Anionically induced decomposition of ethyl 2-(2,2-dimethylethylperoxymethyl)propenoate by amines: an easy access to amino epoxyesters and amino ester peroxides

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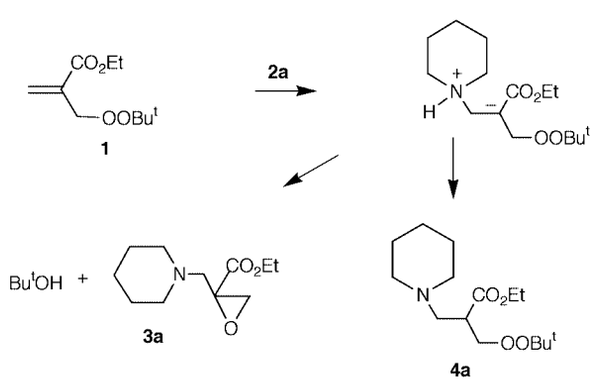
Treatment of ethyl 2-(2,2-dimethylethylperoxymethyl)propenoate with primary and secondary amines led to amino epoxides and/or amino peroxides. These compounds were produced by the addition of the amine to the unsaturation of the peroxide to form a zwitterion, followed, respectively, by a proton transfer and an S_Ni reaction. The formation of one or the other amino derivative was favoured by different reaction conditions (mode of addition of the reactant, solvent). Easy separation of these compounds was possible by chromatography on silica when the reaction was unselective.

Introduction

In the course of a study of the reactivity of unsaturated peroxides,[1] we recently identified the general character of the induced decomposition of ethyl 2-(2,2-dimethylethylperoxymethyl)propenoate **1** provoked by the addition of a nucleophile to the double bond, followed by an S_Ni step to produce an epoxide.[2] While substantiating the mechanism of this process, we studied the reaction of piperidine **2a** with this unsaturated peroxide and discovered the existence of a competition between the S_Ni step, leading to epoxide **3a**, and proton transfer, producing peroxide **4a** (Scheme 1). The potential synthetic usefulness of this type of reaction prompted us to extend this first reaction with piperidine to other amines with the objective of controlling the reaction so as to afford formation of either an amino epoxide **3** or an amino peroxide **4**.



Scheme 1

Results and discussion

Influence of reaction parameters on the selectivity of the reaction of piperidine with peroxide 1

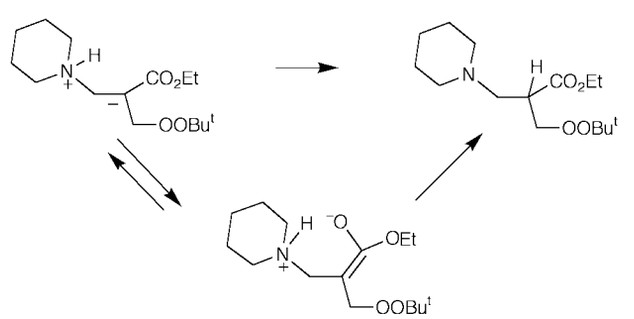
To achieve the selective formation of amino epoxide **3a** or amino peroxide **4a** it appeared possible to adjust several parameters: the concentration of amine **2a**, the solvent polarity and the temperature.

Concentration of amine 2a. In the preliminary account,[2] the reaction of peroxide **1** with piperidine **2a** was reported to produce the amino epoxide **3a** (yield 8%) and the amino peroxide **4a** (yield 72%). Peroxide **1** was added in 5 min to the neat amine **2a**. The zwitterion which was generated in this way was thus still in the presence of an excess of amine **2a**. If the proton transfer is an intermolecular reaction, involving directly or indirectly the piperidine, rather than an intramolecular reaction, the decrease in amine concentration would disfavour the formation of **4a**. Thus, in order to favour the formation of amino epoxide **3a**, addition of piperidine **2a** to the peroxide **1** seemed appropriate (Table 1). These experiments showed that the concentration of the amine **2a** was an important factor for reaction selectivity. However, the formation of similar **3a**/**4a** ratios in the two slower additions of amine **2a** (16 and 30 h) agreed with the existence of inter- and intra-molecular proton transfers. The intramolecular proton transfer mechanism could proceed either from the initial zwiterion produced by the addition or through the enolate (Scheme 2). It appears more difficult to define precisely the intermolecular process. The direct transfer from piperidine **2a** can be excluded because the carbanion (pK_a of conjugated acid ≈ 20–25) is not a strong enough base to deprotonate the piperidine (pK_a ≈ 30). The piperidinium ion is

Table 1 Addition of piperidine **2a** to a solution of **1** in THF at 0 °C

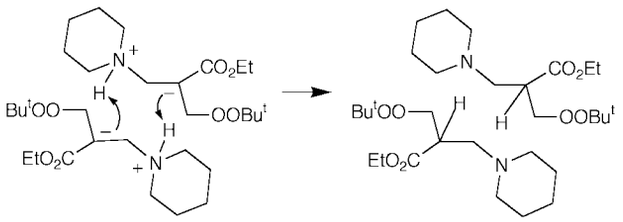
2a addition time	**3a**[a]	**4a**[a]
5 min	28	42
16 h	52	28
30 h	53	28

[a] Isolated yield (%) relative to the starting peroxide **1**.



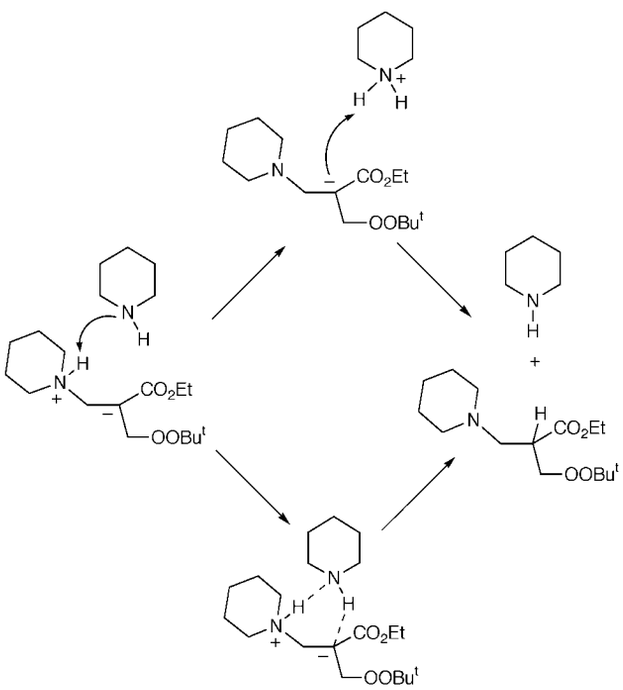
Scheme 2

more acidic ($pK_a \approx 10$) than piperidine and therefore intermolecular proton transfer could occur through its intermediacy. Hence, a proton transfer between two zwitterions (Scheme 3) or a proton transfer *via* piperidinium ion, obtained



Scheme 3

from the reaction of the zwitterion with a molecule of **2a**, either in concerted fashion or not, could be envisaged (Scheme 4).



Scheme 4

Piperidine appears to be a mediator in the proton transfer from trialkylammonium species to the carbanion.

Secondary reactions involving the peroxide or the end products could account for the incomplete balance based on **1**. However, the absence of reaction of peroxide **1** with pure triethylamine showed that a possible secondary reaction between the amino peroxide **4a** or the amino epoxide **3a** and the peroxide **1** can be excluded.

Solvent polarity. Because the decomposition of peroxide **1** induced by piperidine **2a** occurred through reactions involving charged species, the polarity of the solvent appeared to be an important parameter worthy of study. The 16-h additions of piperidine to peroxide solutions at 0 °C were performed in pentane and acetonitrile. The selectivity of the reaction **4a**/**3a** was determined in order to check if this favoured the selective formation of one of the compounds (Table 2). Increasing the solvent polarity favoured proton transfer because the change from THF to acetonitrile increased the production of the amino peroxide **4a** at the expense of the epoxy peroxide **3a**. On the other hand, the use of pentane in place of THF did not promote a great increase in the formation of the epoxide. However, it is worthwhile to note that the reaction in neat piperidine was more favourable to production of amino peroxide (**4a**/**3a** = 9).

Table 2 Products quotients **4a**/**3a** in the 16-h additions of piperidine **2a** to solutions of **1** at 0 °C

Solvent:	Pentane	THF	Acetonitrile
Quotient **4a**/**3a**:	0.4	0.5	7

Table 3 Products obtained in the reaction of secondary amines **2** with peroxide **1** at 0 °C

	Conditions A		Conditions B	
	Amino epoxide (yield)[a]	Amino peroxide (yield)[a]	Amino epoxide (yield)[a]	Amino peroxide (yield)[a]
 **2b**	**3b** (0%)	**4b** (79%)	**3b** (45%)	**4b** (30%)
 **2c**	**3c** (0%)	**4c** (70%)	**3c** (50%)	**4c** (21%)
Et_2NH **2d**	**3d** (25%)	**4d** (27%)	**3d** (0%)	**4d** (0%)

[a] Isolated yield (%) relative to the starting peroxide **1**.

Influence of temperature. No significant effect of temperature between −30 and 0 °C was observed on the reaction in neat piperidine or in solvents.

From the study of the influence of several parameters on the selectivity of the induced decomposition of **1** we could specify conditions leading mainly to the formation of the amino peroxide or to the amino epoxide:

Amino peroxide **4**: addition of the peroxide **1** to the neat amine **2** at 0 °C (conditions A).

Amino epoxide **3**: addition of the amine **2** over 16 h to a solution of the peroxide **1** at 0 °C using a syringe pump (conditions B).

Reaction of amines with peroxide 1: preparation of amino epoxides and amino peroxides

Secondary amines. Peroxide **1** was treated with several secondary amines **2b**–**d** under the conditions defined above. The amino peroxides **4b** and **4c** were selectively formed in good yields from reactions performed under conditions A; however, with diethylamine **2d**, compounds **4d** and **3d** were isolated in similar yields (Table 3). The results obtained from morpholine **2b** and pyrrolidine **2c** under conditions B were similar to those obtained with **2a** when none of the expected products were formed by the reaction of **1** and **2d** in solution (10% of **1** was consumed).

Comparing the cyclic amines, we can conclude that there is no significant difference in their behaviour, judging by the yields of the isolated compounds. The structures of pyrrolidine **2c** and diethylamine **2d** are very similar since, the difference between **2c** to **2d** involves only the replacement of the C–C bond β to the nitrogen atom by two C–H bonds. Their different behaviour in the reaction with peroxide **1** (conditions A) could possibly be attributed to a higher flexibility of **2d**, responsible for a steric effect, disfavouring the proton transfer.

The absence of any reaction in the slow addition of amine **2d** to a THF solution of peroxide **1** prompted us to repeat the same reaction using a syringe pump in the absence of any solvent. Irrespective of the addition time (4 or 16 h), the single amino epoxide **3d** was obtained and isolated in 51% yield. It is important to position the needle of the syringe in the peroxide, to avoid the formation of the amino peroxide since it allows a continuous rather than dropwise addition of **2d**. This method

Table 4 Products obtained in the reaction of primary amines with peroxide **1** at 0 °C

	Conditions A		Conditions C	
	Amino epoxide (Yield %)[a]	Amino peroxide (Yield %)[a]	Amino epoxide (Yield %)[a]	Amino peroxide (Yield %)[a]
 **2e**	**3e** (0%)	**4e** (59%)	**3e** (32%)	**4e** (33%)
 **2f**	**3f** (0%)	**4f** (55%)	**3f** (10%)	**4f** (52%)
 **2g**	**3g** (20%)	**4g** (38%)	**3g** (30%)	**4g** (31%)

[a] Isolated yield (%) relative to the starting peroxide **1**.

did not make any difference when applied to the slow addition of **2a**–**c** in THF.

The extension of this reaction to diisopropylamine and dicyclohexylamine was not successful in inducing the decompositon of **1**. This could be attributed to the low nucleophilicity of these compounds.[3]

Primary amines. The behaviour of primary amines was similar to that of **2d** since no reaction occurred in THF solution. However, amino epoxides and amino peroxides were produced in the 4-h syringe pump addition of the amine to the neat peroxide **1** at 0 °C (conditions C, Table 4). The peroxide was not totally consumed and about 10% remained at the end of the reaction. The conversion of **1**, determined from the products **3** and **4**, was about 60%. The presence in the amino peroxides and amino epoxides of a secondary amine function prompted us to consider the occurrence of a reaction of this amine with a second molecule of peroxide **1**. Under the reaction conditions, whatever was the order of addition, no reaction could be identified between the secondary amino derivative and the peroxide **1**. In fact this result was not surprising considering the known addition of a single molecule of ethyl methacrylate and a primary amine.[4]

Under conditions A and C the amino peroxide **4** was the main product, independent of the starting amine.

Conditions A, designed to prepare the amino peroxide, selectively afforded **4e** and **4f**. However, when *tert*-butylamine was employed, formation of **3g** was observed besides that of **4g**. This could be attributed to a more difficult proton transfer when the group attached to the NH_2 is bulky.

Conditions C, designed to promote the production of the amino epoxide at the expense of the amino peroxide, failed with primary amines, unlike the case with secondary amines. Proton transfer appeared to be the predominant reaction. The low influence of the instantaneous concentration of the amine in the medium, identified in particular for **2f** and **2g** (conditions A and C), on the relative quotients **4/3** is in favour of the involvement of a significant contribution from intramolecular hydrogen transfer. The observed difference between the two classes of amines could be attributed to the presence of two transferable protons in the zwitterion produced from a primary amine instead of one as in the case of a secondary amine.

Conclusions

Primary and secondary unhindered amines, add efficiently to ethyl 2-(2,2-dimethylethylperoxymethyl)propenoate **1** to produce a zwitterion, which in turn generates amino peroxides and amino epoxides. In the case of secondary amines it is possible to orientate the reaction toward the production of one or other of these compounds. Slow addition of the amine to the peroxide led preferentially to the amino epoxide. The amino peroxide was the major reaction product with the reverse order of addition. For primary amines, under both sets of conditions the amino peroxide was the main reaction product, intramolecular proton transfer being the predominant reaction of the zwitterion. However, their easy separation by column chromatography enables amino epoxy esters to be accessed by this type of reaction in a straightforward manner.

Experimental

NMR spectra were recorded at 250 MHz in $CDCl_3$ solutions with $Si(CH_3)_4$ as an internal standard using a Bruker AC 250 spectrometer. ^{13}C Spectra were recorded at 62.9 MHz. Data are reported as δ-values (ppm) and coupling constants (J, Hz).

Microanalyses of the reaction compounds were not performed because of the rapid degradation of the amino epoxy esters and the potential transportation hazard of amino peroxides.

GLC studies were performed with a Varian 3400 coupled to a Spectraphysic Chromjet integrator. The capillary column used was DB5 type (5% Ph), 30 m in length, 0.25 mm in inner diameter and with a film thickness of the stationary phase of 0.25 μm, the carrier gas was nitrogen (0.5 bar †).

Ethyl 2-(2,2-dimethylethylperoxymethyl)propenoate **1** was prepared as described previously.[5]

Amines were purchased from Aldrich and Acros and were distilled before use.

Induced decomposition of 1 by amines

Conditions A. Peroxide **1** (0.0025 mol) was added dropwise, with stirring, to amine **2** (0.003 mol) at 0 °C. The mixture was left under these conditions for 15 min and then for 1 h at room temperature. The disappearance of the peroxide was monitored by GLC. At the end of the reaction, diethyl ether (20 cm^3) was added to the reaction mixture. After several washings with brine the organic phase was dried over magnesium sulfate. The solvent was removed under vacuum and the product was chromatographed on a silica column (petroleum spirit (bp 35–50 °C)–diethyl ether 40 : 60).

Conditions B. To a cooled solution of **1** (0.0025 mol) in 25 cm^3 of THF at 0 °C was added the amine **2** (0.0025 mol) with a syringe pump over 16 h. After observation of the disappearance of the peroxide by GLC, the solvent was evaporated and 20 cm^3 of diethyl ether were added. This reaction mixture was then worked up as under conditions A.

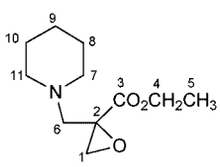
Conditions C. To **1** (0.0025 mol) cooled at 0 °C was added the amine **2** (0.0025 mol) with a syringe pump over 4 h, the extremity of the needle of the syringe being in the peroxide. After observation of the disappearance of the peroxide by GLC, the reaction mixture was then treated as in conditions A.

Reaction of 1 with 2a

Conditions A, **3a** (8%), **4a** (72%). Conditions B, **3a** (52%), **4a** (28%).

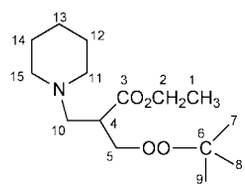
Ethyl 2,3-epoxy-2-(piperidinomethyl)propanoate 3a. ^1H NMR $\delta(CDCl_3)$ 4.18 (q, 2H, J 7.1, CO_2CH_2), 3.07 (A part of AB system, 1H, J 13.8, NCH_2), 2.85 and 2.78 (A′B′ system, 2H, J 5.9, epoxide CH_2), 2.38 (B part of AB system, 1H, J 13.8,

† 1 bar = 10^5 Pa.



NCH_2), 2.51–2.13 [m, 4H, $(CH_2)_2N$], 1.49–1.15 (m, 6H, cycle CH_2), 1.22 (t, 3H, *J* 7.1, $CO_2CH_2CH_3$); ^{13}C NMR δ($CDCl_3$) 171 [C^3], 61.3 [C^4], 59.3 [C^6], 57.1 [C^2], 55.3 [$C^{7,11}$], 48.9 [C^1], 26 [$C^{8,10}$], 24.1 [C^9], 14.1 [C^5].

Ethyl 3-(1,1-dimethylethylperoxy)-2-(piperidinomethyl)propanoate 4a. ^{1}H NMR δ($CDCl_3$) 4.15–3.94 (m, 4H, CH_2OO and

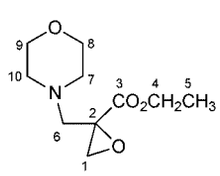


CO_2CH_2), 2.98–2.87 (m, 1H, C*H*$CO_2C_2H_5$), 2.51–2.28 [m, 6H, $(CH_2)_3N$], 1.49–1.31 (m, 6H, cycle CH_2), 1.19 (t, 3H, *J* 7.1, $CO_2CH_2CH_3$), 1.13 [s, 9H, $C(CH_3)_3$]; ^{13}C NMR δ($CDCl_3$) 173.7 [C^3], 80.2 [C^6], 74.2 [C^5], 60.2 [C^2], 57.7 [C^{10}], 54.5 [$C^{11,15}$], 43.2 [C^4], 26.2 [$C^{7,8,9}$], 25.9 [$C^{12,14}$], 24.2 [C^{13}], 14.2 [C^1].

Reaction of 1 with 2b

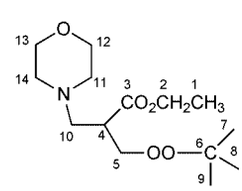
Conditions A, **3b** (0%), **4b** (79%). Conditions B, **3b** (45%), **4b** (30%).

Ethyl 2,3-epoxy-2-(morpholinomethyl)propanoate 3b. ^{1}H



NMR δ($CDCl_3$) 4.12 (q, 2H, *J* 7.1, CO_2CH_2), 3.52 (t, 4H, *J* 4.7, CH_2OCH_2), 3.12 (A part of AB system, 1H, *J* 13.8, NCH_2), 2.79 and 2.73 (A′B′ system, 2H, *J* 5.8, epoxide CH_2), 2.52–2.35 (m, 4H, CH_2NCH_2), 2.28 (B part of AB system, 1H, *J* 13.8, NCH_2), 1.16 (t, 3H, *J* 7.1, $CO_2CH_2CH_3$); ^{13}C NMR δ($CDCl_3$) 169.4 [C^3], 66.8 [$C^{8,9}$], 61.4 [C^4], 59 [C^6], 56.7 [C^2], 54.2 [$C^{7,10}$], 48.6 [C^1], 14 [C^5].

Ethyl 3-(1,1-dimethylethylperoxy)-2-(morpholinomethyl)propanoate 4b. ^{1}H NMR δ($CDCl_3$) 4.13–3.90 (m, 4H, CH_2OO and

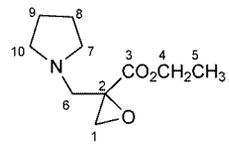


CO_2CH_2), 3.54 (t, 4H, *J* 4.7, CH_2OCH_2), 2.91 (q, 1H, *J* 4.5, C*H*$CO_2C_2H_5$), 2.54–2.25 [m, 6H, $(CH_2)_3N$], 1.16 (t, 3H, *J* 7.1, $CO_2CH_2CH_3$), 1.10 [s, 9H, $C(CH_3)_3$]; ^{13}C NMR δ($CDCl_3$) 173.3 [C^3], 80.2 [C^6], 73.8 [C^5], 66.8 [$C^{12,13}$], 60.3 [C^2], 57.3 [C^{10}], 53.6 [$C^{11,14}$], 42.9 [C^4], 26.1 [$C^{7,8,9}$], 14.2 [C^1].

Reaction of 1 with 2c

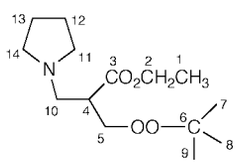
Conditions A, **3c** (0%), **4c** (70%). Conditions B, **3c** (50%), **4c** (21%).

Ethyl 2,3-epoxy-2-(pyrrolidinomethyl)propanoate 3c. ^{1}H



NMR δ($CDCl_3$) 4.16 (q, 2H, *J* 7.1, CO_2CH_2), 3.27 (A part of AB system, 1H, *J* 13.4, NCH_2), 2.89 and 2.82 (A′B′ system, 2H, *J* 5.9, epoxide CH_2), 2.50 (B part of AB system, 1H, *J* 13.4, NCH_2), 2.54–2.47 [m, 4H, $(CH_2)_2N$], 1.68–1.63 (m, 4H, cycle CH_2), 1.21 (t, 3H, *J* 7.1, $CO_2CH_2CH_3$); ^{13}C NMR δ($CDCl_3$) 169.2 [C^3], 61.4 [C^4], 57.1 [C^2], 56.4 [C^6], 55 [$C^{7,10}$], 49.5 [C^1], 23.6 [$C^{8,9}$], 14 [C^5].

Ethyl 3-(1,1-dimethylethylperoxy)-2-(pyrrolidinomethyl)propanoate 4c. ^{1}H NMR δ($CDCl_3$) 4.21–3.98 (m, 4H, CH_2OO and

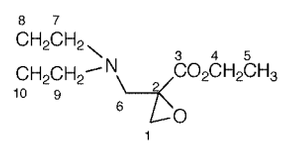


CO_2CH_2), 2.98–2.88 (m, 1H, C*H*$CO_2C_2H_5$), 2.71–2.40 [m, 6H, $(CH_2)_3N$], 1.72–1.61 (m, 4H, cycle CH_2), 1.20 (t, 3H, *J* 7.1, $CO_2CH_2CH_3$), 1.15 [s, 9H, $C(CH_3)_3$]; ^{13}C NMR δ($CDCl_3$) 173.1 [C^3], 79.8 [C^6], 73.7 [C^5], 59.9 [C^2], 54.4 [C^{10}], 53.6 [$C^{11,14}$], 44.4 [C^4], 25.7 [$C^{7,8,9}$], 23 [$C^{12,13}$], 14.7 [C^1].

Reaction of 1 with 2d

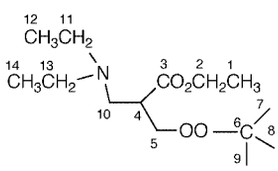
Conditions A, **3d** (25%), **4d** (27%). Conditions C, **3d** (51%), **4d** (0%).

Ethyl 2,3-epoxy-2-(diethylaminomethyl)propanoate 3d. ^{1}H



NMR δ($CDCl_3$) 4.16 (q, 2H, *J* 7.1, CO_2CH_2), 3.19 (A part of AB system, 1H, *J* 14.2, $^6CH_2$), 2.84 and 2.79 (A′B′ system, 2H, *J* 5.9, epoxide CH_2), 2.54 (q, 2H, *J* 7.1, CH_3CH_2N), 2.49 (B part of AB system, 1H, *J* 14.2, $^6CH_2$), 2.46 (q, 2H, *J* 7.1, CH_3CH_2N), 1.22 (t, 3H, *J* 7.1, $CO_2CH_2CH_3$), 0.91 [t, 6H, *J* 7.1, $(CH_3CH_2)_2N$]; ^{13}C NMR δ($CDCl_3$) 169.9 [C^3], 61.3 [C^4], 57.5 [C^2], 53.8 [C^6], 48.8 [C^1], 47.8 [$C^{7,9}$], 14 [C^5], 11.7 [$C^{8,10}$].

Ethyl 2-(diethylaminomethyl)-3-(1,1-dimethylethylperoxy)-propanoate 4d. ^{1}H NMR δ($CDCl_3$) 4.58–3.95 (m, 4H, CH_2OO

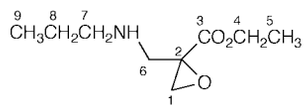


and CO_2CH_2), 2.89–2.81 (m, 1H, C*H*$CO_2C_2H_5$), 2.66–2.36 [m, 6H, $(CH_2)_3N$], 1.19 (t, 3H, *J* 7.1, $CO_2CH_2CH_3$), 1.14 [s, 9H, $C(CH_3)_3$], 0.91 [t, 6H, *J* 7.1, $(CH_3CH_2)_2N$]; ^{13}C NMR δ($CDCl_3$) 174.5 [C^3], 80.3 [C^6], 74.3 [C^5], 60.3 [C^2], 52.2 [C^{10}], 47.2 [$C^{11,13}$], 44.2 [C^4], 26.2 [$C^{7,8,9}$], 14.2 [C^1], 11.8 [$C^{12,14}$].

Reaction of 1 with 2e

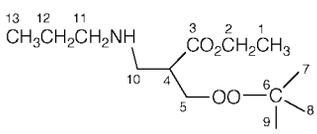
Conditions A, **3e** (59%), **4e** (0%). Conditions C, **3e** (32%), **4e** (33%).

Ethyl 2,3-epoxy-2-(propylaminomethyl)propanoate 3e. ^{1}H



NMR δ($CDCl_3$) 4.17 (q, 2H, *J* 7.1, CO_2CH_2), 3.18 (A part of AB system, 1H, *J* 13.4, $^6CH_2$), 2.97 and 2.91 (A′B′ system, 2H, *J* 6.1, epoxide CH_2), 2.87 (B part of AB system, 1H, *J* 13.4, $^6CH_2$), 2.53 (t, 2H, *J* 7.1, $CH_3CH_2CH_2N$), 1.41 (sextet, 2H, *J* 7.3, $CH_3CH_2CH_2N$), 1.22 (t, 3H, *J* 7.1, $CO_2CH_2CH_3$), 0.83 [t, 3H, *J* 7.3, $CH_3CH_2CH_2N$]; ^{13}C NMR δ($CDCl_3$) 170.1 [C^3], 61.7 [C^4], 58.1 [C^2], 51.7 [C^6], 50.3 [C^7], 49.5 [C^1], 23.1 [C^8], 14.1 [C^5], 11.6 [C^9].

Ethyl 3-(1,1-dimethylethylperoxy)-2-(propylaminomethyl)-propanoate 4e. ^{1}H NMR δ($CDCl_3$) 4.19–3.99 (m, 2H, CH_2OO),

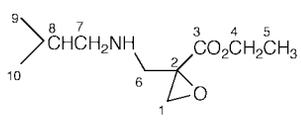


4.10 (q, 2H, *J* 7.1, CO_2CH_2), 2.92–2.47 [m, 5H, $CHCO_2C_2H_5$ and $(CH_2)_2N$], 1.41 (sextet, 2H, *J* 7.4, $CH_3CH_2CH_2N$), 1.20 (t, 3H, *J* 7.1, $CO_2CH_2CH_3$), 1.15 [s, 9H, $C(CH_3)_3$], 0.83 (t, 3H, *J* 7.4, $CH_3CH_2CH_2N$); ^{13}C NMR δ($CDCl_3$) 173.5 [C^3], 80.1 [C^6], 74 [C^5], 60.5 [C^2], 51.6 [C^{10}], 48.5 [C^{11}], 45.1 [C^4], 26.2 [$C^{7,8,9}$], 23 [C^{12}], 14.2 [C^1], 11.6 [C^{13}].

Reaction of 1 with 2f

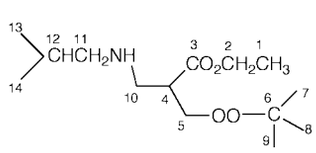
Conditions A, **3f** (0%), **4f** (55%). Conditions C, **3f** (10%), **4f** (52%).

Ethyl 2,3-epoxy-2-(2-methylpropylaminomethyl)propanoate 3f. ^{1}H NMR δ($CDCl_3$) 4.16 (q, 2H, *J* 7, CO_2CH_2), 3.17 (A part



of AB system, 1H, *J* 13.4, $^6CH_2$), 2.96 and 2.90 (A′B′ system, 2H, *J* 6.1, epoxide CH_2), 2.86 (B part of AB system, 1H, *J* 13.4, $^6CH_2$), 2.37 (d, 2H, *J* 6.8, $CHCH_2N$), 1.31–1.02 [m, 1H, $(CH_3)_2CH$], 1.22 (t, 3H, *J* 7, $CO_2CH_2CH_3$), 0.79 [d, 6H, *J* 6.4, $(CH_3)_2CH$]; ^{13}C NMR δ($CDCl_3$) 170.1 [C^3], 61.6 [C^4], 57.1 [C^2], 54.2 and 54.1 [$C^{6,7}$], 47.2 [C^1], 29.5 [C^8], 20.4 [$C^{9,10}$], 14.0 [C^5].

Ethyl 3-(1,1-dimethylethylperoxy)-2-(2-methylpropylamino-methyl)propanoate 4f. ^{1}H NMR δ($CDCl_3$) 4.19–3.98 (m, 2H,

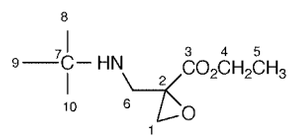


CH_2OO), 4.09 (q, 2H, *J* 7.1, CO_2CH_2), 2.91–2.68 (m, 3H, $CHCO_2C_2H_5$ and $^{10}CH_2$), 2.33 (d, 2H, *J* 6.7, $CHCH_2N$), 1.69–1.58 [m, 1H, $(CH_3)_2CH$], 1.19 (t, 3H, *J* 7.1, $CO_2CH_2CH_3$), 1.14 [s, 9H, $C(CH_3)_3$], 0.81 [d, 6H, *J* 6.6, $(CH_3)_2CH$]; ^{13}C NMR δ($CDCl_3$) 173.3 [C^3], 80.2 [C^6], 73.9 [C^5], 60.4 [C^2], 57.7 [C^{10}], 48.6 [C^{11}], 45.1 [C^4], 28.1 [C^{12}], 26.2 [$C^{7,8,9}$], 20.5 [$C^{13,14}$], 14.1 [C^1].

Reaction of 1 with 2g

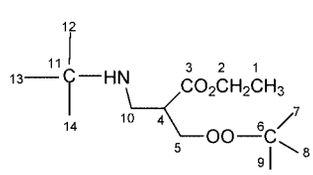
Conditions A, **3g** (20%), **4g** (38%). Conditions C, **3g** (31%), **4g** (30%).

Ethyl 2-(1,1-dimethylethylaminomethyl)-2,3-epoxypropano-ate 3g. ^{1}H NMR δ($CDCl_3$) 4.15 (q, 2H, *J* 7.1, CO_2CH_2), 3.06 (A



part of AB system, 1H, *J* 12.7, NCH_2), 2.95 (s, 2H, epoxide CH_2), 2.86 (B part of AB system, 1H, *J* 12.7, NCH_2), 1.22 (t, 3H, *J* 7.1, $CO_2CH_2CH_3$), 1.01 [s, 9H, $(CH_3)_3$]; ^{13}C NMR δ($CDCl_3$) 171.1 [C^3], 61.5 [C^4], 57.1 [C^2], 50.3 [C^1], 42.9 [C^6], 41.6 [C^7], 28.9 [$C^{8,9,10}$], 14 [C^5].

Ethyl 2-(1,1-dimethylethylaminomethyl)-3-(1,1-dimethylethyl-peroxy)propanoate 4g. ^{1}H NMR δ($CDCl_3$) 4.18–4.01 (m, 2H,



CH_2OO), 4.09 (q, 2H, *J* 7.1, CO_2CH_2), 2.83–2.67 (m, 3H, $CHCO_2C_2H_5$ and $NHCH_2$), 1.19 (t, 3H, *J* 7.1, $CO_2CH_2CH_3$), 1.15 [s, 9H, $(CH_3)_3CO$], 0.99 [s, 9H, $(CH_3)_3CN$]; ^{13}C NMR δ($CDCl_3$) 173.3 [C^3], 80.2 [C^6], 73.9 [C^5], 60.3 [C^2], 50.1 [C^{11}], 46 [C^{10}], 41.5 [C^4], 28.9 [$C^{7,8,9}$], 26.2 [$C^{12,13,14}$], 14.1 [C^1].

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