

Review Article

Synthesis of alkyl-branched fatty acids

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Alkyl-branched fatty compounds are of interest for industrial products in the cosmetics and lubricant areas. In this review, clay- and zeolite-catalyzed isomerizations of unsaturated fatty compounds, especially of oleic acid, are discussed. While clay-catalyzed reactions give most complex mixtures of dimeric fatty acids and of monomeric so-called “isostearic acid”, the zeolite-catalyzed process yields preferentially an isomeric mixture of isostearic acids having the methyl branch on the 8–14 positions of the alkyl chain. Synthetically useful additions of alkyl radicals can only be performed on ω -unsaturated fatty compounds, whereas perfluoroalkyl iodides were added to fatty compounds with terminal as well as internal double bonds using electron transfer-initiated radical addition reactions. Electrophilic additions of alkyl carbenium ions generated by decomposition of alkyl chloroformates by ethylaluminum sesquichloride give well-defined alkyl-branched oleochemicals with good yields.

Keywords: Alkyl-branched fatty compounds / Lewis acid-induced hydro-alkylation / Radical addition / Renewable raw materials / Zeolite- and clay-catalyzed isomerization

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1 Introduction

The unsaturated fatty compounds 1–6 (Fig. 1) are of interest as renewable raw materials. Modern synthetic methods have been applied extensively to fatty compounds for the selective functionalization of the alkyl chain. Radical, electrophilic, nucleophilic, and pericyclic as well as transition metal-catalyzed additions to the C,C double bond of, for example, oleic acid (1) as the prototype of a readily accessible unsaturated fatty acid have led to a large number of novel fatty compounds [1–7]. The synthesis of alkyl-branched fatty compounds is of high importance since they have interesting properties that make them attractive for use in the cosmetics and lubricant areas [8–10]. The biodegradability of some branched-chain fatty acids has been studied [11–13] and reviewed [14]. The synthesis of well-defined and completely characterized alkyl-branched fatty compounds by an addition reaction to, *e.g.*, oleic acid (1) is of significant importance. This review gives a short overview concerning the conversion of linear long-chain unsaturated fatty compounds to give alkyl-branched oleochemicals.

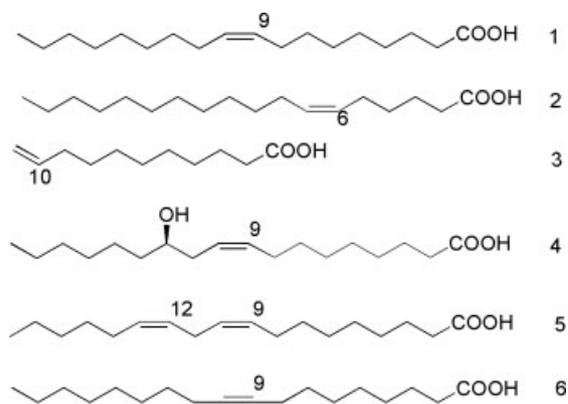


Figure 1. Starting materials for the synthesis of alkyl-branched fatty compounds: oleic acid (1), petroselinic acid (2), 10-undecenoic acid (3), ricinoleic acid (4), linoleic acid (5), stearolic acid (6), and the respective methyl esters 1a–6a.

2 Heterogeneously catalyzed isomerization reactions

Isostearic acid is a commercially available product that is obtained as a by-product in the montmorillonite-catalyzed dimerization process of oleic acid. It is used in the production

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of cosmetics and lubricants, especially because of its positive influence on spreadability, viscosity, and oxidative and hydrolytic stability. However, the commercial isostearic acid is not at all a pure compound; it consists of a mixture of substances with aromatic and cyclic derivatives, among others (Table 1) [15]. The first experiments to identify the products of the montmorillonite clay-induced dimerization of oleic acid (1) were carried out by den Otter [16, 17]. It was shown that the monomeric fraction consisted almost exclusively of straight and branched saturated fatty acids. Haase *et al.* found that it consists of a complex mixture of substances with a high amount of mono methyl-branched fatty acids carrying the methyl groups between C₇–C₁₃ of the alkyl chain [8]. This was shown by GC/MS and ¹³C NMR spectroscopy. Fatty acids with ethyl, propyl and dimethyl side chains could also be observed; however, they were formed only in small amounts. Spittler *et al.* examined the positions of the methyl branches obtained from the monomeric fraction of the dimerization of pure oleic acid [18–20]. The formation of the methyl-branched fatty acids can be rationalized by the protonation of the C,C double bond and following reactions of the adduct carbenium ions with other products of the dimerization, by transfer of a hydride ion [18] on the one hand or by cyclization and following ring opening of the three-membered ring carbocation intermediate on the other hand [21]. Isostearic acids with a branching at C2–C5 were not observed because carbenium ions with the positive charge in these positions cyclize to give the respective lactones [18].

Processes for the production of methyl-branched fatty acids are described in some patents. Using, *e.g.*, bentonite clay as catalyst in dichloromethane [22] as well as montmorillonite clay catalyst in combination with active carbon [23], the conversion of 1 to branched-chain fatty acids or esters was 50 and 30–40%, respectively. In the presence of bentonite clay and a mixture of 1,2-dichloroethane and isobutane as co-catalyst, oleic acid and methyl oleate were reacted under pressure at up to 230 °C to give mixtures of polymerized acids, branched- and straight-chain fatty acids and γ -stearolactones [22]. Recently, Foglia *et al.* described the zeolite Ferrierite- (which

is commercially available) catalyzed isomerization of oleic acid (1), giving, after catalytic hydrogenation with high conversions (98%) and high selectivity (85%), isostearic acids (Fig. 2) [24]. The skeletal isomerization of unsaturated fatty compounds is induced by zeolites having a linear pore structure with a pore size (6.7–7.0 Å) small enough to retard dimerization and large enough to allow diffusion of branched-chain compounds in the presence of water or lower alcohols [25]. Keneally and Connor described the catalyst of choice for the branching of saturated and/or unsaturated fatty acids and/or alkyl esters to be preferably a zeolite catalyst containing Group VIII metal sites [26]. The process was carried out in the presence of hydrogen gas, or a mixture of gases including hydrogen gas, under pressure. Branched fatty acids were obtained from straight-chain unsaturated fatty acid feedstock with strongly acidic catalysts having a three-dimensional channel structure [27]. Acidic and hydrothermally stable mesoporous aluminosilicate and aluminophosphate catalyst materials containing primary and secondary nanosized zeolite structural units gave results with up to 80% isomerization (GC analysis) of methyl oleate. The mechanism of the isomerization using zeolites of large pore size is postulated to proceed through three- and four-membered ring carbocation intermediates (Fig. 3) [14].

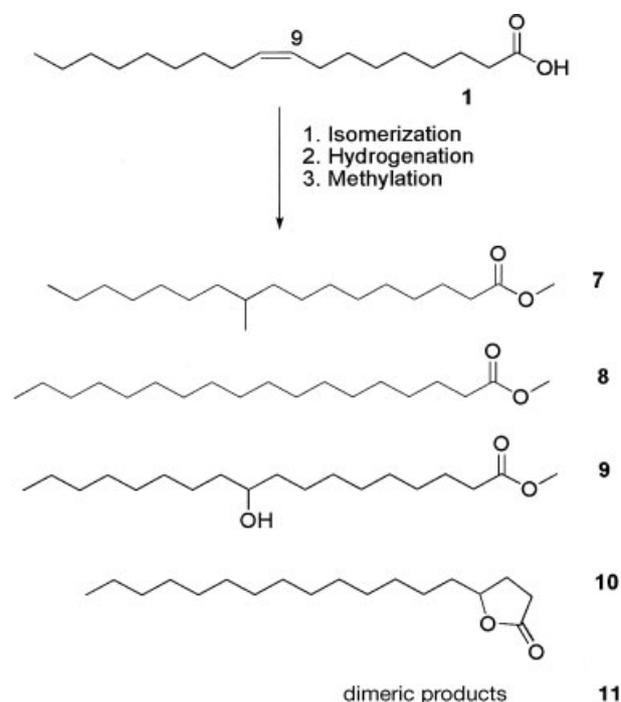


Figure 2. Products obtained from zeolite-catalyzed isomerization of oleic acid (1): isomeric methyl methylheptadecanoates **7** (85% yield). It was determined that 8.3% contain a methyl branch on the 2–7 positions, 84.4% have the methyl branch on the 8–14 positions and 7.3% on the 15 and 16 positions of the alkyl chain. In addition, methyl stearate **8** (6.2%), isomeric methyl hydroxyoctadecanoates **9** and γ -stearolactone **10** (6.9%) as well as dimeric products **11** (2.3%) were obtained [24].

Table 1. Typical composition of isostearic acid (Emersol® 874) [15].

Typical composition	[%]
Straight-chain C ₁₀	0.1
Straight-chain C ₁₂	0.3
Branched-chain C ₁₄	–
Straight-chain C ₁₄	0.2
Branched-chain C ₁₆	4.0
Straight-chain C ₁₆	5.0
Branched-chain C ₁₈	68.3
Straight-chain C ₁₈	2.4
Cyclic C ₁₈	13.9
Straight-chain C ₂₀	0.2
Aromatic C ₁₈	5.6

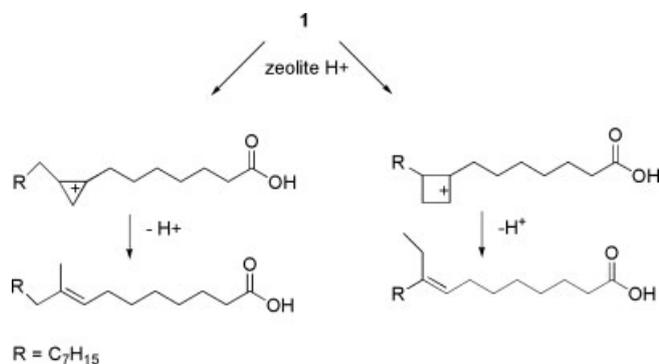


Figure 3. Mechanism of the formation of methyl and ethyl branchings in zeolites with large pore size using, *e.g.*, oleic acid (**1**) as starting material [14].

3 Addition reactions

3.1 Radical additions

3.1.1 Addition of alkanes

Unsaturated fatty compounds are alkenes having an electron-rich C,C double bond that can be functionalized by free-radical additions with the formation of a new C,C bond. Additions of nucleophilic radicals such as alkyl radicals to the internal C,C double bond of alkenes as, *e.g.*, oleic acid (**1**) occur very slowly, as a consequence of polar and steric effects. Additions are possible using the ane-reaction, the thermally initiated free-radical chain addition of alkanes to the C,C double bond of alkenes. At relatively high temperatures of 280–420 °C, methyl oleate (**1a**) reacts with cyclohexane and toluene to give the respective methyl stearate derivatives as regioisomeric mixtures with an alkyl branching in positions C9 and C10 in good yields. However, the reaction seems to be synthetically not useful because of low conversion [28]. In contrast, additions of alkanes, *i.e.* cyclohexane, heptane and toluene, to the ω-C,C double bond of methyl 10-undecenoate (**3a**) are synthetically useful and give long-chain and alkyl-branched alkylation products in yields of 25–50% [29]. The respective reaction with cyclohexane is shown in Fig. 4. 11-Cyclohexylundecanoic acid is the main fatty acid of thermophilic archaeobacteria [30].

3.1.2 Synthesis of perfluoroalkylated fatty acids

Perfluoroalkylated fatty acids may display interesting characteristics because of lipophilic, hydrophilic as well as fluorophilic properties. They can be obtained by electron transfer-initiated radical addition of perfluoroalkyl iodides to unsaturated fatty acids such as oleic acid (**1**) using, *e.g.*, tin(II)chloride/silver(I)acetate as initiator [31, 32]. The reaction of **1a** was performed with perfluorohexyl iodide to give a regioisomeric

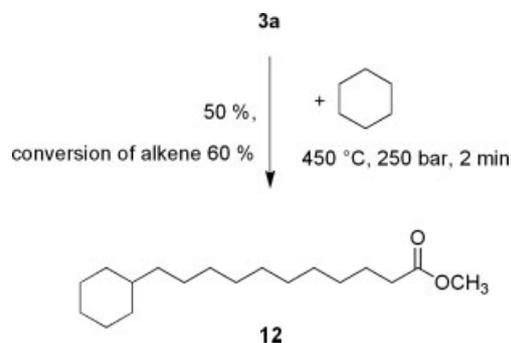


Figure 4. Addition of cyclohexane to methyl 10-undecenoate (**3a**) to give methyl 11-cyclohexylundecanoate (**12**) [29].

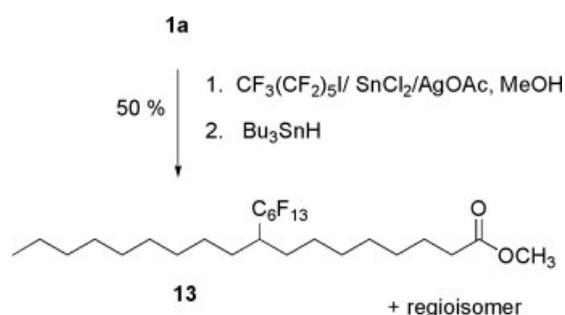


Figure 5. Addition of perfluorohexyl iodide to methyl oleate (**1a**) followed by reduction of the addition product to give methyl 9(10)-perfluorohexyloctadecanoate (**13**) [31, 32].

mixture of methyl 9(10)-perfluorohexyl-10(9)-iodooctadecanoate, which was reduced to methyl 9(10)-perfluorooctadecanoate (**13**) in overall 50% yield (Fig. 5). Furthermore, lead powder together with a catalytic amount of Cu(OAc)₂ in methanol is described to be an excellent reagent for the electron transfer-initiated addition of perfluoroalkyl iodides to, *e.g.*, methyl petroselinat (**2a**) at room temperature. The regioisomeric addition product was obtained in 79% yield. Highest yields of 85% were obtained using copper powder in a solvent-free reaction at about 110 °C. Reduction of the iodides was best performed by catalytic hydrogenation [33]. Tributyltin hydride was used as well [31].

3.2 Lewis acid-induced electrophilic additions

Friedel-Crafts alkylations of alkenes using alkyl halides are rarely used in preparative organic synthesis to form new C,C bonds because they mostly give oligo- and polymers and not the desired monoalkylation products [34]. Recently, a Lewis acid-induced hydro-alkylation reaction using alkyl chloroformates to give saturated alkyl-branched fatty compounds has been developed, being a new method for the alkylation of alkenes in general and of unsaturated fatty compounds in particular [35, 36]. The reaction allows the synthesis of well-

defined hydro-alkylation products in good to moderate yields. Ethylaluminum sesquichloride ($\text{Et}_3\text{Al}_2\text{Cl}_3$) is used as Lewis acid and CH_2Cl_2 as solvent.

The reaction of oleic acid (**1**) with isopropyl chloroformate in the presence of $\text{Et}_3\text{Al}_2\text{Cl}_3$ gave, after a reaction time of 2 h, a 1 : 1 regioisomeric mixture of 9- and 10-isopropyloctadecanoic acid (**14**) in 73% yield (Fig. 6). It is remarkable that the saturated product is formed in this reaction. The reaction mechanism is most interesting. In the presence of $\text{Et}_3\text{Al}_2\text{Cl}_3$, isopropyl chloroformate decomposes by formation of CO_2 and an isopropyl cation, which adds to the C,C double bond of, e.g., an internal alkene to give a secondary adduct carbenium ion I (Fig. 7). 1,2-H shift gives the more stable tertiary carbenium ions. Subsequent transfer of a hydride ion from ethylaluminum sesquichloride to one of the possible tertiary carbenium ions II and III leads to the hydro-alkyl addition product. Compound **14** showed positive results in tests in the cosmetics area as well as an outstanding trans-activation potential on murine and human peroxisome proliferator-activated receptor (PPAR) [37]. In analogy, further secondary alkyl chloroformates such as cyclohexyl (Fig. 8)

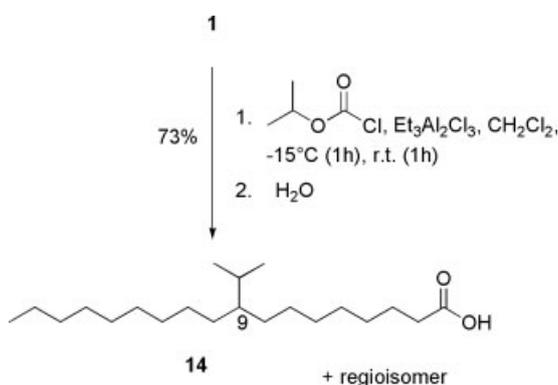


Figure 6. $\text{Et}_3\text{Al}_2\text{Cl}_3$ -induced hydro-alkylation of oleic acid (**1**) with isopropyl chloroformate to give 9(10)-isopropyloctadecanoic acid (**14**) [35, 36].

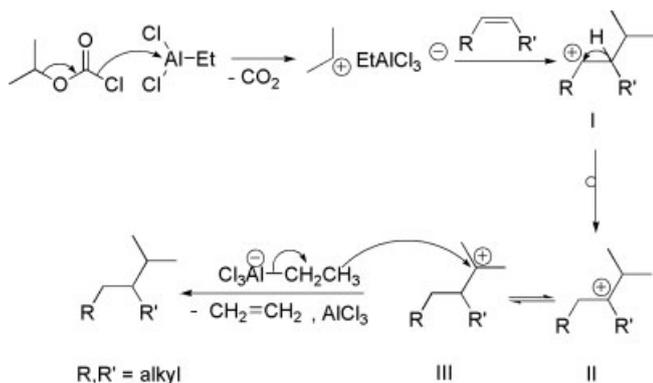


Figure 7. Mechanism of the hydro-alkylation of alkenes with isopropyl chloroformate and $\text{Et}_3\text{Al}_2\text{Cl}_3$ [36].

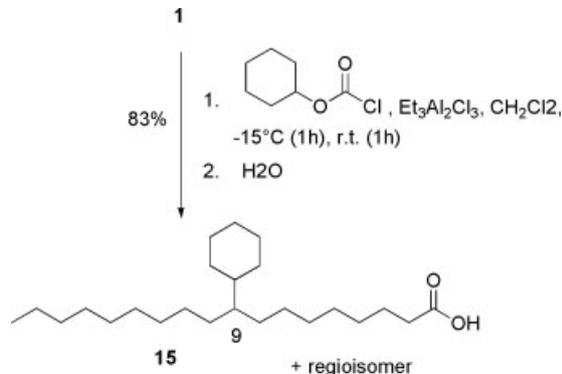


Figure 8. $\text{Et}_3\text{Al}_2\text{Cl}_3$ -induced hydro-alkylation of oleic acid (**1**) with cyclohexyl chloroformate to give 9(10)-cyclohexyloctadecanoic acid (**15**) [36].

and 2-pentyl chloroformate were used. The hydro-alkylation of native oils is also possible and was carried out, e.g., with sunflower oil. All the double bonds included in the oil were isopropylated and the triglyceride structure was preserved.

The isopropylation of methyl ricinoleate (**5a**) afforded the alkylation products in 60% yield as a mixture of two regioisomers, both of which were formed as a pair of diastereomers. The ratio of the diastereomers of the (9)-regioisomer was 7 : 1 and that of the 10-regioisomer was 5 : 3 [36].

The isopropylation of unsaturated fatty compounds with a terminal C,C double bond such as methyl 10-undecenoate (**3a**) has to be carried out in the presence of an equimolar amount of triethylsilane, a more efficient hydride donor, to give methyl 12-methyl-tridecanoate (**16**) in 72% yield (Fig. 9). Under the standard reaction conditions described for oleic acid, the hydro-alkylation occurred with only moderate yield. A product mixture was formed that consisted mainly of oligomers. The reaction of methyl 10-undecenoate (**3a**) and cyclohexyl chloroformate gave methyl 11-cyclohexylundecenoate (**12**), which has been synthesized also in a thermally initiated radical addition reaction (Fig. 4) [29].

Furthermore, fatty acid **3** was treated with linear primary alkyl chloroformates such as 1-butyl chloroformate in the presence of $\text{Et}_3\text{Al}_2\text{Cl}_3$ and Et_3SiH . As expected, the reaction showed the addition of the 2-butyl cation to give 12-methyl-tetradecanoic acid (**17**) in a yield of 72% (Fig. 10).

To introduce the *tert*-butyl group to the C,C double bond of, e.g., oleic acid (**1**), it was necessary to use di-*tert*-butylpyrocarbonate as alkylating agent because of the thermal instability of *tert*-butyl chloroformate. The hydro-alkylation product **18** was formed as a 1 : 1 mixture of the 9- and 10-regioisomers in 81% yield (Fig. 11).

Most interesting, the trialkylated cyclopentane derivatives **19a** and **19b** have been obtained in 82% yield on reaction of methyl stearolate (**6a**) containing a C,C triple bond with isopropyl chloroformate (Fig. 12) [38]. The reaction proceeds

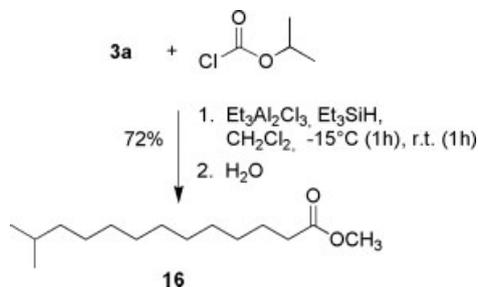


Figure 9. $\text{Et}_3\text{Al}_2\text{Cl}_3$ -induced reaction of methyl 10-undecenoate (**3a**) and isopropyl chloroformate in the presence of triethylsilane to give methyl 12-methyl-tridecanoic acid (**16**) [36].

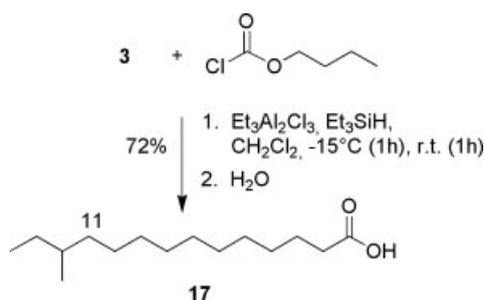


Figure 10. $\text{Et}_3\text{Al}_2\text{Cl}_3$ -induced reaction of 10-undecenoic acid (**3**) and 1-butyl chloroformate in the presence of Et_3SiH to give 12-methyltetradecanoic acid (**17**) [36].

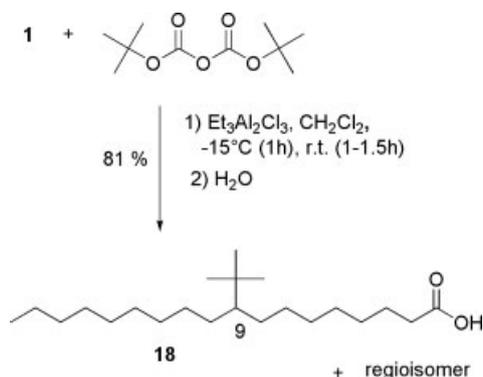


Figure 11. $\text{Et}_3\text{Al}_2\text{Cl}_3$ -induced hydro-alkylation of oleic acid (**1**) with di-*tert*-butylpyrocarbonate to give 9(10)-*tert*-butyloctadecanoic acid (**18**) [36].

by a concerted intramolecular insertion of the primarily formed vinyl cation into a C,H bond to give a cyclopentyl carbenium ion which is trapped by a hydride ion [39].

3.3 Transition metal-catalyzed additions

Behr *et al.* studied the interesting rhodium-catalyzed reaction of methyl linoleate with ethene and observed addition of ethene oligomers to one of the C,C double bonds. Catalytic

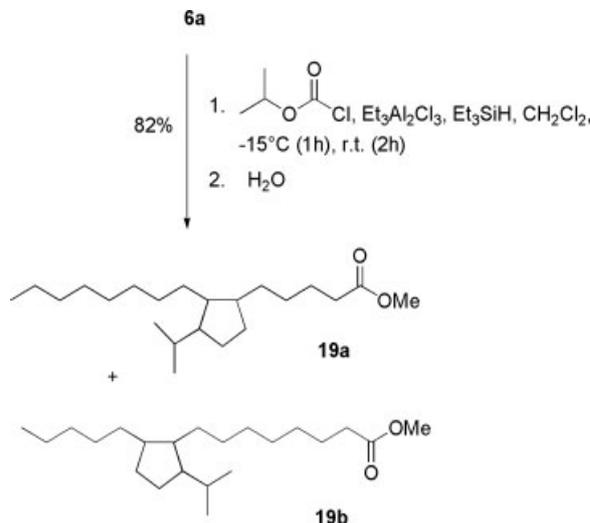


Figure 12. $\text{Et}_3\text{Al}_2\text{Cl}_3$ -induced hydro-alkylation of methyl stearate (**6a**) with isopropyl chloroformate to give the trialkyl-substituted cyclopentane derivatives **19a** and **19b** [38].

hydrogenation yielded 9-, 10-, 12- and 13-alkyl-branched methyl octadecanoate. These branched fatty substances could be synthesized in high yields of up to 98%, and the turn over frequency could be increased from 2 up to 220 h^{-1} [40].

The hydro-alkylation of unbranched 1-alkenes with alkyl halides such as *tert*-butyl bromide in the presence of triethylaluminum and a catalytic amount of Cp_2TiCl_2 was described to yield 2,3-dimethylalkanes [41]. It may be interesting to apply this protocol to fatty compounds.

4 Conclusion

The heterogeneously catalyzed isomerization of unsaturated fatty acids, especially oleic acid (**1**), has been improved considerably during the last years, to give preferentially isostearic acid containing a relatively simple product distribution. The thermally initiated addition of alkanes was applied successfully to ω -unsaturated fatty acids to give cycloalkylated and alkyl-branched fatty acids. The electron transfer-initiated addition of perfluoroalkyl iodides gave perfluoroalkylated fatty compounds with high yields. The $\text{Et}_3\text{Al}_2\text{Cl}_3$ -mediated hydro-alkylation of unsaturated fatty compounds such as acids, methyl esters and native oils using alkyl chloroformates as alkylating agents is a new and interesting method to obtain well-defined oleochemicals with a branched alkyl chain in good yields. With respect to the wide spectrum of applications for these compounds, it should be of interest to modify the reaction conditions to become greener and industrially feasible.

Conflict of interest statement

The authors have declared no conflict of interest.

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