2.54 (1 H, dd, J = 19.65, 5.36 Hz), 2.66 (1 H, d, J = 16.38 Hz), 2.70 (1 H, dd, J = 19.58, 11.64 Hz), 2.89 (1 H, dd, J = 11.81, 4.76 Hz), 3.15 (1 H, s); ^{13}C NMR (125.75 MHz, $CDCl_3$) δ 22.5 (1 C, t), 22.8 (1 C, t), 23.1 (1 C, t), 23.3 (1 C, t), 25.6 (1 C, t), 25.9 (1 C, t), 26.7 (1 C, t), 27.1 (1 C, t), 34.1 (1 C, t), 34.3 (1 C, t), 40.6 (1 C, t), 47.2 (1 C, s), 50.1 (1 C, t), 50.8 (1 C, t), 53.0 (1 C, d), 57.4 (1 C, s), 69.2 (1 C, d), 205.0 (1 C, s), 206.2 (1 C, s), 215.4 (1 C, s); MS (EI, 15 eV) m/z (relative intensity) 316 (M^+, 69.4), 273 (100.0).

Tetracyclo[11.5.2.0^{2,13}.0^{2,16}]eicosane-15,17,19-trione Tris(tosylhydrazone) (23). The trione (22, 22 mg, 0.07 mmol) and tosylhydrazine (64 mg, 0.35 mmol) were dissolved in anhydrous ethanol (3 mL) which contained 2 drops of concentrated HCl. The mixture which resulted was allowed to heat at reflux. The reaction progress was monitored by TLC (EtOAc/hexane, 3:2) on silica gel. After 4 h, examination of the reaction mixture by TLC indicated the presence of a new component and the absence of starting material. The reaction mixture was allowed to cool to 25 °C, and the ethanol was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (100 mL), washed with water and brine, and dried ($MgSO_4$). The solvent was removed in vacuo to provide a crude solid which was chromatographed (EtOAc/hexane, 2:3) to provide tris(tosylhydrazone) (40 mg, 70%) 23: FTIR (KBr) 1650 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 2.42 (3 H, s, CH_3), 2.43 (6 H, s, 2 CH_3), 1.20–3.50 (28 H, m), 7.20–8.05 (12 H, m).

Attempted Preparation of 1,2:16,17-Bisdecanododecahedrane (3) via the Photodimerization of Ellacene (4). Ellacene (4, 30 mg, 0.11 mmol) was dissolved in pentane (0.1 mL) and transferred into a quartz tube (2-mm diameter) with a NMR cap. Argon was carefully bubbled into the solution for 5 min, and then it was placed in a photochemical apparatus (low-pressure Hg lamp with λ = 254 nm). The reaction progress was monitored by GC/MS (temperature 200 °C; initial time, 2 min; program rate, 10 °C/min; final temperature 260 °C; final time, 5 min). The GC/MS results suggested no change over a 3-day period [t_R(4) = 7.0 min]. The reaction was worked up, and the NMR (^{1}H, ^{13}C) spectrum of the entire mixture was identical to that of authentic ellacene. The same reaction was repeated with a light source at 214 nm for 24 h; GC/MS of the reaction mixture indicated no change of the starting triene. The starting ellacene was recovered and found to be identical with an authentic sample of ellacene, 4 (^{1}H NMR, TLC).

Attempted Preparation of 1,2:16,17-Bisdecanododecahedrane (3) via High-Pressure Dimerization of 1,10-Decanotriquinacene (4, Ellacene). High pressure was generated in a gasketed diamond anvil cell, and ellacene was directly introduced via a syringe into the gasket hole, which also contained a ruby chip for pressure calibration. After each high-pressure experiment, the contents of the cell were removed with ca. 2–4 μL of benzene and analyzed by GC/MS on a Finnigan 8230 mass spectrometer using on-columm injection of the entire sample. The GC/MS results indicated that pressurization of ellacene to nearly 20 GPa (1 GPa = 10 kbar) and/or exposure to 308-nm ultraviolet radiation at 5 GPa failed to produce any detectable products except the starting ellacene. Only starting ellacene was obtained. Under the same conditions triquinacene underwent [2 + 2] dimerization.[10f]

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Supplementary Material Available: NMR spectra of 4, 15/16, and 22 (5 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

2-Iminooxetane Chemistry. 3. Synthesis of β-Hydroxy Amides[1,2]

Gaetano Barbaro, Arturo Battaglia,* and Patrizia Giorgianni

Istituto CNR dei Composti del Carbonio Contenenti Eteroatomi, Via della Chimica, 8-I-40064 Ozzano Emilia, Italy

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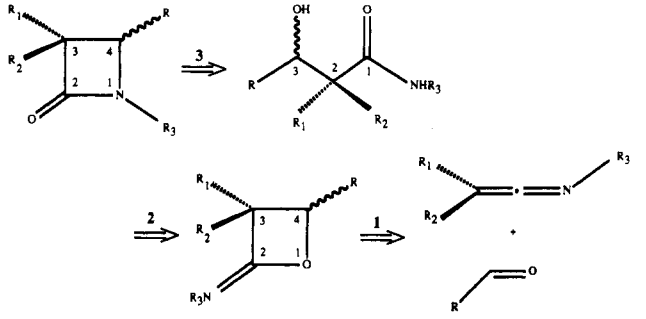
β-Hydroxy amides were synthesized by hydrolysis of the corresponding 2-iminooxetanes, which were prepared in a very simple step by lanthanide-catalyzed cycloaddition of aldehydes to ketene imines. The stereochemical outcome of the hydrolysis, performed under neutral ($DMSO/H_2O$) or acidic (H_2SO_4/H_2O) conditions, depends on the steric and electronic nature of the substituents, which play a crucial role in the ring-opening mechanism. Experiments done with ^{18}O-labeled water showed that two alternatives are possible: one involving ring opening of the oxetane at the C4–O bond, the other involving ring opening at the C2–O bond.

Introduction

We have recently reported the synthesis of 2-iminooxetanes[2] via a heterocycloaddition route. In a preliminary study, it was found[3] that 2-(*N*-*p*-tolylimino)-4-phenyloxetane could be transformed, through medium-controlled ring opening, into the corresponding β-hydroxy amide, β-keto amide, γ-amino alcohol, and β-lactam. This variety of products demonstrates the utility of 2-iminooxetanes for the introduction of functionalized C_2, C_3, and C_4 units into organic compounds. In particular, the possible use of hydrolytic ring opening to obtain β-hydroxy amides

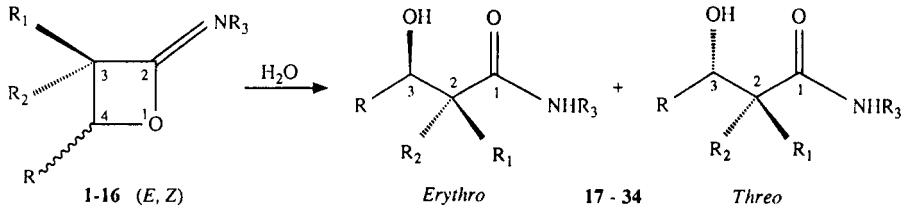
Scheme I



(1) Presented in part at the *Fifth European Symposium on Organic Chemistry*, Jerusalem, Israel, Aug–Sept, 1987.
(2) Part 2: Barbaro, G.; Battaglia, A.; Giorgianni, P. *J. Org. Chem.* **1988**, *53*, 5501.
(3) Barbaro, G.; Battaglia, A.; Giorgianni, P. *Tetrahedron Lett.* **1987**, *26*, 2995.

0022-3263/92/1957-5128$03.00/0

Table I. Isolated Yields and Experimental Erythro/Threo (E:T) Ratios of β-Hydroxy Amides from Neutral[a] (Entries 1–11) and Acid-Induced[b] (Entries 12–30) Hydrolysis of 2-Iminoxetanes



entry	R	R_1	R_2	R_3[c]	2-iminooxetanes	β-hydroxy-amides	E:T[e]	yield (%)
1	C_6H_5	Me	Me	Tol	**1**	**17**	–	82
2	Me_2CH	Me	Me	Tol	**2**	**18**	–	80
3	CH_2=CH	Me	Me	Mes	**3**	**19**	–	75
4	$MeCH_2CH_2$	Me	H	An	(*E*)-**4**	**20**	80:20	52
5	$MeCH_2CH_2$	Me	H	An	(*Z*)-**4**	**20**	16:84	67
6	Me_2CH	Me	H	An	(*E*)-**5**	**21**	40:60	46
7	Me_2CH	Me	H	An	(*Z*)-**5**	**21**	44:56	77
8	C_6H_5	Me	H	Mes	(*Z*)-**6**	**22**	24:76	57
9	C_6H_5	Me	CH_2=CH	Tol	(*E*)-**7**	**23**	42:58	57
10	C_6H_5	Me	CH_2=CH	Tol	(*Z*)-**7**	**23**	49:51	61
11	MeCH=CH	Me	H	An	(*E*/*Z*)-**8**	**24**	30:70	26
12	C_6H_5	Me	Me	Cy	**9**	**27**	–	91
13	$MeCH_2CH_2$	Me	H	An	(*E*)-**4**	**20**	82:16	87
14	$MeCH_2CH_2$	Me	H	An	(*Z*)-**4**	**20**	6:94	90
15	Me_2CH	Me	H	An	(*E*)-**5**	**21**	24:76	92
16	Me_2CH	Me	H	An	(*Z*)-**5**	**21**	59:41	92
17	Me	Me	H	An	(*E*)-**10**	**28**	94:6	89
18	Me	Me	H	An	(*Z*)-**10**	**28**	9:91	85
19	MeC≡C	Me	H	An	(*E*)-**11**	**29**	94:6	94
20	MeC≡C	Me	H	An	(*Z*)-**11**	**29**	5:95	88
21	C_6H_5	Me	H	An	(*E*)-**12**	**30**	29:72	84
22	C_6H_5	Me	H	An	(*Z*)-**12**	**30**	24:76	85
23	2-Pyrido	Me	H	An	(*E*)-**13**	**31**	94:6	94
24	2-Pyrido	Me	H	An	(*Z*)-**13**	**31**	47:53	88
25	Me	Me_3C	H	An	(*E*)-**14**	**32**	erythro	85
26	Me	Me_3C	H	An	(*Z*)-**14**	**32**	erythro	85
27	$MeCH_2CH_2$	$MeCH_2$	H	An	(*E*)-**15**	**33**	86:14	89
28	$MeCH_2CH_2$	$MeCH_2$	H	An	(*Z*)-**15**	**33**	3:97	84
29	C_6H_5	Me_3C	H	An	(*E*)-**16**	**34**	erythro	94
30	C_6H_5	Me_3C	H	An	(*Z*)-**16**	**34**	47:53	84

[a] In DMSO/H_2O. [b] 2-Iminoxetane (0.5 mmol), H_2SO_4 (0.9 mmol), 3:1 acetone/H_2O (20 ml). [c] Tol: C_6H_4-*p*-Me; An: C_6H_4-*p*-OMe; Mes: 2,4,6-Me_3-C_6H_2; Cy: C_6H_{11}. [e] Erythro/threo ratios determined by HPLC analysis.

attracted our attention, since these derivatives constitute an important source for the production of β-lactams by N–C3 ring closure.[4] Consequently, we developed a new retrosynthetic strategy having β-lactams as targets. This strategy suggests the β-lactams can be synthesized from β-hydroxy amides, which in turn are obtained via hydrolytic ring opening of 2-iminooxetanes (Scheme I).

This procedure is valuable because these heterocycles can be easily produced from readily available starting materials such as aldehydes and ketene imines. In this approach, the functionality at C3 of the target is provided by the ketene imine, while that at C4 is provided by the aldehyde. Preliminary studies[2] proved that our procedure for synthesis of 2-iminooxetanes is quite general, due to the high stereoselectivity of the lanthanide-induced heterocycloaddition.

In this paper, we report an extension of our studies on the hydrolytic ring opening to a selected number of 2-iminooxetanes. In particular, the stereochemical outcome of the hydrolysis of several diastereomeric pairs of *E* and *Z* C3,C4-unsymmetrically-monosubstituted derivatives is examined. These studies, supported by experiments with ^{18}O-labeled water, demonstrate that different mechanisms for the ring opening are possible and that the occurrence of a particular mechanism is strictly related to the steric environment of the oxetane mojety.

Results and Discussion

The necessary substituted 2-iminooxetanes (**1–16**) (Table I) were synthesized in one simple step from the corresponding ketene imines and commercially available aldehydes. The unsymmetrically substituted ketene imines afforded diastereomeric mixtures of the corresponding (*E*)- and (*Z*)-oxetanes, which were separated in many cases by flash chromatography (**4**, **5**, **7**, and **10–16**, Table I). Although chromatography was performed with carefully dried solvents and with silica preheated in an oven, the purification of the oxetanes, for analytical purposes, was troublesome because the oxetanes were occasionally contaminated by small amounts of the corresponding β-hydroxy amides, which are formed by hydrolysis during elution. Other impurities were the amides of the corre-

(4) See for example: Bose, A. K.; Saha, D. P.; Manhas, M. S. *J. Org. Chem.* **1981**, *46*, 1229.

sponding ketene imines. The β-hydroxy amides were removed quantitatively by filtration after the oxetanes were dissolved in *n*-pentane and left at −20 °C for 1 day. Solvent was removed under vacuum (0.01 mm) at room temperature in order to prevent a possible retrocycloaddition. After the workup, the oxetanes were always obtained as oily, viscous residues, which still retained some amide of the ketene imine and of ethyl acetate. EtOAc was used as eluant during chromatography. These impurities, revealed by ^{1}H NMR, caused a consistent deviance (0.51–0.69% C) of the analytical data from the theory for (*Z*)-**5**, (*E*)-**10**, (*Z*)-**15**, (*E*)-**15**, and (*E*)-**16** (see Experimental Section). However, the absence of the corresponding β-hydroxy amides, at least on a ^{1}H NMR scale at 200 MHz, was always checked before the hydrolytic experiments were performed.

Ring Opening of 2-Iminooxetanes under Neutral Conditions. Attempts to hydrolyze 2-iminooxetanes in water or water/inert solvent mixtures (dioxane/H_2O or toluene/H_2O, reflux) failed. However, a solvent-assisted ring opening, followed by water addition, was achieved in DMSO/H_2O mixtures at 120–150 °C. A preliminary experiment has been reported for 2-N-p-tolylimino-4-phenyloxetane.[3] In this paper, results for a number of these heterocycles with substituents at C3 and C4 and with different steric and electronic characteristics are reported (entries 1–11, Table I).

The corresponding β-hydroxy amides were always obtained, but yields varied over a wide range and were consistently higher for the C3-disubstituted oxetanes. The higher yields are probably due to a greater tendency of the C3-monosubstituted oxetanes to undergo concurrent cycloreversion under the reaction conditions. In fact, the amide of the corresponding ketene imine was found as the major byproduct of the hydrolyses of **4**–**6**.

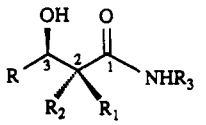
All the β-hydroxy amides exhibit IR, mass, and microanalytical data consistent with the assigned structure. In particular, the assignment of erythro and threo diastereomers was based on the ^{1}H and ^{13}C NMR method used for β-hydroxy carbonyl derivatives.[5]

Entries 1–13 of Table II list the ^{13}C NMR resonances that are of particular interest, namely, C2, C3, and the methyl at C2 of all the β-hydroxy amides isolated with the DMSO/H_2O procedure. The ^{1}H–^{1}H vicinal coupling constants of the C2 and C3 protons of the C2-monosubstituted derivatives are also reported. The carbons of the erythro isomers were generally shifted upfield in the ^{13}C NMR with respect to those of the threo isomers. Larger separations, ranging between 3.0 and 5.0 ppm, were observed in the resonances of the methyl substituents at C2 of the diastereomeric pairs. Smaller separations within a diastereomeric pair were noticed for C2 and C3. The ^{13}C NMR correlations were supplemented by ^{1}H NMR. In fact, the $J_{2,3}$ vicinal coupling constants of the *threo*-β-hydroxy carbonyl derivatives were usually larger than those of the erythro derivatives. The $J_{2,3}$ ^{1}H–^{1}H coupling constants of the threo isomers ranged between 5.1 and 6.8 Hz, while those of the corresponding erythro isomers ranged between 2.5 and 3.6 Hz. We also used the ^{13}C NMR correlations to assign the stereostructure of the C2-unsymmetrically-disubstituted amides *erythro*-**23** and *threo*-**23**. As a consequence, the amide of entry 10, having a methyl at C2 syn to the hydrogen at C3, was assigned as threo, since C2, C3, and the methyl at C3 resonate at higher field (55.0, 78.7, and 20.1 ppm, respectively) with respect to those of *erythro*-**23** (54.2, 78.4, and 17.3 ppm, entry 11).[6]

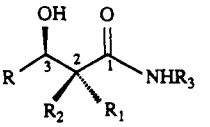
Hydrolysis of a Z/E = 0.85 mixture of oxetanes **8** gave both *erythro*- and *threo*-β-hydroxy amides **24** in 26% overall yield, together with a 1:1 mixture of two major isomers (**25** and **26**, Chart I). Flash chromatography, followed by repeated recrystallizations, yielded pure **25** and **26**.

Analytical data (see Experimental Section) were consistent with a γ-hydroxy amide[7] structure, deriving from

Table II. ^{13}C NMR Chemical Shifts (ppm) and $J_{2,3}$ (Hz) Coupling Constant Values of *threo*- (T-) and *erythro*-(E-)β-Hydroxy Amides



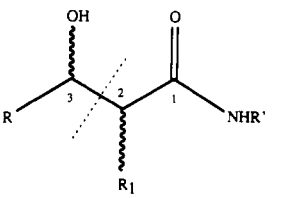
Erythro



Threo

entry	amide	R_1 (ppm)	R_2 (ppm)	C2	C3	$J_{2,3}$
1	**17**	Me	Me	47.1	80.1	–
2	**18**	Me	Me	45.5	83.0	–
3	**19**	Me	Me	45.7	79.2	–
4	*T*-**20**	H	Me (15.8)	47.1	73.8	6.5
5	*E*-**20**	Me (11.4)	H	45.8	72.2	3.0
6	*T*-**21**	H	Me (16.0)	44.4	79.0	5.1
7	*E*-**21**	Me (10.8)	H	43.2	77.1	2.5
8	*T*-**22**	H	Me (16.1)	47.2	76.1	6.0
9	*E*-**22**	Me (11.8)	H	47.3	73.9	3.6
10	*T*-**23**	CH_2=CH	Me (20.1)	55.0	78.7	–
11	*E*-**23**	Me (17.3)	CH_2=CH	54.2	78.4	–
12	*T*-**24**	H	Me (15.1)	44.4	75.2	6.8
13	*E*-**24**	Me (12.0)	H	45.8	74.2	3.3
14	**27**	Me	Me	45.7	80.2	–
15	*T*-**28**	H	Me (15.5)	48.7	69.9	6.0
16	*E*-**28**	Me (11.6)	H	46.5	68.6	3.0
17	*T*-**29**	H	Me (15.0)	48.2	64.9	6.6
18	*E*-**29**	Me (12.6)	H	46.5	64.3	3.2
19	*T*-**30**	H	Me (15.4)	48.6	76.5	7.0
20	*E*-**30**	Me (11.4)	H	48.0	74.2	3.6
21	*T*-**31**	H	Me (15.4)	46.7	75.5	5.0
22	*E*-**31**	Me (11.1)	H	47.3	72.9	3.0
23	*E*-**32**	Me_3C	H	61.7	66.3	2.0
24	*T*-**33**	H	CH_2 (38.1)	54.8	72.1	4.1
25	*E*-**33**	CH_2 (36.2)	H	54.4	72.2	3.4
26	*T*-**34**	H	Me_3C	65.1	75.2	9.2
27	*E*-**34**	Me_3C	H	63.5	72.5	1.8

Chart I



(5) It has been demonstrated that *erythro*- and *threo*-β-hydroxy carbonyl compounds exist as chairlike conformers because of the presence of an intramolecular hydrogen bond between O—H and C=O. The observed upfield shifts in erythro diastereomers are explained by additional gauche interactions with respect to the corresponding threo isomer. For an exhaustive account on this topic see: Heathcock, C. H.; Pirrung, M. C.; Sohn, J. E. *J. Org. Chem.* **1979**, *44*, 4294.

(6) The stereostructure of parent oxetanes **7** has been assigned following Prelog's priority rules, so that the *E*-configuration has been assigned to the oxetane having the vinyl substituent at C3 *anti* to the phenyl at C4. See ref 2.

C4–O bond breaking and attack of a molecule of H_2O on the methyl-substituted carbon of the vinyl substituent of (*Z*)- and (*E*)-**8**.

Hydrolysis of diastereomerically pure (*Z*)- and (*E*)-oxetanes **4–7** gave erythro/threo mixtures of β-hydroxy amides. A change in the sense of the diastereoselection was observed when the steric properties of the substrate were changed: a slight preference for the formation of the threo isomer was observed in the hydrolysis of both oxetanes **7**, irrespective of their *E* or *Z* stereochemistry, while an inversion is the stereochemical relationship between reagents and products in the hydrolysis of (*E*)- and (*Z*)-**4**. However, in these cases product formation was far from quantitative; thus, a general model for the ring-opening stereochemistry cannot be made.

Ring Opening of 2-Iminooxetanes under Acidic Conditions. The low reactivity of 2-iminooxetanes in DMSO/H_2O is similar to that found in the hydrolytic ring opening of trimethylene oxide[8] in both base-induced and neutral "water" reactions. Since much higher rates are reported in the acid-induced hydrolysis of trimethylene oxide, we tested this procedure for 2-(*N*-4-tolylimino)-3,3-dimethyl-4-phenyloxetane. The ring opening in acetone/water mixtures in the presence of HCl, HBr, and HI occurred instantaneously at 25 °C but gave variable mixtures of the expected *N*-(4-tolyl)-2,2-dimethyl-3-hydroxy-3-phenylpropionamide and the corresponding β-halo amide ($C_6H_5CHXCMe_2CONHC_6H_4$-4-Me).[9] Better results were obtained in acetone/water solutions in the presence of H_2SO_4. These reactions were deliberately performed with unbuffered solutions in order to avoid components that might react with the oxetane and hence complicate the hydrolysis.[10] The addition of an equimolar amount of H_2SO_4 with respect to the oxetane produced a considerable catalytic effect. In fact, the reactions were completed in a period ranging from a few minutes to a few hours at 25 °C, depending on the nature of the substituents at C3 and C4.

Entries 12–30 of Table I record our systematic study of the H_2SO_4-induced formation of β-hydroxy amides, and entries 14–27 of Table II report their relevant ^{13}C NMR and $J_{2,3}$ ^1H–^1H coupling constants. Since the yield of product was typically greater than 85%, we investigated the mechanism of the acid-induced hydrolysis of diastereomerically pure C3-monosubstituted oxetanes.

A careful ^1H NMR examination of the geometrical integrity of the 2-iminooxetanes and of the β-hydroxy amides revealed no detectable isomerization at 25 °C. The *E*/*Z* pair of oxetanes **4**, **5**, and **10–16** (0.5 mmol), each of which was >98% isomerically pure, was subjected to the same conditions (a 3:1 acetone/H_2O mixture (20 mL) containing 0.9 mmol of H_2SO_4). Isolated yields and HPLC product analyses are summarized in Table I. The stereospecificity of the reactions depends on the nature of the substituents at C3 and C4 of the oxetane moiety and on the experimental conditions, so a general model for the prediction of the stereochemical outcome of the ring opening cannot be made even for the acid-induced hydrolysis. However, some very important trends can be deduced from these examples. In particular, straight-chain alkyl substituents at C3 and C4 of oxetanes **4**, **10**, **11**, and **15** provided the highest degree of diastereoselection: an inversion is the stereochemical relationship between the reagents, irrespective of their *E*/*Z* stereochemistry, and the predominant products. Interestingly, a very slight relative increase in the retention products with an increase in the relative amount of water was observed in these cases. Typically, the amount of the product of retention (*threo*-**20**) obtained from the hydrolysis of (*E*)-**4** increased from 3% to 16% with a 60-fold relative increase in the amount of water (entries 1–4, Table III). Similarly, *erythro*-**20**, obtained from the hydrolysis of (*Z*)-**4**, increased from 7% to 10% under the same reaction conditions (entries 5, 7, and 8, Table III). The increase in steric requirements of the straight-chain alkyl groups at C4 going from methyl ((*E*/*Z*)-**10**) to *n*-propyl ((*E*/*Z*)-**4**) had no observable effect on the diastereoselection. This trend was consistent also for C3-ethyl-substituted oxetanes (*E*)- and (*Z*)-**15** (entries 27 and 28, Table I).

In contrast, more sterically demanding alkyl substituents at C4, such as the isopropyl group of oxetanes **5**, dramatically decreased the relative amount of product of inversion when the relative amount of water was increased. For instance, inversion is still favored at low H_2O/H_2SO_4 ratios in the hydrolysis of (*E*)-**5** (entries 9, 10, 14, and 15, Table III) and of (*Z*)-**5** (entries 18 and 19), but retention predominates when the relative amount of water is increased (entries 12, 13, 21, and 22).

Table III. Product Distribution of H_2SO_4-Induced Hydrolysis of (*E*)- and (*Z*)-Oxetanes 4, 5, 12, and 16 at 25 °C

entry	oxetane (mmol)	H_2O (mmol)	H_2SO_4 (mmol)	H_2O/H_2SO_4	β-hydroxy amide (erythro:threo)
1	(*E*)-**4** (0.05)	0.28	0.18	1.6	**20** (97:3)
2	(*E*)-**4** (0.05)	0.78	0.18	4.3	**20** (92:8)
3	(*E*)-**4** (0.05)	3.61	0.18	20.0	**20** (88:12)
4	(*E*)-**4** (0.05)	16.7	0.18	93.0	**20** (84:16)
5	(*Z*)-**4** (0.05)	0.28	0.18	1.6	**20** (7:93)
6	(*Z*)-**4** (0.05)	0.78	0.18	4.3	**20** (7:93)
7	(*Z*)-**4** (0.05)	3.61	0.18	20.0	**20** (10:90)
8	(*Z*)-**4** (0.05)	16.7	0.18	93.0	**29** (9:91)
9	(*E*)-**5** (0.04)	0.17	0.09	1.9	**21** (88:12)
10	(*E*)-**5** (0.04)	0.44	0.09	4.9	**21** (80:20)
11	(*E*)-**5** (0.04)	1.28	0.09	14.2	**21** (53:47)
12	(*E*)-**5** (0.04)	5.7	0.09	63.6	**21** (23:77)
13	(*E*)-**5** (0.04)	25.2	0.09	280.0	**21** (24:76)
14	(*E*)-**5** (0.04)	1.8	2.16	0.8	**21** (77:33)
15	(*E*)-**5** (0.04)	1.33	0.45	3.0	**21** (76:24)
16	(*E*)-**5** (0.04)	1.33	0.18	7.4	**21** (63:37)
17	(*E*)-**5** (0.04)	1.28	0.05	28.4	**21** (42:58)
18	(*Z*)-**5** (0.035)	0.17	0.07	2.4	**21** (7:93)
19	(*Z*)-**5** (0.035)	0.44	0.07	6.2	**21** (16:84)
20	(*Z*)-**5** (0.035)	1.22	0.07	17.0	**21** (32:68)
21	(*Z*)-**5** (0.035)	5.67	0.07	81.0	**21** (59:41)
22	(*Z*)-**5** (0.035)	25.1	0.07	358.0	**21** (56:44)
23	(*E*)-**12** (0.035)	0.19	0.09	2.2	**30** (24:76)
24	(*E*)-**12** (0.035)	0.61	0.09	6.8	**30** (27:73)
25	(*E*)-**12** (0.035)	3.17	0.09	35.0	**30** (31:69)
26	(*E*)-**12** (0.035)	19.5	0.09	553.0	**30** (35:65)
27	(*Z*)-**12** (0.035)	0.19	0.09	2.2	**30** (25:75)
28	(*Z*)-**12** (0.035)	0.44	0.09	4.9	**30** (23:73)
29	(*Z*)-**12** (0.035)	1.44	0.09	16.0	**30** (20:80)
30	(*Z*)-**12** (0.035)	5.67	0.09	63.0	**30** (20:80)
31	(*Z*)-**12** (0.035)	22.3	0.09	656.0	**30** (20:80)
32	(*Z*)-**12** (0.035)	1.67	2.38	0.7	**30** (24:76)
33	(*E*)-**16** (0.030)	0.14	0.09	1.5	**34** (erythro)
34	(*E*)-**16** (0.030)	0.69	0.09	7.7	**34** (erythro)
35	(*E*)-**16** (0.030)	8.44	0.09	94.0	**34** (erythro)
36	(*Z*)-**16** (0.030)	0.14	0.09	1.5	**34** (63:37)
37	(*Z*)-**16** (0.030)	0.69	0.09	7.7	**34** (60:40)
38	(*Z*)-**16** (0.030)	0.69	0.09	94.0	**34** (51:49)

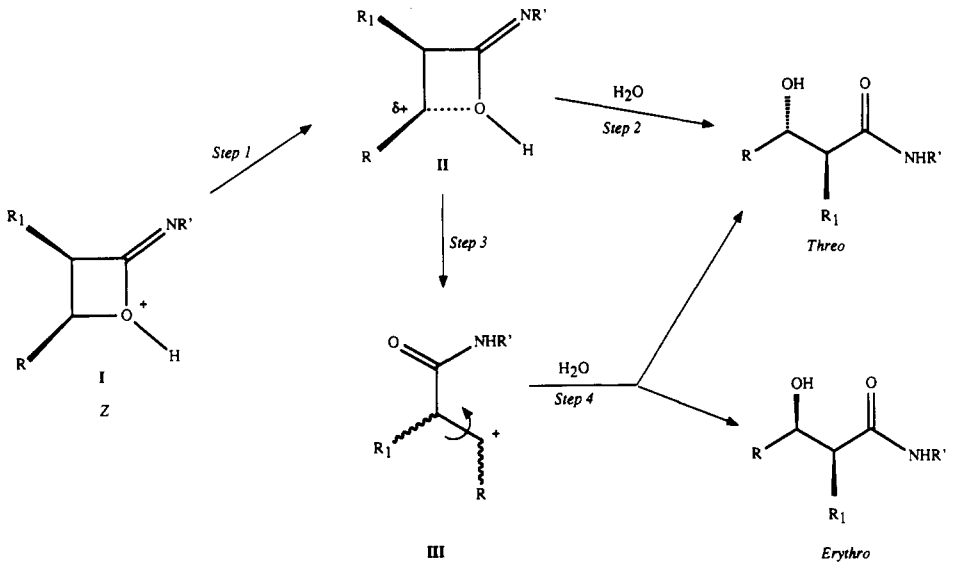
(7) Actually, the ^1H NMR spectra of γ-hydroxamides **25** and **26** showed the presence of a disubstituted double bond, which appears as an ABX_2 spin system. Decoupling experiments simplified the AB region and gave a J_{AB} of 15.0 Hz, which proved that the double bond has the *trans* configuration. The configuration of compounds **25** and **26** differed at C2 and C5, **25** being *syn* and **26** being *anti*, but the differences in their ^1H and ^{13}C NMR spectra (see Experimental Section) were not sufficient to allow assignment of the stereostructure. Attempts to determine the stereostructures of **25** and **26** by a single-crystal X-ray analysis are in progress.

(8) Long, F. A.; Prithchard, J. G. *J. Am. Chem. Soc.* **1958**, *80*, 4162.

(9) The stereochemistry of the addition of acids to 2-iminooxetanes is under investigation.

(10) It is known that normal buffer components frequently react with oxides. See, for example: Ross, W. C. J. *J. Chem. Soc.* **1950**, 2257.

Scheme II



The electronic nature of the substituent also played an important role in the stereoselectivity of the hydrolysis. For example, two of the C4-phenyl substituted oxetanes, (*E*)- and (*Z*)-**12**, gave an approximately equal erythro/threo product distribution of ca. 25:75 under the same reaction conditions (entries 21 and 22, Table I). Only very small product ratio variations were observed with the relative increase in water (entries 23–32, Table III).

The different behavior of the C4-aromatic-substituted oxetanes **12** with respect to the C4-aliphatic-substituted ones suggests that the retention product in the two cases may originate from different reactions. In the first case, an A_1 Ingold-type mechanism[11] is operating; i.e., the aromatic substituent at C4 stabilizes the carbocation (**III** of Scheme II, step 3), which can lose its stereochemical integrity prior to water addition (step 4). As a consequence, the retention and the inversion products are both produced from the same intermediate.

In our opinion, a similar mechanism operates in the hydrolysis of a $E/Z = 0.85$ mixture of oxetanes **8**. In this case, the carbocation is stabilized by the C4-*trans*-1-propenyl substituent; thus, a 1:1 mixture of γ-hydroxy amides is the major product, along with a minor amount of the expected β-hydroxy amides.

The presence of aliphatic substituents at C4, as in oxetanes **4** and **5**, destabilizes the carbocation, so that the retention and inversion products may originate from a competition between two different processes. Namely, the inversion involves breaking the C4–O bond of the H_2SO_4·oxetane complex (**I**) (step 1, Scheme II) and nucleophilic attack of a molecule of water (step 2) from the rear of C4 of the intermediate II. A similar mechanism has been suggested by Pritchard and Long in their studies of acid-induced hydrolysis of trimethylene oxide.[8] Quite interestingly, their kinetic results led to the conclusion that the transition state of the trimethylene oxide ring opening is essentially independent of the nucleophilic activity of the solvent, so that "*the collapse of the transition state by reaction with water molecules occurs immediately after the free energy maximum is attained in the opening of the oxide ring.*" As a consequence, step 1 of Scheme II should be the rate-determining step. The formation of the retention product involves entry of water into the exocyclic C=N bond of the H_2SO_4·oxetane complex (**I**, Scheme III),

Scheme III

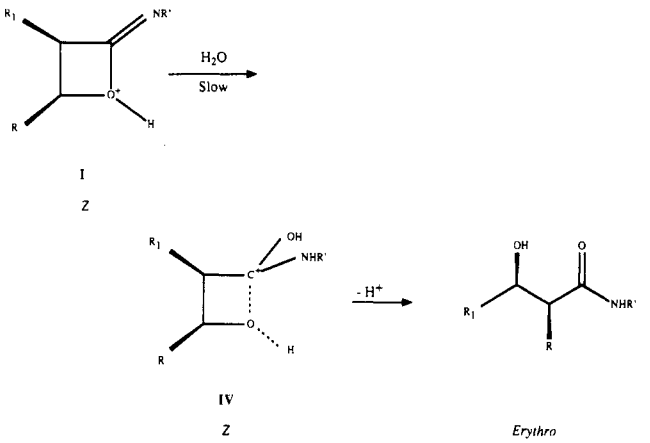


Table IV. Variation on the Rate of Hydrolysis of Oxetane 5 with the Relative Amount H_2O/H_2SO_4

entry	oxetane (mmol, *Z*:*E*)	H_2O:H_2SO_4 (mmol:mmol)	reaction (%)	time (s)	(*Z*/*E*)-oxetane recovered
1	5[a] (0.09, 47:53)	2.8:0.12	15	240	46:54
2	5[a] (0.09, 47:53)	11.7:0.12	80	180	40:60

[a] In 1.5 mL of acetone at 0 °C.

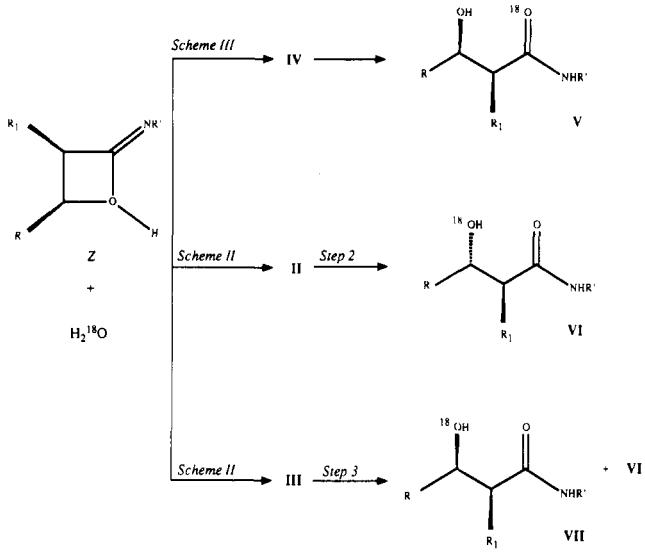
leading to the formation of an H_2SO_4·intermediate complex **IV**. Bond cleavage in this oxocarbonium ion occurs at the endocyclic C_2–O bond because of the presence of electron-rich substituents at C2. A similar mechanism has been proposed in the hydrolysis of 2-methoxy-3,3-dimethyloxetane.[12] In our opinion, a molecule of water acts as an active partner in the rate-determining step of the mechanism that leads to the retention product (Scheme III), and this mechanism is favored by sterically demanding substituents at C4. As supplementary evidence, we have observed that the rate of hydrolysis of oxetane **5** increases when the relative amount of water is increased (Table IV).

In conclusion, the product distribution of C4-aliphatic-substituted oxetanes may be regulated by a competition between a monomolecular process leading to inversion, as suggested by steps 1 and 2 of Scheme II, and a water-dependent bimolecular process leading to retention (Scheme III).

(11) Day, J. N. E.; Ingold, C. K. *Trans. Faraday Soc.* **1942**, *37*, 686.

(12) Atkinson, R. F.; Bruice, T. C. *J. Am. Chem. Soc.* **1974**, *96*, 819.

Scheme IV



The study of the detailed course of the hydrolysis with ^{18}O-labeled water provides valuable supplementary evidence for the mechanism of formation of the retention product.

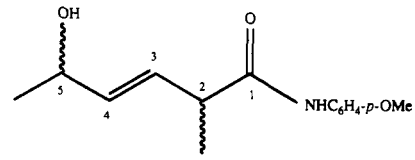
Complex **IV** in Scheme III affords an amide with an ^{18}O-labeled carbonyl function that retains the stereochemistry of the parent oxetane (**V** of Scheme IV). The ring opening of intermediate **II** (step 2 of Scheme II) affords an amide with an ^{18}O-labeled alcohol function inverted with respect to the parent oxetane (**VI** of Scheme IV). Finally, the stabilized carbocation **III** of Scheme II affords a mixture of amides **VI** and **VII** of Scheme IV. Amide **VII**, which has an ^{18}O-labeled alcoholic function, retains the stereochemistry of the reagent.

In order to determine which of these three paths was operating, we hydrolyzed both (*E*)- and (*Z*)-**5** and (*E*)- and (*Z*)-**12** in a mixture of dioxane/$H_2{}^{18}O$. Conditions for the $H_2{}^{18}O$ hydrolysis experiments were chosen to minimize the formation of unlabeled amide, since the presence of unlabeled water was irrelevant. In fact, the ^{18}O-content in $H_2{}^{18}O$ (0.08 mL) was >97%, the content of H_2O in anhydrous dioxane (1.5 mL) was less then 1.5 ppm (measured with the Karl Fischer method), and the amount of H_2SO_4 (96%) used for these experiments was 0.007 mL, so that the $^{18}O/^{16}O$ ratio was estimated to be ≥20. The *erythro*- and *threo*-β-hydroxy amides were separated from the mixture by thick-layer chromatography, and their ^{18}O-content was determined by mass spectrometry. The decomposition paths in the mass spectrometer are similar for the four diastereomers. In every case, there is some intensity from the parent amide ions and relevant peaks resulting from cleavage at C2–C3 of the amide skeleton (Chart II).

Analysis of the ^{18}O-content for our mechanistic studies can best be done by examining the fragment ions containing C1 and C2, since the presence of ^{18}O in the carbonyl function of the product of retention suggests that the mechanism shown in Scheme IV is operating. In contrast, the intensity of the ion containing C3 bearing the alcoholic function is less useful, since other minor masses were always present. The results were the following:

(i) The hydrolysis of oxetane (*Z*)-**5** (0.020 g, 0.09 mmol) gave an erythro:threo = 52:48 mixture of amides **21**. After the products were separated, the mass spectra of the product of inversion (*threo*-**21**) gave a peak at 253 (2.53, rel intensity) for the parent ion ($Me_2CHC^{18}OHCHMeCONHC_6H_4$-4-OMe) and a peak of

Chart II



25 and **26**

mass 178 (3.00, rel intensity) due to the ion $CHMeCONHC_6H_4$-4-OMe. Finally, a peak at *m/e* 75 (7.8, rel intensity) was attributed to $Me_2CHCH^{18}OH$. Analysis of this region was somewhat complicated by the presence of minor peaks at 74, 73, 72, and 71. In contrast, *erythro*-**21**, which retains the stereochemistry of the parent oxetane (*Z*)-**5**, gave a parent ion (rel intensity 7.5), a mass of 180 (9.6, rel intensity) due to the ion $CHMeC^{18}ONHC_6H_4$-4-OMe, and a mass at 73 (13.7, rel intensity) for $Me_2CHCHOH$. Minor peaks were at 74, 72, and 71 with intensities of 6.5, 4.1, and 8.2, respectively. Interestingly, no peaks were observed at mass 178 and 75. These results clearly indicated that the product of retention was formed exclusively via bond breaking at the C2–O bond (Scheme III).

(ii) The results for (*E*)-**5** confirmed those of (*Z*)-**5**. In fact, the hydrolysis of (*E*)-**5** (0.020, 0.09 mmol) gave an erythro:threo = 24:76 mixture of amides **21**. After the products were separated, the mass spectrum of the product of retention (*threo*-**21**) gave peaks at 253 (56.3, rel intensity), 180 (17.6, rel intensity), and 73 (24.5, rel intensity). Minor peaks were observed at 75, 74, and 72 with relative intensities of 4.3, 1.4, and 18, respectively. The product of inversion (*erythro*-**21**) gave peaks at 253 (37.6, rel intensity), 178 (20.1, rel intensity), and 75 (18.76, rel intensity). Minor peaks were observed at 74, 73, and 71 (rel intensities of 1.77, 7.5, and 1.35, respectively). The absence of the mass at 178 ($CHMeCONHC_6H_4$-4-OMe) in the retention product was also noticed in this case.

(iii) The hydrolysis of (*E*)- and (*Z*)-**12** (0.03 g, 0.11 mmol) gave a 22:82 mixture of *erythro*- and *threo*-**30**. Analysis of the mass spectra of the products was potentially complicated by the fact that the fragment at 180 could have been attributed to $CHMeC^{18}ONHC_6H_4$-4-OMe^+, to $C_6H_5CHOHCHMeC^{18}ONH^+$, or to $C_6H_5CH^{18}OHCHMeCONH^+$. Actually, the analysis of these spectra was straightforward, since in neither case was there much intensity from this ion. The relevant fragments of each isomer, together with their relative intensities, are listed below.

erythro-**30** (obtained from (*Z*)-**12**) gave peaks at 287 (M^+, 40.74), 178 (40.74), 108 ($C_6H_5CH^{18}OH^+$, 40.74), and 107 ($C_6H_5CH^{18}O^+$, 62.96). *threo*-**30** (obtained from (*Z*)-**12**) gave peaks at 287 (M^+, 45.68), 178 (31.28), 108 ($C_6H_5CH^{18}OH^+$, 25.34), and 107 ($C_6H_5CH^{18}O^+$, 58.02). *erythro*- and *threo*-**30** obtained from oxetane (*E*)-**12** gave a similar fragmentation pattern. These results clearly indicated that the product of retention was exclusively formed via breaking of the C4–O bond.

Conclusions

We have shown that the hydrolysis of 2-iminooxetanes provides a simple, general procedure for the synthesis of highly functionalized β-hydroxy amides. The hydrolysis proceeds readily in the presence of sulfuric acid, and β-hydroxy amides are formed in good to quantitative yields, irrespective of the steric bulk of the substituents at C3 and C4 of the oxetane moiety. It is worth noting that the hydrolysis also occurs when aliphatic substituents, such

as the cyclohexyl of oxetane **9**, are present at the imino nitrogen. The stereochemistry of these acid-induced reactions is the result of a fine balance among competing mechanisms. One mechanism involves the breaking of the C4–O bond with the formation of a "tight carbocation" (**II**, Scheme II); inversion is the stereochemical result. Another mechanism involves the formation of a "loose carbocation" (**III**, Scheme II) and produces a partial stereochemical scrambling of the reagents and products. These processes are, in essence, two extreme cases of a single mechanism. Finally, another mechanism, evidenced by $H_2{}^{18}O$ experiments, involves the attack of a molecule of water at the exocyclic C=N and breaking of the C2–O bond with total retention.

Similar mechanisms were observed in the hydrolysis of β-lactones. For example, breaking of the C2–O bond occurs in very acidic media during the hydrolysis of β-butyrolactone[13] and of (*R*)-β-(trichloromethyl)-β-propiolactone,[14] while breaking of the C4–O bond with Walden inversion occurs during the hydrolysis of β-butyrolactone in neutral or weakly acidic media. Finally, breaking of the C4–O bond, involving the intermediacy of a carbocation, occurs in the H_2SO_4-induced ring opening of the C-4 sterically hindered 4-*tert*-butyl-substituted β-propiolactone.[15] We have also shown that stereoelectronic effects strongly influence the product distribution during the ring opening of 2-iminooxetanes. For example, electronic effects operate in the hydrolysis of (*E*)- and (*Z*)-2-pyridyloxetanes **13**. These two isomers give quite different product distributions under the same reaction conditions (entries 23 and 24, Table I). Consequently, the formation of the "loose carbocation" **III** can probably be ruled out. One explanation could be that substitution of the phenyl for the electron-poor pyridyl substituent destabilizes the carbocation, so that product distribution is regulated by a competition between different mechanisms.

Steric effects are not easily predictable and require detailed investigations for each case. Our studies revealed the importance of this effect not only at C4 of the oxetane moiety but also at C2. For example, a striking difference was observed when the methyl at C2 was substituted for a *tert*-butyl, other substituents remaining unchanged. In fact, 3,4-dimethyl-substituted oxetanes (*E*)- and (*Z*)-**10** gave almost exclusively the corresponding products of inversion (entries 17 and 18, Table I), while the 3-*tert*-butyl-4-methyl-substituted oxetanes (*E*)- and (*Z*)-**14** afforded only the corresponding *erythro*-β-hydroxy amide **32** (entries 25 and 26, Table I). Similarly, oxetanes (*E*)- and (*Z*)-**12** gave an approximately equal erythro/threo product distribution (ca. 25:75, entries 21 and 22, Table I), oxetane (*E*)-**16** afforded amide *erythro*-**34** exclusively, and (*Z*)-**16** afforded an erythro/threo mixture (entries 33–38, Table III) in which the erythro product was always the major isomer. $H_2{}^{18}O$ experiments, performed on oxetanes **14** and **16**, proved that the product of retention derives from a competition between the mechanisms shown in Schemes II and III. An exhaustive explanation for this selectivity falls beyond the scope of this paper, since it requires a sophisticated kinetic analysis.

Experimental Section

Starting Materials. The aldehydes and the lanthanide shift reagents were commercially available. Ketene imines[16] and 2-iminooxetanes[2] were prepared according to the literature. In particular, 2-iminooxetanes **5**, **10**, **14**, **15**, and **16** were prepared for the first time, and their cis and trans configurational assignment was carried out according to the literature.[2] For the reaction conditions, isomer distributions, and microanalytical, MS, IR, and ^1H NMR ($CDCl_3$) data of 2-iminooxetanes **5**, **10**, and **14–16**, see the supplementary material.

General Procedure for the Synthesis of β-Hydroxy Amides. Hydrolysis in DMSO/H_2O Solutions (Procedure A). The 2-iminooxetanes were hydrolyzed in DMSO:H_2O = 5:1 solutions in a vial sealed under argon. The reaction mixture was held at the selected temperature for the required time. DMSO and water were removed under vacuum (10^{-2} Torr), and the threo/erythro isomer distribution was evaluated directly on the crude reaction mixture by HPLC analysis (5000 Varian on a C-8 reversed-phase column with 10% H_2O/acetonitrile as eluant. The products were separated by flash chromatography (SiO_2, 2:1 CH_2Cl_2/ethyl acetate, unless otherwise stated). Yields and threo/erythro product distributions are given in Table I.

Acid-Catalyzed Hydrolysis in Acetone/H_2O/H_2SO_4 Solutions (Procedure B). Unless otherwise stated, H_2SO_4 (0.9 mmol) was added at 25 °C with stirring to a solution (3:1 acetone/H_2O, 20 mL) of the selected 2-iminooxetane (0.5 mmol). The solution was left at 25 °C for 3–5 h and then neutralized with a 10% solution of $NaHCO_3$. Workup of the reaction mixture was performed as described in procedure A. Yields and erythro/threo product distributions are given in Table I.

For the reaction conditions, isomer distributions, and microanalytical, MS, IR, ^1H NMR ($CDCl_3$), and ^{13}C NMR ($CDCl_3$) data of β-hydroxy amides **17–19**, **21**, **22**, **27–31**, and **33**, see the supplementary material.

***erythro*- and *threo*-*N*-(4-Methoxyphenyl)-2-methyl-3-hydroxyhexanamide (*erythro*-20 and *threo*-20). Procedure A.** Oxetane (*E*)-**4** (0.177 g, 0.76 mmol) was heated at 150 °C for 75 min. Flash chromatography (SiO_2, 1:2 ethyl acetate/CH_2Cl_2) gave 0.020 g (0.08 mmol, 10.5%) of *threo*-**20** and 0.078 g (0.031 mmol, 41%) of *erythro*-**20**, erythro/threo = 3.9. Oxetane (*Z*)-**4** (0.214 g, 0.918 mmol) gave 0.129 g (0.514 mmol, 56.0%) of *threo*-**20** and 0.025 g (0.10 mmol, 11.0%) of *erythro*-**20**, erythro/threo = 0.19. **Procedure B.** (*E*)-**4** (0.117 g, 0.5 mmol) gave an erythro/threo product distribution of 82:16. Flash chromatography afforded *threo*-**20** (0.015 g, 0.060 mmol, 12%) and *erythro*-**20** (0.094 g, 0.374 mmol, 75%). Oxetane (*Z*)-**4** gave an erythro/threo product distribution of 6:94. After chromatography, *threo*-**20** (0.113 g, 0.45 mmol, 90%) and *erythro*-**20** (traces) were obtained. *threo*-**20**: mp 146–147 °C ($CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.8–1.05 (t, Me, 3), 1.32 (d, Me2, 3), 1.33–1.7 (m, CH_2, 4), 2.22–2.57 (m, H2, 1), 3.0–3.18 (m, OH, 1), 3.77 (s, OMe, 3), 3.58–3.88 (m H3, 1), 6.77–7.5 (m, H-arom, 4), 7.77–8.0 (br s, NH, 1); $J_{H,Me2}$ = 7.0, $J_{2,3}$ = 6.5, $J_{H,OH}$ = 2.0 Hz; ^{13}C NMR ($CDCl_3$) δ 14.0 (Me), 15.8 (Me), 19.0 (CH_2), 37.6 (CH_2), 47.1 (CH), 55.6 (OMe), 73.8 CH), 114.2 (2 CH), 122.1 (2 CH), 131.0 (C), 156.5 (C), 174.28 (C); IR (Nujol) 3450–3100, 1660; mass spectrum *m/z* 251 (M^+), 208, 178. Anal. Calcd for $C_{14}H_{21}NO_3$: C, 66.91; H, 8.42; N, 5.57. Found: C, 66.52; H, 8.30; N, 5.50. *erythro*-**20**: mp 154–155 °C ($CHCl_3$); ^1H NMR ($CDCl_3$) δ 0.83–1.03 (t, Me, 3), 1.24 (d, Me2, 3), 1.3–1.67 (m, CH_2, 4), 2.3–2.6 (m, H2, 1), 2.93–3.05 (m, OH, 1), 3.77 (s, OMe, 3), 3.83–4.07 (m, H3, 1), 6.78–7.5 (m, H-arom, 4), 7.73–7.9 (br s, NH, 1); $J_{H,Me2}$ = 7.0, $J_{2,3}$ = 3.0, $J_{H,OH}$ = 2.7 Hz; ^{13}C NMR ($CDCl_3$) δ 11.4 (Me), 14.0 (Me), 19.3 (CH_2), 35.7 (CH_2), 45.8 (CH), 55.5 (OMe), 72.2 (CH), 114.2 (2 CH), 121.9 (2 CH), 130.9 (C), 156.5 (C), 174.1 (C); IR (CCl_4) 3450–3100, 1660; mass spectrum *m/z* 251 (M^+), 2–8, 178. Anal. Calcd for $C_{14}H_{21}HO_3$: C, 66.91; H, 8.42; N, 5.57. Found: C, 67.19; H, 8.44; N, 5.63.

***erythro*- and *threo*-*N*-(4-Tolyl)-2-methyl-2-vinyl-3-hydroxy-3-phenylpropanamide (*erythro*-23 and *threo*-23). Procedure A.** Oxetane (*E*)-**7** (0.230 g, 0.83 mmol) was heated at 150 °C for 30 min. Chromatographic workup of the crude reaction mixture (SiO_2, 6.5:0.5:3 CH_2Cl_2/ethyl acetate/*n*-pentane) gave *erythro*-**23** (0.058 g, 0.2 mmol, 24%) and *threo*-**23** (0.081 g, 0.27 mmol, 33%), erythro/threo = 0.74. From (*Z*)-**7** (0.31 g, 1.12 mmol), 0.099 g (0.336 mmol, 30%) of *erythro*-**23** and 0.102 g (0.347

(13) (a). Olson, A. R.; Miller, R. J. *J. Am. Chem. Soc.* **1938**, *60*, 2687. (b). Olson, A. R.; Hyde, J. L. *J. Am. Chem. Soc.* **1941**, *63*, 2459.

(14) Wynberg, H.; Staring, E. G. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1181.

(15) Asensio, G.; Miranda, M. A.; Perez-Prieto, J.; Sabater, M. J.; Simon-Fuentes, A. *Angew, Chem., Int. Ed. Engl.* **1990**, *20*, 1146.

(16) Battaglia, A.; Dondoni, A.; Giorgianni, P. *J. Org. Chem.* **1982**, *47*, 3998 and references cited therein.

mmol, 31%) of *threo*-**23**, erythro/threo = 0.97, were obtained. ***erythro*-23**: mp 101–102 °C ($CHCl_3$); ^1H NMR ($CDCl_3$) δ 1.22 (s, Me, 3) 2.27 (s, Me, 3), 4.3–4.6 (br s, OH, 1), 4.86 (s, H3, 1), 5–5.32 (m, 2 H of CH=CH_2), 5.88–6.26 (m, 1 H of CH=CH_2), 6.97–7.43 (m, H-arom, 9), 7.97–8.2 (br s, NH, 1); ^{13}C NMR ($CDCl_3$) δ 17.3 (Me), 21.3 (Me), 54.2 (C), 78.4 (CH), 117.5 (CH_2), 120.4 (2 CH), 127.7 (2 CH), 127.8 (CH), 127.9 (2 CH), 129.5 (2 CH), 134.5 (C), 134.8 (C), 139.5 (C), 139.6 (CH), 174.6 (C); IR (Nujol) 3400–3100, 1662; mass spectrum *m*/*z* 295 (M^+), 188. Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26, H, 7.17; N, 4.74. Found: C, 76.99; H, 7.15; N, 4.68. ***threo*-23**: mp 144–146 °C ($CHCl_3$); ^{H} NMR ($CDCl_3$) δ 1.26 (s, Me, 3), 2.29 (s, Me, 3), 3.50–4.00 (br s, OH, 1), 4.93–5.50 (m, 2 H of CH=CH_2), 5.0 (s, H3, 1), 6.23–6.60 (m, 1 H of CH=CH_2), 7.0–7.5 (m, H-arom, 9), 7.67–7.87 (br s, NH, 1); ^{13}C NMR ($CDCl_3$) δ 20.1 (Me), 20.9 (Me), 55.0 (C), 78.7 (CH), 119.1 (CH_2), 120.3 (2 CH), 127.7 (2 CH), 127.8 (CH), 128.0 (2 CH), 129.5 (2 CH), 134.4 (C), 134.9 (C), 137.3 (CH), 140.0 (C), 173.8 (C); IR (Nujol) 3400–3100, 1662; mass spectrum, *m*/*z* 295 (M^+), 188. Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.26, H, 7.17; N, 4.74. Found: C, 77.62; H, 7.11; N, 4.70.

Reaction of *cis*- and *trans*-2-[(4-Methoxyphenyl)imino]-3-methyl-4-(*trans*-1-propenyl)oxetane ((*Z*)-8 and (*E*)-8). Procedure A. A 0.85 *E*/*Z* mixture of oxetanes 8 (1.00 g, 4.33 mmol) was heated at 120 °C for 2 h. HPLC analysis of the crude reaction mixture revealed the presence of three peaks in a relative ratio of 1:2:3 = 68.00:9.52:22.38. Flash chromatography (SiO_2, 14:1 CH_2Cl_2/methanol) afforded the following products: ***threo*-N-(4-methoxyphenyl)-2-methyl-3-hydroxy-4-*trans*-hexenamide** (*threo*-**24**) (0.196 g, 0.788 mmol, 18.2%), corresponding to peak 3 of HPLC [mp 157–158 °C (ethyl ether); ^1H NMR ($CDCl_3$) δ 1.25 (d, Me2, 3), 1.71 (dd, Me5, 3), 2.40 (m, H2, 1), 2.8–2.9 (br s, OH, 1), 3.79 (s, OMe, 3), 4.18 (m, H3, 1), 5.53 (m, H4, 1), 5.77 (m, H5, 1), 6.8–7.4 (m, H-arom, 4), 7.7–7.8 (br s, NH, 1); $J_{2,3}$ = 6.8, $J_{3,4}$ = 7.0, $J_{4,5}$ = 15.5 Hz; ^{13}C NMR ($CDCl_3$) δ 15.1 (Me), 17.7 (Me), 44.4 (CH), 55.5 (OMe), 75.2 (CH), 114.1 (2 CH), 121.9 (2 CH), 129.0 (CH), 130.9 (C), 131.6 (CH), 156.5 (C), 173.4 (C); IR ($CHCl_3$) 3650–3250, 1671; mass spectrum *m*/*z* 249 (M^+). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.14; H, 7.73; N, 5.77] ***erythro*-N-(4-methoxyphenyl)-2-methyl-3-hydroxy-4-*trans*-hexenamide** (*erythro*-**24**) (0.082 g, 0.329 mmol, 7.6%), corresponding to peak 2 of HPLC [mp 134–136 °C (ethyl ether); ^{H} NMR ($CDCl_3$) δ 1.20 (d, Me2, 3), 1.71 (dd, Me5, 3), 2.61 (m, H2, 1), 2.7–3.0 (br s, OH, 1), 3.79 (s, OMe, 3), 4.37 (dd, H3, 1), 5.51 (m, H4, 1), 5.78 (m, H5, 1), 6.8–7.4 (m, H-arom, 4), 8.0–8.1 (br s, NH, 1); $J_{2,3}$ = 3.3, $J_{3,4}$ = 7.0, $J_{4,5}$ = 16.0 Hz; ^{13}C NMR ($CDCl_3$) δ 12.0 (Me), 17.8 (Me), 45.8 (CH), 55.5 (OMe), 74.2 (CH), 114.1 (2 CH), 121.8 (2 CH), 129.5 (CH), 129.7 (C), 131.0 (CH), 156.3 (C), 173.0 (C); IR ($CHCl_3$) 3650–3250, 1671; mass spectrum *m*/*z* 249 (M^+). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.30; H, 7.72; N, 5.67], and **25** and **26** (0.564 g, 2.26 mmol, 52.3%) as a 1:1 mixture of two diastereoisomers, both corresponding to peak 1 of HPLC. Recrystallization from ethyl ether gave analytically pure samples of **25** (mp 114–116 °C) and **26** (mp 78–80 °C). **25**: ^1H NMR ($CDCl_3$) δ 1.26 (d, Me5, 3), 1.31 (d, Me2, 3), 2.2–2.4 (br s, OH, 1), 3.09 (m, H2, 1), 3.76 (s, 3 H, OMe), 4.34 (m, H5, 1), 5.77 (m, H4, 1), 5.81 (m, H3, 1), 6.8–7.4 (m, H-arom, 4), 7.4–7.5 (br s, NH, 1); $J_{H,Me5}$ = 6.3, $J_{H,Me2}$ = 7.1, $J_{2,3}$ = 6.4, $J_{4,5}$ = 5.2, $J_{3,4}$ = 16.0 Hz; ^{13}C NMR ($CDCl_3$) δ 17.3 (Me of C2), 23.2 (Me of C5), 44.5 (CH of C2), 55.4 (OMe), 68.0 (CH of C5), 114.0 (2 CH), 122.0 (2 CH), 129.2 (CH of C3), 131.0 (C), 136.7 (CH of C4), 156.4 (C), 172.7 (C); IR ($CHCl_3$) 3650–3250, 1680–1660; mass spectrum *m*/*z* 249 (M^+). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.03; H, 7.74; N, 5.67. **26**: ^1H NMR ($CDCl_3$) δ 1.26 (d, Me5, 3), 1.29 (d, Me2, 3), 2.6–2.8 (br s, OH, 1), 3.07 (m, H2, 1), 3.76 (s, OMe, 3), 4.29 (m, H5, 1), 5.70 (m H4, 1), 5.74 (m, H3, 1), 6.8–7.4 (m, H-arom, 4), 7.7–7.8 (br s, NH, 1); $J_{H,Me5}$ = 6.3, $J_{H,Me2}$ = 7.1, $J_{2,3}$ = 6.7, $J_{4,5}$ = 5.2, $J_{3,4}$ = 16.0 Hz; ^{13}C NMR ($CDCl_3$) δ 17.4 (Me of C2), 23.2 (Me of C5), 44.5 (CH of C2), 55.4 (OMe), 68.1 (CH of C5), 114.2 (2 CH), 122.0 (2 CH), 129.5 (CH of C3), 131.0 (C), 136.8 (CH of C4), 156.4 (C), 172.7 (C); IR ($CHCl_3$) 3650–3250, 1680–1660; mass spectrum *m*/*z* 249 (M^+). Anal. Calcd for $C_{14}H_{19}NO_3$: C, 67.45; H, 7.68; N, 5.62. Found: C, 67.19; H, 7.73; N, 5.65. **Procedure B.** The same mixture of oxetanes gave a product distribution of **26**:**25**:*threo*-**24**:*erythro*-**24** = 37.4:37.4:18.3:6.9 (91% overall yield).

***erythro*-N-(4-Methoxyphenyl)-2-*tert*-butyl-3-hydroxybutanamide (*erythro*-32).** A *Z*:*E* = 57:43 mixture of oxetanes **14** (0.35 g, 1.41 mmol) was hydrolyzed at 25 °C in a CH_3COCH_3/H_2O solution (20 mL:0.4 mL) containing 0.05 mL of H_2SO_4. The reaction was neutralized after 20 min with a 10% aqueous solution of $NaHCO_3$, extracted with CH_2Cl_2, and dried over Na_2SO_4. After evaporation of the solvent, the ^1H NMR of the crude mixture revealed the presence of unchanged (*E*)-**14** and hydroxy amide *erythro*-**32** ((*E*)-**14**/*erythro*-**32** = 40:60). The crude mixture was further hydrolyzed under the same reaction conditions until the iminooxetane (*E*)-**14** had totally disappeared (24 h). A ^1H NMR spectrum of the curde reaction mixture revealed the presence of hydroxy amide *erythro*-**32**, exclusively. Flash chromatography (SiO_2, 2:1 CH_2Cl_2–ethyl acetate) of the residue gave 0.32 g (1.21 mmol, 86%) of *erythro*-**32**: mp 118–120 °C (ethyl ether); ^1H NMR ($CDCl_3$) δ 1.15 (s, Me, 9), 1.29 (d, Me, 3), 1.96 (d, H2, 1), 3.79 (s, OMe, 3), 3.98 (d, OH, 1), 4.26 (m, H3, 1), 6.8–7.4 (m, H-arom, 4), 8.0–8.1 (br s, NH, 1); $J_{H,Me}$ = 6.5, $J_{2,3}$ = 2.0, $J_{H,OH}$ = 7.3 Hz; ^{13}C NMR ($CDCl_3$) δ 24.3 (Me) 29.2 (3 Me), 33.8 (C), 55.5 (OMe), 61.7 (CH), 66.3 (CH), 114.1 (2 CH), 122.7 (2 CH), 130.5 (C), 156.7 (C), 172.9 (C); IR (Nujol) 3400–3200, 1690; mass spectrum *m*/*z* 265 (M^+), 220, 115. Anal. Calcd for $C_{15}H_{23}NO_3$: C, 67.90; H, 8.74; N, 5.28. Found: C, 68.21; H, 8.65; N, 5.40. The hydrolysis of oxetanes (*Z*)- and (*E*)-**14**, performed under the reaction conditions described in procedure B, gave exclusively amide *erythro*-**32**. **Reaction of Oxetane (*Z*)-14 with $H_2{}^{18}O$.** The reaction of oxetane (*Z*)-**14** (0.024 g, 0.09 mmol) and $H_2{}^{18}O$ (0.08 mL) in 1.5 mL of anhydrous dioxane containing 0.007 mL of H_2SO_4 gave *erythro*-**32**. The mass spectrum of this product of retention gave a mass of 267 for the parent ion (rel intensity of 9.01). Relevant peaks were at 222 ($CHCMe_3C^{18}ONHC_6H_4$-4-OMe, rel intensity of 3.38), 220 ($CHCMe_3CONHC_6H_4$-4-OMe, rel intensity of 3.9), 117 ($MeCH^{18}OHCHCMe_3$, rel intensity of 3.10), and 115 ($MeCHOHCHCMe_3$, rel intensity of 3.10).

***erythro*- and *threo*-N-(4-Methoxyphenyl)-2-*tert*-butyl-3-hydroxy-3-phenylpropanamide (*erythro*-34 and *threo*-34). Procedure B.** HPLC analysis of the crude mixture obtained from hydrolysis of (*E*)-**16** (0.1547 g, 0.5 mmol) revealed the presence of *erythro*-**34**, exclusively. Flash chromatography (SiO_2, 15:0.5 CH_2Cl_2/methanol) gave *erythro*-**34** (0.154 g, 0.47 mmol, 94%). The same amount of oxetane (*Z*)-**16** gave an erythro/threo distribution of 47.1:52.9. Flash chromatography (SiO_2, 15:0.5 CH_2Cl_2/methanol) gave *erythro*-**34** (0.069 g, 0.210 mmol, 42.0%) and *threo*-**34** (0.070 g, 0.226 mmol, 45.0%). *erythro*-**34**: mp 92.94 °C (ethyl ether/*n*-pentane); ^1H NMR ($CDCl_3$) δ 1.23 (s, Me, 9), 2.16 (d, H2, 1), 3.76 (s, OMe, 3), 5.07 (d, OH, 1), 5.17 (m, H3, 1), 6.8–7.4 (m, H-arom, 4), 7.0–7.1 (br s, NH, 1), 7.2–7.4 (m, H-arom, 5); $J_{2,3}$ = 1.8 Hz; ^{13}C NMR ($CDCl_3$) δ 29.1 (3 Me), 34.2 (C), 55.5 (OMe), 63.5 (CH), 72.5 (CH), 114.1 (2 CH), 123.2 (2 CH), 125.4 (2 CH), 127.2 (CH), 128.4 (2 CH), 129.5 (C), 144.8 (C), 157.0 (C), 172.2 (C); IR (Nujol) 3400–3200, 1668; mass spectrum *m*/*z* 327 (M^+), 220. Anal. Calcd for $C_{20}H_{25}NO_3$: C, 73.37; H, 7.70; N, 4.28. Found: C, 72.71; H, 7.32; N, 4.57. *threo*-**34**: mp 179–181 °C (ethyl ether/*n*-pentane); ^1H NMR ($CDCl_3$) δ 1.23 (s, Me, 9), 2.13 (d, OH, 1), 2.31 (d, H2, 1), 3.72 (s, OMe, 3), 5.17 (m, H3, 1), 6.6–6.7 (br s, NH, 1), 6.8–7.4 (m, H-arom, 4), 7.2–7.4 (m, H-arom, 5); $J_{2,3}$ = 9.2 Hz; ^{13}C NMR ($CDCl_3$) δ 29.3 (3 Me), 34.1 (C), 55.4 (OMe), 65.1 (CH), 75.2 (CH), 113.9 (2 CH), 123.0 (2 CH), 126.7 (2 CH), 127.9 (CH), 128.4 (2 CH, 129.9 (C), 143.8 (C), 156.6 (C), 171.2 (C); IR (Nujol) 3400–3200, 1665; mass spectrum *m*/*z* 327 (M^+), 220. Anal. Calcd for $C_{20}H_{25}NO_3$: C, 73.37; H, 7.70; N, 4.28. Found: C, 73.11; H, 7.92; N, 4.03. In another experiment, a *Z*:*E* = 56:44 mixture of **15** was hydrolyzed at 0 °C in a mixture of acetone (1.5 mL), H_2O (0.2 mL), and H_2SO_4 (0.012 mL). After 1.5 min, the reaction was quenched with a 10% aqueous solution of $NaHCO_3$, extracted with CH_2Cl_2, and dried over Na_2SO_4. After evaporation of the solvent, the ^1H NMR analysis of the crude mixture revealed the presence of unchanged (*Z*)-**16** (49%), β-hydroxy amide *erythro*-**34**, and trace amounts of *threo*-**34**. **Reaction of Oxetane (*E*)-16 with $H_2{}^{18}O$.** The reaction of oxetane (*E*)-**16** (0.026 g, 0.09 mmol) and $H_2{}^{18}O$ (0.08 mL) in 1.5 mL of anhydrous dioxane containing 0.007 mL of H_2SO_4 gave *erythro*-**34**. This amide derived from an attack of $H_2{}^{18}O$ on C4 of the oxetane ring and is a product of inversion. Its mass spectrum revealed no intensity for the ion at mass 222 ($C_6H_5CH^{18}OHCHCMe_3CONH^+$). Other relevant fragments, together with their relative intensities, were

at 329 (M^+, 3.48), 328 ($M^+ - 1$, 15.68), 220 ($CHCMe_3CONHC_6H_4$-4-OMe^+, 6.43), 150 ($CONHC_6H_4$-4-OMe^+, 8.34), 109 ($C_6H_5CH^{18}OH^+$, 25.17), 108 ($C_6H_5CH^{18}O^+$, 54.67), and 107 ($C_6H_5C^{18}O^+$, 10.58). The relative ratio of $C_6H_5CH^{18}OH^+$, $C_6H_5CH^{18}O^+$, and $C_6H_5C^{18}O^+$ was 0.46:1:0.193. **Reaction of Oxetane (*Z*)-16 with $H_2{}^{18}O$.** The reaction of oxetane (*Z*)-16 (0.050 g, 0.15 mmol) and $H_2{}^{18}O$ (0.08 mL) in 1.5 mL of anhydrous dioxane containing 0.007 mL of H_2SO_4 gave a 54:48 erythro/threo mixture of amides **34**. They were separated by thick-layer chromatography. The mass spectrum of *threo*-**34** had a pattern similar to that of *erythro*-**34** formed in the reaction of (*E*)-**16** with $H_2{}^{18}O$, since the stereochemical relationship between *threo*-**34** and (*Z*)-**16** was that of inversion. Relevant peaks, together with their relative abundances, were at 329 (5.98), 328 (26.23), 220 (5.64), 150 (5.54), 109 (15.3), 108 (41.0), and 107 (8.96). The relative ratio of the intensity of the peaks at 109, 108, and 107 was 0.37:1:0.21. The relevant masses of *erythro*-**34**, which retains the stereochemistry of (*Z*)-**16**, can be attributed to the amides deriving from an attachment of $H_2{}^{18}O$ at both C4 and C2 of (*Z*)-**16**. Relevant ion masses were at 329 (M^+, 13.99), 222 ($CHCMe_3C^{18}ONHC_6H_4$-4-OMe^+, 1.24), 220 ($CHCMe_3CONHC_6H_4$-4-OMe^+, 5.05), 207 ($CHCMe_3C^{18}ONHC_6H_4$-4-OMe^+ - Me, 3.76), 205 ($CHCMe_3CONHC_6H_4$-4-OMe^+ - Me, 13.02), 109 (14.23), 108 (42.00), and 107 (23.13). The relative ratio of masses at 109, 108, and 107 was 0.34:1:0.56. This isomer revealed an abnormally high 107/108 ratio (0.56) with respect to that observed in the first two cases (0.19 and 0.21). The conclusion is that C_6H_5CHOH rather than $C_6H_5C^{18}O$ contributed to the intensity of this mass.

Supplementary Material Available: Table V, containing reaction conditions, isomer distributions, and microanalytical, MS, IR, and ^1H NMR ($CDCl_3$) data of 2-iminooxetanes **5**, **10**, **14**, **15**, and **16**, and Table VI, containing reaction conditions, isomer distributions, and microanalytical, MS, IR, ^1H NMR ($CDCl_3$), and ^{13}C NMR ($CDCl_3$) data of β-hydroxyamides **17**, **18**, **19**, **21**, **22**, **26**, **27**, **28**, **29**, **30**, **31**, and **33** (9 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current mastehead page for ordering information.

Preparation and Characterization of Crystalline *N*-Acylammonium Salts

Joseph A. King, Jr.,* and Garold L. Bryant, Jr.

General Electric Company, Corporate Research and Development, P.O. Box 8, Schenectady, New York 12301

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The reaction of a tertiary amine with an acid chloride or chloroformate followed by anion exchange with either sodium tetraphenylborate or silver tetrafluoroborate provides stable, nonhygroscopic, crystalline acylammonium salts.

Introduction

Acylammonmium species have been widely invoked as intermediates in organic and biological chemistry.[1-6] Although there has been wide interest in their chemistry and a number of species have been proposed as isolable materials, a convenient, general procedure for the preparation of analytically pure acylammonium salts has not been developed.

Olah used carboxonium salts in sulfur dioxide to acylate pyridine to produce the *N*-acetyl-, *N*-propionyl-, and *N*-benzoylpyridinium hexafluoroantimonates.[7] Paukstelis and Kim treated tertiary amines with acid halides in the presence of hydrogen tetrafluoroborates to yield the corresponding tetrafluoroborate salts;[8] in the course of their work, they developed a more convenient preparation of acylammonium tetrafluoroborates using triethyloxonium tetrafluoroborate. Preformed 4-(dimethylamino)-pyridinium tetrafluoroborate has been used effectively to produce pure onium salts, as well.[9] We wish to report a simple, general method for the preparation of crystalline acylammonium salts.

Results and Discussion

The formation of acylammonium salts in acetonitrile solution in the presence of either sodium tetraphenylborate

(1) Castro, E. A.; Ureta, C. *J. Org. Chem.* **1990**, *55*, 1676. Luther, A. K.; Ba-Saif, S.; Chrystiuk, E.; Williams, A. *Bull. Soc. Chim. Fr.* **1988**, 391. Hammond, R. B.; Williams, I. H. *J. Chem. Soc., Perkin Trans. 2* **1989**, 59. Chrystiuk, E.; Williams, A. *J. Am. Chem. Soc.* **1987**, *109*, 3040. Castro, E. A.; Bórquez, M. T.; Parada, P. M. *J. Org. Chem.* **1986**, *51*, 5072. Bender, M. L. *Chem. Rev.* **1960**, *60*, 53. Battye, P. J.; Ihsan, E. M.; Moodie, R. B. *J. Chem. Soc., Perkin Trans. 2* **1980**, 741. Castro, E. A.: Ureta, C. *J. Chem. Res., Synop.* **1987**, 358 and references therein.

(2) Comins, D. L.: Hong, H. *J. Am. Chem. Soc.* **1991**, *113*, 6672. Comins, D. L.; Mantlo, N. B. *J. Org. Chem.* **1986**, *51*, 5456. Fowler, F. *J. Org. Chem.* **1972**, *37*, 1321. Stout, D. M.; Meyers, A. I. *Chem. Rev.* **1982**, *82*, 223. Sundberg, R. J.; Hamilton, G.; Trindle, C. *J. Org. Chem.* **1986**, *51*, 3672. Yamaguchi, R.; Hata, E.-i.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 1785. Comins, D. L.; Mantlo, N. B. *Tetrahedron Lett.* **1987**, *28*, 759. Keay, J. G. *Adv. Heterocycl. Chem.* **1986**, *39*, 1.

(3) Popp, F. D.; Takeuchi, I.; Kant, J.; Hamanda, Y. *J. Chem. Soc., Chem. Commun.* **1987**, 1765. Katritzky, A. R.; Chen, J.-L.; Wittmann, D. K.; Marson, C. M. *J. Org. Chem.* **1986**, *51*, 2481. Bunting, J. W. *Adv. Heterocycl. Chem.* **1984**, *2*, 165.

(4) Lee, D. U.; Wiegrebe, W. *Bull. Kor. Chem. Soc.* **1991**, *12*(4), 373. Campbell, A. L.; Pilipanskas, D. R.; Khanna, I. K.; Rhodes, R. A. *Tetrahedron Lett.* **1987**, *28*, 2331. Langlois, Y.; Van Bac, N.; Fall, Y. *Tetrahedron Lett.* **1985**, *26*, 1009. Cooley, J. H.; Evain, E. J. *Synthesis* **1989**, 1. Hobson, J. D.; McCluskey, J. G. *J. Chem. Soc. C* **1967**, 2015.

(5) Reissert, A. *Ber.* **1905**, *38*, 1603. Dehn, B.; Ball, A. *J. Am. Chem. Soc.* **1914**, *36*, 2091. Freudenberg, K.; Peters, D. *Ber.* **1919**, *52*, 1463. Hopkins, T. *J. Chem. Soc.* **1920**, *117*, 278.

(6) (a) Sheinkman, A. K.; Suminov, S. I.; Kost, A. N. *Russ. Chem. Rev.* **1973**, *42*, 642. (b) Höfle, G.; Steglich, W.; Vorbruggen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569. (c) Matzner, M.; Kurkjy, R. P.; Cotter, R. J. *Chem. Rev.* **1964**, 645. (d) Hales, J. L.; Jones, J. I.; Kynastron, W. *J. Chem. Soc.* **1957**, 618. (e) Nyquist, R. A.; Potts, W. J. *Spectrochim. Acta* **1961**, *17*, 679.

(7) Olah, G. A.; Szilagyi, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 2949.

(8) Paukstelis, J. V.; Kim, M.-g. *J. Org. Chem.* **1974**, *39*, 1503.

(9) Guibé-Jampel, E.; Wakselman, M. *Synthesis* **1977**, 772. Guibé-Jampel, E.; Wakselman, M. *J. Chem. Soc., Chem. Commun.* **1971**, 267.

(10) (a) King, J. A., Jr. *J. Am. Chem. Soc.* **1988**, 110, 5764. (b) King, J. A., Jr.; Donahue, P. E.; Smith, J. E. *J. Org. Chem.* **1988**, *53*, 6145. (c) King, J. A., Jr.; Bryant, G. L., Jr. *Acta Crystallogr.* **1991**, *C47*, 2249. (d) Bryant, G. L., Jr.; King, J. A., Jr. *Acta Crystallogr.*, in press. (e) King, J. A., Jr.; Bryant, G. L., Jr. *Acta Crystallogr.*, in press.

(11) Sheldrick, G. M. *SHELXTL-Plus. R3m/V Crystallographic Systems Users Guide*; Siemens Analytical X-ray Instruments, Incorporated, Madison, WI, 1988.

(12) Cook, D. *Can. J. Chem.* **1962**, *40*, 2362.

0022-3263/92/1957-5136$03.00/0