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A Convenient Synthesis of Vinyl Epoxides from Glycidic Esters via α-Hydroxy-β,γ-unsaturated Esters

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SYNTHETIC COMMUNICATIONS, 23(17), 2405-2414 (1993)

A CONVENIENT SYNTHESIS OF VINYL EPOXIDES FROM GLYCIDIC ESTERS VIA α-HYDROXY-β,γ - UNSATURATED ESTERS

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Abstract: Glycidic esters, upon isomerisation with $BF_3.Et_2O$ yield α-hydroxy-β,γ-unsaturated esters. These are then reduced with $LiAlH_4$ to vicinal diols which are converted to vinyl epoxides in two steps.

Importance of vinyl epoxides in organic synthesis is well documented in the literature[1]. A variety of methods to prepare them have been reported in recent years[2]. Structural variations in vinyl epoxides and conversion of differently substituted starting compounds to vinyl epoxides are very important and therefore newer approaches to epoxides are still required to be explored. In this paper we wish to report a simple method for vinyl epoxide synthesis from glycidic esters.

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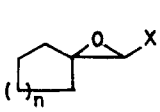
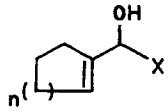
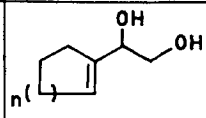
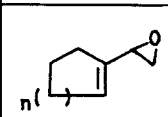
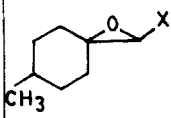
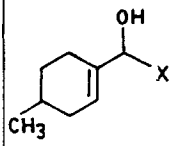
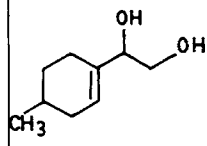
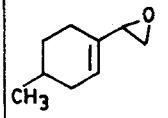
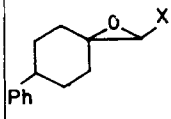
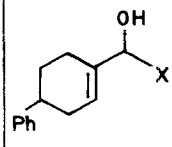
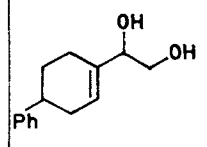
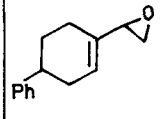
TABLE

CONVERSION OF GLYCIDIC ESTERS INTO VINYL EPOXIDES

Entry	Glycidic ester 1 (% Yield)	Isomerised hydroxy ester 2 (a-e) (% Yield)	Diol 3(a-e) (% Yield) (i)	Vinyl epoxide 6 (a-e)
				
1.	1a[5], n = 1	2a[5], n = 1 (60)	3a, n = 1 (68)	6a, n = 1 (87)
2.	1b[5], n = 2	2b[5], n = 2 (65)	3b, n = 2 (83)	6b, n = 2 (78)
3.	1c[5], n = 3	2c[5], n = 3 (38)	3c, n = 3 (70)	6c, n = 3 (75)
4.	 1d (57)	 2d (58)	 3d (52)	 6d (81)
5.	 1e (56)	 2e (40)	 3e (66)	 6e (71)

(i) This yield is over two steps viz. tosylation followed by NaH treatment.

(ii) X = $-CO_2Et$

Regioselective transformation of glycidic esters 1 into α-hydroxy-β,γ-unsaturated esters 2 using boron trifluoride etherate (or chlorotrimethylsilane) has recently been reported by us[3]. Ready accessibility of these geminal hydroxy esters prompted us to convert them into epoxides. Thus, lithium aluminium hydride reduction of various hydroxy esters (see Table) was easily achieved in good yields in refluxing THF. Treatment of these diols with p-toluenesulphonyl chloride in the presence of pyridine gave tosylates 5. Owing to the instability these tosylates were not characterised and further used as such. Treatment of 5 with NaH in dry ether resulted in the formation of vinyl epoxides 6 in 50-80% yields (Scheme). Results are summarised in Table.

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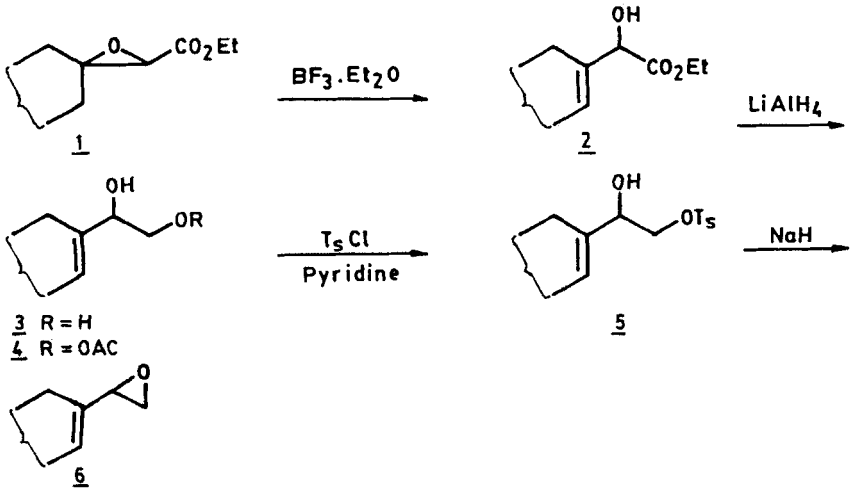
SCHEME



Experimental:

General Methods: ^1H NMR were recorded on Jeol PMX 60 and Bruker WP 80 spectrometers with $(CH_3)_4Si$ as internal standard. IR spectra were recorded on Perkin-Elmer 1320 spectrophotometer by using samples as neat liquids or in $CHCl_3$. Mass spectra were recorded at 70 ev on a Jeol JMS-300 D mass spectrometer. All the chromatographic separations were done by using TLC grade silica gel purchased from E. Merck. Methylene chloride was distilled from P_2O_5 prior to use. Diethyl ether and THF were dried over sodium wire. Glycidic esters were prepared according literature procedures[5].

Glycidic esters 1d and 1e:

1d: Yield: 57%; b.p. 115-120°c/10mm. IR(neat) 1725, 1750 cm^{-1}; ^1H NMR(CCl_4): δ4.2 (2H,q,J=7Hz, $-OCH_2-$), 3.03,3.1(1H, 2s,>C(O)C<u>H</u>), 2.1-0.95(15H,m, methyls, methylenes and methines); mass spectrum,m/e 198; Anal. Calcd. for $C_{11}H_{18}O_3$:C,66.6; H,9.04. Found: C,67.1;H,9.38%.

1e: Yield: 56%; thick liquid. IR(neat) 1725,1750 cm^{-1}; ^1H NMR(CCl_4): δ7.0(5H,s,aromatic), 4.2(2H,q, J=7 Hz, $-OCH_2-$), 3.13,3.16(1H,2s, >C(O)C<u>H</u>), 2.15-1.65(9H,CH_2s and methine), 1.3(3H,t,J=7Hz, $-OCH_2C\underline{H}_3$); mass spectrum, m/e 260; Anal. Calcd. for $C_{16}H_{20}O_3$:C, 73.85; H,7.69. Found C,74.1; H,8.31%.

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Isomerisation of glycidic esters to α-hydroxy β,γ unsaturated esters: 2(a-e)

For the isomerisation of glycidic esters our earlier[3] developed procedure was utilised using $BF_3.Et_2O$.

Ethyl [2-hydroxy-2(4-methyl-1-cyclohexenyl)] acetate 2d: Yield: 58%; thick liquid, IR(neat) 1720, 3480 cm^{-1}; ^1H NMR(CCl_4): δ5.6(1H, br.s, -=CH—), 4.15-3.75(3H,m, $-OCH_2-$,-CH(OH)), 2.8(1H,br.s, -OH),2.5-1.53 (7H,m, CH_2s,-CH(CH_3),1.27 (3H,t,-CH_3),0.97 (3H,d, J=3Hz, -$CHCH_3$); Anal. Calcd. for $C_{11}H_{18}O_3$:C,66.67; H,9.09. Found: C,65.06; H,9.27.

Ethyl [2-hydroxy-2(4-phenyl-1-cyclohexenyl)] acetate 2e: Yield: 40%; m.p. 63°c. IR($CHCl_3$)1720, 3440 cm^{-1}; ^1H NMR(CCl_4):δ 7.1(5H,s, aromatic), 5.75 (1H, br.s, =CH), 4.46-3.73(3H,m, -$COOCH_2CH_3$,-CHOH), 3.1(1H, br. s,-OH), 2.2-1.5(7H,m,CH_2s and -CHPh), 1.3(3H, t, J=7 Hz, -OCH_2CH_3); Anal. Calcd. for $C_{16}H_{20}O_3$: C,73.8; H,7.69. Found: C,74.02; H,8.01%.

$LiAlH_4$ reduction of 1(a-e) to the corresponding diols: 3(a-e):

General Procedure: To a suspension of $LiAlH_4$(2.5 mmol) in dry THF (5ml) was slowly added a solution of the ester (1 mmol) in THF (5 ml). It was then refluxed for 4h. Excess of $LiAlH_4$ was destroyed with ethyl acetate

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(50 ml) followed by water (2 ml) and aq. NaOH(1 ml). It was then filtered through a pad of Na_2SO_4 and the residue thoroughly washed with ethyl acetate. The combined filtrate upon concentration yielded a thick oil which was purified by column chromatography (silica gel; eluent: ethyl acetate/pet. ether:25/75) to yield the diol. These diols were characterised as the corresponding diacetates[4]. A solution of the diol (1 mmol) in dry methylene chloride was treated with pyridine (2.2 mmol) followed by acetic anhydride (2.5 mmol). After stirring for 4h usual work up gave a crude product which was purified by column chromatography (silica gel; eluent:ethyl acetate/pet.ether:5/95) to obtain pure diacetate.

Diacetates 4(a-c) and 4e:

4a: Yield:88%; IR(neat)1750 cm^{-1} ; ^1H NMR(CCl_4): δ 5.73-5.3(2H,m, = CH and -C<u>H</u>OAc), 4.15-3.8(2H,m, -C<u>H</u>$_2$OAc), 2.45-1.3 (12H,m, methylenes and methyls); mass spectrum,m/e 152(M^+-60); Anal. Calcd. for $C_{11}H_{16}O_4$:C,62.26; H,7.54. Found: C,63.05; H,7.65%.

4b: Yield:95%; thick liquid. IR(neat)1745 cm^{-1}; ^1H NMR(CCl_4): δ 5.6(1H, br.s, -C=CH), 5.3-5.00(1H, q, -C<u>H</u>OAc), 4.66-3.75(2H, m, -C<u>H</u>$_2$OAc), 2.3-1.35(14H, m, methylenes and acetates); mass spectrum, m/e166 (M^+-60); Anal. Calcd. for $C_{12}H_{18}O_4$:C,63.72; H,7.96. Found: C,63.12; H,7.09.

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4c: Yield:86%; IR(neat)1740 cm^{-1}; ^1H NMR(CCl_4): δ 5.73-5.26(2H,m, =CH and -CHOAc), 4.3-3.75(2H,m, $-CH_2OAc$), 2.45-1.35(16H, m, methylenes and acetates); mass sspectrum, m/e 180(M^+-60); Anal. Calcd. for $C_{13}H_{20}O_4$: C,65.05; H,8.3. Found: C,66.02; H,8.9%.

4e: Yield:89%; IR(neat)1735 cm^{-1}; ^1H NMR(CCl_4): δ 7.15(5H, s, aromatic), 5.7(1H, br.s, -C=CH), 5.4-5.1(1H, m, -CHOAc), 4.3-3.75(2H, m, -CH(OAc) $-CH_2OAc$), 2.5-1.45 (13H,m,CH_2s,CH_3s and -CH(Ph)); mass spectrum, m/e 242(M^+-60); Anal. Calcd. for $C_{18}H_{22}O_4$: C,71.52; H,7.28. Found: C,72.05; H,7.36%.

General procedure for the preparation of vinyl epoxides 6(a-e):

To a stirred solution of a diol(1 mmol) in dry ether(2 ml) was added pyridine(1.5 mmol) and freshly recrystallised p-toluenesulphonyl chloride (1.2 mmol) at 0°c. It was stirred at 0-10°c for 7 days by the end of which the reaction was generally complete (tlc monitoring as indicator). Solvent was then removed under reduced pressure and the crude product so obtained was used further without purification.

A stirred suspension of NaH (1.2 mmol) in dry ether (2 ml) at 0°c was treated with a solution of crude tosylate, obtained from the above mentioned reaction, in ether (2 ml). The reaction mixture was

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stirred at room temperature for 12 hr. It was then diluted with water (5 ml) and extracted with ether (3 x 10 ml). Evaporation of the solvent yielded a crude product which was purified by column chromatography (silica gel; eluent: pet. ether/ether: 90/10).

6a: Yield: 87%; ^{1}H NMR(CCl_4): δ 5.75(1H, t, J= 2Hz, =CH), 3.3(1H, t, J= 4Hz, -CH  CH_2), 2.83-1.15(8H,m, methylenes); mass spectrum, m/e 111(M +1)$^+$, 110(M^+). Anal. Calcd. for $C_7H_{10}O$: C,76.36; H,9.09. Found: C,75.81; H,8.8%.**6b**: Yield: 78%; ^{1}H NMR(CCl_4): δ 5.75(1H, t, J= 3Hz, =CH), 3.09(1H, t, J= 4 Hz, -CH  CH_2), 2.5-1.15(10H,m, methylenes); mass spectrum, m/e 125(M +1)$^+$, 124(M^+); Anal. Calcd. for $C_8H_{12}O$: C,77.42; H,9.68. Found: C,76.81; H,9.42%.

6c: Yield: 75%; ^{1}H NMR(CCl_4): δ 5.76(1H, t, J= 6Hz, =CH), 3.15(1H, t, J= 4Hz, -CH  CH_2), 2.6-1.15(12H,m, methylenes); mass spectrum, m/e 139(M +1)$^+$, 138(M^+); Anal. Calcd. for $C_9H_{14}O$: C,78.26; H,10.14. Found: C,77.8; H,9.73%.

6d: Yield: 81%; ^{1}H NMR(CCl_4): δ 5.9(1H, br.s, =CH), 3.2(1H, t, J= 3Hz, -CH  CH_2), 2.8-0.66(12H, m, methine, CH_2s and CH_3); mass spectrum, m/e 139(M +1)$^+$, 138(M^+); Anal. Calcd. for $C_9H_{14}O$: C,78.26; H,10.14. Found: C,77.91; H,9.35%.

6e: Yield: 71%; ^{1}H NMR(CCl_4): δ 7.3(5H, br.s,-Ph), 5.73(1H,br.s,=CH),2.96(1H,t, J= 3Hz,-CH  CH_2),

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2.83-1.1(9H,m, methylenes and methine); mass spectrum, m/e 201(M +1)$^+$, 200(M^+). Anal. Calcd. for $C_{14}H_{16}O$: C,84.00; H,8.00. Found: C,83.61; H,7.83%.

Acknowledgement:

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Note: In this paper, table 1 indicates that with $BF_3.Et_2O$ compounds 3a-3f are obtained. It is a printing mistake which has been inadvertantly overlooked so far. In reality, compound 2a-2f should have been mentioned as the products obtained instead of 3a-3f.

4. Compound, **3d** was not characterised as the diacetate instead compound **2d** was characterised as the acetate. The dta for this monoacetate is as follows: Yield:90%; IR(neat) 1745 cm^{-1}; ^1H NMR(CCl_4): δ 5.75(1H,br.s,=CH), 5.15(1H,s, -CH(OAc)), 4.0(2H,q, J=7 Hz,-OCH_2-), 2.2-1.5(10H,m, methylenes and methyl of -OAc), 1.3(3H,t,J= 7 Hz, -OCH_2CH_3), 0.97(3H,d,J=4 Hz,-$CHCH_3$); mass spectrum, m/e 240; Anal.Calcd. for $C_{13}H_{20}O_4$:C,65.00; H,8.33. Found: C,64.81; H,8.01.

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