Anal. Calcd for $C_{17}H_{15}N$: C, 87.51; H, 6.48. Found: C, 87.61; H, 6.63.

Methyl β-(*gem*-Diphenylcyclopropyl)acetate. The nitrile above (2.0 g, 8.5 mmol) in alcohol (15 ml) was added in portions over 15 min to a solution of potassium hydroxide (7.0 g, 0.125 mol) in water (10 ml). After an overnight reflux period, the solution was cooled and acidified. The crude acid so precipitated (1.75 g, 88%) was used directly in the next step. The acid (1.51 g, 6 mmol) in ether was esterified with excess diazomethane. Distillation afforded the ester as an oil (1.20 g, 76%): bp 151–155° (0.4 mm); $n^{28}D$ 1.5602; d_4^{26} 1.242; nmr ($CDCl_3$) δ 3.62 (s, OCH_3); ir (neat) λ 5.84 μ (C=O).

Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.11; H, 6.83.

β-(*gem*-Diphenylcyclopropyl)ethyl Alcohol (9-OH). The acetate ester above (1.2 g, 4.5 mmol) in ether (25 ml) was added dropwise over a 15-min period to lithium aluminum hydride (0.17 g, 4.5 mmol) in ether (25 ml). The solution was stirred under reflux for 3 hr and processed in the usual way. Distillation yielded the alcohol as an oil (1.05 g, 77%): bp 153–158° (0.25 mm); $n^{28}D$ 1.5913; d_4^{26} 1.210; nmr ($CDCl_3$) δ 3.68 (t, $-CH_2OH$); ir (neat) λ 3.02, 9.43–9.69 μ (primary alcohol).

Anal. Calcd for $C_{17}H_{18}O$: C, 85.68; H, 7.61. Found: C, 85.62; H, 7.50.

β-(*gem*-Diphenylcyclopropyl)ethyl Tosylate (9-OTs). Reaction of the alcohol above in pyridine with *p*-toluenesulfonyl chloride in the standard manner[15] gave tosylate **9-OTs** as a colorless solid; mp 95–97° from absolute alcohol; nmr ($CDCl_3$) δ 4.10 (t, $-CH_2OTs$); ir (KBr) λ 8.38, 8.47 μ ($-SO_2-$).

Anal. Calcd for $C_{24}H_{24}O_3S$: C, 73.44; H, 6.16. Found: C, 73.29; H, 6.27.

Solvolysis Studies. A. In Dioxane–Water (80:20 v/v). The kinetic and preparative solvolyses were performed as described earlier.[3] From 4-OTs at 110° for 24 hr there was obtained **bis(*p,p'*-dimethyl)benzhydrylidenenortricyclene (6, 99%)**: mp 103–105° from aqueous methanol; nmr ($CDCl_3$) δ 7.07 (narrow m, ArH), 2.56 (broad s, H-4), 2.33 (s, $ArCH_3$), 1.85–1.26 (m, remaining H's); ir (KBr, prominent absorptions only) λ 6.12, 6.68, 7.32, 7.90, 8.62, 9.25, 9.80, 10.01, 10.69, 11.45, 12.62, 13.10–13.41, 14.25 μ. The spectra were closely analogous to those reported[3] for benzhydrylidenenortricyclene (7).

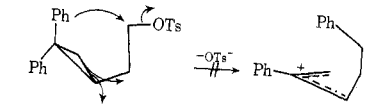
From 5-OTs at 75° for 14 hr there was obtained 8-OH (88%): mp 98–100° from aqueous methanol; nmr ($CDCl_3$) δ 7.65–7.03 (m, ArH), 2.55 (broad s, OH), 2.38 (broad s, H-4), 2.07 (d, exo H-5, $J_{exo-endo}$ = 11 Hz), 1.47 (broad s, H-1), 1.38–0.82 (m, remaining H's); ir (KBr, prominent absorptions only) λ 2.85, 6.81, 7.24, 7.70, 7.81, 8.12, 8.76, 9.35, 10.20, 10.41, 11.25, 12.43–12.72, 14.10–14.55 μ. The spectra were in close analogy to those reported for 2-OH.[3] From tosylate 9-OTs at 130° for 16 hr there was obtained only 9-OH (77%).

B. In Acetic Acid. Tosylate 9-OTs (0.19 g, 0.8 mmol) was heated in dry acetic acid (20 ml) containing sodium acetate (0.04 *M*) at 120° for 46 hr. Reaction work-up yielded only 9-OAc (0.17 g, 87%): nmr ($CDCl_3$) δ 4.05 (t, $-CH_2OAc$, J = 7.5 Hz), 1.91 (s, -OAc); ir neat) λ 5.90 μ (C=O). The nmr total spectrum was in close correspondence to 9-OH and 9-OTs and left no doubt that all three possessed the same parent structure.

Registry No.—3-OTs, 50323-69-8; 3-P, 50323-89-2; 3-OH, 50323-71-2; 3-Δ, 50323-72-3; 4-OTs, 50323-73-4; 4-P, 50323-90-5; 4-OH, 50323-74-5; 4-Δ, 50323-75-6; 5-OTs, 50323-76-7; 5-P, 50323-91-6; 5-OH, 50323-77-8; 5-Δ, 50323-78-9; 6, 50323-92-7; 8-OH, 50323-93-8; 9-OH, 38674-45-2; 9-OTs, 50323-95-0; 9-OAc, 50323-96-1; di-*p*-anisyldiazomethane, 1221-72-3; di-*p*-tolyldiazomethane, 1143-91-5; di-*p*-chlorophenyldiazomethane, 1143-92-6; norbornadiene, 121-46-0; β-(*gem*-diphenylcyclopropyl)acetonitrile, 50323-99-4; β-(*gem*-diphenylcyclopropyl)carbinyl tosylate, 50324-00-0; methyl β-(*gem*-diphenylcyclopropyl)acetate, 38674-44-1.

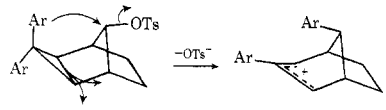
References and Notes

(1) (a) Studies on 3,3-Diaryltricyclo[3.2.1.^{2,4}]octanes. III. (b) Paper II: J. W. Wilt, T. P. Malloy, P. K. Mookerjee, and D. Sullivan, *J. Org. Chem.*, in press.
(2) Taken from portions of the dissertation of J. R. F., 1973.
(3) J. W. Wilt and T. P. Malloy, *J. Org. Chem.*, **38**, 277 (1973).
(4) P. K. Freeman, D. M. Balls, and J. N. Blazevich, *J. Amer. Chem. Soc.*, **92**, 2051 (1970).
(5) The extensive kinetic data for other temperatures and the activation parameters calculated therefrom have been omitted from Table I for the sake of brevity. The interested reader should inquire or consult the dissertation of J. R. F.
(6) The presence of two identical aryl groups in such studies has normally been handled in this fashion. *Cf.* H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).
(7) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).
(8) P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schollkopf, J. Paust, and K. Fellenberger, *J. Amer. Chem. Soc.*, **94**, 133 (1972).
(9) β-(Cyclopropyl)ethyl brosylate itself gave no rearrangement during acetolysis.[10] The same is true for 9-OTs, either in aqueous dioxane or in dry acetic acid. Formolysis of 9-OTs was not investigated, but rearrangement would not be unexpected here. Various substituted β-(cyclopropyl)ethyl brosylates (as well as the parent) do rearrange during solvolysis in this medium.[10,11]
(10) R. R. Sauers and R. W. Ubersax, *J. Org. Chem.*, **31**, 495 (1966).
(11) M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **92**, 6557 (1970).
(12) It might be noted that this solvolysis of 9-OTs involved no proximate aryl migration coupled with cyclopropyl ring opening, as in eq i.



(i)

Such behavior characterizes the solvolysis of the more rigid *exo*-3,3-diaryltricyclo[3.2.1.$0^{2,4}$]oct-*anti*-8-yl tosylates (eq ii).[1b,13]



(ii)

(13) J. W. Wilt and T. P. Malloy, *J. Amer. Chem. Soc.*, **92**, 4747 (1970).
(14) H. M. Walborsky, L. Barasch, A. E. Young, and F. J. Impastato, *J. Amer. Chem. Soc.*, **83**, 2517 (1961).
(15) R. S. Tipson, *J. Org. Chem.*, **9**, 235 (1944).

Novel Products from Oxidation of Hindered Phenols with One-Electron-Transfer Oxidants

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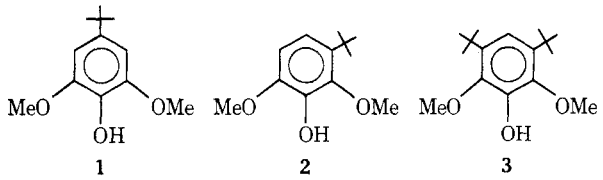
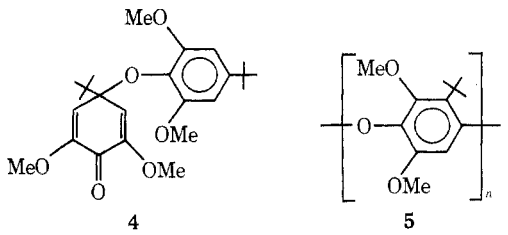
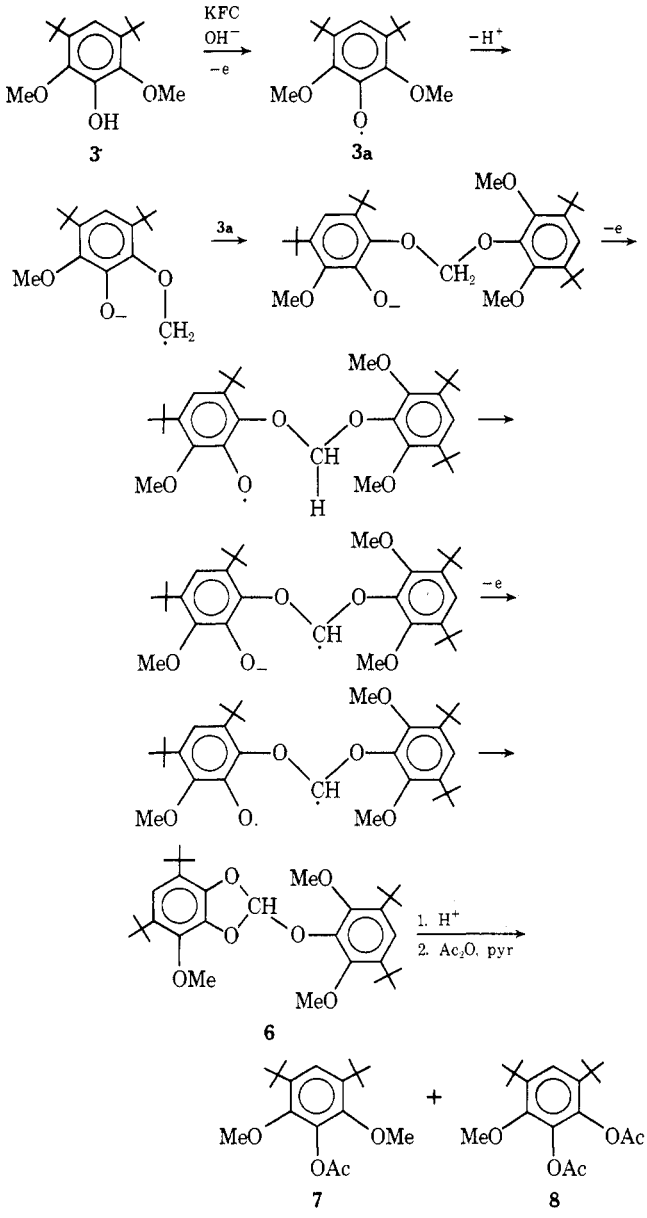
As part of a study of the alkaline oxidation of lignin[2] it was of interest to determine the nature of the products resulting from the oxidation of model phenols **1**, **2**, and **3** by one-electron-transfer reagents such as potassium ferricyanide, lead dioxide, silver oxide, etc. The products of such oxidations are usually dimers and oligomers formed by the coupling of intermediate phenoxy radicals[3] and, indeed, phenol **1** is known to give the quinol ether **4** on treatment with potassium ferricyanide or silver oxide.[4] We found compound **2** to behave in a similar manner, giving, on oxidation by ferricyanide in a benzene–aqueous potassium hydroxide system, an 85% yield of the polyphenylene ether **5** (mol wt *ca.* 2900). The polymer **5**, like **4**, was formed by coupling of the initially produced phenoxy radicals.





Phenol **3** reacted sluggishly under the same conditions and, although the benzene layer showed the intense emer-

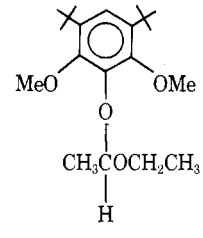
ald green color characteristic of 2,6-dimethoxy-substituted phenoxy radicals,[5] only a few per cent of **3** was altered after 5 hr at room temperature. However, at 70° phenol **3** was in 5 hr completely converted to a complex mixture of products, only one of which was present in significant quantity (26%). This product was characterized as the orthoformate **6** on the basis of analytical and spectral data (see Experimental Section). The structural assignment was confirmed by mild acid hydrolysis of **6** followed by acetylation of the reaction mixture to give the expected phenol acetate **7** (90%), identified by comparison with authentic samples obtained by acetylation of phenol **3**, and catechol diacetate **8** (76%), identified by analytical and spectral data.



This formation of the orthoformate represents a course of reaction which to our knowledge has not previously been reported in the area of phenol oxidation. Coupling between two molecules of phenol has occurred, but not in the usual manner where two mesomeric forms of a phenoxy radical couple with each other. Rather, coupling has occurred between one phenoxy radical and one secondarily formed radical at a methoxyl carbon of another phenol molecule. The same process occurs a second time, albeit intramolecularly, resulting in closure of the five-membered ring.

Apparently, this behavior is due to the bulkiness of the *tert*-butyl groups and probably methoxyl groups as well, which hinder the coupling of one phenoxy radical with an annular position on another. Thus, the reaction follows the normally unfavorable course of hydrogen abstraction from a neighboring methoxyl group, forming a radical which is sufficiently unhindered to couple with a phenoxy radical.

This explanation was further substantiated by repeating the oxidation with lead dioxide, using diethyl ether as solvent instead of benzene. The acetal **9** was isolated in 56% yield, demonstrating the ability of the phenoxy radical to abstract a secondary hydrogen atom from the ether and then couple with this radical. No orthoformate (**6**) was detected by tlc, reflecting as expected the preference for hydrogen abstraction from a secondary carbon, the ether, as opposed to a primary carbon, the methoxyl group, although the much larger concentration of diethyl ether in the reaction mixture undoubtedly also contributes to the overwhelming formation of acetal **9**.



9

Experimental Section

General. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra (ir) were obtained on a Perkin-Elmer Model 521 infrared spectrophotometer. Ultraviolet (uv) and visible spectra were obtained with a Cary Model 15 ultraviolet–visible spectrophotometer. Nuclear magnetic resonance (nmr) spectra were obtained with a Varian Associates Model HA-100 spectrometer using chloroform-*d* as solvent and tetramethysilane as an internal reference. Mass spectra were obtained using either an AEI MS-12 or an AEI MS-902 double-focusing spectrometer. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Ga.

3-*tert*-Butyl-2,6-dimethoxyphenol (2). A petroleum ether (bp 80–110°) solution containing 10.0 g (0.065 mol) of 2,6-dimethoxyphenol and 11.0 g (0.15 mol) of *tert*-butyl alcohol was stirred vigorously and heated to 50°. To this solution, 2 ml of concentrated sulfuric acid was added dropwise over a 0.5-hr period and the reaction solution was then maintained at 50° for another 2.5 hr. After cooling, the reaction mixture was washed twice with 50-ml portions of water, dried over sodium sulfate, and concentrated under reduced pressure.

The residue was placed on a 5.0 × 25.0 cm column of Grace activated silica gel (100–200 mesh) and eluted with benzene. Evaporation of the collected benzene fraction gave 6.20 g (46%) of 3-*tert*-butyl-2,6-dimethoxyphenol: mp 52–53° from 95% ethanol; nmr δ 1.32 (9 H, s, *tert*-butyl), 3.79 (3 H, s, methoxyl), 3.90 (3 H, s, methoxyl), 5.50 (1 H, s, phenolic hydroxyl), 6.50 (1 H, d, J = 9.0 Hz, aromatic), 6.74 (1 H, d, J = 9.0 Hz, aromatic).

Anal. Calcd for $C_{12}H_{18}O_3$: C, 68.57; H, 8.57. Found: C, 68.54; H, 8.61.

3,5-Di-*tert*-butyl-2,6-dimethoxyphenol (3). To a 100-ml three-necked flask equipped with a condenser and a bubble tube were added 7.0 g (0.045 mol) of 2,6-dimethoxyphenol and 12 ml of benzene. This mixture was heated to reflux and isobutylene was bubbled in throughout the entire reaction. Under vigorous stirring, a total of 1 ml of concentrated sulfuric acid was added dropwise over the first 2 hr of reaction. After addition of the sulfuric acid, refluxing was continued for 4.5 hr.

Upon cooling, the desired compound began to crystallize from solution; therefore the reaction mixture was diluted with 100 ml of benzene, washed with two 50-ml portions of water, and dried over sodium sulfate. The benzene was removed under vacuum to leave a residue of crystals and some oil. Recrystallization of the residue from 95% ethanol yielded 6.40 g (53%) of 3,5-di-*tert*-butyl-

2,6-dimethoxyphenol: mp 138–139.5°; nmr δ 1.35 (18 H, s, two *tert*-butyl), 3.84 (6 H, s, two methoxyl), 5.26 (1 H, s, phenolic hydroxyl), 6.79 (1 H, s, aromatic).

Anal. Calcd for $C_{16}H_{26}O_3$: C, 72.18; H, 9.77. Found: C, 72.15; H, 9.82.

Oxidation of 3-*tert*-Butyl-2,6-dimethoxyphenol (2) with Alkaline Potassium Ferricyanide. A solution of 1.20 g of the phenol **2** in 75 ml of benzene was stirred vigorously with a solution of 6.00 g of potassium ferricyanide and 5.60 g of potassium hydroxide in 50 ml of water at 25° for 5 hr. The benzene solution was washed twice with water, dried over sodium sulfate, and evaporated to dryness, and the residue was taken up in chloroform and precipitated with methanol. The precipitate was filtered and dissolved and reprecipitated twice more to give 1.01 g (*ca.* 85%) of the polyphenylene polymer **5**.

The lightly cream colored polymer softened and melted over the range 140–160°. The osmometrically determined molecular weight was 2923 using chloroform as solvent and measurements at three different concentrations. The ir (KBr) showed the following major peaks: 2950 (s), 1595 (s), 1480 (s), 1435 (s), 1383 (s), 1200 (s), 1108 (s), 1060 cm^{-1} (s). The nmr showed peaks at δ 1.57 (s, *tert*-butyl), 3.37 and 3.74 (both s, two different methoxyls), and 5.95 (s, aromatic) in the approximate ratio 9:3:3:1, respectively. One further small peak at δ 1.35 is probably due to the *tert*-butyl group on the terminal unit of the polymer. None of these peaks disappeared upon the addition of deuterium oxide to the sample.

Anal. Calcd for $C_{12}H_{16}O_3$: C, 69.23; H, 7.69. Found: C, 68.47; H, 7.65.

Oxidation of 3,5-Di-*tert*-butyl-2,6-dimethoxyphenol (3) with Alkaline Potassium Ferricyanide. A solution of 1.20 g of the phenol in 75 ml of benzene was stirred vigorously with a solution of 6.00 g of potassium ferricyanide and 5.60 g of potassium hydroxide in 50 ml of water at 70° for 5 hr. The benzene solution was washed twice with water, dried over sodium sulfate, and evaporated to dryness. The residue, a red-brown oil, was dissolved in 8 ml of acetone and allowed to stand in the refrigerator overnight. The precipitated product was filtered and the filtrate was diluted with 15 ml of 95% ethanol and filtered again to remove the second batch of precipitate. The combined precipitates were recrystallized from acetone to give 0.318 g (26%) of the orthoformate **6**: mp 152–153°; ir (KBr) 2960 (s), 1595 (w), 1485 (s), 1418 (s), 04 (s), 1358 (m), 1300 (m), 1230 (s), 1105 (s), 1070 (s), 1008 (s), 990 cm^{-1} (s); nmr δ 1.32 (36 H, narrowly split d, four *tert*-butyl), 3.80 (6 H, s, two methoxyl), 3.96 (3 H, s, methoxyl), 6.77 (1 H, s, trioxymethine), 7.03 (2 H, s, aromatic); none of these peaks disappears upon addition of deuterium oxide to the sample; nuclidic mass, 528.3389 (calcd for $C_{32}H_{48}O_6$, 528.3450); mass spectrum *m/e* (rel intensity) 528 (2.7), 513 (1.0), 266 (1.5), 265 (2.7), 264 (18.8), 263 (100.0), 251 (3.6).

Anal. Calcd for $C_{32}H_{48}O_6$: C, 72.85; H, 9.10. Found: C, 72.67; H, 9.10.

The structure of the orthoformate was confirmed by hydrolysis and subsequent acetylation of the products. Thus, 0.280 g of orthoformate was hydrolyzed in 20 ml of 95% ethanol–chloroform (1:1) containing 5 drops of concentrated hydrochloric acid. The solution was warmed on a steam bath for 1 hr and diluted with water, and the chloroform layer was removed. After drying over sodium sulfate, the chloroform was removed and the residue was acetylated with pyridine–acetic anhydride (1:1). After 24 hr the volatiles were removed under vacuum and ptlc of the residue using benzene–hexane (1:1) gave 0.127 g (76%) of the catechol diacetate **8** and 0.149 g (90%) of the phenol acetate **7**.

The phenol acetate, mp 144–145° from hexane, was identified by comparison of its melting point, mixture melting point, and ir with those of authentic material which was obtained by acetylation of phenol **3**.

Anal. Calcd for $C_{18}H_{28}O_4$: C, 70.10; H, 9.10. Found: C, 70.08; H, 9.19.

The catechol diacetate had mp 130–132° from hexane; ir (KBr) 2960 (m), 1770 (s), 1410 (s), 1200 (s), 1155 (s), 1062 cm^{-1} (s); nmr δ 1.27 and 1.32 (9 H each, both s, two *tert*-butyl), 2.22 and 2.24 (3 H each, both s, two acetyl), 3.77 (3 H, s, methoxyl), 7.21 (1 H, s, aromatic).

Anal. Calcd for $C_{19}H_{28}O_5$: C, 67.90; H, 8.34. Found: C, 68.01; H, 8.31.

Oxidation of 3,5-Di-*tert*-butyl-2,6-dimethoxyphenol (3) with Lead Dioxide in Ether. To a vigorously stirred suspension of lead dioxide (5.0 g) in 100 ml of dry diethyl ether, 2.45 g of the phenol was added. The reaction mixture was maintained at 25° for 4 hr and then filtered to remove the lead dioxide. The solution was washed with two 50-ml portions of water, dried over sodium sulfate, and evaporated to dryness. After tlc on silica gel using benzene–hexane (1:1), a compound was obtained as a partially crystallized oil. The oil was vacuum distilled to give 1.40 g (*ca.* 56%) of the acetal **9** which crystallized in the receiver: mp 36.3°; nmr δ 1.01 (3 H, t, methyl), 1.29 (18 H, s, *tert*-butyl), 1.44 (3 H, d, J = 5 Hz, methyl), 3.49 (2 H, m, methylene), 3.84 (6 H, s, methoxyl), 5.24 (1 H, q, J = 5 Hz, acetal), 6.94 (1 H, s, aromatic); mass spectrum *m/e* 338 (molecular ion), 266, 251, 235, 221, 166, 73, 45.

Anal. Calcd for $C_{20}H_{34}O_4$: C, 71.00; H, 10.07. Found: C, 71.16; H, 10.04.

Registry No.—**2**, 49746-11-4; **3**, 49746-12-5; **5**, 50322-12-8; **6**, 49746-13-6; **8**, 49746-14-7; **9**, 49746-15-8; 2,6-dimethoxyphenol, 91-10-1.

References and Notes

(1) (a) Former graduate student, Department of Wood and Paper Science, North Carolina State University; (b) Associate Professor of Wood and Paper Science; (c) Professor of Chemistry.
(2) R. C. Eckert, H-m. Chang, and W. P. Tucker, *Tappi*, **56** (6), 134 (1973).
(3) H. Musso in "Oxidative Coupling of Phenols," W. I. Taylor and A. R. Battersby, Ed., Marcel Dekker, New York, N. Y., 1967, pp 1–82.
(4) C. J. R. Adderley and F. R. Hewgill, *J. Chem. Soc. C*, 1438 (1968).
(5) C. Steelink, *Advan. Chem. Ser.*, **59**, 51 (1966).

A Facile Synthesis of 2-Aminonicotinaldehyde

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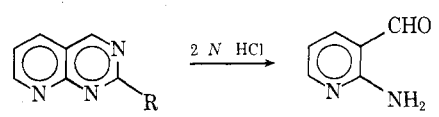
Aromatic *o*-aminoaldehydes are valuable starting materials for a wide variety of *N*-heterocyclic compounds. However, in spite of their seemingly simple array of functionality, they are difficult to synthesize and in fact relatively few compounds possessing this pair of functions have been described. In connection with our investigation of the Friedländer condensation as a synthetic method for the linear annellation of pyridine rings, large quantities of 2-aminonicotinaldehyde (**2**) were required.

The preparation of **2** had previously been accomplished by a multistep synthesis starting from 2-amino-3-picoline,[1,2] but this proved to be a tedious procedure with substantial loss of material upon purification. Therefore, an alternate route to **2** was sought. An attractive possibility was to employ the pyrimidine moiety of pyrido[2,3-*d*]pyrimidine (**1a**) as a source for the *o*-aminoaldehyde functionality. Covalent hydration of this heterocyclic system makes it susceptible to hydrolytic ring opening of the pyrimidine nucleus.[3] This reaction is of no synthetic value, since **1a** was synthesized from **2**.[3] However, sulfamation of nicotinamide with ammonium sulfamate[4] readily provided us with 2-(3′-pyridyl)pyrido[2,3-*d*]pyrimidine (**1b**) in 50% yield together with nicotinonitrile.



1a, R = H
b, R = 3-pyridyl

2

As anticipated, hydrolysis of this crude reaction mixture in 2 *N* HCl gave **2** and nicotinic acid. Separation was readily accomplished by extraction with ether, yielding pure **2** in 50% yield (based on nicotinamide). Proof of structure was obtained by spectroscopic data, by comparison with an authentic sample,[1] and by its conversion into derivatives of 1,8-naphthyridine by Friedländer condensation.[5]