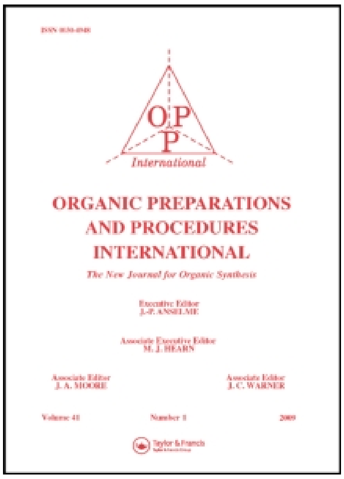

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OXIDATIVE PHOSPHORYIATION OF PHENOLS AND RELATED COMPOUNDS

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OXIDATIVE PHOSPHORYLATION OF PHENOLS AND RELATED COMPOUNDS

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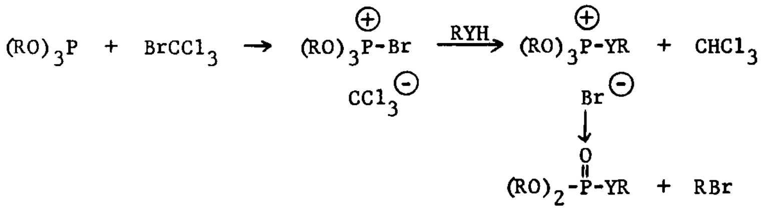
The recent review of indirect oxidative phosphorylation by Blackburn and Cohen[1] has prompted us to report the results of our work which extends the scope of this reaction which can be formulated in general terms as follows.



$$(RO)_3P + BrCCl_3 \rightarrow (RO)_3\overset{\oplus}{P}\text{-}Br\ \ CCl_3^{\ominus} \xrightarrow{RYH} (RO)_3\overset{\oplus}{P}\text{-}YR\ \ Br^{\ominus} + CHCl_3$$

$$(RO)_3\overset{\oplus}{P}\text{-}YR\ \ Br^{\ominus} \rightarrow (RO)_2\text{-}\overset{O}{\overset{\|}{P}}\text{-}YR + RBr$$

Several groups have previously phosphorylated alcohols[2,3], mercaptans[4], and thiophenols[5] (RYH) using this general procedure. We have now shown that phenols, oximes and 4-hydroxy-1,6-dimethyl-2-pyridone can also be phosphorylated conveniently and in high yield with the same procedure. Out interest in the facile preparation of these phosphate esters stems from the fact that, in general, these types of phosphate esters act as insecticides[6].

Our phosphorylation method is simpler than both the conventional one[7] employing phosphorochloridates with acid halide acceptors and the method of Hata and Mukaiyama[8] which utilizes bromocyanoacetamide as the source of positive halogen.

Representative experimental procedures are listed below. Additionally, we have found that acetone oxime and benzaldoxime as well as phenol, p-chlorophenol, and p-methoxyphenol are converted smoothly to the corresponding dialkyl phosphate esters. We obtained an 89% yield of O,O-diethyl-O-phenyl phosphate when phenol was allowed to react with triethyl phosphite in the presence of bromotrichloromethane whereas the same product was obtained in only 34% yield when carbon tetrachloride was used as the halogen source.

EXPERIMENTAL[9]

O,O-Diethyl-O-(p-nitrophenyl)phosphate. A slurry of 13.9g (0.10 mole) of p-nitrophenol in 20g (0.10 mole) of bromotrichloromethane was treated dropwise with 16.6g (0.10 mole) of triethyl phosphite so as to maintain the temperature between 50-60°. The solution was stirred overnight and the solvent was evaporated to afford a pale yellow oil: bp 140° (0.04mm). There was obtained 22.6g (82%) of product, identical in all respects with authentic material[10].

O,O-Dimethyl-O-(m-chlorophenylglyoxylonitriliminyl)phosphate. A slurry of 9.0g (0.05 mole) of m-chlorophenylglyoxylonitrile oxime (prepared by the method of Thurston and Shriner[11]: mp 106-108°) in 40 ml of bromotrichloromethane was treated with 1.0g of trimethyl phosphite. The mixture was stirred for one hour and 5.2g of additional trimethyl phosphite (total of 0.05 mole) was added dropwise. The solution was stirred overnight and the solvent was removed by evaporation. The residue was dissolved in chloroform, washed with 5% sodium hydroxide and then with water. After drying over anhydrous magnesium sulfate, the solution was evaporated to afford 11.1g (77%) of oily product which crystallized on standing and was recrystallized from ether-petroleum ether: mp 60-61°; ir (KBr) 2240, 1640, 1280, 1055 and 950 cm^{-1}; nmr ($CDCl_3$) δ 7.7 (m, 4) and 3.99 ppm (d, 6).

Anal. Calcd for $C_{10}H_{10}ClN_2O_4P$: C, 41.61; H, 3.49. Found: C, 41.54; H, 3.46.

O,O-Dimethyl-O-(1,6-dimethylpyrid-2-on-4-yl)phosphate. A slurry of 27.8g (0.2 mole) of 4-hydroxy-1,6-dimethyl-2-pyridone in 60 ml of bromotrichloromethane was treated with 5.0g of a total of 24.8g (0.2 mole) of trimethyl phosphite. The solution was warmed to 45° when an exotherm took place. The remaining phosphite was added so as to maintain the temperature at 55-60°. The solution was stirred overnight and the solvent evaporated to afford 52.3g of brown oil with spectral characteristics identical to those of material prepared by an alternate route[12]: ir (neat) 1675, 1300, and 1040 (cm^{-1}); nmr ($CDCl_3$) δ 6.12 (m, 2), 3.88 (d, 6), 3.48 (s, 3), and 2.4 ppm (s, 3). In addition, trimethyl phosphate was detected as an impurity: δ 3.78 ppm (d).

O,O-Dimethyl-O-(1-nitroethyliden-1-iminyl)phosphate. A solution of 12.0g (0.115 mole) of 1-nitroacetaldoxime[13,14] in 75 ml of bromotrichloromethane was treated dropwise and with stirring with 15g (0.12 mole) of trimethyl phosphite so as to maintain the temperature below 50°. The cooled solution was stripped of solvent on a rotating evaporator where the pot temperature was not allowed to exceed 50°. There was obtained 26.7g of an amber oil whose infrared spectrum was superimposable on a spectrum of material prepared by an alternate route[15]: ir (neat) 1555, 1255, and 1050 cm^{-1}.

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