butanediol with diisocyanates. All the products described gave characteristic urethan absorption in the infrared spectrum, a strong broad absorption at about 1700 cm.$^{-1}$ as well as a N–H stretching frequency at 3400 cm.$^{-1}$.

A.—A solution of 2.26 g. (0.01 mole) of the diol and 1.74 g. (0.01 mole) of 2,4-tolylene diisocyanate in 30 ml. of benzene and 2 drops of triethylamine was allowed to stand at room temperature for 48 hours. The precipitated polymer was obtained by decantation of the supernatant liquid, dried *in vacuo*, dissolved in acetone and reprecipitated by dropwise addition to a 10-fold excess of benzene. After filtration and drying *in vacuo*, a white solid was obtained, softening range 100–115°, [η] 0.10 determined in acetone at 29.8°.

Anal. Calcd. for $C_{21}H_{24}N_2O_4S$: C, 62.97; H, 6.04; N, 7.00; S, 8.01. Found: C, 63.21; H, 6.09; N, 6.95; S, 8.02.

B.—A solution of 2.26 g. (0.01 mole) of the diol and 1.68 g. (0.01 mole) of hexamethylene 1,6-diisocyanate was prepared as in A and allowed to stand for 48 hours. The resultant precipitate was dissolved in dimethylformamide and precipitated by dropwise addition to a large excess of methanol. The precipitate was filtered and dried *in vacuo*. The product was a white solid, softening range 90–95°, [η] 0.30 determined in dimethylformamide at 29.8°.

Anal. Calcd. for $C_{20}H_{30}N_2O_4S$: C, 60.88; H, 7.66; N, 7.10; S, 8.13. Found: C, 61.13; H, 7.54; N, 6.99; S, 8.35.

C.—A solution of 2.26 g. (0.01 mole) of the diol and 2.50 g. (0.01 mole) of purified diphenylmethane 4,4′-diisocyanate was prepared as in A and allowed to stand for 48 hours. The resultant precipitate was dissolved in dimethyl sulfoxide and precipitated by dropwise addition to a large excess of water. The precipitate was filtered and dried *in vacuo*. The product was a white solid, softening range 110–117° [η] 0.19 determined in dimethylformamide at 29.8°.

Anal. Calcd. for $C_{27}H_{28}N_2O_4S$: C, 68.04; H, 5.92; N, 5.88; S, 6.73. Found: C, 67.91; H, 6.08; N, 5.90; S, 6.72.

Polymer from Adipic Acid and 2-Benzylthiomethyl-1,4-butanediol.—A solution of 6.79 g. (0.03 mole) of 2-benzylthiomethyl-1,4-butanediol and 5.49 g. (0.03 mole) of redistilled adipoyl chloride was refluxed for 18 hours in 100 ml. of benzene. A stream of prepurified nitrogen was used to flush gaseous hydrochloric acid out of the system. The product was isolated by direct lyophilization from the reaction solvent. The oily residue was dried in a vacuum oven at 100° for 4 hours. It was then dissolved in a minimum volume of benzene and precipitated by dropwise addition to a large excess of Skellysolve A, isolated by decantation and dried in a vacuum oven at 60° for 12 hours. An extremely viscous yellow oil resulted, [η] 0.12 determined in benzene at 29.8°. Infrared analysis showed a typical ester peak at 1730 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{24}O_4S$: C, 64.26; H, 7.19; S, 9.53. Found: C, 64.19; H, 7.24; S, 9.71.

Debenzylation of Polyurethan.—This reduction was carried out by adopting some of the features of the methods of Baddiley and Thain[18] and Benkeser, *et al.*[16] A 5-g. sample of polyurethan derived from 2,4-tolylene diisocyanate and 2-benzylthiomethyl-1,4-butanediol (0.0125 mole of benzyl groups) was dissolved in 25 ml. of propylamine and the system flushed with nitrogen. Liquid ammonia was added until the solution became slightly turbid. Freshly cut pieces of sodium were then added periodically with vigorous stirring and external cooling by a Dry Ice–acetone mixture, until a permanent deep blue color was achieved. Excess ammonia was evaporated in a stream of nitrogen and the excess sodium decomposed by careful addition of ethanol. The addition of 200 ml. of deoxygenated water gave a yellow solution which was filtered by gravity under nitrogen and acidified with concentrated hydrochloric acid to a *p*H of 10. The resulting precipitate was allowed to settle under nitrogen at refrigerator temperature, the supernatant liquid decanted and the residue dried *in vacuo* over Drierite. The product was a white solid which gave a strong nitroprusside test and a SH stretching frequency at 2550 cm.$^{-1}$, softening point, 105–115°, [η] 0.21 determined in dimethylformamide at 29.8°.

A sample was allowed to crosslink in alkaline solution in air and the resulting precipitate was filtered, washed with dimethyl sulfoxide and dried.

Anal. Calcd. for $C_{14}H_{17}N_2O_4S$: C, 54.35; H, 5.54; N, 9.06; S, 10.36. Found: C, 54.24; H, 5.78; N, 8.63; S, 10.10.

Acknowledgment.—We wish to acknowledge gratefully the support of this work by a grant from the Charles Pfizer Co., the helpful discussions held with Dr. Richard G. Hiskey and the laboratory assistance of Mr. Robert Liebowitz.

(18) J. Baddiley and E. M. Thain, *J. Chem. Soc.*, 1611 (1953).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Reactions of 2*H*,3*H*-Thieno[3,2-b]pyrrole-3-one. II.[1,2] Acetylation and Formylation

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RECEIVED JANUARY 26, 1960

2*H*,3*H*-Thieno[3,2-b]pyrrol-3-one (I) reacts with hot acetic anhydride to give 3-acetoxy-4-acetylthieno[3,2-b]pyrrole (IV) as the major product, along with a little 3-acetoxy-2,4-diacetylthieno[3,2-b]pyrrole (V). The triacetyl derivative V can be obtained from the diacetyl derivative by the action of acetic anhydride in the presence of a little ferric chloride or iodine, but not acetic anhydride alone; acetic acid formed along with IV probably serves as the catalyst for the formation of the triacetyl derivative obtained in the direct acetylation of I. Hot aqueous sodium carbonate removes the O- and N-acetyl groups of V, leading to 2-acetyl-3-hydroxythieno[3,2-b]pyrrole, which, like the analogous carbethoxy compound, exists as a dimer. Acylation of the ketone I with ethyl formate and sodium methoxide occurs readily, yielding a nearly colorless monomeric derivative, the structure of which is best represented as the internally hydrogen-bonded hydroxyaldehyde X.

In connection with studies of the chemistry of 2*H*,3*H*-thieno-[3,2-b]pyrrol-3-one (I),[4] the acylation of this unique ketone has been investigated. Since I bears a formal resemblance to 2-acetylpyrrole (II), acylation of the two substances might be expected to proceed similarly. Compound II has been reported to undergo nuclear substitution upon treatment with acetic anhydride, yielding 2,5-diacetylpyrrole (III),[5] and there is evidence that carbon substitution is the result of a rearrangement of the initially formed N-acetyl derivative.[6] Therefore, it was anticipated that acylation of I would effect the introduction of an acyl group in the 5-position. Treatment of I with acetic anhy-

(1) For the preceding paper, see W. Carpenter and H. R. Snyder, THIS JOURNAL, **82**, 2592 (1960).

(2) This investigation was supported in part by a grant [C 3969-(C1) Bio] from the National Cancer Institute, Public Health Service.

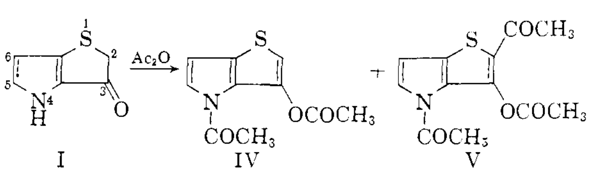
(3) National Science Foundation Fellow, 1958–1959.

(4) H. R. Snyder and D. S. Matteson, THIS JOURNAL, **79**, 3610 (1957).

(5) G. Ciamician and M. Dennstedt, *Ber.*, **17**, 2944 (1884).

(6) A. A. Berlin, *J. Gen. Chem. U. S. S. R.*, **14**, 438 (1944).

dride afforded an excellent yield of a mixture of two products, neither of which, however, was the expected 5-acetyl compound. The major product (*ca.* 83%) was a diacetyl derivative, which by spectral analyses was shown to be 3-acetoxy-4-acetylthieno[3,2-b]pyrrole (IV). The minor product (*ca.* 14%) was the triacetyl derivative, 3-acetoxy-2,4-diacetylthieno[3,2-b]pyrrole (V), as shown by both spectral and chemical evidence.



I IV V

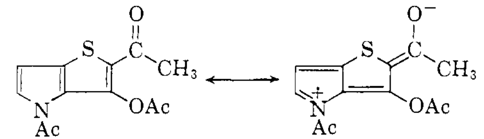
The infrared spectrum of IV lacks the 3120 cm.$^{-1}$ peak, characteristic of the pyrrole -NH, and has carbonyl absorption at 1740 and 1715 cm.$^{-1}$, assigned to the O-acetyl and N-acetyl carbonyl groups, respectively. The ultraviolet spectrum is similar to that of thienopyrrole (260 mμ),[4] having a single peak at 270 mμ. The nuclear magnetic resonance (n.m.r.) spectrum[7] (CDCl$_3$) confirms the structural assignment. There are peaks at -2.36, -2.00 and -1.70 p.p.m. (relative to water), the position[8] and coupling constants (J) of which permit the unequivocal assignments: pyrrole α-hydrogen (5-proton), thiophene α-hydrogen (2-proton) and the pyrrole β-hydrogen (6-proton), respectively. In addition to the expected coupling of pyrrole α- and β-protons (J_{56} = 3.5 c.p.s.), coupling between the α-hydrogen atoms of both rings is observed (J_{25} = 1.2 c.p.s.). This and other examples of this remarkable "cross-ring" coupling will be discussed in more detail elsewhere.[9]

Reconversion of IV to I is effected by either dilute acid or base. Reduction of IV with lithium aluminum hydride effects removal of the N-acetyl group, as well as reduction of the ester, to regenerate I. The change is not surprising in view of the reported deacetylation of N-acetylpyrrole by lithium aluminum hydride.[10]

The by-product V is believed to be formed by a Friedel-Crafts acylation of IV. Since IV is not acetylated upon heating with pure acetic anhydride in a sealed tube, the conversion of IV to V is evidently catalyzed by the acetic acid generated in the formation of IV. Synthesis of V in fair yield was effected by acetylation of IV with acetic anhydride in the presence of weak Friedel-Crafts catalysts like ferric chloride and iodine.

The position of attachment of the third acetyl group in V is shown by the n.m.r. spectrum (CDCl$_3$). The peak attributed to the thiophene α-proton in IV is not present in V, and the "cross-ring" coupling due to it (J_{25}) is not observed. However, the characteristic doublets (J_{56} = 3.5 c.p.s.) of the pyrrole hydrogen atoms are present.

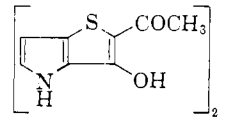
The infrared spectrum has three carbonyl peaks, at 1760, 1710 and 1637 cm.$^{-1}$, the band of lowest frequency being assigned to the 2-acetyl group. The 1637 cm.$^{-1}$ value is somewhat lower than that reported for 2-acetylthiophene (1667 cm.$^{-1}$)[11] but is within instrumental error of that observed for 2-acetylpyrrole (1638 cm.$^{-1}$). In the absence of additional model compounds in this series (in particular, a 3-acylthienopyrrole), the low value may be explained by the fact that V, like II and I, is a vinylog of an amide. The 2-acetyl group is in conjugation with the pyrrole nitrogen atom, making possible a significant contribution by an ionic resonance structure.



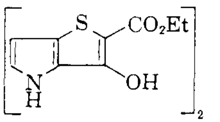
V

The ultraviolet spectrum of V is quite unlike that of IV. The main maximum is at 318 mμ, which represents a surprisingly large bathochromic shift from the 270 mμ absorption of IV. In contrast, a band in this region is reported for some 2-carbethoxy-3-hydroxy derivatives, but it is not present when the hydroxyl group is replaced by a methoxyl or acetoxyl group.[1]

Treatment of V with base gave, upon acidification, a good yield of the high-melting hydrolysis product VI, which like the carbethoxyl analog VII,[1] proved to be dimeric. VI is soluble in dilute sodium hydroxide solution and gives a positive ferric chloride test.[12] The infrared spectrum shows no absorption that can be attributed to a free -OH group,[13] but rather shows broad absorption centered upon the 3200-3000 cm.$^{-1}$ range, which is superimposed upon the normal 3120 cm.$^{-1}$ N-H absorption. This is a familiar phenomenon observed in compounds of the salicylaldehyde type in which the possibility exists for strong hydrogen bonds. In



VI



VII

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[7] The nuclear magnetic resonance spectra were determined on a Varian Associates V-4300-B high resolution n.m.r. spectrophotometer. The spectra were determined with 20% solutions in the indicated solvent with methylene chloride as an external standard. The line positions are given in parts per million (p.p.m.) relative to water and the coupling constants in cycles per second (c.p.s.). Where the line positions are given in terms of τ, the measurement was made with tetramethylsilane (TMS) as the internal reference standard; τ is defined thus

$$\tau \text{ (in p.p.m.)} = 10.000 - 10^6 \frac{H_{\text{TMS}} - H_{\text{obs}}}{H_{\text{TMS}}}$$

$$\textit{i.e.}, \tau_{\text{TMS}} = +10.000$$

This formula and the τ-values for various known substances were taken from G. V. D. Tiers, "Characteristic Nuclear Magnetic Resonance (NMR) Shielding Values (Spectral Positions) for Hydrogen in Organic Structures," Central Research Department, Minnesota Mining and Manufacturing Co., St. Paul, Minn., 1958.

[8] R. Abraham and H. Bernstein, *Can. J. Chem.*, **37**, 1056 (1959).

[9] R. J. Tuite, H. R. Snyder, A. L. Porte and H. S. Gutowsky, forthcoming publication.

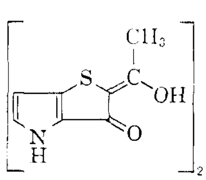
[10] V. M. Micovic and M. L. Mihailovic, *J. Org. Chem.*, **18**, 1190 (1953).

[11] H. D. Hartough, "The Chemistry of Heterocyclic Compounds—Thiophene and Its Derivatives," Interscience Publishers, Inc., New York, N. Y., 1952, p. 120.

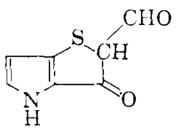
[12] R. Shriner, R. Fuson and D. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 4th Ed., 1956, p. 112.

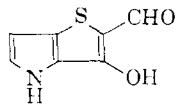
[13] L. Bellamy, "The Infra-Red Spectra of Complex Molecules," Methuen, London, 2nd Ed., 1958.

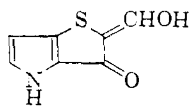
addition there is a broad unresolved absorption at 1610 cm.$^{-1}$, indicating that the carbonyl group is of very low double-bond character. The n.m.r. spectrum (DMF) is consistent with the structure proposed, although the ketomethylene structure VIII is not entirely eliminated by any of the evidence cited. The ultraviolet spectrum of VI shows two intense maxima, at 318 and 352 mμ.


VIII

An attempted formylation of IV with phosphorus oxychloride and dimethylformamide failed. The ketone I was formylated directly, however, by the method of Johnson and Posvic.[14] The reaction of I with ethyl formate in a suspension of sodium methoxide in anhydrous benzene afforded a good yield of a crystalline, nearly colorless, monomeric derivative, for which the structures IX, X and XI might be considered. The product, like the analogous VI, is instantly soluble in dilute sodium hydroxide solution and gives a positive ferric chloride test.[12] Under similar conditions, I does not give a color with ferric chloride reagent, a fact which, in conjunction with spectral evidence to follow, excludes the structure IX.

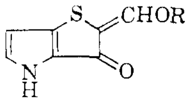

IX


X


XI

The infrared spectrum of the formylation product, like that of VI, shows no free -OH band in the 3000 cm.$^{-1}$ region, but rather reveals broad, weak absorption centered at 2600–2500 cm.$^{-1}$. A peak at 1660 cm.$^{-1}$ is consistent with a carbonyl function attached either to a pyrrole (as in XI) or a thiophene system (as in X). The difference between the representations X and XI, if internal hydrogen bonding occurs in both, is merely in the position of the hydroxylic proton relative to the two oxygen atoms, the electron concentrations portrayed by the double bonds in the oxygen-containing systems being redistributed as a result of resonance. The question then is whether the structure of the formylation product more nearly approximates X than XI. The n.m.r. spectrum (Me_2SO) of the formylation product shows two rather broad bands in the extreme low-field region, assigned to the NH and OH protons. There is no band that could be attributed to an aliphatic $\geqslant$CH proton, a fact that provides further evidence against IX. Furthermore, there is a peak at $\tau = +0.52$ p.p.m., definitely in the range of the proton in an aldehyde function,[7] some examples are: benzaldehyde, $\tau = +0.035$ p.p.m.; *p*-methoxybenzaldehyde, $\tau = +0.199$ p.p.m.; 2-butenaldehyde, $\tau = +0.57$ p.p.m. The hydrogen atom which is aldehydic in X is olefinic in XI; the resonance of olefinic protons occurs at τ-values of 2 to 5.0 p.p.m.,[7] and a peak in this range is observed in the spectra of O-alkyl derivatives (XII) obtained from the formylation product.

The unusual reactivity of the formylation product was first observed in a routine test of its solubility in ethanol. The substance which crystallized from the solution was a higher melting, brightly colored solid to which the structure XII has been assigned on the bases of composition, molecular weight and spectral properties.


XII, R = C_2H_5
XIII, R = CH_3

A similar ether (XIII) was obtained by the action of hot methanol. The ultraviolet spectra of XII and XIII reveal an intense maximum at *ca.* 315 mμ (log ε 4.4). It has been suggested that the absorption in this region exhibited by 2-benzal-1-indanone and its derivatives, which contain a chromophore similar to that in XII and XIII, is characteristic of exocyclic unsaturated ketones.[15] In the n.m.r. spectrum of XIII (Me_2SO), a peak at $\tau = +2.09$ p.p.m. is attributed to the ethylenic proton. The quinoid character of XII and XIII is also indicated by their bright yellow colors.

As a result of these studies it is considered that the formulation X provides a better representation for the structure of the formylation product than does XI. The formation of XII and XIII, which can be regarded as derivatives of XI, presumably proceeds by nucleophilic attack of the alcohols on the exocyclic carbon atom followed by 1,4-elimination of water. That amines can react in the same way was discovered in an attempt to condense X with malonic acid in the presence of pyridine and piperidine. The product, a bright yellow solid, had the composition and spectra properties expected of the nitrogen-containing analog of XII ($-NC_5H_{10}$ instead of OC_2H_5).

A preliminary study of the reduction of the ethyl ether XII with lithium aluminum hydride was undertaken. *o*-Isopropoxymethylenecyclohexanone is reduced in excellent yield to 1-cyclohexenecarboxaldehyde by this reagent[16]; the corresponding reduction product of XII, thieno[3,2-b]pyrrole-2-carboxaldehyde, would be a desirable reagent for use in further syntheses. However, the reduction of XII gave a mixture of unstable products. In its reaction with VII lithium aluminum hydride brought about reduction of the ester group,[1] and it is possible that the same type of reduction complicates the reaction of XII.

Experimental[17]

3-Acetoxy-4-acetylthieno[3,2-b]pyrrole (IV).—A solution of 2.14 g. (0.0154 mole) of I in 40 ml. of acetic anhydride was

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[14] W. S. Johnson and H. Posvic, This Journal, **69**, 1361 (1947).

[15] A. Hassner and N. Cromwell, *ibid.*, **80**, 893 (1958).

[16] A. S. Dreiding and S. N. Nickel, *ibid.*, **76**, 3965 (1954).

[17] All melting points are corrected. The symbol (k) after a melting point indicates that the determination was made on a Kofler hot-stage melting point apparatus. The microanalyses were performed by Mr. Josef Nemeth, Mrs. Maria Stingl, Miss Claire Higham, Miss Jane Liu, and by the Clark Microanalytical Laboratory, Urbana, Ill.

refluxed for 16 hours with the exclusion of moisture. The solvent was removed under reduced pressure (18 mm.), and the black oily residue was dissolved in acetone and transferred to a sublimation tube. After distillation of the acetone, the product was distilled at 130° (0.05 mm.) to give a light yellow oil which crystallized upon scratching, affording 3.39 g. of a white crystalline substance. This material was sublimed at 75–80° (0.05 mm.); after a small amount of oil appeared in the sublimate, the tube was removed, and crystallization was induced by scratching. The white crystalline sublimate melted at 81–82°; 86–88° (k). The yield of pure IV was 2.85 g. (82.9%). An analytical sample was prepared by a second sublimation followed by recrystallization from ethanol–water.

Anal. Calcd. for $C_{10}H_9NO_3S$: C, 53.80; H, 4.06; N, 6.28. Found: C, 53.81; H, 3.83; N, 6.32.

3-Acetoxy-2,4-diacetylthieno[3,2-b]pyrrole (V). (a) As a By-product in the Formation of IV.—After the sublimation of IV at 80° (0.05 mm.) was complete, the temperature was raised to 85–90°. Heating under vacuum was continued for 48 hours during which time only a trace of IV distilled. The solid residue was then sublimed at 130° (0.05 mm.), affording 0.50 g. (14.7%). of impure V. Treatment with Darco and two recrystallizations from benzene were required to purify the product, m.p. 160–162°. An analytical sample, m.p. 162–162.5°, was prepared by an additional recrystallization from benzene.

Anal. Calcd. for $C_{12}H_{11}NO_4S$: C, 54.33; H, 4.18; N, 5.28. Found: C, 54.33; H, 4.04; N, 5.19.

In a control experiment to determine whether the acetylation of IV would proceed in the absence of acetic acid (generated in the formation of IV), a solution of 0.446 g. (2 millimoles) of IV in 5 ml. of acetic anhydride was heated for 5 hours in an evacuated sealed tube at 180°. The only substance isolated was IV, which was recovered in nearly quantitative yield.

(b) By Acetylation of IV with Acetic Anhydride and Ferric Chloride.—To a solution of 0.446 g. (2.00 millimoles) of IV in 1.0 ml. of acetic anhydride was added *ca.* 17 mg. of anhydrous ferric chloride. The resulting purple solution was warmed on the steam-bath for 20 minutes, then was cooled, and 2 ml. of water added. After standing about 15 minutes (or until only one phase was discernible), 3 ml. of chloroform was added. The organic layer was separated, and the aqueous layer was extracted with three 3-ml. portions of chloroform. The resulting solution was cooled to 0° and was washed thoroughly with ice-cold 10% aqueous sodium carbonate solution followed by 10 ml. of water. After drying over magnesium sulfate, the solution was concentrated to dryness and the residue sublimed at 130° (0.05 mm.). The yield of crude V was 0.182 g. or 34.3% of the theoretical amount. After treatment with Darco and recrystallization from benzene, the product had m.p. 160–161.5°, undepressed upon admixture with a pure sample obtained by procedure a. The infrared spectra were also identical.

(c) By Acetylation of IV with Acetic Anhydride and Iodine.—To a solution of 0.446 g. (2.00 millimoles) of IV in 1 ml. of acetic anhydride was added *ca.* 10 mg. of iodine. Within 1 minute the color of the solution changed from orange-red to deep purple. The solution was heated on a steam-bath for 1 hour, the solvent removed under reduced pressure (18 mm.), and the black residue heated at 80° (0.05 mm.) to remove some of the iodine. After the sublimed iodine was washed from the walls of the tube with acetone, the residue was sublimed at 130° (0.05 mm.). The yield of dark, crude product was 0.301 g. After treatment with Darco and recrystallization from benzene, the yield of slightly colored V, m.p. 159–161°, was 0.195 g. (36.8%). A mixed melting point determination and infrared spectrum confirmed the identity of the product with that from procedure a.

Reduction of IV with Lithium Aluminum Hydride.—Six-tenths of a gram of lithium aluminum hydride was added cautiously to an ice-cooled solution of 0.206 g. (0.925 millimole) of IV in 14 ml. of ether. After the vigorous reaction had subsided, the reaction mixture was put under a nitrogen atmosphere and stoppered overnight. The excess lithium aluminum hydride was decomposed by the cautious addition of a few drops of water to the ice-cooled solution; 50 ml. of ether was added, the mixture was filtered, and the precipitate was washed several times with ether. The combined washings were dried over magnesium sulfate and the ether was distilled under reduced pressure. The white residue was sublimed at 115° (0.05 mm.) to give pure I, m.p. 188–191° (k). The yield was 0.048 g. (38%). The identity of the product was substantiated by its infrared spectrum.

The Dimer of 2-Acetyl-3-hydroxythieno[3,2-b]pyrrole (VI).—A suspension of 0.165 g. (0.622 millimole) of V in 10 ml. of 5% aqueous sodium carbonate solution was refluxed for 1 hour; solution was complete before the temperature of reflux was reached. The slightly yellow solution was cooled to 5° and acidified with glacial acetic acid, whereupon a voluminous white precipitate appeared. After cooling for 1 hour in an ice-water-bath, the product was collected on a filter, washed with water, and dried. After sublimation at 130° (0.05 mm.), the yield of crude product was 0.090 g. or 80.0%, m.p. 215–221° (taken in a sealed capillary tube). An analytical sample was prepared by recrystallization from 95% ethanol to give slightly yellow needles, m.p. 216–218° (k).

Anal. Calcd. for $(C_8H_7NO_2S)_2$: C, 53.04; H, 3.90; N, 7.73; mol. wt., 362.3. Found: C, 52.98; H, 3.68; N, 7.70; mol. wt. (ebullioscopic in 2-butanone), 404.

3-Hydroxythieno[3,2-b]pyrrole-2-carboxaldehyde (X).—A suspension of 2.26 g. (0.042 mole) of commercial sodium methoxide in 40 ml. of anhydrous benzene was prepared and about 5 ml. of solvent distilled to remove any traces of water and methanol. To the cooled suspension were added 2.92 g. (0.021 mole) of I and 3.10 g. (0.042 mole) of ethyl formate, and the mixture was refluxed for 2 hours. After cooling, the reaction mixture was poured into 100 ml. of water. The aqueous layer was removed, and the benzene layer was extracted twice with 15-ml. portions of 10% NaOH solution. The combined aqueous extracts were washed once with ether, filtered, and acidified with cold acetic acid. The resulting gray precipitate was washed thoroughly with water and was dried *in vacuo* overnight. The product weighed 2.95 g. (84%). Purification was effected by two sublimations in a cold-finger apparatus using an oil-bath temperature of 120°. (It was found that the sublimate is decomposed if it is allowed to condense on a hot surface.) The light yellow sublimate melted at 155–155.5°.

Anal. Calcd. for $C_7H_5O_2NS$: C, 50.28; H, 3.01; N, 8.38; mol. wt., 167.2. Found: C, 50.78; H, 3.30; N, 8.13, 7.98; mol. wt. (ebullioscopic in 2-butanone), 134.

Reaction of X with Ethanol.—A solution of 1.4 g. of X in 10 ml. of absolute ethanol was gently boiled for 10 min. After treatment with charcoal followed by filtration, the clear yellow solution began to deposit glistening yellow needles. The initial crop weighed 0.7 g., and an additional 0.15 g. could be obtained by slight concentration and cooling. Three crystallizations from ethanol–water yielded material with m.p. 215–216° dec.

Anal. Calcd. for $C_9H_9O_2NS$: C, 55.31; H, 4.65; N, 7.17; mol. wt., 195. Found: C, 55.57; H, 4.69; N, 6.92; mol. wt.[18] (Rast), 206.

Reaction of X with Methanol.—One gram of crude X was dissolved in 10 ml. of absolute methanol and treated as above. There was obtained 0.7 g. of yellow-orange needles which, after three recrystallizations from methanol–water, afforded yellow needles, m.p. 223–226° dec.

Anal. Calcd. for $C_8H_7O_2NS$: C, 53.02; H, 3.90; N, 7.73. Found: C, 52.79; H, 3.86; N, 7.59, 7.51.

Reaction of X with Piperidine.—When a mixture of 100 mg. (0.6 millimole) of X, 187 mg. (1.8 millimoles) of malonic acid, 2 ml. of pyridine and 0.2 ml. of piperidine was heated on the steam-bath for 2 hr., cooled, and poured into 10 ml. of water, a crystalline solid separated. After thorough drying, the olive-colored crystals weighed 120 mg. Three recrystallizations from ethanol-water provided lemon-colored needles, m.p. 272–273° dec.

Anal. Calcd. for $C_{12}H_{14}N_2OS$: C, 61.50; H, 6.03; N, 11.95. Found: C, 61.39; H, 6.01; N, 11.50.

URBANA, ILL.

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[18] Determined by Weiler and Strauss Laboratories, Oxford, England.