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Mendeleev Commun., 2007, **17**, 190–191
Mendeleev Communications

Mild and efficient conversion of oximes into arylhydrazones catalysed by ferric perchlorate

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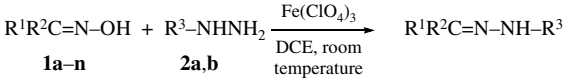
DOI: 10.1016/j.mencom.2007.05.021

Oximes were converted into the corresponding arylhydrazones in 1,2-dichloroethane in the presence of $Fe(ClO_4)_3$.

Interconversions of functional groups are essential steps in organic synthesis. Carbonyl compound derivatives such as oximes, phenylhydrazones, 2,4-dinitrophenylhydrazones, *p*-nitrophenylhydrazones, semicarbazones and tosylhydrazones are used for the characterization and purification of carbonyl compounds and play an important role as protected forms as they are highly crystalline and stable.[1–3] Methods were reported earlier for deoximation into carbonyl compounds.[4–17] To the best of our knowlege, little attention has been paid in recent years to the direct synthesis of hydrazones from oximes.[18,19,†]

In continuation of our studies on the use of ferric perchlorate in organic synthesis,[20] we found that it catalyses the reactions of oximes with arylhydrazines in 1,2-dichloroethane (DCE) to give directly arylhydrazones (Scheme 1, Table 1).[‡]



1a–n **2a,b**

1a $R^1 = 4\text{-}MeOC_6H_4$, $R^2 = H$
1b $R^1 = 4\text{-}O_2NC_6H_4$, $R^2 = H$
1c $R^1 = 4\text{-}Me_2NC_6H_4$, $R^2 = H$
1d $R^1 = 4\text{-}ClC_6H_4$, $R^2 = H$
1e $R^1 = 2\text{-Py}$, $R^2 = H$
1f $R^1 = Ph$, $R^2 = H$
1g $R^1 = PhCH_2CH_2$, $R^2 = H$
1h $R^1 = n\text{-heptyl}$, $R^2 = H$
1i $R^1 = n\text{-nonyl}$, $R^2 = H$
1j $R^1 = PhCH{=}CH$, $R^2 = H$
1k $R^1 = R^2 = Ph$
1l $R^1 = HON{=}C(Me)C(Cl)H$, $R^2 = Me$
1m $R^1 = Me_2C(OH)CH_2$, $R^2 = Me$
1n $R^1 = MeCH{=}CH$, $R^2 = H$

2a $R^3 = Ph$
2b $R^3 = 2,4\text{-}(O_2N)_2C_6H_3$

Scheme 1

The efficiency of this reaction is evident from using a variety of benzaldoximes bearing electron-withdrawing or donating groups on an aromatic moiety, which are converted into the corresponding parent arylhydrazones in good to excellent yields. The catalyst has the ability to tolerate a variety of substituents (Table 1). Substrates carrying electron-withdrawing groups rapidly reacted. Oximes of cinnamaldehyde and various aliphatic carbonyl compounds bearing halogen, hydroxyl or double bond also gave the corresponding hydrazones in good yields (entries 19, 23–28). Ketoximes are also suitable reactants (entries 21–26). We also tested the action of ferric perchlorate (10 mol%) on benzaldehyde phenylhydrazone in DCE (ambient temperature, 24 h) and observed no changes of the starting material.

Table 1 Conversion of oximes to phenyl and 2,4-dinitrophenylhydrazones in the presence of $Fe(ClO_4)_3$.

Entry	Oxime	Hydrazine	Time/h	mp/°C[a]	Yield (%)
1	**1a**	**2a**	8	121	90
2		**2b**	24	254	80
3	**1b**	**2a**	2	159	98
4		**2b**	5	320	95
5	**1c**	**2a**	14	148	92
6		**2b**	24	325	80
7	**1d**	**2a**	7	127	83
8		**2b**	14	270	90
9	**1e**	**2a**	1	90	96
10		**2b**	3	130	95
11	**1f**	**2a**	12	158	98
12		**2b**	24	235	85
13	**1g**	**2a**	2.5	168	99
14		**2b**	8	255	90
15	**1h**	**2a**	2	oil	88
16		**2b**	4	106	93
17	**1i**	**2a**	2	oil	95
18		**2b**	6	104	97
19	**1j**	**2a**	20	173	50
20		**2b**	32	196	70
21	**1k**	**2a**	9	138	80
22		**2b**	12	239	72
23	**1l**	**2a**	8	oil	98
24		**2b**	10	110	90
25	**1m**	**2a**	9	oil	90
26		**2b**	9	202	82
27	**1n**	**2a**	6	56	85
28		**2b**	7	196	76

[a]See ref. 21.

The mechanism of the reaction probably involves ferric perchlorate mediated deoximation[22] followed by an arylhydrazine attack on the *in situ* formed carbonyl compound.

Thus, we have developed a convenient and practical method for the synthesis of arylhydrazones by a one-pot straightforward conversion of oximes catalysed by ferric perchlorate. The significant features of this method involve fairly inexpensive reagents, high yields of products, and the use of relatively non-toxic reagents and solvents.

† Beilstein–Crossfire database contains 83 citations on this reaction dated before 1970 and only two later references (see refs. 18, 19).

‡ *Conversion of oximes into arylhydrazones (general procedure).* A mixture of oxime (1 mmol), arylhydrazine (1 mmol) and $Fe(ClO_4)_3$ (0.1 mmol, 0.05 g) in DCE (5 ml) was stirred at ambient temperature for a specified time (Table 1). After completion of the reaction, as monitored by TLC, DCE (10 ml) was added and filtered through a bed of Na_2SO_4. Then, the solvent was evaporated, and products were recrystallised from light petroleum.

References

1 (*a*) T. W. Green and P. G. M. Wuts, *Protection Groups in Organic Synthesis*, 3rd edn., Wiley, New York, 1999; (*b*) P. J. Kocienski, *Protecting Groups*, 3rd edn., Thieme, Stuttgart, 2004.

2 (*a*) D. Seebach and E. J. Corey, *J. Org. Chem.*, 1975, **40**, 231; (*b*) S. Rozen, I. Shahak and E. D. Bergmann, *Tetrahedron Lett.*, 1972, 1837; (*c*) M. Yus, C. Najera and F. Foubelo, *Tetrahedron*, 2003, **59**, 6147.

3 (*a*) E. J. Corey and H. L. Pearce, *J. Am. Chem. Soc.*, 1979, **101**, 5841; (*b*) E. J. Corey, K. Niimura, Y. Konishi, S. Hashimoto and Y. Hamada, *Tetrahedron Lett.*, 1986, **27**, 2199; (*c*) D. Enders, L. Wortmann and R. Peters, *Acc. Chem. Res.*, 2000, **33**, 157.

4 H. Kumar, B. Kaur and B. Kumar, *Indian J. Chem., Sect. B: Org. Chem. Incl. Med. Chem.*, 1991, **30B**, 869.

5 (*a*) D. H. R. Barton, D. J. Lester and S. V. Ley, *J. Chem. Soc., Chem. Commun.*, 1977, 445; (*b*) B. P. Bandgar, S. I. Shaikh and S. Iyer, *Synth. Commun.*, 1996, **26**, 1163; (*c*) A. Boruah, B. Baruah, D. Prajapati and J. S. Sandhu, *Synlett.*, 1997, 1251.

6 (*a*) J. Drabowicz, *Synthesis*, 1980, 125; (*b*) E. J. Corey, P. B. Hopkins, S. Kim, K. P. Nambiar and J. R. Falck, *J. Am. Chem. Soc.*, 1979, **110**, 71.

7 J. M. Aizpurua and C. Palomo, *Tetrahedron Lett.*, 1983, **24**, 4367.

8 R. Joseph, A. Sudalai and T. Ravindranathan, *Tetrahedron Lett.*, 1994, **35**, 5493.

9 G. A. Olah, Q. Liao, C. S. Lee and G. K. Suryaprakash, *Synlett.*, 1993, 427.

10 N. B. Barhate, A. S. Gajare, R. D. Wakharkar and A. Sendalai, *Tetrahedron Lett.*, 1997, **38**, 653.

11 D. S. Bose and P. Srinivas, *Synlett.*, 1998, 977.

12 H. D. Ayhan and B. A. Tanyeli, *Tetrahedron Lett.*, 1997, **38**, 7267.

13 R. S. Varma and H. M. Meshram, *Tetrahedron Lett.*, 1997, **38**, 5427.

14 (*a*) D. S. Bose and A. V. Narsaiah, *Synth. Commun.*, 1999, **29**, 937; (*b*) S. S. Chaudhari and K. G. Akamanchi, *Tetrahedron Lett.*, 1998, **39**, 3209.

15 B. Subhas and V. Naresaiah, *Synth. Commun.*, 2000, **30**, 1153.

16 B. Subhas, A. V. Narsaiah and V. Lakshminarayana, *Synth. Commun.*, 2000, **30**, 3121.

17 I. Mohmmadpoor Baltork and S. Pouranshirvani, *Synth. Commun.*, 1996, **26**, 1.

18 V. G. Andrianov, V. G. Semenikhina and A. V. Eremeev, *Khim. Geterotsikl. Soedin.*, 1992, 969 [*Chem. Heterocycl. Compd.* (*Engl. Transl.*), 1992, **28**, 808].

19 M. H. Shih, L. H. Lu and M. Y. Yeh, *J. Chin. Chem. Soc.*, 2001, **48**, 883.

20 (*a*) M. M. Heravi, F. K. Behbahani, H. A. Oskooie and R. Hekmat Shoar, *Tetrahedron Lett.*, 2005, **46**, 2543; (*b*) M. M. Heravi, F. K. Behbahani, H. A. Oskooie and R. Hekmat Shoar, *Tetrahedron Lett.*, 2005, **46**, 2775; (*c*) M. M. Heravi, F. K. Behbahani, R. Hekmat Shoar and H. A. Oskooie, *J. Mol. Catal., A: Chem.*, 2005, **244**, 8; (*d*) M. M. Heravi, F. K. Behbahani, R. Hekmat Shoar and H. A. Oskooie, *Catal. Commun.*, 2006, **7**, 136; (*e*) M. M. Heravi, V. Zadsirjan, F. K. Behbahani and H. A. Oskooie, *J. Mol. Catal., A: Chem.*, 2006, **259**, 201.

21 R. L. Shriner R. C. Fuson, D. Y. Curtin and T. S. Morrill, *Systematic Identification of Organic Compounds*, 6th edn., Wiley, New York, 1980.

22 (*a*) M. M. Khodaei, F. A. Meybodi, N. Rezai and P. Salehi, *Synth. Commun.*, 2001, **1**, 2047; (*b*) A. Parmar, R. Goyal, B. Kumar and H. Kumar, *Indian J. Chem. Sect. B: Org. Chem. Incl. Med. Chem.*, 1998, **37**, 941.

Received: 4th September 2006; Com. 06/2780