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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

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To cite this article: Qing-Hua Meng , Jun-Cai Feng , Ning-Sheng Bian , Bin Liu & Chang-Chuan Li (1998) Benzimidazolium Dichromate-A New Reagent for Selective Oxidation Under Microwave Irradiation, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 28:6, 1097-1102, DOI: <u>10.1080/00397919808003079</u>

To link to this article: http://dx.doi.org/10.1080/00397919808003079

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BENZIMIDAZOLIUM DICHROMATE-A NEW REAGENT FOR SELECTIVE OXIDATION UNDER MICROWAVE IRRADIATION

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ABSTRACT: Benzimidazolium dichromate (BIDC), is conveniently prepared and functions as a selective reagent for the oxidation of benzylic and allylic alcohols to the corresponding carbonyl compounds under microwave irradiation.

Oxochromium-amine complexes have long been used as a group of oxidants in organic synthesis. There currently is interest in designing and applicating new chromium(VI) reagents, especially for selective oxidation^[1-3].

During the investigation it has been found that the selectivity depends on the reaction time, selectivity decreased with increasing reaction time^[1]. This fact encouraged us to find a new method to shorten the reaction time to obtain higher selectivity.

Herein we introduce microwave irradiation to the selective oxidation of benzylic and allylic alcohols to the carbonyl compounds. A suitable

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new reagent, benzimidazolium dichromate (BIDC), is also applied under these conditions. It takes less than 5 minutes for most of the reactions to reach a satisfactory yields. Oxidation of chloramphenicol(I) especially illustrates the method's selective advantage (scheme 1).



As analyzed by HPLC, the reaction mixture contained 73% of (II), 23% of (I), which can be recovered, and the total content of by-products is only 4%.

BIDC's selectivity is also shown by the fact that treatment of benzylic and allylic alcohols with 1.3-3.0 mol of BIDC for 1-4 minutes leads to the corresponding carbonyl compounds in 75-98% yield (Table 1).

| entry | alcohol | molar ratio of BIDC/alcohol | solvent | time (min) | yield (%) ^a |
|-------|--|--------------------------------|---------|---------------|---------------------------|
| 1 | C ₆ H ₅ CH ₂ OH | 1.3 | CCl₄ | 1 | 92 |
| 2 | <i>p</i> -CH ₃ C ₆ H₄CH ₂ OH | 1.5 | CCl₄ | 1 | 84 |
| 3 | p-ClC₀H₄CH₂OH | 1.5 | acetone | 1 | 98 |
| 4 | 3,4-(BzO) ₂ C ₆ H ₃ CH ₂ OH | 1.8 | acetone | 2 | 88 |
| 5 | 3,5-(BzO) ₂ C ₆ H ₃ CH ₂ OH | 1.8 | acetone | 2 | 86 |
| 6 | C ₆ H ₅ CH(OH)CH ₃ | 2.0 | CCl₄ | 3 | 97 |
| 7 | C ₆ H ₅ COCH(OH)C ₆ H ₅ | 3.0 | acetone | 4 | 76 |
| 8 | p-CH ₃ OC ₆ H ₄ COCH(OH)C ₆ H ₄ OCH ₃ -p | 3.0 | acetone | 3 | 89 |
| 9 | <i>p</i> -ClC ₆ H ₄ COCH(OH)C ₆ H ₄ Cl- <i>p</i> | 3.0 | acetone | 4 | 92 |
| 10 | CH ₂ =CHCH ₂ OH | 2.5 | CCl₄ | 3 | 75 |
| 11 | C ₆ H ₅ CH=CHCH ₂ OH | 2.5 | CCl₄ | 2 | 88 |

| Table 1: Oxidation of benzylic and all | ylic alcohols by BIDC under |
|--|-----------------------------|
| microwave irradiation | |

a: Yields were determined by HPLC.

However, during oxidation of n-butanol under similar condition, the aldehyde was not detected (HPLC) and 98% of n-butanol can be recovered.

Benzimidazolium dichromate is conveniently prepared from benzimidazole, 6N aqueous hydrochloric acid and chromium trioxide in a molar ratio of 1:1:1. It is a light yellow crystalline solid and is neither hygroscopic nor light sensitive, thus more stable and easily stored as compared to other chromium(VI) reagents and active manganese dioxide^[4]. It is soluble in dimethylformamide and acetone, sparingly soluble in water, and insoluble in carbon tetrachloride, dichloromethane, ether and benzene. We consider BIDC as a promising new oxidant in organic synthesis.

Further investigation on the BIDC's characterization and its application in other reactions is under way.

Experimental:

All reagents were commercially available and used without further purification.

Reactions were carried out in a Sanle WP-500 (2450 MHz, 500W) domestic microwave oven.

Yields were determined on a Varian 5060 HPLC apparatus.

Melting points were measured on a Yanaco Mp-500 apparatus and uncorrected.

IR spectra were recorded on a Nicolet FT-IR 50X FT spectrometer with KBr pellets. ¹H-NMR spectra were recorded on a JEOL JNM-PMX 60 SI spectrometer in CDCl₃ with TMS as an internal standard. MS spectra were obtained by a VG-ZAB-HS spectrometer at 70 ev and elemental analyses were obtained by Perkin-Elmer 240C elemental analyzer.

Preparation of benzimidazolium dichromate (BIDC):

A solution of chromium trioxide (10 g, 0.1 mol) in 12mL water was cooled to room temperature with vigorous stirring, 17mL 6N aqueous hydrochloric acid, which contained 11.8g (0.1mol), benzimidazole was slowly added in. Light yellow powders were produced and the solution was stirred for additional 20 minutes. The product was collected on a sintered glass funnel and dried in a vacuum desiccator. yield 19.8g (81%) mp. 138-140°C. This crude product was

recrystallised from water as orange column crystal, mp. 170-171°C. Anal. calcd for $(C_7H_6)_2 \cdot H_2Cr_2O_7 \cdot 2H_2O$: C, 33.87; H, 3.63; N, 11.29. Found: C, 34.02; H, 4.07; N, 11.26.

General oxidation procedure:

The above reagent (4.0g 16.4mmol) was placed in a round bottom flask equipped with a reflex condenser. A solution of 1.4g (13.0mmol) benzyl alcohol in 15mL carbon tetrachloride was added . The reaction mixture was irradiated in microwave oven for 1 minute. After cooling, the mixture was filtered and washed with carbon tetrachloride (3 ×5mL). The combined filtrates were washed with 10ml water and dried over anhydrous MgSO₄. The solvent was evaporated under reduced pressure to give a pale yellow oil. HPLC [column/Spherisorb C18 5µm (4.6×200mm). column temperature: 18°C; mobile phase: methanol : water = 70:30, (v/v); flow rate: 1mL/min; λ =280nm] analysis of the oil indicated a yield of benzaldehyde in 92%. The product could be isolated as 2,4-dinitrophenylhydrazone derivative which has a melting point of 235-237°C (lit. m.p. 237°C^[5a])

Oxidation of chloramphenicol (I) with 3 equiv. BIDC gave (II) in 73% yield (HPLC analysis). Pure product for spectroscopic analyses was obtained by column chromatography (SiO₂, ethyl acetate / petroleum ether), m.p. 56-58°C.

IR(KBr): 3280, 1700, 1670, 1600, 1520, 1350 cm⁻¹.

¹H NMR(CDCl₃): 8.76 (s,1H), 8.20 (s,2H), 8.12 (s,2H), 7.56 (s,1H), 5.46(m,1H), 4.01 (d,2H), 3.15 (s,1H)ppm.

MS: m/z (relative intensity): 321 (M⁺, 3.14), 303 (7.57), 170 (34.61), 150 (100).

4-methylbenzaldehyde: 2,4-dinitrophenylhydrazone m.p. 231-233°C (lit. m.p. 232.5-234.5°C)^[5b]

4-chlorobenzaldehyde: 2,4-dinitrophenylhydrazone m.p. 263-265°C (lit. m.p. 266°C)^[5c]

3,4-dibenzyloxybenzaldehyde: m.p. 91-94°C (lit. m.p. 93-94°C)^[6] MS:(m/z) 318(M⁺); IR(KBr): 2830, 2730, 1680, 1580, 1510, 1390, 760,

680cm⁻¹; ¹H NMR(CDCl₃): 5.15-5.20(s,4H); 7.05-7.41(m,13H); 9.85(s, 1H)ppm.

3,5-dibenzyloxybenzaldehyde: m.p. 78-80°C (lit.m.p. 81-82°C)^[7] MS:(m/z) 318(M⁺); IR(KBr): 2830, 2740, 1690, 1600, 1460, 1390, 840, 735cm⁻¹; ¹H NMR(CDCl₃): 4.98(s,4H); 6.65-7.30(m,13H); 9.75(s, 1H)ppm.

acetophenone: phenylhydrazone m.p. 104-6°C (lit. m.p. 106°C)^[5d]

Benzil: m.p. 94-95°C (lit. m.p. 93-95°C)^[8]

4,4'-dimethoxybenzil: m.p. 132-134°C (lit. m.p. 133-135°C)^[8]

4,4'-diclorobenzil: m.p.196-198°C (lit. m.p. 197-8°C)^[8]

propenal: 2,4-dinitrophenylhydrazone m.p. 162-164°C (lit. m.p. 165°C)^[5e]

3-phenyl-2-propenal: 2,4-dinitrophenylhydrazone m.p. 251-254°C (lit. m.p. 255°C)^[5f]

Acknowledgments: We thank Professor Xu Jianhua for his helpful discussions. The analysis work was partially supported by the Center of Material Analysis, Nanjing University.

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(Received in the USA 30 September 1997)