The Synthesis of Solvent-Free Glycidic Esters from Diazoesters and Carbonyl Compounds Catalysed by Lanthanide Triflates

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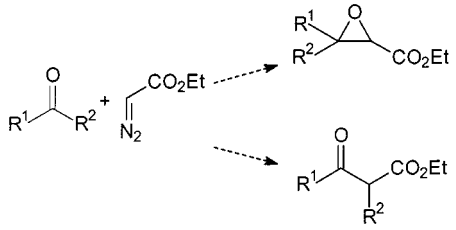
The results of the reaction between ethyl diazoacetate and carbonyl compounds catalysed by lanthanide triflates are described. Aldehydes, and α-unsubstituted and α-monosubstituted cyclohexanones react to give the selective formation of α,β-epoxy esters (glycidic esters), whereas other ketones are unreactive.

Introduction

During the last decade rare earth metal triflates have been found to be unique Lewis acids in that they are water-tolerant, reusable catalysts that can effectively promote several important carbon-carbon and carbon-heteroatom bond formation reactions such as aldol condensation,[1] Diels−Alder and aza Diels−Alder reactions,[2] Friedel−Crafts acylations,[3] Michael additions,[4] allylations of imines[5] and carbonyl compounds,[6] the ring opening of epoxides[7] and aziridines,[8] Mannich reactions,[9] the addition of silyl ketene acetals to nitrones,[10] acetal formation[11] and heterocyclizations.[12,13] Another interesting application is the reaction of diazo derivatives with imines leading to the formation of aziridines.[14]

As part of our ongoing studies to search for new carbon-carbon bond formation processes using diazo compounds, we decided to investigate the use of lanthanide triflates as catalysts in the reaction between ethyl diazoacetate (EDA) and carbonyl compounds. The Lewis acid-promoted reaction between EDA and carbonyl compounds could lead, in principle, to α,β-epoxy esters, also known as "glycidic esters", deriving from a Darzens-type process, or to β-keto esters, deriving from a homologation reaction (Scheme 1).[15]

The use of boron trifluoride etherate, triethyl oxonium tetrafluoroborate, tin(II) chloride, titanium(IV) chloride, zinc dichloride or antimony(V) chloride usually yields only the corresponding homologation adducts in the reaction between EDA and aldehydes or ketones,[16] although α,β-epoxy esters have been obtained as side products in the boron trifluoride etherate catalysed reaction between acetone and EDA at low temperatures[17] or by thermal or Cu^{I}-promoted decomposition of methyl diazomalonate in the presence of benzaldehyde.[18] The only example of the selective formation of glycidic esters starting from diazo compounds is the reaction catalysed by methylrhenium trioxide reported by Espenson and Zhu in 1995,[19] although with some substrates the process was not selective and led to the formation of Δ^3-1,3,4-oxadiazolines as side products in 5−21% yield.



Scheme 1

Results and Discussion

Initially we tested a variety of reaction conditions, employing different solvents such as methanol, dichloromethane, tetrahydrofuran or acetonitrile, but the best results were obtained when the reaction was carried out in solvent-free conditions. We first used aldehydes as substrates and these results are summarized in Table 1.

Both aromatic and aliphatic aldehydes react with EDA in the presence of $Ln(OTf)_3$ (10 mol %) to afford the corresponding α,β-epoxy esters in 73−92% yield. All aldehydes were extremely reactive and the process was complete after 10 minutes. Unfortunately the reaction is not diastereoselective: in all cases we obtained a mixture of *cis* and *trans* epoxides, which could be separated by silica-gel column chromatography. As reported in entry 3 carbon-carbon double bonds were unreactive under these reaction conditions. No homologation (β-keto esters) or carbene dimeriz-

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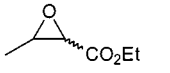
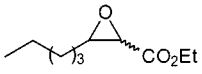
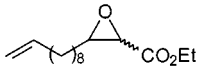
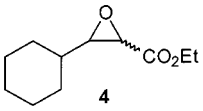
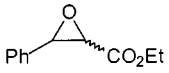
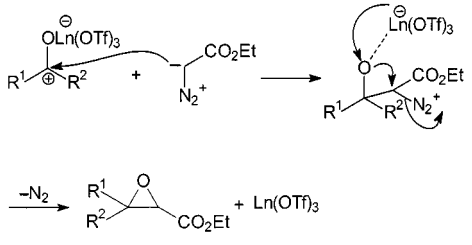
Table 1. Reaction between aldehydes and EDA catalysed by $Ln(OTf)_3$

Entry	Reactant	Product	Yield (%)[a] $La(OTf)_3$	$Eu(OTf)_3$	$Yb(OTf)_3$
1	Acetaldehyde	 **1** *cis/trans* 1:1	92	35	29
2	*n*-Hexanal	 **2** *cis/trans* 1:1	85	41	40
3	10-Undecenal	 **3** *cis/trans* 4:6	82	32	27
4	Cyclohexane-carboxaldehyde	 **4** *cis/trans* 7:3	86	35	30
5	Benzaldehyde	 **5** *cis/trans* 4:6	73	19	18

[a] Isolated yield.

ation products (diethyl maleate and/or fumarate), the latter deriving from Lewis acid-promoted EDA decomposition, were observed, suggesting that the reaction proceeds by nucleophilic addition of EDA to the lanthanide-carbonyl complex, followed by a nucleophilic S_N2 attack of the thus-formed negatively charged oxygen followed by N_2 displacement, as occurs in the Darzens reaction (Scheme 2).



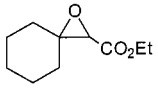
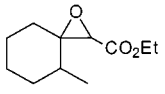
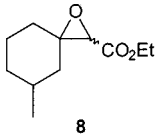
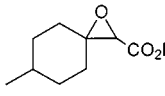
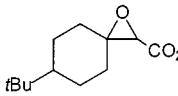
Scheme 2

A similar mechanism was reported by Wang and coworkers to explain aziridine formation.[14] To confirm that carbenes or carbenoids were not involved in the process, in a trial experiment we found that EDA is stable for several days when mixed with 10 mol % $Ln(OTf)_3$.

The best results were obtained using 0.1 equivalents of the catalyst; a lower loading resulted in lower yields, while a higher loading did not significantly reduce reaction times or increase yields. The catalyst could be easily recovered from the reaction media by simple addition of dichloromethane, to precipitate $Ln(OTf)_3$, and subsequent filtration. It could be reused after drying for 2 h at 70 °C. The yields of the second and third runs of the recycled catalyst were similar in all cases to those of the first run. As reported in Table 1, the catalytic activity of $La(OTf)_3$ was far superior to that of heavier lanthanide triflates.

When ketones were used as substrates a different reactivity profile was obtained, and these results are reported in Table 2. Ketones are much less reactive than aldehydes: the process takes up to 72 h to be complete and, in addition, many substrates don't react at all (entries 7−11 and 13). Only in the case of α-unsubstituted and α-monosubstituted cyclohexanones was the process effective, leading to the formation of glycidic esters. A similar pattern of reactivity has been reported for the allylation of cyclohexanone and other cyclic and acyclic ketones with organotitanium species.[20] 3-Methylcyclohexanone (entry 14) yielded a 1:1 mixture of stereoisomers, which could be separated by silica-gel column chromatography; 2-methyl-, 4-methyl- and 4-*tert*-butylcyclohexanone (entries 12, 14 and 15) yielded a single diastereoisomer formed from the thermodynamically more favourable equatorial nucleophilic attack of EDA at the carbonyl function, leading to a *pseudo*-axial configuration at the epoxide C−O bond. The lower yield (25%) obtained

Table 2. Reaction between ketones and EDA catalysed by $Ln(OTf)_3$

Entry	Reactant	Product	Yield (%)[a] $La(OTf)_3$	$Eu(OTf)_3$	$Yb(OTf)_3$
6	Cyclohexanone	 **6**	87	56	46
7	Acetophenone	no reaction	--	--	--
8	3-Heptanone	no reaction	--	--	--
9	Acetone	no reaction	--	--	--
10	Cycloheptanone	no reaction	--	--	--
11	Cyclopentanone	no reaction	--	--	--
12	2-Methyl-cyclohexanone	 **7**	25	15	8
13	2,6-Dimethyl-cyclohexanone	no reaction	--	--	--
14	3-Methyl-cyclohexanone	 **8**	83	34	32
15	4-Methyl-cyclohexanone	 **9**	81	39	34
16	4-*tert*Butyl-cyclohexanone	 **10**	81	39	38

[a] Isolated yield.

using 2-methylcyclohexanone (entry 12), together with the fact that 2,6-dimethylcyclohexanone (entry 13) is not reactive, can be explained by the steric bulk of the α-alkyl substituents preventing the formation of the lanthanide-carbonyl complex., $La(OTf)_3$ also performed as a better catalyst than other lanthanides in the case of ketones.

As a knowledge of the factors that drive the process along one of the two reaction pathways described above could be of synthetic importance, and because we have clearly shown that a completely different selectivity can be obtained simply by changing the catalyst, quantum chemical computational studies to gain further insight into the reaction between diazoesters and carbonyl compounds are now in progress.

Conclusions

From the results presented above we can conclude that lanthanide triflates catalyse the reaction between EDA and carbonyl compounds, acting as a relatively weak and selective catalyst: they allow only the more reactive compounds (i.e. aldehydes and cyclohexanones) to react under milder reaction conditions. The second effect of this "weakness" is that the carbonyl oxygen, although complexing the lanthanide atom, retains sufficient nucleophilicity to allow the subsequent substitution reaction, making glycidic ester formation the preferred pathway. Moreover, we have demonstrated that α,β-epoxy esters can be obtained by $Ln(OTf)_3$-catalysed reactions of carbonyl compounds with EDA. The process can be carried out under mild reaction conditions to afford glycidic esters − which are important intermediates in synthetic organic chemistry as precursors of glycidic acids − the decomposition of these acids yields one-carbon homologated aldehydes starting from carbonyl compounds,[21] in good yield, although only from aldehydes and suitably substituted cyclohexanones. The catalyst can easily be recovered from the reaction medium and recycled.

Experimental Section

General Method: ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Bruker AC 200 spectrometer operating at 200.1 and 50.53 MHz, respectively, in the Fourier transform mode. GC analyses and MS spectra were carried out with an HP 5890 gas chromatograph (dimethyl silicone column 12.5 m) equipped with an HP 5971 Mass Selective Detector. Flash column chromatography was performed on 0.040−0.063 mm (230−400 mesh ASTM) Merck silica gel. Elemental analysis were performed on a Carlo Erba Model 1106 elemental analyzer. Ethyl diazoacetate, $La(OTf)_3$, $Eu(OTf)_3$ and $Yb(OTf)_3$ were purchased from Aldrich Chemical Co. and used without any purification.

General Procedure: A mixture of carbonyl compound (1.0 mmol) and EDA (1.2 mmol) was stirred with $Ln(OTf)_3$ (0.1 mmol) at room temperature for the appropriate time (see Tables 1 and 2). CH_2Cl_2 (5 mL) was then added to precipitate the $Ln(OTf)_3$, and the catalyst was removed by filtration under reduced pressure. The residue was purified by silica-gel column chromatography with CH_2Cl_2 as eluent. The catalyst was washed with dichloromethane and dried at 70 °C for 2 h before being reused for several other experiments without any loss of activity.

Ethyl 3-Methyl-1-oxirane-2-carboxylate (1): Yellow oil. ^1H NMR (*cis* isomer): δ = 1.33 (t, *J* = 7.1 Hz, 3 H), 1.42 (d, *J* = 7.0 Hz, 3 H), 3.19 (d, *J* = 2.0 Hz, 1 H), 3.22−3.36 (m, 1 H), 4.26 (q, *J* = 7.1 Hz, 2 H); (*trans* isomer): δ = 1.33 (t, *J* = 7.0 Hz, 3 H), 1.40 (d, *J* = 6.9 Hz, 3 H), 3.23−3.37 (m, 1 H), 3.52 (d, *J* = 4.4 Hz, 1 H), 4.25 (q, *J* = 7.0 Hz, 2 H). ^{13}C NMR (*cis* isomer): δ = 14.2, 17.1, 53.9, 54.4, 61.5, 168.7; (*trans* isomer): δ = 12.8, 14.1, 52.9, 53.4, 61.4, 169.1. GC-MS: *m*/*z* = 115, 168, 102, 84, 74, 69, 57. $C_6H_{10}O_3$ (130.1): calcd. C 55.37, H 7.74; found C 55.35, H 7.75.

Ethyl 3-Pentyl-1-oxirane-2-carboxylate (2): Yellow oil. ^1H NMR (*cis* isomer): δ = 0.92 (d, *J* = 7.0 Hz, 3 H), 1.32 (t, *J* = 7.1 Hz, 3 H), 1.30−1.85 (m, 8 H), 3.17−3.24 (m, 1 H), 3.27 (d, *J* = 1.8 Hz, 1 H), 4.18 (q, *J* = 7.1 Hz, 2 H); (*trans* isomer): δ = 0.91 (d, *J* = 7.0 Hz, 3 H), 1.31 (t, *J* = 7.1 Hz, 3 H), 1.28−1.80 (m, 8 H), 3.15−3.22 (m, 1 H), 3.57 (d, *J* = 4.0 Hz, 1 H), 4.17 (q, *J* = 7.1 Hz, 2 H). ^{13}C NMR (*cis* isomer): δ = 13.8, 14.0, 22.3, 23.0, 25.7, 31.3, 52.8, 57.6, 61.3, 169.1; (*trans* isomer): δ = 13.8, 14.0, 23.0, 23.1, 27.1, 31.1, 53.0, 58.4, 169.3. GC-MS: *m*/*z* = 170, 158, 143, 129, 113, 102, 85, 83, 69, 55. $C_{10}H_{18}O_3$ (186.2): calcd. C 64.49, H 9.74; found C 64.51, H 9.73.

Ethyl 3-(9-Decenyl)-1-oxirane-2-carboxylate (3): Yellow oil. ^1H NMR (*cis* isomer): δ = 1.12−2.20 (m, 17 H), 2.41−2.51 (m, 2 H), 3.17−3.24 (m, 1 H), 3.25 (d, *J* = 1.8 Hz, 1 H), 4.27 (q, *J* = 7.0 Hz, 2 H), 5.02−5.10 (m, 2 H), 5.85−5.98 (m, 1 H); (*trans* isomer): δ = 1.11−2.20 (m, 17 H), 2.39−2.50 (m, 2 H), 3.15−3.23 (m, 1 H), 3.57 (d, *J* = 4.7 Hz, 1 H), 4.26 (q, *J* = 7.0 Hz, 2 H), 5.73−5.85 (m, 1 H). ^{13}C NMR (*cis* isomer): δ = 14.2, 26.1, 28.8, 29.0, 29.1, 29.2, 29.3, 32.0, 33.7, 52.8, 58.5, 61.5, 114.0, 139.1, 167.8; (*trans* isomer): δ = 14.0, 25.7, 28.8, 29.0, 29.1, 29.2, 29.3, 31.4, 33.7, 53.0, 57.6, 61.4, 114.1, 139.1, 168.0. GC-MS: *m*/*z* = 254, 225, 181, 165, 151, 137, 123, 109, 95, 81, 67, 55. $C_{15}H_{26}O_3$ (254.3): calcd. C 70.83, H 10.30; found C 70.81, H 10.28.

Ethyl 3-Cyclohexyl-1-oxirane-2-carboxylate (4): Yellow oil. ^1H NMR (*cis* isomer): δ = 1.10−1.95 (m, 13 H), 2.97 (dd, $J_{1,2}$ = 1.8 Hz, $J_{1,3}$ = 6.2 Hz, 1 H), 3.28 (d, *J* = 1.8 Hz, 1 H), 4.24 (q, *J* = 7.0 Hz, 2 H); (*trans* isomer): δ = 1.15−1.96 (m, 13 H), 2.84 (dd, $J_{1,2}$ = 4.7 Hz, $J_{1,3}$ = 8.7 Hz, 1 H), 3.54 (d, *J* = 4.6 Hz, 1 H), 4.25 (q, *J* = 7.1 Hz, 2 H). ^{13}C NMR (*cis* isomer): δ = 14.0, 25.3, 25.4, 26.0, 28.7, 29.2, 39.4, 51.9, 61.4, 62.4, 169.4; (*trans* isomer): δ = 14.2, 25.0, 25.2, 28.5, 28.8, 30.5, 36.1, 52.7, 61.2, 61.6, 168.2. GC-MS: *m*/*z* = 198, 141, 125, 115, 107, 95, 81, 67, 55. $C_{11}H_{18}O_3$ (198.2): calcd. C 66.44, H 9.15; C 66.45, H 9.13.

Ethyl 3-Phenyl-1-oxirane-2-carboxylate (5): Yellow oil. ^1H NMR (*cis* isomer): δ = 1.07 (t, *J* = 7.0 Hz, 3 H), 3.52 (d, *J* = 1.9 Hz, 1 H), 4.25 (q, *J* = 7.0 Hz, 2 H), 4.38 (d, *J* = 1.9 Hz, 1 H), 7.23−7.50 (m, 5 H); (*trans* isomer): δ = 1.32 (t, *J* = 7.1 Hz, 3 H), 3.78 (d, *J* = 4.6 Hz, 1 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 4.40 (d, *J* = 4.6 Hz, 1 H), 7.27−7.55 (m, 5 H). ^{13}C NMR (*cis* isomer): δ = 13.8, 56.8, 57.9, 61.5, 125.8, 128.0, 128.6, 129.0, 129.3, 167.8; (*trans* isomer): δ = 14.1, 55.8, 57.4, 61.2, 126.63, 128.4, 128.4, 129.2, 129.9, 133.4, 167.6. GC-MS: *m*/*z* = 192, 163, 119, 103, 77. $C_{11}H_{12}O_3$ (192.2): calcd. C 68.74, H 6.29; found C 68.76, H 6.27.

Ethyl 1-Oxaspiro[2.5]octane-2-carboxylate (6): Yellow oil. ^1H NMR: δ = 1.25 (t, *J* = 7.2 Hz, 3 H), 1.35−1.90 (m, 10 H), 3.25 (s, 1 H), 4.20 (q, *J* = 7.2 Hz, 2 H). ^{13}C NMR: δ = 14.1, 24.6, 24.9, 25.1, 28.5, 34.7, 59.3, 61.1, 64.6, 168.2. GC-MS: *m*/*z* = 184, 167,

156, 144, 138, 127, 111, 99, 81, 67, 55. $C_{10}H_{16}O_3$ (184.2): calcd. C 65.19, H 8.75; found C 65.21, H 8.72.

Ethyl 4-Methyl-1-oxaspiro[2.5]octane-2-carboxylate (7): Yellow oil. ^{1}H NMR: δ = 0.81 (d, *J* = 7.0 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 3.40 (s, 1 H), 1.50−2.40 (m, 9 H), 4.15 (q, *J* = 7.2 Hz, 2 H). ^{13}C NMR: δ = 14.1, 14.0, 23.3, 24.5, 168.5, 27.1, 32.5, 35.5, 57.5, 61.0, 66.5. GC-MS: *m*/*z* = 198, 183, 170, 141, 125, 113, 107, 95, 81, 67, 55. $C_{11}H_{18}O_3$ (198.2): calcd. C 66.64, H 9.15; found C 66.63, H 9.17.

Ethyl 5-Methyl-1-oxaspiro[2.5]octane-2-carboxylate (8): Yellow oil. ^{1}H NMR (isomer 1): δ = 0.84 (d, *J* = 7.0 Hz, 3 H), 1.22 (t, *J* = 7.2 Hz, 3 H), 1.40−1.85 (m, 9 H), 3.25 (s, 1 H), 4.15 (q, *J* = 7.2 Hz, 2 H); (isomer 2): δ = 0.87 (d, *J* = 7.0 Hz, 3 H), 1.23 (t, *J* = 7.0 Hz, 3 H), 1.45−1.85(m, 9 H), 3.26 (s, 1 H), 4.18 (q, *J* = 7.2 Hz, 2 H). ^{13}C NMR (isomer 1): δ = 14.1, 21.8, 23.1, 23.2, 30.5, 33.8, 42.3, 59.2, 61.1, 64.0, 168.0; (isomer 2): δ = 14.1, 21.9, 23.2, 27.4, 30.4, 33.6, 35.9, 59.1, 61.1, 63.9, 168.1. GC-MS: *m*/*z* = 198, 183, 170, 141, 125, 113, 107, 95, 81, 67, 55. $C_{11}H_{18}O_3$ (198.2): calcd. C 66.64, H 9.15; found C 66.61, H 9.16.

Ethyl 6-Methyl-1-oxaspiro[2.5]octane-2-carboxylate (9): Yellow oil. ^{1}H NMR: δ = 0.90 (d, *J* = 7.1 Hz, 3 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 1.52−1.90 (m, 9 H), 3.28 (s, 1 H), 4.20 (q, *J* = 7.2 Hz, 2 H). ^{13}C NMR: δ = 14.1, 21.7, 27.4, 31.4, 32.2, 32.3, 33.7, 59.2, 61.0, 63.9, 168.2. GC-MS: *m*/*z* = 198, 183, 170, 141, 125, 111, 95, 81, 67, 55. $C_{11}H_{18}O_3$ (198.2): calcd. C 66.64, H 9.15; found C 66.65, H 9.15.

Ethyl 6-(*tert*-Butyl)-1-oxaspiro[2.5]octane-2-carboxylate (10): Yellow oil. ^{1}H NMR: δ = 0.90 (s, 9 H), 1.23 (t, *J* = 7.2 Hz, 3 H), 1.40−1.90 (m, 9 H), 3.30 (s, 1 H), 4.20 (q, *J* = 7.2 Hz, 2 H). ^{13}C NMR: δ = 14.5, 24.8, 24.9, 27.4, 27.6, 32.5, 34.4, 47.1, 59.2, 61.1, 64.2, 168.2. GC-MS: *m*/*z* = 240, 225, 183, 167, 155, 137, 123, 107, 93, 81, 67, 55. $C_{14}H_{24}O_3$ (240.3): calcd. C 69.96, H 10.07; found C 69.97, H 10.05.

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