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Oxidations With Acyl Nitrates: a Simple and Rapid Method for Preparing Quinones, Ketones and Aldehydes

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Abstract: Hydroquinones are oxidized rapidly and quantitatively with acyl nitrates or trimethylsilyl nitrates to quinones. Primary and secondary alcohols are oxidized to aldehydes and ketones in good yields with acyl nitrates suported on montmorillonite or chrysotile. A mechaninsm is proposed based on a nitrate intermediate isolated from the reaction mixture.

The acyl nitrates are well known as nitrating agents.[1] There are few reports concerning their oxidative properties. Sulphides react rapidly with acyl nitrates to give sulphoxides in high yields with no sulphone formation.[2] The main product of the reaction of 2,3-diphenylindole with benzoyl nitrate is 3,3-diphenyloxindole, and 2,3-dimethylindole gave a small amount of 3-methyl-2-carbaldehyde.[3] Generally, acetyl nitrate is made from concentrated nitric acid and acetic anhydride at 0° C.[4] We prepared acyl nitrates from the corresponding acyl chlorides with silver nitrate following the literature procedure.[5] Considering the low stability of acyl nitrates we report the impregnation in clay minerals such as montmorillonite, silica, chrysotile, etc., and studied the regioseletivity of nitration of alkylbenzenes and phenol.[6] The obtained acyl nitrate solution was used directly and the quantities were based on the starting amount of acyl chloride and benzoyl chloride used in the preparation with silver nitrate. For each 10 mmol of acyl nitrate in 30 mL of dry solvent (acetonitrile or carbon tetrachloride) at -20°C, we added 2.0g of dry chrysotile or montmorillonite K10, under magnetic stirring during one hour at the same temperature. Then the substrate was added.

In an attempt to nitrate hydroquinone we observed instead a rapid and a quantitative oxidation to 1,4-benzoquinone. The reaction of catechol was nearly instantaneous since after one minute we obtained 1,2-benzoquinone quantitatively. Tetramethyl-1,4-hydroquinone is been quantitatively oxidized to the quinone after 30 minutes. Initially we used supported acyl nitrates but since the reactions were rapid we got the same results without any added mineral clay. Similar results were obtained with trimethylsilyl nitrate[7] but the reaction was slower. The literature describes many methods for the preparative conversion of hydroquinones to quinones using oxidants such as silver oxide, ceric ammonium nitrate, thallic nitrate, lead(IV) oxide, sodium dichromate, nitric acid, gaseous nitrogen oxide, etc.[8-12] Comparing with those methods our procedures also offers excellent yields but with rapidity, neutral conditions and a simple workup.

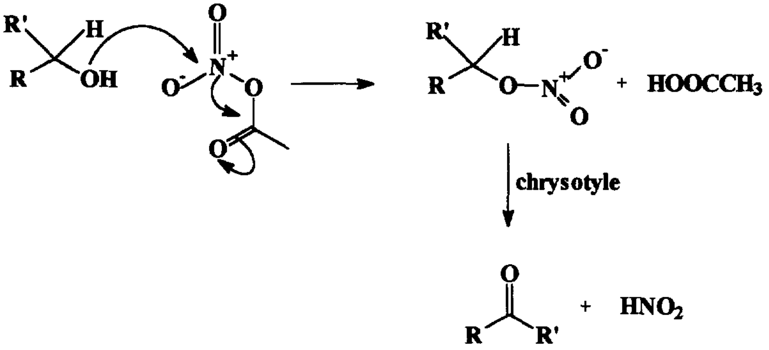
Table. Oxidation of alcohols with acetyl nitrate impregnated on montmorillonite K10 after 2 h of reaction.

substrate	yield % [a]	product
cyclohexanol	99	cyclohexanone
benzydrol	99	benzophenone
benzyl alcohol	67	benzaldehyde
piperonyl alcohol	72	piperonal
cinnamyl alcohol	68	cinnamaldehyde
geraniol	58	citral
1-phenyl-1-ethanol	96	acetophenone
1-phenyl-1-propanol	96	propiophenone

a. Yield determined by gas chromatography.

Alcohol oxidations are slow when compared with the hydroquinones and it is necessary to add a support that stabilizes the acyl nitrates and acceleretes the reaction in order to meliorate the yields. In general, the reactions were run for 2 h and, after filtering the reaction mixture, the yields were determined by gas chromatography and the products were identified by comparison with authentic compounds using also infrared and melting point determinations.[13] Primary alcohols were oxidized to aldehydes in good yields without contamination by carboxylic acids and secondary alcohols were oxidized to ketones. Benzhydrol and cyclohexanol furnish quantitatively benzophenone and cyclohexanone, respectively, after 2 h of reaction. With primary alcohols the reaction takes more time. After 2 h benzylic alcohol gave a 67% yield of benzaldehyde, piperonyl alcohol gave piperonal in 72% yield, cinnamylic alcohol gave cinnamaldehyde in 68% yield and geraniol gave citral in 59% yield. To complete the reactions at least 4 h is necessary. When compared with other procedures that use impregnated oxidants[14-15] acyl nitrates offer a good alternative considering the yield of the products, the selectivity and the simplicity of the method. In general we used acetyl nitrate but benzoyl nitrate can also be used with similar results. The reaction without support is very slow and is not complete. Trimethylsilyl nitrate reacts very slowly and is not a good oxidizing reagent for alcohols. Acetyl nitrate impregnated in chrysotile or montmorillonite K10 also oxidize dibenzylsulfide to dibenzylsulfoxide in above 90% yield.

When the reaction with benzhydrol was carried out for 30 minutes besides the presence of starting material and benzophenone, benzhydryl nitrate was isolated as the major product. This compound was identified by IR (1660 and 1280 cm-1), mass spectra (m/z 229, M+) and by comparison with an authentic sample prepared by an independent synthesis using the procedure of Tojo.[16] The benzhydryl nitrate was treated in chloroform with montmorillonite or with crysotile and after 4 hs gave only benzophenone as product. This reaction is an indication that the nitrate is an intermediate in the oxidation reaction with acetyl nitrate in presence of the support. Also the support seems to be responsible for its transformation to the ketone. The scheme below shows a reaction mechanism that fits the above observation . In the oxidation reaction we also identified the presence of the nitrite ion using the procedure of Feigl and Anger.[17] Acetyl nitrate generated by acetic anhydride and nitric acid was used by others to prepare alkyl nitrates.[18]



Scheme. Proposed oxidation mechanism for alcohols using acyl nitrates impregnated on chrysotile.

In conclusion, we developed a simple method for oxidation of primary and secondary alcohols using as oxidants acyl nitrates supported on montmorillonite or chrysotile to give aldehydes and ketones in high yields. A mechaninsm with an isolated intermediate alkyl nitrate is proposed for the reaction. The oxidation of hydroquinones to quinones is rapid and quantitative.

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13. Experimental procedure for the oxidations: to a suspension of montmorillonite (K10) (1 g) or crysotile in chloroform at -15 ^{0}C was added with magnetic stiring a 10% solution of acetyl nitrate (CAUTION)(10 mL, 6 mmol)^{5}. After 1 h the alcohol (5 mmol) was added and the temperature was left to reach ambient. After 2 or 4 h the reaction was filtered, the solvent evaporated and the yields determined by gas chromatography (Hewlet Packard model HP5890-A with flame ionization detector and a HP1-dimethylsiloxane capillary column, using internal standard). The oven temperature was raised from 2 ^{0}C. min^{-1} to 150 ^{0}C. For quantification, the same response factor was assumed for all compounds. The identity of the peaks was verified by analysis in a HP-5890 II gas chromatograph coupled to a mass detector (HP-9070B) at 70 eV, using the same column.
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