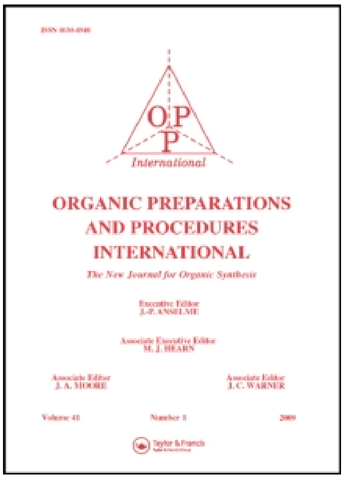

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OXIDATION OF VARIOUS ALCOHOLS WITH *IN SITU* GENERATED MONTMORILLONITE K10-SUPPORTED FERRIC NITRATE REAGENT IN AN APROTIC SOLVENT

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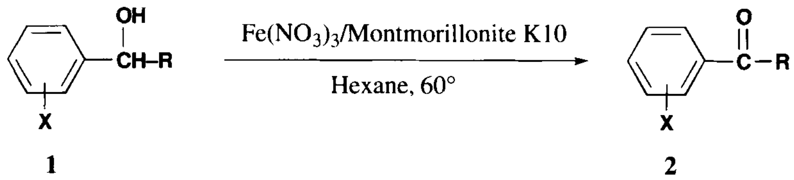
Reactions using supported reagents have recently attracted much attention. Indeed, the introduction of a certain agent onto or into an organic polymeric or an inorganic porous or layered support material (henceforth referred to simply as support) not only exerts modified reactivity of the agent and/or specific product selectivity, but considerably simplifies product isolation. Thus, a great variety of supported reagent systems are currently in wide use in organic synthesis.[1] One of the fascinating examples is *Clayfen* (abbreviation for Montmorillonite K10 doped with ferric nitrate, named by Laszlo), which is a versatile reagent for the conversion of various functional groups in a selective fashion.[2] However, there are serious problems in its use, *viz.*, the necessity of meticulous care upon the preparation of *Clayfen* and its relatively rapid deactivation on storage.[2a] Thus, there is a need of exploring a readily accessible technique to extend the utility of this valuable reagent system.

Our recent attempts to bring about oxidations in aprotic solvents have demonstrated that inorganic supports facilitate the reactions appreciably, affording the products in synthetically useful yields and substantiating the specific product selectivities.[3-6] These reactions can be initiated immediately by simple mixing an aprotic solvent, an oxidant, and a support with a substrate without a need to prepare a supported reagent beforehand; however, the oxidizing media are reminiscent of those used for the supported reagents, thereby making product isolation very straightforward. In the course of related work, we were intrigued by the fact that clay minerals serve as highly reactive sites for certain reagents in the oxidation of sulfides to the sulfoxides[6] or the sulfones,[4] which led us to investigate the clay-assisted organic reaction extensively. This article reports an operationally simple Montmorillonite K10-assisted ferric nitrate oxidation of a series of alcohols.



Several factors markedly affect the efficiency of the reaction. Indeed, the facility of the reaction and selectivity and yield of the carbonyl compounds are dependent on the solvent, water-content of Montmorillonite K10, and reaction temperature and time. For example, use of the clay from the bottle or of a carcinated sample led to poor performance of the reaction, but the optimally water-loaded Montmorillonite K10 (the moist-montmorillonite; *vide* **Experimental Section**) led to efficient oxidation. The effect of solvent and temperature on the yield of the product were also checked by using benzyl alcohol as the test substrate. Of the solvents examined (hexane, carbon tetrachloride, benzene, and acetonitrile), hexane was selected on account of the highest yield of benzaldehyde (GC and isolated yields were 98 and 95%, respectively, based on the starting alcohol). Temperature dependence of the product yield was examined in the range of 30°C-reflux temperature in hexane; optimal yield of benzaldehyde was obtained around 60°C. On the basis of the data collected from preliminary experiments evaluating the influence of these reaction parameters, synthetic reactions of carbonyl compounds were conducted in hexane in the presence of the moist montmorillonite at 60°C; the reactions were allowed to proceed to 100% conversions. Table 1 shows the isolated yields of chromatographically purified carbonyl compounds (**2**) obtained from the oxidations of a wide variety of benzylic alcohols (**1**). In the cases of benzyl alcohol and its *o*-, *m*-, and *p*-substituted derivatives (Entries 1-16), GC analyses of the reaction mixtures revealed that the benzaldehydes were the sole neutral products; no attempt was made to analyze for acidic products. It is of considerable interest that the substituted benzaldehydes are obtained in excellent to essentially quantitative yields, irrespective of the electronic properties of the substituents and their positions on the benzene-ring. Likewise, conversion of secondary benzylic alcohols to the ketones proved successful (Entries 17-33). The isolated yields of benzaldehyde (Entry 1), acetophenone (Entry 17), benzophenone (Entry 27), and benzil (Entry 33) were as high or higher than those reported with the use of *Clayfen*.[2a]

The oxidation of long chain 2-alkanols (C_6-C_{10}) with the present system gave the corresponding 2-alkanones in 85, 86, 89, 90, and 91% isolated yields, respectively after 4 hrs. These results coupled with those in Table 1 clearly imply that independent preparation of a supported reagent is not a necessary prerequisite for effective ferric nitrate oxidations. In addition, work-up and isolation of products did not pose any problem. Thus the *in situ* $Fe(NO_3)_3$/Montmorillonite K10 procedure provides an efficient substitute for *Clayfen*.

EXPERIMENTAL SECTION

^{1}H NMR spectra were measured for solutions in deuteriochloroform at 60 MHz using TMS as standard.

TABLE 1. Oxidation of Various Benzylic Alcohols

Entry No.	Alcohol (1) X	Alcohol (1) R	Time (hrs)	(2) Yield (%)	Entry No.	Alcohol (1) X	Alcohol (1) R	Time (hrs)	(2) Yield (%)
1	H	H	3	95	18	*o*-MeO	Me	2	80
2	*o*-MeO	H	2	92	19	*m*-MeO	Me	2	85
3	*m*-MeO	H	2	97	20	*p*-MeO	Me	2	80
4	*p*-MeO	H	2	80	21	*p*-Me	Me	3	88
5	*o*-Me	H	2	81	22	*p*-Br	Me	4	91
6	*m*-Me	H	2	89	23	*p*-Cl	Me	4	99
7	*p*-Me	H	2	85	24	*o*-NO_2	Me	7	93
8	*o*-Br	H	3	94	25	*m*-NO_2	Me	5	91
9	*m*-Br	H	3	89	26	*p*-NO_2	Me	5	97
10	*p*-Br	H	3	99	27	H	Ph	3	92
11	*o*-Cl	H	3.5	90	28	*p*-MeO	Ph	2	85
12	*m*-Cl	H	3	97	29	*p*-Me	Ph	3	89
13	*p*-Cl	H	3	92	30	*p*-Br	Ph	4	98
14	*o*-NO_2	H	3	96	31	*p*-Cl	Ph	4	99
15	*m*-NO_2	H	3	99	32	*p*-NO_2	Ph	5	98
16	*p*-NO_2	H	3	99	33	H	PhCO	3	99
17	H	Me	3	90					

IR spectra were recorded for thin films (neat) or KBr disks. GC was equipped with a 2 m glass column packed with 5% PEG-20M or 1.5% Silicone OV-17 on Chromosorb WAW-DMCS. Ferric nitrate nonahydrate and Montmorillonite K10 (*Aldrich*) were commercial chemicals. Alcohols in Entries 18-26, 28, 30, and 32 were synthesized by reductions of the parent ketones either with $NaBH_4$ in 90% aqueous ethanol or with $LiAlH_4$ in dry ether. The other alcohols were commercially available.

Preparation of the Moist-Montmorillonite and Oxidation Procedure.-The moist montmorillonite was prepared by adding distilled water (1 g) to Montmorillonite K10 (10 g) in several portions followed by vigorous shaking of the mixture after every addition for a few minutes until a free-flowing powder was obtained.

The following oxidation procedure for benzyl alcohol is representative. A 30 mL two-necked round-bottom flask, equipped with a stir bar, a 25 cm long reflux condenser and a glass tubing connected to an argon-filled balloon, was arranged for conducting the reaction under inert atmosphere by connecting the top of the condenser to a liquid paraffin trap in order to exclude air oxidation. The flask was charged with benzyl alcohol (0.108 g, 1 mmol), hexane (10 mL), and finely pulverized ferric nitrate nonahydrate (0.404 g, 1 mmol) and stirring was started. After addition of the moist montmorillonite (1 g), a gentle stream of the argon was passed through a system. The cloudy heterogeneous mixture was vigorously stirred for 3 hrs at 60°. The whole mixture was filtered through a sintered glass funnel in order to remove insoluble material, which was thoroughly washed with dry ether (required *ca.* 100 mL). Rotary evaporation of the combined filtrate *in vacuo* left an oil, which was immediately chromatographed on a silica gel column (*Merk 60*) by elution with a mixture of hexane and ethyl acetate (7:3 by volume) to afford benzaldehyde (0.101 g, 95%) (Entry 1).

Oxidations of the other alcohols were carried out as above, and each carbonyl compound was identified by spectral comparison (^{1}H NMR and IR) with authentic sample synthesized separately.

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