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NaIO₄–DMF: a novel reagent for the oxidation of organic halides to carbonyl compounds

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Abstract—NaIO₄–DMF oxidises various primary and secondary halides to the corresponding aldehydes and ketones under mild conditions ($150^{\circ}C/40-60$ min) in high yields (70-90%). © 2003 Elsevier Science Ltd. All rights reserved.

Oxidation of organic halides to the corresponding carbonyl compounds is a well known transformation in organic synthesis. In 1949, the Hass-Bender reaction was reported for the oxidation of halides.¹ Several methods have been developed to carry out this conversion^{2,3} such as the Sommelet reaction⁴ which is limited to benzylic halides, the Krohnke reaction (pyridine followed by p-nitrosodimethylaniline)⁵ and the Kornblum reaction (DMSO/NaHCO₃)⁶ which is limited to active halides and requires very high tempera-ture. Various amine N-oxides⁷⁻⁹ are also used for this oxidation. Masaki et al.¹⁰ have reported the photooxidation of aryl bromides with mesoporous silica FSM-16. More recently, 2-dimethylamino-N,N-dimethyl aniline-N-oxide¹¹ was used for this conversion in high yield. All the above procedures are limited and required high temperatures. To circumvent all these obstacles, we planned to explore the use of NaIO₄-DMF for the oxidation of halides to the corresponding carbonyl compounds. We wish to report here a new and convenient method for the preparation of aldehydes and ketones from the corresponding halides.

The importance of sodium metaperiodate in organic synthesis prompted us to examine the behaviour of sodium metaperiodate and dimethyl formamide on different halogen compounds. Primary and secondary halides were reacted with NaIO₄–DMF to give the corresponding aldehydes and ketones, respectively. It was found that different primary halides (Table 1) and secondary halides (Table 2) gave the corresponding carbonyl compounds in good yields in short time periods. Octyl bromide was converted into octanal in an 85% yield (Table 1, entry 1). Benzyl bromide (entry 2) and a substituted benzyl bromide (entry 3) gave the corresponding aldehydes in good yields. Different

halomethyl naphthalenes (entries 4, 5 and 6) were also converted to the corresponding aldehydes in 80–85% yields. Cinnamyl bromide and chloride (entries 7 and 8) also gave cinnamaldehyde in 90 and 84% yields in 50 and 55 min, respectively.

Secondary halides gave the corresponding ketones, as shown in Table 2. For example, cyclohexyl bromide (Table 2, entry 1) gave cyclohexanone in an 84% yield. Bromodiphenyl methane was converted to benzophenone in 90% yield and chlorodiphenyl methane (Table 2, entry 3) took a little more time but gave benzophenone in 80% yield. 9-Bromofluorene (Table 2, entry 4) give 9-fluorenone in good yield in 45 min.

The behaviour of this reagent towards the α -halocarbonyl compounds, i.e. phenacyl bromide was also examined, but to our surprise benzaldehyde was isolated instead of phenyl glyoxal. Phenacyl bromide might have undergone the same oxidation (Scheme 1) as primary halides to give phenyl glyoxal which is further oxidized to phenylglyoxalic acid which undergoes decarboxylation to give benzaldehyde (85% yield based upon GC–MS).

In conclusion, we have developed a new method to convert primary and secondary halides to the corresponding aldehydes and ketones, using for the first time the oxidising property of a mixture of $NaIO_4$ and DMF.

Typical reaction procedure: Benzyl bromide (0.34 g, 2 mmol) was taken in a round bottom flask along with sodium metaperiodate (NaIO₄) (0.42 g, 2 mmol). The above mixture was dissolved in 30 ml of *N*,*N*-dimethyl formamide (DMF). The reaction mixture was heated at reflux. The progress of the reaction was monitored by thin layer chromatography by comparison with the

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Table 1. Reactions of primary halides with NaIO₄ and DMF



starting material (10% ethyl acetate in hexane). The reaction was completed in 40 min. The reaction mixture was cooled and treated with 20 ml of water and then

extracted with ether $(2 \times 30 \text{ ml})$. The combined ether layers were dried over anhydrous magnesium sulphate

(MgSO₄), then filtered off and concentrated. GLC anal-

ysis of the reaction mixture showed the presence of

benzaldehyde (80%). Purification by column chro-

matography on 60-100 mesh silica gel gave (0.18 g,

Table 2. Reactions of secondary halides with $NaIO_4$ and DMF



a) Isolated yields; analytical data were compared with those of authentic samples.

80%) of benzaldehyde. The formation of benzaldehyde was further confirmed by the melting point of its 2,4-dinitrophenylhydrazone derivative.

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References

- 1. Hass, H. B.; Bender, M. L. J. Am. Chem. Soc. 1949, 7, 1767–1769.
- Kileny, S. N. In *Comprehensive Organic Synthesis*; Trost, B. M.; Ley, S. V., Eds.; Pergamom Press: Oxford, 1991; Vol. 7, pp. 653–670.



- Smith, M. B.; March, J. March's Advanced Organic Chemistry, 5th ed.; Wiley-Interscience Publication: New York, 2001; pp. 1535–1536.
- 4. Larock, R. C. *Comprehensive Organic Transformations*; VCH Publication: NewYork, 1989; pp. 599–600.
- 5. Krohnke, F. Angew. Chem., Int. Ed. 1963, 2, 380-393.
- Kornblum, N.; Jones, W. J.; Anderson, G. J. J. Am. Chem. Soc. 1959, 81, 4113.
- 7. Franzen, V. Org. Synth. 1973, 5, 872-874.
- Mukaiyama, S.; Inanga, J.; Yamaguchi, M. Bull. Chem. Soc. Jpn. 1981, 54, 2221.
- Suzuki, S.; Onishi, T.; Fujita, Y.; Misawa, H.; Otera, J. Bull. Chem. Soc. Jpn. 1986, 59, 3287.
- Itoh, A.; Kodana, T.; Inagaki, S.; Masaki, Y. Org. Lett. 2000, 2, 2455–2457.
- 11. Chandrasekhar, S.; Sridhar, M. Tetrahedron Lett. 2000, 41, 5423-5425.