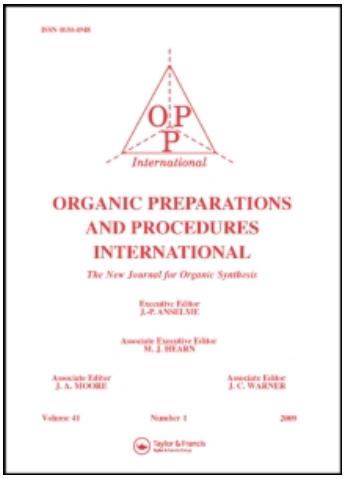

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A SIMPLE PROCEDURE FOR THE SYNTHESIS OF LABILE ARYL OXIRANES BY EPOXIDATION

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A SIMPLE PROCEDURE FOR THE SYNTHESIS OF LABILE ARYL OXIRANES BY EPOXIDATION

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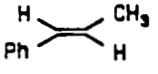
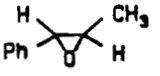
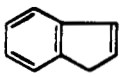
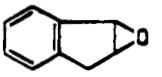
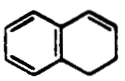
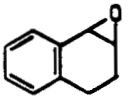
Aryl oxiranes have biological[1a] and synthetic importance[1b] but their preparation is difficult because of their sensitivity to acids and oxidants.[2] Synthesis by a two-step procedure *via* the halohydrin gives satisfactory results when there is no possibility to obtain diastereoisomers. Thus styrene and α-methylstyrene afford the corresponding epoxides in 68% and 78% yield respectively,[3] but *trans*-β-methylstyrene gives a 2:5 mixture of *cis*- and *trans*-1-phenyl-2-methylethylene oxide.[4] Direct epoxidation with peroxyacids is in principle the simplest synthetic path but low yields are obtained because of the lability of aryl oxiranes under the reaction conditions.[2] Improved procedures of direct epoxidation by m-chloroperoxybenzoic acid (MCPBA) have been proposed in recent years. Ziffer and Imuta[4] note that epoxidation at room temperature with MCPBA in a two phase buffered system gives high yields of aryl epoxides in 7-14 hrs. In our hands these results were not always successful and

the procedure also failed for the epoxidation of α-methylstyrene.[5] Camps[5] epoxidized (24 hrs, 90%) α-methylstyrene with a 1:2 MCPBA-KF complex in methylene chloride at room temperature. The MCPBA-KF system is not highly stable; at room temperature after 40 min. or at -20° after one week, its active oxygen content dropped to ca. 20% of the initial value. Epoxidation by polymeric epoxyacids gives low yields of aryloxiranes (7-62%) and sometimes a complex mixture of oxidation products as with α-methylstyrene.[2b] Aryloxiranes can be prepared in organic solvent ($CHCl_3$, 3 hrs, 60°, 50-70%) by 2-(phenylsulfonyl)-3-(p-nitrophenyl)oxaziridine, an aprotic and neutral oxidizing reagent.[6]

We report here a mild and simple epoxidation procedure of liquid and low-melting arylalkenes by MCPBA and peroxybenzoic acid (PBA) in the presence of an aqueous solution of sodium bicarbonate (pH = 8.3). The reaction conditions and the results are described in the Table. Both reactants are insoluble in the aqueous buffered solution; however, the reaction is rapid and the pure epoxide is isolated in good or excellent yield. PBA gives better results than MCPBA with highly acid sensitive olefins and labile epoxides (entries 2 and 4). The reaction of α-methylstyrene with MCPBA (entry 2) gives, besides the epoxide (70%), acetophenone (14%), α-phenylpropionaldehyde (10%) and other by-products (1-phenyl-1-methyl-1,2-ethanediol (3%), 1-phenyl-1-hydroxy-propionaldehyde (3%), detected by mass spectrometry); all the by-products except acetophenone (15%) were absent when PBA was used. When α-methylstyrene oxide was treated with the aqueous

$NaHCO_3$ solution in the absence of peroxyacids for 3 hrs at room temperature, it was quantitatively recovered; however in the presence of PBA, small amounts of acetophenone (4%) and diol (4%) were detected. This could be an indication that acetophenone does not originate mainly by a rearrangement-degradation reaction of the epoxide but rather from a side-reaction of the oxidation process.

TABLE. Epoxidation Reactions of Arylalkenes in Water

Entry	Alkene	Peroxyacid	Epoxide[a]	Reaction Temp.(°C)	Reaction Time (hr)	Yield(%)[b]
1		MCPBA		20	1.5	100 (95)
2		MCPBA		0	1	70[c] (63)
		PBA		0	3	85[d] (80)
3		MCPBA		0	1	100 (93)
4		MCPBA		0	1	60 (53)
		PBA		0	3	73 (65)
5		MCPBA		0	0.75	80 (70)

a) Identified by comparison with authentic samples (see Experimental Section). b) Yields determined by g.l.c. and yields of isolated epoxide in parentheses. c) For the remaining 30%, see text. d) The remaining 15% is acetophenone.

EXPERIMENTAL SECTION

MCPBA was purified[7a] but identical results were obtained with the commercial compound with 85% purity. PBA was prepared as described.[7b] GLC analyses were performed on a Hewlett-Packard 5880A chromatograph with SPB-5 fused silica capillary column (30m, 0.25mm diameter;temperature: 40-250°, 10°/min), an "on

column" injector system and hydrogen as the carrier gas. ^{1}H-NMR spectra were obtained on a Bruker AW-80 and chemical shifts are reported in ppm downfield from TMS. The reaction products were identified by comparison with authentic samples (bp.,mp.,GLC, ^{1}H-NMR), prepared by various procedures.[2,4,8-12]

General Epoxidation Procedure.- To a stirred heterogeneous mixture of 0.3 N sodium bicarbonate solution (60 ml) and aryl-alkene (0.01 mole) was added the powdered peroxyacid (0.011 mole) in small portions over a 5-10 min. period at 0°. The mixture was vigorously stirred at the temperature for the time indicated in the Table and then extracted with ether. The organic phase was washed with a cooled solution of 10% NaOH, then with saturated brine and dried (Na_2SO_4). The solvent was removed under reduced pressure and the crude arylepoxide purified by flash chromatography on silica gel eluting with n-pentane-ethyl ether 95:5. The yields of isolated epoxides are reported in the Table in parentheses.

Styrene oxide,[4,8] bp. 80°/16 mmHg; ^{1}HNMR ($CDCl_3$): δ 3.70 (dd, 1H, CH, J = 2.5 Hz, J = 4.0 Hz), 2.98 (dd, 1H, CH_2, J = 4.0 Hz, J = 6.0 Hz), 2.58 (dd, 1H, CH_2, J = 2.5 Hz, J = 6.0 Hz), 7.33 (m, 5H, C_6H_5).

α-Methylstyrene oxide,[2b,3b] bp. 85°/16 mmHg; ^{1}HNMR ($CDCl_3$): δ 1.70 (s, 3H, CH_3), 2.75 (d, 1H, CH_2, J = 4.0 Hz), 2.95 (d, 1H, CH_2, J = 4.0 Hz), 7.30 (m, 5H, C_6H_5).

trans-β-Methylstyrene,[4,9,12] bp. 80/16 mmHg; ^{1}HNMR ($CDCl_3$): δ 1.42 (d, 3H, CH_3, J = 5.0 Hz), 2.97 (dq, 1H, $CHCH_3$, J = 5.0 Hz, J = 2.0 Hz), 3.52 (d, 1H, C_6H_5CH, J = 2.0 Hz), 7.22 (m, 5H, C_6H_5).

Indene oxide,[4,10] mp. 30°C (from petroleum ether); ^{1}HNMR ($CDCl_3$): δ 3.00 (m, 1H, CH_2), 3.10 (m, 1H, CH_2), 4.10 (m, 1, CH_2CH), 4.23 (d, 1H, ArCH, J = 3.0 Hz), 7.20 (m, 4H, C_4H_4)

1,2,3,4-Tetrahydronaphthalene-1,2-oxide,[4,11] bp. 75°/0.4 mmHg; ^{1}HNMR ($CDCl_3$): δ 1.74 (m, 1H, $ArCH_2$), 2.52 (m, 3H, $ArCH_2CH_2$), 3.72 (m, 1H, CH_2CH), 3.80 (d, 1H, ArCH, J = 4.0 Hz), 7.20 (m, 4H, C_4H_4).

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