

### Experimental Section

A typical phenol oxidation by solid  $\text{KMnO}_4$  was carried out in the following manner. 2,6-Diisopropylphenol (2.14 g, 12 mmol) in 25 mL of chloroform was stirred magnetically at 51 °C with 7.6 g (48 mmol) of solid  $\text{KMnO}_4$  (Baker reagent used as received). After 1.5 h the reaction was judged complete from the disappearance of the phenol peak in a gas chromatogram. The inorganic solids were then removed by filtration, and the resulting filtrate was evaporated to dryness under reduced pressure. This gave a 95% yield of 3,3',5,5'-tetraisopropylidiphenoquinone with a melting point of 202–204 °C (lit.<sup>16</sup> mp 202–203 °C) and reasonable NMR spectra.<sup>10</sup> The corresponding tetramethyl and tetra-*tert*-butyl compounds were prepared in 92% and 97% yields, respectively; the former had a "shrinking" point of 205 °C in agreement with the literature,<sup>16</sup> and the latter melted at 241–241.5 °C (lit.<sup>16</sup> mp 245–247 °C). NMR spectra of all products were reasonable.<sup>10</sup> Oxidation of 2,6-dimethylphenol by solid  $\text{K}_2\text{MnO}_4$  (Aldrich, used as received) was carried out in a manner identical with the  $\text{KMnO}_4$  reactions, but the product was a 90% yield of poly(2,6-dimethyl-1,4-phenylene oxide) with a mp >300 °C and with an NMR spectrum identical with that reported in the literature.<sup>10</sup>

**Acknowledgment.** This work was supported by the National Institutes of Health.

**Registry No.**  $\text{KMnO}_4$ , 7722-64-7;  $\text{K}_2\text{MnO}_4$ , 10294-64-1; 2,6-diisopropylphenol, 2078-54-8; 3,3',5,5'-tetraisopropylidiphenoquinone, 2178-51-0; 2,6-dimethylphenol, 576-26-1; 3,3',5,5'-tetramethylidiphenoquinone, 4906-22-3; 2,6-di-*tert*-butylphenol, 128-39-2; 3,3',5,5'-tetra-*tert*-butylidiphenoquinone, 2455-14-3; poly(2,6-dimethyl-1,4-phenylene oxide), 25134-01-4.

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### A Polymer-Bound 4-Aminopyridine: Synthesis and Reactivity

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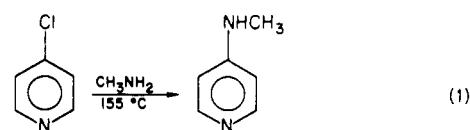
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For over a decade 4-(dimethylamino)pyridine (DMAP) has experienced widespread use as an acylation and alkylation catalyst.<sup>1,2</sup> The efficacy of DMAP is illustrated by kinetic work of Litvinenko et al.<sup>3</sup> who showed that benzoylation of *m*-chloroaniline proceeds  $10^4$  times faster with DMAP than with pyridine. DMAP is the catalyst of choice for acylating sterically hindered alcohols such as 1-methylcyclohexanol.<sup>4</sup> DMAP has also found applications in silylations,<sup>5</sup> phosphorylations,<sup>6</sup> condensations,<sup>7</sup> and polymerizations<sup>8</sup> to name a few.

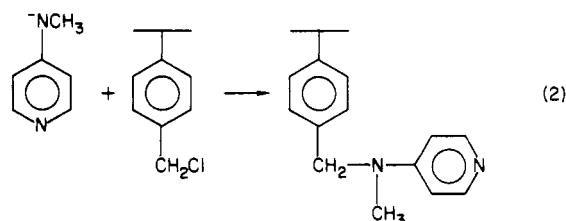
We report herein the behavior of a 4-aminopyridine grouping rendered insoluble via attachment to a poly-

styrene backbone. Potential advantages of the polymer include a simple reaction workup (i.e., removal of the catalyst by filtration), recycling of "spent" (protonated) catalyst, and the development of flow systems. No doubt it was just these advantages that led to the recent development of a host of immobilized reagents and catalysts.<sup>9</sup> To our knowledge, only three polymeric forms of (di-alkylamino)pyridine have been published. Klotz et al.<sup>10</sup> covalently linked 3-[*N*-methyl-*N*-(4-pyridyl)amino]-propionic acid to laurylated poly(ethylenimine). Shinkai et al.<sup>11</sup> obtained catalytic beads by reacting polystyrene bearing (methylamino)methyl substituents with 4-chloropyridine at 150 °C for 4 days. And Tomoi et al.<sup>12</sup> polymerized a styrene derivative functionalized at the para position with an aminopyridine unit. Our method constitutes the fourth, and perhaps the simplest, approach to the problem.

The polymer was prepared in a two-step sequence beginning with the formation of 4-(methylamino)pyridine according to eq 1. Since replacing the Cl by N requires moderately severe conditions, it is best performed with a simple amine as opposed to a polymeric amine used in the Shinkai procedure.<sup>11</sup> 4-(Methylamino)pyridine was then



attached to a polymer by means of an  $\text{S}_{\text{N}}2$  displacement on commercial poly(vinylbenzyl chloride) (eq 2). Prior to the coupling, the pyridine was converted into its anion, with the aid of NaH, in order to ensure attack by the substituent nitrogen alone.<sup>13,14</sup>



Our polymeric product, a fine yellow powder, was assayed by combustion analysis and by a nonaqueous titration. The former indicated an 82–89% nitrogen yield assuming one nitrogen per repeat unit; the latter gave yields near 75%, in rough agreement. A less heavily loaded polymer, namely one with only one catalytic group for every six styrene monomers, displayed too little reactivity to be useful. NMR characterization of the polymers was not possible, owing to their insolubility in the usual solvents.

Seven different polymer-catalyzed reactions were examined:

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(2) Scriven, E. F. V. *Chem. Soc. Rev.* 1983, 12, 129.

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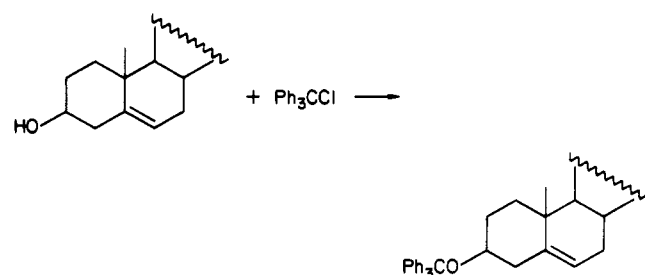
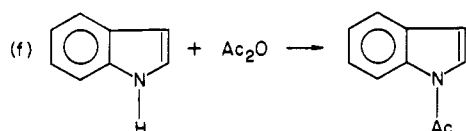
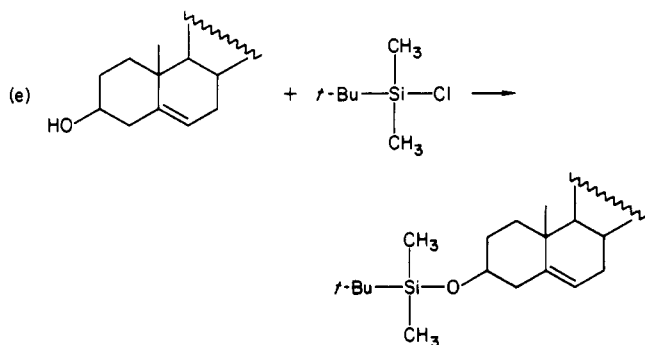
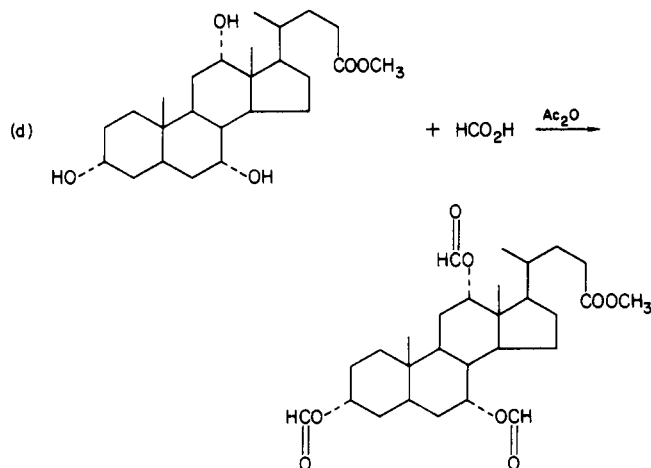
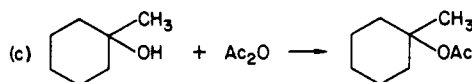
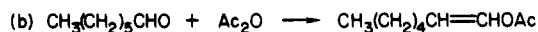
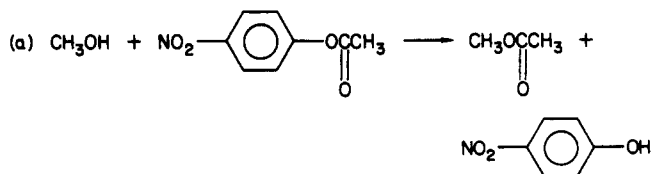
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The isolated yields of these reactions, as well as those from reactions catalyzed by monomeric DMAP under equivalent conditions, are presented in Table I. Although the DMAP reactions are seen to be more efficient (at least under one given set of experimental parameters), the differences are often not great. The polymeric catalyst might well be preferred if simple workup and catalyst recyclability are important considerations.

### Experimental Section

**4-(Methylamino)pyridine.** This compound was synthesized according to the procedure of Wibaut and Broekman.<sup>19</sup> Two or

**Table I. Comparison of Yields from Seven Reactions Catalyzed by DMAP and Polymer<sup>a</sup>**

reacn	catal	yield, %	
		lit. (ref)	this work
1	polymer		100
2	DMAP	64 (15)	60
3	polymer		59
3	DMAP	86 (4)	83
4	polymer		45
4	DMAP	97 (16)	98
5	polymer		82
5	DMAP	68 (5)	64
6	polymer		48
6	DMAP	89 (17)	64
7	polymer		60
7	DMAP	68 (18)	79
	polymer		63

<sup>a</sup> All yields are isolated yields except that of reaction 1, where formation of product was followed spectrophotometrically. Equivalent conditions were used for the corresponding DMAP- and polymer-catalyzed reactions, and no attempt was made to optimize either of them.

three crystallizations from ether produced a white solid, mp 122–123 °C, in 50% yield.

**Synthesis of Polymer.** Sodium hydride (0.34 g, 14.2 mmol, Aldrich, 60% dispersion) was mixed with 5 mL of tetrahydrofuran (dried over sodium) in a magnetically stirred three-neck flask under a blanket of nitrogen. (*N*-Methylamino)pyridine (0.86 g, 7.9 mmol), dissolved in 15 mL of dry tetrahydrofuran by sonication, was injected through a septum into the reaction flask. The mixture was heated to reflux for 1 h and cooled, whereupon 0.90 g poly(vinylbenzyl chloride) (Aldrich, 60/40 mixture of 3- and 4-isomers) was added. Within 5 min after applying modest heat (50 °C), a gummy material appeared, which prevented further magnetic stirring. If, after addition of the polymer the gum did not form, the temperature was increased slightly. After removing the dark brown product, we placed it in a vacuum desiccator for drying until it could be cut into small pieces. The product was then dried further and ground into a powder. The powder was washed with 0.01 N NaOH (2 × 15 mL) and with water until the water was neutral. Drying under reduced pressure overnight gave the final product, which was stored in a desiccator.

**Analysis of Polymer.** Perchloric acid (8.6 mL, 72%) in glacial acetic acid (800 mL) and acetic anhydride (20 mL) were mixed and standardized with potassium acid phthalate according to Day and Underwood.<sup>20</sup> This was used as a titrant for 20-mg samples of polymer in 15 mL of glacial acetic acid. End points were reached when the indicator, methyl violet, remained blue for greater than 2 min.

**Reactions.** Reactions were carried out as described in the references cited in Table I. An illustrative procedure is given here for the acylation of 1-methylcyclohexanol. 1-Methylcyclohexanol (11.4 g, 0.10 mol), acetic anhydride (20 mL, 0.21 mol), DMAP (0.50 g, 4.1 mmol) or polymer (0.92 g, 4.1 mmol), and triethylamine (20 mL, 0.14 mol) were stirred magnetically for 16 h at room temperature. If polymer was used as the catalyst, it was removed by gravity filtration at this point. Water (50 mL) was added either to the reaction mixture (in the case of DMAP) or to the filtrate (in the case of polymer) and the product extracted with benzene. The benzene was washed with 1 N HCl (2 × 50 mL), 2 N NaOH (2 × 50 mL), and water, after which it was dried over MgSO<sub>4</sub>. The benzene was removed on a rotary evaporator, giving a yellow liquid, which was distilled under vacuum (using a 200 mL boiling flask and microporous boiling chips owing to a "bumping" problem). The product, with correct IR and NMR spectra, was obtained as a colorless liquid in the yields shown in Table I.

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(20) Day, R. A.; Underwood, A. L. "Quantitative Analysis", 4th ed.; Prentice-Hall: New York, 1980; p 572.

**Acknowledgment.** This work was supported by the Army Research Office.

**Registry No.** CH<sub>3</sub>OH, 67-56-1; *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OAc, 830-03-5; CH<sub>3</sub>OAc, 79-20-9; *p*-O<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>OH, 100-02-7; CH<sub>3</sub>(CH<sub>2</sub>)<sub>5</sub>CHO, 111-71-7; CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>CH=CHOAc, 35468-97-4; 4-(methylamino)pyridine, 1121-58-0; *p*-(chloromethyl)styrene polymer, 29296-32-0; 1-methylcyclohexanol, 590-67-0; 1-methylcyclohexyl acetate, 16737-30-7; indole, 120-72-9; 1-acetylindole, 576-15-8; methyl (3 $\alpha$ ,7 $\alpha$ ,12 $\alpha$ )-trihydroxy-5 $\beta$ -cholan-24-oate, 1448-36-8; methyl (3 $\alpha$ ,7 $\alpha$ ,12 $\alpha$ )-triaceoxy-5 $\beta$ -cholan-24-oate, 33744-75-1; 3 $\beta$ -cholest-5-en-3-ol, 57-88-5; 3 $\beta$ -cholest-5-en-3-ol TBDMS ether, 57711-50-9; 3 $\beta$ -(triphenylmethoxy)cholest-5-ene, 51414-56-3.

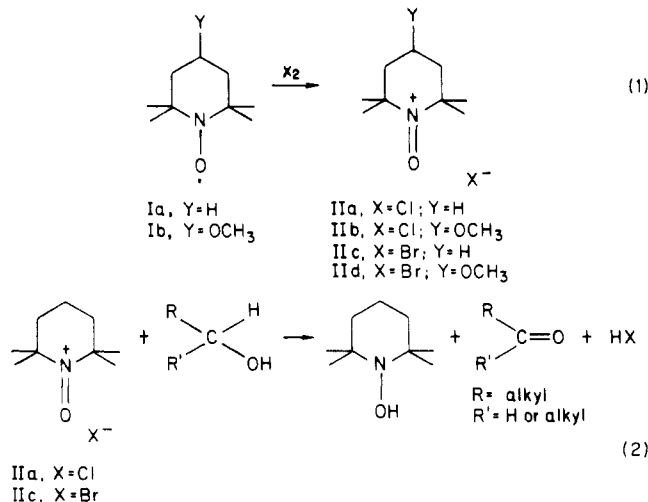
## Oxidation of Diols with Oxoammonium Salts

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2,2,6,6-Tetramethylpiperidine-1-oxyl (Ia) known as a stable radical<sup>1</sup> can be easily oxidized by chlorine or bromine to obtain the corresponding oxoammonium salts (IIa)<sup>2</sup> and (IIc)<sup>3</sup> (eq 1). As shown in eq 2, primary or secondary



alcohols are oxidized to the corresponding carbonyl compounds with IIa or IIc, respectively, and oxoammonium salt itself is reduced to hydroxylamine in the oxidation of alcohols.<sup>4,5</sup> The most recent report of selective oxidation of alcohols by M. F. Semmelhack<sup>6</sup> involves this oxoammonium ion as a mediator for the electrolytic oxidation.

Some oxidative methods are available for the selective oxidation of diols.<sup>7</sup> A most typical reagent for the oxidative lactonization is silver carbonate on Celite<sup>8</sup> (Fetizon's reagent). However, this oxidation requires the large excess of silver carbonate. Other methods using ruthenium<sup>9,10</sup> or

- (1) Rozantsev, E. G.; Neiman, M. B. *Tetrahedron* 1964, 20, 131.
- (2) Golubev, V. A.; Zhdanov, R. I.; Rozantsev, E. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1970, 184.
- (3) Zhdanov, R. I.; Golubev, V. A.; Rozantsev, E. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* 1970, 186.
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- (6) Semmelhack, M. F.; Chou, C. S.; Cortes, D. A. *J. Am. Chem. Soc.* 1983, 105, 4492.
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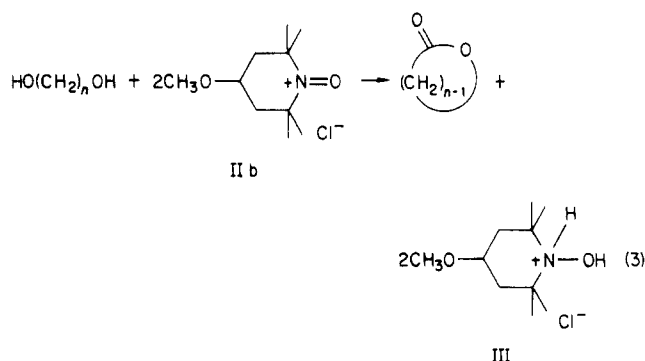
Table I. Oxidation of 1, $\omega$ -Diols with IIb<sup>a</sup>

diol	product	time, min	yield, <sup>b</sup> %	bp, °C/mmHg
HO(CH <sub>2</sub> ) <sub>3</sub> OH		60	trace	
HO(CH <sub>2</sub> ) <sub>4</sub> OH		10	100 (81) <sup>c</sup>	90/24
HO(CH <sub>2</sub> ) <sub>5</sub> OH		30	61 (40) <sup>c</sup>	80/4
HO(CH <sub>2</sub> ) <sub>6</sub> OH		60	trace	

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub> at 25 °C. <sup>b</sup> GLC yield based on the starting alcohol. <sup>c</sup> Isolated yield.

bromine with nickel(II) benzoate<sup>11</sup> or alkanooates<sup>12</sup> have been reported.

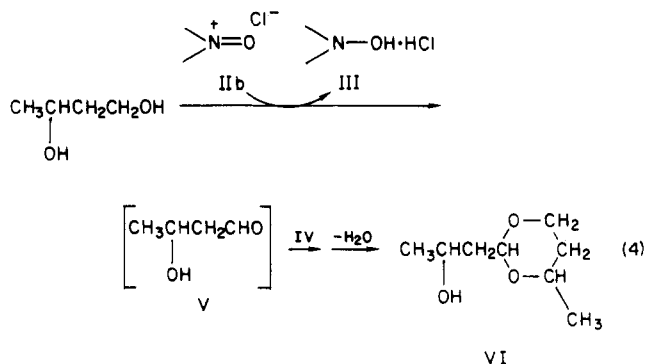
We now report the oxidation of diols with oxoammonium salt IIb under mild conditions. As shown in eq 3, 1, $\omega$ -diols



were oxidized with IIb (2 equiv) in methylene chloride at room temperature to afford the corresponding lactones, and IIb was reduced to the corresponding hydroxylamine hydrochloride (III). As shown in Table I, the oxidation is successful for 1,4-butanediol to afford  $\gamma$ -butyrolactone quantitatively. However,  $\delta$ -valerolactone is obtained in good yield, and the lactones of four- or seven-membered rings are detectable as the trace by GLC.

As shown in Table II, 1,4-pentanediol containing primary and secondary hydroxyl groups was oxidized by IIb to give  $\gamma$ -valerolactone in 83% yield and no other carbonyl compounds such as hydroxy ketone or aldehyde were obtained. This result might support the selective oxidation of primary alcohol by IIb.

1,3-Butanediol (IV) was also oxidized by IIb to give acetal VI in quantitative yield (eq 4). As shown in Table



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