Pergamon

Tetrahedron, Vol. 53, No. 33, pp. 11369-11376, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00718-7

Diastereoselective Epoxidation of Allylic Alcohols by t-Butyl Hydroperoxide/Zeolites System

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Abstract : Commercial zeolites promotes the epoxidation of unsaturated alcohols in chemo- and diastereoselective way. © 1997 Elsevier Science Ltd.

Introduction

Zeolites are porous crystalline aluminosilicates characterized by very interesting chemical and physical properties, such as variable acidity/basicity, shape selectivity and thermal stability.[1]

Besides their well-known employment as highly selective adsorbants, many other applications have been achieved by modifying the chemical properties of zeolites, for example, through cation exchange. In particular, the possibility of incorporation of certain transition metals, e.g. Ti, V, Fe, Cr, etc, has been conveniently exploited for the elaboration of new catalytic procedures for the oxidation of alkanes,[2] amines,[3] thioethers,[4,5] alcohols,[6] hydroxylation of aromatic compounds,[7] epoxidation of olefins.[8,9] The ever increasing interest in this field can be attributed to the strong demand of new, selective and non polluting processes.

Epoxyalcohols of defined configuration are useful key-intermediates in the synthesis of bioactive natural products : Adam has recently reported an interesting procedure for diastereoselective epoxidation of allylic alcohols with the urea-hydrogen peroxide adduct, catalyzed by titanium silicalite TS-1.[9]

However, as confirmed by preliminary reports,[10,11] zeolites cannot be simply considered inert supports, but, in the absence of any previous transition metal incorporation, they show unusual catalytic properties in oxidative processes, as the epoxidation of unsaturated alcohols.

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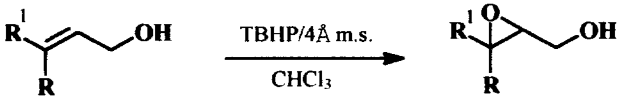
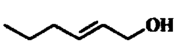
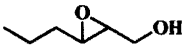
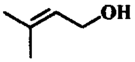
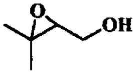
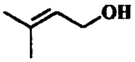
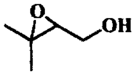
Epoxidation of Primary Alcohols 1

When allylic alcohols **1** are submitted to the action of an excess of t-butyl hydroperoxide (TBHP), in the presence of thermally activated 4Å molecular sieves, the formation of epoxyalcohols **2** takes place in appreciable way (Table 1).



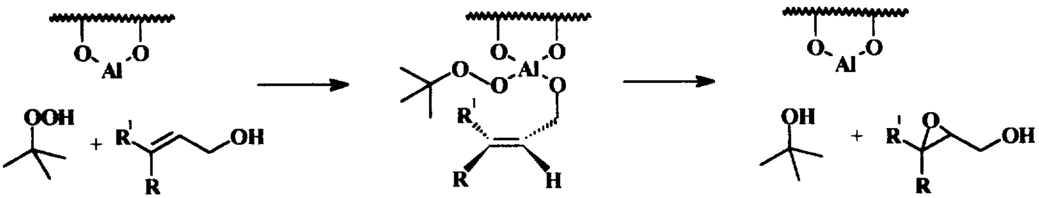
1 **2**

Table 1.Zeolite-Catalyzed Epoxidation of Primary Allylic Alcohols **1**

Entry	**Substrates**	**Products**	**Temp. (°C)**	**React. Time (h)**	**Yields (%)[a,b]**
a			45	96	63
b			50	96	52
c	Geraniol	2,3-epoxygeraniol	r.t.	144	67
d	Geraniol	2,3-epoxygeraniol	60	48	67
e	Geraniol	2,3-epoxygeraniol	r.t.	144	60
f	Farnesol[c]	2,3-epoxyfarnesol	r.t.	96	50
g			50	24	66
h			50	24	>95[d]

[a] All the yields refer to isolated, chromatographically pure compounds. [b] In all entries allylic alcohol/zeolite have been used 2 mmol/0.6 g ratio with the exception of entry **h** (2 mmol/2 g). [c] Farnesol was used as mixture of stereo isomers (Fluka). [d] ^{1}H-NMR yield.

In entries **c-f** high regioselectivity was observed since no evidence of formation of isomeric epoxides could be detected. This result can be reasonably explained through a Sharpless-type reaction :



A

In fact, cohordinatively unsaturated Al atoms of the zeolite surface can undergo addition of TBHP and allylic alcohol affording the intermediate **A** : then, cleavage of the polarized O—O bond by π electrons of the olefinic residue leads to the epoxidation products. It is noteworthy that an analogous path has been proposed for the epoxidation of allylic alcohols by $Al(OR)_3$ catalysis.[12]

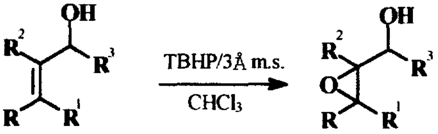
Since penetration of TBHP into 4Å pores of the molecular sieves is not possible,[13] oxidation takes place on the external surface and the low reaction rate can be attributed to the very reduced number of outer active sites.

However, reaction rate can be satisfactory increased performing the oxidation at higher temperatures ($\geq$ 45°C) (entry **d**) or in the presence of greater amounts of zeolites (entry **h**). No significant improvement has been obtained by using a threefold excess of TBHP (entry **e**).

Since a Sharpless-type process should have involved a diastereoselective control, a series of experiments has been performed on secondary allylic alcohols.

Epoxidation of Secondary Allylic Alcohols 3

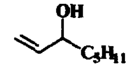
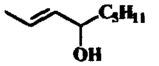
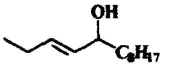
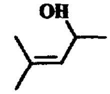
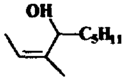
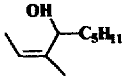
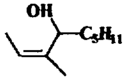
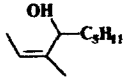
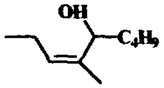
Under the conditions reported in Table 1 for entry **h** the conversion **3**→**4** proceeds with very satisfactory efficiency and selectivity (α,β-unsaturated ketones have been usually obtained, as by-products, in < 5% yield). (Table 2)



3 **4**

Furthermore, epoxidation has shown to take place with the same stereoselectivity observed with $TBHP/VO(acac)_2$ system. As known, in transition metal catalyzed epoxidation 1,2- and 1,3-allylic strains (origined respectively by R^2-R^3 and R^1-R^3 steric interactions) usually represent determining factors for the diastereoselectivity of the process. In the zeolite-catalyzed epoxidation the presence of only 1,3-allylic strain (entry **d**) involves the formation of *threo*-epoxyalcohol **4d** as far predominant product. However, 1,2-allylic strain has proven to be more effective than 1,3-allylic strain (entries **e-i**) so that the corresponding *erythro*-epoxyalcohol is generally isolated in very high yields. In the absence of both 1,2- and 1,3-allylic strain (entries **a-c**) the moderate *erythro* diastereoselectivity can be reasonably attributed to preferential steric interactions with the zeolite lattice. It is noteworthy that epoxidation of 1-octen-3-ol (entry **a**) proceeds very slowly and a competitive process of oxidation leads to the corresponding α,β-unsaturated ketone with comparable yields (18%).

Table 2. Zeolite-Catalyzed Epoxidation of Secondary Allylic Alcohols **3**

Entry	Alcohol 3	T/°C	Reac. time/h	Yield (%)[a,b]	TBHP/VO(acac)$_2$/C$_6$H$_6$ d.r. (E/T)
a		40	72	23 (76/24)	80/20
b		40	20	70 (63/37)	71/29
c		45	48	81 (66/34)	36/64
d		45	18	50 (18/82)	14/86
e		40	18	71 (86/14)[c]	93/7
f		40	17	73 (88/12)[c]	
g		40	20	52 (83/17)[c]	
h		40	18	75 (95/5)[d]	
i		45	72	89 (88/12)	-

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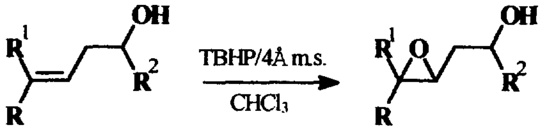
[a] All the yields refer to isolated, chromatographically pure compounds, whose structures have been confirmed by ^{1}H-NMR data. [b] Values in parentheses refer to erythro/threo diastereoisomeric ratios[Ø]. [c] In entries **e**, **f**, and **g**, have been respectively used 3Å, 4Å, and 5Å molecular sieves. [d] Solvent: n-hexane.

The pore diameter does not seem to have a significant influence on the diastereoselectivity of the reaction (entries **e**-**g**) ; however, reduced yields have been obtained when 5Å molecular sieves have been used. More interestingly, the employment of a more safe solvent, as n-hexane, has allowed very good results both in terms of efficiency and stereoselectivity (entry **h**).

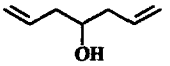
Epoxidation of Homoallylic Alcohols 5

Although in very long reaction times, zeolite/TBHP oxidant system has proven to be effective in the epoxidation of homoallylic alcohols 5 (Table 3).



5 **6**

Table 3. Zeolite-Catalyzed Epoxidation of Homoallylic Alcohols **5**

Entry	alcohol	react. time/h	T/°C	Yield (%)[a,b]
a		120	45	53
b		120	45	50
c		96	55	29(65/35)

[a] All the yields refer to isolated, chromatographically pure compounds. [b] Value in parentheses refers to syn/anti ratio determined by ^{1}H-NMR data[14].

In fact, carefully controlled reaction conditions have to be chosen in order to avoid competitive process of decomposition of β,γ-epoxyalcohols promoted by temperature enhancement and/or high molecular sieves/alcohol ratios. At last, it has to be noted that in entry c only product of monoepoxidation has been isolated as 65/35 syn/anti mixture, i.e. the same ratio observed in the epoxidation with TBHP/VO(acac)$_2$ system.

This result supports the previously reported hypothesis of a Sharpless-type pathway involving contemporary cohordination of TBHP and unsaturated alcohol by the active sites of molecular sieves.

In our opinion the possibility of exploitation of the catalytic properties of zeolites (without any previous metal doping) satisfies many requirements of a synthetic methodology : simplicity, ease of set-up and work-up, cheapness and selectivity.

Acknowledgements: We wish to thank MURST and CNR (Roma) for financial support.

Experimental

***General information*:** ^{1}H-NMR and ^{13}C-NMR spectra were recorded with Varian Gemini-200 spectrometer. Splitting patterns are designated as s (singlet), d (doublet), t(triplet), q (quartet), qp (quintet), hept (heptuplet), m (multiplet), dd (double doublet), ss (sharp singlet), bs (broad singlet), bdd (broad double doubled). Chemical shifts are reported in (δ) ppm relative to internal $CHCl_3$ δ (7.27) for ^{1}H-NMR and $CDCl_3$ δ (77.0) for ^{13}C-NMR. Silica gel (230-400 mesh Merck) was used for flash chromatography. Analytical thin layer chromatography (TLC) were carried out on Merck Kieselgel F_{254} plates. Spots on TLC were visualized under iodine and by spraying with H_2SO_4 (10% in ethanolic solution) followed by heating.

Commercial 3Å 4Å and 5Å molecular sieves (Aldrich) have been activated by heating at 200°C for 6h under a reduced pressure (0.1 mmHg). TBHP has been employed as iso-octane 3M solution (Fluka). Most of the allylic and homoallylic alcohols were commercially available; allylic alcohols **3b-g** have been prepared by Grignard reaction with the appropriate α,β-unsaturated aldehydes and their structures have been confirmed by ^{1}H-NMR data.

General procedure for the epoxidation of unsaturated alcohols : A mixture of unsaturated alcohols (3 mmol), activated zeolites (0.9 g) (3 g for substrates **3**), TBHP (6 mmol) in $CHCl_3$ (10 ml) was stirred under the conditions reported in Tables and the reaction, monitored by TLC and/or GLC, was prolonged until >80% conversion. Then dimethyl sulphide (1 ml) was added and, after 1h, the filtered solution was directly poured onto the top of a silica gel chromatographic column. Elution with n-pentane/diethyl ether mixtures afforded pure epoxyalcohols.

2a: ^{1}H-NMR data: 0.90 (3H, t, J=7.1 *Hz*); 1.50-1.58 (4H, m); 2.50 (1H, bs); 2.82-2.95 (2H, m); 3.54 (1H, dd, J_1=12.5 *Hz*, J_2=4.5 *Hz*); 3.85 (1H, dd, J_1=12.5 *Hz*, J_2=2.4 *Hz*). ^{13}C-NMR data: 13.61, 18.98, 33.34, 55.78, 58.49, 61.69. Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04; H, 10.41%. Found: C, 62.10; H, 10.35%.

2b: ^{1}H-NMR data: 0.93 (3H, t, J=7.0 *Hz*); 1.30-1.58 (4H, m); 2.98-3.08 (1H, m); 3.10-3.18 (1H, m); 3.62 (1H, dd, J_1=11.7 *Hz*, J_2=6.7 *Hz*); 3.82 (1H, dd, J_1=11.7 *Hz*, J_2=6.7 *Hz*). ^{13}C-NMR data: 13.83, 19.86, 29.84, 56.94, 57.12, 60.81. Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04; H, 10.41%. Found: C, 62.10; H, 10.38%.

2c: ^{1}H-NMR data: 1.27 (3H, s); 1.58 (3H, s); 1.66 (3H, s); 2.05 (4H, bq); 2.94 (1H, dd, J_1=6.7 *Hz*, J_2=4.3 *Hz*); 3.59-3.70 (1H, m); 4.99-5.10 (2H, m). ^{13}C-NMR data: 16.92, 17.82, 23.87, 25.86, 38.73, 61.53, 61.76, 63.33, 123.81, 132.69. Anal. Calcd. for $C_{10}H_{18}O_2$: C, 70.55; H, !0.66%. Found: C, 70.50; H, 10.62%.

2f (*inseparable mixture of two stereoisomers*): ^{1}H-NMR data: 1.28-1.33 (6H, m); 1.59 (3H, s); 1.66 (3H, s); 1.75-2.18 (8H, m); 2.90-3.00 (1H, m); 3.72 (2H, bdd); 4.70-4.80 (1H, m); 5.05-5.15 (1H, m). Anal. Calcd. for $C_{15}H_{26}O_2$: C, 75.58; H, 10.99%. Found: C, 75.55 ; H, 10.97%.

2g: ^{1}H-NMR data: 1.38 (3H, s);1.42 (3H, s); 2.95 (1H, dd, J_1=6.0 *Hz*, J_2=4.0 *Hz*); 3.57-3.72 (1H, m); 3.74-3.91 (1H, m). ^{13}C-NMR data: 18.52, 24.50, 58.76, 61.18, 63.91. Anal. Calcd. for $C_5H_{10}O_2$: C, 58.80; H, 9.87%. Found: C, 58.76% H, 9.85%.

4a (*inseparable mixture of two diastereomers*): ^{1}H-NMR data (*erythro isomer*): 0.85 (3H, bt); 1.10-1.70 (8H, m); 2.67-2.72 (1H, m); 2.77-2.82 (1H, m); 2.97-3.02 (1H, m); 3.77-3.87 (1H, m). ^{1}H-NMR data (*threo isomer*): 0.85 (3H, bt); 1.10-1.70 (8H, m); 2.67-2.72 (1H, m); 2.77-2.82 (1H, m); 2.92-2.97 (1H, m); 3.35-3.45 (1H, m). ^{13}C-NMR data (*erythro isomer*): 13.81, 22.38, 24.80, 31.69, 33.25, 43.26, 54.44, 68.34. ^{13}C-NMR data (*threo isomer*): 13.81, 22.38, 24.80, 31.62, 34.24, 45.27, 55.42, 71.63. Anal. Calcd. for $C_8H_{16}O_2$: C, 66.63; H, 11.18%. Found : C, 66.68; H, 11.22%.

4b (*inseparable mixture of two diastereomers*): ^{1}H-NMR data (*erythro isomer*): 0.85 (3H, bt); 1.10-1.60 (11H, m); 2.10 (1H, bs); 2.68 (1H, dd, J_1=2.5 *Hz*, J_2=5.4 *Hz*); 3.03 (1H, dq, J_1=2.5 *Hz*, J_2=5.3 *Hz*); 3.78-3.30 (1H, m). ^{1}H-NMR data (*threo isomer*): 0.85

(3H, bt); 1.10-1.60 (11H, m); 2.27 (1H, bd); 2.64 (1H, dd, J_1=2.32, J_2=5.4); 2.93 (1H, dq, J_1=2.32, J_2=5.3); 3.35-3.42 (1H, m). ^{13}C-NMR data (*erythro isomer*): 13.77, 17.01, 22.34, 24.76, 31.67, 33.32, 50.91, 61.88, 68.59. ^{13}C-NMR data (*threo isomer*): 13.77, 17.01, 22.34, 24.76, 31.60, 34.10, 52.76, 68.77, 71.31. Anal. Calcd. for $C_9H_{18}O_2$: C, 68.31; H, 11.47%. Found: C, 68.37; H, 11.40%.

4c (*inseparable mixture of two diastereomers*): ^{1}H-NMR data (*erythro isomer*): 0.88 (3H, bt); 0.99 (3H, t, J= 7.6 *Hz*); 1.15-1.65 (16H, m); 2.1 (1H, bs); 2.73 (1H, m); 2.97 (1H, dt, J_1= 5.6 *Hz*, J_2= 2.4 *Hz*); 3.70-3.80 (1H, m). ^{1}H-NMR data (*threo isomer*): 0.88 (3H, bt); 0.99 (3H, t, J= 7.6 *Hz*); 1.15-1.65 (16H, m); 2.1 (1H, bs); 2.71 (1H, m); 2.86 (1H, dt, J_1= 5.5 *Hz*, J_2= 2.2 *Hz*); 3.35-3.45 (1H, m). ^{13}C-NMR selected data *(diagnostic signals for the erythro isomer)*: 31.81, 33.52, 56.07, 60.82, 68.47. ^{13}C-NMR selected data *(diagnostic signals for the threo isomer)*: 32.71, 34.26, 58.06, 61.73, 71.51. Anal. Calcd. for $C_{13}H_{26}O_2$: C, 72.85; H, 12.23%. Found: C, 72.89; H, 12.26%.

4d (*inseparable mixture of two diastereomers*): ^{1}H-NMR data (*erythro isomer*): 1.18 (3H, d, J= 6.2 Hz); 1.24-1.34 (6H, m); 2.60 (1H, d, J= 7.8 Hz); 2.90-3.00 (1H, bs); 3.52-3.66 (1H, m). ^{1}H-NMR data (*threo isomer*): 1.18 (3H, d, J= 6.2 Hz); 1.24-1.34 (6H, m); 2.68 (1H, d, J= 8.0 Hz); 2.90-3.00 (1H, bs); 3.52-3.66 (1H, m). ^{13}C-NMR data (*erythro isomer*): 18.62, 20.84, 24.75, 59.23, 66.07, 67.04. ^{13}C-NMR data (*threo isomer*): 19.00, 19.11, 24.84, 59.23, 66.88, 68.56. Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04; H, 10.41%. Found : C, 61.97; H, 10.38%.

4e (*erythro isomer*): ^{1}H-NMR data: 0.88 (3H, bt); 1.15-1.68 (11H, m); 2.15 (1H, s); 3.13 (1H, q, J=5.6 *Hz*); 3.60 (1H, bs). ^{13}C-NMR data: 13.51, 13.97, 14.05, 22.52, 25.23, 31.85, 32.62, 54.91, 62.70, 72.59. Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70%. Found: C, 69.76; H, 11.68%.

4e (*threo isomer*): ^{1}H-NMR data: 0.88 (3H, bt); 1.10-1.68 (11H, m); 2.1 (1H, s); 2.96 (1H, q, J=5.6 *Hz*); 3.15 (1H, bs). ^{13}C-NMR data: 13.52, 13.99, 14.09, 22.49, 25.32, 31.77, 32.97, 57.67, 63.60, 76.95. Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72 ; H, 11.70%. Found: C, 69.75 ; H, 11.75%.

4i (*erythro isomer*): 0.88 (3H, bt); 0.99 (3H, t, J=7.6 *Hz*); 1.2-1.7 (8H, m); 2.28 (1H, bs); 2.95 (1H, dd, J_1=J_2=6.6 *Hz*); 3.65-3.55 (1H, m). ^{13}C-NMR data: 10.39, 13.94, 14.18, 21.38, 21.71, 27.73, 32.39, 60.36, 62.87, 72.46. Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70%. Found: C, 69.72; H, 11.66%.

4i (*threo isomer*): 0.90 (3H, bt); 1.01 (3H, t, J=7.6 *Hz*); 1.15-1.70 (8H, m); 1.97 (1H, bs); 2.79 (1H, dd, J_1=J_2=6.6 *Hz*); 3.10-3.22 (1H, m). ^{13}C-NMR data: 10.40, 10.94, 13.99, 21.44, 22.69, 27.87, 32.73, 63.43, 63.73, 77.13. Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.72; H, 11.70%. Found: C, 69.73; H, 11.66%.

6a: 0.98 (3H, t, J=7.4 *Hz*); 1.45-1.75 (3H, m); 1.85-2.02 (1H, m); 2.71-2.80 (1H, m); 2.81-2.90 (1H, m); 3.75 (2H, t, J=5.8 *Hz*). ^{13}C-NMR data: 9.75, 24.94, 34.23, 56.54, 59.41, 59.87. Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04 ; H, 10.41. Found: C, 62.02; H, 10.37%.

6b: 0.98 (3H, t, J=7.4 *Hz*); 1.40-1.90 (4H, m); 2.83-2.93 (1H, m); 3.00-3.10 (1H, m); 3.65-3.85 (2H, m). ^{13}C-NMR data: 10.31, 21.05, 30.39, 55.02, 57.98, 60.16. Anal. Calcd. for $C_6H_{12}O_2$: C, 62.04 ; H, 10.41. Found : C, 62.04 ; H, 10.37%.

6c: (*inseparable mixture of two diastereomers*): ^{1}H-NMR data (*syn isomer*): 1.49-1.65 (1H, m); 1.73 (1H, m); 2.15-2.40 (2H, m); 2.51 (1H, dd, J_1=2.5 *Hz*, J_2=5.0 *Hz*); 2.75-2.85 (1H, m); 3.0-3.2 (1H, m); 3.80-4.00 (1H, m); 5.05-5.20 (2H, m); 5.70-5.95 (1H, m). ^{1}H-NMR data (*anti isomer*): 1.49-1.65 (1H, m); 1.78 (1H, m); 2.15-2.40 (2H, m); 2.58 (1H, dd, J_1=2.5 *Hz*, J_2=5.0 *Hz*); 2.75-2.85 (1H, m); 3.0-3.2 (1H, m); 3.80-4.00 (1H, m); 5.05-5.20 (2H, m); 5.70-5.95 (1H, m). ^{13}C-NMR data (*syn isomer*): 38.96, 41.79, 46.58, 50.29, 69.16, 118.33, 134.22. ^{13}C-NMR data (*anti isomer*): 38.64, 42.01, 46.93, 50.04, 68.22, 118.33, 134.22. Anal. Calcd. for $C_7H_{12}O_2$: C, 65.60; H, 9.44%. Found: C, 65.56; H, 9.50.

References and Notes

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[Ø] Diastereoisomeric ratios have been determined on the ground of isolated epoxyalcohols (**4e**, **4i**) or by ^{1}H-NMR analysis of the crude mixture, involving accurate integration of the signals relative to C$\underline{H}$—OH of *threo* and *erythro* epoxyalcohols for **4a**, **4b**, **4c**, relative to C$\underline{H}_3$CH(OH)- for **4d**.

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(*Received in UK* 15 *April* 1997; *revised* 16 *June* 1997; *accepted* 19 *June* 1997)