-[2.2.1]heptadiene: Synthesis of Five- and Six-membered Heterocycles[2]

By **Hiroshi Matsukubo** and **Hiroshi Kato,*** Department of Chemistry, Faculty of Science, Shinshu University, Asahi, Matsumoto 390, Japan

The reaction of dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (1) with some five-membered mesoionic compounds [(2) and (10)] gave five-membered aromatic heterocycles [(6)—(9) and (12)] by thermal double fragmentation of the initially formed cycloadducts [(3), (4), and (11)]. The periselectivity of the cycloaddition varies according to the mesoionic compound employed. With a dithiolone (10a) and a thiazolone (10b), the cycloadducts (11) were isolable, and the corresponding *S*-oxides (13) were prepared. Pyrolysis of the *S*-oxides gave a thiopyranone (14a) and a pyridone (14c).

We have reported[3] that the cycloaddition reactions of five-membered-ring mesoionic compounds with small ring olefins and concomitant extrusion and ring cleavage afford a convenient route for the preparation of six-membered aromatic heterocycles. Stabilisation of the intermediate ylides and relief of ring strain by ring cleavage facilitate these reactions. We now report the reactions of some mesoionic compounds with dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (1). In these reactions, the unstable intermediate ylides, expected to be produced by fragmentation of the initially formed cycloadducts, may undergo further fragmentation to give two aromatic heterocycles. Thus, this cycloaddition–double fragmentation reaction may constitute a novel approach to heterocycles by retro-cycloaddition reactions.[4] A similar reaction[5] of a mesoionic dithiolone and norbornadiene gives a stable cycloadduct, which undergoes thermal fragmentation at 180 °C to a thiophen, COS, and cyclopentadiene. However, no major product was isolated from the reactions of mesoionic 4-thiazolones with norbornene and norbornadiene.[6] In reactions with some cyclic olefins, the intermediate ylides have been intercepted by the olefins to give bis-adducts.[7]

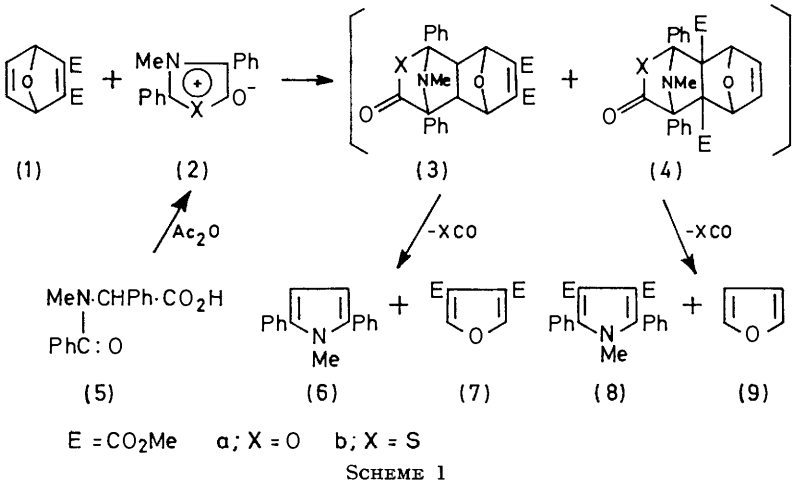
Dimethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (1) reacted rapidly at room temperature with the mesoionic 3-methyl-2,4-diphenyloxazol-5-one (2a), giving 1-methyl-2,5-diphenylpyrrole (6) (16%) and its dimethyl 3,4-dicarboxylate (8) (24%). This indicates that the cycloaddition of the oxazolone (2a) took place across both the less substituted and the fully substituted double bonds to give the cycloadducts (3a) and (4a), which then underwent spontaneous double fragmentation to give the pyrroles (6) and (8), and the furans (7) and (9). The furans were not isolated, but the n.m.r. spectrum of the crude reaction mixture showed appropriate peaks. The n.m.r. measurements also showed that the reaction was complete within a few minutes. The pyrroles (6) and (8) were isolated in 24 and 16%

[1] Part 5, H. Matsukubo and H. Kato, preceding paper.
[2] Preliminary report, H. Matsukubo and H. Kato, *J.C.S. Chem. Comm.*, 1975, 840.
[3] H. Matsukubo and H. Kato, *J.C.S. Chem. Comm.*, 1974, 412; *J.C.S. Perkin I*, 1975, 632; H. Matsukubo, M. Kojima, and H. Kato, *Chem. Letters*, 1975, 1153; *cf.* also K. T. Potts and J. Baum, *J.C.S. Chem. Comm.*, 1973, 833; T. Eicher and V. Schäfer, *Tetrahedron*, 1974, **30**, 4025; H.-D. Martin and M. Hekman, *Angew. Chem. Internat. Edn.*, 1972, **11**, 926.
[4] H. Kwart and K. King, *Chem. Rev.*, 1968, **68**, 415.
[5] H. Gotthardt and B. Christl, *Tetrahedron Letters*, 1968, 4751.
[6] K. T. Potts, J. Baum, and E. Houghton, *J. Org. Chem.*, 1974, **39**, 3631.
[7] H. Gotthardt and R. Huisgen, *Chem. Ber.*, 1968, **101**, 552; 1970, **103**, 2625; R. Huisgen, H. Gotthardt, and H. O. Bayer, *ibid.*, p. 2368.

yield, respectively, when the diene (1) and 2-(*N*-methylbenzamido)-2-phenylacetic acid (5) were warmed together in acetic anhydride. The reaction of the diene (1) with the corresponding 5-thiazolone (2b) proceeded more slowly but more selectively and in higher yields than with (2a), and gave, *via* the unisolated adducts (3b) and (4b), the pyrroles (6) (79%) and (8) (7%) when heated in benzene for 13 h.

When the mesoionic 2,5-diphenyl-1,3-dithiol-4-one (10a) and the diene (1) were heated in dichloromethane, the cycloaddition took place specifically across the less substituted double bond, and the cycloadduct (11a) (82%) was isolated. The *exo,exo*-configuration of the adduct was assigned by comparison of its n.m.r. data with those of similar systems,[6,8] particularly on the basis of the small coupling constant of the bridgehead protons and the markedly different chemical shift values of the two angular methine protons. The mass spectrum of (11a) showed no molecular ion but a base peak at *m/e* 236 corresponding to diphenylthiophen. In agreement with this fragmentation, pyrolysis of the adduct (11a) in refluxing xylene resulted in a clean double fragmentation to 2,5-diphenylthiophen (12a) (92%) and dimethyl furan-3,4-dicarboxylate (7) (91%). Irradiation of the adduct (11a) in benzene through a Pyrex filter also resulted in the thiophen (12a) (71%).

The reaction of the mesoionic 2,3,5-triphenyl-4-thiazolone (10b) with the diene (1) in benzene under reflux slowly gave two major adducts and a minor one, together with dimethyl 2,5-diphenylthiophen-3,4-dicarboxylate (12c) (3%). The two major products are formed by cycloaddition across the less substituted double bond (11b) (48%) and the fully substituted double bond (11c) (33%), respectively. The assignments of structures and configurations are based mainly on mass and n.m.r. spectra; the latter show that the two bridgehead protons are magnetically almost equivalent, the two methine protons of (11b) are in a markedly different magnetic environments, and the methyl protons of (11c) are shielded. The spectral data (see Experimental) of the minor product (11b') (1% yield) show that it is a configurational isomer of (11b). The cycloadduct (11b) was thermally stable, and only partial pyrolysis occurred on boiling in xylene for 40 h. It was pyrolysed by heating in *o*-diethylbenzene under reflux for 27 h, but the reaction gave, besides the expected thiophen (12b) (73%), a product (3%) which arose by elimination of the furan (7) from the adduct. The by-product no longer retained a bicyclic structure (15); it showed no n.m.r. signal assignable to protons on a non-conjugated olefin, had a u.v. maximum at 314 nm, and contained an unstrained carbonyl group ($\nu_{max.}$ 1 648 cm^{-1}). Thiazepinone structures (16a or b) may be



SCHEME 1

assigned but shortage of material did not allow degradation studies. As suggested by the partial formation of the thiophen (12c) under the conditions of cycloaddition, the *peri*-isomeric adduct (11c) underwent a ready fragmentation on heating in xylene for 4 h, and the thiophen (12c) (84%) was isolated.

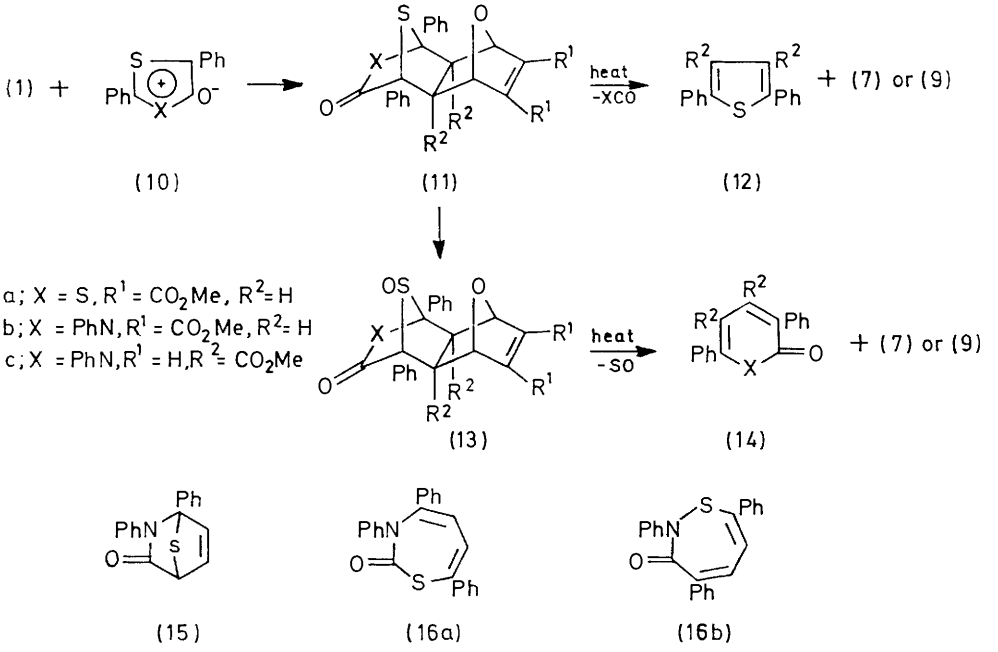
Oxidation of the dithiolone adduct (11a) with *m*-chloroperbenzoic acid gave the corresponding *S*-oxide (13a) (94%). The sulphoxide oxygen was considered to be oriented *anti* to the oxygen bridge because the chemical shift values of the methine protons of (13a) are almost identical with those of (11a). When the *S*-oxide (13a) was heated in xylene, extrusion of sulphur monoxide occurred exclusively to give diphenylthiopyranone (14a) (81%). Photolysis of (13a) also gave (14a), albeit in low yield. Similar oxidation of the thermally stable thiazolone adduct (11b) gave the corresponding *S*-oxide (13b) (97%). This *S*-oxide was also thermally stable, and prolonged heating in xylene or heating in a higher boiling solvent resulted in a complex product mixture which we could not purify. Oxidation of the isomer (11c) gave the unstable *S*-oxide

[8] (*a*) K. T. Potts, J. Baum, E. Houghton, D. N. Roy, and U. P. Singh, *J. Org. Chem.*, 1974, **39**, 3619; (*b*) J. D. Slee and E. LeGoff, *J. Org. Chem.*, 1970, **35**, 3897; T. Sasaki, K. Kanematsu, and K. Hayakawa, *J.C.S. Perkin I*, 1972, 1951; and references cited in M. P. Cava and M. V. Lakshmikantham, *Accounts Chem. Res.*, 1975, **8**, 139.

(13c), which could not be isolated pure because of its ready decomposition to the pyridone (14c) during attempted recrystallisation. Brief heating of the *S*-oxide (13c) in benzene caused extrusion of sulphur monoxide and fragmentation to give dimethyl 1,6-dihydro-6-oxo-1,2,5-triphenylpyridine-3,4-dicarboxylate (14c) (70%).

The above survey shows that the reactions of this type provide an alternative synthesis of five-membered heterocycles from mesoionic compounds, especially valuable when they are not readily formed by direct cycloaddition–extrusion reactions with the corresponding acetylenes. The reactions of mesoionic compounds with electron-deficient acetylenes proceed rapidly whereas those with non-conjugated or electron-rich acetylenes occur sluggishly or give complex products.[8a,9,10] The of mesoionic compounds, controlled by substituents[10] and by photochemical and thermal control[12] has been reported.

The double fragmentation of the adducts described above may not proceed by the same mechanism in all cases. At the outset of the present investigation, it was expected that initial formation of an unstable ylide by extrusion of the XCO group from the cycloadduct should facilitate the ensuing fragmentation to two aromatic heterocycles. However, the markedly different reaction conditions required for the fragmentation show that the tendency for extrusion of the XCO groups is not completely uninfluenced by the molecular framework and/or the substituent groups; alternatively the two fragmentation steps may be concerted. Moreover, the isolation



SCHEME 2

periselectivity in avoidance of the fully substituted double bond of the bicycloheptadiene system is greatly increased by replacement of the oxygen atom of (1) by a bulky group such as tosylimino.[11] Moreover, by a simple modification of the initial cycloadduct, these reactions provide a novel method of preparation of six-membered heterocycles from mesoionic compounds. Although we have earlier reported a method of preparation of fully conjugated six-membered heterocycles from mesoionic compounds,[3] the present method is unique in that the mesoionic system provides a four-atom unit for cycloaddition reactions. Selective extrusion of two potentially extrudable groups from adducts of a small amount of (16) by pyrolysis of the adduct (11b) shows that the first step of the double fragmentation may be fragmentation of the furan (7), at least for the adduct (11b). Indeed, the reactions of some mesoionic compounds with a cyclo-octatetraene–acetylene adduct give fragmentation products in which the XCO group of the original mesoionic ring system remains intact.[1] On the other hand, we have recently found that the cycloadducts of some mesoionic compounds with naphthalene 1,4-epoxide lose XCO first to form a transient ylide intermediate, which can be trapped successfully by added dipolarophiles before further fragmentation into isobenzofuran.[13]

[9] *Cf. e.g.* R. Huisgen and H. Gotthardt, *Chem. Ber.*, 1968, **101**, 1059; R. Knorr, R. Huisgen, and G. K. Staudinger, *ibid.*, 1970, **103**, 2639.

[10] K. T. Potts, E. Houghton, and U. P. Singh, *J. Org. Chem.*, 1974, **39**, 3627.

[11] H. Matsukubo and H. Kato, *Bull. Chem. Soc. Japan*, 1976, **49**, 3314.

[12] H. Kato, S. Nakazawa, T. Koyosawa, and K. Hirakawa, *J.C.S. Perkin I*, 1976, 672.

[13] H. Kato, M. Nishiwaki, and H. Matsukubo, unpublished results.

EXPERIMENTAL

General experimental directions are given in the preceding paper.[1]

Reactions of Dimethyl 7-Oxabicyclo[2.2.1]*hepta-2,5-diene-2,3-dicarboxylate* (1) *with Mesoionic Compounds.*—3-*Methyl-2,4-diphenyloxazol-5-one* (2a). (*a*) A suspension of the oxazolone (2a)[14] (2.3 mmol) in benzene (25 cm³) was slowly added with stirring, under nitrogen, to a solution of the diene (1)[15] (2.3 mmol) in benzene (5 cm³). After 15 min, the solution was concentrated *in vacuo* and the residue was recrystallised (from benzene–n-hexane) to give 1-methyl-2,5-diphenylpyrrole (6). Chromatography on silica (benzene) of the mother liquor gave more of (6), and dimethyl 1-methyl-2,5-diphenylpyrrole-3,4-dicarboxylate (8). The pyrrole (6) (16%) had m.p. 206—207 °C (lit.,[16] 204—205 °C) (Found: C, 87.75; H, 6.3; N, 6.0. $C_{17}H_{15}N$ requires C, 87.5; H, 6.5; N, 6.0%), u.v. and i.r. data as reported,[16] δ 7.47—7.20 (10 H, m, ArH), 6.27 (2 H, s, =CH), and 3.57 (3 H, s, Me), *m/e* 233 (100%, M^+). The diester (8) (24%) had m.p. 148—149 °C (lit.,[16] 147—148 °C) (Found: C, 72.4; H, 5.35; N, 3.95. $C_{21}H_{19}NO_4$ requires C, 72.2; H, 5.5; N, 4.0%), $\lambda_{max.}$ 215sh (log ε 4.39) and 272 nm (4.16), i.r. data as reported,[16] δ 7.38 (10 H, s, ArH), 3.63 (6 H, s, OMe), and 3.20 (3 H, s, NMe), *m/e* 349 (100%, M^+). The crude reaction mixture showed additional n.m.r. peaks at δ 7.81, 3.82, and 6.20, assignable to the furan (9) and dimethyl furan-3,4-dicarboxylate (7).

(*b*) In situ *reaction*. A mixture of the diene (1) (2 mmol) and 2-(*N*-methylbenzamido)-2-phenylacetic acid (5) (2 mmol) in freshly distilled acetic anhydride (10 cm³) was warmed under nitrogen at 50—55 °C for 3 h. The precipitate of (6) which separated on cooling was collected and the filtrate was worked up by a method similar to that described above to give the pyrroles (6) (24%) and (8) (16%), both identical with authentic specimens.

3-*Methyl-2,4-diphenyl-5-thiazolone* (2b). A solution of the diene (1) (4.4 mmol) and the thiazolone (2b)[17] (4.4 mmol) in benzene (60 cm³) was heated under reflux in an atmosphere of nitrogen for 13 h. The precipitate of (6) which separated on cooling was collected, and similar work up of the filtrate gave the pyrrole (6) (79%) and the pyrroledicarboxylate (8) (7%), both identical with authentic specimens.

2,5-*Diphenyl-1,3-dithiol-4-one* (10a). A solution of the diene (1) (2.9 mmol) and the dithiolone (10a)[18] (2.9 mmol) in dichloromethane (30 cm³) was refluxed for 38 h. The solvent was removed and the residue was chromatographed on silica (chloroform) to give dimethyl 3,4,4a,5,8,8a-*hexahydro-3-oxo-1,4-diphenyl-1,4-epithio-5,8-epoxy-1H-benzothiopyran-6,7-dicarboxylate* (11a) (82%) as prisms (from chloroform–ether), m.p. 165—166 °C (Found: C, 62.3; H, 4.1. $C_{25}H_{20}O_6S_2$ requires C, 62.5; H, 4.2%), u.v. (MeOH) end absorption, $\nu_{max.}$ 1 750 and 1 713 cm⁻¹, δ 7.66—7.25 (10 H, m, ArH), 5.00 and 4.85 (each 1 H, d, *J* 1 Hz, OCH), 3.80 and 3.34 (each 1 H, dd, *J* 6.5 and 1 Hz, CH), and 3.80 (6 H, s, Me), *m/e* 236 [100%, $(12a)^+$], 184 [14, $(7)^+$], 153 [65, $(7)^+$ — OMe], and 60 (55, COS^+).

2,3,5-*Triphenyl-4-thiazolone* (10b). A mixture of the diene (1) (17.6 mmol), the thiazolone (10b)[19] (17.6 mmol), and benzene (150 cm³) was heated under reflux for 50 h. The solution was concentrated and the residue was fractionally recrystallised from methanol and benzene. The combined mother liquor was chromatographed on silica (chloroform) to give the following compounds: *dimethyl* 1,2,3,4,4a,5,8,8a-*octahydro-3-oxo-1,2,4-triphenyl-1,4-epithio-5,8-epoxyisoquinoline-6,7-dicarboxylate* (11b) (48%), prisms (from methanol), m.p. 203—204 °C (Found: C, 69.05; H, 4.55; N, 2.55. $C_{31}H_{25}NO_6S$ requires C, 69.0; H, 4.65; N, 2.6%), u.v. (MeOH) end absorption, $\nu_{max.}$ 1 745, 1 722sh, and 1 708 cm⁻¹, δ 7.57—6.62 (15 H, m, ArH), 5.06 and 5.03 (each 1 H, d, *J* 1 Hz, OCH), 3.82 and 3.78 (each 3 H, s, Me), and 3.72 and 3.31 (each 1 H, dd, *J* 6.5 and 1 Hz, CH), *m/e* 355 [9%, M^+ — (7)], 236 [100, $(12a)^+$], 184 [23, $(7)^+$], 153 [99, $(7)^+$ — OMe], and 119 (50, $PhNCO^+$); *dimethyl* 1,2,3,4,4a,5,8,8a-*octhydro-3-oxo-1,2,4-triphenyl-1,4-epithio-5,8-epoxyisoquinoline-4a,8a-dicarboxylate* (11c) (33%) prisms (from methanol), m.p. 181—182 °C (decomp.) (Found: C, 68.75; H, 4.6; N, 2.55. $C_{31}H_{25}NO_6S$ requires C, 69.0; H, 4.65; N, 2.6%), u.v. (MeOH) end absorption, $\nu_{max.}$ 1 749, 1 722sh, and 1 715 cm⁻¹, δ 7.75—7.82 (15 H, m, ArH), 6.77 and 6.57 (each 1 H, d, *J* 6 Hz, =CH), 5.37br (2 H, s, OCH), and 3.13 and 3.07 (each 3 H, s, Me), *m/e* 352 [34%, $(12c)^+$], 119 (100, $PhNCO^+$), and 68 [53, $(9)^+$]; an isomer of (11b) (1%), prisms (from chloroform–ether), m.p. 259—260 °C (Found: C, 68.6; H, 4.8; N, 2.5%), u.v. (MeOH) end absorption, $\nu_{max.}$ 1 750, 1 721sh, and 1 715 cm⁻¹, δ 7.68—6.78 (15 H, m, ArH), 5.46 and 5.21 (each 1 H, s, OCH), 3.95 (2 H, s, CH), and 3.87 and 3.85 (each 3 H, s, Me), *m/e* 537 (trace, M^+), 355 [57%, M^+ — (7)], 236 [100, $(12b)^+$], 180 (38, $PhCNPh^+$), and 153 [79, $(7)^+$ — OMe]; dimethyl 2,5-diphenylthiophen-3,4-dicarboxylate (12c) (3%), prisms (from methanol), m.p. 167—169 °C (lit.,[10,20] 167—168 °C) (Found: C, 67.95; H, 4.45. $C_{20}H_{16}O_4S$ requires C, 68.15; H, 4.6%) (i.r., n.m.r. and mass spectral data were virtually identical with the reported values[10]).

Pyrolysis and Photolysis of the Adducts (11).—*Dithiolone adduct* (11a). (a) *Pyrolysis*. A solution of the adduct (11a) (0.42 mmol) in xylene (10 cm³) was heated under reflux for 20 h, then concentrated, and the residue was recrystallised (from methanol) to give 2,5-diphenylthiophen (12a) (92%) as plates, m.p. 154—155 °C (lit.,[21] 152—153 °C) (Found: C, 81.25; H, 4.95. $C_{16}H_{12}S$ requires C, 81.3; H, 5.1%), $\nu_{max.}$ 1 599, 1 486, 1 452, 804, 749, and 685 cm⁻¹, δ 7.70—7.12 (m), *m/e* 236 (100%, M^+). The mother liquor was concentrated, ether–light petroleum was added to the residue, and the mixture was kept in a refrigerator. The crystals which were slowly deposited were recrystallised (ether–light petroleum) to give slightly impure dimethyl furan-3,4-dicarboxylate (7) (91%), m.p. 42—43.5 °C (lit.,[22] 47.5 °C) (Found: C, 51.05; H, 4.25. $C_8H_8O_5$ requires C, 52.2; H, 4.4%), $\nu_{max.}$ 3 155, 1 747, and 1 730sh cm⁻¹, δ 7.81 (2 H, s, =CH) and 3.82 (6 H, s, Me), *m/e* 184 (22%, M^+) and 153 (100, M^+ — OMe).

[14] H. O. Bayer, R. Huisgen, R. Knorr, and F. C. Schaefer, *Chem. Ber.*, 1970, **103**, 2581.
[15] W. Eberbach, M. Perroud-Arguelles, H. Achenbach, E. Druckrey, and H. Prinzbach, *Helv. Chim. Acta*, 1971, **54**, 2579.
[16] R. Huisgen, H. Gotthardt, H. O. Bayer, and F. C. Schaefer, *Chem. Ber.*, 1970, **103**, 2611.
[17] R. Huisgen, E. Funke, F. C. Schaefer, H. Gotthardt, and E. Brunn, *Tetrahedron Letters*, 1969, 1809.
[18] H. Gotthardt, M. C. Weisshuhun, and B. Christl, *Chem. Ber.*, 1976, **109**, 740.
[19] M. Ohta, H. Chosho, C. Shin, and K. Ichimura, *J. Chem. Soc. Japan*, 1964, **85**, 440.
[20] K. T. Potts, E. Houghton, and U. P. Singh, *J.C.S. Chem. Comm.*, 1969, 1129.
[21] E. Baumann and E. Fromm, *Ber.*, 1895, **28**, 890.
[22] S. Oae, N. Furukawa, T. Watanabe, Y. Otsuji, and M. Hamada, *Bull. Chem. Soc. Japan*, 1965, **38**, 1247.

(b) *Photolysis*. A solution of the adduct (11a) (0.42 mmol) in benzene (900 cm^3) was deaerated by passing nitrogen and irradiated through a Pyrex filter with a 400 W immersion type high-pressure mercury lamp for 5 h below 30 °C. The solution was concentrated, the crystals were collected, and the residue was chromatographed on silica (chloroform) to give diphenylthiophen (12a) (71%), identical with an authentic sample.

Thiazolone adduct (11b). A suspension of the adduct (11b) (0.93 mmol) in *o*-diethylbenzene (10 cm^3) was heated under reflux for 27 h. The solvent was removed and the residue was chromatographed on silica (benzene) to give 2,5-diphenylthiophen (12b) (73%), identical with an authentic specimen, and needles (from benzene–n-hexane) tentatively identified as 3,4,7-triphenyl-1,3-thiazepin-2(3*H*)-one (16a) or 2,4,7-triphenyl-1,2-thiazepin-3(2*H*)-one (16b) (3%), m.p. 205.5—206 °C (Found: C, 77.55; H, 4.6; N, 3.85. Calc. for $C_{23}H_{17}NOS$: C, 77.7; H, 4.8; N, 3.95%), $\lambda_{max.}$ (MeOH) 265 (log ε 4.32) and 314 nm (4.27), $\nu_{max.}$ 1 648, 1 600, 1 552, 1 494, 1 442, and 1 319 cm^{-1}, δ 7.75—6.95 (m), *m/e* 355 (30%, M^+), 263 (100, M^+ — PhNH), and 234 (28, M^+ — PhCS).

Thiazolone adduct (11c). A solution of the adduct (11c) (0.37 mmol) in xylene (10 cm^3) was heated under reflux for 4 h. The solution was concentrated and the residue was chromatographed on silica (chloroform) to give dimethyl 2,5-diphenylthiophen-3,4-dicarboxylate (12c) (84%), m.p. 167—169 °C, identical with an authentic specimen.

S-*Oxides* (13).—*From the adduct* (11a). A solution of the dithiolone adduct (11a) (0.63 mmol) and *m*-chloroperbenzoic acid (0.65 mmol; 70% purity) in dichloromethane (10 cm^3) was stirred for 4 h at room temperature. The solution was washed (aqueous sodium hydroxide; water), dried (Na_2SO_4), and concentrated, and the residue was recrystallised (from chloroform–ether) to give needles of the S-*oxide* (13a) (94%), m.p. 201—202 °C (Found: C, 60.2; H, 3.95. $C_{25}H_{20}O_7S_2$ requires C, 60.45; H, 4.05%), u.v. (MeOH) end absorption, $\nu_{max.}$ 1 749, 1 712, and 1 077 cm^{-1}, δ 7.83—7.30 (10 H, m, ArH), 5.09 and 4.98 (each 1 H, d, *J* 1 Hz, OCH), 3.81 and 3.79 (each 3 H, s, Me), and 3.81 and 3.21 (each 1 H, d, *J* 7.5 Hz, CH), *m/e* 264 [27%, $(14a)^+$], 236 [87, $(12a)^+$], 153 [100, $(7)^+$ — OMe], 60 (17, COS^+), and 48 (8, SO^+).

From the adduct (11b). A solution of the thiazolone adduct (11b) (0.56 mmol) and *m*-chloroperbenzoic acid (0.61 mmol) in dichloromethane (10 cm^3) was stirred for 8 h at room temperature. Similar work-up and recrystallisation (from methanol) gave prisms of the S-*oxide* (13b) (97%), m.p. 206—207 °C (Found: C, 66.8; H, 4.4; N, 2.45. $C_{31}H_{25}NO_7S$ requires C, 67.0; H, 4.55; N, 2.5%), u.v. (MeOH) end absorption, $\nu_{max.}$ 1 740sh, 1 729, 1 714sh, and 1 058 cm^{-1}, δ 7.90—6.94 (15 H, m, ArH), 5.33 and 5.14 (each 1 H, d, *J* 1 Hz, OCH), 3.92 and 3.83 (each 3 H, s, Me), and 3.81br and 3.36br (each 1 H, d, *J* 7.8 Hz, CH), *m/e* 323 [55%, $(14b)^+$], 295 [17, $(6)^+$], and 153 [100, $(7)^+$ — OMe].

From the adduct (11c). The adduct (11c) (0.19 mmol) was treated similarly. Reprecipitation with benzene–n-hexane gave the crude *S*-oxide (13c) (107% crude), which decomposed gradually at 110—210 °C (Found: C, 68.25; H, 4.7; N, 2.5. Calc. for $C_{31}H_{25}NO_7S$: C, 67.0; H, 4.55; N, 2.5%), $\nu_{max.}$ 1 739sh, 1 729, and 1 084 cm^{-1}, δ 7.85—6.90 (15 H, m, ArH), 6.78 and 6.66 (each 1 H, dd, *J* 6 and 1.5 Hz, =CH), 5.70 and 5.46 (each 1 H, t, *J* 1.5 Hz, OCH), and 3.23 and 3.11 (each 3 H, s, Me). Attempts at purification by recrystallisation or chromatography resulted in partial decomposition to (14). Accordingly, this crude sample was used directly for the pyrolysis.

Pyrolysis and Photolysis of the S-*Oxides* (13).—S-*Oxide* (13a). (a) *Pyrolysis*. A solution of the *S*-oxide (13a) (0.2 mmol) in xylene (10 cm^3) was heated under reflux for 12 h. The solution was concentrated and the residue was chromatographed on silica (chloroform) to give dimethyl furan-3,4-dicarboxylate (7) (14%), identical with an authentic specimen, and 3,6-diphenylthiopyran-2-one (14a) [57%; 81% based on consumed (13a)], m.p. 187—187.5 °C (lit.,[23] 183.5—184 °C) (Found: C, 77.35; H, 4.6. Calc. for $C_{17}H_{12}OS$: C, 77.25; H, 4.6%), $\lambda_{max.}$ (MeOH) 222 (log ε 4.39), 275 (3.94), and 379 nm (4.13), $\nu_{max.}$ 1 627 cm^{-1}, δ 7.50—7.22 (11 H, m, ArH and =CH) and 7.07 (1 H, d, *J* 7.5 Hz, =CH), *m/e* 264 (31%, M^+) and 236 (100, M^+ — CO). A later fraction gave unchanged (13a) (30%).

(b) *Photolysis*. Irradiation of a solution of the *S*-oxide (13a) (0.2 mmol) in benzene for 15 h with a 400 W high-pressure mercury lamp through Pyrex and chromatography gave unchanged *S*-oxide (13a) (30%) and the thiopyranone (14a) (19%), identical with authentic specimens.

S-*Oxide* (13c). A solution of the crude *S*-oxide (13c) (0.14 mmol) in benzene (5 cm^3) was heated under reflux for 5 h, then concentrated. The precipitate of (14c) was collected, and the filtrate was chromatographed on silica (chloroform) to give dimethyl 1,6-dihydro-6-oxo-1,2,5-triphenylpyridine-3,4-dicarboxylate (14c) (70% combined yield) as prisms (from methanol), m.p. 231—232 °C (227—228 °C in a capillary tube) (lit.,[6] 219—221 °C) (Found: C, 37.45; H, 4.7; N, 3.1. $C_{27}H_{21}NO_5$ requires C, 73.8; H, 4.8; N, 3.2%), u.v. and i.r. data virtually identical with the reported values,[6] δ 7.40—6.94 (15 H, m, ArH), and 3.58 and 3.40 (each 3 H, s, Me), *m/e* 439 (86%, M^+), 411 (46, M^+ — CO), 380 (73, M^+ — CO — OMe), 180 (68, $PhCNPh^+$), and 77 (100, Ph^+).

We are indebted to Kyorin Chemical Laboratories for elemental analyses and mass spectra, and to Mr. Naomi Takagi for experimental assistance.

[6/1230 *Received*, 25*th June*, 1976]

[23] G. Laban and R. Mayer, *Z. Chem.*, 1967, **7**, 227 (*Chem. Abs.*, 1967, **67**, 64184).