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(54) **Title:** A PROCESS FOR THE PREPARATION OF FATTY CYCLIC CARBONATES BY OXIDATIVE CARBOXYLATION

(57) **Abstract:** The present invention relates to the development of novel one-pot process for the preparation of fatty cyclic carbonates from unsaturated fatty derivatives using *t*-butyl hydroperoxide (TBHP; 70 wt.% in water) and carbon dioxide (CO₂) through oxidative carboxylation. This process uses recyclable metal salen complexes, in particular, Mn (III) salen complexes, as catalyst and the reactions are performed under ambient conditions (26 ± 2 °C and 1 bar). Varied forms of fatty compounds such as fatty alkyl esters, fatty acids and fatty glyceryl esters including vegetable oils were converted into fatty cyclic carbonates with moderate to excellent yields. Ethyl linoleate was converted into fatty cyclic carbonates at 88% conversion with 86% selectivity in 4 h. This process efficiently uses abundantly available CO₂ as one of the raw materials for the preparation bio-based oleochemicals that can serve as alternate for presently used petroleum-based products.



“A PROCESS FOR THE PREPARATION OF FATTY CYCLIC CARBONATES BY OXIDATIVE CARBOXYLATION”

FIELD OF THE INVENTION

5 The present invention relates to a one-pot process for the preparation of fatty cyclic carbonates from unsaturated fatty derivatives, including triglyceride sources such as vegetable oils, using aqueous *t*-butyl hydroperoxide (TBHP; 70wt.%) and carbon dioxide (CO₂) through oxidative carboxylation in high yields. Particularly, present invention relates to a one-pot process for the preparation of fatty cyclic carbonates using salen complexes, and
10 in particular manganese (Mn) salen complexes, as catalysts and the reactions are performed under ambient conditions ($26 \pm 2^\circ\text{C}$ and 1 bar).

BACKGROUND OF THE INVENTION

Oil based oleochemicals have gained significant interest in recent years because of their
15 diverse reaction scope and environmental friendly nature. Developing new molecules from vegetable oil derivatives are not only sustainable but also provide opportunity to substitute many petro-derived products. Generally, applications of vegetable oils depend on their physical properties such as fatty chain length, degree of unsaturation and presence of functional groups in the fatty chains. Functionalization/derivatization of unsaturated fatty
20 centres improves/modifies the physical properties of oils/fatty derivatives that makes them suitable for many applications. Carbon dioxide (CO₂), besides known for its deleterious influence in global-warming and related issues, is available in abundance at low cost and therefore a promising C1 feedstock in organic synthesis. Oxidation of olefins to epoxides and cycloaddition of epoxide with CO₂ for the preparation of cyclic carbonates are well-studied
25 organic transformations and the same strategy was used for the preparation of fatty cyclic carbonates in two steps. Fatty cyclic carbonates have the potential in making specialty polyurethane polymers, and can be used as lubricants, emollients, fuel additives and as solvents.

R.A. Holser reported the preparation of the carbonated methyl soyates by the insertion of CO₂
30 to epoxy methyl soyate (methyl esters of soybean oil) in presence of tetrabutylammonium bromide as catalyst (Carbonation of epoxy methyl soyate at atmospheric pressure. *J. Oleo Sci.* (2007) 56 (12), 629-632). A epoxy methyl soyate conversion of 42% was obtained in 18

h. Requirement of longer reaction time as well as lower conversion of epoxides are the main drawbacks of this work.

K.M. Doll and S.Z. Erhan in their paper titled “Synthesis of carbonated fatty methyl esters using supercritical carbon dioxide” in *J. Agric. Food Chem.* **(2005)**, 53, 9608-9614 discussed the preparation of carbonated fatty methyl esters by epoxidation followed by carbonation route. In this work the carbonation step was carried out by using supercritical CO₂. Further, they extended the work for preparation of carbonated soybean oil (The improved synthesis of carbonated soybean oil using supercritical carbon dioxide at a reduced reaction time. *Green Chem.* **(2005)** 7, 849–854). Though isolated yield obtained was high (97% for fatty methyl ester and 81% for epoxy soybean oil), requirement of sensitive reaction conditions (high temperature and pressure -100 °C and 10.3 MPa; supercritical conditions) and additional chemicals are the drawbacks of their work, besides being a two-step process.

N. Mann et al. reported in their paper titled “Synthesis of carbonated vernonia oil”, in *J. Am. Oil Chem. Soc.* **(2008)** 85, 791–796) wherein Vernonia oil, an oil that naturally has epoxy ring in its triglycerides structure, was converted into cyclic carbonate under the pressure of <13.8 MPa at 100 °C for 46 h. After the completion of reaction, the catalyst (TBAB – tetrabutyl ammoniumbromide) was decomposed at high temperature (175 °C) and obtained 72% of carbonated oil. Requirement of harsh reaction conditions including during post-work up and longer reaction time are the main drawback of their work besides being substrate specific, for oil rich in epoxy content.

Interestingly, one-pot synthesis of fatty cyclic carbonates from fatty derivatives by oxidative carboxylation (combining both epoxidation and CO₂ insertion) is not yet documented.

OBJECTIVES OF THE INVENTION

The main objective of the present invention is to provide a one pot process for the preparation of fatty cyclic carbonates from unsaturated fatty derivatives including vegetable oils through a one-step oxidative carboxylation process in high yields.

Another objective of the present invention is to use environmentally-concerned and abundantly available CO₂ as reactant in an easy handling manner.

Yet another objective of the present invention is to carry out the reaction under ambient conditions ($26 \pm 2^\circ\text{C}$ and 1 bar).

Still another objective of the present invention is to use Mn (III) salen complexes as recyclable catalyst.

- 5 Still another objective of the present invention is to use aqueous *t*-butyl hydroperoxide (TBHP; 70 wt.%) as oxidant.

Still another objective of the present invention is to achieve higher selectivity of fatty cyclic carbonates.

- 10 Still another objective of the present invention is to develop a simple technique to recycle the catalyst.

Still another objective of the present invention is to demonstrate the process on higher scale.

SUMMARY OF THE INVENTION

- Accordingly, the present invention provides a one-step process for the preparation of fatty cyclic carbonates from unsaturated fatty derivatives using metal salen complexes as catalysts
15 comprising the steps of:

- i. mixing unsaturated fatty derivative and solvent at room temperature in the range of 24 to 28°C to obtain a mixture;
- ii. adding 0.5 to 5 wt.% catalyst to the mixture as obtained in step (i) followed by adding oxidant in molar ratio ranging between 0.3 to 4.5 with respect to fatty
20 derivative to obtain a mixture;
- iii. continuously purging CO_2 to the mixture as obtained in step (ii) with stirring in the range 600-800 rpm for the period in the range 15 min to 12 h.
- iv. removing solvent and water from the mixture as obtained in step (iii) followed by adding higher alkanes and centrifuging to separate the catalyst to
25 obtain the fatty cyclic carbonates.

- In an embodiment of the present invention, the unsaturated fatty derivatives used in step (i) is selected from the group consisting but not limited to fatty alkyl esters such as ethyl linoleate (technical grade whose assay is $\sim 70\%$), methyl oleate, methyl ricinoleate, fatty acids such as linoleic acid, glyceryl esters including oils such as glyceryl trioleate, sunflower oil and castor
30 oil.

In yet another embodiment of the present invention, the metal in metal salen catalyst used in step (ii) is selected from Mn, Cr, Al and V.

In yet another embodiment of the present invention, the catalyst used in step (ii) is Mn salen complex in different structural environment, preferably C-7.

- 5 In yet another embodiment of the present invention, the oxidant used in step (iii) includes 70 wt.% *t*-butyl hydroperoxide (TBHP) in water and 5-6 M TBHP soln. in decane preferably 70wt% of TBHP in water.

In yet another embodiment of the present invention, the solvents used in step (i) is selected from the group consisting of toluene, xylenes, tetrahydrofuran, acetonitrile, dimethyl
10 formamide and acetone preferably toluene.

In yet another embodiment of the present invention, the amount of catalyst used in step (ii) is preferably 2.5 wt.% with respect to fatty derivative.

In yet another embodiment of the present invention, the reaction time in step (iii) is preferably 4 h.

- 15 In yet another embodiment of the present invention, the conversion percentage of fatty derivative used in step (i) is in the range of 24-88% with the epoxide and cyclic carbonate selectivity in the range of 14-34 and 66-86% respectively.

In yet another embodiment of the present invention, the fatty derivative used in step (i) is ethyl linonate whose conversion is 58% with the epoxide and cyclic carbonate selectivity is
20 32 and 68% respectively over a recycled catalyst.

In still another embodiment of the present invention the ethyl linoleate used in step (i) is technical grade with an assay of ~70%.

In still another embodiment of the present invention the conversion of ethyl linoleate is 88%
25 with fatty cyclic carbonate selectivity of 86%.

In still another embodiment of the present invention, the catalyst was reusable successfully for two cycles.

In still another embodiment of the present invention, the process could be demonstrated on higher scale with similar efficacy as that of lower scale.

BRIEF DESCRIPTION OF DRAWINGS

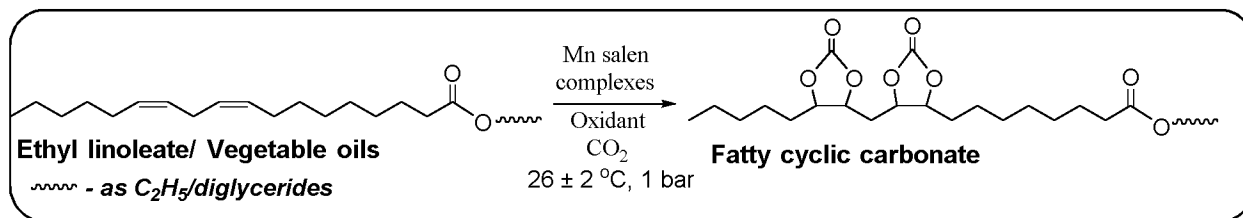
Figure 1: Structure of Mn (III) salen complex **1** (C-1).

Figure 2: Structure of Mn (III) salen complexes **2-7** (C-2 to C-7).

DETAILED DESCRIPTION OF THE INVENTION

The present invention aims to replace the conventional two-step process namely epoxidation of fatty derivatives followed by carboxylation by CO₂ insertion to the epoxide derivatives for the preparation of fatty cyclic carbonates in high yields from unsaturated fatty derivatives by one-step oxidative carboxylation process using *t*-butyl hydroperoxide (TBHP; 70 wt.%), CO₂ and in presence of metal salen Mn (III) salen complexes as reusable catalysts under ambient conditions (26 ± 2 °C and 1 bar).

Different unsaturated fatty derivatives (esters, acid, glyceryl esters including oils) were converted to fatty cyclic carbonates by environmentally benign one-step oxidative carboxylation route. Mn (III) salen complexes with different structural environments were prepared by well-known methods and were used as catalysts for this process. The oxidative carboxylation reactions were carried out in different solvents namely toluene, xylenes, tetrahydrofuran, acetonitrile, dimethyl formamide and acetone with the catalyst range of 0.5 to 5 wt.% at 26 ± 2 °C for 15 min to 12 h reaction time by using *t*-butyl hydroperoxide (TBHP; 70 wt.% in water) as oxidant under bubbling CO₂. The catalyst was separated by simple solubility technique using n-dodecane followed by centrifugation and the recovered catalyst was recycled. The collected organic layer was concentrated by rotary evaporator and the conversion of reactant and selectivity of products were computed using ¹H NMR. Different unsaturated fatty derivatives rendered moderate to excellent conversion (24-88%) with good selectivity (>75%) in 4-10 h reaction time. Reaction only with oxidant or carbon dioxide did not render the desired product suggest co-operative effect of both for the preparation of fatty cyclic carbonates. 88% conversion of ethyl linoleate with 86% selectivity of fatty cyclic carbonates was achieved within 4 h reaction time using 2.5 wt.% of catalyst. The recovered catalyst showed 58% conversion of ethyl linoleate with 68% selectivity of cyclic carbonate. The reaction was successfully scaled for ethyl linoleate and castor oil up to 6 g scale to prove the efficacy of the catalyst that showed 85 and 41% conversion respectively with > 85% selectivity of cyclic carbonates.



The main embodiment of the present invention provides a one-step process for the preparation of fatty cyclic carbonates from unsaturated fatty compounds using metal salen complexes preferably Mn (III) salen complexes as catalyst which comprises of the following steps:

- (i) mixing of fatty derivative and solvent at room temperature ($26 \pm 2^\circ C$);
- (ii) adding catalyst to the mixture obtained in step (i);
- (iii) adding oxidant (70 wt.% TBHP in water or 30 wt.% H_2O_2 in water or 5-6 M TBHP soln. in decane) to mixture obtained in step (ii);
- (iv) tightly closing the mixture obtained in step (iii) by a rubber septum;
- (v) purging of CO_2 by using needle to the mixture as obtained in step (iii);
- (vi) stirring of reaction mixture mentioned in step (v) at a rate in the range 600-800 rpm;
- (vii) carrying out the reaction for different time in the range from 15 min to 12 h;
- (viii) removing the solvent and water (came from TBHP) from the mixture obtained in step (vii) by rotary evaporator;
- (ix) adding higher alkanes to the mixture obtained in step (viii) and centrifuge to separate the catalyst to obtain the fatty cyclic carbonates along with fatty derivative;
- (x) fatty cyclic carbonates can be separated from the mixture obtained in step (ix) using suitable techniques.

In another embodiment of the present invention, the unsaturated fatty derivatives used in step (i) is selected from the group consisting but not limited to fatty alkyl esters such as ethyl linoleate (technical grade whose assay is $\sim 70\%$), methyl oleate, methyl ricinoleate, fatty acids such as linoleic acid, glyceryl esters including oils such as glyceryl trioleate, sunflower oil and castor oil.

In another embodiment of the present invention, the metal in metal salen catalyst used in step (ii) is selected from Mn, Cr, Al and V.

In another embodiment of the present invention, the catalyst used in step (ii) is Mn salen complex in different structural environment, preferably C-7.

- 5 In another embodiment of the present invention, the oxidant used in step (iii) includes 70 wt.% *t*-butyl hydroperoxide (TBHP) in water and 5-6 M TBHP soln. in decane preferably 70wt% of TBHP in water.

In another embodiment of the present invention, the solvents used in step (i) is selected from the group consisting of toluene, xylenes, tetrahydrofuran, acetonitrile, dimethyl formamide
10 and acetone, preferably toluene.

In another embodiment of the present invention, the amount of catalyst used in step (ii) is preferably 2.5 wt.% with respect to fatty derivative.

In another embodiment of the present invention, the reaction time in step (iii) is preferably 4 h.

- 15 In another embodiment of the present invention, the conversion percentage of fatty derivative used in step (i) is in the range of 24-88% with the epoxide and cyclic carbonate selectivity in the range of 14-34 and 66-86% respectively.

In another embodiment of the present invention, the fatty derivative used in step (i) is ethyl linonate whose conversion is 58% with the epoxide and cyclic carbonate selectivity is 32 and
20 68% respectively over a recycled catalyst.

EXAMPLES

Following examples are given by way of illustration and therefore should not be construed to limit the scope of the invention.

Example 1

- 25 200 mg of technical grade ethyl linoleate (EL) (Assay = ~70%; Mol. wt. 308) was taken along with 1 ml of toluene in a 10 ml glass tube. 5 mg (2.5 wt.% with respect to (w.r.t.) EL) of Mn salen complex **1** (C-1) (structure given in Fig. 1) and 280 μ L of *t*-butyl hydroperoxide (TBHP; 70 wt.% in water) were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO₂) gas was bubbled in the system continuously using a

needle. The contents in the glass tube were stirred well for 4 h at 26 °C. The reaction mixture was distilled out to get the product mixture. Solvent free sample was analyzed by ¹H NMR provide data of NMR. The conversion of EL was 79% and the selectivity of epoxides and cyclic carbonates are 25 and 75% respectively.

5

Example 2

200 mg of EL was taken along with 1 ml of toluene in a 10 ml glass tube. 5 mg (2.5 wt.% w.r.t. EL) of various metal salen complex **1** (C-1 to C₃-1) and 280 µL of TBHP (70 wt.% in water) were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO₂) gas was bubbled in the system continuously using a needle. The contents in the glass tube were stirred well for 4 h at 25 °C. The remaining procedure was followed as given in Example 1. The catalytic activity of different metal salen complexes are given in **Table 1**.

Table 1: Catalytic activity of metal salen complexes

Catalyst	Conversion (%)	Selectivity (%)	
		Epoxide	Cyclic carbonate
Mn (III) salen complex 1 (C-1)	79	25	75
Cr (III) salen complex 1 (C ₁ -1)	65	35	65
Al (III) salen complex 1 (C ₂ -1)	25	35	65
V (V) salen complex 1 (C ₃ -1)	25	52	48

Example 3

200 mg of EL was taken along with 1 ml of toluene in a 10 ml glass tube. 5 mg (2.5 wt.% w.r.t. EL) of Mn salen complexes **2-7** (C-2 to C-7) and 280 µL of TBHP (70 wt.% in water) were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO₂) gas was bubbled in the system continuously using a needle. The contents in the glass tube were stirred well for 4 h at 25 °C. The remaining procedure was followed as given in Example 1. The catalytic activity of different Mn (III) salen complexes are given in Table 2

25

Table 2: Catalytic activity of Mn (III) salen complexes (C-2 to C-7)

Catalyst	Conversion (%)	Selectivity (%)	
		Epoxide	Cyclic carbonate
Mn (III) salen complex – 2 (C-2)	77	25	75
Mn (III) salen complex – 3 (C-3)	82	32	68
Mn (III) salen complex – 4 (C-4)	80	36	64
Mn (III) salen complex – 5 (C-5)	81	23	77
Mn (III) salen complex – 6 (C-6)	81	21	79
Mn (III) salen complex – 7 (C-7)	88	14	86

Example 4

200 mg of EL was taken along with 1 ml of toluene in a 10 ml glass tube. 5 mg (2.5 wt.% w.r.t. EL) of C-7 and 292 μ L of hydrogen peroxide (H_2O_2 ; 30 wt.% in water) were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO_2) gas was bubbled in the system continuously using a needle. The contents in the glass tube were stirred well for 4 h at 27 °C. The remaining procedure was followed as given in Example 1. The conversion of EL was 8% and the selectivity of epoxides/cyclic carbonates was 0/0%.

Example 5

200 mg of EL was taken along with 1 ml of toluene in a 10 ml glass tube. 5 mg (2.5 wt.% w.r.t. EL) of C-7 and 292 μ L of *t*-butyl hydroperoxide (abbreviated as TBHP; 5-6 M soln. in decane) were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO_2) gas was bubbled in the system continuously using a needle. The contents in the glass tube were stirred well for 4 h at 26°C. The remaining procedure was followed as given in Example 1. The conversion of EL was 9% and the selectivity of epoxides/cyclic carbonates was 89/11%.

Example 6

200 mg of EL was taken along with 1 ml of toluene in a 10 ml glass tube. 5 mg (2.5 wt.% w.r.t. EL) of C-7 and 280 μ L of TBHP (70 wt.% in water) were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO_2) gas was bubbled in the system continuously using a needle. The contents in the glass tube were stirred well for

15 min. at 26°C. The remaining procedure was followed as given in Example 1. The conversion of EL was 76% and the selectivity of epoxides/cyclic carbonates was 36/64%.

Example 7

5 200 mg of EL was taken along with 1 ml of xylene in a 10 ml glass tube. 5 mg (2.5 wt.% w.r.t. EL) of C-7 and 280 μ L of TBHP (70 wt.% in water) were added to the tube were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO₂) gas was bubbled in the system continuously using a needle. The contents in the glass tube were stirred well for 4 h at 26 °C. The remaining procedure was followed as given in
10 Example 1. The conversion of EL was 69% and the selectivity of epoxides/cyclic carbonates was 20/80%.

Example 8

200 mg of EL was taken along with 1 ml of tetrahydrofuran (THF) in a 10 ml glass tube. 5
15 mg (2.5 wt.% w.r.t. EL) of C-7 and 280 μ L of TBHP (70 wt.% in water) were added to the tube were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO₂) gas was bubbled in the system continuously using a needle. The contents in the glass tube were stirred well for 4 h at 25 °C. The remaining procedure was followed as given in Example 1. The conversion of EL was 22% and the selectivity of
20 epoxides/cyclic carbonates was 43/57%.

Example 9

600 mg of EL was taken along with 2 ml of toluene in a 10 ml glass tube. 15 mg (2.5 wt.% w.r.t. EL) of C-7 and 840 μ L of TBHP (70 wt.% in water) were added to the tube. The glass
25 tube was then sealed well with a rubber septum and carbon dioxide (CO₂) gas was bubbled in the system continuously using a needle. The contents in the glass tube were stirred well for 4 h at 27 °C. The remaining procedure was followed as given in Example 1. Small amount of n-dodecane was added to the reaction mixture to precipitate the catalyst and was separated by centrifugation. The recovered complex was used for the next cycle as per the conditions
30 given in Example 1. The conversion of EL was 58% and the selectivity of epoxides/cyclic carbonates was 32/68%.

Example 10

200 mg of methyl oleate (MO) was taken along with 1 ml of toluene in a 10 ml glass tube. 5 mg (2.5 wt.% w.r.t. LA) of C-7 and 280 μ L of TBHP (70 wt.% in water) were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO₂) gas was bubbled in the system continuously using a needle. The contents in the glass tube were stirred well for 4 h at 26 °C. The remaining procedure was followed as given in Example 1. The conversion of MO was 32% and the selectivity of epoxides/cyclic carbonates was 24/76%.

Example 11

200 mg of methyl ricinoleate (MR) was taken along with 1 ml of toluene in a 10 ml glass tube. 5 mg (2.5 wt.% w.r.t. LA) of C-7 and 280 μ L of TBHP (70 wt.% in water) were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO₂) gas was bubbled in the system continuously using a needle. The contents in the glass tube were stirred well for 4 h at 26 °C. The remaining procedure was followed as given in Example 1. The conversion of MR was 24% and the selectivity of epoxides/cyclic carbonates was 18/82%.

Example 12

200 mg of linoleic acid (LA) was taken along with 1 ml of toluene in a 10 ml glass tube. 5 mg (2.5 wt.% w.r.t. LA) of C-7 and 280 μ L of TBHP (70 wt.% in water) were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO₂) gas was bubbled in the system continuously using a needle. The contents in the glass tube were stirred well for 4 h at 27°C. The remaining procedure was followed as given in Example 1. The conversion of LA was 52% and the selectivity of epoxides/cyclic carbonates was 34/66%.

Example 13

200 mg of glyceryl trioleate (GTO) was taken along with 1 ml of toluene in a 10 ml glass tube. 5 mg (2.5 wt.% w.r.t. LA) of C-7 and 280 μ L of TBHP (70 wt.% in water) were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO₂) gas was bubbled in the system continuously using a needle. The contents in the glass tube were stirred well for 10 h at 26 °C. The remaining procedure was followed as given in

Example 1. The conversion of GTO was 34% and the selectivity of epoxides/cyclic carbonates was 18/82%.

Example 14

- 5 200 mg of sunflower oil (SO) was taken along with 1 ml of toluene in a 10 ml glass tube. 5 mg (2.5 wt.% w.r.t. LA) of C-7 and 280 μ L of TBHP (70 wt.% in water) were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO₂) gas was bubbled in the system continuously using a needle. The contents in the glass tube were stirred well for 10 h at 26°C. The remaining procedure was followed as given in Example 1.
- 10 The conversion of SO was 69% and the selectivity of epoxides/cyclic carbonates was 24/76%.

Example 15

- 200 mg of castor oil (CO) was taken along with 1 ml of toluene in a 10 ml glass tube. 5 mg
- 15 (2.5 wt.% w.r.t. CO) of Mn salen complex-7 (C-7) and 280 μ L of *t*-butyl hydroperoxide (abbreviated as TBHP; 70 wt.% in water) were added to the tube. The glass tube was then sealed well with a rubber septum and carbon dioxide (CO₂) gas was bubbled in the system continuously using a needle for 8 h at 25 °C. Further, processes were done as mentioned earlier in Example 1. The conversion of CO was 66% and the selectivity of epoxides/cyclic
- 20 carbonates was 24/76%.

Example 16

- 6 g of ethyl linoleate was taken along with 30 ml of toluene in a 100 ml round bottom (R.B.) flask. 150 mg (2.5 wt.% w.r.t. reactant) of C-1 and 8400 μ L of TBHP (70 wt.% in water)
- 25 were added to the tube. Then R.B. flask was sealed well with a rubber septum and carbon dioxide (CO₂) gas was bubbled in the system continuously using a needle. The contents of the flask were stirred well for 4 h at 27 °C. The remaining procedure was followed as given in Example 1. The conversion of EL was 85% and the selectivity of epoxides/cyclic carbonates was 14/86%. Scale up study was done for castor oil with 6 g scale by following
- 30 the same procedure. The conversion of castor oil was 41% and the selectivity of epoxides/cyclic carbonates was 11/89%.

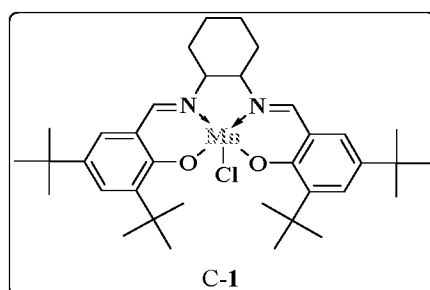
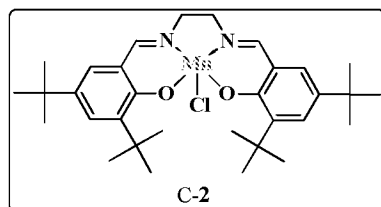
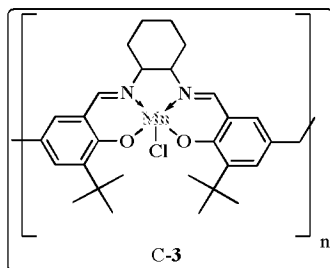
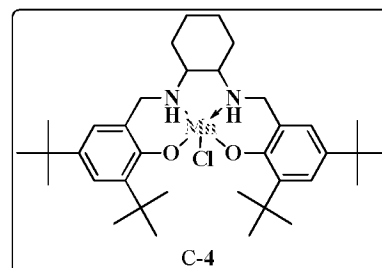
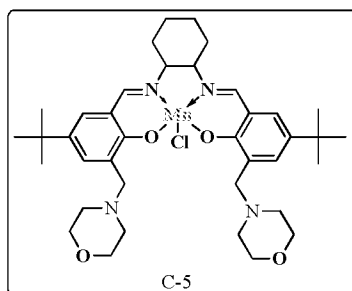
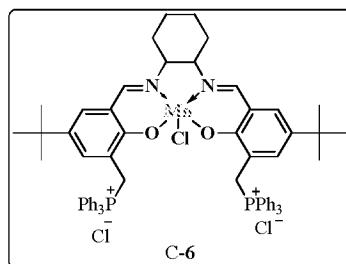
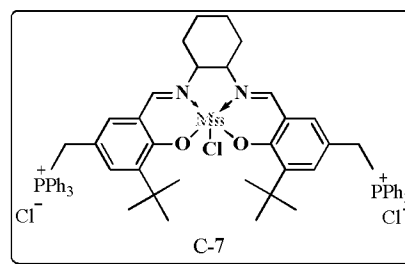
ADVANTAGES OF THE INVENTION

1. One-step process for the preparation of fatty cyclic carbonates from unsaturated fatty derivatives (acids, esters, glyceryl esters including oils)
2. Reaction is easily extendable to varied forms of fatty compounds such as fatty alkyl esters, fatty acids and fatty glyceryl esters including vegetable oils.
3. Easy handling process as it does not require high pressure reactor or supercritical reactor as reported in some of the prior art
4. Using environmentally abundant and low cost CO₂ as C₁ feedstock
5. Reaction performed using bubbling CO₂ at atmospheric pressure (1 bar; 50-100 cc/min; preferably around 60-80 cc/min)
6. Reaction carried out at room temperature (26 ± 2 °C)
7. A maximum conversion of 88% was achieved for ethyl linoleate with high selectivity of fatty cyclic carbonate (86%) under ambient conditions (26 ± 2 °C and 1 bar)
8. High activity of Mn salen complex as catalyst than reported catalytic systems
9. Higher yield of fatty cyclic carbonates in shorter reaction time (4 h)
10. Simple separation process
11. The complex catalyst is recyclable
12. Easily scalable with same efficacy

THE CLAIMS

1. A one-step process for the preparation of fatty cyclic carbonates from unsaturated
5 fatty derivatives using metal salen complexes as catalysts and the process comprising the steps of:
 - i. mixing unsaturated fatty derivative and solvent at room temperature in the range of 24 to 28 °C to obtain a mixture;
 - ii. adding 0.5 to 5 wt.% catalyst to the mixture as obtained in step (i) followed by
10 adding oxidant in molar ratio ranging between 0.3 to 4.5 with respect to fatty derivative to obtain a mixture;
 - iii. continuously purging CO₂ to the mixture as obtained in step (ii) with stirring in the range 600-800 rpm for the period in the range 15 min to 12 h.
 - iv. removing solvent and water from the mixture as obtained in step (iii)
15 followed by adding higher alkanes and centrifuging to separate the catalyst to obtain the fatty cyclic carbonates.
2. The process as claimed in claim 1, wherein the unsaturated fatty derivatives used in step (i) is selected from the group consisting but not limited to fatty alkyl esters such as ethyl linoleate (technical grade whose assay is ~70%), methyl oleate, methyl
20 ricinoleate, fatty acids such as linoleic acid, glyceryl esters including oils such as glyceryl trioleate, sunflower oil and castor oil.
3. The process as claimed in claim 1, wherein metal in metal salen catalyst used in step (ii) is selected from Mn, Cr, Al and V.
4. The process as claimed in claim 3, wherein the catalyst used in step (ii) is Mn salen
25 complex in different structural environment, preferably C-7.

5. The process as claimed in claim 1, wherein the oxidant used in step (iii) includes 70 wt.% *t*-butyl hydroperoxide (TBHP) in water and 5-6 M TBHP soln. in decane preferably 70 wt% of TBHP in water.
6. The process as claimed in claim 1, wherein the solvents used in step (i) is selected from the group consisting of toluene, xylenes, tetrahydrofuran, acetonitrile, dimethyl formamide and acetone, preferably toluene.
7. The process as claimed in claim 1, wherein amount of catalyst used in step (ii) is preferably 2.5 wt.% with respect to fatty derivative.
8. The process as claimed in claim 1, wherein reaction time in step (iii) is preferably 4 h.
9. The process claimed in claim 1, wherein conversion percentage of fatty derivative used in step (i) is in the range of 24-88% with the epoxide and cyclic carbonate selectivity in the range of 14-34 and 66-86% respectively.
10. The process as claimed in claim 1, wherein the fatty derivative used in step (i) is ethyl linonate whose conversion is 58% with the epoxide and cyclic carbonate selectivity is 32 and 68% respectively over a recycled catalyst.

**Figure 1****Mn(III) salen complex 2****Mn(III) salen complex 3****Mn(III) salen complex 4****Mn(III) salen complex 5****Mn(III) salen complex 6****Mn(III) salen complex 7****Figure 2**

INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2015/050064

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07D317/36 C11C3/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C07D C11C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KENNETH M DOLL ET AL: "Synthesis of Carbonated Fatty Methyl Esters Using Supercritical Carbon Dioxide", JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY, AMERICAN CHEMICAL SOCIETY, US, vol. 53, 1 January 2005 (2005-01-01), pages 9608-9614, XP007921633, ISSN: 0021-8561, DOI: 10.1021/JF0516179 [retrieved on 2005-10-29] cited in the application abstract Scheme 1	1-10
A	WO 2008/132474 A1 (UNIV NEWCASTLE [GB]; NORTH MICHAEL [GB]) 6 November 2008 (2008-11-06) claim 1 ----- -/--	1-10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search

24 November 2015

Date of mailing of the international search report

02/12/2015

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INTERNATIONAL SEARCH REPORT

International application No
PCT/IN2015/050064

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 824 969 A (AUSTIN RICHARD G [US] ET AL) 25 April 1989 (1989-04-25) abstract example 1	1-10
A	----- CN 1 789 258 A (LANZHOU CHEM PHYS INST [CN]) 21 June 2006 (2006-06-21) abstract -----	1-10

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IN2015/050064

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		EP 2146977 A1	27-01-2010
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		US 2010130752 A1	27-05-2010
		WO 2008132474 A1	06-11-2008

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CN 1789258 A	21-06-2006	NONE	
