The mixture of benzene–chloroform eluted: triphenylmethane, m.p. 92–93°, unchanged on admixture with an authentic sample[3]; *p*-trityl-*N*,*N*-dimethylaniline, m.p. 210–211°, not depressed with an authentic sample[3] and *p*-trityl-*N*-methylaniline, m.p. 211–212°, unchanged with the pure compound.[3] Yields were: *p*-trityl-*N*,*N'*-dimethylaniline, 32.8%; *p*-trityl-*N*-methylaniline, 27.4%; and triphenylmethane, 22.5%.

Method B.—With the same procedure as in A, but when heated at 140–145°, the yields were: *p*-trityl-*N*,*N'*-dimethylaniline, 29.5%; *p*-trityl-*N*-methylaniline, 27.4%; and triphenylmethane, 24.2%.

Method C.—As in A, but when refluxed under nitrogen, the yields were: *p*-trityl-*N*,*N'*-dimethylaniline, 2.8%, and triphenylmethane, 77.5%.

II. Competition of *N*,*N'*-Dimethylaniline and Aniline. Method A.—*N*,*N'*-Dimethylaniline (0.05 mole), aniline (0.05 mole), and triphenylmethyl perchlorate (0.005 mole) were heated at 90–100°. The reaction mixture was treated in the same way as in (IA) and the crude product passed through a column of alumina with the benzene–chloroform mixture as indicated. The separation gave: *p*-trityl-*N*,*N'*-dimethylaniline, 54.5%; and triphenylmethane, 20.8%.

Method B.—As in A, but when heated at 140–145°, the yields were: *p*-trityl-*N*,*N'*-dimethylaniline, 54.5%; and triphenylmethane, 24.2%.

Method C.—As in A, but refluxed under nitrogen. The first fraction eluted all the triphenylmethane reported and there were no other products, except a small amount of oily material removed by the acetone. The yield was: triphenylmethane, 79.2%.

III. Competition of *N*-Methylaniline and Aniline. Method A.—*N*-Methylaniline (0.05 mole), aniline (0.05 mole), and triphenylmethyl perchlorate (0.005 mole) were heated at 90–100°. Following the general procedure described in (IA) the products separated and identified were: *p*-trityl-*N*-methylaniline, 62.8%; and triphenylmethane, 16.7%.

Method B.—As in A, but at 140–145°. The yields were: *p*-trityl-*N*-methylaniline, 62.2%, and triphenylmethane, 23.3%.

Method C.—As in A, but refluxed under nitrogen. The yield was: triphenylmethane, 85.0%.

IV. Competition of *N*,*N'*-Dimethylaniline and Phenol. Method A.—*N*,*N'*-dimethylaniline (0.05 mole), phenol (0.05 mole), and triphenylmethyl perchlorate (0.005 mole) were heated at 90–100°. Following the procedure already described (IA), the resulting products were identified as indicated and the yields were: *p*-trityl-*N*,*N'*-dimethylaniline, 50.5%; and triphenylmethane, 22.5%.

Method B.—As in A, but at 140–145°. The chloroform fraction eluted in this case some *p*-trityl phenol, identified by mixed melting point with an authentic sample of *p*-tritylphenol.[3] The yields were: *p*-trityl-*N*,*N'*-dimethylaniline, 34.0%; *p*-tritylphenol, 1.2%; and triphenylmethane, 37.5%.

Method C.—As in A, but refluxed under nitrogen. Yields were: *p*-trityl-*N*,*N'*-dimethylaniline, 1.1%, and triphenylmethane, 89.2%.

V. Competition of *N*-Methylaniline and Phenol. Method A.—*N*-Methylaniline (0.05 mole), phenol (0.05 mole), and triphenylmethyl perchlorate (0.005) were heated at 90–100°. The chromatographic procedure described in (IA) gave: *p*-trityl-*N*-methylaniline, 70.3%; and triphenylmethane, 15.0%.

Method B.—As in A, but at 140–145°. The yields were: *p*-trityl-*N*-methylaniline, 45.6%; and triphenylmethane, 35.0%.

Method C.—As in A, but refluxed under nitrogen. The yield was: triphenylmethane, 87.5%.

Reactions of 2*H*,3*H*-Thieno[3,2-*b*]pyrrol-3-one. IV.[1,2] Benzylation

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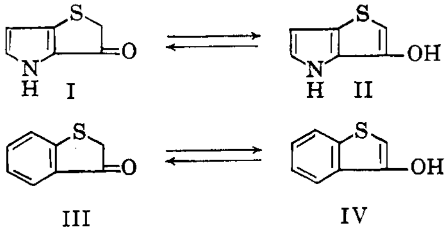
The heterocyclic ketone 2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (I) reacts with benzyl chloride in the presence of sodium hydride to give the tribenzyl derivative Vd, in which nitrogen and carbon, but not oxygen, have been alkylated. Similar treatment of either the *N*-benzyl derivative (VIII) or the C-benzyl derivative (VII), prepared by other means, yields the same tribenzyl ketone Vd. Hydrogen peroxide in acetic acid attacks the sulfur atom of the tribenzyl ketone Vd, producing the dioxide. Preparations of the dioxides by similar oxidation of the parent ketone (I) and its benzylidene derivative (VI) also are described.

Past investigations in this laboratory have been concerned with the synthesis of substitution products of 2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (I)[4,5] such as carbethoxy,[6] acetyl,[7] formyl-,[7,8] and arylidene[1] derivatives. In continuation of this program we have now studied the benzylation of this unique ketone.



It is known that the comparable system present in 3-thianaphthenone (III), under appropriate conditions, yields derivatives of both the keto and

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[1] For the preceding paper, see R. J. Tuite and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 4364 (1960).

[2] This investigation was supported by a grant [C3969-Bio] from the National Cancer Institute, Public Health Service.

[3] Postdoctoral Research Associate.

[4] D. S. Matteson and H. R. Snyder, *J. Am. Chem. Soc.*, **79**, 3610 (1957).

[5] D. S. Matteson and H. R. Snyder, *J. Org. Chem.*, **22**, 1500 (1957).

[6] W. Carpenter and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 2592 (1960).

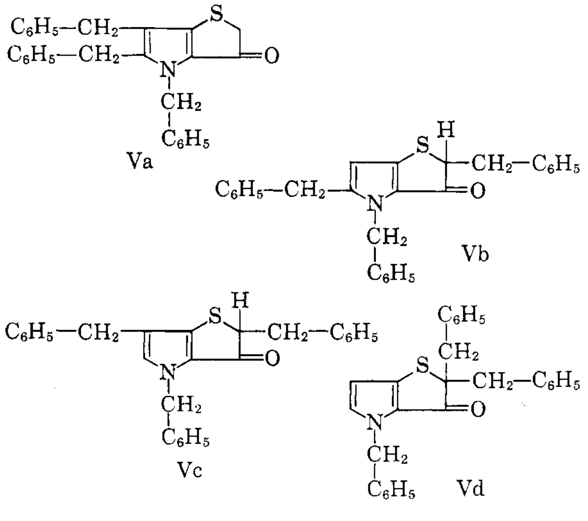
[7] R. J. Tuite, A D. Josey, and H. R. Snyder, *ibid.*, **82**, 4360 (1960).

[8] J. Witt, thesis, Doctor of Philosophy, University of Illinois, 1961.

enol forms (III and IV).[9] In contrast, the carbonyl group of I is very inert towards typical carbonyl reagents such as hydroxylamine, phenylhydrazine,[10] and 2,4-dinitrophenylhydrazine[11] as well as liquid hydrogen cyanide[11] and Grignard reagents.[12] It seemed possible that the failure of I to react with these reagents might be due to its rapid change to an enol form according to the tautomerism I $\rightleftharpoons$ II, and it was therefore of interest to attempt the formation and isolation of an *O*-alkyl derivative.

The initial reaction of I in tetrahydrofuran solution with two moles of benzyl chloride in the presence of sodium hydride dispersion yielded as the only isolated reaction product a colorless solid, which by elemental analysis was shown to be a tribenzyl derivative. On repeating this experiment under similar conditions with three moles of benzyl chloride we obtained the same reaction product in 50.6% yield.

The infrared spectrum (KBr) of this product displays a peak at 1645 cm.$^{-1}$, characteristic of a carbonyl absorption, but lacks the typical NH band around 3120 cm.$^{-1}$; in contrast to the very broad carbonyl band of the original ketone (I) with a maximum at 1625 cm.$^{-1}$, the corresponding absorption of the tribenzyl ketone is very sharp. These results are consistent with the assignment of a *N*-benzyl ketone structure to this compound. Therefore, only the following four structures Va, b, c, and d have to be discussed for the purpose of assigning the correct locations of the remaining two benzyl groups.


Va Vb Vc Vd

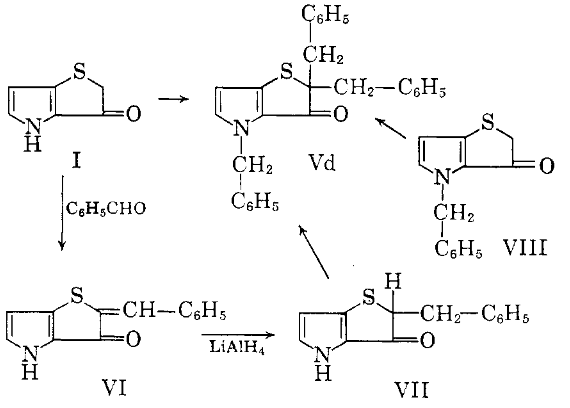
The nuclear magnetic resonance (NMR) spectrum[13] of V proved to be sufficient for the elucidation of the structure (Chart I). The spectrum indicated the presence of both 5- and 6-protons of the pyrrole ring, represented by two doublets (J_{56} = J_{65} = 2.8 c.p.s.) of equal intensity at τ = 3.34 and 4.35; on the basis of these results only structure Vd is indicated for the tribenzyl ketone V, since no other possible structure carrying substituents in the pyrrole ring could give rise to the observed splitting pattern. Additional support for structure Vd is given by the appearance of two superimposed four-line spectra of the methylene groups (AB system) in the 2-position; the protons of each methylene group are nonequivalent. The exact analysis[14] of the AB spectra yields chemical shifts of τ = 6.73 and 6.99 (J = 13 c.p.s.).

CHART I[13]

NMR SPECTRUM OF Vd

Frequency (in τ-values), Intensity ratio	Multiplicity, Coupling Constant (c.p.s.)	Assignment
2.92 (15)	Multiplet	Aromatic protons
3.34 (1)	Doublet (J_{56} = 2.8)	5-Proton
4.35 (1)	Doublet (J_{65} = 2.8)	6-Proton
4.88 (2)	Singlet	*N*-Methylene protons
6.73 (4)	Four-line spectra	Gem.
6.99	(J = 13)	*C*-Methylene protons

Both of the possible intermediate monobenzylation products, VII and VIII, were converted to the tribenzyl ketone. When 2-benzyl-2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (VII),[1] readily accessible by reduction of the benzylidene ketone VI[1] with an excess of lithium aluminum hydride, was treated with two moles of benzyl chloride in the presence of sodium hydride, the tribenzyl ketone was formed in 62% yield; elemental analysis, mixed melting point, and spectral data showed it to be identical



[9] H. D. Hartough and S. L. Meisel, "The Chemistry of Heterocyclic Compounds-Compounds with Condensed Thiophene Rings," Interscience Publishers, Inc., New York, N. Y., 1954, Chap. VI.

[10] D. S. Matteson, thesis, Doctor of Philosophy, University of Illinois, 1957.

[11] W. R. Carpenter, thesis, Doctor of Philosophy, University of Illinois, 1959.

[12] R. J. Tuite, thesis, Doctor of Philosophy, University of Illinois, 1960.

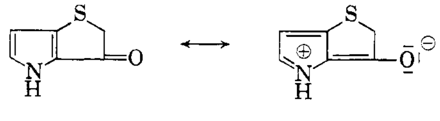
[13] The NMR spectra were recorded by Mr. O. Norton with a Varian Associates high resolution spectrometer (Model V-4300B) working at a frequency of 60 megacycles per second. Spectra were obtained in deuteriochloroform (15% solution) using tetramethylsilane as an internal standard. Chemical shifts are expressed as shielding values τ in parts per million as defined by G. V. D. Tiers [*J. Phys. Chem.*, **62**, 1151 (1958)]. $Si(CH_3)_4$ = 10.00 τ units.

[14] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y., 1959, p. 89.

[15] A. D. Josey, R. J. Tuite, and H. R. Snyder, *J. Am. Chem. Soc.*, **82**, 1597 (1960).

with the product obtained directly from I. Similarly, the benzylation of 4-benzyl-2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (VIII)[15] with two moles of benzyl chloride resulted in the formation of Vd in 79.5% yield.

The low carbonyl reactivity of I and the preference for *N*-benzylation rather than *O*-benzylation suggest a relationship to the structure of an amide, as might be depicted by the zwitterionic form shown.



Treatment of the tribenzyl ketone Vd with 30% hydrogen peroxide in glacial acetic acid afforded 2,2,4-tribenzyl-2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one-1,1-dioxide (IX) in 59% yield. The structure of the sulfone is proved by its infrared spectrum (KBr); a sharp band at 1688 cm.$^{-1}$ is to be attributed to the 3-keto group and two strong absorption bands at 1132 and 1294 cm.$^{-1}$ are characteristic of the sulfone grouping.[16]

The oxidation of thieno[3,2-*b*]pyrrole derivatives with hydrogen peroxide in acetic acid seems to be a method of general application for the formation of sulfones in this series. For instance, under conditions analogous to those described for the preparation of IX the dioxides X and XI derived from I and VI could be isolated in 85% and 57% yield, respectively (see Experimental).

Experimental[17]

2,2,4-Tribenzyl-2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (Vd).—The reaction apparatus used for the preparation of Vd consisted of a 50-ml., three-necked flask equipped with a magnetic stirrer, thermometer, dropping funnel, and reflux condenser with gas inlet tube. The entire system was baked dry and thoroughly flushed with dry nitrogen for about 15 min. The sodium hydride was weighed out rapidly, transferred to the flask and, without interrupting the nitrogen flow, immediately covered with anhydrous solvent. Reactions were carried out as described below.

(A). **From 2*H*,3*H*-Thieno[3,2-*b*]pyrrol-3-one (I).**—A suspension of 0.72 g. (0.015 mole) of 50% sodium hydride dispersion in paraffin oil[18] and 1.89 g. (0.015 mole) of benzyl chloride in 20 ml. of freshly distilled tetrahydrofuran was heated to 60° under a nitrogen atmosphere. The mixture was stirred while a solution of 0.70 g. (0.005 mole) of 2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (I) in 10 ml. of dry tetrahydrofuran was added dropwise over a period of 5 min. so as to maintain a convenient rate of reaction (indicated by hydrogen evolution).

After addition of the ketone was complete, the deep purple-colored reaction mixture was stirred at 55–60° for another 4 hr. The mixture was allowed to cool to room temperature and 2 ml. of methanol was added cautiously to destroy any unchanged sodium hydride. A small amount of precipitated sodium chloride was filtered off, the residue was washed thoroughly with 5 ml. of tetrahydrofuran, and the washings were added to the original filtrate. Evaporation of the solvent under reduced pressure yielded a dark oily residue which solidified upon cooling in the refrigerator at 5° overnight. The crude product was triturated with a mixture of 5 ml. of 95% ethanol and 1 ml. of hexane and again kept at 5° for 45 hr. After this time a pinkish precipitate had formed which was filtered, washed with a small amount of cold ethanol–hexane (1:1), and dried *in vacuo* overnight. The yield of nearly pure Vd was 1.04 g. (50.6%). An analytical sample was prepared by two recrystallizations from 95% ethanol to give pure Vd as colorless, glistening platelets, m.p. 172–174°.

The infrared spectrum[19] (KBr pellet) showed major bands[20] at 3030 w (aromatic CH), 1645 s (C=O), 1495 s, 1453 m (aromatic C=C), 1178 w, 1079 m, 1062 m, 1025 m, 768 m, 758 w, 746 w, 732 m, 714 m, and 698 s cm.$^{-1}$ (monosubstituted aromatic); there was essentially no NH absorption. Bands of medium to strong intensity are also present at 1398, 1323, 1251, 1203, 1196, 993, 964, 916, and 876 cm.$^{-1}$.

Anal. Calcd. for $C_{27}H_{23}NOS$: C, 79.16; H, 5.66; N, 3.42. Found: C, 79.18; H, 5.84; N, 3.32.

(B). **From 2-Benzyl-2*H*,3*H*-thieno-3,2-*b*]pyrrol-3-one (VII).**—2-Benzyl-2*H*,3*H*-thieno[3,2 *b*]pyrrol 3-one (VII) was prepared by reduction of the benzylidene ketone VI with lithium aluminum hydride following the procedure previously described by R. J. Tuite and H. R. Snyder.[1]

A mixture of 0.48 g. (0.01 mole) of 50% sodium hydride dispersion in paraffin oil[18] and 1.26 g. (0.01 mole) of benzyl chloride in 20 ml. of freshly distilled tetrahydrofuran was heated under nitrogen to 55° and stirred rapidly. A solution of 1.10 g. (0.005 mole) of VII in 10 ml. of anhydrous tetrahydrofuran was added dropwise at such a rate that the reaction proceeded smoothly, indicated by evolution of hydrogen. When the addition of VII was complete, the reddish brown reaction mixture was stirred for 4 hr. while the temperature was kept at 55–60° and finally allowed to cool to room temperature. Excess sodium hydride was destroyed by dropwise addition of 3 ml. of ethanol; precipitated sodium chloride was filtered off and was washed several times with small portions of tetrahydrofuran. The combined solutions were concentrated *in vacuo* to give 1.76 g. of a dark brown oil which solidified upon refrigeration overnight.

A mixture of 5 ml. of 95% ethanol and 1 ml. of hexane was added to the crude product, and the solution was again cooled in a refrigerator for 36 hr. The resulting light tan-colored crystals were filtered, washed with a small amount of cold ethanol–hexane (1:2), and dried *in vacuo* overnight, affording 1.01 g. (51%) of Vd, m.p. 171–173°. After concentrating the mother liquor and cooling, an additional 0.22 g. of Vd could be obtained, increasing the yield to 62%.

A mixed melting point determination and infrared spectrum confirmed the identity of the product with that from procedure A.

(C). **From 4-Benzyl-2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (VIII).**—The 4-benzyl-2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one (VIII), m.p. 105–106.5°, was prepared from *N*-benzylpyrrole according to the method of A. D. Josey, R. J. Tuite, and H. R. Snyder.[15]

To a stirred mixture of 0.19 g. (0.004 mole) of 50% sodium hydride dispersion in paraffin oil[18] and 0.50 g. (0.004 mole) of benzyl chloride in 15 ml. of freshly distilled tetrahydrofuran, heated to 60° under a nitrogen atmosphere, was slowly added a solution of 0.46 (0.002 mole) of VIII in 14 ml. of dry tetrahydrofuran over a period of 5 min. The reaction started immediately, evidenced by the evolution of hydrogen, and within a few minutes the color of the reaction mixture turned deep red. After all the ketone had been added, stir-

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[16] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 360.

[17] Melting points are uncorrected. Microanalyses were performed by Mr. J. Nemeth and his associates, University of Illinois.

[18] Metal Hydrides Inc., Beverly, Mass.

[19] The infrared spectra were obtained from a Perkin-Elmer Model 21B spectrophotometer by Mr. Paul E. McMahon and Mr. W. Dalton, University of Illinois.

[20] The abbreviations used in describing the relative intensity of the absorption maxima are: s, strong; m, medium; w, weak.

ring was continued at 55–60° for 4 hr. The mixture was then cooled to room temperature; precipitated sodium chloride was filtered off and washed with a small amount of tetrahydrofuran. Evaporation of the combined solutions *in vacuo* provided 0.81 g. (98%) of crude Vd as a deep red crystalline solid. After treatment with Darco and recrystallization from 95% ethanol, the yield of colorless Vd, m.p. 172.5–174°, was 0.65 g. (79.5%).

The identity of the product with samples of Vd prepared by methods A and B was substantiated by infrared analysis and a mixed melting point determination.

2,2,4-Tribenzyl-2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one-1,1-dioxide (IX).—To a solution of 0.41 g. (1.0 mmole) of Vd in 3 ml. of boiling glacial acetic acid was added 0.5 ml. of 30% hydrogen peroxide and the mixture was refluxed for 5 min. After this period, an additional 0.5 ml. of 30% hydrogen peroxide was added and refluxing was continued for 45 min. The colorless solution was then allowed to cool to room temperature over a period of 2 hr. (slow cooling is necessary in order to avoid precipitation of the reaction product as an oil) and finally was refrigerated overnight. The resulting colorless precipitate was filtered, washed with a small amount of ice water, and dried *in vacuo* overnight. The crude sulfone IX, m.p. 155–157°, weighed 0.19 g. (43.0%). Additional product (0.07 g.) was obtained by concentration of the mother liquor under reduced pressure, bringing the total yield to 0.26 g. (59.0%).

An analytical sample of IX was prepared by two recrystallizations from 95% ethanol yielding colorless, glistening needles, m.p. 159–160°.

The infrared spectrum of IX (KBr pellet) showed characteristic bands at 1688 s (C=O), 1494 m and 1454 (aromatic C=C), 1294 s and 1132 s (sulfone), 1080 m, 1073 m, 773 m, 753 m, 740 m, 732 m, 716 s, and 704 s cm.$^{-1}$ (monosubstituted aromatic).

Anal. Calcd. for $C_{27}H_{23}NO_3S$: C, 73.43; H, 5.25; N, 3.18. Found: C, 73.03; H, 5.24; N, 3.11.

2*H*,3*H*-Thieno[3,2-*b*]pyrrol-3-one-1,1-dioxide (X).—A mixture of 1.39 g. (0.01 mole) of I in 8 ml. of glacial acetic acid and 6.6 ml. of 30% hydrogen peroxide was refluxed for 1 hr. and then kept at room temperature for 60 hr. The crystalline product which separated partially was filtered and dried to give 0.60 g. (35.1%) of sulfone X, m.p. 237–239°. The major amount of reaction product (0.92 g., m.p. 228–232°) was obtained upon evaporation of the acetic acid solution *in vacuo;* total yield 88.8%. A sample recrystallized twice from 95% ethanol afforded colorless needles, m.p. 239–241°. The infrared spectrum of X (Nujol/HCBD) showed characteristic bands at 3240 m (N—H), 1693 s (C=O), 1307 s and 1126 s cm.$^{-1}$ (sulfone).

Anal. Calcd. for $C_6H_5NO_3S$: C, 42.09; H, 2.95; N, 8.18. Found: C, 41.76; H, 2.86; N, 8.07.

2-Benzylidene-2*H*,3*H*-thieno[3,2-*b*]pyrrol-3-one-1,1-dioxide (XI).—To a solution of 1.0 g. (4.4 mmoles) of benzylidene compound VI in 6 ml. of boiling glacial acetic acid was added 1 ml. of 30% hydrogen peroxide. After refluxing for 5 min., an additional 1 ml. of 30% hydrogen peroxide was added, and refluxing was continued for another 30 min. until the color of the solution had changed to light yellow. The reaction mixture was allowed to cool to room temperature and the resulting colorless precipitate was filtered, washed with 15 ml. of water, and dried overnight. The crude sulfone XI, m.p. 233–234°, weighed 0.84 g. (73.7%). An additional 0.13 g. of XI could be obtained by addition of water to the mother liquor, bringing the total yield to 0.97 g. (85%). Two recrystallizations from 95% ethanol afforded colorless needles, m.p. 236–238°.

The infrared spectrum of XI (Nujol/HCBD) showed bands at 3160 m (N—H), 1682 s and 1666 s (C=O), 1308 s and 1142 s cm.$^{-1}$ (sulfone); other major absorptions at 1598 s, 1455 m, 1158 m, 1082 m, 1059 m, 777 s, 736 m, and 682 m cm.$^{-1}$.

Anal. Calcd. for $C_{13}H_9NO_3S$: C, 60.21; H, 3.50; N, 5.41. Found: C, 60.46; H, 3.60; N, 5.45.

Cleavage of Alkyl *o*-Hydroxyphenyl Ethers

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A facile cleavage of the vanillin methoxyl group has been discovered and the reaction has been successfully extended to a number of other alkyl *o*-hydroxyphenyl ethers.

The ready availability of vanillin from lignin has prompted a study of various reactions which could conceivably lead to greater utilization of this material. Foremost among the reactions under study was demethylation, for a facile cleavage of the vanillin methoxyl group would provide a good route to protocatechualdehyde, which is an intermediate with interesting possibilities. A cheap, efficient reaction of this type has been singularly lacking.

The demethylation of vanillin has been effected by the use of dilute hydrochloric acid,[1] by 48% hydrobromic acid in glacial acetic acid,[2] and by phosphorus pentachloride,[3] but the yields were less than 50%. These results were confirmed in the present investigation.

The stability of the vanillin or isovanillin (3-hydroxy-4-methoxybenzaldehyde) structures toward the usual demethylating conditions is illustrated by the behavior of veratraldehyde toward diverse reagents; treatment with boiling 43% hydrobromic acid for three hours gave a 27% yield of isovanillin,[4] while heating at 60° for six hours with anhydrous aluminum chloride and benzene afforded vanillin in 67% yield.[5] Apparently,

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[1] F. Tiemann and W. Haarmann, *Ber.*, **7**, 608 (1874).

[2] R. Stoermer, *Ber.*, **41**, 321 (1908).

[3] K. Freudenberg and W. Heel, *Chem. Ber.*, **86**, 190(1953).

[4] A. Lovecy, R. Robinson, and S. Sugasawa, *J. Chem. Soc.*, 817 (1930).

[5] H. E. Ungnade and E. W. Crandall, *J. Am. Chem. Soc.*, **71**, 2209 (1949).