

Note

Ferric perchlorate adsorbed on silica gel : An efficient reagent for cleavage of carbon-nitrogen double bond

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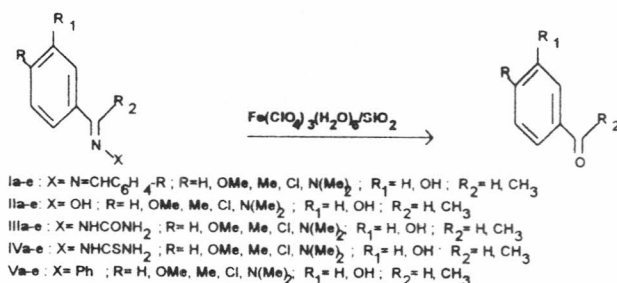
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Adsorption of $\text{Fe}(\text{ClO}_4)_3(\text{H}_2\text{O})_6$ on to chromatographic grade silica gel produces a supported reagent $\text{Fe}(\text{ClO}_4)_3(\text{H}_2\text{O})_6/\text{SiO}_2$. This reagent, has been found effective for the rapid and high yield regeneration of the carbonyl compounds from azines **1a-e**, oximes **2a-e**, semicarbazones **3a-e**, thiosemicarbazones **4a-e** and schiff's base's **5a-e** on grinding in the solid state using pestle & mortar.

Regeneration of the carbonyl compounds from their derivatives under mild conditions is an important synthetic reaction. Several methods¹⁻⁵ have been developed for regeneration of carbonyl compounds from their corresponding derivatives. Acidic hydrolysis of oximes to carbonyl compounds is not found satisfactory in the presence of an acid sensitive functional group in the molecule⁶. Some reductive and oxidative methods^{4,7-11} have been reported, but these methods still lack in terms of cost, convenience and yield.

We now report a simple and efficient method of regeneration of carbonyl compounds from their corresponding azines **1a-e**, oximes **2a-e**, semicarbazones **3a-e**, thiosemicarbazones **4a-e** and schiff's bases **5a-e** derivatives. We have observed that $\text{Fe}(\text{ClO}_4)_3(\text{H}_2\text{O})_6$ adsorbed on to chromatographic grade silica gel cleaved **1a-e**, **2a-e**, **3a-e**, **4a-e** and **5a-e**, to the corresponding carbonyl compounds (Scheme I) on grinding in solid state using pestle and mortar. The carbonyl compounds obtained were characterized by direct comparison with authentic samples and preparation of their phenyl hydrazone derivatives (Table I).

The "supported reagent" $\text{Fe}(\text{ClO}_4)_3(\text{H}_2\text{O})_6\text{-SiO}_2$ has the advantage^{12,13} of being easily removed from



Scheme I

the organic product by filtration. Further, advantage of this supported reagent is its improved storage stability in comparison to $\text{Fe}(\text{ClO}_4)_3(\text{H}_2\text{O})_6$ which is very sensitive to moisture.

The "supported reagent" of interest was prepared by simple dissolution of $\text{Fe}(\text{ClO}_4)_3(\text{H}_2\text{O})_6$ in water followed by addition of an appropriate amount of dried chromatographic grade silica gel. Evaporation of the excess water gave $\text{Fe}(\text{ClO}_4)_3(\text{H}_2\text{O})_6\text{-SiO}_2$ complex as a homogeneous, free flowing, light yellow to creamish powder. The formation of such complexes $[\text{Fe}(\text{ClO}_4)_3(\text{S})_6]$; S=solvent] from $\text{Fe}(\text{ClO}_4)_3(\text{H}_2\text{O})_6$ has already been reported¹⁴. The amount of iron present in each batch of reagent was accurately determined by titration¹⁵.

In conclusion, the "supported reagent" used here for the regeneration of carbonyl compounds is simple, unaffected by moisture, have greater storage stability, easy to use, efficient and easily separable from the reaction mixture and avoid many disadvantages of the previous methods like formation of side products. The regeneration of cyclic (entry-8; Table I) and acyclic aliphatic carbonyl compounds was not so efficient in comparison to the aromatic carbonyl compounds.

Experimental Section

All melting points recorded are uncorrected (open capillary measurements, using sulphuric acid bath). IR spectra were recorded in KBr on a Perkin-Elmer spectrophotometer, NMR spectra on EM-390, 90 MHz instrument using TMS as internal standard. All product spectra were compared with spectra of authentic samples taken on the same instrument.

Table I—Yield (%) of the products* from the corresponding azines **1a-e**, oximes **2a-e**, semicarbazones **3a-e**, thiosemicarbazones **4a-e** and schiff's bases **5a-e**

Sl. No.	Product	(Yield %)				
		1a-e	2a-e	3a-e	4a-e	5a-e
1	Benzaldehyde	95	90	96	96	98
2	Vanillin	97	80	95	87	81
3	Anisaldehyde	60	62	50	66	69
4	<i>N,N</i> -Dimethylamino-benzaldehyde	91	83	84	86	88
5	Acetophenone	90	73	80	71	70
6	4-Cl-acetophenone	87	70	72	80	75
7	4-Me-acetophenone	80	77	74	78	83
8	Cyclohexanone	60	51	62	67	48

*Products were isolated as phenyl hydrazone derivatives

All solvents were reagent grade and used as received. Silica gel for column chromatography was used as received from E Merck.

Preparation of $\text{Fe}(\text{ClO}_4)_3(\text{H}_2\text{O})_6/\text{SiO}_2$ reagent.

An appropriate amount of $\text{Fe}(\text{ClO}_4)_3(\text{H}_2\text{O})_6$ (about 30 g) was dissolved in water. To this solution added the appropriate amount of dried chromatographic grade silica gel (about 25 g). The mixture was mixed properly and allowed to stand for 1 hr. The excess water was filtered off *in vacuo*. The supported reagent at this point was reproducibly a homogeneous, free flowing, cremish powder. It was stored in a bottle after drying in air for 1-2 days. The reagent is unaffected by light or moisture.

Determination of iron (III) present in $\text{Fe}(\text{ClO}_4)_3(\text{H}_2\text{O})_6/\text{SiO}_2$ reagent: A weighed sample of $\text{Fe}(\text{ClO}_4)_3(\text{H}_2\text{O})_6/\text{SiO}_2$ reagent was analysed for determining the amount of iron present by a series of redox reactions¹⁵.

General procedure for oxidation. Equimolar amount of "supported reagent" and the carbonyl derivative (**1a-e/ 2a-e/3a-e/4a-e/5a-e/6a-e**) were mixed together and grinded in a pestle and mortar for 15 min. Usually an immediate colour change was observed. The reaction mixture was allowed to stand for 2 hr. To this crude reaction mixture was added methylene chloride (50 mL) and distilled water (5 mL) to quench the reaction mixture as well as to destroy any inorganic complexes that may have formed during the reaction. The mixture was stirred for 1 min and then suction filtered. The spent reagent was washed twice with methylene chloride (10 mL each). The combined organics were washed with saturated NaHCO_3 solution

followed by 1% HCl, water, dried over Na_2SO_4 and solvent was removed under reduced pressure. This crude reaction mixture was analyzed and purified by crystallization after isolation as phenyl hydrazone derivatives. Products (Table I) formed were identified by comparison of NMR, IR and in some cases mass spectra with authentic samples.

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References

- 1 Mahto S K, Hamal S & Gajural C L, *Indian J Chem*, 35B, 1996, 998 and references cited therein.
- 2 Hamal S, Mahto S K & Gajural C L, *Indian J Chem*, 35B, 1996, 1116 and references cited therein.
- 3 Wali A, Guneshpure P A & Satish S, *Bull Chem Soc Jpn*, 66, 1993, 1847.
- 4 Lee J G, Kwak K H & Hwang J P, *Tetrahedron*, 31, 1990, 6677.
- 5 Kumar H, Kaur B & Kumar B, *Indian J Chem*, 30B, 1991, 869.
- 6 Donaldson R E, Saddler J C, Byrn S, McKenzie A T & Fucks P L, *J Org Chem*, 48, 1983, 2167 and references cited therein.
- 7 Tamami B & Goudarzian N, *Eur Polym*, 28, 1992, 1035.
- 8 Tamami B, Hatam M & Mohadjev D, *Polymer*, 32, 1991, 2666.
- 9 Salmon M, Miranda R & Angelels E, *Synth Commun*, 16, 1986, 1827.
- 10 Aizpurua J M & Palomo C, *Tet Lett*, 24, 1983, 4367.
- 11 Aizpurua J M, Juaristi M, Lecea B & Palomo C, *Tetrahedron*, 15, 1981, 2903.
- 12 McKillop A & Young D W, *Synthesis*, 401, 1979, 481.
- 13 Possner G W, *Angew Chem (Int)*, 17, 1978, 487.
- 14 Kotani E, Kobayashi S & Ishii Y, *Chem Pharm Bull*, 32, 1984 4281.
- 15 Fritz J S & Schenk G H (Jr), *Quantitative analytical chemistry* (Allyn and Bacon, Rockleigh, NJ), 1969, 271.