matographs. The expert assistance of E. Demgar, Hercules, Inc., in obtaining NMR spectra is gratefully acknowledged. Special thanks are due to William H. Bunnelle for invaluable discussions.

Registry No. 2-Ethynylcyclohexanol ethyl vinyl ether acetal (isomer 1), 97690-73-8; 2-ethynylcyclohexanol ethyl vinyl ether acetal (isomer 2), 97747-34-7; 2-ethynylcyclohexanol (methoxyethoxy)methyl ether, 97690-74-9; 2-ethenylcyclohexanol ethyl vinyl ether acetal (isomer 1), 97690-75-0; 2-ethenylcyclohexanol ethyl vinyl ether acetal (isomer 2), 97747-35-8; 2-ethenylcyclohexanol (methoxyethoxy)methyl ether, 97690-76-1; (2A,4AA,8AB)-4-chloro-2-methyl-4a,5,6,7,8,8a-hexahydro-2*H*-benzopyran, 97690-77-2; *trans*-4-chloro-4a,5,6,7,8,8a-hexahydro-2*H*-benzopyran, 97690-78-3; (2A,4A,4AA,6AB)-4-chloro-2-methyloctahydro-2-*H*-benzopyran, 97690-79-4; (4A,4AA,8AB)-4-chlorooctahydro-2*H*-benzopyran, 97690-80-7; $TiCl_4$, 7550-45-0.

Comparison of Phenolic Couplings on $KMnO_4$ and K_2MnO_4 Surfaces

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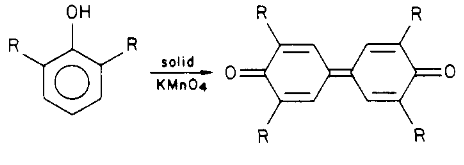
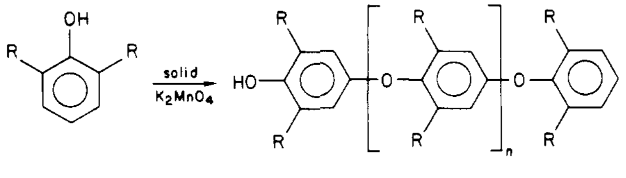
Received December 11, 1984

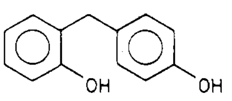
Several synthetically exploitable oxidations using solid permanganate systems have been recently reported. Examples include zinc permanganate on silica gel (tetrahydropyran to valerolactone, 69%),[1] potassium permanganate on molecular sieves (benzyl alcohol to benzaldehyde, 80%),[2] solid potassium permanganate with ultrasonication (1-octanol to octanoic acid, 81%),[3] potassium permanganate on bentonite (1-octen-3-ol to 1-octen-3-one, 92%),[4] and crystalline sodium permanganate (5α-androstan-17β-ol to 5α-androstan-17-one, 84%).[5] Easy workup ranks as the most valuable feature of such oxidations; a satisfactory state of purity is often achieved by mere filtration of solids and removal of solvent. The heterogeneous oxidations also manifest a selectivity not present with corresponding solution systems. Whereas olefins, for example, are inert toward solid permanganate,[6] carbon–carbon double bonds oxidize almost instantly in aqueous permanganate.[7]

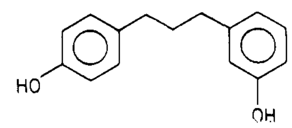
We report here an interesting reactivity difference between solid potassium permanganate ($KMnO_4$) and solid potassium manganate (K_2MnO_4) in the oxidative coupling of phenols.[8] Thus, $KMnO_4$ oxidation of 2,6-dimethylphenol, 2,6-diisopropylphenol, and 2,6-di-*tert*-butylphenol (12 mmol phenol, 48 mmol $KMnO_4$, 25 mL $CHCl_3$, 51 °C, 1.5 h) gave the corresponding diphenoquinone in >90% yield. This far exceeds the yields listed for other transition-metal compounds (e.g., Ag^{II}, 32%; Cu^{II} + $S_2O_8^{2-}$, 47%; MnO_2, 53%).[9] When K_2MnO_4 was used instead of $KMnO_4$, but with the reaction conditions kept otherwise constant, the product is exclusively poly(2,6-dialkyl-1,4-phenylene oxide).[10] Addition of pulverized KOH (12 mmol) to the $KMnO_4$ system also gave the polyphenylene oxide (85%) along with the diphenoquinone (15%). This behavior resembles that found by Tsuruya et al.[11] in the oxidation of 2,6-dimethylphenol by $KOH/CuCl_2$; C–O coupling increases at the expense of C–C coupling as the $KOH/CuCl_2$ ratio is elevated.





The high efficiency of diphenoquinone formation with solid $KMnO_4$ suggested a possible application in the intramolecular oxidative coupling of diphenolic substrates. Although this is an important process in the biosynthesis of natural products, attempts to emulate the biological reaction in the laboratory have been often troubled by low yields.[12] To test the efficacy of the solid $KMnO_4$ method in intramolecular systems, we synthesized (2-hydroxyphenyl)(4-hydroxyphenyl)methane and 1-(3-hydroxyphenyl)-3-(4-hydroxyphenyl)propane by known procedures.[12,13] Unfortunately, both substrates displayed absolutely no reaction even after 24 h of refluxing in $CHCl_3$ over solid $KMnO_4$. The only observable change was a decrease in the original NMR peak amplitudes, suggesting that substrate was being partially adsorbed onto the solid. Proof that adsorption blocks the reactive sites on the permanganate crystals comes from the following experiment: 2-Octanol (1.0 mmol) in heptane was treated with solid $KMnO_4$ (4.0 mmol) in the usual manner.[5] When about half of the 2-octanol had been oxidized to 2-octanone, a bisphenol (0.45 mmol) was added to the reaction mixture. Oxidation of the 2-octanol ceased immediately. The unhindered phenols must bind competitively, via their hydroxyls, to the permanganate surface where further reaction does not take place.[14]





$KMnO_4$ and K_2MnO_4 also behaved differently in the oxidation of aliphatic alcohols. Thus, refluxing 2-octanol in heptane over powdered $KMnO_4$ (<210 mesh) for 4 h gave ketone in 80% yield. On the other hand, reaction of 2-octanol with K_2MnO_4 under identical conditions gave <2% ketone. Solid $K_3(MnO_4)_2$, a mixed-valence salt comprised of alternating MnO_4^- and MnO_4^{2-} centers sufficiently close to allow site-transfer electronic conductivity,[15] likewise failed to oxidize alcohols.

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Experimental Section

A typical phenol oxidation by solid $KMnO_4$ 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 $KMnO_4$ (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′-tetraisopropyldiphenoquinone with a melting point of 202–204 °C (lit.[16] mp 202–203 °C) and reasonable NMR spectra.[10] 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,[16] and the latter melted at 241–241.5 °C (lit.[16] mp 245–247 °C). NMR spectra of all products were reasonable.[10] Oxidation of 2,6-dimethylphenol by solid K_2MnO_4 (Aldrich, used as received) was carried out in a manner identical with the $KMnO_4$ 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.[10]

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

Registry No. $KMnO_4$, 7722-64-7; K_2MnO_4, 10294-64-1; 2,6-diisopropylphenol, 2078-54-8; 3,3′,5,5′-tetraisopropyldiphenoquinone, 2178-51-0; 2,6-dimethylphenol, 576-26-1; 3,3′,5,5′-tetramethyldiphenoquinone, 4906-22-3; 2,6-di-*tert*-butylphenol, 128-39-2; 3,3′,5,5′-tetra-*tert*-butyldiphenoquinone, 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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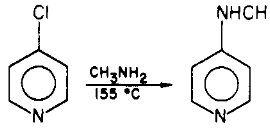
Received March 25, 1985

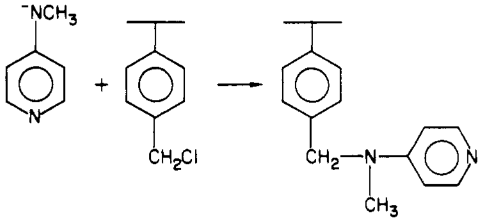
For over a decade 4-(dimethylamino)pyridine (DMAP) has experienced widespread use as an acylation and alkylation catalyst.[1,2] The efficacy of DMAP is illustrated by kinetic work of Litvinenko et al.[3] who showed that benzoylation of *m*-chloroaniline proceeds 10^4 times faster with DMAP than with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

We report herein the behavior of a 4-aminopyridine grouping rendered insoluble via attachment to a polystyrene 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.[9] To our knowledge, only three polymeric forms of (dialkylamino)pyridine have been published. Klotz et al.[10] covalently linked 3-[*N*-methyl-*N*-(4-pyridyl)amino]propionic acid to laurylated poly(ethylenimine). Shinkai et al.[11] obtained catalytic beads by reacting polystyrene bearing (methylamino)methyl substituents with 4-chloropyridine at 150 °C for 4 days. And Tomoi et al.[12] 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.[11] 4-(Methylamino)pyridine was then attached to a polymer by means of an S_N2 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.[13,14]



(1)



(2)

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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