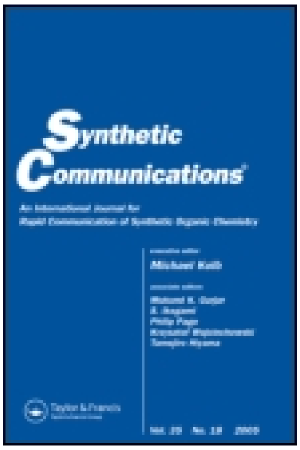

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A MILD AND CONVENIENT PROCEDURE FOR THE OXIDATION OF AROMATIC ALDEHYDES TO CARBOXYLIC ACIDS USING UREA-HYDROGEN PEROXIDE IN FORMIC ACID

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A MILD AND CONVENIENT PROCEDURE FOR THE OXIDATION OF AROMATIC ALDEHYDES TO CARBOXYLIC ACIDS USING UREA–HYDROGEN PEROXIDE IN FORMIC ACID

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ABSTRACT

Mild and safe oxidation of aromatic and heteroaromatic aldehydes to the corresponding acids was achieved by using UHP in formic acid.

A large number methods have been reported for the transformation of aromatic aldehydes into their corresponding carboxylic acids.[1] The conventional methods of carrying out this reaction make use of oxidant agents, *i.e.* potassium permanganate, chromium (VI) oxide, pyridinium dichromate, pyridinium chlorochromate, silver (I) oxide or molecular oxygen.[2] Hydrogen peroxide has been also used for this purpose under strongly basic conditions[3] itself or in combination with other reagents.[4–7] However, most of the existing methods are deficient in some respect such as: low yields, high cost, severe acidic or basic reaction conditions and formation of heterogeneous mixture. On the other hand concentrated H_2O_2 is very dangerous to handle and not readily available. Hence this agent is now replaced by more stable and safe compounds. Urea–hydrogen peroxide

(UHP)[8] is a safe alternative to anhydrous H_2O_2, relatively stable, inexpensive and commercially available.

Several systems containing UHP with some carboxylic acid or their anhydrides were used as efficient, oxidizing agents.[9–11] Recently we reported that performic acid obtained by the combination of UHP and formic acid appeared to be an effective reagent for mild N-oxidation of N-heteroaromatics[12] and organic sulfides to sulfones.[13] These results have prompted us to extend the studies on the oxidizing ability of this novel reagent system.

In this paper we wish to report on a safe and efficient oxidation of aromatic and heteroaromatic aldehydes **1** to the respective carboxylic acid **2** by use of UHF/HCOOH system. The reaction is very easy and proceeds within 1.5–3 hours upon addition of the substrate **1** to the solution of UHP in formic acid at room temperature to afford the corresponding carboxylic acid **2**.

The optimum ratio substrate **1** to UHP was found to be 1:4. Use in the place of formic acid other carboxylic acids alone or in their methanolic solutions gave less satisfactory results.

Several examples illustrating this novel and efficient procedure for the oxidation of aromatic aldehydes **1** to the corresponding carboxylic acids **2** are presented in Table. The reaction proceeds well with aldehydes containing electron-withdrawing (**1h–g**) or mildly activating (**1h–i**) groups. The presence of powerful electron-donating groups (**1j–l**) gave less satisfactory results. Oxidation of pyridine carboxaldehydes (**1m–p**) afforded the corresponding acids in high yield, although the traces of the N-oxides were also formed.

In conclusion, this new method for converting aromatic aldehydes to the corresponding carboxylic acids offers the following advantages: (a) safe and cheap oxidizing agent is used, (b) the oxidation is mild and fast giving in most cases the carboxylic acids in high yields, (c) the method is efficient also for the oxidation N-heteroaromatic aldehydes (entries **1m–p**), (d) the procedure is facile and isolation of the products is easy. For the above reasons the procedure described herein may be method of choice for the conversion aldehydes into carboxylic acids.

EXPERIMENTAL

Typical Procedure: The corresponding aromatic aldehyde **1** (2 mmol) was introduced portionwise to the stirred solution of UHP (8 mmol) in 95% formic acid (15 cm^3) at room temperature. The mixture was stirred at this temperature until tlc analysis indicated completion of reaction (1. 5–3 hr). The water (20 cm^3) was then added to the reaction mixture. The aqueous

Table. Oxidation of (Hetero)aromatic Aldehydes to Carboxylic Acids

$$\underset{\mathbf{1}}{\text{Ar—CHO}} \xrightarrow[\text{r.t.}]{\text{UHP/HCOOH}} \underset{\mathbf{2}}{\text{Ar—COOH}}$$

Aldehyde **1** Entry	Ar	Reaction time	Yield[a,b] of **2**, %	m.p. (°C)[c]
1a	Ph	1.5	96	119–121 (121–123)
1b	2-NO_2-Ph	2.0	79	145–147 (146–148)
1c	3-NO_2-Ph	2.0	78	139–140 (140–142)
1d	2-Cl-Ph	1.5	78	137–139 (138–140)
1e	4-Cl-Ph	2.5	82	240–241 (239–241)
1f	3-Cl-Ph	3.0	77	154–157 (155–157)
1g	4-F-Ph	3.0	75	183–185 (184–187)
1h	4-CH_3-Ph	2.5	85	180–183 (180–182)
1i	3-CH_3-Ph	2.0	87	108–111 (108–110)
1j	3-CH_3O-Ph	2.5	51	103–105 (106–108)
1k	2-CH_3O-Ph		–[d]	
1l	4-CH_3O-Ph	3.0	54	179–181 (182–185)
1m	4-pyridyl	1.5	91[e]	> 308 (310–315)
1n	3-pyridyl	1.5	90[e]	233–236 (236–239)
1p	3-quinolyl	2.0	90[e]	277–281 (277–280)

[a] All products were characterized by their ^{1}H-NMR and MS spectra.

[b] Yields of isolated crude acids.

[c] Literature m.p's in parantheses taken from Aldrich Chemical Co., catalogue.

[d] Intractable complex reaction mixture was obtained.

solution was extracted with $CHCl_3$ ($3 \times 10\,cm^3$) and organic layer washed with water ($2 \times 10\,cm^3$), saturated aq. $NaHCO_3$ solution ($2 \times 10\,cm^3$) and again with water ($2 \times 10\,cm^3$). The combinated extracts were then dried over anhydrous Na_2SO_4, filtered and evaporated to give product **2** (Table).

REFERENCES

1. Ogliaruso, M.A.; Wolfe J.F. "*Synthesis of Carboxylic Acids, Esters and Their Derivatives*", Patai, S., Rappaport, Z., Eds., Wiley, Chichester, 1991, pp. 40–51.
2. Yamada, T.; Rhode, O.; Takai, T.; Mukaiyama, T. Chem. Lett. **1991**, 5.
3. Birkinshaw, J.H.; Raistrick, H.; Ross, D.J.; Stickings, C.E. Biochem. J. (London) **1952**, *5*, 610.

4. Ganem, B.; Heggs, R.P.; Biloski, R.P. Tetrahedron Lett. **1980**, *21*, 685.
5. Delcanale, E.; Montanari, F. J. Org. Chem. **1986**, *51*, 567.
6. Choi, J.K.; Chang, Y.K.; Hong, S.Y. Tetrahedron Lett. **1988**, *29*, 1667.
7. Dodd, R.H.; Le Hyaric, M. Synthesis **1993**, 295.
8. Lu, C.; Hughes, E.W.; Giguere, P.A. J. Am. Chem. Soc. **1941**, *53*, 1507.
9. Balicki, R.; Kaczmarek, Ł.; Nantka-Namirski, P. Justus Liebigs Ann. Chem. **1992**, 883.
10. Ballini, R.; Marcantoni, E.; Petrini, M. Tetrahedron Lett. **1992**, *33*, 385.
11. Balicki, R.; Synth. Commun. **1999**, *29*, 2235.
12. Balicki, R.; Goliñski, J. Synth. Commun. **2000**, *30*, 1529.
13. Balicki, R. J. Prakt. Chem. **1999**, *341*, 183.

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