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ULTRASONIC ACCELERATION OF OXIDATION WITH SOLID POTASSIUM PERMANGANATE

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Ultrasonic irradiation facilitates heterogeneous oxidation of secondary alcohols to ketones with solid potassium permanganate in nonpolar organic solvents.

Successful applications of ultrasound to organic synthesis have been reported in a number of recent papers.1) However, most of them have been concerned with the reaction of metals, e. g., lithium,1a) zinc,1b,c) mercury,1d) etc.; heterogeneous reactions of other inorganic reagents in organic solvents have been rare.2) We herein report that oxidation with potassium permanganate in nonpolar organic solvents is accelerated by ultrasonic irradiation.

It has been pointed out that oxidation with solid permanganate salts in organic solvents is facilitated by the addition of inorganic solid supports.3-6) Traces of water are critical to the reaction, and the permanganate reagents become unreactive when extremely dried.4) Thus, Menger concluded that a primary function of solid supports is to supply the necessary trace quantities of water.4) With the idea that ultrasound may play the role of traces of water in mind, permanganate oxidation of alcohols was carried out under ultrasonic irradiation. Typical results are summarized in Table 1.

In order to compare the effects of ultrasound and mechanical agitation, small scale experiments were run with a mixture of 1.0 mmol of an alcohol, 6.4 mmol of dried and powdered $KMnO_4$, and 3.0 ml of a solvent in a test tube with a Teflon-coated screw cap (run 1-5). The results clearly show that the heterogeneous oxidation proceeds even under the dry conditions when ultrasonically irradiated. Without irradiation the reaction was very slow. Excellent to moderate isolated yields were attained in preparative scale experiments (run 6-11). Attempts to obtain aldehydes from primary alcohols turned out to be of limited success (run 11 and 12), and an acid was isolated in a good yield in one case (run 13). Olefins and alkylbenzenes are rather resistant to the oxidation but prolonged reaction time caused the C-C bond cleavage to a small extent; butylbenzene gave a 21% yield of benzoic acid after 90 h. Thus, the ultrasonically accelerated oxidation with potassium permanganate is a good alternative method for small scale preparation of ketones from secondary alcohols.

Interestingly, addition of traces of water hindered the ultrasonic acceleration of the reaction. When a mixture of $KMnO_4$ and alumina (Merck, neutral, Type 90) was used as an oxidant, the reaction proceeded smoothly even by mechanical agitation, and the additional acceleration effect of ultrasound was not obvious. Study of solvent effects on the heterogeneous oxidation revealed that the reaction was faster in a more polar solvent when mechanically agitated, but that this solvent dependence almost disappeared when ultrasound was applied; under the conditions applied to run 1 of Table 1, the yield of 2-octanone after 24 h of mechanical agitation was 7.9, 36.8, and 78.5% in hexane, benzene, and acetone, respectively, whereas the yield after 5 h of ultrasonic irradiation was 92.8, 87.2, and 82.5%, respectively.

Although the function of ultrasound is not clearly understood at present, our results obviously demonstrated that it is effective for various types of heterogeneous reactions not only of metals but also of inorganic salts.

Table 1. Oxidation by Solid Potassium Permanganate under Ultrasonic Irradiation[a]

Run	Substrate	Product	Solvent	Time/h	Yield/%[b]	
					Ultrasound[c]	Mech. Agit.[d]
1	2-octanol	2-octanone	hexane	5	92.8[e]	2.6[e]
2	cyclohexanol	cyclohexanone	hexane	5	53.2[e]	4.2[e]
3	cyclododecanol	cyclododecanone	benzene	24	85.7[e]	15.7[e]
4	$PhCH=CHCH_2OH$	PhCH=CHCHO	benzene	3	82.8[e]	4.5[e]
5	1-octene-3-ol	1-octene-3-one	benzene	24	43.6[e]	0.8[e]
6	2-decanol	2-decanone	benzene	40	89.4	
7	4-decanol	4-decanone	benzene	40	89.7	
8	PhCH(OH)Ph	PhCOPh	benzene	5	98.9	
9	cyclododecanol	cyclododecanone	benzene	32	84.1	
10	cholestanol	cholestanone	benzene	20	65.3	
11	$PhCH=CHCH_2OH$	PhCH=CHCHO	benzene	14	74.7	
12	$PhCH_2OH$	PhCHO	benzene	1.5[f]	29.7[g]	
13	1-octanol	octanoic acid	hexane	14	80.5	

a) At 50 °C unless otherwise noted. b) Isolated yields unless otherwise noted. c) A thermostated ultrasonic cleaner (Branson, 200 W, 55 kHz) was used. d) A Vapor Mix vibrating apparatus (Tokyo Rikakikai S-10) was used. e) Calibrated GLPC yields. f) At 20 °C. g) Starting material (47.4%) was recovered.

References: 1) See, for example: a) J.-L. Luche and J.-C. Damiano, J. Am. Chem. Soc., 102, 7926 (1980); b) B. H. Han and P. Boudjouk, J. Org. Chem., 47, 751 (1982); c) T. Kitazume and N. Ishikawa, Chem. Lett., 1982, 1453; d) A. J. Fry, G. S. Ginsburg, and R. A. Parente, J. Chem. Soc., Chem. Commun., 1978, 1040. 2) S. L. Regen and A. Singh, J. Org. Chem., 47, 1587 (1982); B. H. Han and P. Boudjouk, Tetrahedron Lett., 23, 1643 (1982); S. Raucher and P. Klein, J. Org. Chem., 46, 3558 (1981). 3) S. L. Regen and C. Koteel, J. Am. Chem. Soc., 99, 3837 (1977). 4) F. M. Menger and C. Lee, J. Org. Chem., 44, 3446 (1979); Tetrahedron Lett., 22, 1655 (1981). 5) N. A. Noureldin and D. G. Lee, Tetrahedron Lett., 22, 4889 (1981); J. Org. Chem., 47, 2790 (1982). 6) J. H. Clark and D. G. Cork, J. Chem. Soc., Chem. Commun., 1982, 635.

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