became quite thick and difficult to stir as the reaction proceeded. The mixture was cooled and 25 ml. of methanol was added to decompose any unused sodium hydride. Then 600 ml. of 7% hydrochloric acid solution was added. The organic phase was separated and distilled to give, after removal of toluene and other low-boiling materials, 126 g. (66%) of 2,2-dimethyl-4-pentenoic acid, b.p. 82–83° (4 mm.), n_D^{20} 1.4337; reported[3] b.p. 104–108° (20 mm.)

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.4; neut. equiv. 128. Found: C, 65.7; H, 9.5; neut. equiv. 129.

2,2,4-Trimethyl-4-pentenoic acid. Under the conditions described above, methallyl isobutyrate and sodium hydride gave 2,2,4-trimethyl 4 pentenoic acid in 68% yield, b.p. 78–81° (1.5–2 mm.), n_D^{20} 1.4421.

Anal. Calcd. for $C_8H_{14}O_2$: C, 67.6; H, 9.9; neut. equiv. 142. Found: C, 67.2; H, 9.9; neut. equiv. 143.

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[3] R. F. Brown and N. M. Van Gulick, *J. Am. Chem. Soc.*, 77, 1092 (1955).

Catalytic Interaction of 2-Vinylpyridine and Hydrogen Sulfide[1]

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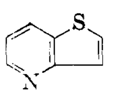
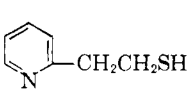
Moore and Greensfelder[2] have described the synthesis of benzothiophene in 60% yield from styrene and hydrogen sulfide using a flow apparatus, a ferrous sulfide–alumina catalyst, and a temperature of 600–625°. Besides benzothiophene and unchanged starting materials other substances identified in the effluent were hydrogen, a tar-like polymer, and small amounts of benzene, ethene, and probably ethane. By use of similar conditions we have been able to isolate, albeit in only 1.6% yield, a compound which appears to be the previously unknown thieno[3,2-*b*]pyridine (I) from 2-vinylpyridine and hydrogen sulfide. Other products identified in the gases condensable above −70° from the reaction effluent were ethyl mercaptan, diethyl sulfide, pyridine, thiophene, sulfur, and hydrogen sulfide, but not unchanged 2-vinylpyridine. A material balance showed that at least half of the nitrogen atoms in the influent were retained on the column, perhaps as polymeric or strongly adsorbed[3] species. The formation of the products can be rationalized by the assumption that hydrogen sulfide adds to 2-vinylpyridine to form the intermediate 2-(2-pyridyl)ethyl mercaptan (II) which undergoes hydrogenolysis (by hydrogen sulfide) to ethyl mercaptan, pyridine, and sulfur and dehydrocyclization to I. In addition, condensation of ethyl mercaptan with 2-vinylpyridine followed by hydrogenolysis and subsequent dehydrocyclization could account for the formations of diethyl sulfide and thiophene, respectively.



I



II

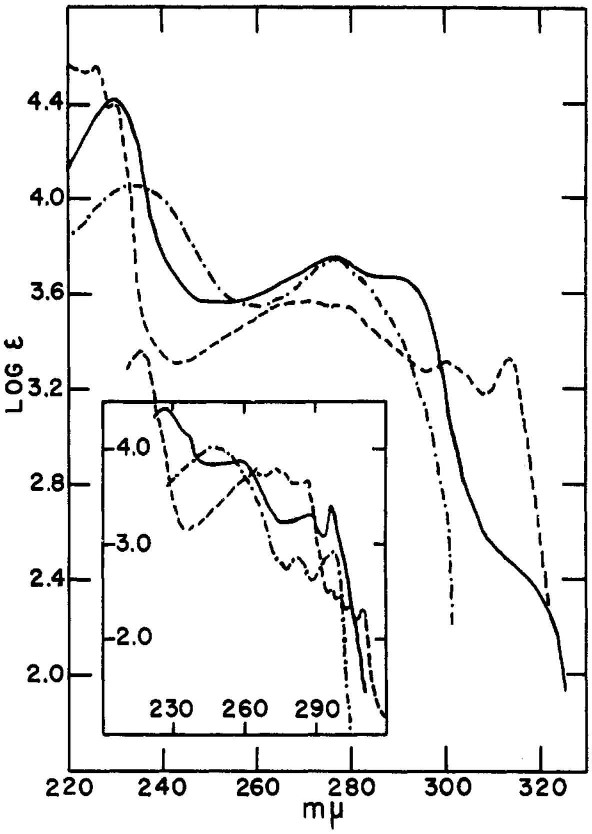


Fig. 1. Comparison of ultraviolet spectra. Large graph: ——— thieno[3,2-*b*]pyridine; - - - - quinoline; -·-·-· 2-vinylpyridine. Inset graph: ——— benzothiophene; - - - - naphthalene; -·-·-· styrene.

Structure I was assigned to the faintly yellow liquid obtained from fractional distillation of the crude reaction product on the basis of its b.p. (82–84°/2 mm., estimated b.p. 240°/760 mm.; *cf.* quinoline,[4] b.p. 239°), its ultraviolet absorption spectrum (nearly a composite of the spectra of quinoline[5] and 2-vinylpyridine,[6] *cf.* the spectrum

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[1] Abstracted from the M.S. thesis of David D. Reed, University of Oregon, June 1957. Further details concerning the apparatus used may be obtained by consultation of this thesis.

[2] R. J. Moore and B. S. Greensfelder, *J. Am. Chem. Soc.*, 69, 2008 (1947).

[3] In preliminary chromatographic studies conducted in this laboratory the unusually strong adsorbability of aromatic nitrogen heterocycles (as compared to the corresponding arenes) on alumina has been noted.

[4] R. L. Shriner, R. C. Fuson, D. Y. Curtin, *The Systematic Identification of Organic Compounds*, 4th ed., J. Wiley & Sons, New York, 1956, p. 297.

[5] R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, J. Wiley & Sons, New York, 1951.

[6] R. P. Mariella, L. F. A. Peterson, and R. C. Ferris, *J. Am. Chem. Soc.*, 70, 1494 (1948).

of benzothiophene[5] with the spectra of naphthalene[5] and styrene,[7] Fig. 1),[8] its reaction with methyl iodide to form a high melting solid containing both nitrogen and sulfur, and its conversion to a crystalline picrate of elementary analyses appropriate for I monopicrate.

Hansch and Carpenter[9] were unable to isolate any thienopyridine upon treating 4-vinylpyridine with hydrogen sulfide in the manner of Moore and Greensfelder.[2] Instead, they obtained a yellow liquid which formed a crystalline dipicrate and was presumed to be β,β-di(4-pyridyl)ethyl sulfide.

EXPERIMENTAL

The apparatus used was modified from that previously reported.[1, 2] The ferrous sulfide–alumina catalyst was prepared by impregnating activated alumina (Fisher Scientific Co., 8–14 mesh) with 1.25*M* aqueous ferric nitrate solution, sulfiding, and calcining.[2] Commercial hydrogen sulfide was used directly from the cylinder. 2-Vinylpyridine (Reilly Tar and Chemical Corp., Indianapolis) was distilled from its inhibitor just prior to use. In a typical run which furnished maximum yields of total products condensable above 0°, the reaction temperature was 603 ± 3°; the flow rates of hydrogen sulfide and 2-vinylpyridine were 475 ml./min. and 29.5 g./hr., respectively (molar ratio 4.1:1); the calculated contact time (assuming the catalyst bed was a total void, *i.e.*, 700 ml.) was 24 sec.; and the total reaction time was 80 min.

The dark liquid (15 g.) which collected in air- and ice water–cooled receivers was distilled under reduced pressure in a nitrogen atmosphere. From earlier fractions of distillate were obtained ethyl mercaptan (positive colorimetric test with sodium nitroprusside, converted to ethyl 2,4-dinitrophenyl sulfide), diethyl sulfide (converted to sulfone), pyridine (converted to picrate), thiophene (converted to 2-mercurichloride derivative), and sulfur. Sulfur and each of the preceding crystalline derivatives were identified by melting point and mixture melting point with authentic samples of the same substances.

Thieno[3,2-b]pyridine (I) was collected from the higher boiling fraction as a yellow liquid, b.p. 82–84° (2 mm.), yield 0.8 g. (1.6%); $\lambda_{max}^{C_2H_5OH}$ 230 mμ (log ε 4.42), 278 (3.71), 285–290 (3.65)-shoulder, *ca.* 315 (2.4)-shoulder; soluble in ethanol, ether, benzene, and dilute hydrochloric acid; insoluble in water and aqueous sodium hydroxide. I darkened upon exposure to air at room temperature for a few hours, but it remained yellow for several weeks when stored under nitrogen at 0°.

Treatment of I with an equimolar quantity of picric acid in methanol gave green-yellow needles of *picrate*, recrystallized from ethyl acetate to constant m.p., 195.5–197.5°.

Anal. Calcd. for $C_{13}H_8N_4O_7S$: C, 42.86; H, 2.21; N, 15.38; S, 8.80. Found: C, 43.17; H, 2.18; N, 15.38; S, 8.26.

Treatment of I with excess methyl iodide gave pale yellow needles, presumably the methiodide, m.p. 217–219.5° with previous darkening, not obtained sufficiently pure for elementary analysis but giving positive qualitative sodium-fusion tests for the presence of nitrogen and sulfur.

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(7) G. Allard, *Helv. Chim. Acta*, **19**, 1270 (1936).

(8) W. Herz and L. Tsai, *J. Am. Chem. Soc.*, **75**, 5122 (1953) have noted a "marked resemblance" between the spectra of isoquinoline and thieno[2,3-*c*]pyridine.

(9) C. Hansch and W. Carpenter, *J. Org. Chem.*, **22**, 936 (1957).

3-Hydroxycoumarins

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3-Hydroxycoumarin has an inhibiting effect on the growth of *avena* roots[1] and 3-aminocoumarins, which are intermediates in the synthesis of 3-hydroxycoumarins, are found to have antibacterial properties.[2] The present work deals with the synthesis of some substituted 3-hydroxycoumarins and a study of the pattern of substitution in 3-hydroxycoumarin.

5-Bromo-, 3,5-dibromo-, 3-nitro-, 5-nitro-, and 3,5-dinitrosalicylaldehyde, methyl 2,4-dihydroxy-3-formylbenzoate and 2,4-dihydroxy-3-formylacetophenone were condensed according to Shaw, McMillen, and Armstrong[3] with acetylglycine in the presence of sodium acetate and acetic anhydride and the 3-acetamidocoumarins formed hydrolyzed with alcoholic 3*N*-hydrochloric acid to the 3-hydroxycoumarins. The intermediate 3-aminocoumarins could not be isolated even under controlled hydrolysis with acid or alkali.

The ketonic character of the 3-hydroxycoumarin has been shown by the formation of a phenylhydrazone and a quinoxaline derivative with *o*-phenylenediamine.[4] It is now found that 3-hydroxycoumarin gives the isonitroso derivative with nitrous acid. With bromine in acetic acid it gave the 4-bromoderivative and with iodine and iodic acid the 4-iodo derivative, both of which gave the original coumarin on reduction with zinc and acetic acid. Further bromination did not succeed, but the 6-bromo- and 6,8-dibromo-3-hydroxycoumarin were brominated in the 4-position. 3-Acetoxycoumarin underwent Fries migration to give the 4-acetyl derivative which was also obtained in the Friedel-Crafts acetylation of 3-hydroxycoumarin. On oxidation it gave salicylic acid. 3-Hydroxycoumarin when treated with formaldehyde gave 4-4′-methylenebis(3-hydroxycoumarin).

EXPERIMENTAL

Synthesis of 3-hydroxycoumarins. An equimolecular mixture of the salicylaldehyde derivative, acetylglycine, and anhydrous sodium acetate and acetic anhydride (2 moles) was heated on a steam bath for 1 hr. The 3-acetamidocoumarin derivative obtained on dilution with water was crystallized from acetic acid (Table I).

The acetamidocoumarin was dissolved in a minimum quantity of alcohol and refluxed with 3*N* hydrochloric acid for 3 to 4 hr. The 3-hydroxycoumarin obtained on cooling

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(1) R. H. Goodwin and G. Taves, *Am. J. Botany*, **37**, 224 (1950).

(2) G. Rodighiero and C. Antonello, *Bull. Chim. Farm.*, **97**, 592 (1958).

(3) K. N. F. Shaw, A. McMillen, and M. D. Armstrong, *J. Org. Chem.*, **21**, 601 (1956).

(4) E. Erlenmeyer, Jr., and W. Stadlin, *Ann.*, **337**, 283 (1904).