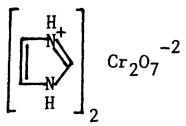
Imidazolium Dichromate. A New Reagent for the Oxidation of Alcohols to Carbonyl Compounds

Sunggak KIM* and Dong Chul LHIM
Department of Chemistry, Korea Advanced Institute of Science and Technology, Seoul 131, Korea
(Received September 21, 1985)

Synopsis. Imidazolium dichromate, a stable yellow crystalline compound, is found to be a mild selective reagent for the oxidation of allylic and benzylic alcohols to the corresponding carbonyl compounds.

Among many useful and reliable oxidation methods available in the literature,[1] the use of chromium(VI) reagents is the most convenient and efficient. Chromium trioxide–pyridine complex,[2] pyridinium chlorochromate,[3] and pyridinium dichromate,[4,5] have been widely utilized as oxidizing agents in most cases.

We have had occasion to study chromium trioxide–imidazole complex as an oxidizing agent and found that imidazolium dichromate (IDC) is very useful and reliable for the oxidation of allylic and benzylic alcohols to the corresponding carbonyl compounds in high yields under mild conditions.



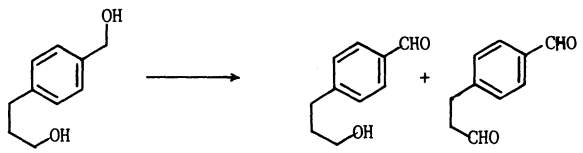
IDC

IDC is conveniently prepared by the addition of imidazole to a solution of an equimolar amount of chromium trioxide in a minimum of water and obtained in 80% yield as a nonhygroscopic and air-stable yellow crystals. IDC is readily soluble in *N,N*-dimethylformamide and dimethyl sulfoxide, while very slightly soluble in dichloromethane, chloroform, and acetone.

The choice of solvent in the oxidation of alcohols with IDC appeared to be important. The oxidation of 1-phenylethanol with 2 equiv of IDC in dichloromethane at room temperature for 16 h gave 35% of acetophenone along with the recovery 55% of the original alcohol, while the reaction in *N,N*-dimethylformamide under the same conditions was complete, yielding acetophenone in 83% yield. Thus, remaining reactions were carried out with 2 equiv of IDC in *N,N*-dimethylformamide at room temperature.

Table 1 includes several experimental results and shows the efficiency, the applicability, and the scope of this method. Under the present conditions, allylic alcohols such as cinnamyl alcohol and carveol were rapidly oxidized to α,β-unsaturated carbonyl compounds in high yields. The oxidation of geraniol to geranial resulted in isomerization of double bond to some extent. GLC analysis indicated the 6% E→Z isomerization at double bond took place. The oxidation of benzylic alcohols was somewhat slower than that of allylic alcohols and required 4—16 h for completion of the reaction.

The oxidation of saturated aliphatic alcohols occurred very slowly. For example, when the oxidation of 1-undecanol was carried out with 2 equiv of IDC in *N,N*-dimethylformamide at room temperature for 24 h, undecanal was obtained in 38% yield along with the recovery of the starting material in 53% yield. Similar results were realized with several saturated aliphatic alcohols, though relatively sterically-hindered cyclohexanol derivatives such as 2-*t*-butylcyclohexanol and 3,3,5-trimethylcyclohexanol were cleanly and completely oxidized to the corresponding carbonyl compounds in high yields under the same conditions.



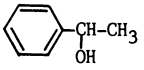
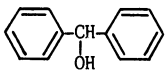
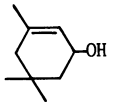
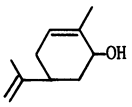
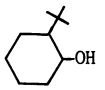
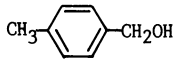
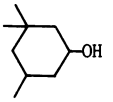
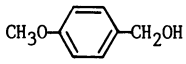
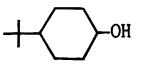
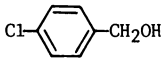
Since the possibility of selective oxidation of benzylic and allylic alcohols in the presence of saturated aliphatic alcohols was indicated by the oxidation results obtained herein, the oxidation of an equimolar mixture of isophorol (3,5,5-trimethyl-2-cyclohexen-1-ol) and 1-nonanol with 2 equiv of IDC was carried out in *N,N*-dimethylformamide at room temperature for 1 h. GLC analysis indicated the presence of a 98:11 mixture of isophorone and nonanal. Even better selectivity was obtained with *p*-(3-hydroxypropyl)benzyl alcohol. Reaction of *p*-(3-hydroxypropyl)benzyl alcohol with 2 equiv of IDC in *N,N*-dimethylformamide at room temperature for 4 h gave *p*-(3-hydroxypropyl)-benzaldehyde in 68% yield along with less than 3% of the corresponding dialdehyde. The selectivity achieved with IDC is comparable to 4-(dimethylamino)pyridinium chlorochromate.[5]

In conclusion, the use of imidazolium dichromate as an oxidizing agent offers some distinct advantages such as easy preparation and stability of the reagent, the selective oxidation of allylic and benzylic alcohols, and mild conditions.

Experimental

Preparation of Imidazolium Dichromate. Imidazole (13.6 g, 0.2 mol) was slowly added to a cooled solution of chromium trioxide (20.0 g, 0.2 mol) in water (16 ml). After 0.5 h, the reaction mixture was diluted with acetone (20 ml) and cooled to −20 °C. The yellow crystals were collected, washed with acetone (40 ml), and dried in vacuo at room temperature to give imidazolium dichromate (28.3 g, 80%). Mp 130—131 °C (decomp); NMR (DMSO-d_6) δ=7.50 (s, 2H), 8.96 (s, 1H), 12.37 (s, 2H); IR (KBr) 930, 890, 765 cm^{-1}. Found: C, 20.80; H, 2.90; N, 16.19%. Calcd for $C_6H_{10}O_7N_4Cr_2$: C, 20.35; H, 2.85; N, 15.82.

Table 1. Oxidation of Alcohols to Carbonyl Compounds with IDC in DMF at Room Temperature[a)]

Alcohol	Time/h	Yield/%[b)]	Alcohol	Time/h	Yield/%[b)]
t-C_6H_5-CH=CH-CH_2OH	1	91		16	83
t-C_6H_5-CH=CH-CH(OH)CH_3	1	94			
Geraniol	2	82 [c)]		12	93
	2	88			
	2	91		24	84
	6	75		24	87
	6	75		24	58(25)
	6	71	$CH_3CH(OH)(CH_2)_8CH_3$	24	77(13)
			$CH_3(CH_2)_9CH_2OH$	24	38(53)

a) The reaction was carried out with 2 equiv of IDC. b) The yields refer to isolated products. The numbers in parentheses indicate the isolated yields of the recovered starting materials. c) 6% E→Z isomerization was detected by GLC.

General Procedure for Oxidation of Alcohols. To a solution of an alcohol (2 mmol) in *N,N*-dimethylformamide (5 ml) was added imidazolium dichromate (4 mmol) and the reaction mixture was stirred at room temperature. After completion of the reaction, water (30 ml) was added to the reaction mixture and the product was extracted three times with diethyl ether. The ether extracts were washed with water and aqueous $NaHCO_3$, dried over anhydrous $MgSO_4$, and evaporated to dryness. The crude product was purified by distillation with a Kugelrohr apparatus or crystallization. The oxidation products obtained here were known products in all cases and were readily available compounds in most cases.

Selective Oxidation of *p*-(3-Hydroxypropyl)benzyl Alcohol. To a solution of *p*-(3-hydroxypropyl)benzyl alcohol (165 mg, 1 mmol) in *N,N*-dimethylformamide (3 ml) was added imidazolium dichromate (705 mg, 2 mmol) and the mixture was stirred at room temperature for 4 h. After usual workup as described above, the crude product was subjected to silica-gel column chromatography with dichloromethane–ethyl acetate (4:1) as an eluant to yield *p*-(3-hydroxypropyl)-benzaldehyde (112 mg, 68%) and 3-(4-formylphenyl)propanal (4 mg, 3%). *p*-(3-Hydroxypropyl)benzaldehyde: NMR ($CDCl_3$) δ=1.80—2.30 (m, 2H), 2.77 (s, 1H), 2.93 (t, 2H, J=6 Hz), 3.80 (t, 2H, J=6 Hz), 7.40—7.98 (m, 4H), 10.10 (s, 1H). IR (film) 1700 cm^{-1}. 3-(4-Formylphenyl)propanal: ^1H NMR ($CDCl_3$) δ=2.45—3.21 (m, 4H), 7.31—7.85 (m, 4H), 9.81 (s, 1H), 9.95 (s, 1H).

We thank Korea Advanced Institute of Science and Technology for financial support.

References

1) L. J. Chinn, "Selection of Oxidants in Synthesis," Marcel Dekker, New York (1971); J. G. Moffatt, "Oxidation," Marcel Dekker, New York (1971), Vol. 2; H. O. House, "Modern Synthetic Reactions," 2nd ed. W. A. Benzamin, Inc., New York (1972); K. Omura and D. Swern, *Tetrahedron*, **34**, 1651 (1978).

2) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, **1968**, 3363.

3) E. J. Corey and J. W. Suggs, *Tetrahedron Lett.*, **1975**, 2647.

4) E. J. Corey and G. Schmidt, *Tetrahedron Lett.*, **1979**, 399.

5) For recently developed chromium(VI) reagents, see: F. S. Guziec and F. A. Luzzio, *Synthesis*, **1980**, 691; F. S. Guziec and F. A. Luzzio, *J. Org. Chem.*, **47**, 1787 (1982); M. N. Bhattacharjee, M. K. Chaudhuri, H. S. Dasgupta, N. Roy, and D. T. Khathing, *Synthesis*, **1982**, 588; X. Huang and C. Chan, *Synthesis*, **1982**, 1091; J. Herscovici, M-J. Egron, and K. Antonakis, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 1967; J. M. Aizpurua and C. Palomo, *Tetrahedron Lett.*, **24**, 4367 (1983).