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Oxidation of Benzyl Ethers via Phase Transfer Catalysis

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OXIDATION OF BENZYL ETHERS VIA PHASE TRANSFER CATALYSIS

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Abstract: A convenient procedure for the oxidation of benzyl ethers to benzoate esters is reported. Potassium permanganate in dichloromethane with phase transfer catalysis by triethylbenzylammonium chloride (TEBAC) affords products regiospecifically in fair to excellent yields.

We have previously observed that tertiary benzylamines were oxidized to benzamides by potassium permanganate via phase transfer catalysis.¹ We now report the application of that methodology to benzyl ethers. The results are presented in the Table. Although there are procedures known to effect this transformation, the present method offers the advantages of convenience, simplicity, and economy. Prior reports involved longer times, lower yields, additional products, more stringent conditions, or less accessible reagents.^{3, 7-20} Recently D.G. Lee and coworkers utilized KMnO₄ and a phase transfer catalyst in dichloromethane for the oxidation of benzyl methyl ether (1).²⁰ Their study, however, addressed only the mechanistic aspects of *para* substituents of 1.

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Our study encompassed a wide variety of benzyl ethers. Regioselectivity was assessed with 1 and 3: no benzyl formate was observed from 1 and less than 1% of benzyl acetate was detected from 3. Such regiospecificity was in contrast to the isomeric amides obtained from the analogous benzyldialkylamines. Phenyl ether 7 was far less reactive than its N analog, benzyldiphenylamine.¹ With cyclic ethers the five-membered ring system 9 was less stable to the reaction conditions. In the case of 11 none of the isomeric product, 3-isochromanone, was formed. From the observed regiospecificities and the absence of any reaction with ethers 19-21 the oxidation site was exclusively benzylic. The facile oxidation of xanthene



(15) reflected its structure as a vinylogous benzyl ether. Finally, the greater selectivity of Ovs. N for this type of oxidation was demonstrated by a competitive reaction between dibenzyl ether (5) and tribenzylamine (22) from which it was estimated that 22 was oxidized twenty-three times more rapidly than 5.

In conclusion, we have found that benzyl ethers were oxidized to benzoate esters by $KMnO_4$ via phase transfer catalysis with TEBAC. These mild conditions, which were effective for an extensive series of such ethers, proved more selective than the analogous oxidation of benzylamines.

Experimental Section

Starting materials and products were commercially available or were prepared by literature methods and purified to the reported physical properties.

References for the latter are included for individual compounds in the Table. Product analyses were performed on a Hewlett-Packard 5890II gas chromatograph with a SPB-5 polydiphenyl(5%)-dimethyl(95%)siloxane column (30 m x 200 µm with 0.2 μ m film) and Hewlett-Packard 5971A mass spectrometer (EI, 70 eV). Products were identified by comparison with authentic compounds. Product yields were determined in duplicate (±2%) with naphthalene as an internal standard and included detector response calibration factors. NMR spectra were obtained in CDCl₃ on a Brucker DPX 300 spectrometer; chemical shifts are reported in ppm downfield relative to tetramethylsilane. IR spectra were obtained as thin films on NaCl plates with a Nicolet 550 FT-IR spectrophotometer.

Oxidation of Benzyl Ethers; Analytical Procedure

To a stirred solution of the ether (1.00 mmol) and TEBAC (0.683 g, 3.00 mmol) in dichloromethane (10 mL) was added finely ground potassium permanganate (0.474 g, 3.00 mmol), and the purple solution was stirred at reflux for the times specified. The mixture was cooled in an ice bath and a solution of sodium bisulfite (2 g) in water (10 mL) was added slowly with vigorous stirring, which was continued until the color was completely discharged. The biphasic mixture was separated; the aqueous phase was extracted with chloroform (2 x 10 mL). The combined organic extract was washed with water (15 mL), dried (anhydrous Na₂SO₄), filtered into a 50-mL volumetric flask containing naphthalene (0.128 g, 1.00 mmol), and the flask was filled to the mark with chloroform. An aliquot (5 mL) was diluted similarly (to 50 mL) and analyzed by GC/MS.

Oxidation of 2,2-Dimethyl-4H-1,3-benzodioxin (17); Preparative Procedure

The oxidation of 17^5 (1.73, 10.5 mmol) was carried out by the above procedure for 5 h. Removal of the solvent gave 2,2-dimethyl-4*H*-1,3-benzodioxin-4-one (**18**) (1.54 g, 82.2%) as a pale yellow crystalline solid (purity > 99% by GC/MS), which was recrystallized from cyclohexane to give **18**: m.p. 58-59°, lit.²¹ m.p. 58-59°; ¹H NMR δ 1.74 (s, 6H), 6.95-7.97 m (4H), IR 1743 cm⁻¹; lit.²² ¹H NMR (CDCl₃) δ 1.71, IR (CCl₄) 1750 cm⁻¹.

Etherª	Ester ^a	Time (h)	Yield ^b (%)
PhCH ₂ —OCH ₃ 1	$Ph - C - OCH_3$	3 6	80 85
PhCH ₂ —OCH ₂ CH ₃ 3 ²	$Ph - C - OCH_2CH_3$	3	87
(PhCH ₂) ₂ O 5	$Ph - C - OCH_2Ph$	3	87
PhCH ₂ —OPh 7	O II Ph —C—OPh 8	3 6 18	22 51 55
9		1.5 3 6	59 51 36

Table. Oxidation of Ethers by KMnO₄

Table. Continued









175





100

3 6

3







18⁶

the compund was prepared.

^b Yields determined by GC/MS analysis; yield of isolated product in brackets.

Oxidation of Dibenzyl Ether (5) and Tribenzylamine (22); Competitive Procedure

To a stirred solution of 5 (0.198 g, 1.00 mmol), 22, (0.287 g, 1.00 mmol), and TEBAC (0.683 g, 3.00 mmol) in dichloromethane (10 mL) was added finely ground potassium permanganate (0.474 g, 3.00 mmol), and the purple mixture was stirred at reflux for 30 min. The work up and GC/MS analysis were the same as for the analytical procedure. The crude product mixture contained only 5, 6, 22, and N,N-dibenzylbenzamide (23); relative areas were adjusted for detector responses in the calculation of relative reactivity.

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References

- Markgraf, J. H.; Sangani, P. K.; Finkelstein, M. Synth. Commun. 1997, 27, 1285.
- 2. Rojahn, C. A.; Schulten, J. Ber. 1926, 59, 499.
- 3. Bonadies, F.; Bonini, C.; Di Fabio, R. J. Org. Chem. 1984, 49, 1647.
- 4. (a) Burnham, J. W.; Eisenbraun, E. J.; Hamming, M. C.; Keen, G. W. Org. Prep. Proced. Int. 1973, 4, 35; (b) Anderson, J. E.; Jørgensen, F. S. J. Chem. Soc., Perkin Trans. 1 1981, 741.
- 5. Sargent, M.; Sala, T. J. Chem. Soc., Perkin Trans. 1 1981, 877.
- 6. Ziegler, E.; Hanus, H. D. Monatsh. Chem. 1964, 95, 1053.
- Maitte, P. Colloq. Intern. Centre Natl. Recherche Sci. 1955, No. 64, 197; Chem. Abstr. 1961, 55, 104126a.
- Masui, M.; Hara, S.; Ueshima, T.; Kawaguchi, T.; Ozaki, S. Chem. Pharm. Bull. 1983, 31, 4209.
- 9. Balavoine, G.; Eskenazi, C.; Meunier, F. J. Molec. Catal. 1985, 30, 125.

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- 10. Li, P.; Alper, H. J. Molec. Catal. 1992, 72, 143.
- (a) Nakayama, K.; Hamamoto, M.; Nishiyama, Y.; Ishii, Y. Chem. Lett.
 1993, 1699; (b) Fujibayashi, S.; Nakayama, K.; Hamamoto, M.; Sakaguchi, S.; Nishiyama, Y.; Ishii, Y. J. Molec. Catal. 1996, 110, 105.
- 12. Sommovigo, M.; Alper, H. J. Molec. Catal. 1994, 88, 151.
- 13. Zhao, D.; Lee, D. Synthesis 1994, 915.
- Miyamoto, M.; Minami, Y.; Ukaji, Y.; Kinoshita, H.; Inomata, K. Chem. Lett. 1994, 1149.
- Einhorn, C.; Einhorn, J.; Marcadal, C.; Pierre, J. J. Chem. Soc., Chem. Commun. 1997, 447.
- Sakaguchi, S.; Kikuchi, D.; Ishii, Y. Bull. Chem. Soc. Jpn. 1997, 70, 2561.
- 17. Bovicelli, P.; Sanetti, A.; Bernini, R. Tetrahedron 1997, 53, 9755.
- Kim, Y. H.; Kim, Y. I.; Kim, J. Y. J. Chem. Soc., Perkin Trans. 1 1998, 633.
- 19. Lee, N. H.; Lee, C.-S.; Jung, D.-S. Tetrahedron Lett. 1998, 39, 1385.
- Rankin, K. N.; Liu, Q.; Hendry, J.; Yee, H.; Noureldin, N. A.; Lee, D. G. Tetrahedron Lett. 1998, 39, 1095.
- Mowry, D. T.; Yanko, W. H.; Ringwald, E. L. J. Am. Chem. Soc. 1947, 69, 2358.
- 22. Rüchardt, C.; Rochlitz, S. Liebigs Ann. Chem. 1974, 15.

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