

## The Isolation and Spectroscopic Characterization of Products from the Metatheses of Alkyl Oleates

Rose Aini Kamarudin, Nor Asikin Mohamad Nordin  
and Nor Aziah Buang

*Department of Chemistry,  
Faculty of Science,  
Universiti Teknologi Malaysia,  
Lockbag 791, 80990 Johor Bahru, Malaysia.*

Received 17 April 1993

### ABSTRAK

Hasil daripada tindak balas metatesis metil oleat dan etil oleat dipisahkan dengan kromatografi turus. Komponen berasingan yang diperolehi dicirikan dengan menggunakan spektroskopi infra merah, RMN  $^1\text{H}$  dan RMN  $^{13}\text{C}$  dan kromatografi gas yang digandingkan dengan spektrometer jisim.

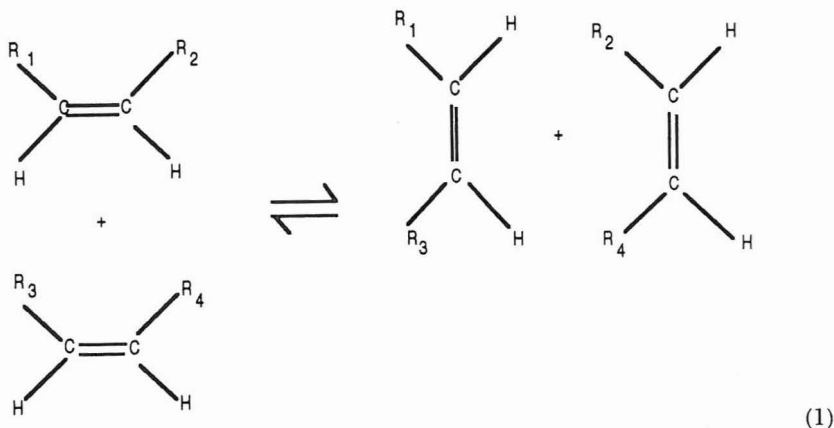
### ABSTRACT

The products from the metathesis reactions of methyl and ethyl oleate were isolated using column chromatography. The various components obtained were characterized using infrared (IR),  $^1\text{H}$  and  $^{13}\text{C}$  nuclear magnetic resonance spectroscopy (NMR) and gas chromatography mass spectrometry (GC-MS).

**Keywords:** metathesis, homogeneous catalyst, separation, characterization, gas chromatography, spectroscopy

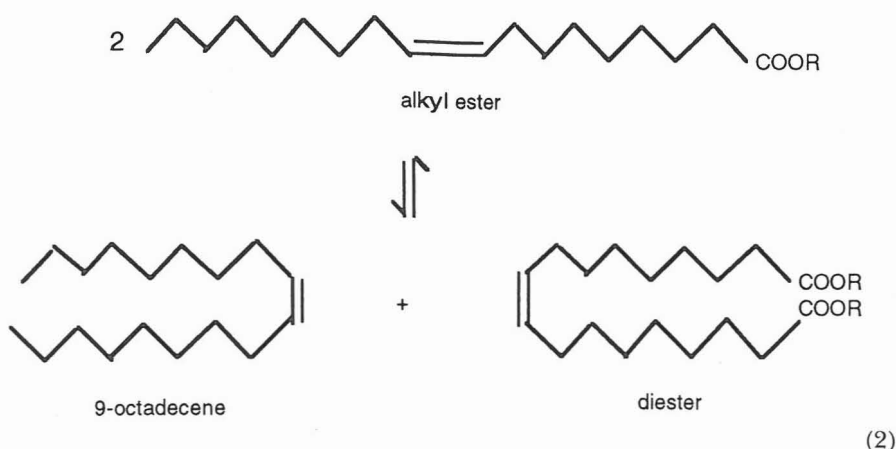
### INTRODUCTION

In general, the metathesis reaction of unsaturated hydrocarbons can be represented by equation 1.



A variety of catalysts, both homogeneous and heterogeneous, have been used to catalyse the above metathesis reaction. The most active are those based on the transition metals; W, Mo, and Re (Boelhouwer and Mol 1985; Boelhouwer *et. al.* 1972, 1974). A catalyst system for homogeneous metathesis is generally composed of a principal catalyst and a co-catalyst. The most successful combination for the metathesis of functionalised olefins is the mixed oxide catalyst,  $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3\text{-MR}_4$  ( $\text{M} = \text{Sn}$  or  $\text{Pb}$ ;  $\text{R} = \text{Me}$ ,  $\text{Et}$  or  $\text{Bu}$ ) which was discovered by Xu *et. al.* (1985). This system, however, is a heterogeneous system.

The metathesis of alkyl oleate yielded 9-octadecene and the diester (Equation 2).



So far, very few studies on the separation of the metathesis reaction mixtures have been reported (Tsuji and Hashiguchi 1980).

The diesters have been shown to have many uses. They can be converted to polyesters and polyamides. Both polymers have been used successfully as stationary phases in gas liquid chromatography for the separation of unsaturated hydrocarbons and mono- and dicarboxylic esters (Boelhouwer and Mol 1985). The diester can also be converted to civetone which is an important base material for the perfume industry (Tsuji and Hashiguchi 1980).

The objective of this research was two-fold :-

- (i) to separate the products of metathesis of methyl and ethyl oleate using column chromatography.
- (ii) to identify the separated products using IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

## MATERIALS AND METHODS

The infrared spectra were recorded on a Perkin Elmer PE 727B as a thin film. Both  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  on a JEOL FX-

400 operating at 400 MHz with TMS as internal standard. The mass spectra of the compounds were analysed by a Hewlett Packard HP 5917A using Chemstation software with a Wiley library search. The capillary column used in this analysis was 35% methylphenyl silicone. Operating oven temperature was 70-270°C. Column chromatography was carried out on a silica gel column. Methyl oleate and ethyl oleate were purchased from TCI and Aldrich respectively, were of 99% purity and were used without purification. No other isomers of these compounds were found based on the gas chromatographic analysis. The catalyst, tungsten hexachloride, and the co-catalyst, tetramethyltin, were purchased from Aldrich. The former was purified by fractional sublimation under vacuum. Chlorobenzene from Merck was used as solvent after prior purification by distillation over phosphorus pentoxide. All reactions were carried out under nitrogen.

#### *General Procedure for the Metathesis Reaction*

The alkyl oleate (1 g) in PhCl (5.00 ml) was degassed 3-4 times in a round three-neck bottle flask. A solution of the catalyst in PhCl (0.20 g solution prepared as 0.03 mol/60 ml) and the co-catalyst (0.18 g) was added. The reaction mixture was heated at 70°C for 24 hours and the reaction terminated by air. The purple mixture obtained was filtered, dried and analysed by column chromatography using silica gel with hexane : ether (25:1) as the initial solvent and 25 : 4 as the final solvent.

## RESULTS AND DISCUSSION

In this study  $\text{WCl}_6/\text{SnMe}_4$  catalyst system was used to metathesise methyl oleate and ethyl oleate. These reactions have been reported before in the literature (Boelhouwer *et. al.* 1974). The objective of this study was two-fold. Firstly, to isolate the different products from the metatheses of alkyl oleates and secondly, to identify and confirm each product isolated using spectroscopic methods.

Throughout this study all products were isolated by column chromatography using silica gel. No yields are given as the main concern was to isolate and confirm the products of the metathesis reactions by various spectroscopic techniques.

Both systems used hexane:ether (25:1) as eluent. Two fractions were collected and on increasing the polarity of the eluent (hexane:ether 25:4), a third fraction was eluted. All the fractions collected were subjected to analyses by GC-MS, IR and NMR.

#### *GC-MS Analyses*

The GC-MS chromatograms from the metathesis products of methyl and ethyl oleates before separation by column chromatography were examined. Four peaks were observed in both chromatograms. Upon separation by column chromatography, three fractions were isolated for both systems. The  $m/z$

values obtained for each fraction which contained the different peaks from GC-MS analyses are given in Tables 1(a) and 1(b).

TABLE 1(a)  
m/z values for the different fractions collected from the metathesis of methyl oleate

Fractions	Peaks	Methyl Oleate System	Retention Time (min)
1	1	252	24.550
2	2	296	30.324
	3	296	33.920
3	4	340	35.391

TABLE 1(b)  
m/z values for the different fractions collected from the metathesis of ethyl oleate

Fractions	Peaks	Ethyl Oleate System	Retention Time (min)
1	1	252	24.566
2	2	310	31.432
	3	310	34.904
3	4	368	37.566

Based on the m/z values obtained from GC-MS analysis, fraction 1 contains 9-octadecene, fraction 2 contains alkyl ester (starting material) and its isomer and fraction 3 contains the diester. Peak 3 is proposed to be an isomer of alkyl oleate and it is probably the *trans*-isomer.

### IR Spectra

The IR spectra of the three fractions isolated were recorded as neat liquid and are similar to those of 9-octadecenedioate, dimethyl 9-octadecenedioate and diethyl 9-octadecenedioate as reported in the literature (Tsuji and Hashiguchi 1980). All the spectra showed the presence of *cis* (724-740 cm<sup>-1</sup>) and *trans* (966-969 cm<sup>-1</sup>) C=C and for the diester an absorption band due to C=O stretching was also observed at 1739-1741 cm<sup>-1</sup>. The identification of the three compounds was further confirmed by their <sup>1</sup>H and <sup>13</sup>C spectra.

### <sup>1</sup>H and <sup>13</sup>C NMR Spectra

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of fraction 1 are shown in Fig. 1 and Fig. 2. Alkenic protons are observed at  $\delta$  5.45 p.p.m. in the <sup>1</sup>H NMR spectrum. Resonances due to the methylene protons bonded to alkenic carbons at  $\delta$

2.0 p.p.m.(m), methyl protons at  $\delta$  0.9 (t,  $J \sim 7$  Hz) and the rest of the  $\text{CH}_2$  protons in the structure were observed at  $\delta$  1.3 p.p.m. (br. s).

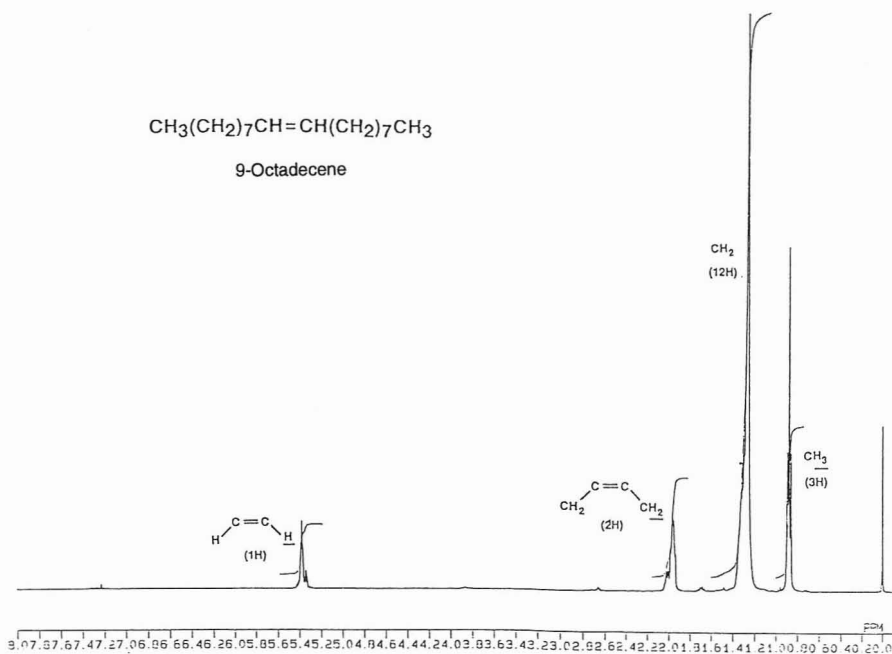


Fig. 1.  $^1\text{H}$  NMR spectrum of 9-octadecene

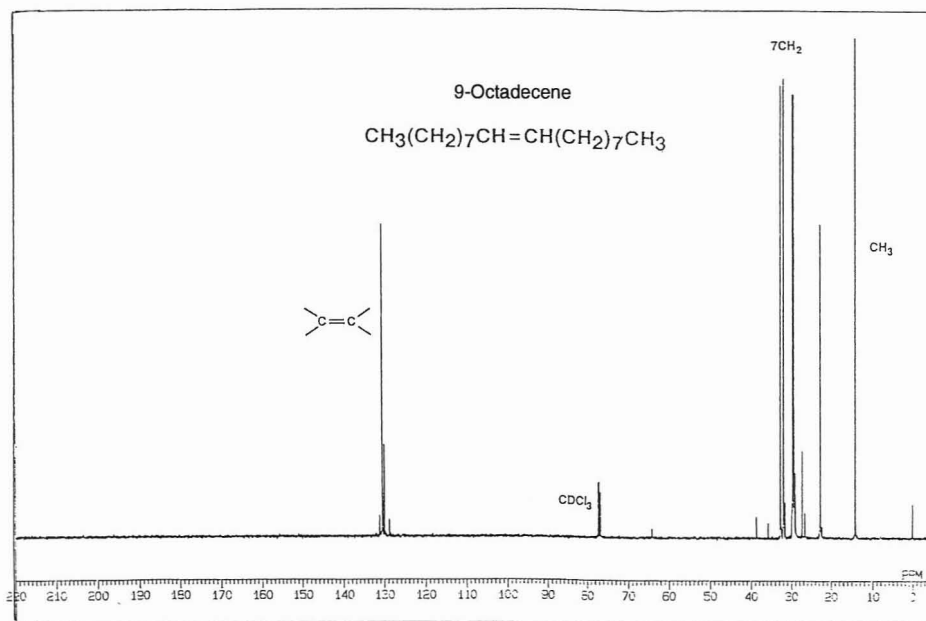


Fig. 2.  $^{13}\text{C}$  NMR spectrum of 9-octadecene

The  $^{13}\text{C}$  NMR spectrum of fraction 1 showed the presence of 9 carbons. An alkene carbon was observed at  $\delta$  130.43, seven methylene carbons at  $\delta$  22.79 - 32.74 and a methyl carbon at  $\delta$  14.16 p.p.m. The presence of a shorter peak at  $\delta$  130.43 may imply the presence of the other isomer of 9-octadecene. The assignment for the different types of carbon atoms observed in fraction 1 is consistent with that of 9-octadecene.

The  $^1\text{H}$  NMR spectrum of fraction 3 from the metathesis of methyl oleate is given in Fig. 3. Examination of the  $^1\text{H}$  NMR spectrum showed the presence of 18 protons. A multiplet at  $\delta$  5.35 p.p.m. for an alkenic proton, a singlet at  $\delta$  3.65 p.p.m. due to a methoxy group, a multiplet centred at  $\delta$  2.29 p.p.m. due to a methylene group next to a carbonyl group, two very broad singlets at  $\delta$  1.97 and  $\delta$  1.62 respectively assigned to the  $\text{CH}_2$  protons bonded to the alkenic carbons and a broad singlet at  $\delta$  1.43 due to the rest of the methylene protons were observed in the  $^1\text{H}$  NMR spectrum. The presence of two very broad singlets for the  $\text{CH}_2$  protons implies that the compound may be present in both the *cis* and *trans* forms. From the  $^1\text{H}$  NMR spectrum, the isomers exist in equal amounts.

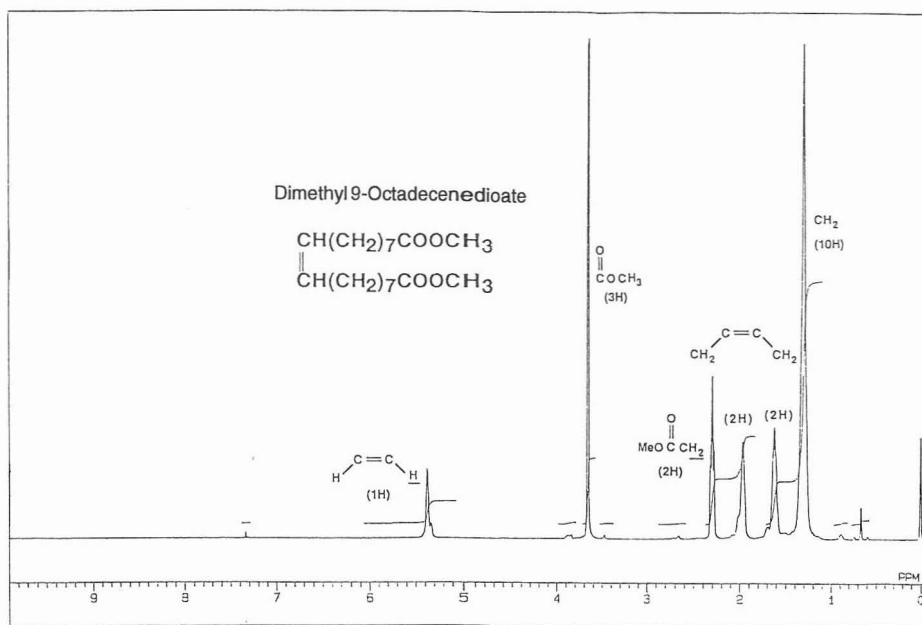


Fig. 3.  $^1\text{H}$  NMR spectrum of dimethyl diester

The  $^{13}\text{C}$  NMR spectrum of fraction 3 is shown in Fig. 4. The spectrum showed the presence of a keto group at  $\delta$  174.18, an alkenic carbon at  $\delta$  130.32, a methoxy carbon at  $\delta$  51.37 and the seven methylene carbons at  $\delta$  24.96-38.55 p.p.m. Both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra observed for fraction 3 are in agreement with the compound dimethyl 9-octadecenedioate.

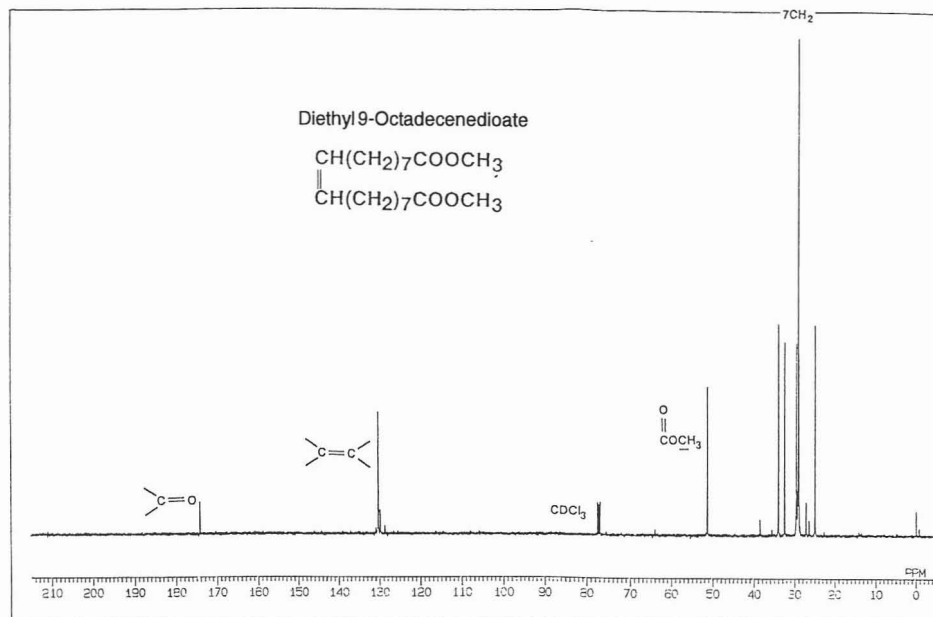


Fig. 4.  $^{13}\text{C}$  NMR spectrum of dimethyl diester

The structural assignment for fraction 3 as dimethyl 9-octadecenedioate was further confirmed by its 2-D heteronuclear COSY spectrum (Fig. 5). The alkenic carbons at  $\delta$  130.13 p.p.m. were correlated to the alkenic proton at  $\delta$  5.3 p.p.m. The methyl carbon at  $\delta$  51.4 p.p.m. was correlated to the methoxy protons at  $\delta$  3.7 p.p.m. The methylene carbon adjacent to the carbonyl group was correlated to the methylene protons adjacent to the carbonyl group. The COSY spectrum confirmed the presence of a symmetrical diester, dimethyl 9-octadecenedioate, in fraction 3.

The  $^1\text{H}$  NMR spectrum of fraction 3 from the metathesis of ethyl oleate is similar to that of diethyl 9-octadecenedioate as reported in the literature (Tsuji and Hashiguchi 1980). This is shown in Fig. 6. An examination of the  $^1\text{H}$  NMR spectrum showed the presence of alkenic protons which appeared as a multiplet at  $\delta$  5.37, methylene protons of the ethoxy group appeared as a quartet centred at  $\delta$  4.12 ( $J = 7$  Hz), methylene protons bonded to a keto group appeared as a triplet at  $\delta$  2.28, two broad multiplets centred at  $\delta$  1.96 and  $\delta$  1.61 respectively and another set of multiplets centred at  $\delta$  1.25 p.p.m. due to the methylene protons in the molecule. The multiplet centred at  $\delta$  1.96 and  $\delta$  1.61 p.p.m. as in the case of dimethyl 9-octadecenedioate implied the presence of both *cis* and *trans* isomers and again the isomers are present in equal amounts.

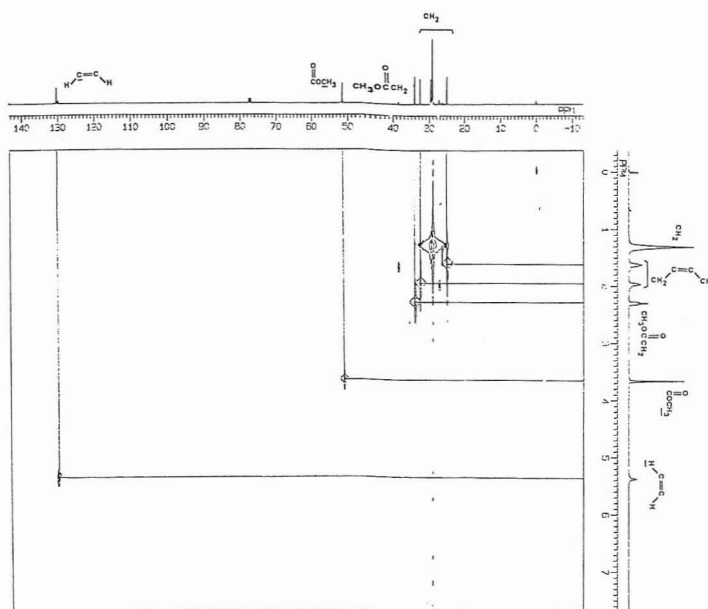


Fig. 5. 2 - D COSY heteronucleus spectrum of dimethyl 9-octadecenedioate

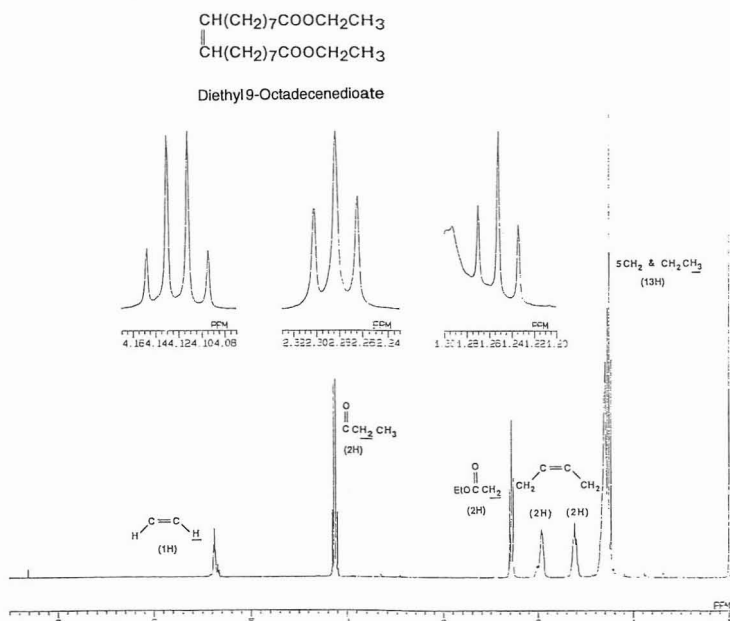


Fig. 6.  $^1\text{H}$  NMR spectrum of diethyl diester



The  $^{13}\text{C}$  NMR spectrum of fraction 3 from the metathesis of ethyl oleate system is shown in Fig. 7. The spectrum showed the presence of a keto group ( $\delta$  173.85), alkenic carbon ( $\delta$  130.32), methylene carbon of an ethoxy group ( $\delta$  60.13), methyl carbon on an ethoxy group ( $\delta$  14.27) and the rest of the methylene carbons ( $\delta$  24.98 -  $\delta$  34.37). Both the  $^1\text{H}$  and  $^{13}\text{C}$  NMR data supported the presence of a symmetrical diester, diethyl 9-octadecenedioate, in fraction 3 of the metathesis product from the ethyl oleate system.

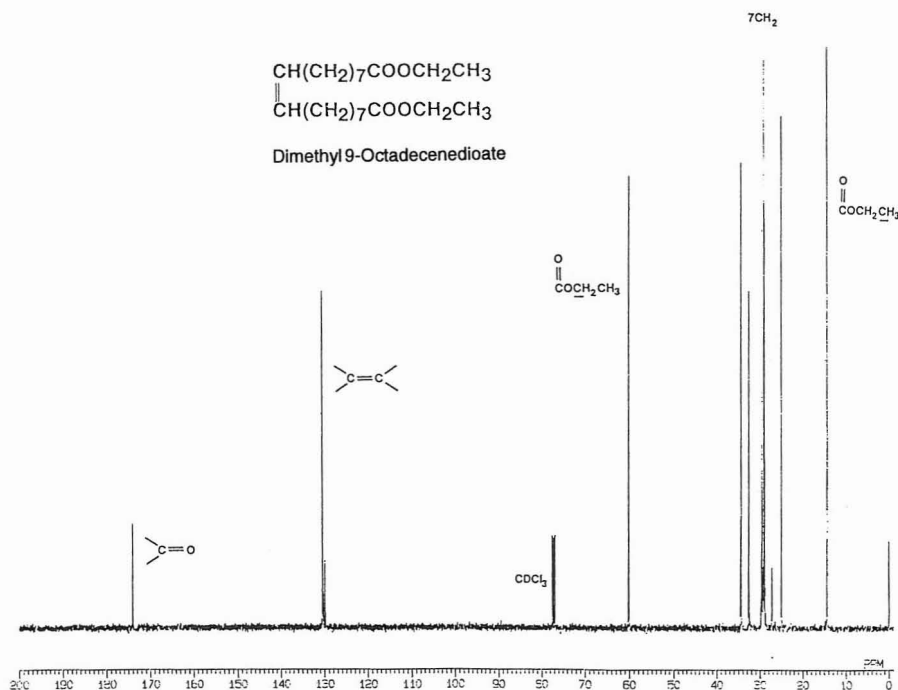


Fig. 7.  $^{13}\text{C}$  NMR spectrum of diethyl diester

## CONCLUSION

The products from the metatheses of methyl oleate and ethyl oleate have been successfully separated by using column chromatography to give three components, i.e. 9-octadecene, starting material and diester. The two products have been characterized based on their GC-MS, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Based on their  $^1\text{H}$  NMR spectra, the ratio of the *cis* to *trans* isomer in both the diesters is about 1:1.

## ACKNOWLEDGEMENTS

This research was funded partly by the Ministry of Science and Technology under the Sixth Malaysia Plan. One of the authors (RAK) was awarded a research fellowship from Rikkyo University to carry out part of the research in collaboration with Profesor Horiuchi Akira at the Department of Chemistry,

Rikkyo University. Special thanks to Profesor Horiuchi for recording the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

### REFERENCES

- BOELHOUWER, C. and J.C. MOL. 1985. Metathesis reactions of fatty acids. *Prog. Lipid Res.* **32**: 243.
- BOELHOUWER, C., F.P.B. VAN DAM and M.C. MITTELMEIJER. 1972. Metathesis of unsaturated fatty esters by a homogeneous tungsten hexachloride-tetra-methyltin catalyst. *J. Chem. Soc., Chem. Commun.* **122**.
- BOELHOUWER, C., F.P.B. VAN DAM and M.C. MITTELMEIJER. 1974. Homogeneous catalytic metathesis of unsaturated fatty esters - new synthetic method for preparation of unsaturated monocarboxylic and dicarboxylic acids. *J. Amer. Oil Chem. Soc.* **51**: 389.
- TSUJI, T. and S. HASHIGUCHI. 1980. Application of olefin metathesis to organic synthesis. Synthesis of civetone and macrolides. *Tet. Lett.* **2955**.
- XU XIAODING, P. IMHOFF, G.C.N. VAN DEN AARDWEG and C. MOL. 1985. Mixed-oxide catalysts for the methathesis of functionalized alkenes. *J. Chem. Soc. Chem. Commun.* **273**.