

Synthesis of a Palm-Based Star-Shaped Hydrocarbon via Oleate Metathesis

Yuen-May Choo*, Kay-Eng Ooi, Ing-Hong Ooi, and Daniel D.H. Tan

Palm Oil Research Institute of Malaysia, 50720 Kuala Lumpur, Malaysia

ABSTRACT: 10,11-Dioctyleicosane, a star-shaped hydrocarbon, has been successfully synthesized from 9-octadecene (a product from metathesis of methyl oleate or ethyl oleate) through dimerization followed by hydrogenation. The product was determined by ^{13}C nuclear magnetic resonance spectroscopic and gas chromatography/mass spectrometric techniques. This hydrocarbon likely exhibits lubricating properties that can be used as high-performance functional fluids in automotive lubrication. We also report the presence of a novel product, a trimer that was formed during the synthesis. *JAACS* 73, 333–336 (1996).

KEY WORDS: Diethyl 9-octadecenedioate, 10,11-dioctyl eicosane, ethyl and methyl oleates, metathesis, 9-octadecene, palm oil, star-shaped hydrocarbon.

Oleochemical products such as alkyl oleates are obtained through transesterification of palm oil and palm oil products or direct esterification of oleic acid with alcohol (e.g., methanol or ethanol). Metathesis of alkyl oleates provides two main products, 9-octadecene and dialkyl 9-octadecenedioate. In a previous paper, we have reported the synthesis of civetone from the dialkyl 9-octadecenedioate via Dieckmann condensation/hydrolysis-decarboxylation reactions (1). This paper describes the preparation of a star-shaped hydrocarbon, 10,11-dioctyleicosane. 9-Octadecene can undergo dimerization, and further hydrogenation gives rise to this saturated highly branched C_{36} hydrocarbon.

Various catalysts are known for synthesizing various types of star-branched hydrocarbons, more generally known as hydrogenated α -olefin oligomers. The catalysts used include cationic, free-radical, and anionic types. Early reports showed the use of a cationic catalyst, AlCl_3 , in preparing the 1-octene oligomer (2,3). BF_3 , together with a protonic co-catalyst such as RCOOH , ROH , or H_2O , produces hydrogenated α -olefin oligomers, which have excellent lubricating properties (4–7).

This paper reports the synthesis of 10,11-dioctyleicosane from 9-octadecene derived from palm oil and palm-based fatty acids via dimerization, followed by hydrogenation.

EXPERIMENTAL PROCEDURES

Materials. WCl_6 and SnMe_4 were purchased from Aldrich Chemical Co. (Milwaukee, WI). WCl_6 was purified by vacuum sublimation at 200°C . Benzene, purchased from Merck (Darmstadt, Germany), was dried over CaCl_2 and distilled onto 3\AA molecular sieves. Other solvents used were of reagent grade. Thin-layer chromatography (TLC) was performed on Merck Analtech glass plates precoated with silica gel (UV $_{254}$, 0.25 mm thickness, Merck 9385, 230–400 mesh).

Methods. ^{13}C Nuclear magnetic resonance (NMR) spectra were obtained on JEOL JNM-PMX60 SI and JNM-FX100 spectrometers (JEOL, Tokyo, Japan) with tetramethylsilane as internal standard. Electron-impact/mass spectra (EIMS) were obtained from a JEOL JMS-DX303 spectrometer.

Preparation of ethyl oleate. The preparation of ethyl oleate was carried out by transesterification of crude palm oil or direct esterification of oleic acid with ethanol.

Transesterification of crude palm oil and palm oil products. Transesterification of crude palm oil and palm oil products has been well established, and detailed experimental procedures have been described elsewhere (8).

Direct esterification of oleic acid with ethanol. Purified oleic acid was esterified with dry ethanol in the presence of catalytic amounts of concentrated sulfuric acid at 110°C for 2 h. Water, produced during esterification, was continuously removed with a Dean & Stark distillation apparatus. Excess ethanol was distilled off at the end of the reaction. NaHCO_3 solution was added to neutralize the acid. The product was extracted with petroleum ether ($60\text{--}80^\circ\text{C}$) three times. The extract was then dried over NaSO_4 and filtered, and the solvent was removed. The pure ethyl oleate ($\sim 100\%$) was obtained by distillation under reduced pressure.

Metathesis of alkyl oleates. Metathesis of alkyl oleate to yield 9-octadecene and diethyl 9-octadecenedioate was discussed in detail in a previous paper (1).

9-Octadecene. The starting material obtained in 97% yield was obtained from metathesis of ethyl oleate with catalyst $\text{WCl}_6/\text{SnMe}_4$. 9-Octadecene was separated from other metathesis products in the earlier fraction with petroleum ether in a silica column. The ^1H NMR (CDCl_3) data showed the chemical shift at δ 5.43–5.35 (*m*, olefinic proton, 2H), 1.99 (*m*, 4H), 1.27 (*m*, 24H), 0.94–0.83 (*t*, 6H); infrared (NaCl)

*To whom correspondence should be addressed at Chemistry and Technology Division, Palm Oil Research Institute of Malaysia, P.O. Box 10620, 50720 Kuala Lumpur, Malaysia.

spectrum at λ_{\max} 3012, 2964, 2932, 1470, 970 cm^{-1} ; EIMS showed m/e at 252 (M^+), 224, 209, 195, 181, 168, 154, 139, 125, 111, 98, 82, 71, 54.

Synthesis of star-shaped hydrocarbon: 10,11-dioctyleicosane. The desired compound of interest has been successfully synthesized by following the scheme shown in Scheme 1.

Dimerization. 9-Octadecene (1 g) and 0.5 mL of absolute ethanol were placed in a 25-mL reaction flask. The flask was carefully placed into a high-pressure reactor with stirring. The reaction mixture was cooled to ice temperature and was placed under vacuum for 10 min. BF_3 gas was then introduced slowly to reach about 30 psi. Then, the reaction mixture was heated to 90°C in an oil bath and maintained for 1 h. At the end of the reaction, diluted ammonia solution was added to destroy the remaining BF_3 gas. The yellowish solution was then extracted by 2×20 mL *n*-hexane. The extract containing the dimerized product was washed with distilled water, dried, and roto-evaporated to remove excess solvent. The dimerized product was further pumped dry and was ready for the hydrogenation reaction.

Hydrogenation. A sample of 0.3 g dimer was weighed in a 25-mL round-bottom flask, and 0.05 g of Pd catalyst (10% on carbon) was added. The flask was placed into a high-pressure Soxhlet reactor. The content of the extractor was then vacuum-pumped for 10 min. Hydrogen gas was then slowly in-

troduced to reach a pressure of 300 psi. The reaction was maintained for 1 h at 165°C . At the end of the reaction, *n*-hexane was used for extraction of the reaction product, and the extract was dried with Na_2SO_4 . Excess solvent was removed. The final product was initially checked by gas chromatography (GC). Further confirmation and structural elucidation was done by mass-spectrometric (MS) and ^{13}C NMR spectroscopic techniques.

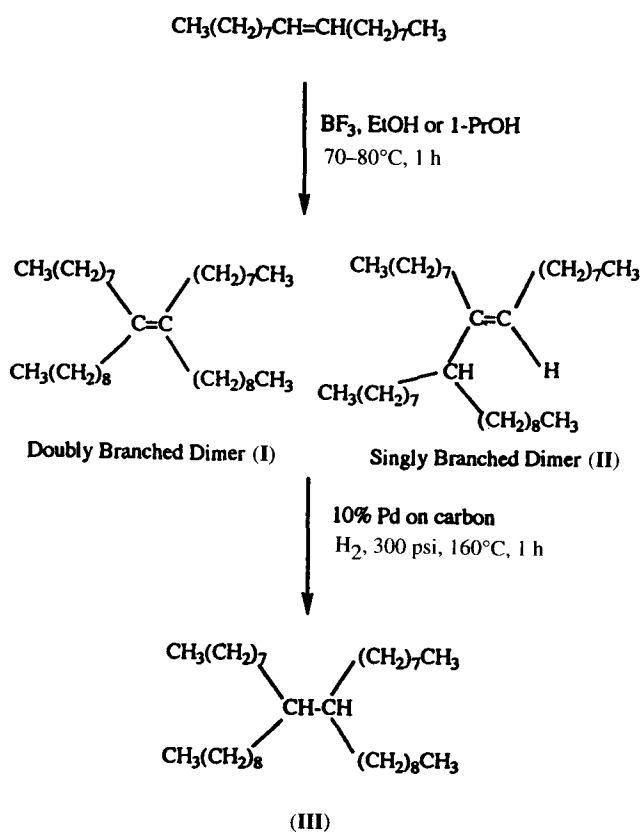
RESULTS AND DISCUSSION

Metathesis of alkyl oleates. Tungsten hexachloride (WCl_6) is the most commonly used catalyst in olefin metathesis reactions. A number of references have shown that the catalyst system with WCl_6 as the principal catalyst and $\text{Sn}(\text{CH}_3)_4$ as the co-catalyst is the most active system for metathesis (9–11).

The presence of impurities, such as oxygen or water, however, may affect the effectiveness of this WCl_6 -based catalyst system, as well as the yield of the metathesis products. Thus, to minimize such problems, the metathesis reaction should be carried out under an inert gas atmosphere. WCl_6 was purified by careful sublimation to remove WOCl_4 and WO_2Cl_2 impurities and was stored in an inert-atmosphere chamber maintained at less than 5 ppm oxygen and water. The solvents used (benzene or other aromatic solvents) were dried by refluxing over CaCl_2 and sodium metal, distilled under N_2 , and then stored over activated alumina. All reaction vessels were oven-dried ($\sim 110^\circ\text{C}$) and flushed with nitrogen gas before introduction of starting materials.

Among the solvents used in the reaction, benzene was the best for metathesis of alkyl oleate and provided the highest yields of 9-octadecene (97%) and diethyl 9-octadecenedioate (97%). Other solvents, such as anisole, xylenes, and *tert*-butylbenzene, provided a lower yield (85%) of almost equal amounts of the two desired products. It was also found that metathesis could be carried out without solvents, but the yields were much lower. The results of methyl oleate metathesis in different solvents are shown in Table 1.

The molar ratio of substrate to catalyst affects the rate of reaction, whereas an excess of catalyst suppresses the conver-



SCHEME 1

TABLE 1
Metathesis of Methyl Oleate^a with WCl_6 and SnMe_4
in Various Solvents

Experiment number	Time (h)	Solvent	Yield ^b (%)	
			A	B
1	20	Toluene	59 [24]	61 [25]
2	22	Xylene	87 [41]	79 [38]
3	21	<i>t</i> -Butylbenzene	80 [28]	90 [31]
4	20.5	Anisole	91 [37]	84 [34]
5	22	Benzene	96 [42]	96 [41]
6	22	No solvent	38 [6]	49 [8]
7	22	Nitrobenzene	No reaction	

^aReactions were carried out at 70°C under N_2 .

^bPercent yield was based on % methyl oleate (in brackets) consumed; A = 9-octadecene, B = diethyl 9-octadecenedioate.

TABLE 2
Metathesis of Ethyl Oleate^a with WCl_6 and $SnMe_4$

Experiment number	WCl_6 (mol%)	$SnMe_4$ (mol%)	Time (h)	Yield ^b (%)	
				A	B
1	5.4	6	20	94 [36]	60 [23]
2	6	7.2	20	90 [46]	90 [46]
3	6.6	7.3	20	97 [50]	99 [51]
4	7	7.7	20	92 [45]	85 [42]
5	12	12	20	42 [32]	45 [28]
6	20	20	20	27 [15]	24 [12]

^aAll reactions were carried out at 70°C under N_2 in benzene, except Experiment number 6, where toluene was used instead.

^bPercent yield was based on % methyl oleate (in brackets) consumed; A = 9-octadecene, B = diethyl 9-octadecenedioate.

sion. Accordingly, when 6.3 mole% of WCl_6 was used with respect to ethyl oleate, the conversion was 50%, yielding 97% 9-octadecene, and 99% diethyl 9-octadecenedioate. Results are shown in Table 2.

Confirmation of 10,11-dioctyleicosane by GC/MS. The analysis of 10,11-dioctyleicosane was initially carried out by HP5890 series II gas chromatograph with an HT5 25 m × 0.53 mm i.d. capillary column (Hewlett-Packard, Palo Alto, CA). The synthetic product was co-injected with the authentic normal hydrocarbon standards of C_{20} to C_{40} . Calculation with Kovat's Index showed that the hydrocarbon carbon number was equivalent to 36.

Further confirmation of 10,11-dioctyleicosane was done by GC/MS. The presence of a low-intensity ion fragment with m/z at 506 (the molecular ion, M^+) confirmed the molecular weight of 10,11-dioctyleicosane with a molecular formula of $C_{36}H_{74}$. The presence of other more prominent ion fragments due to fragmentation at the branched points of m/z at 379/378, 253/252, and 127/128 further confirmed the molecular structure of this hydrogenated dimer.

¹³C NMR data of 10,11-dioctyleicosane. In the ¹³C NMR spectrum of the dimerized product, 10,11-dioctyl-10-eicosene, the presence of higher absorption signals at chemical shift δ 10 to 40 ppm is due to the resonances of the car-

bons on the long-chain tail, namely, the methylene and methyl carbons. At the lower field region, the olefinic carbons of the doubly branched (I) and singly branched (II) dimers are indicated by the resonance of the absorption signals at δ 133.5 and 141.9 ppm, respectively. However, these lower-field resonance absorption signals were not detected in the carbon-13 spectrum of the hydrogenated product, 10,11-dioctyleicosane (III); instead, an absorption signal was observed at about δ 50 ppm, which was assigned to the resonances of the CH carbons.

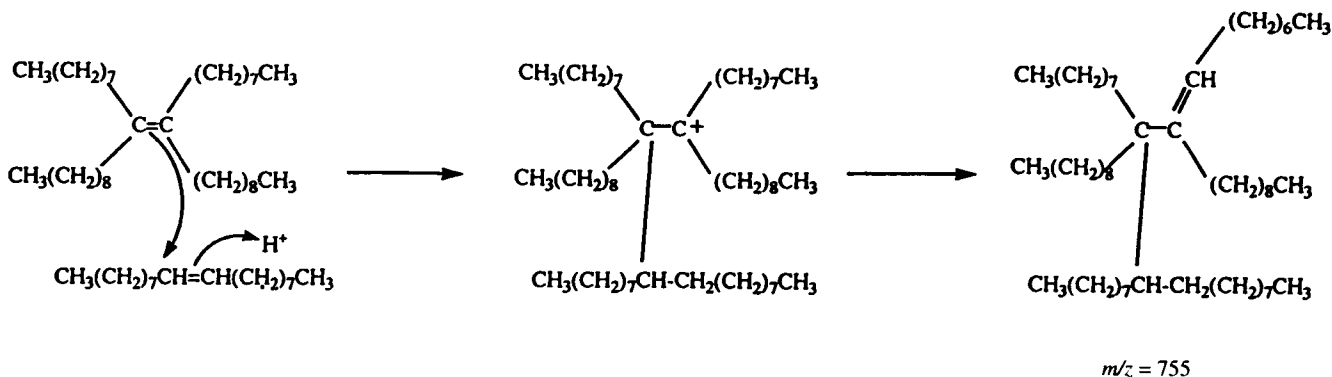
Detection of trimer. In the course of reaction, a trimer has also been isolated and identified as confirmed by GC and MS (the presence of $M^+ - 1$ ion fragment of m/z at 755). The mechanism of trimer formation has also been postulated as shown in Scheme 2. The trimer might be another important lube-based material.

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SCHEME 2

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