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EFFICIENT CLEAVAGE OF CARBON-NITROGEN DOUBLE BONDS UNDER SOLVENT FREE CONDITIONS

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ABSTRACT

The conversion of oximes, hydrazones and semicarbazones into the corresponding carbonyl compounds is obtained conveniently using $(NH_4)_2Cr_2O_7$ in the presence of $ZrCl_4$ and wet SiO₂ under solvent free conditions.

Regeneration of carbonyl compounds from stable and readily prepared oximes, hydrazones and semicarbazones has received attention in recent years.^[1-4] Since oximes can be prepared from olefins,^[5] esters,^[6] nitriles,^[6] nitro compounds,^[7,11–13] nitrites,^[8] alcohols,^[9] and primary aliphatic amines,^[10] the regeneration of carbonyl compounds from oximes provides an alternative method for the preparation of aldehydes and ketones. However, many of these methods of generating carbonyl compounds from oximes involve reagents which are either expensive or not readily available.^[14–22]

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Table 1. Regeneration of Aldehydes and Ketones from Oximes, Hydrazones, and Semicarbazones

Entry	Substrate	Time (min)	Product ^a	Yield(%) ^b	
1	4-Chlorobenzaldoxime	10	4-Chlorobenzaldehyde	80	
2	Acetophenone oxime	90	Acetophenone	82	
3	4-Methylacetophenone oxime	15	4-Methylacetophenone	80	
4	Benzophenone oxime	60	Benzophenone	90	
5	3-Nitrobenzaldoxime	8	3-Nitrobenzaldehyde	60	
6	4-Phenylcyclohexanone oxime	30	4-Phenylcyclohexanone	75	
7	Cyclohexanone oxime	10	Cyclohexanone	85	
8	4-Methylbenzaldehyde hydrazone	15	4-Methylbenzaldehyde	90	
9	4-Methoxybenzaldehyde hydrazone	20	4-Methoxybenzaldehyde	85	
10	4-Chlorobenzaldehyde hydrazone	15	4-Chlorobenzaldehyde	87	
11	4-Nitrobenzaldehyde	20	4-Nitrobenzaldehyde	92	
12	3-Nitrobenzaldehyde	25	3-Nitrobenzaldehyde	90	
13	4-Methylacetophenone	35	4-Methylacetophenone	95	
14	4-Phenylcyclohexanone hydrazone	40	4-Phenylcyclohexanone	89	
15	Benzaldehyde	40	Benzaldehyde	65	
16	2-Hydroxybenzaldehyde semicarbazone	12	2-Hydroxybenzaldehyde	43	
17	4-Methoxybenzaldehyde semicarbazone	16	4-Methoxybenzaldehyde	70	
18	3-Nitrobenzaldehyde semicarbazone	35	3-Nitrobenzaldehyde	88	
19	Acetophenone semicarbazone	45	Acetophenone	90	
20	1-Naphthaldehyde semicarbazone	65	1-Naphthaldehyde	85	
21	Cyclohexanone semicarbazone	15	Cyclohexanone	80	

^aAll products were characterized by IR and ¹H-NMR spectra and by comparison with authentic samples.

^bIsolate yield.

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Table 2. Comparison of Some of the Results Obtained from Ammonium Dichromate in the Presence of $ZrCl_4$ and Wet SiO₂ (1) with Some of Those Reported with Pyridinium Chlorochromate (2),^[1] Methyl Ammonium Chlorochromate Adsorbed on Alumina (3),^[2] and Chlorotrimethylsilane–sodium Nitrate (4).^[3]

	Substrate	Product	Yield(%)			
Entry			1	2	3	4
1	Benzophenone oxime	Benzophenone	90	55	61	_
2	Benzaldehyde Phenylhydrazone	Benzaldehyde	65	65	_	_
3	Acetophenone semicarbazone	Acetophenone	90	15	_	80

Little attention has been paid to the cleavage of carbon–nitrogen double bonds of hydrazones and semicarbazones, and only a few reports are available dealing with the conversion of the derivatives into their corresponding carbonyl compounds.^[4,23,24]

In this communication we report that ammonium dichromate in the presence of $ZrCl_4$ and wet SiO_2 is able to perform the cleavage of carbonnitrogen double bonds of oximes, hydrazones and semicarbazones under solvent free conditions (Table 1). Our experiments show that oximes, hydrazones and semicarbazones are converted into their corresponding carbonyl compounds from good to high yields. It should be noted that these deoximation, dehydrazonation and desemicarbazonation reactions did not proceed using either ammonium dichromate, $ZrCl_4$ or wet SiO_2 alone, even after prolonged heating. In order to show the ability of this system we have compared some of the results with some of those reported in the literature (Table 2).

In summary, ammonium dichromate in the presence of $ZrCl_4$ and wet SiO_2 can serve as an efficient reagent for the cleavage of carbon–nitrogen double bonds of oximes, hydrazones and semicarbazones. The yields are almost quantitative and the procedure is simple and convenient.

EXPERIMENTAL

General Procedure

A mixture of the substrate (1 mmol), ammonium dichromate (1 mmol), $ZrCl_4$ (4 mmol) and wet $SiO_2[(SiO_2/H_2O: 20\% \text{ ww}), 0.4 \text{ g}]$ was heated in a

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water-bath (80°C) for the specified time (Table 1). The reaction was monitored by TLC or GLC. After completion of the reaction, CH_2Cl_2 (5 mL) was added to the mixture and the resultant mixture was filtered. Anhydrous MgSO₄ was added to the filtrate and filtered. Evaporation of the solvent, being followed by column chromatography on silica gel, gave the corresponding carbonyl compounds from good to high yields.

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REFERENCES

- 1. Yang, Y.-L.; Li, T.-S.; Li, Y.-L. Synth. Commun. 1993, 23, 1121.
- 2. Zhang, G.-S.; Yang, D.-H.; Chen, M.-F.; Cai, K. Synth. Commun. 1998, 28, 607.
- 3. Khan, R.H.; Mathur, R.K.; Ghosh, A.C. J. Chem. Res.(S) 1995, 506.
- Khurana, J.M.; Ray, A.; Sahoo, P.K. Bull. Chem. Soc. Jpn. 1994, 67, 1091.
- 5. Kadzyauskas, P.P.; Zefirov, N.S. Russ. Chem. Rev. 1968, 37, 543.
- 6. Touster, O. Org. React. 1953, 7, 327.
- 7. Fujisawa, T.; Kurita, Y.; Sato, T. Chem. Lett. 1983, 1537.
- Barton, D.H.R.; Beaton, J.M.; Geller, L.E.; Pechet, M.M. J. Am. Chem. Soc. 1961, 83, 4076.
- 9. Barton, D.H.R.; Beaton, J.M. J. Am. Chem. Soc. 1961, 83, 4083.
- 10. Kahr, K.; Berther, C. Chem. Ber. 1960, 93, 132.
- 11. Stiver, S.; Yates, P. J. Chem. Soc. Chem. Commun. 1983, 2, 50.
- 12. Hanson, J.R.; Organ, T.D. J. Chem. Soc. C 1970, 1182.
- 13. Zeilstra, J.J.; Engberts, J.B.F.N. Synthesis 1974, 49.
- 14. Depuy, C.H.; Ponder, B.W. J. Am. Chem. Soc. 1959, 81, 4629.
- 15. Chamberlin, E.M.; Chamerda, J.M. J. Am. Chem. Soc. 1955, 77, 1221.
- 16. Vankar, P.; Rathore, R.; Chandrasekaran, S. J. Org. Chem. **1986**, *51*, 3036.
- 17. Moriarty, R.M.; Praksh, O.; Vivilikolarn, R. Synth. Commun. **1986**, *16*, 1247.
- 18. Kim, S.B.; Kim, K.; Kim, Y.H. Tetrahedron Lett. 1987, 28, 645.
- Naraya, C.R.; Ramaswamy, O.S.; Wadia, M.S. Chem. Ind. (London) 1977, 454.
- 20. Drabowicz, J. Synthesis 1980 125.

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CLEAVAGE OF CARBON–NITROGEN DOUBLE BONDS

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- 21. Olah, G.A.; Ho, T.C. Synthesis 1976, 610.
- 22. Barton, D.H.R.; Lester, D.J.; Ley, S.V. J. Chem. Soc. Chem. Commun. 1977, 445.
- 23. BartonD.H.R.; Lester, D.J.; Ley, S.V. J. Chem. Soc. Chem. Commun. 1978, 276.
- 24. Barton, D.H.R.; Lester, D.J.; Ley, S.V. J. Chem. Soc. Perkin Trans. 1 1980, 1212.

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