Chromium(VI) Based Oxidants; II[1]. Zinc Dichromate Trihydrate: A Versatile and Mild Reagent for the Oxidation of Organic Compounds

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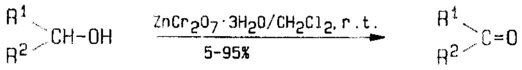
Zinc dichromate trihydrate is an easily prepared, stable, and cheap reagent for the efficient oxidation of organic compounds in aprotic organic solvents at room temperature.

Oxidations with the two commonly used oxidants; potassium permanganate and potassium dichromate in aqueous media are PH dependent and encounter problems in modern organic synthesis[2,3]. Oxidation of organic substrates in aprotic organic solvents and under mild conditions is of practical importance.

Several chromium(VI) based oxidants[1,4-20] and permanganates[21-32] have been prepared for this purpose, and used efficiently for the oxidation of organic compounds. Unfortunately many of these reagents suffer at least from one of the following disadvantages[1]: (1) cost of preparation, (2) hygroscopic, (3) photosensitive and unstable, (4) long reaction time, (5) high acidity of the media, (6) powerful oxidant without selectivity, and (7) dangerous procedure for their preparation. Therefore, search for new oxidizing agents is still a neccessity.

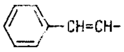
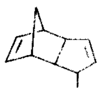
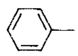
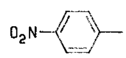
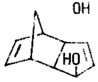
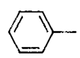
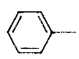
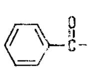
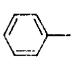
In connection with work on bis[pyridine]silver permanganate[28] and bis[2,2'-bipyridyl]copper(II) permanganate[29], we observed that zinc permanganate and tetrakis[pyridine] zinc permanganate were highly reactive and unstable reagents. Therefore, they were recognized as impractical oxidizing agents in organic synthesis. Very recently it has been reported that zinc permanganate supported on silica gel[32] is moderately stable and could be used as an oxidizing reagent. This reagent also suffers from cost of its preparation from barium manganate[32,33,34], and in some cases, from long reaction times and moderate yields of the oxidized products[32]. Having all these points in mind and also the drastic effect of the zinc cation upon the reactivity of permanganate anion, we decided to investigate the properties of oxoanions with a zinc cation for the oxidation of organic compounds. Now we report the use of zinc dichromate trihydrate[35], a red, crystalline compound, for the effective oxidation of different classes of organic substrates.

Zinc dichromate trihydrate [$ZnCr_2O_7 \cdot 3H_2O$] in dichloromethane oxidizes primary and secondary alcohols (**1a–f**) to their corresponding aldehydes or ketones (**2a–f**) in good yields. Allyl alcohols such as cinnamyl alcohol (**1g**) and the tricyclic allyl alcohols (**1h**, **1h'**) are resistant towards oxidation with this reagent under the same reaction conditions and the corresponding aldehyde (**2g**) and ketone (**2h**) are isolated in poor yields, respectively. The reagent has also been successfully applied to the oxidation of benzoin (**1i**) to benzil (**2i**).

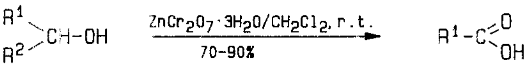


$$\mathrm{R^1R^2CH{-}OH} \xrightarrow[\text{5-95\%}]{\mathrm{ZnCr_2O_7\cdot 3H_2O/CH_2Cl_2,\ r.t.}} \mathrm{R^1R^2C{=}O}$$

1a-i **2a-i**

1, 2	R^1	R^2	1, 2	R^1	R^2
a	n-C_6H_{11}	H	g		H
b	-$(CH_2)_5$-				
c	n-$C_{11}H_{23}$-	H	1h		
d		H			
e		H	1h'		
f			i		

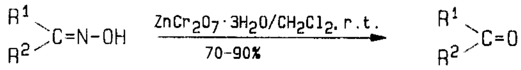
Zinc dichromate trihydrate in dichloromethane also oxidizes primary alcohols (**1a, c–e**) to their corresponding carboxylic acids (**3**) in good yields. The pathway of this reaction is dependent on the molar ratio of oxidant towards reactant.



$$\mathrm{R^1R^2CH{-}OH} \xrightarrow[\text{70-90\%}]{\mathrm{ZnCr_2O_7\cdot 3H_2O/CH_2Cl_2,\ r.t.}} \mathrm{R^1{-}COOH}$$

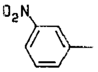
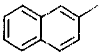
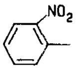
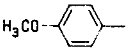
1a, c–e (R^2=H) **3a, c–e**

Aldoximes and ketoximes **4** in dichloromethane are successfully converted to their corresponding aldehydes and ketones **2e, f, j–m**.



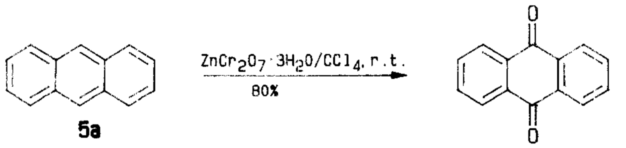
$$\mathrm{R^1R^2C{=}N{-}OH} \xrightarrow[\text{70-90\%}]{\mathrm{ZnCr_2O_7\cdot 3H_2O/CH_2Cl_2,\ r.t.}} \mathrm{R^1R^2C{=}O}$$

4e, f, j–m **2e, f, j–m**

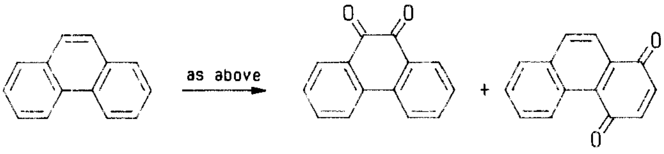
2, 4	R^1	R^2	2, 4	R^1	R^2
j		H	l		H
k		H	m		H

Similarly, further demonstrating the scope of the reaction, benzaldehyde (**2d**) was oxidized to benzoic acid (**3d**) and *m*-nitrobenzaldoxime (**4j**) was oxidized to *m*-nitrobenzoic acid (**3j**), both in good yields.

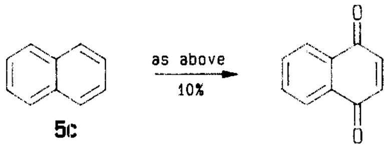
Oxidations of anthracene (**5a**), phenanthrene (**5b**), and naphthalene (**5c**) are performed in carbon tetrachloride at room temperature. Anthraquinone (**6a**) is isolated in 80%, 9,10- and 1,4-phenanthroquinone (**6b** and **6b'**) are isolated in 30%, 10%, and naphthoquinone (**6c**) in only 10% yields.



5a **6a**

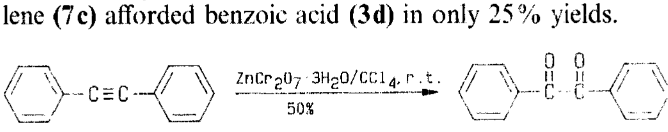


5b **6b** **6b'**

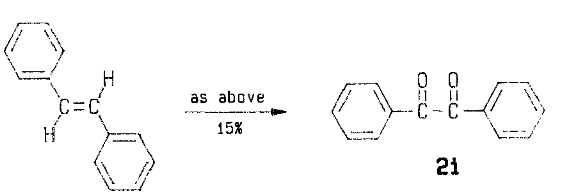


5c **6c**

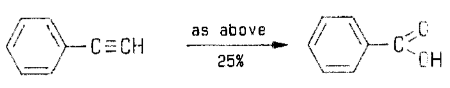
Diphenylacetylene (**7a**) produced benzil (**2i**) in 50%, *trans*-stilbene (**7b**) produced benzil (**2i**) in 15%, and phenylacetylene (**7c**) afforded benzoic acid (**3d**) in only 25% yields.



7a **2i**

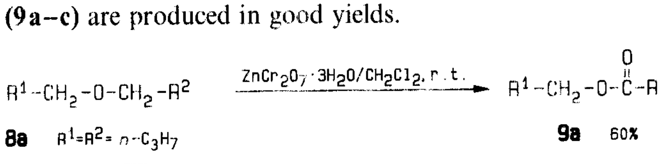


2i **7b**



7c **3d**

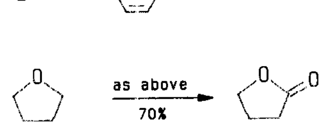
Ethers (**8a–c**) in dichloromethane are reactive towards oxidation with this reagent and their corresponding esters (**9a–c**) are produced in good yields.



$$R^1-CH_2-O-CH_2-R^2 \xrightarrow[]{ZnCr_2O_7\cdot 3H_2O/CH_2Cl_2,\ r.t.} R^1-CH_2-O-\overset{O}{\overset{\|}{C}}-R^2$$

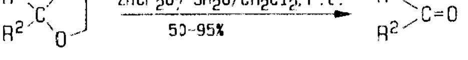
8a $R^1=R^2=n\text{-}C_3H_7$ **9a** 60%

b $R^1=R^2=$ **b** 85%



8c **9c**

This reagent is also suitable for the deacetalization reaction where the mild acidity of the media is essential. Ethylene acetals of cyclohexanone and benzophenone (**10b, f**) undergo this reaction and their corresponding ketones (**2b, f**) are isolated in good yields.



10b, f **2b, f**

The acidity of zinc dichromate trihydrate (pH of a 0.01 molar solution: 2.85) is less pronounced than those reported for pyridinium chlorochromate (pH of a 0.01 molar solution: 1.75) and pyridinium fluorochromate[6] (pH of a 0.01 molar solution: 2.45). The lower acidity of this reagent in comparison with the pyridinium halochromates, ease of its preparation, its stability, rate of the oxidation reaction, cost of its preparation, the ease of the work up of the reaction mixture, and also the results obtained, make zinc dichromate trihydrate a versatile and a practical reagent for the oxidation of organic compounds and a useful addition to the presently available bench reagents in organic synthesis.

All oxidation products are known compounds; they were identified by comparison of their spectral and physical data with those of authentic samples. I. R. spectra were run on a Perkin-Elmer IR 157 G spectrophotometer. Melting points were determined in open capillaries on a Büchi 510 apparatus and are not corrected. The purity determinations of the liquid products were accomplished by G.L.C. on a Gow-Mac 750P instrument with a flame ionization detector and using a column of 10% Apiezon L/Chromosorb-W 80–100 mesh.

Zinc Dichromate Trihydrate[35]:

To the cold solution of chromic acid (236 g, 2 mol), prepared by the addition of chromium trioxide (200 g, 2 mol) to a 3.4 molar solution of sulfuric acid (590 ml), zinc carbonate (125 g, 1 mol) is added in portions within 15 min. A dark reddish solution is produced. Evaporation of the solvent under vacuum affords an orange-red slurry, which is completely dried on the surface of a highly dried clay plate in the air; yield: 268 g (80%).

Oxidation of Benzhydrol (1f); Typical Procedure:

In a round-bottomed flask (50 ml), equipped with a condenser, a solution of benzhydrol (**1f**; 184 mg, 1 mmol) in dichloromethane (20 ml) is prepared and the oxidant (672 mg, 2 mmol) is added to this solution. The reaction mixture is stirred magnetically at room temperature for 0.1 h. The mixture is filtered and the filtrate evaporated. The resulting mixture is chromatographed on a silica gel column (70–230 mesh), eluting with 1/1 *n*-hexane/benzene. Evaporation of the solvent affords an oily material which crystallizes on standing. Recrystallization from *n*-hexane gives pure benzophenone (**2f**); yield: 173 mg (95%); m.p. 48–51 °C (Ref.[34], m.p. 49–51 °C).

Oxidation of Benzyl Alcohol (1d) to Benzoic Acid (3d); Typical Procedure:

In a round-bottomed flask (50 ml), equipped with a condenser, a solution of benzyl alcohol (**1d**; 108 mg, 1 mmol) in dichloromethane (25 ml) is prepared and the oxidant (2 g) 6 mmol) is added to this solution. The mixture is stirred magnetically at room temperature for 6 h. The mixture is filtered, the filter cake washed with dichloromethane (20 ml), the filtrates are combined, and evaporated. The resulting mixture is chromatographed on a silica gel column (30–270 mesh) and first was eluted with benzene (20 ml) and then with benzene/dichloromethane (75/25). Evaporation of benzene/dichloromethane mixture affords benzoic acid (**3d**) as white crystals; yield: 110 mg (90%); m.p. 119–121 °C (Ref.[34], m.p. 122–123 °C).

Oxidation of Dibenzyl Ether (9b); Typical Procedure:

In a round-bottomed flask (50 ml), equipped with a condenser, a solution of dibenzyl ether (**8b**; 396 mg, 2 mmol) in dichloromethane (25 ml) is prepared, the oxidant (2 g, 6 mmol) is added, and the

Table. Oxidations with Zinc Dichromate Trihydrate

Substrate	Molar Ratio oxidant/ substrate	solvent	Time	Product	Yield [%]	m.p. [°C] or b.p. [°C]/torr	
						found	reported
1a	0.5	CH_2Cl_2	0.2 h	**2a**	90[a]	153°/760	153°/760[34]
1b	2.0	CH_2Cl_2	0.3 h	**2b**	80[a]	153°/760	155°/760[34]
1c	0.5	CH_2Cl_2	0.6 h	**2c**	80[a]	187°/100	185°/100[34]
1d	2.0	CH_2Cl_2	0.1 h	**2d**	95[a]	174–180°/760	178–185°/760[34]
1e	2.5	CH_2Cl_2	0.7 h	**2e**	50	102–104°	105–108°[34]
1f	2.0	CH_2Cl_2	0.1 h	**2f**	95	48–51°	49–51°[34]
1g	2.0	CH_2Cl_2	2.0 h	**2g**	5[a]	241–245°/760	248°/760[34]
1h	2.0	CH_2Cl_2	0.5 h	**2h**	5[a]	79–81°	80°[6]
1h′	2.0	CH_2Cl_2	0.5 h	**2h**	5[a]		
1i	2.0	CH_2Cl_2	0.5 h	**2i**	90	93–95°	94–95°[34]
1a	1.5	CH_2Cl_2	0.2 h	**3a**	90[a]	218–220°/760	223°/760[34]
1c	1.5	CH_2Cl_2	0.3 h	**3c**	75–80	223°/100	225°/100[34]
1d	6.0	CH_2Cl_2	6.0 h	**3d**	90	119–121°	122–123°[34]
1e	6.0	CH_2Cl_2	6.04	**3e**	70	236–238°	239–241°[34]
4e	3.0	CH_2Cl_2	1.5 h	**2e**	70	107–108°	105–108°[34]
4j	3.0	CH_2Cl_2	1.5 h	**2j**	70	57–59°	57–59°[34]
4k	3.0	CH_2Cl_2	1.5 h	**2k**	75	150°/23	153°/23[34]
4l	3.0	CH_2Cl_2	3.0 h	**2l**	90	59–62°	59–62°[34]
4f	3.0	CH_2Cl_2	0.5 h	**2f**	90		
4m	3.0	CH_2Cl_2	0.25 h	**2m**	90	221°/760	226°/760[34]
4k	6.0	CH_2Cl_2	3.5 h	**3k**	90	139–142°	140–142°[34]
2d	3.0	CH_2Cl_2	3.0 h	**3d**	85		
5a	10.0	CCl_4	3.5 h	**6a**	80[b]	280–283°	284–286°[36]
5b	10.0	CCl_4	5.0 h	**6b**	30[b]	203–206°	205–207°[36]
				6b′	10[b]	148–150°	152–153°[36]
5c	8.0	CCl_4	6.0 h	**6c**	10[b]	123°	123–125°[36]
7a	10.0	CCl_4	8.0 h	**2i**	50[b]	93–95°	94–95°[34]
7b	8.0	CCl_4	7.0 h	**2i**	15[b]		
7c	10.0	CCl_4	13.0 h	**3d**	25		
8a	3.0	CH_2Cl_2	3.0 h	**9a**	60[a]	163–168°/760	164–167°/760[37]
8b	3.0	CH_2Cl_2	0.4 h	**9b**	85[a]	317–332°/760	323°/760[34]
8c	3.0	CH_2Cl_2	1.0 h	**9c**	70[a]	200–203°/760	204°/760[34]
10b	4.0	CH_2Cl_2	0.5 h	**2b**	50–60[a]		
10f	4.0	CH_2Cl_2	0.5 h	**2f**	95		

[a] Purity of liquid products by G.L.C.: ≥96%.
[b] Yield based on recovered starting material.

mixture is magnetically stirred for 0.4 h at room temperature. The mixture is filtered, the filtrate is evaporated, and the resulting mixture is chromatographed on a silica gel column (30–270 mesh). Elution with benzene affords liquid benzyl benzoate (**9b**). Microdistillation of the liquid product at 317–322 °C under atmospheric pressure affords the purified ester; yield: 360 mg (85%). G.L.C. analysis shows > 96% purity.

Oxidation of Anthracene (7a); Typical Procedure:

In a round-bottomed flask (50 ml), equipped with a condenser, a solution of anthracene (178 mg, 1 mmol) in carbon tetrachloride (30 ml) is prepared and the oxidant (3.4 g, 10 mmol) is added. The mixture is stirred magnetically for 3.5 h at room temperature. The mixture is filtered and the filter cake washed with boiling dichloromethane (20 ml). The filtrates are combined and evaporated. The resulting mixture is chromatographed on a silica gel column (30–270 mesh), eluting with benzene. Evaporation of the solvent affords anthraquinone (**8a**), which is recrystallized from glacial acetic acid; yield: 165 mg (80%); m.p. 280–283 °C (Ref.[34], m.p. 283–285 °C).

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