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Bismuth(III) Trifluoromethanesulfonate Catalyzed Ring-Opening Reaction of Mono Epoxy Oleochemicals To Form Keto and Diketo Derivatives

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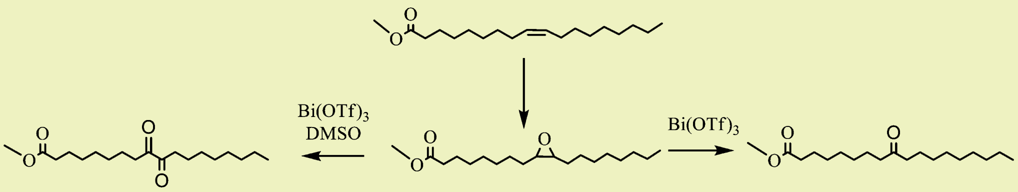

ABSTRACT: Using a catalytic system, methyl oleate is transformed into long-chain keto and diketo derivatives via an epoxide route. Methyl 9(10)-oxooctadecanoate and methyl 9,10-dioxooctadecanoate were made by a ring-opening reaction of epoxidized methyl oleate using bismuth(III) trifluoromethanesulfonate (bismuth triflate) catalyst. Lower reaction temperatures favor the ketone, whereas higher temperatures are required to produce the diketone. The second synthesis also requires the use of dimethylsulfoxide to serve as an oxygen atom donor and that reagent also is needed to keep the catalyst in its active form. The ketone was also evaluated as a lubricity additive in soybean oil, where it was found that it had a minimal effect in reducing wear and did not improve oxidative stability. This drawback, while not good in lubricant formulations, is desirable in many applications such as paint and linoleum production. Also, the structure of the ketone could make it a desirable dielectric fluid, where the water sequestering ability of the carbonyl group would be desirable. Overall, this is an effective synthesis of promising materials, with high biobased content, useful for industries of the future.

KEYWORDS: *Bismuth(III) trifluoromethanesulfonate, Bismuth triflate, Diketone, Long-chain dioxo compound, Epoxidized methyl oleate*

■ INTRODUCTION

For the chemical industry to achieve sustainability, a broad range of strategies are required. Some of those strategies have been put forth a decade ago in the well-cited 12 principles of green chemistry.[1,2] These principles include the use of catalytic reagents, maximizing the incorporation of reagents into the final product, and using a feedstock of renewable material whenever practical. Much progress has been made in these areas, especially in the use of biobased sources to produce modern chemicals and materials.[3,4] One area of past focus has been on the industrial use of soybean oil, which has yielded products in the ink,[5] lubricant,[6] and polymer industries.[7−10] However, problems that have come along with this biobased sourcing are the lack of catalytic reactions and the environmentally unfriendly nature of many of the stoichiometric reagents needed to form these products. For example, the ring-opening of epoxidized soybean oil has been done using boron trifluoride dietherate in dichloro methane[11] or with a ~25 wt % loading of perchloric acid.[12]

Ketones of soybean oil are highly sought after for several purposes. For example a large oil company has filed for a patent in which they are favored for formulation of lubricants, hydraulic fluids, and dielectric fluids.[13] In this latest application, the value of the incorporation of ketone structures is especially evident given the literature mechanism for the insulation breakdown of biobased dielectric fluids.[14] In that mechanism, the carbonyl is essential for the sequestration of water in the oil, making it a much more useful fluid. However, formation of these highly desired ketone containing oleochemicals are problematic. Oxidations of soybean oil are environmentally unfriendly, with stoichiometric osmium tetroxide and potassium permanganate being the most published routes.[15−19]

Trifluoromethanesulfonic acid (triflic acid) has been shown to be an effective reactant in a variety of chemical reactions,[20,21] where its combination of superacidity and weakly coordinating ionic behavior provides unique conditions. It has been used for the chemical modification of soybean oil and oil-based acids in reactions such as dimerization,[22] phenolation,[23] and in the formation of estolides and lactones.[24]

Bismuth(III) trifluoromethanesulfonate (bismuth triflate) has found recent use in a variety of chemical reactions including the poly condensation of diols and anhydrides,[25] the transesterification of triacylglycerols and fatty acids using microwave technology,[26] the polymerization of caprolactone,[27] the production of vinyl chlorides,[28] and most interestingly, in the catalyzed cyclization of a molecule with both epoxy and olefin groups.[29] There is also interesting debate as to the actual active species in some of these reactions where metal involved catalysis or "hidden bronsted acid" catalysis are alternative

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hypotheses for the dominant mechanism.[30] Specifically of interest here is the use of bismuth triflate in the ring-opening reactions of epoxides, which were demonstrated in aryl systems,[31,32] to form a variety of carbonyl-containing ketone and aldehyde compounds. This is similar to some chemistry performed using stoichiometric reagents, such as boron trifluoride-diethyl etherate[33] or lithium perchlorate-diethyl ether,[34] and through Wacker type chemistry using palladium.[35,36] However, the bismuth chemistry has the advantage of being both cheap, catalytic, and also versatile enough to catalyze a similar reaction system where diketones can be produced.[37,38]

This manuscript reports the extension of this chemistry into the modification of agriculturally based substrates by transformation of epoxidized methyl oleate (EMO) into ketone and diketone materials. The ketone was also evaluated as an additive in a soybean oil lubricant.

■ MATERIALS AND METHODS

Reagents. Methyl oleate (Nu-Check Prep, Elsyian, MN, >99%), methyl linoleate (Nu-Check Prep, Elsyian, MN, >99%), methyl ricinoleate (Nu-Check Prep, Elsyian, MN, >99%), soybean oil (KIC Chemical, New Paltz, NY, RBD grade), hydrogen peroxide as a 30% aqueous solution (Sigma-Aldrich, St. Louis, MO, A.C.S. Reagent), formic acid (Sigma-Aldrich, St. Louis, MO, 96%, A.C.S. reagent), n-heptane (EMD, Gibbstown, NJ, Omnisolve), sodium chloride, (Fisher, Fairlawn, NJ, A.C.S. Reagent), sodium bicarbonate (Fisher, Fairlawn, NJ, A.C.S. Reagent), bismuth triflate (Strem Chemical, Newburyport, MA, 98%), dimethyl sulfoxide (Fisher, Fairlawn, NJ, A.C.S. spectrophotometric grade), 2,6-dimethylbenzoquinone (Sigma-Aldrich, St. Louis, MO, 99%), magnesium sulfate (J.T. Baker, Phillipsburg NJ, 99.8%), poly alpha olefin synthetic fluid (Synfluid Polyalphaolefin, PAO 8, Chevron-Phillips, Woodlands, TX), group III mineral oil (UCBO 7R, Chevron, San Ramon, CA), hexadecane (Aldrich, St. Louis, MO, 99% anhydrous), toluene (Sigma-Aldrich, St. Louis, MO, >99.5% ACS reagent), and zinc dialkyl dithiophosphate (RheinChemie, Leverkusen, Germany, Additin RC3180) were used as received. Molecular sieves (Sigma-Aldrich, St. Louis, MO, 4 Å) were dried at 100 °C under vacuum overnight before use.

Instruments. The gas chromatograph−mass spectrometer (GC-MS) used was an Agilent (Santa Clara, CA) 7890A gas chromatograph equipped with a 7683B series injector, a 5975 C quadrapole mass detector, and an Agilent/J&W DB35-MS (30m × 320um, 0.25um film thickness) column. Injections of 1 uL were made using a 50:1 split with the temperature program: 40 °C held for 3 min, ramped 25 °C min^{-1} to 190 °C, then at 10 °C min^{-1} to 240 °C, held for 5 min, then ramped 25 °C min^{-1} to 340 °C and held for 6 min. Agilent MSD Enhanced Chemstation version E01.00.237 was employed for instrument control and data processing. The detector was run in the electron impact mode and set to scan for m/z ratios from 50 to 500 Da. Samples of ∼10 mg were diluted in 1 mL of heptane.

Nuclear magnetic resonance (NMR) spectroscopy was performed on a Bruker (Boston, MA) Avance 500 NMR spectrometer operating at 125 MHz to give appropriate ^{13}C spectra. Peaks were referenced to tetramethyl silane 0.00 ppm. Simulations of ^{13}C NMR spectra were performed by ACD/Laboratories 6.00 ACD/CNMR predictor software.

Wear testing was performed on a Falex Multi-Specimen Friction and Wear instrument, controlled by Falex 330 Software. The instrument was set in a four-ball configuration according to ASTM method D-4172 at a temperature of 75 °C, a speed of 1200 rpm, a test duration time of 60 min, and a load of 40 kg. The specimen balls (52100 steel, 12.7 mm diameter, 64−66 Rc hardness, and extreme polish) were thoroughly cleaned with dichloromethane and hexane before each experiment. Wear scars diameters were measured using a microscope (6SD with L2 fiber-optic light, Leica, Bannockburn, IL) equipped with a digital microscope camera (PAXcam, Vill Park, IL) controlled by Pax-it 6.4 software. On each ball, the scars were measured along perpendicular x- and y-axes, and the value reported value for a given experiment was the mean average of the six measurements. Replicate experiments were performed and standard deviations were calculated.

In order to determine oxidation stability, a Q10 (TA Instruments, New Castle, DE) pressurized differential scanning calorimeter (PDSC) was used. This method has been shown to be a convenient and reliable measure of oxidation of oleochemicals.[39] The software employed was Q Advantage software version 2.8.0 ran on an IBM ThinkCentre Pentium 4 processor with a 3.0 GHz processor. In aluminum pans with a pinhole lid, samples of ∼2 mg were used, and air pressure of 1379 kPa was introduced and kept over the sample throughout the run. A temperature ramp rate of 10 °C min^{-1} was utilized, and an oxidation onset temperature was determined by the start of the large exothermic reaction peak.

Synthesis of Epoxidized Methyl Oleate (EMO). Following a modified literature method,[40] 150 g of methyl oleate and 75 g of formic acid were placed in an ∼500 mL Parr glass reactor, which was cooled in an ice bath. A total of 120 mL of 30% hydrogen peroxide was added to the reactor dropwise with continuous stirring of the solution. The ice bath was removed but returned whenever the reaction temperature approached 30 °C. Reaction progress was monitored by taking aliquots of the reaction, dissolving in heptane, and analyzing by GC-MS. The reaction was complete in 8 h, where the product was isolated by dissolving in 50 mL heptane, separating from the aqueous layer, then shaking the organic layer several times with a total of 100 mL saturated aqueous sodium bicarbonate solution to neutralize residual acid, then three times with 100 mL of deionized water, and finally, with 100 mL saturated sodium chloride solution to aid drying. The final EMO yield was 136.4 g and had identical spectra to those reported earlier.[41] Epoxide content of the material, as determined by integration of ^{1}H and ^{13}C NMR, was as expected, demonstrating complete reaction.

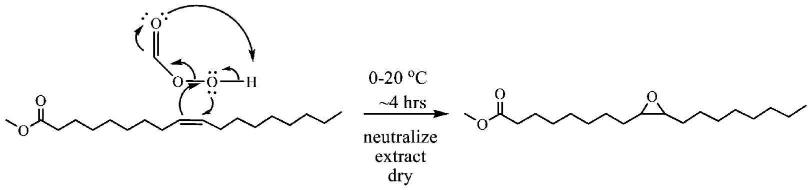
Synthesis of Methyl 9(10)-oxooctadecanoate. The catalytic ketone reactions were prepared in a model IL2GB nitrogen filled inert atmosphere glovebox (Innovative Technologies, Amesbury, MA), where the catalyst and EMO were weighed into a dried 10 mL vial along with a small stir-bar. Typically, 3.00 g of EMO and 0.060 g of catalyst were used, and the septa-capped vial was heated to temperature from 30 to 90 °C, depending on the reaction, in a model 18970 Reacti-vap (Pierce, Rockford, IL). Utilizing a Schlenk line, a needle with argon flow was placed into the reactor to maintain the inert atmosphere and atmospheric pressure.

After the reaction, the product was taken up in heptane and in a separatory funnel and washed with saturated sodium bicarbonate solution, water, and saturated sodium chloride. The heptane layer was dried over magnesium sulfate, vacuum filtered, then dried under vacuum by rotary evaporation at 40 °C for 3 h.

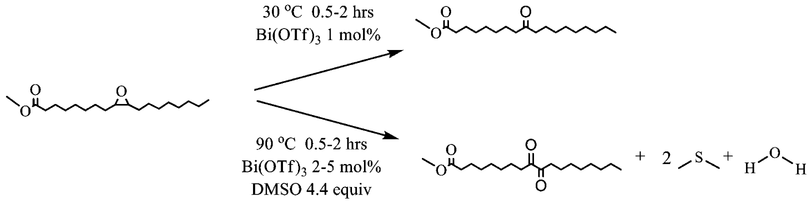
Representative isolated yield is 2.67 g (89% yield) of the two isomers of the product that were characterized and confirmed by mass spectrometry and NMR spectroscopy: ^{13}C NMR (125 MHz, $CDCl_3$): δ 211.6, 211.5 (C═O), 174.24, 174.20 (OC═O), 51.4 (H_3CO), 42.8−42.7 (C−C═O), 34.1 (C−C═OO), 31.9−14 many signals. This spectrum was similar to that predicted from simulation. Of note is that the presence of the potential side product ketal (Scheme 3) is evident, in samples where it was formed, from a pair of ^{13}C NMR signals at δ 110.9. Other side slight impurities were noted by small signals in the hydroxy or ether region of between δ 81−70. The product was miscible with a wide variety of hydrocarbons including heptane, hexadecane, toluene, Group III mineral oil, and poly alpha olefin synthetic fluid.

Synthesis of Methyl 9,10-dioxooctadecanoate. The diketone was prepared in a similar manner to the ketone, with the catalyst and EMO added to the vial in the inert atmosphere glovebox, typically, 3.0 g of EMO and 0.060 g of catalyst. The DMSO was injected through the septa, and the reaction vials were heated to temperature in a Reacti-vap. Reaction workup was similar to the ketone as well, except an initial filtration was necessary to remove a small amount of solid material. The material was isolated as a mixture, 35% diketone and 65% ketone, which were not separated but characterized in the

Scheme 1. Typical Synthesis of EMO from Methyl Oleate Utilizing In Situ Performic Acid from Formic Acid and Hydrogen Peroxide



Scheme 2. Reaction of EMO with $Bi(OTf)_3$ with and without DMSO[a]



[a] In the ketone product, only the 9 isomer is shown.

mixture. The GC-MS signals and NMR spectroscopy of the compound gave good agreement with both simulated data and with the values reported in the literature.[18] The ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.1, 200 0.5 (C=O), 174.23, 174.21 (OC=O), 51.4 (H_3CO), 42.8–42.7 (C–C=O) 34.0 (C–C=OO), 31.9–14 many signals.

Wear Reduction Experiments. The lubrication evaluation was performed by blending 0.5–1 wt % solutions of the ketone in soybean oil. The solutions were stirred for at least 12 h to ensure complete mixing, although no solubility problems were observed. Both methyl oleate and zinc dialkyl dithiophosphate were used as comparative samples. The blends were analyzed by for wear reduction using the four-ball test.

Oxidation experiments. The soybean oil blends of the ketone and of methyl oleate were evaluated using the PDSC method described above. Neat samples of these two materials, as well as methyl linoleate and methyl ricinoleate, were also analyzed using the same method.

■ RESULTS AND DISCUSSION

Epoxidation of methyl oleate with a peracid system to form EMO has been known for many decades.[40,42,43] A modified version of this synthesis (Scheme 1) has been used extensively in literature reports,[44,45] to produce a high quality starting material for further derivatization into esters,[46,47] ethers,[48] amines,[6] and cyclic carbonates.[41]

Bismuth(III) compounds are well-known for their usefulness in organic oxidations,[49] such as the cleavage of styrene epoxide by bismuth mandelate.[50,51] The ring-opening reaction of EMO with $Bi(OTf)_3$ was studied at various temperatures (Scheme 2). At the convenient temperature of 30 °C, it proceeds rapidly with 1 mol % catalyst loading giving complete conversion in less than 2 h (Figure 1). The 9 and 10 isomers are expected to form in nearly equal quantities due to equal chemical reactivity. Possible side reactions that would involve the cleavage of the bond between carbon 9 and carbon 10 were not observed indicating the suitability of these conditions. The synthetic method applied here produced a high yield of the desired product that was characterized by GC-MS and NMR spectroscopy and used for the lubricity evaluation. An important observation was that if the reaction mixture or the catalyst was not kept dry, the yields were lower and less reproducible, putatively from inactivation of the catalyst by water. The possibility of using multiepoxy substrates was also considered but avoided due to the tendency of those materials to form furan structures instead of the desired ketones.[52]

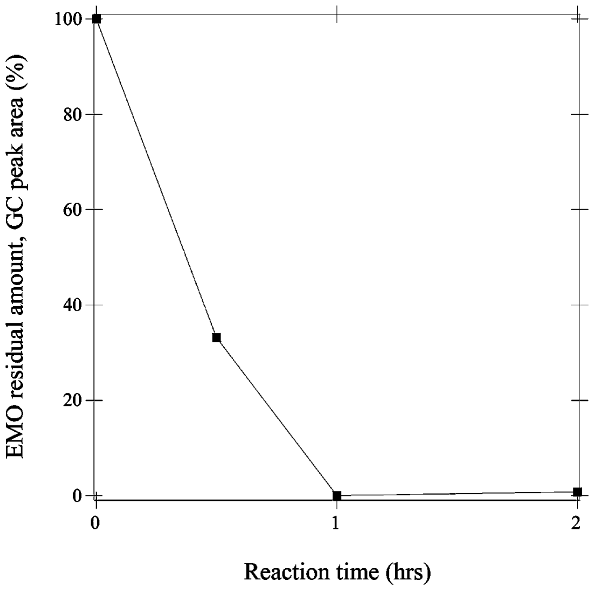
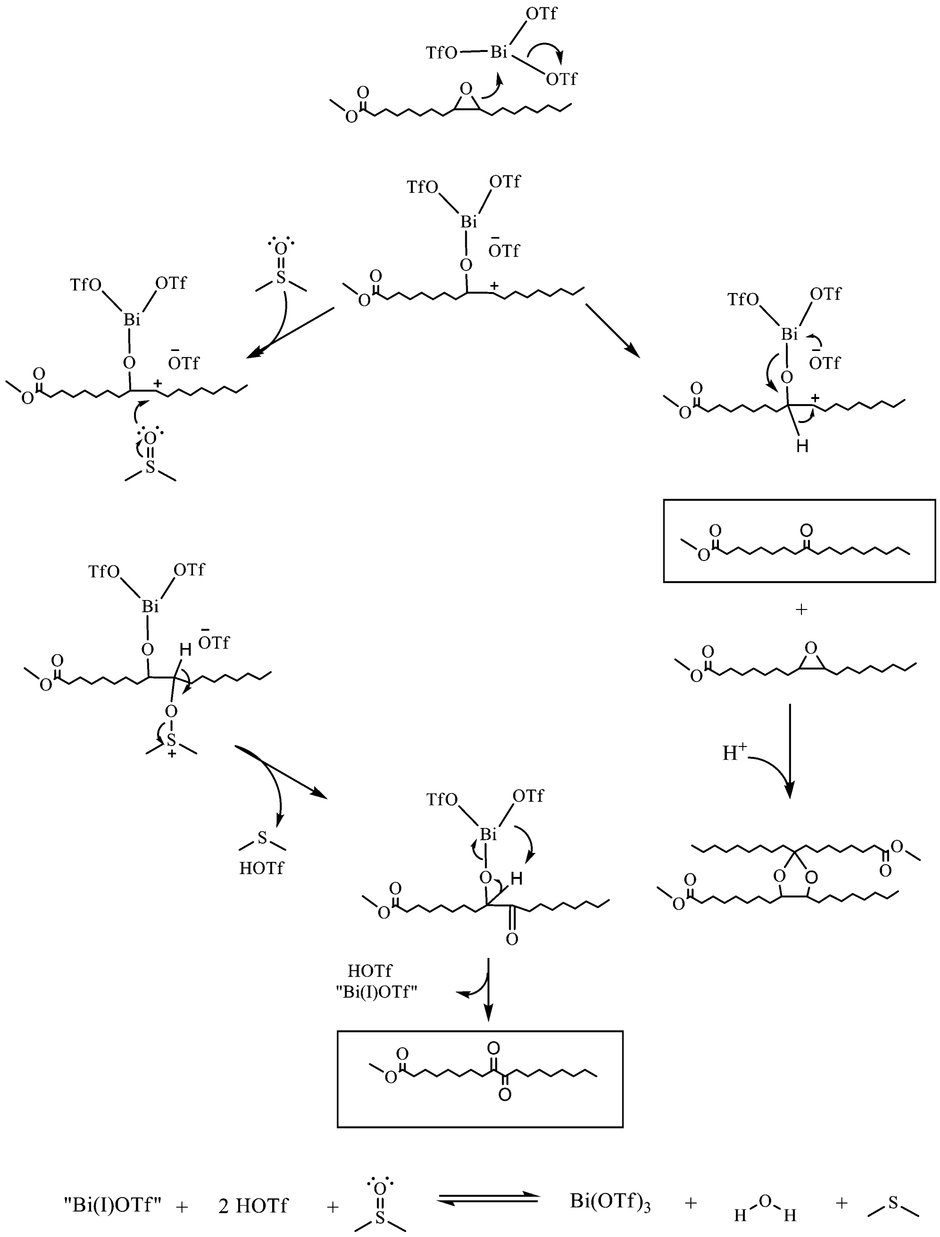


Figure 1. Conversion of EMO to the ketone product at 30 °C with 1 mol % $Bi(OTf)_3$ vs time.

When the reaction was run at the higher temperature of 90 °C, an interesting side product was produced. Under these conditions the formation of a cyclic acetal was observed, in ~22% yield. This side product remained stable during purification and, hence, could be detected in the isolated product. Looking at a possible mechanism (Scheme 3),[32,38] it appears that the acidity of the system is sufficient to catalyze the coupling of a product ketone with the epoxy group of the starting material. In other words, protecting group chemistry is at play in this system. Although prior work teaches that EMO sourced ketals have many interesting properties,[53] in this system, the side reaction only leads to ~22% lower yields.

The vicinal diketone system also proved to be interesting (Scheme 2). Within the literature, diketones of this type have been prepared previously by a couple of different approaches. The oxidant used on these alkene substrates range from

Scheme 3. Catalytic Reaction of EMO to Ketone and Diketone Products



potassium permanganate[18] to ruthenium tetroxide.[54] Diols are also used as substrates where they undergo oxidation with ruthenium oxides[54] or N-bromosuccinimide in carbon tetrachloride.[55] These methods are not catalytic, and these oxidants are not environmentally friendly.

This system has the advantage of utilizing a catalytic amount of the much more environmentally benign bismuth reagent with DMSO serving as the oxygen donor. Initial experiments utilizing 1.5 equivalents of DMSO at 30 °C were tried with 1% catalyst loading, the same temperature and loading used to form the ketone, and less than 5% of the diketone product was synthesized, as observed by GC-MS and confirmed by ^{13}C NMR spectroscopy. Instead, what was synthesized was a mixture of ketone and unreacted starting material. However, utilizing 90 °C as a reaction temperature, ~8% yield was observed (Figure 2), which could be further improved to 29% by the increase of the catalyst concentration to 5 mol %. Further increases in temperature to 130 °C, the bubbling of dry O_2 during the reaction, the addition of 2,6-dimethylbenzoquinone, or the addition of 4 Å molecular sieves were each ineffective in improving the reaction yield. What was effective was increasing the added amount of DMSO to 4.4 equivalents, where 38% yield was possible. This demonstrates the dual roles of that compound in the catalytic cycle where it serves as both the oxygen donor and in the reformation of the active catalyst. Further increases in DMSO concentration to 15 equivalents did not improve the reaction yield perhaps due to changes in the rates of other reaction steps. Catalyst recycling could make the new process even more advantageous, although that was not undertaken here. Alternatives to DMSO are of interest but were not discovered in this study. Overall, this reaction is advantageous over previous state of the art in use of reagents, time, and number of steps. Literature syntheses of compounds of this type use potassium permanganate or acetic anhydride in the initial synthesis, which must be reacted for 72 h.[18] Extraction, recrystallization, and cold filtering are required next.

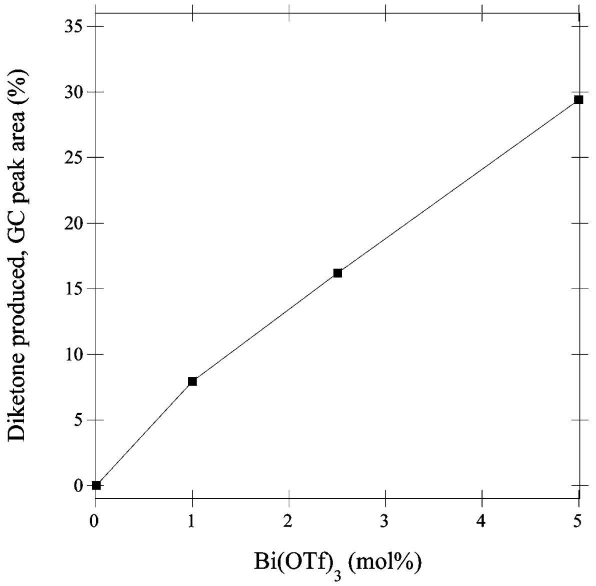


Figure 2. Production of diketone in the presence of DMSO for 2 h at 90 °C with various catalyst loading.

Earlier work also sometimes requires a further purification utilizing pyridine and hydrochloric acid.[56] Literature preparations also have reported yields of only 40−50%.

As a potential application of these materials, the ketone was tested as a lubricant additive in a soybean oil lubrication system. The results show that the ketone was able to slightly reduce the scar diameter (Figure 3) observed in the four-ball wear scar test when a concentration of 1 wt % was used. This effect was on the order of that observed in a control experiment in which ordinary methyl oleate was used as the lubricant additive. However, results also show that this material was not as effective as the commercial product, zinc dialkyl dithiophosphate, indicating that the product's use as an antiwear additive is somewhat limited.

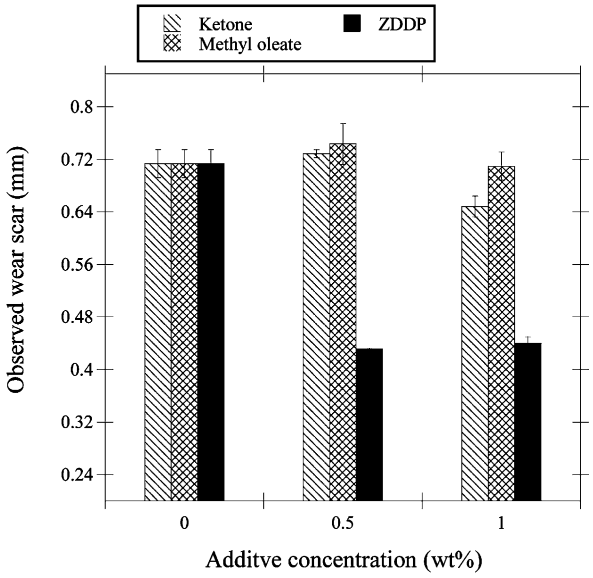


Figure 3. Effectiveness of the ketone as a lubricant additive in ordinary soybean oil, compared to methyl oleate and also to the commercial product, zinc dialkyl dithiophosphate (ZDDP).

The oxidation stability of the oil in the presence of the ketone compound, measured by pressurized differential scanning calorimetry (Table 1), show poor performance of the ketone, which actually made the low oxidative stability of the soybean oil even worse. Because the oxidation of vegetable oils is quite complicated, the oxidation of the ketone was more closely by looking at the oxidation of the product directly.[57] The ketone stability lies between that of the monounsaturated material, methyl oleate, and the diunsaturated material, methyl linoleate. It is also slightly less stable than a material that contains one unsaturation and one hydroxyl group, methyl ricinoleate. Because the oxidation onset is an important factor in the performance of many industrial fluids, this research shows the limits where the ketone is expected to exhibit good performance.

Table 1. Oxidation Onset Temperature of Soybean Oil with Additives Studied by Pressurized Differential Scanning Calorimetry

	oxidation onset temperature of soybean oil (°C)	
additive (% wt)	ketone	methyl oleate
0	175 (±0.8)	
0.5	164 (±0.2)	170 (±0.6)
1	163 (±1.2)	169 (±0.6)

Table 2. Oxidation Onset Temperature of the Ketone Product Compared to That of Common Unsaturated Methyl Esters[a]

	oxidation onset temperature (°C)
methyl oleate	178 (±0.9)
methyl linoleate	140 (±0.8)
methyl ricinoleate	173 (±0.3)
ketone product	167 (±2.5)

[a]The diketone product mixture did not display a clean oxidation onset temperature, so a proper comparison was not possible.

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Notes

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The authors declare no competing financial interest.

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