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Solid State Deoximation with Ammonium Persulfate-Silica gel: Regeneration of Carbonyl Compounds Using Microwaves

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Abstract: Ammonium persulfate on silica gel rapidly regenerates carbonyl compounds from their corresponding oxime derivatives using microwaves under solventless 'dry' conditions.

Oximes are useful protecting groups[1a] and are extensively used for purification of the carbonyl compounds. Their synthesis from non-carbonyl compounds[1b] provides an alternative pathway to aldehydes and ketones. The hydrolytic stability of oximes has inspired the development of several deoximation reagents[2a] such as trimethylammonium chlorochromate,[2b] dinitrogen tetraoxide,[2c] pyridinium chloroformate,[2d] trimethylsilyl chloroformate,[2e] titanium silicalite-1,[2f] zirconium sulfophenyl phosphonate,[2g] and N-haloamides[2h] with certain limitations. Even among the newer reagents, the use of dimethyl dioxirane[3a] is restricted to ketoximes whereas pyridinium chloroformate–H_2O_2[3b] suffers from the disadvantage of overoxidation of ensuing aldehydes.

The reagents impregnated on mineral solid supports, especially that are efficient in 'dry' media,[4,5] have gained popularity in organic synthesis because of their selectivity, and ease of manipulation. During the course of our investigations on organic manipulations in solventless systems,[5] we have observed a relatively useful microwave (MW) effect.[6] The salient feature of MW approach are the much improved reaction rates, cleaner and rapid reactions.[4-7] The microwave-assisted reactions in dry media condition[4,5] are especially appealing as they provide an opportunity to work with open vessels, thus avoiding the risk of high pressure development and with a possibility of upscaling the reaction on preparative scale. Ammonium persulfate has been used once for deoximation of steroidal ketones in sulfuric acid (room temperature, 8 days)[8] under a corrosive environment. In continuation of our ongoing efforts,[5] we envisioned the applicability of silica-supported ammonium persulfate to fulfill a variety of oxidative needs under solvent-free reaction conditions using microwaves. We wish to report here a facile deoximation protocol using ammonium persulfate 'doped' silica gel.

Among the various solid supports examined such as alumina, montmorillonite K 10 clay etc., silica gel is found to be the best. In the absence of silica, however, mixture of products are obtained using both, microwave irradiation (1 min) and heating in an oil bath at 98° C (20 min). The reactions on clay predominantly result in the formation of Beckmann rearranged products.[4a] The optimum ratio of substrate to reagent is found to be 1:5; the reaction remains incomplete with lower amounts of the oxidant even after extended exposure to microwaves (5 min). Unlike other oxidative hydrolytic methods, the major drawback of overoxidation is not encountered.

An environmentally benign and safe oxidant on a solid support is introduced in this efficient transformation. The use of recyclable silica gel support and the general applicability of this reaction to a variety of aldoximes and ketoximes under solvent-free conditions are other attractive features of this protocol.

General procedure: Neat oxime (1 mmol) or dissolved in dichloromethane (2-3 mL) is combined with silica gel (10 times, w/w) and the 'dry' powder is mixed with ammonium persulfate (5 mmol) using a vortex mixer. The contents are irradiated at full power in an alumina bath inside a Kenmore MW oven (2450 MHz, 800 Watts).

After completion of the reaction (monitored by TLC) the product is extracted into dichloromethane (4x30 mL) and purified by column chromatography. In the case of aldehydes, the crude product is filtered through a small bed of neutral alumina with dichloromethane. Our results for various oximes are summarized in the **Table.**

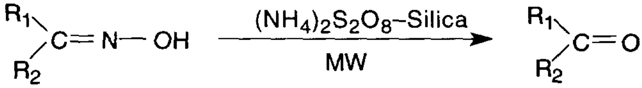
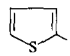
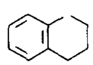


Table: Microwave-assisted deoximation reactions using ammonium persulfate-silica

Entry	R_1	R_2	Time (min)	Yield[a] (%)
1	C_6H_5	CH_3	1.5	65
2	*p*-Cl-C_6H_4	CH_3	1.8	72
3	*p*-OMe-C_6H_4	CH_3	1.5	59
4	*p*-Me-C_6H_4	CH_3	1.6	73
5	C_6H_5	H	1.7	83
6	1-Naphthyl	H	1.8	76
7	*p*-NO_2-C_6H_4	H	0.8	66
8	3,4-$(OMe)_2$-C_6H_3	H	2.5	69
9		H	1.5	75
10			1.8	64

[a]Unoptimized yields of pure isolated products that exhibited physical and spectral properties in accord with the assigned structures.

In conclusion, we have developed a solid state method for the facile deoximation of protected aldehydes and ketones using ammonium persulfate and silica gel under microwave irradiation conditions.

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REFERENCES AND NOTES

1. a) Greene, T.W.; Wuts, P.G.M. *Protective Groups in Organic Synthesis*, Wiley, New York, **1991**, p 214 and references cited therein; b) Kabalka, G.W.; Pace, R.D.; Wadgaonkar, P.P. *Synth. Commun.* **1990**, *20*, 2453.
2. a) Curran, D.P.; Brill, J.F.; Rakiewicz, D.M. *J. Org. Chem.* **1984**, *49*, 1654; b) Rao, C.G.; Radhakrishna, A.S.; Singh, B.B.; Bhatnagar, S.P. *Synthesis* **1983**, 808; c) Shim, S.B.; Kim, K.; Kim, Y.H. *Tetrahedron Lett.* **1987**, *28*, 645; d) Meloney, J.R.; Lyle, R.E.; Saavedra, J.E.; Lyle, G.G. *Synthesis* **1978**, 212. e) Aizpurua, J.M.; Juaristi, M.; Lecea, B.; Palomo, C. *Tetrahedron* **1987**, *41*, 2903; f) Joseph, R; Sudalai, A.; Ravindranathan, T. *Tetrahedron* **1994**, *35*, 5493; g) Curini, M.; Rosati, O.; Pisani, E. *Synlett* **1996**, 333; h) Bandgar, B.P.; Kunde, L.B.; Thote, J.L. *Synth. Commun.* **1997**, *27*, 1149.
3. a) Olah, G.A.; Liao, Q.; Lee, C.S.; Surya Prakash, G.K. *Synlett* **1993**, 427; b) Drabowicz, J. *Synthesis* **1980**, 125.
4. a) Bosch, A.I.; Cruz, P.; Diez-Barra, E.; Loupy, A.; Langa, F. *Synlett* **1995**, 1259; b) Oussaid, A.; Thach, L. N.; Loupy, A. *Tetrahedron Lett.* **1997**, *38*, 2451; c) Villemin, D.; Benalloum, A. *Synth. Commun.* **1991**, *21*, 1 and 63.
5. a) Varma, R.S.; Chatterjee, A.K.; Varma, M. *Tetrahedron Lett.* **1993**, *34*, 3207; b) Varma, R.S.; Chatterjee, A.K.; Varma, M. *Tetrahedron Lett.* **1993**, *34*, 4603; c) Varma, R.S.; Varma, M.; Chatterjee, A.K. *J. Chem. Soc.. Perkin. Trans. 1* **1993**, 999; d) Varma, R.S.; Lamture, J.B.; Varma, M. *Tetrahedron Lett.* **1993**, *34*, 3029; (e) Varma, R.S.; Dahiya, R.; Kumar, S. *Tetrahedron Lett.* **1997**, *38*, 2039; (f) Varma, R.S.; Dahiya, R. *Tetrahedron Lett.* **1997**, *38*, 2043; (g) Varma, R.S.; Saini, R.K. *Tetrahedron Lett.* **1997**, *38*, 2623; (h) Varma, R.S.; Dahiya, R.; Kumar, S. *Tetrahedron Lett.* **1997**, *38*, in press.
6. For recent reviews on microwave-assisted chemical reactions, see a) Abramovich, R.A. *Org. Prep. Proced. Int.* **1991**, *23*, 683; b) Whittaker, A.G.; Mingos, D.M.P. *J. Microwave Power Electromagn. Energy* **1994**, *29*, 195; c) Majetich, G.; Hicks, R. *J. Microwave Power Electromagn. Energy* **1995**, *30*, 27; d) Caddick, S. *Tetrahedron* **1995**, *51*, 10403; e) For commentary on the First World Congress on Microwave Processing, see Dagani, D. *Chem. Eng. News* Feb. 10, **1997**, 26.
7. Bose, A.K.; Jayaraman, M.; Okawa, A.; Bari, S.S.; Robb, E.W.; Manhas, M.S. *Tetrahedron Lett.* **1996**, *37*, 6989.
8. Brooks, S.G.; Evans, R.M.; Green, G.F.H.; Hunt, J.S.; Long, A.G.; Mooney, B.; Wyman, L.S. *J. Chem. Soc.* **1958**, 4614.

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