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A Green Route to Petroleum Feedstocks: Photochemistry of Fats and Oils

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ABSTRACT: We demonstrate that it is possible to generate long chain olefins from different fat sources, i.e., animal fat, vegetable oils/fats, and waste cooking oil. Our results show that, independent of the source of fat, irradiation using UV−C light produces 1-tetradecene, 1-hexadecene, 1,7-hexadecadiene, and 1,7,10-hexadecatriene. Fats undergo transesterification with primary alcohols rendering the corresponding esters. These, following irradiation, produce the olefins described, in addition to lower molecular weight esters.

KEYWORDS: *Photochemistry, Fats, Oils, Fatty acids, Triglycerides, Norrish type II reaction*

INTRODUCTION

The increased demand for sustainable development, together with the ever fluctuating cost of petroleum-based raw materials, makes the development of new processes that provide more economical and greener alternatives to conventional methods in forming base feedstocks for commercial polymers imperative. One approach, the development of the *biodiesel* industry, generates biofuel from vegetable/animal oil sources.[1−8] Another development is that of biobased routes that generate carbon-containing building blocks, some of which may be more conventionally obtained from petroleum derivatives.[9−25]

We report the use of animal fats, tallow, and lard as synthetic raw materials for preparation of simple organic starting materials and products that until now have been made from petroleum feedstocks. We employ animal fats as reagents in a unique photochemical route to low molecular weight products using a new methodology that will provide an alternative greener route to the synthesis of both long chain olefins and glycerol.[26,27] Fats, both animal and vegetable, are composed of triglycerides containing saturated and unsaturated fatty acids. Although the percentage composition of each fatty acid varies from one fat to another, the fatty acids found are generally the same. For example, lard is composed of esterified palmitic acid (26%), stearic acid (14%), oleic acid (44%), and linoleic acid (10%). Tallow has a similar composition but a differing ratio of fatty acids: palmitic acid (24%), stearic acid (19%), oleic acid (43%), and linoleic acid (3%). Our method involves irradiation of animal and vegetable fats with UV light to produce long chain alkenes, dienes, trienes, and glycerol as the byproduct. Independent of the source of fat, irradiation of these triglycerides with deep UV light results in the products of Norrish type II cleavage.[28−31] Although extensively studied for ketone systems, to the best of our knowledge, this is the first report that uses this reaction with animal and vegetable fat sources. Product glycerol can be transformed through catalytic processes into acrylic acid and other essential raw materials for the plastic industry.[9−13]

EXPERIMENTAL SECTION

General Procedures and Materials. Lard and olive oil were purchased from Giant Eagle and irradiated in their original form unless otherwise noted. Canola oil was purchased from Kroger and used as obtained. Waste cooking oil (canola) was used obtained as the residue from a small deep fryer for at least three cycles before irradiation (sediments were separated using a cheesecloth). Tallow was obtained from beef fat by “cooking” the fat at medium heat on a stove, separating the grease from the tissue, and allowing it to cool at room temperature. For irradiation, 2 g of the corresponding fats/oils were dissolved in 1 mL of hexane and/or ethanol. Hexane and ethanol were used as obtained without further purification. 1-Tetradecene, ethyl palmitate, glyceryl tripalmitate, glyceryl 1,3-dipalmitate, glyceryl monopalmitate, glyceryl trioleate, benzyl alcohol, cyclohexyl methanol, tetrahydrofurfuryl alcohol, and (*R*)-(−)-2,2-dimethyl-1,3-dioxolane-4-methanol were obtained from Aldrich and used as received. Transesterification reactions were carried out following reported procedures.[1−8] Irradiation was performed using either a Hanovia Hg lamp immersed in a quartz sleeve or a Fusion system equipped with a H-bulb. GC-MS analysis was performed in a Shimadzu QP-2010 SE. UV−vis absorption spectra were measured with a Cary 50 Bio spectrophotometer accurate to ±2 nm. [Oxygen concentrations in most solvents approach 2 mM. With high intensity UV light, as is the case with the Fusion lamp system, free radicals generated early in the reaction are sufficient to consume all the oxygen. Rates of diffusion are not sufficient to overcome these anaerobic conditions, and the reactions—for all intents and purposes—occur in the absence of oxygen.]

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Scheme 1. Structure of Triglycerides and Photoproducts

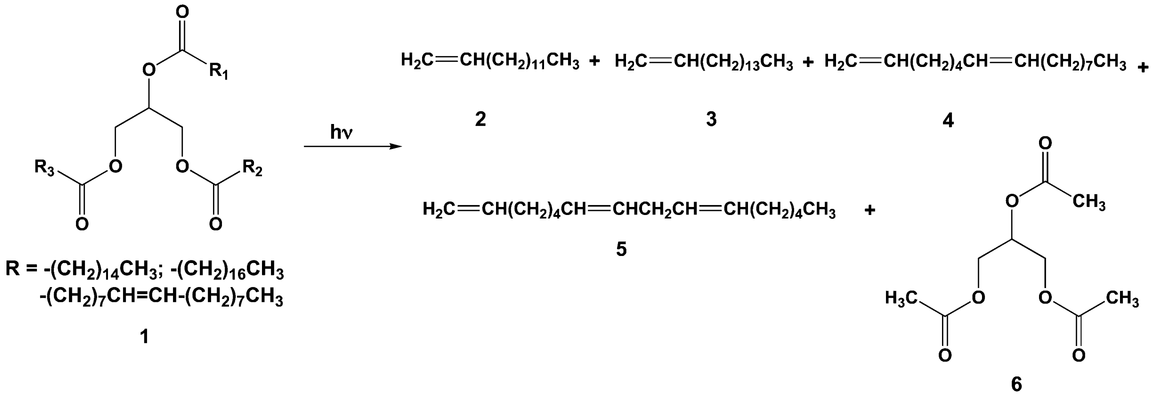
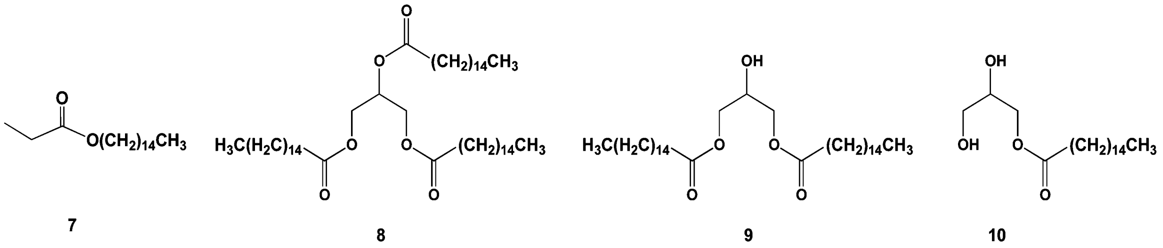


Table 1. Photoproducts and Yields Obtained after Irradiation of Fats and Model Systems in Hexane

	products (% yield)			
fats and/or model systems	1-tetradecene	1-hexadecene	1,7-hexadecadiene	1,7,10-hexadecatriene
lard	5	12	7	7
tallow	10	9.8	13	n/a
ethyl palmitate	34	n/a	n/a	n/a
glyceryl tripalmitate	36	n/a	n/a	n/a
glyceryl dipalmitate	34	n/a	n/a	n/a
glyceryl monopalmitate	32	n/a	n/a	n/a

Scheme 2. Structures of Model Systems



RESULTS AND DISCUSSION

Different fat samples were irradiated in a quartz cuvette using two different light sources that produced deep UV irradiation. Among the samples tested were lard, tallow, olive oil, canola oil, and waste cooking oil (canola). The photochemical reactions, carried out in solvents that were not degassed,[1] were followed by GC-MS to determine times of reactions and yields. For the yields, calibration curves using 1-tetradcene and ethyl palmitate were performed. The response of the instrument did not change for these two compounds. Structures of products were determined by comparing GC-MS spectra to standards and/or the compound library. Reactions proceed more slowly with a Hanovia Hg lamp, while a Fusion system equipped with an H-bulb with a higher intensity of UV−C light shortened reaction times. [It does not escape our attention that irradiation with deep UV light, followed by GC/MS analysis, is an excellent way to determine glyceride compositions in fats.]

Lard and tallow have similar triglyceride compositions (Scheme 1). Oleic acid is present in the highest percentage (33−44%), followed by palmitic (26%) and stearic acids (14−18%). Linoleic acid (10%) is only observed in lard. Olive oil and canola oil have a low content of saturated fats (i.e., palmitic and/or stearic acids). Irradiation of lard in hexane and ethanol produced 1-tetradecene (2), 1-hexadecene (3), 1,7-hexadecadiene (4), and 1,7,10-hexadecatriene (5). These photoproducts can be predicted from the Norrish type II cleavage (γ-H abstraction) at the carbonyl moiety.[28,30,31] Irradiation in the Fusion system could continue for 6−8 h before a decline in yield. Each photoproduct was produced in about 10% yield.[2]

A similar irradiation of tallow produced just the first three products because tallow does not have an appreciable amount of glyceryl linoleate in its composition. The irradiation times required and yields for tallow were similar to those observed for lard. Irradiation of olive oil produced mainly 4 with a small percentage of 2 and 3, while canola oil and its wasting cooking oil only showed the formation of 4. Though not observed, a byproduct of these photoreactions should be glyceryl triacetate (6). The absence of this product and low yields are an indication that not all the functions on the triglyceride are undergoing photochemical cleavage. This was further demonstrated by the presence of mono- and 1,3-diglycerides in the GC-MS analysis, suggesting that C-2 in the triglyceride has a higher reactivity.[32] Another possibility is that saturated fatty acids (palmitic and stearic) are more reactive than unsaturated fatty acids (oleic and linoleic). Control experiments were performed using ethyl palmitate (7), glyceryl tripalmitate (8), glyceryl 1,3-dipalmitate (9), and glyceryl monopalmitate (10), following the procedure outlined earlier (Scheme 2). In each case, the photoproduct was 1-tetradecene. Lower molecular weight ester fragments, presumably formed by the α-cleavage of the fatty acid from the triglyceride unit that decompose when analyzed, were not detected using our experimental conditions. Irradiation of (7) for 1.5 h in both hexane and ethanol produces 1-tetradecene in 34% yield. A 36% yield was observed when glyceryl tripalmitate was irradiated for 1.5 h, perhaps further evidence that only one of the positions undergoes cleavage. Glyceryl 1,3-dipalmitate and glyceryl monopalmitate exhibit slightly lower yields, 34% and 32% respectively, relative to their triglyceride counterpart. A somewhat higher reaction time (2 h) was required as well. These yields, although not sufficient for commercial use, are 3-fold higher than the yields observed for lard and tallow. Glyceryl trioleate was used as a control for the unsaturated fatty acids; however, irradiation for 2 h yielded 4 in only 1%. These data support the hypothesis that saturated fatty acids are more reactive toward the photochemical cleavage than the unsaturated ones and reactivity depends on the position of the fatty acids on the triglyceride unit.

Reactions were followed using UV−vis spectroscopy as well. Throughout irradiation, the formation of an absorption band at 284 nm was observed (Figure 1), independent of the solvent and fat source used. The nature of this band is unclear, and no species other than the olefins were observed in the GC-MS.

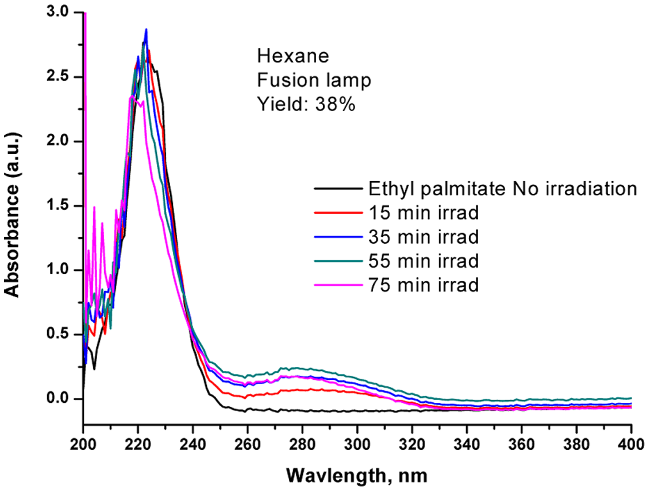


Figure 1. UV−vis spectrum of ethyl palmitate (hexane) as function of irradiation time.

Unfortunately, due to the high energy transition of the carbonyl moiety in the triglyceride, no sensitizer complied with the energetic requirements of such a high energy transition, and we were unable to sensitize the process. We tried benzophenone (E_t = 287 kJ mol^{-1}), acetone (E_t = 330 kJ mol^{-1}), benzene (E_t = 352 kJ mol^{-1}), toluene (E_t = 346 kJ mol^{-1}), methyl acetate, and ethyl acetate (both with E_t > 330 kJ mol^{-1}).[33] The reactions showed no improvement in yield, and in some cases, photochemistry from the sensitizer itself was observed.

It is well known that animal fats can also be transesterified in different alcohols using either basic or acid catalysis.[1−8,34] Reaction of tallow with methanol and ethanol produced methyl and ethyl esters, respectively, of palmitic, oleic, and stearic acids, while benzyl alcohol produced benzyl palmitate, benzyl stearate, and benzyl oleate. Analogous esters were observed when cyclohexyl methanol, tetrahydrofurfuryl alcohol, and (*R*)-(−)-2,2-dimethyl-1,3-dioxolane-4-methanol were used.

The products of transesterification were irradiated without separation. Regardless of the nature of the esters, 2, 3, and 4 were observed as photoproducts. Conversely, when the benzyl ester mixture was irradiated, no photoproducts were obtained, leading us to conclude that the chromophore is centered on the benzyl ring rather than on the carbonyl group, hindering the Norrish type II cleavage.

We hesitate to comment on the mechanism of these decompositions beyond saying that the Norrish type II cleavage has been demonstrated as possible with different sources of fat and UV−C light. Whether there is a preliminary homolysis step as suggested by the Givens review[35] is still to be determined. In any case, all a preliminary homolysis might do is to reduce the quantum yield,[36] though likely not the chemical yield, of product formation. Moreover, in this study, we have shown that olefins often prepared from petroleum derivatives can be synthesized in an environmentally friendly fashion from animal fats. Because of the high-energy transition of these molecules, high-intensity UV−C light is required. Further transformation of the triglycerides into ketones would considerably lower the energy of those transitions, allowing for the use of longer wavelengths. Additional experiments are in progress.

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Notes

The authors declare the following competing financial interest(s): Biosolar LLC is wholly owned by the senior author.

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REFERENCES

(1) Tekade, P. V.; Mahodaya, O. A.; Khandeshwar, G. R.; Joshi, B. D. Green synthesis of biodiesel from various vegetable oil and characterization by FT-IR spectroscopy. *Sci. Rev. Chem. Commun.* **2012**, *2*, 208−211.

(2) Rabu, R. A.; Janajreh, I.; Honnery, D. Transesterification of waste cooking oil: Process optimization and conversion rate evaluation. *Energy Convers. Manage.* **2013**, *65*, 764−769.

(3) Borugadda, V. B.; Goud, V. V. Biodiesel production from renewable feedstocks: Status and opportunites. *Renewable Sustainable Energy Rev.* **2012**, *16*, 4763−4784.

(4) Sharma, Y. C.; Singh, B.; Agrawal, S. A low-cost synthesis of biodiesel at room temperature and purification of by-product glycerol for reuse. *Biomass Convers. Biorefin.* **2012**, *2*, 63−71.

(5) Ronda, J. C.; Lligadas, G.; Galia, M.; Cadiz, V. Vegetable oils as platform chemicals for polymer synthesis. *Eur. J. Lipid Sci. Technol.* **2011**, *113*, 46−58.

(6) Bhatti, H. N.; Hanif, M. A.; Munir, U. F.; Sheikh, A. Acid and base catalyzed transesterification of animal fats to biodiesel. *Iran. J. Chem. Chem. Eng* **2008**, *27*, 41−48.

(7) Lotero, E.; Liu, Y.; Lopez, D. E.; Suwannakarn, K.; Bruce, D. A.; James, G.; Goodwin, J. Synthesis of biodiesel via acid catalysis. *Ind. Eng. Chem. Res.* **2005**, *44*, 5353−5363.

(8) Freedman, B.; Pryde, E. H.; Mounts, T. L. Variables affecting the yields of fatty esters from transesterified vegetable oils. *J. Am. Oil Chem. Soc.* **1984**, *61*, 1638−1643.

(9) Chieregato, A.; Basile, F.; Concepcion, P.; Guidetti, S.; Liosi, G.; Soriano, M. D.; Trevisanut, C.; Cavani, F.; Lopez-Nieto, J. M. Glycerol oxidehydration into acrolein and acrylic acid over W-V-Nb-O bronzes with hexagonal structure. *Catal. Today* **2012**, *197*, 58−65.

(10) Ekman, A.; Borjesson, P. Environmental assessment of propionic acid produced in an agricultural biomass-based biorefinery system. *J. Cleaner Prod.* **2011**, *19*, 1257−1265.

(11) Witsuthammakul, A.; Sooknoi, T. Direct conversion of glycerol to acrylic acid via integrated dehydration-oxidation bed system. *Appl. Catal., A* **2012**, *413−414*, 109−116.

(12) Lunelli, B. H.; Duarte, E. R.; Toledo, E. C. V. d.; Maciel, M. R. W.; Filho, R. M. A new process for acrylic acid synthesis by fermentative process. *Appl. Biochem. Biotechnol.* **2007**, *136−140*, 487−500.

(13) Katryniok, B.; Paul, S.; Capron, M.; Dumeignil, F. Towards the sustainable production of acrolein by glycerol dehydration. *ChemSusChem* **2009**, *2*, 719−730.

(14) García-Sancho, C.; Moreno-Tost, R.; Mérida-Robles, J.; Santamaría-González, J.; Jiménez-López, A.; Maireles-Torres, P. Zirconium doped mesoporous silica catalysts for dehydration of glycerol to high added-value products. *Appl. Catal., A* **2012**, *433−434*, 179−187.

(15) Shen, L.; Yin, H.; Wang, A.; Feng, Y.; Shen, Y.; Wu, Z.; Jiang, T. Liquid phase dehydration of glycerol to acrolein catalyzed by silicotungstic, phosphotungstic and phosphomolybdic acids. *Chem. Eng. J.* **2012**, *180*, 277−283.

(16) Liu, L.; Ye, X. P.; Bozell, J. J. A comparative review of petroleum-based and bio-based acrolein production. *ChemSusChem* **2012**, *5*, 1162−1180.

(17) Soriano, M. D.; Concepcion, P.; Lopez-Nieto, J. M.; Cavani, F.; Guidetti, S.; Trevisanut, C. Tungsten-Vanadium mixed oxides for the oxidehydration of glycerol into acrylic acid. *Green Chem.* **2011**, *13*, 2954−2962.

(18) Lauriol-Garbey, P.; Millet, J. M. M.; Loridant, S.; Bellière-Baca, V.; Rey, P. New efficient and long-life catalyst for gas phase glycerol dehydration to acrolein. *J. Catal.* **2011**, *281*, 362−370.

(19) Wang, F.; Dubois, J.-L.; Ueda, W. Catalytic dehydration of glycerol over vanadium phosphate oxides in the presence of molecular oxygen. *J. Catal.* **2009**, *268*, 260−267.

(20) Wang, F.; Xu, J.; Dubois, J.-L.; Ueda, W. Catalytic oxidative dehydration of glycerol over a catalyst with iron oxide domains embedded in an iron orthovanadate phase. *ChemSusChem* **2010**, *2*, 1383−1389.

(21) Halit, L.; Hoşgün, M. Y.; Ferdi Gerçel, H. Hydrogenolysis of aqueous glycerol over Raney nickel catalyst: Comparison of pure and biodiesel by-product. *Ind. Eng. Chem. Res.* **2012**, *51*, 3863−3869.

(22) Zhao, H.; Zhou, C. H.; Wu, L. M.; Lou, J. Y.; Li, N.; Yang, H. M.; Tong, D. S.; Yu, W. H. Catalytic dehydration of glycerol to acrolein over sulfuric acid-activated montmorillonite catalyst. *Appl. Clay Sci.* **2013**, *74*, 154−162.

(23) Deleplanquea, J.; Duboisb, J. L.; Devauxb, J. F.; Uedac, W. Production of acrolein and acrylic acid through dehydration and oxydehydration of glycerol with mixed oxide catalysts. *Catal. Today* **2010**, *157*, 351−358.

(24) Zhang, J.; Zhao, Y.; Pan, M.; Feng, X.; Ji, W.; Au, C.-T. Efficient acrylic acid production through bio-lactic acid dehydration over NaY Zeolite modified by alkali phosphates. *ACS Catal.* **2011**, *1*, 32−41.

(25) Omata, K.; Izumi, S.; Murayama, T.; Ueda, W. Hydrothermal synthesis of W-Nb complex metal oxides and their application to catalytic dehydration of glycerol to acrolein. *Catal. Today* **2013**, *201*, 7−11.

(26) Neckers, D. C. Photochemical Method for Producing Hydrocarbons. U.S. Patent US 8,110,074 B1, 2012 .

(27) Neckers, D. C. Photochemical Method for Producing Hydrocarbons. U.S. Patent US 2012/0103787 A1, 2012.

(28) Neckers, D. C. Developmental photochemistry. The Norrish type II reaction. *J. Org. Chem.* **1971**, *36*, 1838−1840.

(29) DeCosta, D. P.; Bennett, A. K.; Pincock, J. A. The Norrish type II photofragmentation of esters induced by intramolecular electron transfer. *J. Am. Chem. Soc.* **1999**, *121*, 3785−3786.

(30) Evans, T. R.; Leermakers, P. A. The Norrish type II process in α-keto acids. Photolysis of α-ketodcanoic acid in benzene. *J. Am. Chem. Soc.* **1968**, *90*, 1840−1842.

(31) Hartley, G. H.; Guillet, J. E. Photochemistry of ketone polymers. II. Studies of model compounds. *Macromolecules* **1968**, *1*, 413−417.

(32) Silva, A. C. H. d.; Kuhnen, C. A.; Silva, S. C. d.; Dall'Oglio, E. L., Jr.; P. T., d. S. DFT Study of alkaline-catalyzed methanolysis of pentyli acid triglyceride: Gas phase and solvent effects. *Fuel* **2013**, *107*, 387−393.

(33) Carmichael, I.; Hug, G. L. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. *I*, p 369−404.

(34) Stelmachowski, M. Utilization of glycerol, a by-product of the transesterification process of vegetable oils: A review. *Adv. Chem. Res.* **2011**, *9*, 59−92.

(35) (a) Givens, R. S. In *Organic Photochemistry*; Padwa, A., Ed.; Marcel Dekker, Inc.: New York, 1981; Vol. *5*, pp 227−342. (b) Givens, R. S.; Matuszewski, B.; Levi, N.; Leung, D. Photodecarboxylation. A labeling study. Mechanistic studies in photochemistry. 15. *J. Am. Chem. Soc.* **1977**, *99*, 1896−1903.

(36) Neckers, D. C.; Sponsler, M. Quantum Yields of Photo Reduction of Para Benzoylbenzoic Acid Esters. 1979, unpublished.