



Fatty ketones from the rearrangement of epoxidized vegetable oils

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ABSTRACT

The rearrangement of epoxidized vegetable oils to produce fatty ketones, catalyzed by acidic resins, is disclosed. The non-microbial production of fatty ketones from epoxidized vegetable oils has not been previously reported. Some of the variables affecting the ketone formation such as acidic strength of the catalyst, temperature and solvent are studied in order to determine the conditions that favor the rearrangement. Epoxidized vegetable oils can be easily transformed to the respective ketones via a rearrangement reaction catalyzed by acidic resins. Other kind of acidic catalysts are active for this reaction if their Brönsted acid sites are accessible to protonate the epoxide. Formation of ketones, from the rearrangement of epoxidized methyl oleate, is favored in the presence of strongly acidic catalysts and enhanced by increasing temperature. Polar-protic solvents increase the ketone yield but decrease the ketone selectivity because they are added to the epoxide ring. The mechanism for the epoxide rearrangement is very likely to take place through a hydride migration to the carbocation generated in the acid-catalyzed epoxide ring opening.

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1. Introduction

Epoxidation of vegetable oils is a commercially important reaction because the epoxides obtained from these renewable raw materials and from their alkyl esters, their transesterification products, have applications in such materials as plasticizers and polymer stabilizers [1,2]. Furthermore, these epoxides can be used as intermediates in the production of a variety of derivatives, because of the high reactivity of the strained epoxide ring. For example, monoalcohols, diols, alkoxyalcohols, hydroxyesters, N-hydroxyalkylamides, mercaptoalcohols, aminoalcohols, and hydroxynitriles could be produced via epoxide ring-opening reactions with suitable reactants [3]. Among these products, it was recently reported the addition of alcohols and organic acids to epoxidized vegetable oils to obtain derivatives that have shown good properties as biocompatible lubricants [4–7].

During our investigations dealing with the production of fatty epoxides and their transformation into other valuable products [4–9] we realized that ketones were produced as by-products, through an epoxide rearrangement reaction. Rearrangement of epoxides to ketones has been reported but for short-chain epoxides such as ethylene oxide and propylene oxide [10–13]. This reaction has been used to obtain important commercial products like

phenylacetaldehydes, methyl isopropyl ketone and campholenic aldehyde from the respective epoxides and using heterogeneous catalysts such as acidic zeolites [14]. Yates [15] reported a method to oxidize olefins to the less substituted carbonyl compounds, involving two steps: hydroboration with borane dimethyl sulfide, followed by oxidation of the resulting alkylboranes with tetrapropylammonium perruthenate and N-methylmorpholine-N-oxide. Only short chain olefins were studied, with the unsaturation in terminal or cyclic position. The reaction was accomplished in ca. 4 h at room temperature. On the other hand, Deshmukh et al. [16] reported a method to convert olefins into the corresponding α -bromo ketones in the presence of 1.1 equivalents each of o-iodoxybenzoic acid and tetraethylammonium bromide. Similarly, Maksimchuk et al. [17] established that the mesoporous metal-organic framework MIL-101 (chromium terephthalate-based mesoscopic metal-organic framework) is an efficient heterogeneous catalyst for the selective allylic oxidation of alkenes with tert-butyl hydroperoxide. They found that the selectivity toward α,β -unsaturated ketones reached 86–93% and the temperature of the catalyst activation strongly affected the ketone yield. Wang and Jiang [18] developed a method for palladium-catalyzed dihydroxylation and oxidative cleavage of olefins (monosubstituted aromatic and aliphatic terminal alkenes, 1,2-disubstituted, and 1,1-disubstituted olefins) with oxygen to produce 1,2-diols, aldehydes, and ketones. Microbial production of ketones from fatty epoxides using *Rhodococcus rhodochrous* and *Nocardia cholesterolicum* [19,20] has been reported. To the best of our knowledge, the

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non-microbial production of fatty ketones from epoxidized vegetable oils has not been previously disclosed. The disclosure of the rearrangement of epoxidized vegetable oils is a very important issue that will help to better understand previous and future experimental results on reactions dealing with these epoxides. For instance, there are many reports using epoxidized oils as reactants where the reactions were monitored by measuring the decrease in the epoxide content, via titration (oxirane value) or infrared spectroscopy. Most of these reports have assumed that the measured decrease in the epoxide content is due to the formation of the desired product and do not take into account the possible ketone formation.

This paper is devoted to this reaction, i.e., the rearrangement of epoxidized vegetable oils to produce fatty ketones. Some of the variables affecting the ketone formation, such as acidic strength of the catalyst, temperature and solvent are studied in order to determine the conditions that favor the rearrangement.

2. Materials and methods

2.1. Materials

Oleic acid methyl ester was used as a substrate (Fuchs Petrolub AG, 97 wt% *cis*-9-octadecenoic acid methyl ester). Amberlyst 15 was purchased from Aldrich, SAC13 was kindly provided by DuPont. Amberlyst 15 is a copolymer of styrene and divinylbenzene (DVB). SAC13 is a composite material made of Nafion nanoparticles entrapped in a silica matrix. Nafion itself is a copolymer of tetrafluoroethene and perfluor-2-(fluorosulfonylethoxy)-propylvinyl ether. All the other reactants were from analytical grade and purchased from Aldrich.

The total amount of Brönsted acid sites in Amberlyst 15 and SAC13 was 4.72 and 0.22 meq H^+ /g respectively, determined by ion exchange with NaCl solution 1.0 M (10 mL per gram of catalyst) and titrating the residual solution with NaOH 0.01 M. Surface area and porosity were measured with a Micromeritics Gemini V employing the BET method, prior to this measurement samples were degassed for 4 h at 100 °C and 10^{-2} Pa.

2.2. Characterization of reaction mixtures

Reaction mixtures were analyzed by gas chromatography on a Hewlett Packard HP 6890 using 60 m of the slightly polar column FS-SE54. Products were characterized by GC-Mass Spectrometry (GC Varian 3400 CX, MS Varian Saturn 3 at 70 eV and electron ionization), infrared spectroscopy (Nicolet Protégé 460, NaCl windows) and 1H and ^{13}C NMR. 1H (300 MHz) and ^{13}C NMR (75 MHz) were recorded in $CDCl_3$ as the solvent using a Mercury-300 BB spectrometer. For 1H NMR spectra, a total of 16 scans were performed with a relaxation delay of 0.100 s and width of 8103.7 Hz. 320 scans were recorded for ^{13}C NMR spectra with a relaxation delay of 0.100 s and width of 19607.8 Hz.

2.3. Catalytic experiments

Oleic acid methyl ester was used as substrate. Epoxidized oleic acid methyl ester was produced following a known procedure [1]. Rearrangement reactions were carried out in round-bottom glass reactors immersed in a heated oil bath at 57 °C. The agitation was performed using a turbine impeller (2 cm radius, 500 rpm) to prevent attrition of the catalyst. Solvents and substrate were kept over a molecular sieve (UOP type 3A) to prevent water contamination that could lead to the hydrolysis of the epoxide. Catalysts were evacuated overnight at 120 °C under high vacuum and kept under argon atmosphere. Epoxide and solvent were mixed for 15 min at the desired temperature, then the catalyst (10% weight with respect

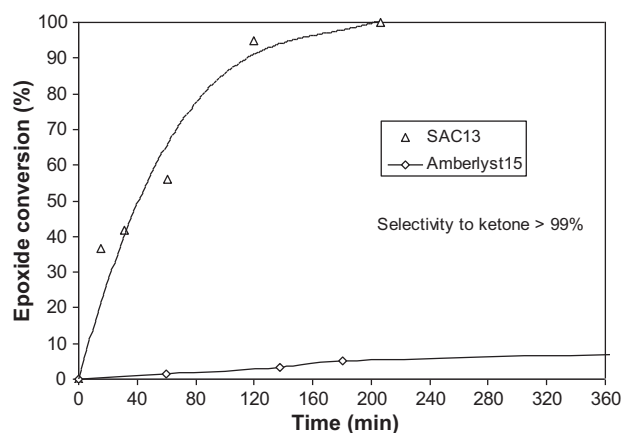


Fig. 1. Effect of the catalyst acid strength on the ketone formation rate from epoxidized methyl oleate. Epoxide/catalyst = 10 g/g, temperature = 70 °C.

to the epoxide) was added. To investigate the effect of stirring speed on the three-phase reaction system, reactions were carried out over a range of stirring speeds (100–1000 rpm). It was observed that the epoxides conversion increased with the stirring speed, but beyond 500 rpm there was no appreciable change in the rate of reaction. Therefore, all the subsequent experiments were carried out under a stirring speed of 500 rpm to ensure that there was no mass-transfer limitation in the liquid phases. Data plotted in the accompanying figures correspond to the means of triplicate experiments with a relative standard deviation <5% in all cases.

3. Results and discussion

Experiments on the rearrangement of epoxidized methyl oleate were carried out to analyze the effect of the catalyst's acid strength, reaction temperature and solvent on the epoxide conversion and ketone yield. Fig. 1 shows the results with the first variable, i.e. acid strength of the catalyst.

The catalyst SAC13 (13% Nafion® entrapped in silica) is quite better than the catalyst Amberlyst15 for the ketone production. At 70 °C, ca. 3.5 h are required for complete epoxide conversion on SAC13 while Amberlyst15 needs ca. 30 h to completely convert the epoxide at 100 °C. SAC13 is a very strong acid, which explains its superior activity; Hammet acidity and NMR of mesityl oxide (Table 1) indicate that the acidity of this catalyst is equivalent to 85% sulfuric acid solution, while the acidity of Amberlyst 15 is equivalent to 45% sulfuric acid solution. This fact is a consequence of the fluor atom in the Nafion resin (component of SAC13), which owing its high electronegativity increases the dissociation of the acidic proton.

When different temperatures were studied, the results shown in Figs. 2 and 3 were obtained for the epoxide rearrangement on Amberlyst15 and SAC13, respectively. It is clear that the temperature plays a crucial role on the ketone formation rate, which is favored by increasing the temperature. If the ketone formation is to be minimized then mildly acidic catalysts, like Amberlyst15, and temperatures lower than 70 °C have to be used. When the catalyst is strongly acidic (SAC13) the ketone formation is appreciable even at temperatures as low as 50 °C. The reaction order was estimated from data of Figs. 2 and 3. By plotting $-\ln(1 - \eta)$ vs. t , where η is the conversion and t the reaction time, it was found that the reaction exhibits the first order kinetics typical for intramolecular (rearrangement) reactions. This result is supported by the high values obtained for the correlation coefficients (R^2), which were higher than 0.96 in all cases (for both catalysts at 50, 70 and 100 °C). Rate constants (k) and correlation coefficients (R^2) are shown in Table 2.

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