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Synthesis of 3-Hydroxythienopyrimidine-2,4(1*H*,3*H*)-diones from 2,3- and 3,4-Thiophenedicarboxylic Acids

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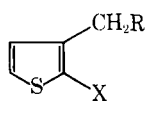
The modified Lossen rearrangement of sodium 2,3-thiophenedicarbohydroxamate with benzenesulfonyl chloride furnished a mixture of 3-benzenesulfonyloxythieno[2,3-*d* and 3,2-*d*]pyrimidine-2,4(1*H*,3*H*)-diones (54%, in the ratio of 1:3). The structure of these isomers was established by means of their proton magnetic resonance spectra. A similar rearrangement of sodium 3,4-thiophenedicarbohydroxamate produced 3-benzensulfonyloxythieno[3,4-*d*]pyrimidine-2,4(1*H*,3*H*)-dione in 67% yield. Each of these sulfonates was hydrolyzed to the corresponding *N*-hydroxy compound.

A number of thienopyrimidines have been reported during the past six years.[1] The majority of these syntheses commenced with vicinal 2- (or 3-) amino-3- (or 2-) thenoic acid derivatives and built up the pyrimidine ring by standard methods. Our approach utilized the partial Lossen degradation of one of the carboxylic acid groups from vicinal thiophenedicarboxylic acids to arrive at the title compounds.

2,3- and 3,4-Thiophenedicarboxylic Acids. The literature preparations for these acids, particularly that for the 2,3 isomer, were unsatisfactory, and reliable large-scale syntheses were developed. Friedel–Crafts acylation of 3-methylthiophene[2] furnished predominantly 2-acetyl-3-methylthiophene (**1**, R = H, X = $COCH_3$; 75%) which was separated from the accompanying 2-acetyl-4-methylthiophene by column (Al_2O_3) or gas chromatography. However, this ideal precursor was oxidized to **2** in poor yield, the major product being 3-methyl-2-thenoic acid.[2,3] Although



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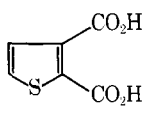
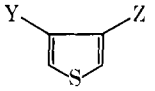


2

2-thenoic acid derivatives have been made with a functionalized 3-methyl substituent (*e.g.*, **1**, R = Br, X = CO_2Et), their preparations were tedious and subsequent oxidation to **2** was not assured.[5]

An attractive route for the synthesis of **2** appeared feasible from 3-thenyl ethers. It was observed that functionalized 3-thenyl derivatives [*e.g.*, **1**, R = OCH_3 or $N(CH_3)_2$, X = H] were lithiated exclusively at the 2 position. Subsequent exposure of these lithio intermediates to electrophilic substrates, such as D_2O, DMF, C_6H_5CN, or $(C_6H_5)_2CO$, furnished 2,3-disubstituted thiophenes in excellent yields.[6,7] Thus, 3-thenyl methyl ether was lithiated and carbonated and furnished 3-methoxymethyl-2-thenoic acid (**1**, R = OCH_3, X = CO_2H). Permanganate oxidation of this acid completed the sequence to produce **2** in 86% yield.

Another synthesis of **2** was based on 2,3-dilithiothiophene.[8] Lithiation of 2,3-dibromothiophene[9] followed by carbonation gave **2** and 3-bromo-2-thenoic acid in 37 and 38% yields, respectively. A similar transformation converted 3,4-dibromothiophene (**3**) into the dicarboxylic acid (**4**). Sicé[4] had reacted 3,4-diiodothiophene with butyllithium and carbonated acid to obtain **4** in 74% yield. We planned to use the more accessible 3,4-dibromothiophene (**3**). Although two methods were explored for the synthesis of **3**,

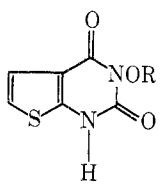


3, Y = Z = Br
4, Y = Z = CO_2H
5, Y = Br; Z = CO_2H

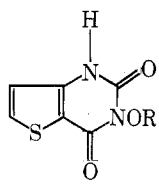
the first one of these was preferred, although it involved larger quantities of bromine. Thiophene was brominated in carbon tetrachloride to tetrabromothiophene, which was reduced with zinc and acetic acid to **3** in good overall yields.[10] The alternate method started with bromination of thiophene in benzene which furnished 2,5-dibromothiophene in excellent yield (80%).[11] However, the rearrangement of the 2,5 isomer to **3** by sodamide proceeded in considerably lower yield (42%) than had been reported (73%).[12] Lithiation of **3**, followed by Dry Ice produced **4** (40%) and

3-bromo-4-thenoic acid (**5**) (17%). These methods of converting **3** into **4** do not greatly improve on (yieldwise) a method published while this work was in progress. That procedure converted **3** first into the bis-nitrile, which was then hydrolyzed to **4** in 59% yield.[13a]

Rearrangement. Conversion of **2** into the ethyl ester and then to the corresponding bis-hydroxamate was accomplished in the usual way.[14] Treatment of this hydroxamate with benzenesulfonyl chloride under conditions developed in this laboratory resulted in a mixture of **6** and **8** in the ratio of 1:3. Separation of these two isomers was achieved when it was found that **8** precipitated first at pH 8, while the isomer **6** was recovered at a lower pH. Mild hydrolysis of **6** or **8** provided the isomeric *N*-hydroxy compounds **7** and **9**, respectively.



6, R = $C_6H_5SO_2$
7, R = H

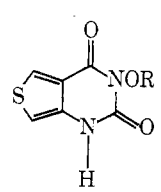


8, R = $C_6H_5SO_2$
9, R = H

To prove the structure of **7** and **9**, we resorted to pmr spectral analysis. There were extensive pmr data available on both the thieno[3,2-*d*]- and -[2,3-*d*]pyrimidine systems. The close resemblance of the chemical shift and coupling constants of the two thiophene ring protons in **7** and **9** with those found in related ring systems permitted structure assignments.[1c,d,f,i]

In DMSO-d_6, a number of thieno[3,2-*d*]pyrimidine-4(3*H*)-ones showed resonances of the two thiophene ring protons as two doublets consistently between δ 8.23–8.26 for H-6 and 7.43–7.50 for H-7 for that ring system.[1c] Isomers in the [2,3-*d*] system presented the thiophene ring proton resonances (in DMSO-d_6) further upfield either as an AB pattern between δ 7.40 and 7.55 or as a singlet in that region. When an AB pattern was observed, these authors could not assign the chemical shifts of H-5 and H-6 in the thieno[2,3-*d*]pyrimidine-4(3*H*)-one system. As members of the thieno[2,3,-*d*]pyrimidine system, **6** and **7** both showed singlets for H-5 and H-6 around δ 7.15 in DMSO-d_6. On the other hand, the proton magnetic resonances spectra clearly revealed two doublets assignable to the thiophene ring protons: H-6 and H-7 at δ 8.20 and 6.95, 8.05 and 6.94 for **8** and **9**, respectively. The coupling constant, $J_{6,7}$ = 5.2 Hz, was of similar magnitude as had been reported for the [3,2-*d*] system.[1c] It was found that for the [2,3-*d*] system, coupling constants were usually a little larger (J = 5.6–5.9 Hz). Therefore, on the basis of the chemical shift data, **8** and **9** were assigned structures in the thieno[3,2-*d*]pyrimidine system, while **6** and **7** belong to the isomeric [2,3-*d*] system.[1c]

In a similar series of reactions, 3,4-thiophenedicarboxylic acid was converted into the thieno[3,4-*d*]pyrimidine derivatives **10** and **11**.



10, R = $C_6H_5SO_2$
11, R = H

There was no problem in proving the structure of **10** or **11**. The aromatic nature of these compounds is attested to by the chemical shift of the ring protons. It is reasonable to assign the furthest downfield proton δ 8.40 to the thiophene ring proton flanked by the C=O.[1c] Furthermore, both **10** and **11** showed a coupling constant expected for "meta" type of coupling through sulfur, J = 3.2 Hz. This coupling resembles that reported for a number of unsymmetrical 3,4-disubstituted thiophenes[13b] and a number of thieno[3,4-*d*]pyrimidines.[1k]

Experimental Section

All melting points are uncorrected and were determined in capillary tubes on a Thomas Hoover Unimelt up to 300° and over 300° on a Mel-Temp melting point apparatus. Nitrogen analyses were determined by means of a Coleman Nitrogen Analyzer, Model D-29, and those for other elements by Micro-Tech Labs, Skokie, Ill. Ir spectra were obtained on a Perkin-Elmer 337 recording infrared spectrophotometer. Pmr spectra were recorded by means of a Varian A-60 spectrometer in ppm (δ), downfield from $(CH_3)_4Si$. Mass spectra were obtained by R. Dvorak at 70 eV using a Hitachi Perkin-Elmer RMU-6D single focusing mass spectrometer and substantiated the proposed structures. Thin layer chromatographs (tlc) were developed over 15 min on 7.2-cm slides coated with silica gel and a fluorescent indicator (Eastman Chromagram Sheet 6060) using ethyl acetate. Spots were detected by uv light.

Methyl 3-Thenyl Ether. Details for the preparation of this ether have not been reported.[15] The reaction of thenyl bromide[16] and sodium methoxide in methanol gave considerably lower yield due to the azeotropic distillation of the product with methanol. The following procedure gave reproducible results.

Sodium (18.4 g, 0.8 g-atom) was dissolved in absolute methanol (150 ml) and the solution evaporated to dryness, *in vacuo*. The last traces of methanol were removed by azeotropic distillation with benzene (twice with 200 ml). Residual sodium methoxide was suspended in anhydrous ether (250 ml), and thenyl bromide[16] (129 g, 0.73 mol) was added with occasional swirling (20 min). The vigorous exothermic reaction was controlled by immersing the reaction flask in an ice–water bath so as to maintain gentle reflux. After the exothermic reaction ceased, the mixture was boiled for 2 hr. The mixture was filtered and after removal of the ether, the product (82 g, 89%) boiled at 78° (10 Torr) [lit.[15] bp 65–67° (17 Torr)]: pmr ($CDCl_3$) δ 3.34 (s, CH_3), 4.40 (s, CH_2), 6.95–7.40 (m, thiophene protons).

3-Methoxymethyl-2-thenoic Acid. To a suspension of freshly prepared ethereal solution of butyllithium (0.4 mol)[17] in a 300-ml pressure bottle was added cautiously methyl 3-thenyl ether (38.4 g, 0.3 mol) in a stream of nitrogen. The flask was then filled up with anhydrous ether, stoppered, and kept at 25° for 10 hr. The mixture was poured slowly into a slurry of Dry Ice in anhydrous ether under a blanket of nitrogen. The mixture was permitted to stand at 25° for 3 hr and was then mixed with water (375 ml). The ether layer was separated and was washed with water (2 × 50 ml). The combined aqueous phase was extracted with ether (2 × 50 ml) and then heated on the steam bath to expel dissolved ether. After cooling to 25°, the solution was acidified with concentrated HCl to pH < 2. After 3 hr at 5°, the acid (46 g, 89%) was collected and washed with water and dried; mp 115–120°. The product was recrystallized from water (charcoal): mp 126–127°; ir (Nujol) 3300–2200 (broad, COOH), 1675 (CO) cm^{-1}; pmr ($CDCl_3$) δ 3.46 (s, CH_3), 4.86 (s, CH_2), 7.31, 7.64 (AB pattern, H-4, H-5, $J_{4,5}$ = 5.2 Hz), 10.8 (broad, s, exchangeable with D_2O).

Anal. Calcd for $C_7H_8O_3S$: C, 48.84; H, 4.68. Found: C, 48.73; H, 4.59.

2,3-Thiophenedicarboxylic Acid. Method A. To a stirred solution of 3-methoxymethyl-2-thenoic acid (16 g, 0.1 mol) in 10% NaOH solution (500 ml) was added potassium permanganate (30 g, 0.2 mol). After stirring at 50° for 1 hr, manganese dioxide was filtered off, and the filter cake was washed with boiling water (2 × 50 ml). The combined filtrate was acidified and cooled to 5° to afford **2** (12 g, 75%), mp 264°; recrystallization from water raised the melting point to 270° (lit.[3,18] mp 270°, 271–272°,[19] 277–278°).[4] An additional batch (1.7 g) was obtained by evaporating the mother liquor to half-volume (total yield, 86%). The acid was identical to a sample prepared by a literature method.[3]

Method B. To a stirred suspension of ethereal butyllithium (0.4 mol) at −70° was added 2,3-dibromothiophene[9] (26.3 g, 0.1 mol) over 5 min. The mixture was stirred at −70° for 0.5 hr and then

poured slowly into a slurry of Dry Ice in anhydrous ether. After 3 hr, water (200 ml) was added to the ethereal suspension. The aqueous layer was separated and the ether layer was extracted several times with water (3 × 200 ml). The combined aqueous phase was washed with ether (2 × 100 ml) and then warmed to remove dissolved ether. After cooling to 25°, a small amount of a solid was filtered off. The filtrate was acidified to pH 1 with concentrated HCl and immersed in an ice–water bath. Several hours later the solid was filtered and recrystallized from water (charcoal) to give 3-bromo-2-thenoic acid (7.8 g, 38%), mp 190–193° (lit.[20] mp 195–197°); its ir spectrum was identical with the one reported in the literature.[20]

The combined mother liquors were concentrated *in vacuo*, to about 350 ml. After several hours, at 5°, **2** was isolated (6.9 g, 37%), which was identical with the sample prepared in method A. Attempts to increase the yield of **2** by increasing the reaction time or the ratio of butyllithium to 2,3-dibromothiophene were unsuccessful.

Esterification of **2** was achieved by refluxing the *acid* (4.9 g) with ethanol (200 ml), toluene (100 ml), and concentrated sulfuric acid (1 ml) (Dean–Stark apparatus attached). During the first 5 hr, 50 ml were withdrawn every hour and replenished by an equal volume of the ethanol–toluene mixture. The solution was then concentrated *in vacuo*, to 10 ml and neutralized with cold saturated $NaHCO_3$, and the organic phase was extracted into benzene (4 × 30 ml). The extract was dried ($MgSO_4$) and distilled to yield the ester (5.6 g, 86%): bp 109° (0.015 Torr); ir (neat) 3120, 3000, 1720 cm^{-1}; pmr (CCl_4) δ 1.34 (t, CH_3's), 4.34 (q, CH_2's), 7.24, 7.45 (AB pattern, H-4, H-5, $J_{4,5}$ = 5.2 Hz).

Anal. Calcd for $C_{10}H_{12}O_4S$: C, 52.63; H, 5.30. Found: C, 52.67; H, 5.30.

3,4-Thiophenedicarboxylic Acid. A sample of 3,4-dibromothiophene[10,12] (30.5 g, 0.126 mol) was lithiated and then carbonated as described in method B for **2**. The aqueous extract was acidified and the first precipitate proved to be 4-bromo-3-thenoic acid (4.5 g, 17%) which was recrystallized from water, mp 153–156° (lit.[21] mp 157–159°). Its ir spectrum was identical to the published one.

The aqueous mother liquors were concentrated to 200 ml *in vacuo*, and the hot solution was charcoaled to give **4** (8.5 g, 40%); mp 225–229° (lit.[22] mp 223–225°, 230–231°,[4] 225–226°[13a]).

Esterification of **4** (8.5 g) was achieved as described under method B above, producing the ethyl ester (6.8 g, 77%): bp 136–142° (1 Torr) [lit.[23] bp 156–157° (8 Torr)]; ir (neat) 3150, 3020, 1720 (CO) cm^{-1}; pmr ($CDCl_3$) δ 1.32 (t, CH_3's), 4.33 (q, CH_2's), 7.81 (s, thiophene protons).

Sodium 2,3-Thiophenedicarbohydroxamate. An ethanolic solution of hydroxylamine was prepared by stirring a suspension of finely powdered dry hydroxylammonium chloride in absolute ethanol (14.6 g in 400 ml) with a solution of sodium ethoxide in absolute ethanol (4.8 g in 200 ml) at temperatures below 25°, until neutral to wet litmus. Sodium chloride was filtered off and ethyl 2,3-thiophenedicarboxylate (24 g, see method B, above) was added in one portion to the alcoholic hydroxylamine solution, followed by more sodium ethoxide solution (4.8 g in 200 ml of absolute ethanol) after the mixture had been stirred for 0.5 hr. The yellow suspension was then stirred for 18 hr. The mixture was cooled to 5° and the hydroxamate (17.6 g) was filtered off, washed with small amounts of absolute ethanol and dry ether, and dried *in vacuo* at 25° (over sulfuric acid) for 4 hr. It was used immediately without further purification.

3-Benzenesulfonyloxythieno[2,3-*d* and 3,2-*d*]pyrimidine-2,4(1*H*,3*H*)-diones, 6 and 8, Respectively. To a stirred suspension of the finely powdered hydroxamate (19 g) prepared as described above, in tetrahydrofuran (650 ml) was added dropwise a solution of benzenesulfonyl chloride (32 g, 0.18 mol) in tetrahydrofuran (150 ml) over 1 hr. The temperature was maintained between 10 and 13° by submersing the flask occasionally in an ice–water bath. After 0.5 hr, sodium acetate trihydrate (18 g) was added and stirring continued for 8 hr at 25°. The solids were filtered and washed several times with tetrahydrofuran. The tetrahydrofuran filtrates were concentrated *in vacuo*, to produce an oily residue.

This residue was partitioned between water (800 ml) and petroleum ether (bp 30–60°, 900 ml) and the mixture stirred vigorously until the oil solidified. The solid was filtered and washed with water and ether. It weighed 15.8 g (54% yield based on original ester) and proved to be a mixture of **6** and **8** in the ratio of 1:3 (pmr).

When the following procedure was used, reproducible results were obtained in the separation of the isomers. It was critical to adhere closely to the pH VALUES USED HERE/[24] It was also found that adjustment of the pH of the original alkaline solution (~10) to pH 8 relatively quickly gave the cleanest separation. Fractions were examined by tlc to ensure their purity.

The crude mixture of **6** and **8** (2 g) was dissolved in 80 ml of dilute ammonium hydroxide solution (1:7, aqueous solution) at 5°. A very small amount of an insoluble substance was filtered off. To the filtrate at 5° was added of 10% aqueous acetic acid (~80 ml) until pH 8 was reached. This neutralization was accomplished quickly (~2 min). After several minutes at 5°, **8** (1 g) precipitated. Its purity was checked by tlc and, if contaminated by **6**, this operation had to be repeated. Recrystallization of **8** from absolute ethanol (charcoal) furnished colorless crystals (0.9 g): mp 222–224° dec; tlc R_f 0.48; ir (Nujol) 3190 (NH), 1755, 1720, 1695 (CO) cm^{-1}; pmr (DMSO-d_6) δ 6.95 (d, H-7), 7.40–8.08 (5, m, benzene ring protons), 8.20 (d, H-6, $J_{6,7}$ = 5.2 Hz).

Anal. Calcd for $C_{12}H_8N_2O_5S_2$: C, 44.46; H, 2.49; N, 8.64. Found: C, 44.30; H, 2.39; N, 8.87.

The filtrate from **8**, above, was acidified further to pH 5 with 10% aqueous acetic acid to give **6** (0.5 g). This sulfonate was recrystallized from methanol (charcoal) to afford colorless needles (0.4 g): mp 250–252° dec; tlc R_f 0.24; ir (Nujol) 3200 (NH), 1745, 1690 (CO) cm^{-1}; pmr (DMSO-d_6) δ 7.15 (2, s) (thiophene protons), 7.45–8.12 (5, m, benzene ring protons).

Anal. Calcd for $C_{12}H_8N_2O_5S_2$: C, 44.46; H, 2.49; N, 8.64. Found: C, 44.31; H, 2.44; N, 8.86.

3-Hydroxythieno[3,2-*d*]pyrimidine-2,4(1*H*,3*H*)-dione. A solution of **8** (1.9 g) in 20 ml of 10% sodium hydroxide solution was heated at 95° for 10 min. After dilution with water (10 ml) the solution was acidified with concentrated hydrochloric acid to pH 5. After 10 min at 5°, **9** (1.0 g, 93%) was collected. It was recrystallized from water (with 80% recovery): mp 305–308° dec; ir (Nujol) 3145 (broad, NH and OH), 1700, 1650 (CO) cm^{-1}; pmr (DMSO-d_6) δ 6.94 (d, H-7), 8.05 (d, H-6, $J_{6,7}$ = 5.2 Hz), 11.32 (broad, NH and OH); uv max (ethanol) 207 nm (log ϵ 4.19), 257 (3.96), 289 (3.75).

Anal. Calcd for $C_6H_4N_2O_3S$: C, 39.14; H, 2.19; N, 15.22. Found: C, 39.01; H, 2.04; N, 15.19.

3-Hydroxythieno[2,3-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (7). The hydrolysis of **6** (0.5 g) was carried out as described for **8** to yield **7** (0.3 g, 100%): mp 275–277° dec; ir (Nujol) 3260, 3120, (NH and OH), 1700, 1670, 1630 (CO) cm^{-1}; pmr (DMSO-d_6) δ 7.16 (s, H-5 and H-6); uv max (ethanol) nm (log ϵ) 205 sh (4.08), 224 (4.41), 250 sh (3.76), 275 sh (3.53).

Anal. Calcd for $C_6H_4N_2O_3S$: C, 39.14; H, 2.19; N, 15.22. Found: C, 39.06; H, 2.12; N, 15.31.

3-Benzenesulfonyloxythieno[3,4-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (10). The 3,4-bishydroxamate (6.1 g, prepared as for the 2,3 isomer, above) reacted with benzenesulfonyl chloride (10.6 g) as described for the synthesis of **6** and **8** to furnish **10** (6.5 g, 67%, based on the ester used). The sulfonate was recrystallized from ethanol (charcoal): mp 232–233° dec; tlc R_f 0.52; ir (Nujol) 3250 (NH), 1750, 1710 (CO) cm^{-1}; pmr (DMSO-d_6) δ 6.95 (d, H-7), 7.48–8.20 (5, m, benzene ring protons), 8.54 (d, H-5, $J_{5,7}$ = 3.2 Hz).

Anal. Calcd for $C_{12}H_8N_2O_5S_2$: C, 44.46; H, 2.49; N, 8.64. Found: C, 44.21; H, 2.44; N, 8.65.

3-Hydroxythieno[3,4-*d*]pyrimidine-2,4(1*H*,3*H*)-dione (11). The hydrolysis of **10** (1.6 g) was carried out as described for **8**. After adjusting the pH of the resultant solution to 1, **11** was collected. The product was recrystallized from water to brown needles (0.75 g, 83%); mp 306° dec; ir (Nujol) 3130 (NH and OH), 1720, 1700, 1665 (CO) cm^{-1}, pmr (DMSO-d_6) δ 6.89 (d, H-7), 8.40 (d, H-5, $J_{5,7}$ = 3.2 Hz), 10.40, 11.32 (broad, NH and OH); uv max (ethanol) 211 nm (log ϵ 4.51), 259 (3.96), 302 (3.69).

Anal. Calcd for $C_6H_4N_2O_3S \cdot 0.25\ H_2O$: C, 38.21; H, 2.40; N, 14.85. Found: C, 38.46; H, 2.27; N, 14.85.

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Registry No.—**1** (R = OCH_3, X = H), 53229-44-0; **1** (R = Br, X = H), 34846-44-1; **1** (R = OCH_3, X = CO_2H, 53229-45-1; **2**, 1451-95-2; **2** diethyl ester, 53229-46-2; **3**, 3141-26-2; **4**, 4282-29-5; **4** diethyl ester, 53229-47-3; **5**, 16694-17-0; **6**, 53229-48-4; **7**, 53229-49-5; **8**, 53229-50-8; **9**, 53229-51-9; **10**, 53229-52-0; **11**, 53229-53-1; sodium methoxide, 12441-4; 2,3-dibromothiophene, 3140-93-0; 3-bromo-2-thenoic acid, 7311-64-0; sodium 2,3-thiophenecarbohy-

droxamate, 53229-54-2; hydroxylamine, 7803-49-8; benzenesulfonyl chloride, 98-09-9; sodium 3,4-thiophenecarbohydroxamate, 53229-55-3.

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Photochromic Aziridines. On the Photochemical Valence Tautomerization and Cycloaddition Reactions of a Substituted Indano[1,2-*b*]aziridine[1]

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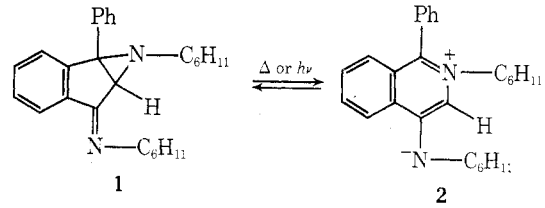
Heat or ultraviolet light partially converts 1-cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine to an aromatic valence tautomer, the red isoquinolinium imine. The red color associated with the 1,3 dipole is rapidly discharged upon exposure to visible light, oxygen, or acetylenic dipolarophiles. The regiochemistry of the initial 1,3-dipolar adducts obtained with acetylenic dipolarophiles is discussed in light of some earlier results published in the literature. The initial cycloadducts were found to undergo a novel rearrangement to a benzazocine derivative whose structure was determined by X-ray crystallography. The details of each reaction are described and evidence is presented demonstrating the existence of transient intermediates in some of the irradiation experiments.

During the past decade, systematic studies of molecules or complexes which undergo reversible photoinduced color changes have contributed greatly to the basic understanding of the factors which govern the behavior of a photochromic system.[2,3] Although these systems have been the subject of valuable and penetrating mechanistic investigations, there are still many gaps in our understanding of this phenomenon.[4] Irradiation of solutions of acyclic[5,6] or bicyclic[7-9] aziridines with ultraviolet light is known to produce red colors which fade spontaneously in the dark. The colored species produced in these photoinduced reversible reactions were assigned as 1,3 dipoles (azomethine ylides).[9] Reactions involving the thermal and photochemical cleavage of aziridines to azomethine ylides and their subsequent 1,3-dipolar additions to reactive carbon–carbon multiple bonds have been studied by several groups of investigators.[10-14] Huisgen and coworkers have firmly established that the thermal ring cleavage of aziridines involves stereospecific, conrotatory ring opening. A disrotatory course has been found to occur from the excited state. Lown and Matsumoto[15] have recently pointed out that when the aziridine ring is constrained in a bicyclic structure of medium size, disrotatory photochemical ring opening is allowed, but thermal conrotatory ring opening is not permitted by the geometry of the system.[16,17] These workers reported, however, that 1-cyclohexyl-6-(cyclohexylimino)-1a-phenylindano[1,2-*b*]aziridine (**1**) undergoes thermal conversion to the tautomeric isoquinolinium imine (**2**), despite the geometrical restrictions imposed by the molecule. The driving



1 2

force for the thermally disallowed valence tautomerization in this system was attributed to the relief of ring strain in **1** and to the gain in resonance energy in **2**. Our interest in 1,3-dipolar cycloaddition reactions also led us to study independently the thermal and photochemical behavior of the phenylindano[1,2-*b*]aziridine ring system.[18] The present paper reports on the photochemical valence tautomerization and cycloaddition reactions of the indano[1,2-*b*]aziridine ring, as well as some of the interesting ground-state chemistry encountered with this system which differs, in