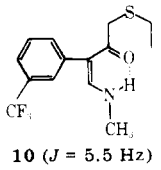
(3) J. N. Bonfiglio, I. Hasan, J. I. Piwinski, B. Weinstein, and F. W. Fowler, *J. Am. Chem. Soc.*, **98**, 2344 (1976).
(4) H. G. Viehe, G. J. de Voghel, and F. Smets, *Chimia*, **30**, 189 (1976).
(5) K. Takabe, H. Fujiwara, T. Katagiri, and J. Tanaka, *Tetrahedron Lett.*, 4375 (1975).
(6) A. L. Cossey, R. L. N. Harris, J. L. Huppatz, and J. N. Phillips, *Aust. J. Chem.*, **29**, 1039 (1976).
(7) J. Becher and E. G. Frandsen, *Tetrahedron*, **33**, 341 (1977).
(8) L. E. Overman and S. Tsuboi, *J. Am. Chem. Soc.*, **99**, 2813 (1977).
(9) G. Dauphin, B. Jamilloux, A. Kergomard, and D. Planat, *Tetrahedron*, **33**, 1129 (1977).
(10) S. Barnela, R. S. Pandit, and S. Seshadri, *Indian J. Chem., Sect. B*, **14B**, 665 (1976).
(11) E. E. Kilbourne and M. C. Seidel, *J. Org. Chem.*, **37**, 1145 (1972); I. El-Kholy, M. Mishrikey, and R. F. Atmeh, *J. Heterocycl. Chem.*, **11**, 487 (1974); T. Kato, *Acc. Chem. Res.*, **7**, 265 (1974).
(12) These refer to *isolated yields* of chromatographically homogeneous materials based on starting enamine. All pyridinones described in this communication were fully characterized by combustion analysis, mass spectral fragmentation spectra, and infrared and proton magnetic resonance spectra. Liquid intermediates were purified by column chromatography on Woelm silica gel using dichloromethane/ethyl acetate gradient elution and characterized by infrared, proton magnetic resonance spectra, and mass spectral fragmentation analysis.
(13) Fused sodium acetate at 300 °C led to recovered starting material. In addition, we were unable to generate hetarynes from these compounds via the use of *tert*-butoxide in anhydrous *tert*-butyl alcohol. Therefore, the 3-halogenated pyridinones would not serve as intermediates for the synthesis of the 3-alkylthio and 3-substituted aminopyridinones or of the 3-oxypyridinones we had already obtained via Scheme I.
(14) In one run an aliquot of the toluene solution was stripped to dryness to give **10** as a viscous oil that crystallized under pentane to an orange solid: mp 47–48 °C; IR (Nujol) $\bar{\nu}$ 3175 (broad), 1645 cm^{-1}; NMR ($CDCl_3$) δ 1.17 (t, 3 H), 2.53 (q, 2 H), 3.05 (d, 3 H), 3.17 (s, 2 H), 6.80 (d, J = 12 Hz, 1 H), 7.40 (broad s, 4 H). Compound **10** could also be prepared using methanol in place of toluene and 40% aqueous methylamine.



10 (J = 5.5 Hz)

Convenient Method for the Preparation of Reactive Oxiranes by Direct Epoxidation

Mitsuru Imuta and Herman Ziffer*

Laboratory of Chemical Physics, National Institute of Arthritis, Metabolism, and Digestive Diseases, National Institutes of Health, Bethesda, Maryland 20014

Received October 10, 1978

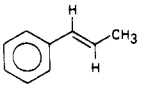
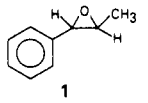
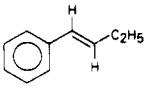
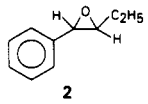
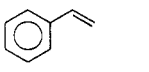
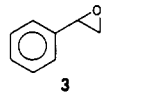
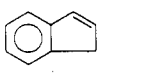
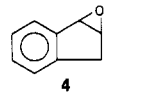
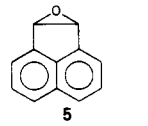
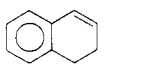
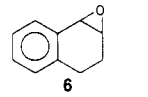
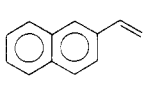
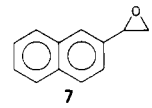
As part of another study we recently required pure samples of *trans*-β-methylstyrene oxide, **1**, and *trans*-β-ethylstyrene oxide, **2**. Related oxides, such as styrene oxide, **3**, are usually prepared from the olefin via an intermediate halohydrin; when this reaction sequence was used for *trans*-β-methylstyrene and β-ethylstyrene, mixtures of cis and trans oxides were obtained. Similar results were recently reported by Marshall and Prager,[1] who prepared their halohydrin intermediate by sodium borohydride reduction of the corresponding ketone. As these oxides were intended to be starting materials in a study of the stereochemistry of ring openings of oxides, a tedious separation of these sensitive compounds into the constituent isomers did not appear practical. Pure cis and trans oxides have been prepared by direct epoxidation of the appropriate olefin; however, aryl oxides are very sensitive to acids and therefore unstable under the usual epoxidizing conditions.[2a] Several methods[2b] have been employed to minimize the amount of acid present; we wish to report here the successful preparation of **1**, **2**, **3**, and several other related reactive oxides using a two-phase system similar to one described by Anderson and Veysoglu.[3]

Although samples of **1** and **2** were required, we were also interested in the methodology associated with the preparation of related labile aryl oxiranes. The reactivity of one such oxirane, indene oxide, **4**, has been studied in some detail by Berti et al.[4] Consequently this compound was chosen as our initial target molecule. Berti et al. have shown that **4** is easily opened by weak acids to yield mixtures of cis and trans diols.[5] In order to minimize destruction of **4**, we chose therefore to examine two-phase systems, dichloromethane and aqueous phosphate buffer (pH 8).[6] On oxidizing indene with 1 equiv of *m*-CPBA in dichloromethane in the presence of the phosphate buffer, reaction was not complete; however, when a second equivalent of *m*-CPBA was added, all the indene present was consumed and very little, if any, ring-opened product formed. If two or more equivalents of *m*-CPBA were added initially in one portion, epoxidation was not complete.

Epoxidation of *trans*-β-methylstyrene and *trans*-β-ethylstyrene with 2 equiv of *m*-CPBA in the two-phase system developed for indene yielded the trans oxides, in each case in high yield (90%) and uncontaminated by the cis isomer. In addition to the two styrene derivatives, 2-vinylnaphthalene, styrene, and 1,2-dihydronaphthalene were oxidized to the respective oxiranes in high yield (see Table I).

Although acenaphthene can be oxidized to 1,2-epoxyacenaphthene[8,9] under carefully controlled conditions using *m*-CPBA by a procedure using only one solvent, the reported yield was relatively low (35%). Furthermore, formation of acenaphthenone and other compounds complicated the isolation of the oxirane. We therefore subjected acenaphthene to the above-mentioned two-phase oxidation and obtained

Table I. Summary of Results from Two-Phase Epoxidations [c,d]

Aryl Olefin	Product	Reaction Time (hr.)	Yield (%)[a]
	 **1**	10	90[b]
	 **2**	11	90[b]
	 **3**	7	95[11]
	 **4**	10	100[12]
	 **5**	8	100[7]
	 **6**	14	95[13]
	 **7**	9	90[14]

[a] Determined by NMR. [b] The yields of these oxiranes prepared via bromohydrin are given in the Experimental Section. [c] Registry no. for the aryl olefins from top to bottom: 873-66-5; 1005-64-7; 100-42-5; 95-13-6; 208-96-8; 447-53-0; 827-54-3. [d] Registry no.—**1**, 23355-97-7; **2**, 69140-50-7; **3**, 96-09-3; **4**, 768-22-9; **5**, 22058-69-1; **6**, 2461-34-9; **7**, 20861-99-8.

the corresponding epoxide in essentially quantitative yield; no detectable amounts of the ketone or ring-opened products formed. The oxide was readily identified by a comparison with authentic material prepared via the intermediate bromohydrin. Thus, this two-phase procedure appears superior to the previously described direct epoxidation.

The above results establish that this two-phase procedure enables one to prepare by direct epoxidation a number of reactive aryl oxiranes. The procedure has proven to be invaluable for the preparation of *cis*- or *trans*-oxiranes where other methods have yielded mixtures.

Experimental Section

Synthesis of Epoxides Using *m*-CPBA in a Two-Phase System. To a stirred solution of 1.16 g of indene in dichloromethane–phosphate buffer (the buffer was prepared by adding sufficient aqueous 0.1 M Na_2HPO_4 to 0.1 M NaH_2PO_4 until the pH was 8.0) (200 mL; 1:1) was added *m*-CPBA (1.73 g) in small portions over a 10-min period at 0 °C. After stirring for 5 h at room temperature, 1.73 g of *m*-CPBA was added in small portions to the mixture at 0 °C over a second 10-min period. The mixture was stirred at room temperature for 5 h and the organic layer was separated, washed with saturated sodium thiosulfate and water, and dried over anhydrous sodium sulfate. The NMR spectrum of the crude reaction product showed that indene epoxide (4) was produced in ~100% yield. A pure sample of 4 (1.26 g 91% yield, mp 30 °C (lit.[4] mp 29–30 °C)) was prepared by crystallization from petroleum ether. The NMR and mass spectra of this sample were identical with that of an authentic sample prepared from *trans*-1-hydroxy-2-bromoindane. The same yield of oxirane formed when a sodium bicarbonate solution (pH 8.0) was substituted for the phosphate buffer.

This procedure was also used to prepare the epoxides listed in Table I.

(*E*)-1-Phenyl-2-methylethylene oxide (1): colorless oil; MS 134 (M^+); NMR ($CDCl_3$) δ 1.43 (3 H, d, J = 5.0 Hz), 3.00 (1 H, m), 3.55 (1 H, d, J = 1.8 Hz), 7.20–7.32 (5 H, m).

(*E*)-1-Phenyl-2-ethylethylene oxide (2): colorless oil; MS 148 (M^+); NMR ($CDCl_3$) δ 1.06 (3 H, t, J = 7.5 Hz), 1.71 (2 H, qd, J = 7.5, 5.6 Hz), 2.94 (1 H, td, J = 5.6, 1.7 Hz), 3.62 (1 H, d, J = 1.7 Hz), 7.28–7.36 (5 H, m).

1,2-Epoxyacenaphthene (5): mp 83–84 °C (lit.[8] mp 83–84 °C); MS 168 (M^+); NMR ($CDCl_3$) δ 4.81 (2 H, s), 7.39–7.77 (6 H, m).

1,2-Epoxy-1,2,3,4-tetrahydronaphthalene (6): colorless oil; bp 89–91 °C/1 mm Hg (lit.[13] bp 73–75 °C/0.4 mm Hg); NMR ($CDCl_3$) δ 1.73 (1 H, m), 2.40 (1 H, m), 2.53 (1 H, m), 2.78 (1 H, m), 3.72 (1 H, m), 3.84 (1 H, d, J = 4.0 Hz), 7.09–7.40 (4 H, m).

(2-Naphthyl)ethylene oxide (7): mp 55–56 °C (lit.[10] mp 54–56 °C); MS 170 (M^+); NMR ($CDCl_3$) δ 2.89 (1 H, dd, J = 5.0, 2.5 Hz), 3.21 (1 H, dd, J = 5.0, 4.0 Hz), 4.00 (1 H, dd, J = 4.0, 2.5 Hz), 7.27–7.84 (7 H, m).

Synthesis of Epoxides via the Trans Halohydrins. (*E*)-1-Phenyl-2-methylethylene Oxide (1). When *trans*-β-methylstyrene was converted to a halohydrin and treated with 2 N KOH as described for acenaphthene, a mixture of trans and cis epoxides in the ratio of 5:2 (determined by NMR) was obtained. Because of their instabilities the two isomers were not separated. Cis epoxide: NMR ($CDCl_3$) δ 1.05 (3 H, d, J = 5.0 Hz), 3.29 (1 H, m), 4.02 (1 H, d, J = 4.8 Hz), 7.17–7.36 (5 H, m).

(*Z*)-1-Phenyl-2-ethylethylene Oxide. When *trans*-β-ethylstyrene was subjected to the above procedure a mixture of trans and cis epoxides formed (ratio of 5:3 (determined by NMR)). Cis epoxide: NMR ($CDCl_3$) δ 0.89 (3 H, t, J = 7.5 Hz), 1.00 (1 H, m), 1.23 (1 H, m), 3.09 (1 H, m), 4.05 (1 H, d, J = 4.6 Hz), 7.23–7.36 (5 H, m).

1,2-Epoxyacenaphthene (5). To a solution of acenaphthene (152 mg) in THF (100 mL) and H_2O (25 mL) was added freshly purified NBS (213 mg) and the solution was stirred overnight at room temperature. The reaction mixture was poured into cold water, extracted with ether, dried over anhydrous sodium sulfate, and concentrated. The crude *trans*-1-bromo-2-hydroxyacenaphthene was isolated by thick-layer chromatography (silica gel, ethyl acetate–hexane, 1:4) and the NMR ($CDCl_3$) spectrum of this compound showed resonances at δ 2.81 (1 H, broad s, OH), 5.46 (1 H, s), 5.81 (1 H, s), and 7.45–7.79 (6 H, m). The bromohydrin thus obtained without further purification was treated with 2 N KOH (100 mL) in $CHCl_3$ (100 mL) at 50 °C for 2 h. The organic layer was separated, washed with water, and dried over anhydrous sodium sulfate. The solvent was removed in vacuo and the residue was purified by recrystallization (ether–petroleum ether (1:1)) to give 1,2-epoxyacenaphthene (5), mp 83–84 °C, 89 mg (53% overall yield). The NMR and mass spectra of this compound were identical with those of a sample prepared by a two-phase system using *m*-CPBA.

1,2-Epoxyacenaphthene was converted to 1-acenaphthenol by $LiAlH_4$ reduction. To a slurry of $LiAlH_4$ (18 mg) in 10 mL of dry THF was added 20 mg of 1,2-epoxyacenaphthene and the solution was stirred overnight at room temperature under N_2. The reaction mixture was decomposed using cold water and worked up as usual to yield 1-acenaphthenol, mp 147–148 °C, 16 mg (80% yield). The NMR spectrum of this compound was identical with that of an authentic sample.

Registry No.—*cis*-1-Phenyl-2-methylethylene oxide, 4541-87-1; *cis*-1-phenyl-2-ethylethylene oxide, 69140-51-8; *trans*-1-bromo-2-hydroxyacenaphthene, 69140-52-9; 1-acenaphthenol, 6306-07-6.

References and Notes

(1) P. A. Marshall and R. H. Piager, *Aust. J. Chem.*, **30**, 151 (1977).
(2) (a) N. C. Yang, W. Chiang, D. Leonov, E. Leonov, I. Bilyk, and B. Kim, *J. Org. Chem.*, **43**, 3425 (1978); (b) R. P. Hanzlik and J. M. Hilbert, *ibid.*, **43**, 610 (1978).
(3) W. K. Anderson and T. Veysoglu, *J. Org. Chem.*, **38**, 2267 (1973).
(4) A. Balsamo, G. Berti, P. Crotti, M. Ferretti, B. Macchia, and F. Macchia, *J. Org. Chem.*, **39**, 2596 (1974).
(5) For a good review of stereoselective epoxide cleavage see J. B. Buchanan and H. Z. Sable in "Selective Organic Transformations", Vol. 2, B. S. Thyagarajan, Ed., Wiley-Interscience, New York, 1972, pp 1–95.
(6) Griffin et al.[7] have recently described the use of a similar two-phase system in the direct peracid oxidation of polynuclear hydrocarbons to arene oxides.
(7) K. Ishikawa, H. C. Charles, and G. W. Griffin, *Tetrahedron Lett.*, 427 (1977).
(8) T. H. Kinstle and P. J. Ihrig, *J. Org. Chem.*, **35**, 257 (1970).
(9) A recent report by S. Krishman, D. G. Kuhn, and G. A. Hamilton, *J. Am. Chem. Soc.*, **99**, 8121 (1977), described the preparation of 1,2-epoxyacenaphthene by oxidation of acenaphthene with sodium hypochlorite in the presence of a phase-transfer catalyst in 70% yield.
(10) R. P. Hanzlik, M. Edelman, W. J. Michaely, and G. Scott, *J. Am. Chem. Soc.*, **98**, 1952 (1976).
(11) The reported yield of the bromohydrin from styrene and NBS is 76%: D. R. Dalton, V. P. Dutta, and D. C. Jones, *J. Am. Chem. Soc.*, **90**, 5498 (1968).
(12) The reported yield of *trans*-1-hydroxy-2-bromoindane from indene and NBS is 59%: C. O. Guss and R. Rosenthal, *J. Am. Chem. Soc.*, **77**, 2549 (1955).
(13) The oxirane was prepared in 60% yield according to the procedure of H. E. Audier, J. F. Dupin, and J. Jullien, *Bull. Soc. Chim. Fr.*, **9**, 3844 (1968).
(14) This oxirane was prepared according to the procedure described by Hanzlik[10] in 70% yield.

Bis(phenylthio)methaneboronic Esters as Sources of Carbanions and Ketene Thioacetals

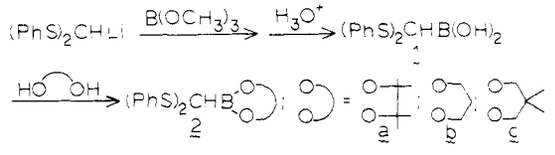
Abel Mendoza and Donald S. Matteson*

Department of Chemistry, Washington State University, Pullman, Washington 99164

Received November 21, 1978

Boron-substituted carbanions show considerable promise as synthetic intermediates and have proved especially effective in Wittig-type condensations with carbonyl compounds to form substituted alkenes.[1–5] The synthesis of bis(phenylthio)methaneboronic esters from the readily available bis(phenylthio)methyllithium[6] was undertaken as a logical extension of this work.

Reaction of trimethyl borate with bis(phenylthio)methyllithium followed by workup with aqueous acid yielded bis(phenylthio)methaneboronic acid (1), which proved unstable to storage and was not fully purified, but was readily converted to the cyclic esters 2 by treatment with pinacol, 1,3-propanediol, or 2,2-dimethyl-1,3-propanediol.



0022-3263/79/1944-1352$01.00/0