ArH), 7.48–7.22 (m, 2, ArH), 5.00 (m, 1, HOC**H**), 4.00 (d, 2, *J* = 17 Hz, CH_2S), 3.50 (d, 2, *J* = 17 Hz, CH_2S), 3.03 (m, 2, $SC\mathbf{H}_2CHOH$), and 2.77 ppm (m, 1, CHO**H**, disappeared on exchange with D_2O).

Anal. Calcd for $C_{11}H_{10}OS_2$: C, 59.42; H, 4.53; S, 28.85. Found: C, 59.35; H, 4.71; S, 28.58.

Thianaphtheno[2,3-*c*]thiapyrylium Perchlorate (4).—A refluxing solution of 0.88 g (0.004 mol) of **21** in 15 ml of acetic acid was treated with a solution of 1.37 g (0.004 mol) of trityl perchlorate in 15 ml of nitromethane, and the product was isolated as in the preparation of **1**. The crude product, yield 1.10 g (91%), was recrystallized several times from glacial acetic acid to give the pure thiapyrylium salt (**4**): mp 207.0–208.0°; visible and uv max (1% perchloric acid in acetonitrile) 292 mμ (log ε 4.24), 354 (4.18), and 433 (3.52); nmr (CF_3CO_2D) δ 10.40 (m, 1, *J* = 2 Hz, H-1), 9.55 (2 s, 2, H-3 and H-4), 8.77 (m, 1), and 8.32–7.68 ppm (m, 3, H-6–9).

Anal. Calcd for $C_{11}H_7ClO_4S_2$: C, 43.64; H, 2.33; S, 21.18. Found: C, 43.82; H, 2.37; S, 21.10.

Registry No.—**1**, 22482-76-4; **2**, 22482-77-5; **3a**, 22482-78-6; **3b**, 22482-79-7; **4**, 22482-80-0; **6**, 22316-07-0; **7**, 22314-71-2; **8**, 22294-31-1; **10**, 22482-83-3; **11**, 22482-84-4; **12**, 22482-85-5; **13**, 22482-86-6; **15a**, 22482-87-7; **15b**, 22482-88-8; **16a**, 22482-89-9; **16b**, 22482-90-2; **17a**, 22482-91-3; *cis*-**17b**, 22528-36-5; *trans*-**17b**, 22486-17-5; **19**, 22482-92-4; **20**, 22482-93-5; **21**, 22482-94-6; thieno[3,2-*b*]thiapyrylium perchlorate, 22482-95-7; thieno[2,3-*b*]thiapyrylium perchlorate, 22482-96-8; thieno[3,2-*c*]thiapyrylium perchlorate, 22431-16-9; thieno[2,3-*c*]thiapyrylium perchlorate, 22482-98-0.

Notes

Dithia Aromatic Systems. II. Thieno[3,2-*c*]- and Thieno[2,3-*c*]thiapyrylium Perchlorates[1]

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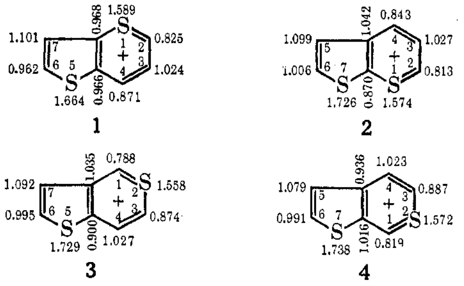
Received July 8, 1969

For reasons cited more explicitly in a companion article,[3] we became interested in the isomeric thienothiapyrylium cations (**1**–**4**) as representatives of a new class of dithia aromatic systems having 10 π electrons. While this work was in progress, the first examples of this class of compounds, thieno[3,2-*b*]- and thieno[2,3-*b*]thiapyrylium perchlorates (**1** and **2**, respectively), were reported by Degani and coworkers,[4] who made a quantitative study of the hydrolysis equilibria (pK_R^+) of these two cations and interpreted their nmr spectra in the light of electron densities calculated from Hückel molecular orbital (HMO) theory. More recently, syntheses of the 2,4-dimethyl derivatives of **1** and **2** have also been revealed in a preliminary communication, along with charge densities and bond orders for all four cations (**1**–**4**) and electronic transition frequencies predicted (for ions **1**–**3**) from semiempirical SCF calculations.[5] We have already presented syntheses of thianaphtheno[3,2-*c*]- and -[2,3-*c*]thiapyrylium perchlorates[3] and now wish to complete this picture with a description of some salts containing the isomeric thieno[*c*]thiapyrylium nuclei (**3** and **4**), which were readily obtained as shown in the accompanying formulas (**5** → **6** → **3** and **7** → **8** → **4**).

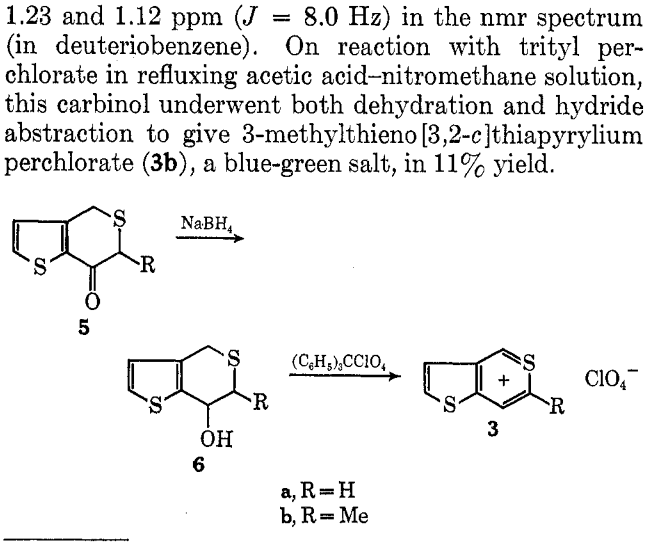
CHART I

STRUCTURES AND ELECTRON DENSITIES OF THE THIENOTHIAPYRYLIUM CATIONS[a]



[a] All isolated as the perchlorates.

Reduction of 3-methyl-3,4-dihydro-1H-thieno[3,2-*c*]thiapyran-4-one (**5b**)[6] with sodium borohydride in refluxing isopropyl alcohol gave the corresponding carbinol (**6b**) (84%), which had a broad melting range (64–75°) and was clearly a mixture of *cis* and *trans* isomers, as shown by the appearance of the methyl resonance as two well-defined doublets centered at δ 1.23 and 1.12 ppm (*J* = 8.0 Hz) in the nmr spectrum (in deuteriobenzene). On reaction with trityl perchlorate in refluxing acetic acid–nitromethane solution, this carbinol underwent both dehydration and hydride abstraction to give 3-methylthieno[3,2-*c*]thiapyrylium perchlorate (**3b**), a blue-green salt, in 11% yield.



a, R = H
b, R = Me

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(1) Based on the Ph.D. Dissertation of C. R. Hamel, Lehigh University, 1969. Supported in part by National Science Foundation Grant GP-8597.

(2) National Science Foundation Trainee, 1967–1969.

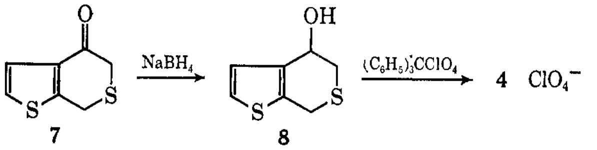
(3) Part I: T. E. Young and C. R. Hamel, *J. Org. Chem.*, **35**, 816 (1970).

(4) I. Degani, R. Fochi, and G. Spunta, *Ann. Chim.* (Rome), **58**, 263 (1968).

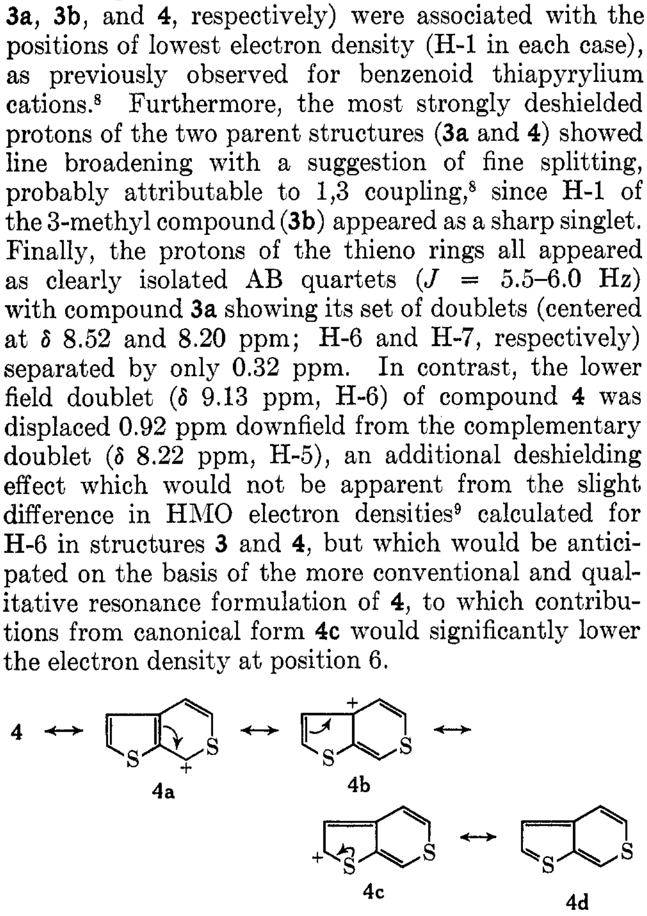
(5) J. Fabian and H. Hartmann, *Tetrahedron Lett.*, 239 (1969).

(6) P. Cagniant and D. Cagniant, *Bull. Soc. Chim. Fr.*, 2597 (1967).

In exactly analogous fashion, 3,4-dihydro-1H-thieno[3,2-*c*]thiapyran-4-one (**5a**)[6] and the isomeric [2,3-*c*]-fused ketone **7**[7] were converted *via* the carbinols **6a** and **8** into the parent thieno[3,2-*c*]- and thieno[2,3-*c*]thiapyrylium perchlorates **3a** and **4**, respectively.



These salts (**3a**, **3b**, and **4**) all dissolved in deuteriotrifluoroacetic acid to give stable solutions that exhibited well-defined nmr spectra (reproducible even after a month of standing) in which the most strongly deshielded protons (δ 10.60, 10.33, and 10.67 ppm for **3a**, **3b**, and **4**, respectively) were associated with the positions of lowest electron density (H-1 in each case), as previously observed for benzenoid thiapyrylium cations.[8] Furthermore, the most strongly deshielded protons of the two parent structures (**3a** and **4**) showed line broadening with a suggestion of fine splitting, probably attributable to 1,3 coupling,[8] since H-1 of the 3-methyl compound (**3b**) appeared as a sharp singlet. Finally, the protons of the thieno rings all appeared as clearly isolated AB quartets (J = 5.5–6.0 Hz) with compound **3a** showing its set of doublets (centered at δ 8.52 and 8.20 ppm; H-6 and H-7, respectively) separated by only 0.32 ppm. In contrast, the lower field doublet (δ 9.13 ppm, H-6) of compound **4** was displaced 0.92 ppm downfield from the complementary doublet (δ 8.22 ppm, H-5), an additional deshielding effect which would not be apparent from the slight difference in HMO electron densities[9] calculated for H-6 in structures **3** and **4**, but which would be anticipated on the basis of the more conventional and qualitative resonance formulation of **4**, to which contributions from canonical form **4c** would significantly lower the electron density at position 6.



The ultraviolet spectrum of **4** (in MeCN-HClO$_4$) was closely comparable with that of **3a**, except that the longest wavelength absorption of **4** (381 mμ) was more intense and bathochromically shifted from that of **3a** (357 mμ). In turn, the spectrum of **3a**, as well as its methyl derivative (**3b**), was very similar to that of thieno[2,3-*b*]thiapyrylium perchlorate (**2**)[4,10] showing the overall similarity of the electronic structures of these isomeric thienothiapyrylium cations.

Experimental Section[11]

3,4-Dihydro-1H-thieno[3,2-*c*]thiapyran-4-ol (6a).—To a solution of 3.40 g (0.020 mol) of 3,4-dihydro-1H-thieno[3,2-*c*]thiapyran-4-one (**5a**)[6] dissolved in 250 ml of warm isopropyl alcohol was added 0.76 g (0.020 mol) of finely powdered sodium borohydride. The mixture was stirred magnetically at reflux overnight. The reaction mixture was cooled and then poured into 250 ml of cold water. The aqueous mixture was extracted with three 100-ml portions of benzene and the combined extracts were washed with 100 ml of water, dried (MgSO$_4$), filtered, and evaporated on a rotary evaporator to leave an oil. Distillation at 107–109° (0.10 mm) yielded 3.00 g (87%) of 3,4-dihydro-1H-thieno[3,2-*c*]thiapyran-4-ol (**6a**): ir (neat) 3600–3120 (hydrogen-bonded OH), 3090 m (Ar-H), 2900 (methylene), and other strong bands at 1420, 1400, 1378, 1192, 1032, 990, 710, and 680 cm^{-1}; nmr (C$_6$D$_6$) δ 6.92 (d, 1, J = 5 Hz, H-6), 6.45 (d, 1, J = 5 Hz, H-7), 4.72 (br s, 1, HO**CH**), 3.80 (m, 1, **HO**CH), 3.32 (s, 2, CH$_2$S), and 2.65 ppm (d, 2, J = 5 Hz, S**CH$_2$**CHOH).

Anal. Calcd for C$_7$H$_8$OS$_2$: C, 48.80; H, 4.68; S, 37.23. Found: C, 48.93; H, 4.67; S, 37.42.

3-Methyl-3,4-dihydro-1H-thieno[3,2-*c*]thiapyran-4-ol (6b).—By an analogous procedure, 2.40 g (0.013 mol) of **5b**[6] was reduced with 0.49 g (0.013 mol) of sodium borohydride to yield 2.05 g (84%) of **6b**, bp 112° (0.20 mm). Upon standing, the oil solidified to a waxy solid: mp 64–75°; nmr (C$_6$D$_6$) δ 6.82 (d, 1, J = 5.5 Hz, H-6), 6.35 (d, 1, J = 5.5 Hz, H-7), 4.40 (m, 1, HO**CH**), 3.67–2.37 [m, 4, **CH$_2$**S**CH**(Me)CH**OH**], and 1.28–1.07 ppm (m, 3, CH$_3$).

Anal. Calcd for C$_8$H$_{10}$OS$_2$: C, 51.57; H, 5.41; S, 34.43. Found: C, 51.72; H, 5.51; S, 34.17.

3,4-Dihydro-1H-thieno[2,3-*c*]thiapyran-4-ol (8).—This compound was similarly prepared by reduction of 0.90 g (0.0053 mol) of **7**[7] with 0.22 g (0.0053 mol) of sodium borohydride in 100 ml of isopropyl alcohol. The yield of **8** was 0.85 g (94%): bp 118.5–120° (0.28 mm); ir (neat) 3600–3120 (hydrogen-bonded OH), 3080 (weak, Ar-H), 2900 (methylenes), and other strong bands at 1415, 1195, 1030, 915, 875, 715, and 660 cm^{-1}; nmr (C$_6$D$_6$) δ 6.90 (d, 1, J = 5.5 Hz, H-6), 6.80 (d, 1, J = 5.5 Hz, H-5), 4.55 (m, 1, HO**CH**), 3.58 (m, 1 **HO**CH), 3.35 (s, 2, CH$_2$S), and 2.62 ppm (d, 2, J = 4.5 Hz, S**CH$_3$**CHOH).

Anal. Calcd for C$_7$H$_8$OS$_2$: C, 48.80; H, 4.68; S, 37.23. Found: C, 49.10; H, 4.74; S, 37.17.

Thieno[3,2-*c*]thiapyrylium Perchlorate (3a).—To a magnetically stirred, refluxing solution of 3.00 g (0.0174 mol) of **6a** in 45 ml of glacial acetic acid was added 5.96 g (0.0174 mol) of trityl perchlorate in 50 ml of nitromethane during a 2-min period. The solution turned dark red (nearly black) as reflux was continued for 15 min. The reaction mixture was then allowed to cool to room temperature, and the solvents were removed on a rotary evaporator. The resulting oil solidified on dilution to 450 ml with ether. After overnight refrigeration, the crystalline product was collected by filtration and air dried to give 5.50 g of crude material, mp 142–145°, with much prior softening. The product was slurried in 175 ml of boiling glacial acetic acid and a black, insoluble tar was removed by filtration. On being cooled to room temperature, the solution deposited 1.70 g of crystals, which, after two further recrystallizations from glacial acetic acid (Norit), gave 0.90 g (20%) of thieno[3,2-*c*]thiapyrylium perchlorate (**3a**): mp 165–167°; uv max (1% perchloric acid in acetonitrile) 263 mμ (log ε 4.57), 304 (3.53), and 357 (3.44); nmr (CF$_3$COOD) δ 10.60 (m, 1, H-1), 9.43 (m, 2, H-3 and H-4), 8.52 (d, 1, J = 6 Hz, H-6), and 8.20 ppm (d, 1, J = 6 Hz, H-7).

Anal. Calcd for C$_7$H$_5$ClO$_4$S$_2$: C, 33.27; H, 1.99; Cl, 14.03; S, 25.38. Found: C, 33.16; H, 2.06; Cl, 14.20; S, 25.27.

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(7) P. Cagniant, D. Cagniant, and A. Pancrazi, *Bull. Soc. Chim. Fr.*, 1534 (1964).

(8) T. E. Young and C. J. Ohnmacht, *J. Org. Chem.*, **32**, 1558 (1967).

(9) The HMO calculations were carried out as already described[3] using the parameters $\alpha_S = \alpha + 0.9\beta$ and $\beta_{CS} = 0.6\beta$ for both sulfur atoms, in order to be consistent with our previous calculations.[3,8]

(10) This compound (**2**) was also prepared in this laboratory essentially as described by Degani.[4] Our sample (*Anal.* Calcd for C$_7$H$_5$ClO$_4$S$_2$: C, 33.27; H, 1.99; S, 25.38. Found: C, 33.55; H, 1.93; S, 25.14) gave an electronic absorption spectrum (MeCN–HClO$_4$) [262 mμ (log ε 4.47), 333 (3.66), 361 sh (3.36)] essentially identical with that reported in sulfuric acid solution.[4] The nmr spectrum was also comparable; however, our sample had a melting point (255–257° dec) significantly higher than the literature value (142° dec),[4] which appears to be in error (possibly typographical).

(11) Melting points were determined on a Mel-Temp apparatus (Laboratory Devices, Cambridge, Mass.) precalibrated with standards having known corrected melting points. The microanalyses were performed by the late Dr. V. B. Fish of Lehigh University and by Galbraith Microanalytical Laboratories, Knoxville, Tenn. Infrared spectra were determined on a Perkin-Elmer 257 spectrophotometer and the ultraviolet spectra were run on a Beckman DK-2A instrument. Nuclear magnetic resonance spectra were run on a Varian A-60 spectrometer using tetramethylsilane as internal standard, and data are presented in the order δ (multiplicity, number of protons, assignment).

3-Methylthieno[3,2-c]thiapyrylium Perchlorate (3b).—Carbinol **6b** (1.00 g, 0.0054 mol) dissolved in 16 ml of acetic acid reacted analogously with 1.85 g (0.0054 mol) of trityl perchlorate in 16 ml of nitromethane to yield (after a similar work-up) 1.75 g of crude product, mp 135–140°, which, after two recrystallizations from glacial acetic acid (Norite), afforded 0.15 g (11%) of pure 3-methylthieno[3,2-c]thiapyrylium perchlorate (**3b**) as slightly colored (blue-green) plates: mp 156–158°, uv max (1% perchloric acid in acetonitrile) 229 mμ (log ε 4.32), 264 (4.61), 306 (4.60), and 366 (3.52); nmr (CF_3COOD) δ 10.33 (s, 1, H-1), 9.17 (s, 1, H-4), 8.33 (d, 1, J = 5.5 Hz, H-6), 8.07 (d, 1, J = 5.5 Hz, H-7), and 3.23 ppm (s, 3, CH_3).

Anal. Calcd for $C_8H_7ClO_4S_2$: C, 36.02; H, 2.65; Cl, 13.29; S, 24.04. Found: C, 36.16; H, 2.87; Cl, 13.33; S, 23.93.

Thieno[2,3-c]thiapyrylium Perchlorate (4).—By a procedure similar to that for **3a**, 2.45 g (0.014 mol) of carbinol **8** in 50 ml of glacial acetic acid and 4.88 g (0.014 mol) of trityl perchlorate in 50 ml of nitromethane reacted to give 3.30 g (92%) of crude thiapyrylium salt (**4**), mp 175–182°. Three recrystallizations from glacial acetic acid (Norit) afforded 0.80 g (22%) of pure thieno[2,3-c]thiapyrylium perchlorate (**4**): mp 192–194°; uv max (1% perchloric acid in acetonitrile) 225 mμ (log ε 4.25), 262 (4.29), 304 (3.78), and 381 (4.01); nmr (CF_3COOD) δ 10.67 (br, s, 1, H-1), 9.28 (m, 2, H-3 and H-4), 9.13 (d, 1, J = 5.5 Hz, H-6), and 8.22 ppm (d, 1, J = 5.5 Hz, H-5).

Anal. Calcd for $C_7H_5ClO_4S_2$: C, 33.27; H, 1.99; Cl, 14.03; S, 25.38. Found: C, 33.30; H, 2.06; Cl, 14.09; S, 25.11.

Registry No.—**3a**, 22431-16-9; **3b**, 22431-17-0; **4**, 22482-98-0; **6a**, 22431-18-1; *cis*-**6b**, 22433-06-3; *trans*-**6b**, 22433-03-0; **8**, 22431-19-2.

A Novel Synthesis of Dihydro-*p*-dithiins and Dihydro-1,4-dithiepins[1a,b] Involving an Amide Leaving Group

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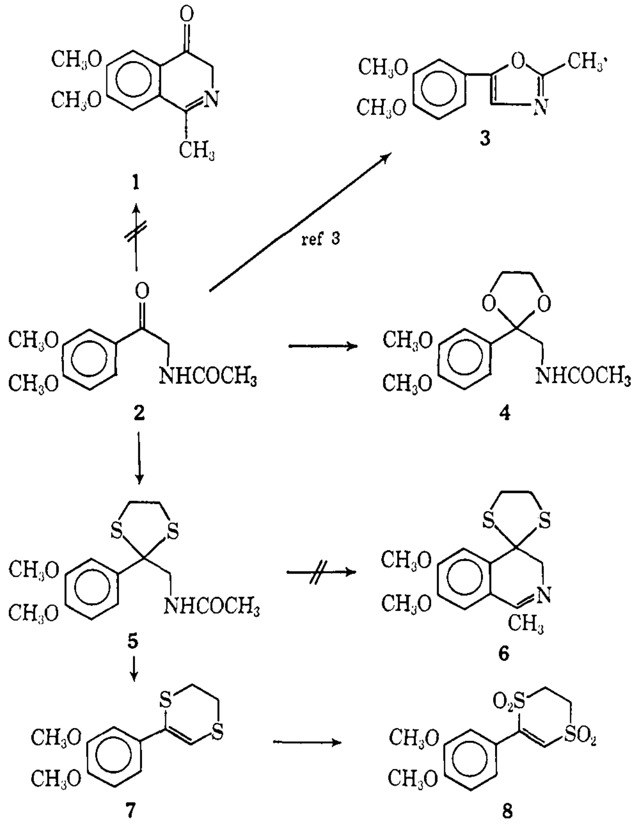
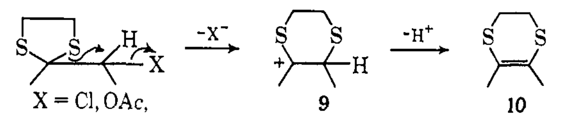
Received July 10, 1969

During an investigation of the structures of certain cactus alkaloids,[2] the synthesis of the 4-oxoisoquinoline derivative **1** from the corresponding ring-opened acetamido ketone **2** was contemplated. Since direct cyclization would be expected[3] to lead to the oxazole **3**, a modified Bischler-Napieralski[4] reaction *via* the ethylene ketal **4** was attempted. The oxazole **3** was the only product isolated, perhaps owing to hydrolysis of **4** to the ketone **2** under the reaction conditions. Cyclization of the hydrolytically more stable thioketal **5** therefore was attempted.

Instead of the desired isoquinoline derivative **6**, however, a sulfur-containing, nitrogen-free product was isolated whose infrared and nmr spectra suggested the structure **7**, 2,3-dihydro-5-(3′,4′-dimethoxyphenyl)-*p*-dithiin. This hypothesis was supported by the elemental analyses of both the compound and its tetroxide derivative **8**.



Several other syntheses of dihydro-*p*-dithiins are known in which an ethylene thioketal is either the starting material or a possible intermediate.[5–8] The common feature of each of these reactions is that the position α to the original carbonyl carbon atom may develop electrophilic character by loss of acetate ion[5] or chloride ion[6,8] or by opening of an epoxide ring.[7] This process in turn could initiate (or occur simultaneously with) the 1,2 migration of sulfur to give a carbonium ion (**9**), which on loss of a proton would lead to the dihydro *p*-dithiin **10**. An analogous mechanism for the formation of **7** from **5** would require loss of the elements of acetamide. Under the conditions of the reaction (P_2O_5 in pyridine), this might occur by elimination of acetonitrile from an intermediate Vilsmeir-Haack adduct (**11**).[9] This hypothesis is supported by



X = Cl, OAc,
OR (epoxide)

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[1] (a) Reported in part at the 23rd Southwest Regional Meeting of the American Chemical Socieity, Little Rock, Ark., Dec 1967. (b) Taken in part from the Ph.D. Dissertation of J. L. Massingill, Jr., Texas Christian University, 1968. (c) To whom inquiries should be addressed.

[2] J. E. Hodgkins, S. D. Brown, and J. L. Massingill, Jr., *Tetrahedron Lett.*, 1321 (1967).

[3] (a) R. Robinson, *J. Chem. Soc.*, 275 (1933); (b) J. S. Buck, *ibid.*, 740 (1933). (c) E. Zalay, *Vegyip. Kut. Intez. Kozlem.*, **4**, 101 (1954); *Chem. Abstr.*, **52**, 16273*b* (1958).

[4] N. Itoh and S. Sugasawa, *Tetrahedron*, **6**, 16 (1959).

[5] L. F. Fieser, C. Yuan, and T. Goto, *J. Amer. Chem. Soc.*, **82**, 1996 (1960).

[6] G. Karmas, *J. Org. Chem.*, **32**, 3147 (1967).

[7] M. Tomoeda, M. Ishizaki, H. Kayashi, S. Kantomo, T. Koga, M. Inuzuka, and T. Furuta, *Tetrahedron*, **21**, 733 (1965).

[8] (a) L. Levine, Abstracts, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, p 24. (b) After this paper was accepted for publication another example of this type of synthesis of dihydro-*p*-dithiins was reported utilizing α-bromo ketones as starting materials: H. Rubenstein and M. Weurthele, *J. Org. Chem.*, **34**, 2762 (1969).

[9] (a) Z. Arnold and A. Holy, *Collect. Czech. Chem. Commun.*, **27**, 2886 (1962). (b) A related, acid-catalyzed, N-alkyl cleavage of amides is the subject of a recent paper by A. G. Mohan and R. T. Conley, *J. Org. Chem.*, **34**, 3259 (1969).