

Selective Mono-Ozonolysis of a Cyclic 1,5,9-Cyclododecatrien

Hussein Habeeb Mustafa and Noorhan Ali Chelebi

Department of Basic Sciences, Faculty of Dentistry, University of Kerkuk, Kerkuk, Iraq

Abstract: Some unsaturated compounds with the required (Z,Z)-double bonds configuration are synthesized through controlled ozonolysis process of 1,5,9-cyclododecatriene by determining the necessary amount of ozone passing through to selectively guarantee the breakage of a double bond while leaving other two bonds as (Z,Z). The products were diagnosed by using NMR spectrum, infrared (IR) and mass spectrometer techniques. It is concluded that these products could widely be used in the synthesis of insect pheromones instead of insecticides and as useful intermediate compounds in many chemical reactions.

Key words: Ozonolysis, cyclododecatriene, alkenes, pheromone synthesis.

1. Introduction

Ozonolysis does imply the cleavage of analkene or alkyne with ozone form organic compounds in which the multiple carbon-carbon bond has been replaced by a double bond to oxygen [1]. It is considered to be a recognized method for establishing the location of a double bond in non-saturated compounds which has become an important technique of synthetic organic chemistry within 1960-1970s [2]. Since then, methods and expedients were developed for the ozonolysis of alkenes in order to obtain carbonic acids, aldehydes, and alcohols [3-6]. An ketones oxidative decomposition stage (as a rule, under the action of hydrogenperoxide) of peroxide products formed due to that ozonization is of important value in the synthesis of carbonic acids based on the ozonolysis of alkenes [2].

Alkenes could be oxidized with ozone form alcohols, aldehydes, ketones or carboxylic acids. However, in a typical procedure, ozone is bubbled through a solution of the alkene in methanol at -78 °C until the solution takes on a characteristic blue color, which is due to un-reacted ozone indicating a complete consumption of the alkene. Alternatively,

various other chemicals can be used as indicators of this endpoint by detecting the presence of ozone. If ozonolysis is performed by bubbling a stream of ozone-enriched oxygen through the reaction mixture, the gas that bubbles out can be directed through a potassium iodide solution and when the solution has stopped absorbing ozone, the ozone in the bubbles oxidizes the iodide toiodine, which can easily be observed by its violet color [7].

The invention discussed in this paper is basically designed to facilitate the process of transforming a cyclic non-conjugated polyolefin into a beneficial product. Such an invention may further exceed for selective mono-ozonolysis of a non-conjugated poly olefin cyclododecatriene. It might also be appropriate for a selective oxidization of the product obtained from selective monozonolysis. Cyclic non-conjugated polyolefinse-1,4-cyclohexadiene, 1,5-cyclooctadiene and 1,5,9-cyclododecatrieneare necessary for initiating the process used for developing the project (Preparation of the compound 1,5,9-cyclododecatriene) has thoroughly been described [8-10]. These polyolefins are all non-conjugated while their double bonds have approximately the same reactivity as that of the chemical reaction [11]. Furthermore, in order to deliver an olefinic mono ozonolysis product, these

Corresponding author: Noorhan Ali Chelebi, Ph.D., main research field: protein purification. E-mail: nchelebi@liv.ac.uk.

olefinic bonds do pose some grave concerns with respect to selective conversion and the possible solution including selective monozonization.

The objectives of this work have been to prepare a number of useful intermediates which contain (1Z and 5Z) double bond formation. These products could possibly be used easily in several fields to prepare both pheromones and polyunsaturated compounds. It may also lead to selectivity in choosing the processing conditions of ozonolysis and to reduce manufacturing costs via moving away from the use of expensive starting materials such as acetylene.

An acceptable mechanism for the ozonolysis reaction could be undergoing as following steps. The first step in the mechanism of ozonolysis is the initial electrophilic addition of ozone to the carbon-carbon double bond, which then forms the molozonide intermediate. Due to the unstable molozonide molecule, it continues further with the reaction and breaks apart to form a carbonyl and a carbonyl oxide molecule. Then, continuous with the next additions as shown in Fig. 1.

2. Methodology

The ozonolysis step was the main process in this work, which depended on control pushing ozone amount monitoring the reaction temperature to be limited. The ozonolysis of cyclododeca-1,5,9-triene, involved reacting of 12.3 mmol of triene dissolved in 50% (DCM/methanol) (-62 °C to -48 °C), with 0.6 equivalent of ozone. The methods of synthesis and

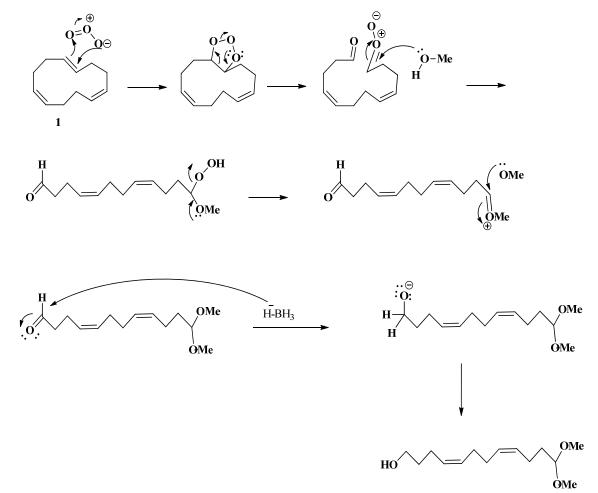


Fig. 1 An acceptable mechanism for the ozonolysis reaction as the initial electrophilic addition of ozone to the carbon-carbon double bond produce molozonide intermediate which would further continue with the reaction and breaks apart to form a carbonyl and a carbonyl oxide molecule.

chemical properties of 1,5,9-cyclododecatriene (the butadiene cyclo-trimerisation product), which is manufactured on an industrial scale, are examined. Syntheses based on this interesting compound have played a major role in the development of organic chemistry of medium and large rings [12]. After completion the reaction of nitrogen, the ozone was passed through the mixture for 160 sec to eliminate excess ozone and oxygen. To the ozonidep-toluene sulfonic acid, the mono-hydride was added, followed by addition of sodium borohydride (strongly exothermic) in small portions, to keep the temperature at low level [8].

3. Results and Discussion

3.1 Synthesis of (4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-ol

The ozonolysis reaction (1E,5Z,9Z)-cyclododeca-1,5,9-triene (1) has been oxidized with ozone to form alcohols which contain two isolated double bonds in Cis configuration. In a typical procedure, ozone is bubbled through a solution of the triene in a mix of methanol/dichloromethane at -62 °C for a limited time followed by addition of *p*-Toluensulfonic acid monohydrate. The reaction mixture was treated with sodium borohydride as a

reduction agent to obtain the (4*Z*,8*Z*)-12,12-dimethoxydodeca-4,8-dien-1-ol (2) (Fig. 2).

The general ozonolysis reaction has been the subject of numerous studies [2]. This technique was applied on (1E,5E,9Z)-cyclododeca-1,5,9-triene, but the resulting alcohol had usually been contained two double bonds in (1E,5Z) or (1E,5E) formation, while the ozonolysis of (1Z,5Z,9Z)-cyclododeca-1,5,9-triene led to the formation of (1Z,5Z) double bond. In the present work, the ozonolysis process was applied on (1Z,5E,9E)-cycloocta-1,5,9-triene while the NMR spectrums confirmed that the resulted products are a mixture of these expected structures (Fig. 3).

Moreover, the same ozonolysis conditions has successfully been used on (1E,5Z,9Z)-cyclododeca-1,5,9-triene which is cheaper than other starting materials for the synthesis of (1Z,5Z)double bonds alcohol. Surprisingly, according to the rules and references transforms, it should be more stable than Cis. This method does not appear to have been reported before.

The HNMR spectrum of compound (2) showed a multiplet at $\delta 5.44$ -5.38 for the four olefinic protons, a triplet at $\delta 4.38$ for acetal proton and a quartet at $\delta 3.67$ for the methylene protons as a next alcohol group. The

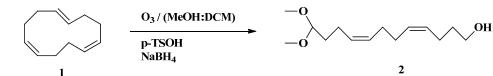


Fig. 2 Preparation of (4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-ol.

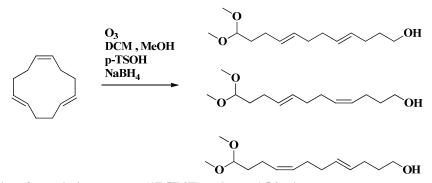


Fig. 3 The application of ozonolysis process on (1Z,5E,9E)-cycloocta-1,5,9-triene.

six protons of methoxy group have appeared as a singlet at δ 3.33, the signals as a multiplet at δ 2.17-2.04, corresponding to the four methylene groups next to the double bonds and at δ 1.69-1.62 for the remaining methylene groups. Additionally, ¹³C NMR and IR used to confirm the structure. The ¹³C NMR showed four signals at δ 129.9, δ 129.8, δ 129.4 and δ 129.1; for the alkene carbons, at δ 103.9; for acetalcarbonat, at δ 62.4 and for carbon of the methyl next to the alcohol while the remaining methylene group signals appeared between δ 52.6 and δ 22.4. The IR spectrum showed a broad peak at 3,430 cm⁻¹ for the OH stretch.

Morimoto et al. [13] had synthesized new antitumor and antibiotic agents using (5Z,9Z,13Z)-Octadeca-5,9,13-triene in their works, but prepared it using acetylenic derivatives as the starting materials. In these works, the same required compound was successfully but more easily prepared, and with cheaper starting material and via reducing the reaction steps (Fig. 4).

The (4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-ol (2) was used as a starting material for preparation of molecules with (Z,Z)-double bond groups. Following the above described methods, the tosylate (3) was prepared by dissolving the alcohol in pyridine and

treating with tosyl chloride. The reaction lasted overnight at 0 °C and produced a tosylate yield of 87% which has not been reported before. Transformation into the tosylate was confirmed by the appearance of significant aromatic signals at δ 7.80 and δ 7.35 in the ¹HNMR and at δ 144.6, δ 133.2, δ 129.7 and δ 127.8 in the ¹³C NMR. In addition, there was no OH band at 3,430 cm⁻¹ in the IR spectrum, which had been introduced at the starting material [14].

The (4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-yl 4-methylbenzenesulfonate was undergone several reaction throughout the present work: firstly, the tosylate compound (3) was reduced with lithium aluminum hydride in THF and secondly, quenched with saturated aqueous sodium sulfate dehydrate to give (4Z,8Z)-1,1-dimethoxydodeca-4,8-diene (4) in an 89% yield. The ¹H NMR and ¹³C NMR spectra were analyzed contributing to the confirmation of its structure. Analyzing the ¹H NMR spectrum of the product (4) revealed a triplets at $\delta 0.92$ (3 H, t) while the carbon NMR spectrum showed a peak at $\delta 13.77$ ppm for the terminal methyl group.

Second reaction was involved coupling tosylate compound (3) by Grignard reaction to give (4Z,8Z)-1,1-Dimethoxytrideca-4,8-diene (5) in 79% yield. An excess of the available Grignard reagent methyl-magnesium bromide was reacted with tosylate compound in a dry THF in the presence of lithiume-tetrachloro-cuprate catalyst. The ¹H NMR

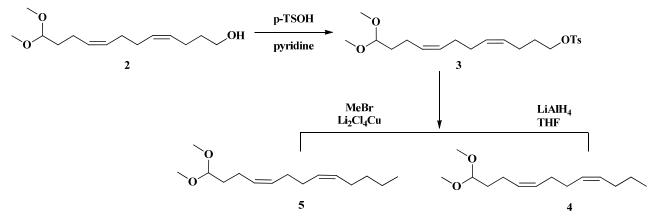


Fig. 4 Preparation of the same required compound more easily, cheaper cost and with reducing the reaction steps.

spectrum showed a triplet at $\delta 0.89$ (3 H, t, Hz) to indicate the presence of a terminal methyl group and a doublet or triplet further high field from $\delta 4.03$ to $\delta 1.33$ due to the CH₂-O protons to CH₂-CH₃. The latter confirmed that the tosylate, at the end of the chain, had been replaced by a methyl group. Furthermore, the carbon NMR showed a new peak at 13.96 ppm corresponding with the terminal methyl group carbons.

3.3 Preparation of (5Z,9Z,13Z)-Octadeca-5,9,13-Triene

Deprotection of acetyl group was carried out as in previous sections. Compound (5) was treated with 80% formic acid in dioxane to give rise to (4Z,8Z)-trideca-4,8-dienal in 89% yield. The unstable aldehydes had coupled without purification in a Wittig reaction with pentyltri-phenylphosphonium bromide to obtain (5Z,9Z,13Z)-octadeca-5,9,13-triene (6) in 88% yield (Fig. 5) [10, 15].

The ¹H NMR spectrum of compound (6) showed a multiplet at $\delta 5.38$ for the six Olefinic protons (-CH=CH-), a multiplet at $\delta 2.09$ for the 12 protons (-CH₂-C=), a multiplet at $\delta 1.34$ for the other eight protons of methylene groups and at $\delta 0.9$ for the two terminal methyl groups [16]. The ¹³C NMR spectrum had confirmed the result because the carbon of the acetyl group was disappeared.

3.4 Preparation of Unsaturated Intermediate with Isolated Double Bonds

A stirred solution of Trans, Cis, Cis-1,5,9-cyclododecatriene (2 gm, 12.3 mmol) in 50% (DCM/methanol) (100 mL) in a three-neck round bottom flask was fitted with three glass tubes to admit

ozone, digital thermometer and condenser [10, 15, 17]. The flask was cooled down to (-62 °C to -48 °C) (liquid nitrogen/IMS). Then, ozone was passed through a stirred solution for 160 sec (4 L/min O₂, 6 mmol/min). After completion of the reaction, nitrogen was passed through the reaction mixture over 10 minutes and the cooling bath was then removed. A p-Toluensulfonic acid monohydrate (0.5 g, 2.6 mmol) was added at (-35 °C to -20 °C) after replacing the ozone inlets with stoppers. The solution was allowed to reach room temperature then stirred for three hours. The reaction mixture was cooled to -10 °C and sodium borohydride (2 gm, 53 mmol) was added in small portions. The reaction was allowed to reach room temperature over 30 minutes. The reaction mixture was quenched with ice water (100 mL) and the product was extracted with dichloromethane (3×150) mL). The combined organic layers were dried over anhydrous MgSO4 filtered and evaporated under vacuum. The crude product was purified by column chromatography eluting with petrol: ethylacetate (5:2) to give (4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-ol (0.86 gm, 30%) (Fig. 6).

3.4.2Preparationof(4Z,8Z)-12,12-Dimethoxydodeca-4,8-Dien-1-yl4-Methylbenzene-Sulfonate

A p-Toluenesulfonyl chloride (0.4 gm, 2 mmol) was added to a stirring solution of (4Z,8Z)-12, 12-dimethoxydodeca-4,8-dien-1-ol (0.2 gm, 0.8 mmol) in pyridine (2 mL) at 0 °C. The reaction mixture was allowed to react with continuous stirring for two hours at 0 °C and then it was left overnight in the fridge. After that, water (5 mL) was added slowly to the mixture at 0 °C, followed by pouring it into separating funnel contained water (10 mL). Then the product was extracted with dichloromethane (3 × 20 mL). The

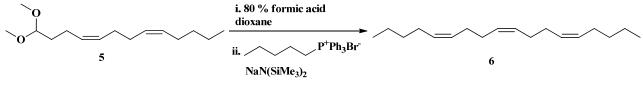
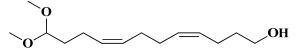


Fig. 5 Preparation of (5Z,9Z,13Z)-octadeca-5,9,13-triene.



(4Z,8Z)-12,12-Dimethoxydodeca-4,8-dien-1-ol

Fig. 6 The chemical structure of (4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-ol.

Table 1	Mass, NMR and II	R analysis of th	e compound	(4Z,8Z)-12,12	-dimethoxydodeca-4,8-dien	-1-ol.

Mass	242
$\delta_{H(400\;MHz)}$	5.44-5.38 (4 H, m), 4.38 (1 H, t, J, 5.72 Hz), 3.67 (2 H, q, J, 6.2 Hz), 3.33 (6 H, s), 2.17-2.04 (8 H, br, m), 1.69-1.62 (4 H, m).
δc (126 MHz)	129.9, 129.8, 129.4, 129.1, 103.9, 62.4, 52.6, 32.5, 32.3, 27.2, 27.2, 23.5, 22.4.
$v_{\rm max}/{ m cm}$	3,430, 3,007, 2,929, 1,656, 1,598, 1,494, 1,364, 1,176, 823

combined organic solution was transferred into a 100 mL round bottom flask with a magnetic stirrer bar. The flask was cooled to -5 °C and a solution of 2 M hydrochloric acid (15 mL) was added over a period maintaining the temperature below 5 °C. The organic layer was separated and the water layer was re-extracted with dichloromethane 20 mL. The combined organic layers were dried over magnesium sulphate, filtered and evaporate to give a crude product. The crude product was purified by column chromatography on silica eluting with a proportion of petrol: ethylacetate (10:1)to give (4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-yl 4-methylbenzenesulfonate (0.28 g, 87%) (Fig. 7). 3.4.3 Preparation of

(4Z,8Z)-1,1-Dimethoxytrideca-4,8-Diene

Methyl magnesium bromide of (0.3 gm, 2.5 mmol) added was to а stirred solution of lithium-tetrachloro-cuprate (2 mL) in a dry THF (5 mL) at -30 °C [14]. The reacted mixture was stirred for 1 hour before addition of (4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-yl

4-methylbenzene-sulfonate (0.2 gm, 0.5 mmol) in THF (2 mL) at -30 °C. The mixture was stirred at -30 °C for 2 hours, then, allowed to reach room temperature and stirred for 16 hours. The reaction mixture was quenched with a saturated solution of ammonium chloride (4 mL) at -10 °C. The product was extracted with ethyl acetate (3 \times 20 mL), the combined organic layers were dried over MgSO₄ and evaporated to give a yellow residue. The latter was

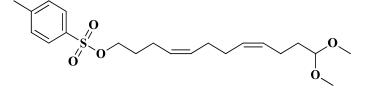
purified by column chromatography on silica eluting with petrol: ethylacetate (10:1)to give (4Z,8Z)-1,1-dimethoxytri-deca-4,8-diene (0.95) gm, 79%) (Fig. 8).

A solution of an 80% formic acid (6 mL) was added dropwise to a stirred solution of (4Z,8Z)-1, 1-dimethoxytrideca-4,8-diene (0.4 gm, 1.66 mmol) in a dioxane (6 mL), the reaction mixture was quenched as above to give (4Z,8Z)-trideca-4,8-dienal (0.3 gm, 93%) which was used immediately in the next step.

Sodium bis (trimethylsilyl)amide (2 mL, 2 mmoL) was added dropwise to a stirred slurry of pentyl-triphenyl-phosphonium bromide (0.55 gm, 1.33 mmol) in dry THF (25 mL), under nitrogen atmosphere. The reaction mixture was allowed to reach room temperature and stirred for 30 minutes, then cooled down again to -78 °C and a (4Z,8Z)-trideca-4,8-dienal (0.2 gm, 1 mmol) in dry THF (3 mL) was added. The reaction mixture was stirred and allowed slowly to reach room temperature, then the reaction was quenched as above to obtain (5Z,9Z,13Z)-octadeca-5,9,13-triene (0.22 gm, 88%) (Fig. 9).

(4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-yl 4-methylbenzenesulfonate (0.5 gm, 1.26 mmol) in tetrahydrofuran (5 mL) was added dropwise to a suspension solution of Lithium Aluminium hydride (0.3 gm, 7.9 mmol) in tetrahydrofuran (10 mL) at 0 °C [10, 15, 18]. The reaction mixture was stirred 16 hours and was worked up as above to give

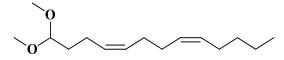
(4Z,8Z)-1,1-dimethoxydodeca-4,8-diene (0.25 gm, 89%) (Fig. 10). The above products were diagnosed by using NMR spectrum, infrared (IR) and mass spectrometer techniques are given in Fig. 11.



(4Z,8Z)-12,12-Dimethoxydodeca-4,8-dien-1-yl 4- Methylbenzenesulfonate

Fig. 7 The chemical structure of (4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-yl 4-methylbenzene-sulfonate.

Mass	Required
8	7.80 (2 H, br, d, J, 6.12 Hz), 7.35 (2 H, br, d, J, 8.04 Hz), 5.35 (4 H, br, m), 4.36 (1 H, br, t, J, 5.68 Hz),
0 _{H (400 MHz)}	4.03 (2 H, br, dt, J, 3, 6.4 Hz), 3.32 (6 H, s), 2.45 (3 H, s), 2.05 (8 H, m), 1.66 (4 H, m).
δc (126 MHz)	144.6, 133.2, 130.7, 129.7, 129.6, 129.2, 127.8, 103.9, 69.9, 52.6, 32.3, 28.8, 27.1, 27.0, 23.0, 22.4, 21.6.
$v_{\rm max}/{ m cm}$	2,929, 2,861, 1,655, 1,598, 1,494, 1,363, 1,189, 824.



(4Z,8Z)-1,1-Dimethoxytrideca-4,8-diene

Fig. 8 The chemical structure of (4Z,8Z)-1,1-dimethoxytrideca-4,8-diene.

Table 3	Mass, NMR and	IR analysis of	compound	(4Z,8Z)-1,1-	-dimethoxytri-d	leca-4,8-diene.
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Mass	Required
$\delta_{H(500\;MHz)}$	5.38 (4 H, br, m), 4.36 (1 H, br, t, J, 5.76 Hz), 3.32 (6 H, s), 2.09 (8 H, m), 1.65 (2 H, br., q, J, 6.04 Hz), 1.33 (4 H, br. m), 0.89 (3 H, t, J, 6.76, Hz).
δc (126 MHz)	130.40, 130.00, 128.99, 128.96, 104.00, 52.64, 32.39, 31.89, 27.31, 27.27, 26.94, 22.46, 22.31, 13.96.
$v_{\rm max}/{ m cm}$	2,954, 1,609, 1,493, 1,452, 1,066, 824

(5Z,9Z,13Z)-Octadeca-5,9,13-triene

Fig. 9 The chemical structure of (5Z,9Z,13Z)-octadeca-5,9,13-triene.

Table 4	Mass, NMR and l	R analysis of compound	(5Z,9Z,13Z)-octadeca-5,9,13-triene.
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Mass	Required	
$\delta_{H(400MHz)}$	5.38 (6 H, br, m), 2.09 (12 H, br, m), 1.34 (8 H, m), 0.90 (6 H, br, t, J, 6.96 Hz).	
δc (126 MHz)	130.3, 129.6, 129.1, 31.9, 27.4, 27.3, 26.9, 22.3, 13.9.	
$v_{\rm max}/{\rm cm}^{-1}$	2,927, 2,859, 1,655, 1,493, 1,455, 1,377, 824	

0

(4Z,8Z)-1,1-Dimethoxydodeca-4,8-diene

Fig. 10 The chemical structure of (4Z,8Z)-1,1-dimethoxydodeca-4,8-diene.

Selective Mono-Ozonolysis of a Cyclic 1,5,9-Cyclododecatrien

ass	Requires				
(500 MHz)	5.44-5.34 (4 H, br, m), 4.3'	7 (1 H, t, J 5.76 H	Iz), 3.32 (6 H, s	s), 2.12-1.98 (8 H, br, m)	, 1.68-1.62 (2 H, m
	1.36 (2 H, sext, J, 7.4 Hz), 130.19, 130.01, 129.20, 123		27 21 27 20 22 22 22	16 12 77	
101 MHz)	2,929, 2,861, 1,607, 1,493,			, 27.31, 27.29, 22.83, 22.	40, 13.77.
_{ax} /cm	2,929, 2,801, 1,007, 1,495,	1,431, 1,120, 1,0.	50, 824		
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	H ₃ C_0	OH			
	H ₃ C_0	OH			

Table 5	Mass,	NMR and	l IR ana	lvsis of	compound	(4 Z,8 Z)-	-1,1-di	imethox	vdodeca-4	.8-diene.

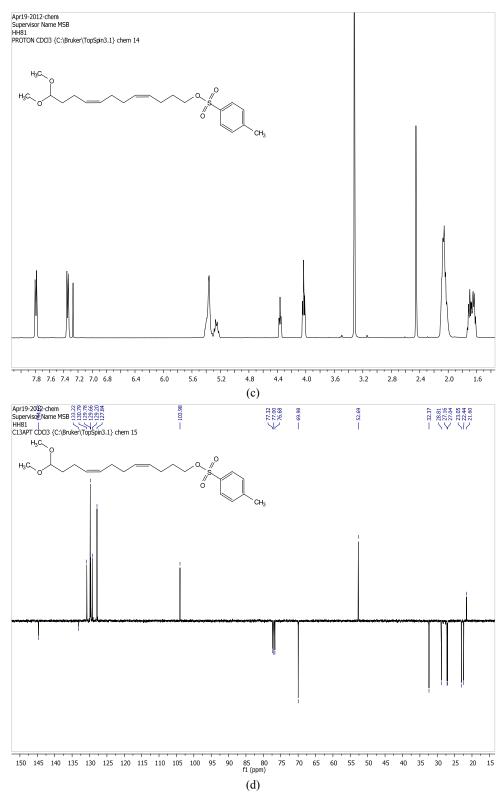


Fig. 11 The diagnosing process of the above products using NMR spectrum ((a) ¹H NMRof (4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-ol in CDCl₃, (b) ¹³C NMR of (4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-olin CDCl₃, (c) ¹H NMRof (4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-yl 4-methylbenzene-sulfonate in CDCl₃ and (d) Dept-CNMRof (4Z,8Z)-12,12-dimethoxydodeca-4,8-dien-1-yl 4-methylbenzene-sulfonatein CDCl₃).

4. Conclusion

Controlled ozonolysis process sustains a suitable technique to break unsaturated double chemical compounds alkenes or alkynes form organic compounds in which the multiple carbon-carbon bond has been replaced by a double bondtooxygen. These products could widely be used in the synthesis of insect pheromones instead of insecticides and may also be as useful intermediate compounds in many chemical reactions.

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