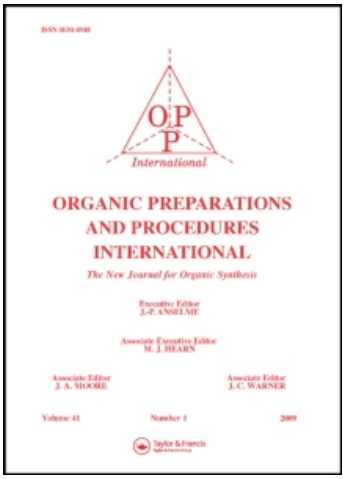

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RING OPENING OF SOME SUBSTITUTED STYRENE OXIDES

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RING OPENING OF SOME SUBSTITUTED STYRENE OXIDES#

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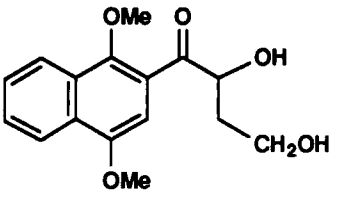
Intermediate **1**, which carries an oxygen function at C-2 in the side-chain, was required in connection with the synthesis of 9-deoxynanaomycin A.[1] Since keto ester **2** is readily available, transposition of oxygen from C-1 to C-2 thus appeared to be an attractive approach for the synthesis of diol **1**. As part of a program of transforming **2** to **1**, the transposition of oxygen of ketone **3** was examined by converting it to the key epoxide intermediates **5a**, **5b**, and **5c** and studying the ring opening of these epoxides. The results are presented in this paper.



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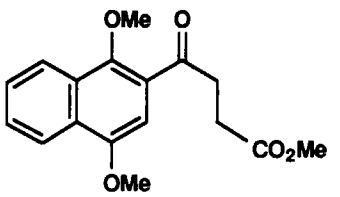

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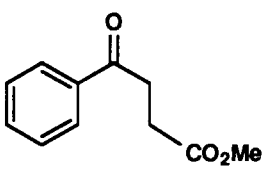


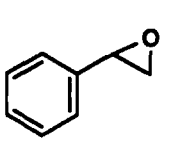
3

The epoxide ring opening of styrene oxide **4** with hydrides under a variety of experimental conditions has been studied.[2] Reduction with $LiAlH_4$ (LAH) involves attack almost exclusively at the less substituted carbon atom due to steric reasons to furnish the secondary alcohol **6**. The opposite ring opening of styrene oxide **4** to afford almost exclusively the alcohol **7** takes place when the reaction is carried out with "mixed hydrides" or sodium cyanoborohydride/BF_3.[3] In contrast to the LAH reduction of styrene oxide **4**, reduction of epoxide **5a** with LAH is not highly regioselective, a 70:30 mixture of alcohols **8a** and **9a** being obtained (Table).[4] The decrease in selectivity is presumably due to the presence of a substituent at C-2 in epoxide **5a**. The formation of **8a** in larger amounts than **9a** may be due to the lesser steric demand of the substituent at C-2 than that at C-1 in **5a**. Though reduction of **5a** with "mixed hydrides" or sodium cyanoborohydride/BF_3 reagent favors attack at the benzylic carbon, the selectivity is not as high as in the case of the reduction of **4** (Table).

Ring opening of **5a** with methanol in the presence of *p*-toluenesulfonic acid proceeds regioselectively and stereoselectively to furnish exclusively the *threo* alcohol **10a**.[5] The high selectivity in

the preparation of **10a** suggests that under the conditions employed, the ring opening of **5a** probably proceeds through a "border line SN_2" mechanism.[7] The phenyl substituent in **5a** is well suited to accommodate the developing positive charge at C-1 in the transition state leading to **10a**, while the substituent at C-2 is less able to accommodate a positive charge at C-2. Oxidation of alcohol **10a**

Scheme 1



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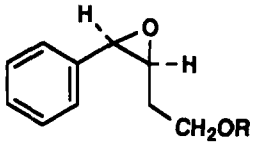
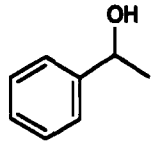


5

a) R = CH_2Ph
b) R = H
c) R = Ac



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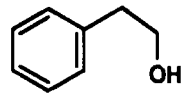

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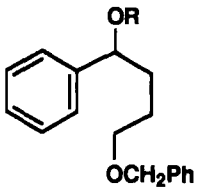
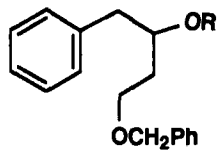


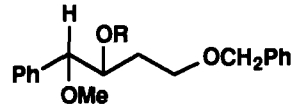
8

a) R = H
b) R = Ac



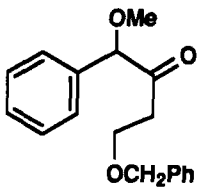
9

a) R = H
b) R = Ac



10

a) R = H
b) R = Ac



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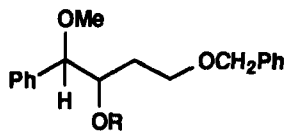
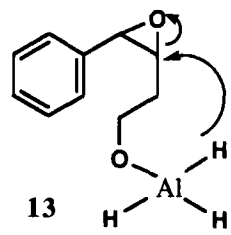


12

a) R = H
b) R = Ac



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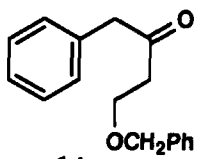

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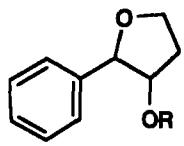
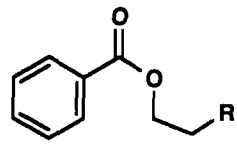


15

a) R = Ac
b) R = H



16

a) R = CO_2H
b) R = CH_2OH

TABLE. Regioselectivity of Epoxide Ring Cleavage with Hydrides[a]

Substrate[b]	Reagent[b]	Benzylic attack (%)	Ref.
4	A	5-10	2
4	B	90-98	2
4	C	97	3
5a	A	30	This work
5a	B	75	This work
5a	C	60	This work
5b	A	10	This work
5b	B	55	This work
5b	C	55	This work
5c	A	10	This work
5c	B	55	This work
5c	C	55	This work

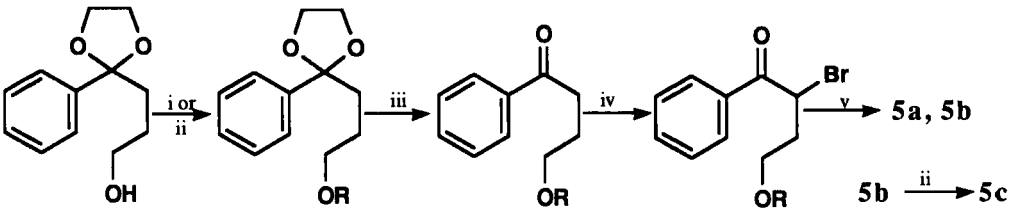
a) *Reagents and Conditions:* A, LAH / ether, 0°, 1 hr; B, Mixed hydride LAH + $AlCl_3$ (3:1.5), 0°, 1 hr; C, $NaBH_3CN/BF_3$, 25°, 1 hr. b) Reagent and substrate (1:1).

afforded ketone **11** which was reduced with $NaBH_4$ to a mixture of the alcohols **10a** and **12a** (*erythro* isomer).[6] LAH reduction of alcohol **5b** and of acetate **5c** gave higher amounts of benzylic alcohols when compared to the $LiAlH_4$ reduction of ether **5a**. It is likely that epoxy alcohol **5b** undergoes intramolecular attack *via* intermediate **13**. The same intermediate may also be involved in the reduction of **5c**. When compared to the reduction of **5a**, a higher degree of homobenzylic attack takes place during the reduction of **5b** and **5c** with i) "mixed hydrides" and ii) sodium cyanoborohydride/BF_3. This difference may be rationalized by postulating an intramolecular hydride delivery as indicated in **13** (Scheme 1). Epoxide **5a** rearranges to ketone **14** on treatment with BF_3•etherate. However, epoxide **5c** rearranges to **15a** on treatment with BF_3•etherate. The structure assigned (**15a**) is supported by its NMR spectrum and the chromic acid oxidation of its hydrolysis product **15b** to acid **16a**, identified by direct comparison with an authentic sample prepared from **16b** (Scheme 1).

The *cis*-epoxides **5a**, **5b**, and **5c** were prepared as shown in Scheme 2. The *cis* stereochemistry of the epoxides is to be anticipated on the basis of analogy with related work[8] and is confirmed by the observed coupling constants of the benzylic hydrogens in the NMR spectra.

In summary, we have shown that the epoxide **5a** can be prepared from the keto ester **3**. The epoxide **5a** can be readily converted to compounds **9a** and **14** which carry a oxygen function at C-2. We have successfully employed this methodology for the synthesis of the methyl ester of 9-deoxynanaomycin A starting with the compound **2**.[1]

Scheme 2



17 **18** **19** **20**

a) R = CH_2Ph b) R = Ac

i) NaH, $PhCH_2Br$, 25°; ii) Ac_2O/Py; iii) H^+, acetone; iv) Br_2/CCl_4; v) $NaBH_4$, KOH.

EXPERIMENTAL SECTION

IR spectra were recorded on a Perkin-Elmer 599B infra-red spectrophotometer. ^1H NMR Spectra were recorded on a Varian FT-80, Brüker WH-90, Varian T-60 or Jeol T-60, with tetramethylsilane as internal standard. Bps and mps which were measured on a Büchi apparatus, and together with bps. are not corrected. Na_2SO_4 (anhydrous) was used as a drying agent in all the work up procedures. The compound **17** was prepared from **3**[9] and compounds **5a**, **5b**, **5c**, **19a**, **19b**, **20a**, and **20b** were prepared according to the procedure given in the reference 8.

4-Benzyloxy-1,2-epoxy-1-phenylbutane (5a).- The epoxy ether **5a** was obtained as a colorless oil, bp. 110-115° (bath)/0.8 mmHg, in 83% yield from **20a**. IR (neat): 2940, 2880, 1500, 1460, 1360, 1110(b), and 750 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.53-1.76 (2H, m, CH_2); 3.31-3.76 (1H, m, CH_2CHO); 4.13 (1H, d, J = 4 Hz, PhC*H*O); 4.50 (2H, s, $PhCH_2O$); 7.36 (10H, s, ArH).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.22; H, 7.07

4-Phenyl-3,4-epoxy-1-butanol (5b).-The epoxide **5b** was obtained as a colorless oil, bp. 80-90° (bath)/0.6 mmHg, in 85% yield. IR (neat): 3400 (OH) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.60-1.78 (3H, m, CH_2 and O*H*); 3.22-3.44 (1H, m, $OCHCH_2$); 3.73 (2H, t, J = 6 Hz, CH_2OH); 4.27 (1H, d, J = 4 Hz, PhC*H*O); 7.31 (5H, s, ArH).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.10; H, 7.30

4-Phenyl-3,4-epoxy-1-acetoxybutane (5c).- The colorless liquid acetate **5c**, bp. 95-100° (bath)/0.6 mmHg, was prepared in 97% yield by acetylation of **5b** with pyridine and acetic anhydride. IR (neat): 2980, 1740 (C=O), 1450, 1260 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.60 (2H, m, CH_2); 2.00 (3H, m, $OCOCH_3$); 4.10 (3H, PhC*H*O, and CH_2OAc); 7.35 (5H, s, ArH).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.81; H, 6.78

4-Benzyloxy-1-acetoxy-1-phenylbutane (8b).- The ketone **19a** (1.2 g, 4.7 mmol) was reduced with $NaBH_4$ (0.179 g, 4.7 mmol) in methanol (50 mL) at 0°. The resulting colorless liquid was isolated according to the procedure given for **5a** and acetylated with acetic anhydride-pyridine to furnish the colorless acetate **8b** (1.29 g, 92%), bp. 130-135° (bath)/0.8 mmHg. IR (neat): 2940, 1735 (C=O), 1600 cm^{-1}. ^1H NMR (CCl_4): δ 1.40-1.83 [4H, m, $(CH_2)_2$]; 1.90 (3H, s, $OCOCH_3$); 3.3 (2H, t, J = 6

Hz, CH_2O); 4.33 (2H, s, PhCH_2O); 5.60 (1H, t, J = 6 Hz, PhC*H*OAc); 7.10 (5H, s, ArH).

Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48, H, 7.43. Found: C, 76.40; H, 7.68

***threo*-4-Benzyloxy-2-acetoxy-1-methoxy-1-phenylbutane (10b).**- A mixture of epoxide **5a** (0.38 g, 1.5 mmol), dry methanol (15 mL) and *p*-toluenesulfonic acid (15 mg) was stirred at 25° for 24 hrs. The volatiles were removed by distillation under reduced pressure (10 mmHg). The resulting residue was diluted with water (50 mL) and extracted with ether (2 x 25 mL). The combined ethereal layers were washed with water, brine and dried. Removal of solvent gave product **10a** which was acetylated with acetic anhydride-pyridine to furnish the colorless product **10b** (0.478 g, 97%), bp. 130-135° (bath)/0.8 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.40-2.00 (2H, m, CH_2); 1.80 (3H, s, OCOCH_3); 3.13 (3H, s, OCH_3) 3.90 (2H, t, J = 6 Hz, CH_2O), 4.07 (1H, d, J = 6 Hz, PhC*H*O); 4.30 (2H, s, PhCH_2O); 4.90-5.27 (1H, m, *H*COAc); 7.20 (10H, s, ArH).

Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.06. Found: C, 72.23; H, 6.91

4-Benzyloxy-2-oxo-1-methoxy-1-phenylbutane (11).- Jones oxidation of **10a** at 0° furnished the ketone **11** which was purified by chromatography on grade I neutral alumina. The ketone **11** was eluted with 4:1 mixture of pet. ether (bp. 40-60°) and ethyl acetate to furnish the colorless oil, bp. 125-130° (bath)/0.8 mmHg, in 81% yield. IR (neat): 2940, 1720 (C=O); 1600 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.70 (2H, t, J = 6 Hz, COCH_2); 3.25 (3H, s, OCH_3); 3.60 (2H, t, J = 6 Hz, CH_2O); 4.35 (2H, s, PhCH_2O); 4.65 (1H, s, PhC*H*CO); 7.20 (5H, s, ArH); 7.25 (5H, s, ArH).

Anal. Calcd for $C_{18}H_{20}O_3$: C, 76.03; H, 7.09. Found: C, 75.90; H, 7.08

$NaBH_4$ Reduction of 11.- Sodium borohydride (0.12 g, 3.17 mmol) was added to the solution of ketone **11** (0.92 g, 3.17 mmol) in methanol (25 mL) at 0°. The reaction mixture was stirred for 2 hrs at 25°. Methanol was removed under reduced pressure (10 mmHg). The residual oil was diluted with ether (2 x 30 mL). The combined ethereal layers were washed with water, brine and dried. Removal of solvent furnished a mixture of alcohols **10a** and **12a** which was acetylated with acetic anhydride-pyridine. GC analysis showed that the acetylation product is a 3:1 mixture of two compounds; the major component had the same retention time as **10b**. ^{1}H NMR ($CDCl_3$): δ 1.73-2.07 (2H, m, CH_2); 1.89 (0.75H, s, OCOCH_3); 1.96 (2.25H, s, OCOCH_3); 3.22 (0.75H, s, OCH_3); 3.27 (2.25H, s, OCH_3); 3.44 (3H, t, J = 6 Hz, CH_2O); 4.25 (0.25H, d, J = 6 Hz, PhC*H*OCH$_3$); 4.31 (0.75H, d, J = 6 Hz, PhC*H*OCH$_3$); 4.40 (0.5H, s, PhCH_2O); 4.44 (1.5H, s, PhCH_2O); 5.0-5.33 (1H, m, PhC*H*OAc); 7.24 (2.5H, s, ArH); 7.33 (7.5H, s, ArH).

4-Benzyloxy-2-oxo-1-phenylbutane (14).- A solution of BF_3•etherate (0.55 g, 3.9 mmol) in dry benzene (5 mL) was added to the epoxide **5a** (1.0 g, 3.9 mmol) in benzene (30 mL) at 25°. The reaction mixture was poured on water after 10 minutes. The organic layer was washed with water, 1% aqueous Na_2CO_3 solution, water, brine and dried. Removal of solvent furnished the product which was chromatographed on grade I neutral alumina. Elution with a 4:1 mixture of pet. ether (bp. 40-60°) and ethyl acetate furnished the colorless ketone **14** (0.75 g, 75%), bp. 130-135° (bath)/ 1 mmHg. IR (neat): 2940, 1720 (C=O), 1510 cm^{-1}. ^{1}H NMR (CCl_4): δ 2.50 (2H, t, J = 7 Hz, COCH_2); 3.45 (2H, t, J = 7 Hz, CH_2O); 3.50 (2H, s, PhCH_2CO); 4.30 (2H, s, PhCH_2O); 7.15 (10H, bs, ArH).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.29; H, 7.14. Found: C, 80.28; H, 7.12

2-Phenyl-3-acetoxytetrahydrofuran (15a).- A solution of BF_3•etherate (0.941 g, 6.63 mmol) in dry benzene (5 mL) was added to the epoxide **5c** (1.3 g, 6.33 mmol) in dry benzene (30 mL) at 25°. The reaction mixture was treated with water (10 mL) after 10 minutes. After the work up procedure, as given for the compound **14**, the product **15a** was obtained and distilled to give the colorless oil (1.15 g, 88%), bp. 110-115° (bath)/1 mmHg. IR (neat): 2960, 1735 (C=O), 1360 cm^{-1}. ^1H NMR (CCl_4): δ 1.80-2.23 (2H, m, CH_2); 2.00 (3H, s, $OCOCH_3$); 3.83-4.23 (2H, m, OCH_2); 4.85 (1H, bs, PhC*H*); 5.00-5.31 (1H, m, *H*COCOCH$_3$); 7.00-7.45 (5H, m, ArH).

Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.79; H, 6.78

2-Phenyl-3-hydroxytetrahydrofuran (15b).- A mixture of **15a** (1.0 g, 4.85 mmol), KOH (0.272 g, 4.85 mmol), water (0.1 mL) and methanol (30 mL) was heated under reflux for 2 hrs. The volatiles were removed by distillation under reduced pressure (10 mmHg). The reaction mixture was diluted with water (25 mL) and extracted with ether (2 x 30 mL). The combined extracts were washed with water brine and dried. Removal of solvent furnished the product **15b** which was purified through distillation to give the colorless liquid (0.58 g, 73%), bp. 120-125° (bath)/2 mmHg. IR (neat): 3400 (OH); 2880, 1450 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.80-2.35 (2H, m, CH_2); 4.00-4.30 (3H, m, CH_2O, and C*H*OH); 4.70 (1H, t, J = 3Hz, PhC*H*O); 7.30 (5H, s, ArH).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.14; H, 7.37. Found: C, 73.06; H, 7.29

β-Benzyloxypropionic acid (16a).- Alcohol **15b** (0.5 g, 3 mmol) was oxidized with Jones reagent. Recrystallization of the oxidation product from ether furnished **16a** (0.385 g, 65%), mp. 80°. Mixed mp. of acid thus obtained was undepressed on admixture with an authentic sample prepared by oxidizing **16b** with Jones reagent (alcohol **16b** was prepared by benzoylation of 1,3-propanediol). IR ($CHCl_3$): 2900-3000, 1710 (C=O), 1450 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.80 (2H, t, J = 6 Hz, CH_2COOH); 4.50 (2H, t, J = 6 Hz, CH_2OCO); 7.25-7.5 (3H, m, ArH); 7.85-8.1 (2H, m, ArH); 9.00 (1H, bs, COOH).

Anal. Calcd for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 61.80; H, 5.12

2-(3-Benzyloxypropyl)-2-phenyl-1,3-dioxolane (18a).- The ketal ether **18a** as a colorless liquid, bp. 135-140° (bath)/ 0.9 mmHg, was prepared in 86% yield. ^1H NMR (CCl_4): δ 1.43–2.00 [4H, m, $(CH_2)_2$]; 3.27 (2H, t, J = 6 Hz, CH_2O); 3.53-3.93 (4H, m, $O(CH_2)_2O$); 4.37 (2H, s, $PhCH_2O$); 6.90-7.33 (5H, m, ArH).

Anal. Calcd for $C_{19}H_{22}O_3$: C, 76.48; H, 7.43. Found: C, 76.39; H, 7.38

2-(3-Acetoxypropyl)-2-phenyl-1,3-dioxolane (18b).- The acetate **18b** as a colorless liquid, bp. 110-115° (bath)/0.8 mmHg, was prepared in 96% yield by acetylation of **17** with acetic anhydride and pyridine. IR (neat): 2980, 2900, 1740(C=O) cm^{-1}. ^1H NMR (CCl_4): δ 1.40-1.87 [4H, m, $(CH_2)_2$]; 1.93 (3H, s, $OCOCH_3$); 3.50-4.17 [6H, m, $O(CH_2)_2O$, and CH_2OAc]; 7.10-7.50 (5H, m, ArH.)

Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.15; H, 7.20

4-Benzyloxy-1-oxo-1-phenylbutane (19a).- The ketone **19a** was obtained, as a colorless liquid, bp.

140-150° (bath)/1 mmHg, in 94% yield from **18a**. IR (neat): 1690 (C=O) cm^{-1}. ^1H NMR (CCl_4): δ 1.70-2.27 (2H, m, CH_2); 3.90 (2H, t, J = 6 Hz, CH_2O); 3.53 (2H, t, J = 6 Hz, $PhCOCH_2$); 4.30 (2H, s, $PhCH_2O$); 6.90-7.37 (8H, m, ArH); 7.53-7.90 (2H, m, ArH).

Anal. Calcd for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.19; H, 7.09

4-Oxo-4-phenyl-1-acetoxybutane (19b).- Deketalization of **18b** furnished **19b** as a colorless oil, bp. 115-120° (bath)/2 mmHg, in 96% yield. IR (neat): 2950, 1740 (C=O); 1690 (PhCO) cm^{-1}. ^1H NMR (CCl_4): δ 1.92 (3H, s, $OCOCH_3$); 1.73-2.23 (2H, m, CH_2); 2.97 (2H, t, J = 7 Hz, $PhCOCH_2$); 4.10 (2H, t, J = 7 Hz, CH_2OAc); 7.06-7.57 (2H, m, ArH); 7.73-8.00 (2H,m,ArH).

Anal. Calcd for $C_{12}H_{14}O_4$: C, 69.85; H, 6.89. Found: C, 69.81; H, 6.78

4-Benzyloxy-2-bromo-1-oxo-1-phenylbutane (20a).- The bromo ketone **20a** was obtained as a pale yellow liquid, bp. 140-145° (bath)/1 mmHg, in 90% yield. IR (neat): 1690 (C=O). ^1H NMR (CCl_4): δ 2.10-2.60 (2H, m, CH_2); 3.63-3.67 (2H, m, CH_2O); 4.33 (2H, s, $PhCH_2O$); 5.30 (1H, t, J =7 Hz, CHBr); 7.10 (5H, s, ArH); 7.17-7.6 (3H, m, ArH); 7.70-8.00 (2H, m, ArH).

Anal. Calcd for $C_{17}H_{17}O_2Br$: C, 61.26; H, 5.10. Found: C, 61.18; H, 4.70

4-Oxo-4-phenyl-3-bromo-1-acetoxybutane (20b).- The **19b** was converted into the **20b**, a colorless liquid, bp. 120-125° (bath)/1 mmHg, in 90% yield. IR (neat): 2960, 1740 (C=O), 1690 (PhCO) cm^{-1}. ^1H NMR (CCl_4): 1.97 (3H, s, $OCOCH_3$); 2.17-2.68 (2H, m, CH_2); 4.22 (2H, t, J = 6 Hz, CH_2OAc); 5.12 (1H, t, J = 7 Hz, CHBr); 7.13-7.62 (2H, m, ArH); 7.83-8.12 (2H, m, ArH).

Anal. Calcd for $C_{12}H_{13}O_3Br$: C, 50.53; H, 4.59. Found: C, 50.48; H, 4.49

Study of the Reduction of Epoxides 5a, 5b, and 5c with Hydrides.-The data given in the table was obtained in the following manner. The epoxide is reduced with hydride reagent according to the conditions reported in Table. The mixture of products is acetylated and the composition determined through i) GC studies and ii) examination of the NMR spectrum.

REFERENCES

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1. U. P. Dhokte and A. S. Rao, *Synth. Commun.*, **21**, 1263 (1991).

2. E. L. Eliel and D. W. Delmonte, *J. Am. Chem. Soc.*, **78**, 3226 (1956).

3. R. O. Hutchins, I. M.Traffer, and W. Burgoyne, *J. Org. Chem.*, **46**, 5214 (1981).

4. The alcohols **8a** and **9a** obtained were acetylated to the respective acetates **8b** and **9b** by using Ac_2O/pyridine (Scheme 1), and they were compared by GC and ^1H NMR analysis with the

authentic acetates prepared from the reduction ($NaBH_4$) followed by acetylation (Ac_2O/Py) of the keto compounds **19a** and **19b**.

5. *threo*-Alcohol **10a** was acetylated to **10b**.

6. Mixture of *threo*- and *erythro*-alcohols **10a** and **12a** were acetylated (Ac_2O/Py) to the respective acetates **10b** and **12b** and compared with the above *threo*-acetate **10b** by GC and ^1H NMR analysis.

7. R. E. Parker and N. S. Issacs, *Chem. Rev.*, **59**, 737 (1959).

8. K. S. Bhat and A. S. Rao, *Indian J. Chem.*, **20B**, 355 (1981).

9. W. G. Dauben and H.Tilles, *J. Org. Chem.*, **15**, 785 (1950).

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