G. Wilson, J. Org. Chem., 40, 124 (1975).
(6) J. H. Lee, A. Matsumoto, O. Simamura, and M. Yoshida, Chem. Commun., 1393 (1969).
(7) A. Matsumoto, J. H. Lee, M. Yoshida, and O. Simamura, Chem. Lett., 455 (1973).
(8) J. H. Lee, A. Matsumoto, M. Yoshida, and O. Simamura, Chem. Lett., 951 (1974).
(9) M. Yoshida, A. Matsumoto, and O. Simamura, Bull. Chem. Soc. Jpn., 43, 3587 (1970).
(10) M. J. Haddadin and N. C. Chelhot, Tetrahedron Lett., 5185 (1973); R. Bonnett, R. F. C. Brown, and R. G. Smith, J. Chem. Soc., Perkin Trans. 1, 1432 (1973); J. D. White, M. E. Mann, H. D. Kirshenbaum, and A. Mitra, J. Org. Chem., 36, 1048 (1971).
(11) (a) K. T. Potts, J. Baum, E. Houghton, D. N. Roy, and U. P. Singh, J. Org. Chem., 39, 3619 (1974); (b) H. O. Bayer, R. Huisgen, R. Knorr, and F. C. Schaefer, Chem. Ber., 103, 2581 (1970).
(12) L. M. Jackman and S. Sternhell, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry", 2nd ed., Pergamon Press, London, 1969.
(13) K. T. Potts and S. Zurawell, unpublished observations.
(14) H. Gotthardt, M. C. Weisshuhn, and B. Christl, Chem. Ber., 109, 740 (1976).
(15) K. T. Potts, E. Houghton, and U. P. Singh, J. Org. Chem., 39, 3627 (1974).
(16) Spectral characterization and reaction workup conditions were as described in ref 4b.
(17) H. Brandsma, "Preparative Acetylenic Chemistry", Elsevier Publishing Co., New York, 1971, p 117.
(18) K. Bowden, I. M. Heilbron, E. H. R. Jones, and B. C. L. Weedon, J. Chem. Soc., 39 (1946).

Notes

Mesoionic Compounds. 47. Cycloadditions with the 4(5*H*)-Oxazolone System[1]

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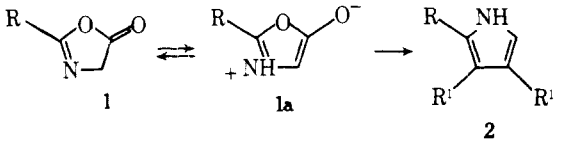
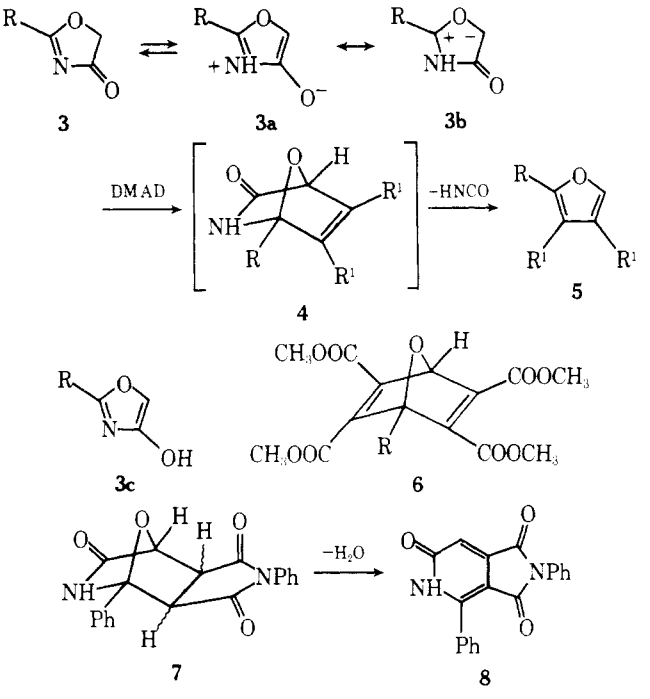
Cycloadditions with a variety of mesoionic ring systems have been utilized as convenient routes to other heterocyclic systems. With those ring systems containing nitrogen, the final product always contained a substituted nitrogen atom, restricting somewhat the appeal of this route. Ring systems capable of undergoing tautomerism such as the 5(4*H*)-oxazolones (**1**) undergo[2] cycloaddition with acetylenic dipolarophiles via the tautomer **1a** giving pyrroles **2**. 4(5*H*)-Thiazolones also react with olefinic dipolarophiles[3a] forming thiophenes and pyridones depending on the substitution pattern, and the corresponding 5(4*H*)-thiazolones form a variety of cycloadducts and Michael adducts with electron-deficient olefins.[3b] 3-Hydroxypyridine, via its tautomer, has been shown to undergo cycloaddition with benzyne[4a] and also with acrylonitrile and ethyl acrylate.[4b] We now report our utilization of the 4(5*H*)-oxazolones in cycloaddition reactions leading to 2,3,4-trisubstituted furans, this being a useful complement to the formation of furans from *anhydro*-2,5-disubstituted-4-hydroxyoxazolium hydroxides.[5]



The reaction of 2-phenyl-4(5*H*)-oxazolone (**3**, R = Ph) with excess dimethyl acetylenedicarboxylate (DMAD) in refluxing acetic anhydride gave dimethyl 2-phenylfuran-3,4-dicarboxylate (**5**, R = Ph, R^1 = $COOCH_3$) (26%). Under similar conditions, 2-(4-chlorophenyl)-4(5*H*)-oxazolone (**3**, R = *p*-ClC_6H_4) yielded dimethyl 2-(4-chlorophenyl)furan-3,4-dicarboxylate (**5**, R = *p*-ClC_6H_4; R^1 = $COOCH_3$) (29%), as well as a second product, identified as tetramethyl 1-(4-chlorophenyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3,5,6-tetracarboxylate (**6**; R= *p*-ClC_6H_4) (19%), the latter product resulting from a Diels–Alder reaction of **5** (R = *p*-ClC_6H_4; R^1 = $COOCH_3$) with dimethyl acetylenedicarboxylate. The structures of these products were evident from analytical and spectral data (Experimental Section). The mode of formation of the furans **5** is less clear, the tautomer **3a** and the carbonyl ylide dipole **3b** being likely contributors to the reaction.



Thermal extrusion of isocyanic acid from the intermediate 1:1 cycloadduct **4** would lead to **5**, a sequence consistent with that shown to be in effect with the 5(4*H*)-oxazolones and with the *anhydro*-4-hydroxyoxazolium hydroxide system. An alternative route involves Diels–Alder addition of DMAD to the 4-hydroxyoxazole tautomer **3c**, oxazoles having been shown to act in this fashion giving furans after extrusion of a nitrile from the initial 1:1 adduct.[7] The latter route appears unlikely as the 5(4*H*)-oxazolones were shown not to react in this fashion[2] and in the 4(5*H*)-thiazolones, the 4-alkoxy- and 4-acetoxythiazoles did not undergo cycloaddition under reaction conditions successful with the unblocked thiazolones.

Evidence in favor of the dipolar mechanism comes from the increased yield of **5** obtained with increase in solvent polarity in the cycloaddition. Thus in changing from Ac_2O to sulfolane the reaction was completed in a significantly shorter time and the yield of **5** (R = Ph; R^1 = $COOCH_3$) increased from 26 to 45%. Further increases in the yield of **5** (to 61%) resulted from the use of the hydrochloride salt of **3** (R = Ph) in sulfolane as solvent. Although Lewis acids are known[7,8] to exert a catalytic effect on certain Diels–Alder reactions, the above indications make us favor the dipolar mechanism in the present case.

Dibenzoylacetylene also reacted readily with **3** (R = Ph) giving 3,4-dibenzoyl-2-phenylfuran (**5**, R = Ph; R^1 = COPh)

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(30%) and 2-methyl-4(5*H*)-oxazolone hydrobromide (**3**, R = CH_3), and DMAD in sulfolane gave dimethyl 2-methylfuran-3,4-dicarboxylate (**5**, R = CH_3; R^1 = COPh) (19%), none of the corresponding secondary adduct **6** being obtained. This is an important route to this type of 2-alkylfuran.

The cycloaddition of **3** to acetylenic dipolarophiles and the isolation of the furan reaction product is probably aided by the thermodynamic stability of the extruded fragment (HNCO) and of the furan produced. It is not surprising that attempts to cycloadd **3** to a number of olefinic dipolarophiles were generally unsuccessful. Of several olefins examined (e.g., fumaronitrile, diethyl fumarate, diethyl maleate), only *N*-phenylmaleimide was found to result in a characterizable product. The product isolated proved to be not the expected primary adduct **7** but rather the pyridone **8**, derived from **7** by elimination of water.[9]

Experimental Section[10]

2-(4-Chlorophenyl)-4(5*H*)-oxazolone (3, R = *p*-ClC_6H_4). To a solution of 4-chlorobenzoyl isocyanate[11] (12.6 g, 0.07 mol) in sodium-dried Et_2O (175 mL) was added dropwise with stirring a sodium-dried ethereal solution of diazomethane (6.0 g, 0.14 mol). The resulting colorless solid was collected by filtration and crystallized from benzene as very pale yellow irregular prisms: 8.9 g (66%); NMR ($CDCl_3$) δ 8.19 (d, 2, aromatic), 7.55 (d, 2, aromatic), 4.77 (s, 2, CH_2).

Anal. Calcd for $C_9H_6ClNO_2$: C, 55.26; H, 3.09; N, 7.16. Found: C, 55.49; H, 3.15; N, 7.40.

Reaction of 2-Phenyl-4(5*H*)-oxazolone with Dimethyl Acetylenedicarboxylate. A. In Acetic Anhydride. A solution of 2-phenyl-4(5*H*)-oxazolone[12] (0.8 g, 0.005 mol) and DMAD (2.5 mL) in acetic anhydride (5 mL) was heated at 130 °C for 18 h. The volatile components were removed in vacuo and the residue taken up in benzene and chromatographed (silica gel, 75 g, eluted with Et_2O–petroleum ether, 2:3) to afford as the only isolable component dimethyl 2-phenylfuran-3,4-dicarboxylate (**5**; R = Ph; R^1 = $COOCH_3$), 0.32 g (26%). It crystallized from CH_3OH as colorless plates: mp 70–71 °C; IR (KBr) 3170, 3030, 2980 (CH), 1730, 1720 (CO) cm^{-1}; λ_{max} (CH_3OH) 259 nm (log ϵ 3.34); NMR ($CDCl_3$) δ 7.89 (s, 1, C_5–H), 7.16–7.84 (m, 5, phenyl), 3.82 (d, 6, methyl); M^+ · 260 (60).

Anal. Calcd for $C_{14}H_{12}O_5$: C, 64.61; H, 4.65. Found: C, 64.52; H, 4.60.

In a similar fashion 2-(4-chlorophenyl)-4(5*H*)-oxazolone (1.0 g, 0.005 mol), DMAD (2.5 mL, ca. 0.02 mol), and Ac_2O (7 mL) were heated at 130 °C for 18 h. The volatile components were removed by evaporation and the residue chromatographed (silica gel, 40 g, eluted with Et_2O–petroleum ether 1:1) to give as the first component dimethyl 2-(4-chlorophenyl)furan-3,4-dicarboxylate (**5**, R = *p*-ClC_6H_4; R^1 = $COOCH_3$) crystallizing from CH_3OH as fine colorless needles: 0.43 g (29%); mp 93–93.5 °C; IR (KBr) 1760, 1735 (CO) cm^{-1}; λ_{max} (CH_3OH) 278 nm (log ϵ 4.24); NMR ($CDCl_3$) δ 7.97 (C_5–H), 7.61 (d, 2, aromatic), 7.32 (d, 2, aromatic), 3.77 (d, 6, CH_3); M^+ · 296 (32), 294 (100).

Anal. Calcd for $C_{14}H_{11}ClO_5$: C, 57.06; H, 3.76. Found: C, 57.20; H, 3.81.

A second fraction crystallized from CH_3OH to afford tetramethyl 1-(4-chlorophenyl)-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3,5,6-tetracarboxylate (**6**, R = *p*-ClC_6H_4) as colorless irregular prisms: 0.42 g (19%); mp 126–127 °C; IR (KBr) 1753, 1735 (CO) cm^{-1}; λ_{max} (CH_3OH) 332 nm (log ϵ 3.69), 224 (4.15); NMR ($CDCl_3$) δ 7.42 (s, 4, aromatic), 6.10 (s, 1, bridgehead CH), 3.80 (b, 12, CH_3); M^+ · 377 (6), 294 (100).

Anal. Calcd for $C_{20}H_{17}ClO_9$: C, 54.99; H, 3.92. Found: C, 55.10; H, 3.84.

B. In Sulfolane. 2-Phenyl-4(5*H*)-oxazolone (0.8 g, 0.005 mol), DMAD (2 mL), and sulfolane (5 mL) were heated at 125 °C for 6 h. The volatile components were removed under vacuum and the residual oil was taken up in H_2O and extracted with Et_2O. The organic layer was dried (Na_2SO_4) and evaporated to leave a brown oil which was chromatographed (silica gel, 18 g, eluted with Et_2O–petroleum ether, 1:1) to afford as the first fraction dimethyl 2-phenylfuran-3,4-dicarboxylate (**5**, R = Ph; R^1 = $COOCH_3$), 0.58 g (45%). A second fraction was collected which crystallized from CH_3OH to yield tetramethyl-1-phenyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3,5,6-tetracarboxylate (**6**, R = Ph) as colorless prisms: 0.05 g (4%); mp 108–110 °C; IR (KBr) 1755, 1730 (CO) cm^{-1}; λ_{max} (CH_3OH) 275 nm (sh) (log ϵ 3.00), 216 (sh) (3.27), 207 (sh) (3.29); NMR ($CDCl_3$) δ 7.21–7.82 (m, 5, aromatic), 6.09 (s, 1, bridgehead), 3.80 (d, 12, methyl); *m/e* (rel intensity) M^+ · 402 (7), $(M - DMAD)^+$ · 260 (100).

Anal. Calcd for $C_{20}H_{18}O_9$: C, 59.70; H, 4.51. Found: C, 59.64; H, 4.54.

Reaction of 2-Phenyl-4(5*H*)-oxazolone Hydrochloride with Dimethyl Acetylenedicarboxylate. A solution of 2-phenyl-4(5*H*)-oxazolone (2.2 g, 0.014 mol) in CH_3OH was cooled to 5 °C and dry HCl gas was introduced with stirring to precipitate the hydrochloride as colorless irregular prisms, mp 110–120 °C. A mixture of this material (1.0 g, 0.005 mol) and DMAD (2.5 g, 0.012 mol) in sulfolane (7 mL) was heated at 115 °C for 6 h. Most of the solvent was removed by evaporation and the residual oil was taken up in Et_2O, washed with H_2O, dried (Na_2SO_4), and chromatographed (silica gel, 30 g, eluted with Et_2O–petroleum ether 1:1). The first fraction crystallized from CH_3OH as colorless plates (0.8 g, 61%) identical[13] with dimethyl 2-phenylfuran-3,4-dicarboxylate (**5**, R = Ph; R^1 = $COOCH_3$) obtained as described above.

A second fraction from the column also crystallized from CH_3OH as colorless prisms (0.15 g, 7%) identical[13] with tetramethyl 1-phenyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3,5,6-tetracarboxylate (**6**, R = Ph) obtained as described above.

3,4-Dibenzoyl-2-phenylfuran (5, R = Ph; R^1 = COPh). 2-Phenyl-4(5*H*)-oxazolone (4.9 g, 0.03 mol) and dibenzoylacetylene (5.7 g, 0.04 mol) in acetic anhydride (50 mL) were heated at 130 °C for 6 h and then at 110 °C overnight. The solvent was removed by evaporation and the tarry brown residue was chromatographed (silica gel, 100 g, eluted with Et_2O–petroleum ether 1:1) to afford, after crystallization from CH_3OH, 3.2 g (30%) of small colorless prisms: mp 148.5–149 °C; IR (KBr) 1685, 1655 (CO) cm^{-1}; NMR ($CDCl_3$) δ 7.02–8.04 (m, 19, aromatic); M^+ · 352 (69), 105 (100) (PhCO).

Anal. Calcd for $C_{24}H_{16}O_3$: C, 81.80; H, 4.58. Found: C, 81.62; H, 4.54.

Reaction of 2-Methyl-4(5*H*)-oxazolone Hydrobromide with Dimethyl Acetylenedicarboxylate. 2-Methyl-4(5*H*)-oxazolone hydrobromide[14] (1.2 g, 0.0067 mol) and DMAD (2.0 g, 0.014 mol) were heated in sulfolane (5 mL) at 105 °C for 18 h, then poured into H_2O and the mixture extracted with Et_2O. The organic layer was dried (Na_2SO_4), solvent removed by evaporation, and the resulting residue chromatographed (silica gel, 14 g, eluted with benzene) to afford dimethyl 2-methylfuran-3,4-dicarboxylate (**5**, R = CH_3; R^1 = $COOCH_3$) as a pale yellow oil which crystallized from CH_3OH as fine colorless needles: 0.25 g (19%); mp 30–31 °C (lit.[7] bp 88–91 °C (1 mm)); IR (KBr) 2965 (CH_3), 1730 (broad, C=O) cm^{-1} (lit.[7] 1731, 1737 cm^{-1}); NMR ($CDCl_3$) δ 7.65 (s, 1, C_5–H), 3.85 (d, 6, ester $COOCH_3$), 1.85 (s, 3, C_2–CH_3) (lit.[7] δ 7.65, 3.85, 1.86).

Reaction of 2-Phenyl-4(5*H*)-oxazolone Hydrochloride with *N*-Phenylmaleimide. A mixture of 2-phenyl-4(5*H*)-oxazolone hydrochloride (1.0 g, 0.005 mol) and *N*-phenylmaleimide (1.0 g, 0.006 mol) in sulfolane (5 mL) was heated at 120 °C for 18 h and cooled to deposit *N*-6-diphenyl-1,2-dihydro-2-oxopyridine-4,5-dicarboximide (**8**) as a brown solid which crystallized from a large volume of EtOH as fine, very pale yellow needles: 0.4 g (22%); mp 305–307 °C; IR (KBr) 3450 (NH or OH), 1730, 1675 (CO); λ_{max} (CH_3OH) 298 nm (log ϵ 4.15), 245 (4.15); NMR ($CDCl_3$) δ 7.20–7.97 (m, 10, aromatic), 6.85 (s, 1, C_3–H), 3.30 (bs,[15] 1, NH or OH).

Anal. Calcd for $C_{19}H_{12}N_2O_3$: C, 72.14; H, 3.82; N, 8.86. Found: C, 71.73; H, 3.86; N, 9.17.

When the above oxazolone (free base) (0.8 g, 0.005 mol) and *N*-phenylmaleimide were refluxed in pyridine (8 mL) for 12 h and the reaction mixture cooled, yellow prisms were collected which crystallized from DMF/H_2O as cream-colored irregular prisms (0.20 g, 13%) identical[13] with **8** obtained above.

Registry No.—**3** (R = *p*-ClC_6H_4), 26254-10-4; **3** (R = Ph), 30216-01-4; **3** (R = Ph) hydrochloride, 68475-21-8; **3** (R = Me) hydrobromide, 15059-26-4; **5** (R = Ph; R^1 = $COOCH_3$), 37674-31-0; **5** (R = *p*-ClC_6H_4; R^1 = $COOCH_3$), 68475-22-9; **5** (R = Ph; R^1 = COPh), 37674-32-1; **5** (R = CH_3; R^1 = $COOCH_3$), 6141-60-2; **6** (R = *p*-ClC_6H_4), 68475-23-0; **6** (R = Ph), 68510-68-9; **8**, 68475-24-1; 4-chlorobenzoyl isocyanate, 4461-36-3; diazomethane, 334-88-3; DMAD, 762-42-5; dibenzoylacetylene, 1087-09-8; *N*-phenylmaleimide, 941-69-5.

References and Notes

(1) (a) Partial support of this work by U.S. Public Health Service Research Grant CA 08495, National Cancer Institute, is gratefully acknowledged; (b) NDEA Trainee; abstracted from the Ph.D. thesis of J.L.M., RPI, 1975; (c) for a preliminary communication see: K. T. Potts and J. L. Marshall, *Chem. Commun.*, 1000 (1972).

(2) H. Gotthardt, R. Huisgen, and H. O. Bayer, *J. Am. Chem. Soc.*, **92**, 4340 (1970); A. Padwa, M. Dharan, J. Smolanoff, and S. I. Wetmore, *ibid.*, **95**, 1945 (1973).

(3) (a) A. Robert, M. Ferrey, and A. Foucaud, *Tetrahedron Lett.*, 1377 (1975); (b) G. C. Barrett and R. Walker, *Tetrahedron*, **32**, 571 (1976).
(4) (a) N. Dennis, A. R. Katritzky, T. Matsue, S. K. Parton, and Y. Takeuchi, *J. Chem. Soc., Perkin Trans. 1*, 746 (1974); N. Dennis, A. R. Katritzky, and S. K. Parton, *ibid.*, 2285 (1976); (b) J. Banerji, N. Dennis, J. Frank, A. R. Katritzky, and T. Matsuo, *ibid.*, 2334 (1976).
(5) T. Ibata, M. Hamaguchi, and H. Kiyohara, *Chem. Lett.*, 21 (1975); M. Hamaguchi and T. Ibata, *Tetrahedron Lett.*, 4475 (1974).
(6) E.g., see O. Diels and S. Olsen, *J. Prakt. Chem.*, **156**, 289 (1940); C. D. Weis, *J. Org. Chem.*, **27**, 3520 (1962).
(7) R. Grigg and J. L. Jackson, *J. Chem. Soc. C*, 552 (1970).
(8) P. Yates and P. Eaton, *J. Am. Chem. Soc.*, **82**, 4436 (1960); G. I. Frey and R. Robinson, *ibid.*, **83**, 249 (1961).
(9) The acid-catalyzed elimination of water from similar Diels–Alder type adducts is well documented: R. Weiss, A. Abeles, and E. Knapp, *Monatsh. Chem.*, **61**, 162 (1932); Ch. Dufraisse and R. Priou, *Bull. Soc. Chim. Fr.*, **502**, 611 (1938).
(10) Spectral characterizations were carried out with the following instrumentation: infrared spectra, Perkin-Elmer Model 337 spectrophotometer; ultraviolet and visible spectra, Cary 14 spectrophotometer; NMR spectra, Varian T-60 and HA-100 spectrometers, using Me_4Si as internal standard; mass spectra, Hitachi Perkin-Elmer RMU-6E mass spectrometer at 70 eV, utilizing the direct inlet probe, with a source temperature of ca. 150 °C. Melting points were determined in capillaries and are uncorrected. Evaporations were performed using a Rotovap apparatus. Microanalyses were performed by Instranal Laboratories, Inc., Rensselaer, N.Y. and Galbraith Laboratories, Inc., Knoxville, Tenn.
(11) A. J. Speziale and L. R. Smith, *J. Org. Chem.*, **28**, 1805 (1963).
(12) J. H. Sheehan and P. T. Izzo, *J. Am. Chem. Soc.*, **71**, 4059 (1949).
(13) Criteria used for establishing identity include superimposable infrared spectra, no depression in mixed melting point, and identical R_f values in at least two different TLC systems.
(14) I. V. Smolanka, S. M. Zhripak, and V. I. Staninets, *Ukr. Khim. Zh.*, **30**, 265 (1964); *Chem. Abstr.*, **60**, 14490 g. (1964).
(15) Proton exchanged with D_2O.

Air Oxidation of Oxindoles to Isatins

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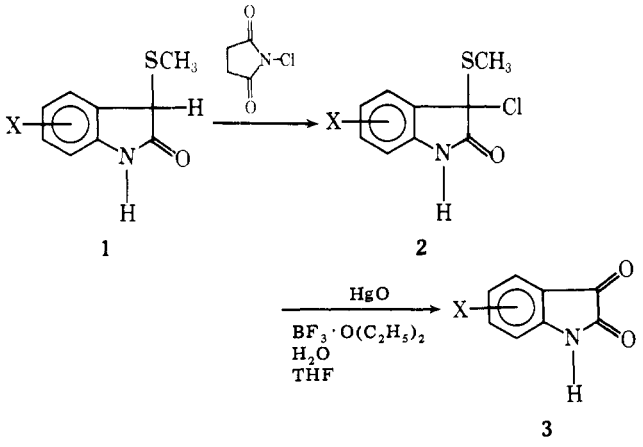
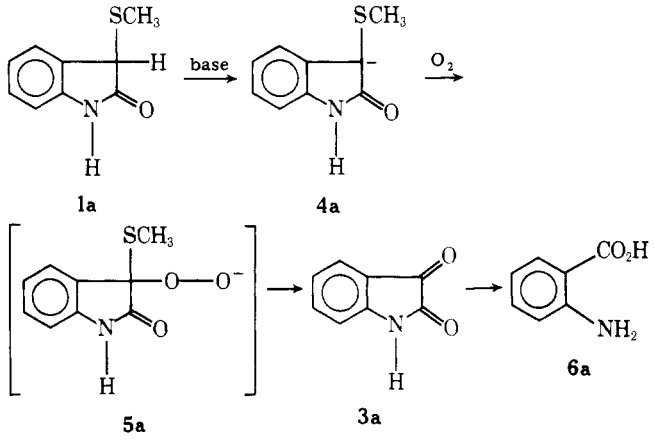
Recently, we described a general method for the synthesis of isatins.[2] This method involved the chlorination of readily available oxindoles[3] of general formula **1** to give 3-chloro-3-methylthiooxindoles, **2**. Hydrolysis of **2** using red mercuric oxide and boron trifluoride etherate in aqueous tetrahydrofuran then gave the desired isatin, **3**. In view of the problems associated with the use of mercuric oxide and boron trifluoride etherate on a large scale, and considering the long history of isatins as valuable synthetic intermediates in the preparation of both pharmaceuticals and dyes, we decided to seek a more direct route for the conversion of **1** into **3**. We now wish to report on the direct air oxidation of the anion of **1** into **3**.



1 **2** **3**

In our initial studies, we attempted to utilize aqueous base in the direct oxidation of **1a** to **3a**. It was hoped that the base would convert **1a** into **4a**,[4] which would react with oxygen to give **5a**. Breakdown of **5a** under the reaction conditions should have yielded **3a**. Utilizing sodium carbonate, sodium bicarbonate, or potassium hydroxide with air in aqueous methanol



1a **4a** **5a** **3a** **6a**

appeared to give the desired oxidation of **1a** to **3a**. Unfortunately **3a** was unstable under these reaction conditions and was further converted into anthranilic acid (**6**). This was demonstrated by an increase in the amount of anthranilic acid and a decrease in the amount of isatin with increased reaction time.[5] Under the best conditions, we obtained approximately a 2:1 ratio of **6a** to **3a**.

The difficulties encountered in the use of aqueous base prompted us to turn our attention to nonaqueous conditions. We found that the nonnucleophilic base potassium *tert*-butoxide in either ether or anhydrous tetrahydrofuran worked very well for the desired conversion. Table I lists the yields and melting points obtained by this method. In general, contamination by anthranilic acid was not a problem under the anhydrous conditions. In fact, in all of the examples listed, purification of the product was achieved by recrystallization without any prior chromatography of the product.

Experimental Section[10]

General Procedure. In a general procedure, 0.3 to 2.0 g of sublimed potassium *tert*-butoxide was suspended in 200–250 mL of dry ether or tetrahydrofuran (THF) at 0 °C and an equimolar amount of the corresponding 3-methylthiooxindole was added. The solution immediately became colored. The reaction mixture was then stirred

Table I. Yields of Isatins Obtained from the Air Oxidation of 3-Methylthiooxindoles

oxindole	registry no.	% yield of isatin (3)	registry no.	mp, °C	lit. mp, °C
3-methylthiooxindole (**1a**)	40800-64-4	32	91-56-5	199–200	200–202,[2] 200–201[6]
5-carboethoxy-3-methylthiooxindole (**1b**)	61394-56-7	60	25128-35-5	205–206	206–207[2]
5-methyl-3-methylthiooxindole (**1c**)	40800-66-6	41	608-05-9	184–185	185–187[2]
7-methyl-3-methylthiooxindole (**1d**)	40800-67-7	40	1127-59-9	268–270	270–272,[2] 267[7]
5-chloro-3-methylthiooxindole (**1e**)	61394-53-4	49	17630-76-1	246–247	249–252[2], 247[8]
5-methoxy-3-methylthiooxindole (**1f**)	50461-38-6	27	39755-95-8	201–203	202–204,[2] 201–202[9]
5-cyano-3-methylthiooxindole (**1g**)	61394-58-9	35	61394-92-1	273–274 dec	270–272 dec[2]

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