1,1,3,3-Tetramethylguanidinium Dichromate. A New Mild Reagent for the Oxidation of Alcohols

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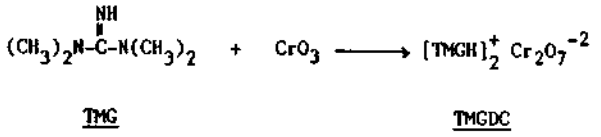
The oxidation of alcohols to carbonyl compounds is one of the fundamental reactions in synthetic organic chemistry and the development of new oxidizing agents and the modification of known reagents have been actively studied in recent years.[1,2] Among many useful reagents for oxidation of alcohols, chromium trioxide-pyridine,[3] pyridinium chlorochromate,[4] and pyridinium dichromate[5] have been widely used for this purpose.

In connection with our ongoing research program directed toward the development of new oxidizing agents, we wish to report the oxidizing property of a new mild oxidizing agent, 1,1,3,3-tetramethylguanidinium dichromate (TMGDC). TMGDC was prepared by the addition of 1,1,3,3-tetramethylguanidine (TMG)[6] to a solution of an equimolar amount of chromium trioxide in a minimum of water at −10°C and obtained in 85% yield as a bright orange solid. TMGDC was stable when kept at room temperature for a long period of time but moderately light sensitive. The structure of TMGDC was determined by elemental analysis and infrared spectral data (950, 930, 885, 77 cm^{-1}). Furthermore, TMGDC was soluble in water, dimethylformamide, and dimethyl sulfoxide, while it is slightly soluble in most organic solvents such as dichloromethane, acetone, and acetonitrile.

The oxidation of benzhydrol with 2 equiv of TMGDC in several solvents such as dichloromethane, acetonitrile, and dimethylformamide did not occur to an observable extent, even after prolonged stirring for 24 h. Since it has been known that chromate oxidation is facilitated by the addition of acids such as 2,2,2-trichloroacetic acid, p-toluenesulfonic acid,[7] and pyridinium trifluoroacetate,[5] the oxidation was carried



TMG TMGDC

out with equimolar amounts of TMGDC and pyridinium p-toluenesulfonate (PPTS)[8] in dichloromethane at room temperature. Under the present conditions, various benzylic alcohols were cleanly oxidized to the corresponding carbonyl compounds in high yields. The reaction was generally complete within 4 h. Similarly, various allylic alcohols were cleanly and rapidly oxidized as shown in Table 1. Secondary saturated aliphatic alcohols such as 2-octanol, cycloheptanol, and 2-t-butylcyclohexanol was relatively slow, as compared to above results obtained with benzylic and allylic alcohols. In general, the reaction required 24 h for completion of the reaction as shown in Table 1. However, the oxidation of primary saturated aliphatic alcohols with TMGDC and PPTS gave somewhat capricious results. For instance, reaction of phenethyl alcohol with 4 equiv of TMGDC and PPTS in dichloromethane at room temperature for 24 h gave phenylacetic acid in 27% yield along with two unidentified products. Similar results were obtained with n-nonyl alcohol.

We are planning to study oxidation of primary saturated aliphatic alcohols to the corresponding carboxylic acids and selective oxidation of allylic and benzylic alcohols in the presence of saturated aliphatic alcohols.

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Table 1. Oxidation of Alcohols to Carbonyl Compounds with TMGDC and PPTS[a]

Alcohol	Time, h	Product	Yield, %[b]
$C_6H_5CH_2OH$	4	C_6H_5CHO	93
p-$CH_3OC_6H_4CH_2OH$	4	p-$CH_3OC_6H_4CHO$	92
p-$ClC_6H_4CH_2OH$	4	p-ClC_6H_4CHO	93
$C_6H_5CH(OH)C_6H_5$	8	$C_6H_5COC_6H_5$	98
$C_6H_5CH(OH)CH_3$	12	$C_6H_5COCH_3$	90
t-$C_6H_5CH=CHCH_2OH$	1	t-$C_6H_5CH=CHCHO$	85
geraniol	1	geranial	93
carveol	1	carvone	94
isophorol	1	isophorone	90
$CH_3(CH_2)_5CH(OH)CH_3$	24	$CH_3(CH_2)_5COCH_3$	88
cyclohexanol	16	cyclohexanone	(88)
cycloheptanol	16	cycloheptanone	(91)
2-t-butylcyclohexanol	16	2-t-butylcyclohexanone	84
$C_6H_5CH_2CH_2OH$[c]	24	$C_6H_5CH_2COOH$	27
$CH_3(CH_2)_7CH_2OH$[d]	24	$CH_3(CH_2)_7COOH$	30

[a]The reaction was carried out with 2 equiv of TMGDC and PPTS in dichloromethane at room temperature. [b]Isolated yields. The numbers in parentheses indicate GLC yields. [c]11% of E→Z isomerization occurred. [d]4 equiv of TMGDC and PPTS was employed.

References

1. (a) L.J. Chinn, "Selection of Oxidants in Synthesis," Marcel Dekker, New York, 1971; (b) J.G. Moffatt, "Oxidation," Vol. 2, Marcel Dekker, New York, 1971; (c) H.O. House, "Modern Synthetic Reactions," 2nd Ed., W.A. Benzamin, Inc., New york, 1972; (d) K. Ogura and D. Swern, *Tetrahedron*, 34, 1651 (1978).
2. For recently developed chromium (VI) reagents, see: (a) F.S. Guziec and F.A. Luzzio, *Synthesis*, 691 (1980); (b) M.N. Bhattacharjee, M.K. Chaudhuri, H.S. Dasgupta, N. Roy, and D.T. Khathing, *Synthesis*, 588 (1982); (c) X. Huang and C. Chang, *Synthesis*, 1091 (1982); (d) J. Herscovici, M-J. Egron, and K. Antonakis, *J.C.S. Perkin I*, 1967 (1982); (e) J.M. Aizpurua and C. Palomo, *Tetrahedron Lett.*, 4367 (1983).
3. J.C. Collins, W.W. Hess, and F.J. Frank, *Tetrahedron Lett.*, 3363 (1969).
4. E.J. Corey and J.W. Suggs, *Tetrahedron Lett.*, 2647 (1975).
5. E.J. Corey and G. Schmidt, *Tetrahedron Lett.*, 399 (1979).
6. (a) G.P. Pollini, A. Barco, and G. DeGuili, *Synthesis*, 44 (1972); (b) F.S. Alvarez and D. Wren, *Tetrahedron Lett.*, 569 (1973); (c) S. Kim and H. Chang, *Synth. Commun.*, **14**, 899 (1984).
7. K.K. Banerji, *Bull. Chem. Soc. Jpn.*, **51**, 2732 (1978).
8. N. Miyashita, A. Yoshikoshi, and P.A. Grieco, *J. Org. Chem.*, **42**, 3772 (1977).

A New Direct Esterification Method Using Di-2-pyridyl Sulfite As a New Coupling Agent

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In connection with our continuous studies on the synthetic utility of 2-pyridyl related active carbonates and active esters,[1] we have reported that di-2-pyridyl carbonate (2-DPC) is an efficient coupling agent for the direct esterification of carboxylic acids under mild conditions.[2] However, the preparation of 2-DPC requires the use of highly toxic phosgene. Therefore, we investigated the possibility of using thionyl chloride, readily available and easy to handle, instead of phosgene.

Di-2-pyridyl sulfite was easily prepared by treatment of thionyl chloride with 2 equiv of 2-hydroxypyridine and triethylamine in methylene chloride at 0 °C. Di-2-pyridyl sulfite could not be isolated as a pure form due to its instability and so it was used as a crude form.

Table 1. Esterification of Carboxylic Acids Using Di-2-pyridyl Sulfite

Acid	Alcohol	Method[a]	Time, h	Yield, %[b]	
RCOOH	R'OH			RCOOR'	RCOO-2-py
$CH_3(CH_2)_6$	$C_6H_5CH_2$	A	4	91	0
	CH_3CH_2	A	8	89	0
	CCl_3CH_2	A	2	95	0
	$(CH_3)_3C$	A	0.3	0	88
		B	24	58	34
$C_6H_5CH_2$	CH_3CH_2	A	6	93	0
	$(CH_3)_2CH$	A	24	81	9
		B	5	93	0
	CH_3CH_2	A	10	88	0
	$C_6H_5CH_2$	A	5	87	0
	$(CH_3)_2CH$	A	24	59	36
		B	24	86	0
C_6H_5	CH_3CH_2	A	24	55	36
		B	36	90	0
$(C_6H_5)_2CH$	CH_3	A	4	90	0
	$C_6H_5CH_2$	A	3	92	0
$(CH_3)_3C$	$C_6H_5CH_2$	A	0.3	58	23 (9)[c]
		B	30	77	0 (7)[c]

[a]Method A: in CH_2Cl_2 at room temperature. Method B: in CH_3CN at 60 °C. [b]Isolated yields. [c]Isolated yields of pivalic anhydride.