Elimination from Diastereoisomeric Methyl 3-Acetoxy-2-halogeno- and 2,3-Dihalogeno-3-phenylpropanoates

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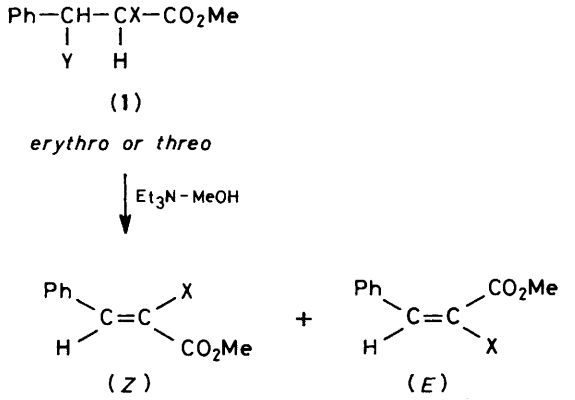
The rates of elimination of a number of *erythro*- and *threo*-PhCHYCXHCO$_2$Me in methanolic triethylamine have been measured. The kinetic evidence together with the stereochemical results suggest that elimination of the dihalogeno-compounds occurs by an $(E1cB)_I$ process for the *erythro*-substrates and by a concerted pathway for the *threo*-isomers. In the case of the acetoxy derivatives the former mechanism seems to be operative for both diastereoisomers.

From comparison between the kinetic data for the dehydroacetoxylation reactions of methyl *erythro*-3-acetoxy-2-chloro-3-arylpropanoates with triethylamine in methanol, and those obtained for the elimination with methanolic sodium methoxide,[1] it became apparent that the former reaction proceeded by an *E*1cB irreversible mechanism. As a result of studies in this area, we now report an examination of the kinetics and stereochemistry of the methanolic triethylamine-induced elimination of a series of methyl *erythro*- and *threo*-2-halogeno-3-phenylpropanoates (**1**; X = Cl, Br, or I; Y = OAc, F, Cl, or Br).



Results

The ^{1}H n.m.r. spectra of the reaction products showed that the substrates gave exclusively the corresponding alkene, methyl 2-X-cinnamate, except for the reactions with the *erythro*-3-acetoxy derivatives where elimination was accompanied by small amounts of epoxide formation, and for that with *erythro*-3-chloro-2-iodo-3-phenylpropanoate which afforded (*E*)-methyl cinnamate. The isomeric alkene distribution is shown in Table 1. The kinetics were monitored by following the appearance of the alkene by u.v. spectroscopy. Since the concentration of the substrates were fifty-fold smaller than that of triethylamine, pseudo-first-order relationships were obtained in all cases. The second-order rate coefficients were calculated as usual from those of first order. Kinetic plots were linear to more than 80% reaction. Runs were performed in triplicate and agreement between triplicates was usually better than ±1.5%. Results are recorded in Table 1

Table 1. Kinetics and isomeric product composition (PhCH=CXCO$_2$Me) for the reaction of PhCHYCXHCO$_2$Me (0.001M) with triethylamine (0.05M) and triethylamine hydrochloride (0.02M) in methanol at 30 °C

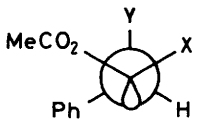
		erythro		*threo*		
X	Y	k^a	*Z*/*E*	k^a	*Z*/*E*	$k_{threo}/k_{erythro}$
Cl	OAc	0.104	98 : 02[b]	0.12	98:02	1.15
	F	1.95	98:02	0.93	100:00	0.48
	Cl	0.202	92:08	6.06	100:00	30
	Br	0.196	61:39	58.0	100:00	296
Br	OMe[c]	0.0031	—	0.0028	—	0.90
	OAc	0.055	98:02[b]	0.058	98:02	1.05
	F	0.992	100:00	0.69	98:02	0.70
	Cl	0.065	88.12	3.72	100:00	57
	Br	0.058	54:46	23.1	98:02	398
I	Cl	*d*		1.27	100:00	—

[a] In dm^3 mol^{-1} min^{-1}. [b] Together with 1—2% of *trans*-methyl 3-phenylglycidate. [c] Rate coefficients for diastereoisomerisation reactions. [d] (*E*)-Methyl cinnamate obtained as the only product.

Discussion

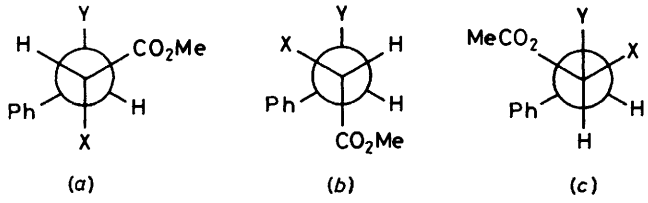
Among the different mechanisms consistent with the observed second-order kinetics[2] *E*2, $(E1cB)_R$, and $(E1cB)_I$, that involving reversible carbanion formation can be dismissed on the grounds of the observed stereochemistry, the nature of the leaving groups,[3] and from the lack of diastereoisomerisation of the starting material under the reaction conditions. Inspection of Table 1 reveals that there is a dependence of the elimination rate of the *erythro*-compounds on the electron-withdrawing ability of the leaving group. With the exception of the 3-fluoro compounds, the sensitivity of the reactions of the remaining substrates to the change in the leaving group is rather small and consistent with the relative reactivity expected on the basis of the Taft correlation for C-2 carbanion-forming reactions in carbonyl compounds.[1] Thus, simple inductive electron attraction seems insufficient to account for the increase in reaction rate on changing the leaving group in the *erythro*-isomers from chlorine to fluorine. A similar behaviour was reported for elimination of 9-fluoro-X,X′-bifluorenyl.[4] Anionic hyperconjugation appears inadequate as an explanation for this observation since the importance of interaction of carbanionic negative charge with a carbon–halogen dipole is expected to increase in the order C–F < C–Cl < C–Br.[5] However, the effectiveness with which hyperconjugative interaction occurs partially depends on the angle defined by the axis of the developing *p*-orbital resulting from loss of the 2-hydrogen and the C–halogen bond. One might argue that non-bonded interactions between the 3-halogen and the 2-substituent in the required *anti* geometry for anionic hyperconjugation,[6] which should be increasingly important with the larger halogens, will make hyperconjugative opportunity in the 3-fluoro compounds more likely. It should be recognised that the terms we use for

this description involve significant oversimplification. Whatever the interpretation, however, it is clear that the observed reactivity trend for the *erythro*-dihalogeno compounds is not as would be predicted for a concerted elimination pathway. Moreover, the sequence of leaving group reactivities suggests an interpretation in terms of the *E*1cB irreversible process.[2]



The sensitivity of the reaction rates to the effect of changing the 2-substituent in the *erythro*-compounds from chlorine to bromine is the opposite to that expected of the ability of the α-halogen to stabilise a carbanion (see Table 1).[7] The relative rates of α-halogenocarbanion formation are thought to be the result of a balance between *d*-orbital resonance, polarisability, and inductive effect.[8] It is likely that due to the stabilisation of the incipient negative charge exerted by the carbonyl, polarisation and delocalisation of the charge in the *d*-orbitals of the halogen are reduced, thus making the inductive component dominant in determining the relative reactivity of these compounds.

The fact that the elimination from the *erythro*-compounds produces predominantly the (*Z*)-alkene[1] (Table 1) is not as expected on the basis of the *anti* stereochemical preference observed for concerted eliminations from β-halogeno-activated substrates.[9] The subsequent observation of the response of the stereochemical course of the reaction to the influence of the 3-halogeno substituent is also difficult to reconcile with an *E*2 process. Models of the three possible conformations of the *erythro*-isomer show that a concerted pathway leading to the (*E*)-alkene should necessarily require *anti*-elimination from (*c*)



conformation. An indication that the latter is not the predominant rotamer is readily obtained from vicinal coupling constants (Table 2).[10] Furthermore, consideration of non-bonded interactions suggests that increasing size of the halogen leaving group (F < Cl < Br) would disfavour relative contribution of that conformer to the rotamer equilibrium, thus decreasing the propensity of the 3-halogeno substrates to form the (*E*)-alkene. This conclusion is supported by the observed variation in the magnitude of $J_{2,3}$ (Table 2) with a change of the 3-halogen identity, since it seems to indicate an increase of (*a*) at expense of (*b*) and (*c*) populations in the order F < Cl < Br. The experimental results, which are not in accordance with the aforementioned predictions, are consistent with the *syn-anti* dichotomy occurring with a single *E*1cB mechanism[11] and can be taken as additional evidence for the carbanionic pathway. We believe that the degree of stereospecificity of these eliminations may be attributed to the result of a balance between the rate of internal rotation of the anionic intermediate and that of the leaving-group expulsion in the product controlling step. It is not unreasonable to assume that whereas better leaving groups may depart directly from the carbanions configurationally related to the conformations of the starting compound, sluggish leaving-group departure occurs after they attain the appropriate geometry which leads to the more stable alkene (*Z*).

Table 2. Proton coupling constants (Hz) for *erythro*-PhCHYCXHCO$_2$Me in carbon tetrachloride

X	Y	$J_{2,3}$
Cl	Br	11.5
Cl	Cl	11.0
Cl	F	8.5
Br	Br	11.5
Br	Cl	11.0
Br	F	9.5
I	Cl	11.8

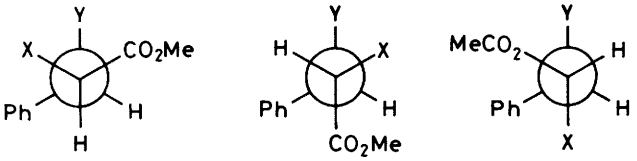
Comparison between the rate constants for the elimination of the *erythro*- and *threo*-acetoxy substrates clearly indicates that their reactions do not depend on the stereochemical nature of the starting compound. Previous work on methoxide-induced dehydroacetoxylation of these diastereoisomers provided evidence which was interpreted in terms of the irreversible *E*1cB mechanism.[1] It might be suggested that the observed insensitivity of the kinetic behaviour of the present reactions to the stereochemistry of the substrates is also caused by the operation of a common mechanism for both diastereoisomers. Consistent with this proposal is the similarity in the kinetic acidity of methyl *erythro*- and *threo*-2-bromo-3-methoxy-3-phenylpropanoate estimated from their respective rates of diastereoisomerisation[1] which suggests an insensitivity of the isomerisation rates to configurational differences (see Table 1). The apparently unexpected enhanced reactivity of the acetoxy compounds over that of the corresponding methoxy derivatives was also observed when the reactions were induced by methanolic sodium methoxide.[1] Our previous suggestion of some direct interaction involving the acetoxy group and the 2-H appears to be an attractive explanation, but it must remain tentative until independent evidence is found to support it. The operation of a carbanionic process seems to be general for β-activated dehydroacetoxylation reactions. Fedor[12] has interpreted his results from elimination of β-acetoxy ketones in terms of an irreversible *E*1cB mechanism. On the basis of comparison of rates of elimination and predicted ionisation rates of a series of β-activated systems, Stirling[13] suggested that acetate is expelled by the (*E*1cB)$_I$ process irrespective of the nature of the activating group. Ahlberg and Thibblin[14] also found indications of the intermediacy of a carbanion in the elimination from 1-(2-acetoxy-2-propyl)indene with tertiary amines. Similarly the irreversible carbanion pathway has been assigned by More O'Ferrall[15] to dehydroacetoxylation of 9-acetoxy-X,X′-bifluorenyl.

The fact that only the reaction with the *erythro*-3-acetoxy-derivatives is accompanied by a small contribution of epoxide formation (*trans*-methyl 3-phenylglycidate)[16] can be interpreted in terms of a process involving (*a*) conformation with internal displacement of the 2-halogen by the oxyanion resulting from partial saponification of the acetoxy group. In the case of the *threo*-3-acetoxy isomers, it is likely that the increased Ph–CO$_2$Me interaction in the corresponding internal S_N2 transition state arising from (*f*) conformation will make the pathway energetically unfavourable. This isomer, however, also failed to provide the halogenohydride arising from the corresponding oxyanion, but this could be attributed to inability to detect its presence by the available spectrometric methods.

In contrast to the *erythro*-substrates, the evidence from the halogen leaving-group influence upon the reactivity of the *threo*-isomers seems to favour the concerted mechanism, since there is a trend for the rate of elimination to increase with leaving-group

abilities. The observed variation in reaction rates, however, is smaller than that reported in *E*2 reactions.[17] This behaviour is probably a reflection of elimination taking place by a concerted process having a transition state of nearly carbanion type with a rather small extent of cleavage of the bond to the 3-substituent, thus making the reaction less sensitive to leaving group identity.[18]

The stereochemical results for the *threo*-compounds indicate that the reactions occur with virtually complete stereospecificity (≥98%). In terms of the concerted pathway, the stereochemistry of the reaction demands exclusively a predominant *anti*-elimination from (*d*) conformation. From inspection of the



models and predictions based on the assumption that Ph and CO_2Me have larger steric requirements one should except that such a conformation will be somewhat favoured with respect to the others, a situation which will then facilitate the concerted elimination pathway.

Returning to the *erythro*-isomers, the increased relative reactivity of the 3-fluoro compounds could alternatively have been accommodated by assuming a change in the rate-determining step from *E*1cB to an *E*2 process in the carbanion region of the mechanistic spectrum.[19] In that case, the observed stereochemistry would be consistent with the *syn*-pathway often associated with *E*1cB-like transition states.[20] If this assumption is correct then there is no apparent reason why the *threo*-3-fluoro compounds, for which the appropriate orientation for *anti*-periplanar elimination seems to be favoured, should not eliminate more readily than the corresponding *erythro*-isomers. Alternatively, it is difficult to imagine why the factors governing the ionisation of the *erythro*-3-fluoro substrates do not apparently operate in the case of the *threo*-isomers, for which the possibility of the carbanionic pathway appears easier than for their corresponding diastereoisomers. We cannot offer justification for this discrepancy which might perhaps be the reflection of some conformation-dependent interaction involving fluorine.*

Experimental

Materials.—Triethylamine[21] and methanol[15] were purified according to described procedures.

Methyl *erythro*-3-acetoxy-2-bromo-,[1] 3-acetoxy-2-chloro-,[1] 2,3-dibromo-,[1] 2-bromo-3-chloro-,[1] 3-bromo-2-chloro-,[1] 2-bromo-3-methoxy-,[1] 2,3-dichloro-,[1] and 3-chloro-2-iodo-3-phenylpropanoates,[22] and methyl *threo*-3-acetoxy-2-bromo-[1] and 3-acetoxy-2-chloro-3-phenylpropanoates[23] were prepared as described. Methyl *threo*-2,3-dichloro-3-phenylpropanoate was obtained together with *ca.* 20% of the corresponding *erythro*-isomer according to the reported procedure.[10] *Methyl* erythro-2-*bromo*-3-*fluoro*-3-*phenylpropanoate* was obtained by a slight modification of the method employed for preparation of the corresponding ethyl ester.[24] (*E*)-Methyl cinnamate (6.2 mmol) and *N*-bromoacetamide (8 mmol) were added to a solution of hydrogen fluoride (2.5M; 20ml) in ether–dichloromethane (1:1) at −30 °C. After 1 h the mixture was allowed to warm up to 0 °C, kept at this temperature for 48 h, and then poured into aqueous 5% sodium hydrogencarbonate and extracted with carbon tetrachloride (50 ml). Evaporation of the solvent and recrystallisation from methanol at 0 °C afforded the product, m.p. 58—59 °C (Found: C, 45.6; H, 3.8; Br, 29.8. $C_{10}H_{10}BrFO_2$ requires C, 46.0; H, 3.9; Br, 30.6%); δ(CCl_4) 7.17 (5 H, s, ArH), 5.47 (1 H, dd, $J_{3,2}$ 9.5 and $J_{3,F}$ 45.0 Hz, 3-H), 4.20 (1 H, dd, $J_{2,3}$ 9.5 and $J_{2,F}$ 6.5 Hz, 2-H), and 3.70 (3 H, s, CO_2Me). *Methyl* threo-2-*bromo*-3-*fluoro*-3-*phenylpropanoate* was obtained following the same procedure described for the preparation of the *erythro*-isomer except that (*Z*)-methyl cinnamate was used as the substrate. The reaction product obtained after work-up contained a mixture of *erythro*- and *threo*-isomer (68:32), which were then taken up in methanol and kept at 0 °C overnight. The crystals which formed were filtered off, the filtrate evaporated, and the *oily residue* was shown (^1H n.m.r.) to contain the two isomers (45:55). Column chromatography on silica gel and elution with hexane–carbon tetrachloride (2:3) did not change the isomeric composition and the mixture was used as such (Found: C, 45.7; H, 3.6; Br, 29.9. $C_{10}H_{10}BrFO_2$ requires C, 46.0; H, 3.9; Br, 30.6%); δ(CCl_4) 7.13 (5 H, s, ArH), 5.46 (1 H, dd, $J_{3,2}$ 8.5 and $J_{3,F}$ 45.0 Hz, 3-H), and 4.30 (1 H, dd, $J_{2,3}$ 8.5 and $J_{2,F}$ 10.8 Hz, 2-H). Methyl *threo*-2-bromo-3-methoxy-3-phenylpropanoate[1] was prepared free of the *erythro*-isomer by esterification of the corresponding acid with diazomethane. The *threo*-2-bromo-3-methoxy-3-phenylpropionic acid was obtained according to the method reported elsewhere.[25] Methyl *erythro*- and *threo*-2-chloro-3-fluoro-3-phenylpropanoate have been previously reported but their configurations poorly characterised.[26] The *erythro*-isomer was prepared following the same procedure described for the 2-bromo-3-fluoro analogue except that t-butyl hypochlorite was used instead of *N*-bromoacetamide. After work-up the product was recrystallised from methanol–water (9:1), giving a pure sample of methyl *erythro*-2-chloro-3-fluoro-3-phenylpropanoate, m.p. 40—41 °C; δ(CCl_4) 7.20 (5 H, s, ArH), 5.47 (1 H, dd, $J_{3,2}$ 8.5 and $J_{3,F}$ 43.8 Hz, 3-H), 4.21 (1 H, dd, $J_{2,3}$ 8.5 and $J_{2,F}$ 8.3 Hz, 2-H), and 3.68 (3 H, s, CO_2Me). When (*Z*)-methyl cinnamate was used as the substrate, the procedures described above gave an oily product which was found (^1H n.m.r.) to be a mixture of *erythro*- and *threo*-isomer (79:21). The mixture was taken up in methanol–water (9:1) (3 ml) and stored at −10 °C for 36 h. The precipitate which formed was isolated by filtration; ^1H n.m.r. analysis showed the presence of the isomers in equimolar proportions. Attempted isolation of the *threo*-compound by column chromatography did not lead to any improvement in the isomeric composition; δ(CCl_4) 7.15 (5 H, s, ArH), 5.43 (1 H, dd, $J_{3,2}$ 7.0 and $J_{3,F}$ 45.5 Hz,), 4.21 (1 H, dd, $J_{2,3}$ 7.0 and $J_{2,F}$ 14.0 Hz, 2-H), and 3.38 (3 H, s, CO_2Me). Methyl *threo*-2,3-dibromo-3-phenylpropanoate[27] was obtained *via* bromination of (*E*)-cinnamic acid in methylene dichloride at −5 °C in the dark and in the presence of a trace of iodine. The resulting precipitate was filtered off, and the filtrate was evaporated to afford a mixture of the *erythro*- and *threo*-acid (55:45). Consecutive crystallisations from methylene dichloride, carbon tetrachloride, and hexane afforded the diastereoisomerically pure acid which was converted into the ester by reaction with diazomethane. *Methyl* threo-3-*bromo*-2-*chloro*-2-*phenylpropanoate* was obtained as a diastereoisomeric mixture by reaction of methyl *threo*-2-chloro-3-hydroxy-3-phenylpropanoate (16 mmol) with a mixture of ether–phosphorus tribromide (1:1) (30 ml) at 0 °C. After 24 h small portions of water (0.8 ml) were added at intervals of 12 h and the mixture maintained at the same temperature for 72 h. The mixture was then allowed to warm up to room temperature, stand for a

* A referee has suggested that the increased reactivity of the *erythro*-3-fluoro compounds could be a manifestation of geminal interaction with the carbanion, similar to the stabilising interaction that accompanies the attachment of fluorine atoms to the same carbon atom.[29]

further 7 days, and then poured onto ice–water and extracted with aqueous 10% sodium hydrogencarbonate and dried (Na_2SO_4), and the solvent evaporated off to give *erythro*- and *threo*-2-bromo-3-chloro-3-phenylpropanoate (3:2). Recrystallisation from methanol at 4 °C gave the product which was found by ^1H n.m.r. to contain 80% of the threo-*isomer*. Further purification was not attempted. (Found: C, 43.0; H, 3.5; Cl, 10.9. $C_{10}H_{10}BrClO_2$ requires C, 43.3; H, 3.6; Cl, 11.5%); δ(CCl_4) 7.15 (5 H, s, ArH), 5.05 (1 H, d, *J* 9.3 Hz, 3-H), 4.50 (1 H, d, *J* 9.3 Hz, 2-H), and 3.43 (3 H, s, CO_2Me). Methyl *threo*-2-bromo-3-chloro-3-phenylpropanoate was obtained together with 14% of the *threo*-2,3-dichloro derivative by esterification of the mixture of the corresponding acids prepared according to the described procedure.[28] After repeated silica gel column chromatography the compound could not be freed from the 2,3-dichloro analogue and was used as such; δ(CCl_4) 7.15 (5 H, s, ArH), 5.00 (1 H, d, *J* 9.5 Hz, 3-H), 4.43 (1 H, d, *J* 9.5 Hz, 2-H), and 3.40 (3 H, s, CO_2Me). Methyl *erythro*-3-chloro-2-iodo-3-phenylpropanoate was obtained according to the reported procedure;[22] δ(CCl_4) 7.19 (5 H, s, ArH), 5.11 (1 H, d, *J* 12.0 Hz, 3-H), 4.60 (1 H, d, *J* 12.0 Hz, 2-H), and 4.60 (3 H, s, CO_2Me). *Methyl* threo-3-*chloro*-2-*iodo*-3-*phenylpropanoate* was obtained as a diastereoisomeric mixture by reaction of (*Z*)-methyl cinnamate (12 mmol) with iodine chloride (14 mmol) in carbon tetrachloride (15 ml) at room temperature. After the reaction was complete (15 min), the usual work-up of the mixture afforded the compound together with 12% of the *erythro*-isomer (Found: C, 36.8; H, 3.1; Cl, 9.3. $C_{10}H_{10}ClIO_2$ requires C, 37.0; H, 3.1; Cl, 9.9%); δ(CCl_4) 7.15 (5 H, s, ArH), 4.99 (1 H, d, *J* 10.3 Hz, 3-H), 4.62 (1 H, d, *J* 10.3 Hz, 2-H), and 3.40 (3 H, s, CO_2Me).

Kinetic Procedure.—The elimination reactions were started by the addition of a methanolic solution of triethylamine (0.07M)–triethylamine hydrochloride (0.028M) buffer (50 ml) to a solution of the substrate in methanol (0.0035M; 20 ml) both solutions being at 30 ± 0.05 °C. Aliquots were extracted by a calibrated automatic pipette at suitable intervals and diluted with 0.1M aqueous hydrochloric acid by a factor of 20. The optical densities of the resulting solutions were determined at the following wavelengths (nm): 284, methyl 2-chlorocinnamate; 286, methyl 2-bromocinnamate; and 288, methyl 2-iodocinnamate. The fraction of elimination product (x) was calculated from the equation $x = O.D._t - O.D._0/O.D._\infty - O.D._0$, or directly from $x = O.D._t/O.D._\infty$, where $O.D._0$, $O.D._t$, and $O.D._\infty$ are optical densities obtained from samples drawn initially, after time t, and after eight half-lives, respectively. The contribution of the reactants to the optical density of the appropriate wavelength was insignificant. For the reactions carried out on substrates containing some proportion of their corresponding diastereoisomers or analogues, the absorbance values were corrected for the contribution arising from the accompanying compound by substraction of their corresponding optical densities estimated from the knowledge of its coefficient rate.

The rate constants observed for the *erythro*-acetoxy derivative runs are a composite of elimination and a small amount of epoxide formation. However, since the product of the latter reaction was shown to be transparent at the wavelengths stated above no correction was required. The proportions of epoxide were estimated from ^1H n.m.r. measurements. It was independently prepared by esterification of the acid[16] with diazomethane; δ(CCl_4) 7.10 (5 H, s, ArH), 5.05 (1 H, d, *J* 1.7 Hz, 3-H), 4.08 (1 H, d, *J* 1.7 Hz, 2-H), and 3.80 (3 H, s, CO_2Me).

The ionisation rates were also determined at 30 ± 0.05 °C by measuring the proportions of equilibrated material by ^1H n.m.r. spectroscopy.[1] Reactions were started by mixing triethylamine (5 mmol) and triethylamine hydrochloride (2 mmol) with the substrate (9 mmol) in methanol (10 ml). Aliquots (1.5 ml) were withdrawn and worked up according to the method previously described.[1]

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