

OZONOLYSIS OF CYCLODODECENE

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Abstract—Ozonolysis of cyclododecene was carried out to produce an ω -formyl carboxylic acid (12-oxododecanoic acid) which is derived from zwitterion and aldehyde moiety that are formed during the reaction. The ozonolysis was performed to examine the product distribution under such reaction variables as temperature, kinds of solvent, and presence of catalyst. The yield of polymeric ozonide, which is undesirable product, was measured to be dominantly 86% without pyridine catalyst, whereas, only 10.25% with the catalyst. The optimum reaction condition was to be in MC (methylene chloride) solvent, and in the presence of equimolar olefin and pyridine catalyst at 0°C, at which the yields of polymeric ozonide, 1,12-dodecanedialdehyde, 1,12-dodecanedicarboxylic acid, and 12-oxo-dodecanoic acid were 10.25%, 26.72%, 26.31%, and 36.72%, respectively.

Key words: Ozonation, Cyclododecene, Pyridine

INTRODUCTION

Ozone is a powerful oxidizing agent for olefin in ozonolysis and it attacks selectively the double bond. According to the Criegee mechanism [1, 2], the reaction results eventually in the cleavage of double bond, and it proceeds stepwise with the formation of a series of peroxidic intermediates. In the first step, the first intermediate, an ozone-olefin adduct, the structure of which Criegee left in doubt, was assumed to be very unstable and to be cleaved to a zwitterion and an aldehyde or ketone. Zwitterion or carbonyl oxide, the key intermediate in the Criegee mechanism, is proposed earlier by Harries [3-5] and Staudinger [6, 7]. The fate of such a zwitterion or carbonyl oxide, according to the Criegee mechanism, depends partly on its source and partly on its environment. It was suggested that there were at least three ways in which it can stabilize itself: (a) reaction with an aldehyde or ketone, usually an aldehyde, to give an ozonide; (b) dimerization and polymerization to give dimeric and polymeric ozonide (favored by aprotic solvents and by aldehyde moiety); (c) reaction with a protic, nucleophilic solvent molecule to give α -substituted hydroperoxide [2]. It is a common feature of the peroxidic compound that it has limited stability. This imposes considerable limitation on its utility as industrial products, and for that reason, the ozonolysis has long been disregarded as a potential oxidation technique in industrial chemistry.

In recent year, non-peroxidic products could be obtained by the judicious selection and application of specific catalyst, pyridine. One example for such reaction is the pyridine-catalyzed rearrangement of mono-substituted carbonyl oxide to give carboxylic acid. This type of reaction has been discovered by the K. Griesbaum [8, 9] and the present study was encouraged in cooperation with his numerous laboratory advice. In 1973, Odinokov et al. [10] reported that the ozonolysis of cyclohexene in mixed solvent (pyridine-AcOH) afforded 29.5% α,ω -dicarboxylic acid and 35-40% ω -formyl carboxylic acid, isolated as its 2,4-dinitrophenylhydra-

zone (DNP) and that of its methyl-ester. And Kim [11] reported that the ozonolysis of cyclohexene in the presence of pyridine catalyst obtained 6% α,ω -dicarboxylic acid, 82% ω -formyl carboxylic acid, and 12% α,ω -dialdehyde by analyzing NMR itself without its pretreatment and effects on amount of catalyst. Among the products, an ω -formyl carboxylic acid is a very essential precursor for making terminally bifunctional molecules such as ω -hydroxy carboxylic acid, ω -amino acid and α,ω -dicarboxylic acid [12]. Also Kim et al. [13] reported that pyridine catalyzed the isomerization of zwitterionic carbonyl oxide moieties to give the corresponding carboxylic acids.

In this study, ω -formyl carboxylic acid (12-oxododecanoic acid) is prepared by the ozonolysis of cyclododecene, which is derived from zwitterion and aldehyde moiety that are formed during the reaction. The yield of ω -formyl carboxylic acid was examined by varying temperature, kinds of solvent, and the presence of pyridine catalyst.

EXPERIMENTAL SECTION

1. Reagent

Solvents used in the present experiment, ethylether (EE, 95%), ethylacetate (EA, 95%), and methylene chloride (MC, 95%) were purchased from Duksan Chemical Co.. They were dried and deoxygenated by distillation over sodium metal under a nitrogen atmosphere. A substrate cyclododecene (>95%) purchased from Aldrich Co. was used without further purification. Pyridine (96%, Kanto Chemical Co.) was used as a catalyst.

2. Experimental Procedure

For the ozonolysis, ozone was generated by electric discharge in an oxygen stream, using a Sander or Fisher 500 ozone generator. Ozone concentration in oxygen, which served also as a carrier gas, averaged 0.5-1.0 mmole/l. The ozone concentration was determined by percolation of ozone-oxygen mixture through a 2% aqueous solution of potassium iodide (KI) and subsequent titration of the liberated iodine with a 0.1 N aqueous sodiumthiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) solution. For the reaction, the following procedure has

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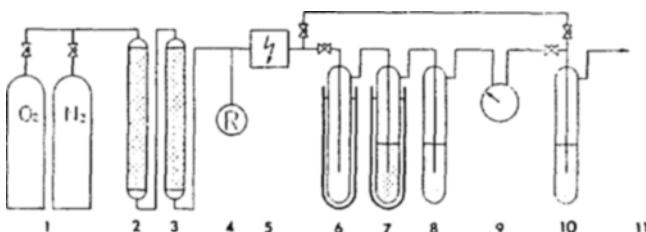


Fig. 1. Experimental apparatus of ozonolysis.

1. Gas bomb (O ₂ , N ₂)	7. Reactor
2. Drying tube (silicagel)	8. KI solution bottle (0.1 N)
3. Drying tube (CaCl ₂)	9. Gas meter
4. Manometer	10. NaOH solution bottle (10 wt%)
5. Ozone generator	
6. Cool trap (-78°C)	11. Hood

been used. A mixture consisted of 2.41 g (14.5 mmole) of cyclododecene and equimolar pyridine on the basis of olefin was dissolved in 100 ml of EE, EA, or MC and transferred into the reactor (7) (Fig. 1). The mixture was stirred and cooled to the desired reaction temperature and then the reaction was started. During the whole course of run, the gas stream was adjusted to the flow rate of 0.5 l/min through the reactor and contained 0.5 mmole of ozone per liter of O₃/O₂ mixed gas. The completion of the reaction was confirmed by the change of color in KI trap (8) (change to right-brown due to the excess ozone and iodine), and the O₃/O₂ mixed gas was stopped and then nitrogen was purged for ca. 20 minutes to kick out remained ozone in the reactor. The product in the reactor was used for further analysis after removing solvent by a rotary vacuum evaporator.

The reaction mixture obtained in this reaction was treated as stated before. These products consisted of polymeric ozonide, 1,12-dodecanedialdehyde, 12-oxododecanoic acid, and 1,12-dodecanedicarboxylic acid. Of these products, the polymeric ozonide having a characteristic insolubility in n-pentane was isolated easily [13], and then the remaining product, containing 1,12-dodecanedialdehyde, 12-oxododecanoic acid, and 1,12-dodecanedicarboxylic acid, was treated with a 10 wt% aqueous solution of sodium bicarbonate (NaHCO₃). The molecules having the carboxylic functional group, that is 12-oxododecanoic acid and 1,12-dodecanedicarboxylic acid, readily dissolved in the aqueous solution and so the 1,12-dodecanedialdehyde was obtained easily. The aqueous layer containing 12-oxododecanoic acid and 1,12-dodecanedicarboxylic acid was acidified with conc. hydrochloric acid (HCl) and then cooled in an ice bath, and the extracts were obtained by MC as an extractant.

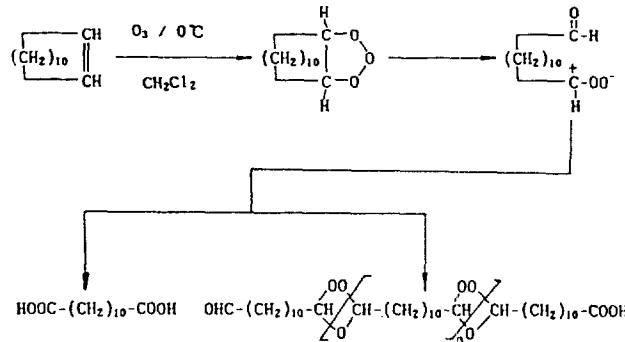
3. Analyses

The sample of ca. 40 mg of the product was dissolved in acetone-d₆ or CDCl₃ and analyzed by ¹H-NMR spectroscopy. The spectra were recorded on a Bruker FT-80A NMR spectrometer using tetramethylsilane (TMS) as a reference.

(1) Identification of polymeric ozonide, 1,12-dodecanedicarboxylic acid, 12-oxododecanoic acid, and 1,12-dodecanedialdehyde

*Polymeric ozonide : colorless viscous liquid; ¹H-NMR (80 MHz, acetone-d₆/TMS) : δ=9.77-9.78 (t, 1H), 5.6-5.8 (m, 1H), 1.2-1.4 (m, 12H), 1.9-2.1 (m, 4H), 3.2-3.3 (s, 2H), 3.5-3.6 (s, 2H); IR (KBr/Film) : 2950-3600, 2700, 1715, 1110, 910 cm⁻¹.

*1,12-dodecanedicarboxylic acid : ¹H-NMR (80 MHz, CDCl₃/TMS) : δ=9.30 (s, 2H), 1.0-1.85 (m, 12H), 2.15-2.25 (m, 4H), 2.30-2.50 (t, 4H); IR (KBr/Film) : 2980-3600, 1725 cm⁻¹.



Scheme 1. Products obtained from the ozonolysis of cyclododecene without pyridine catalyst in MC at 0°C.

*12-oxododecanoic acid : ¹H-NMR (80 MHz, CDCl₃/TMS) : δ=9.85 (t, 1H), 9.3 (s, 1H), 0.95-1.45 (m, 12H), 1.5-1.65 (m, 4H), 2.2-2.25 (m, 2H), 2.4-2.6 (t, 2H); IR (KBr/Film) : 2980-3600, 2700, 1725 cm⁻¹.

*1,12-dodecanedialdehyde : ¹H-NMR (80 MHz, acetone-d₆/TMS) : δ=9.85 (t, 2H), 1.0-1.8 (m, 12H), 2.1-2.15 (m, 4H), 2.25-2.5 (t, 4H); IR (KBr/Film) : 2950-3500, 2700, 1720 cm⁻¹.

(2) Calculation of product yield without internal standard material [14]

$$n_x = \frac{G \times I_x}{\sum_i (I_i / H_i) \times H_x \times M_x}$$

$$\text{Yield}(\%) = \frac{G \times I_x \times 100}{\sum_i (I_i / H_i) \times H_x \times M_x \times n_{\text{initial}}}$$

Where,

- G : weight of total product [g]
- I_x : sum of integral value for product x
- I_i : sum of member of hydrogen atom product i
- H_x : sum of member of hydrogen atom for product x
- H_i : sum of member of hydrogen product i
- M_x : molecular weight of product x
- n_{initial} : mole of reactant
- n_x : mole of product x

For Infrared (IR) analysis, the product and KBr powder were mixed and pressed into a thin self-supporting pellet. The IR spectra have been recorded with Perkin Elmer 1600 series FT-IR spectrometer using KBr as a reference.

*Separation of the polymeric ozonide

The solvent of reaction mixture was removed by the rotary vacuum evaporator and the crude product was kept stirring with n-pentane at room temperature for ca. 1 hour and it stopped. The polymeric ozonide was separated by simple vacuum filtration [13].

RESULTS AND DISCUSSION

1. Without Pyridine (Scheme 1)

The ozonolysis of cyclododecene was performed in the aprotic non-participating solvent (MC) without pyridine catalyst at 0°C. The mixture obtained after reaction was treated as mentioned above (separation of the polymeric ozonide). The yield of polymeric ozonide was 86% [12] and that of 1,12-dodecanedicarboxylic acid was 14%. Fig. 2 and Fig. 3 are the ¹H-NMR and IR spectra

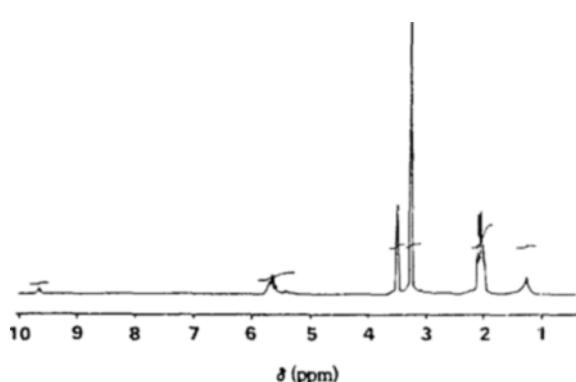


Fig. 2. $^1\text{H-NMR}$ Spectrum (80 MHz, acetone- d_6 /TMS) of polymeric ozonide obtained from the ozonolysis of cyclododecene in the absence of pyridine in CH_2Cl_2 at 0°C.

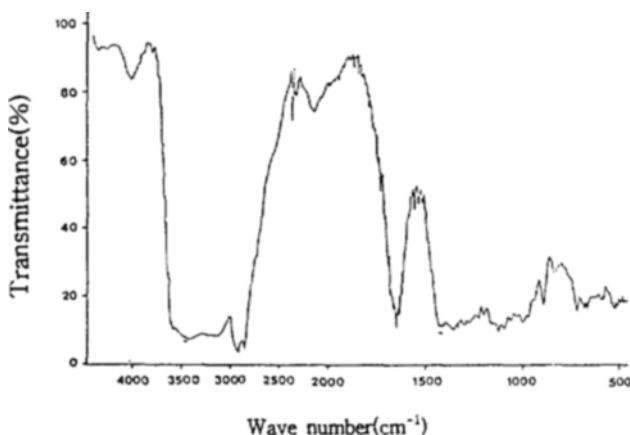
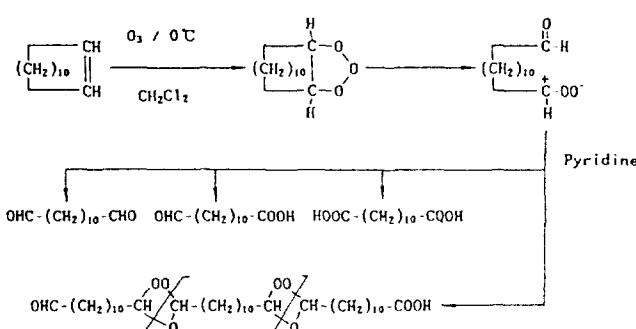


Fig. 3. IR Spectrum of polymeric ozonide obtained from the ozonolysis of cyclododecene in the absence of pyridine in CH_2Cl_2 at 0°C.



Scheme 2. Products obtained from the ozonolysis of cyclododecene with pyridine catalyst in MC at 0°C.

for the polymeric ozonide. The ozonide was a colorless, viscous liquid. The $^1\text{H-NMR}$ spectrum showed a triplet at 3.5-3.6 ppm for the methylene protons next to aldehyde and at 3.2-3.3 ppm for the protons next to carboxylic acid and at 9.77-9.78 ppm for the aldehydic protons and a multiplet at 1.2-1.4 ppm for the internal methylene protons and at 1.9-2.1 ppm for the remaining methylene protons and at 5.6-5.8 ppm for the ozonide peroxy protons. The IR spectrum of polymeric ozonide showed a carbonyl absorption at ca. 1715 cm^{-1} and C-H of aldehyde group at ca. 2700 cm^{-1} and C-O combined with peroxy bonding at 910 and 1110 cm^{-1} .

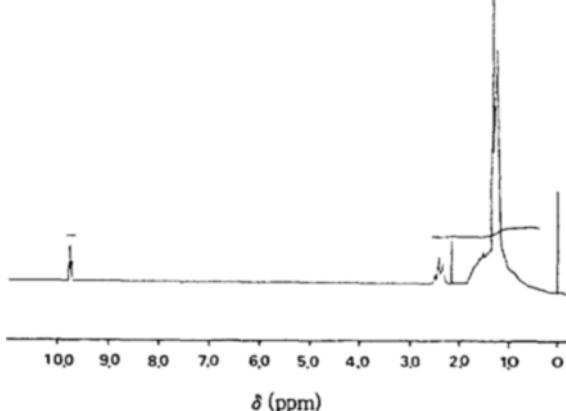


Fig. 4. $^1\text{H-NMR}$ Spectrum (80 MHz, acetone- d_6 /TMS) of extracts after treatment in aqueous NaHCO_3 solution of raw products obtained from the ozonolysis of cyclododecene in the presence of equimolar pyridine in CH_2Cl_2 at 0°C.

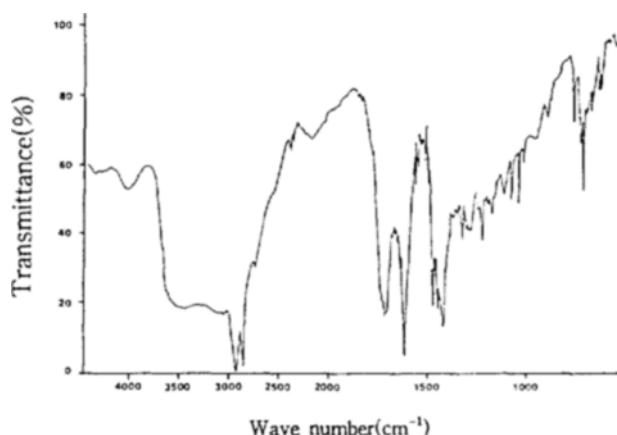


Fig. 5. IR Spectrum of extracts after treatment in aqueous NaHCO_3 solution of raw products obtained from the ozonolysis of cyclododecene in the presence of equimolar pyridine in CH_2Cl_2 at 0°C.

This indicates that there exist terminal aldehyde groups and, hence, that the polymeric ozonide is an open chain [15].

2. With Pyridine (Scheme 2)

Fig. 4 and Fig. 5 are the $^1\text{H-NMR}$ and IR spectra of 1,12-dodecanedialdehyde. The $^1\text{H-NMR}$ spectrum showed a triplet at 9.85 ppm for the aldehyde protons and at 2.25-2.5 ppm for the methylene protons next to aldehyde and a multiplet at 1.0-1.8 ppm for the internal methylene protons and at 2.1-2.15 ppm for the remaining methylene protons. The IR spectrum of 1,12-dodecanedialdehyde showed a broad hydroxyl absorption band at ca. $2950\text{-}3500\text{ cm}^{-1}$ and C-H of aldehyde group at ca. 2700 cm^{-1} and carbonyl at ca. 1720 cm^{-1} .

Fig. 6 and Fig. 7 are the $^1\text{H-NMR}$ and IR spectra for a mixture of 12-oxododecanoic acid and 1,12-dodecanedicarboxylic acid. The $^1\text{H-NMR}$ spectrum showed a triplet at 9.85 ppm for the aldehydic protons and a singlet at 9.3 ppm for the carboxylic protons and a triplet at 2.4-2.6 ppm for the methylene protons next to carboxylic group and a multiplet at 0.95-1.45 ppm for the internal methylene protons and at 1.5-1.65 ppm for the remaining methylene protons. The IR spectrum showed a broad hydroxyl absorption

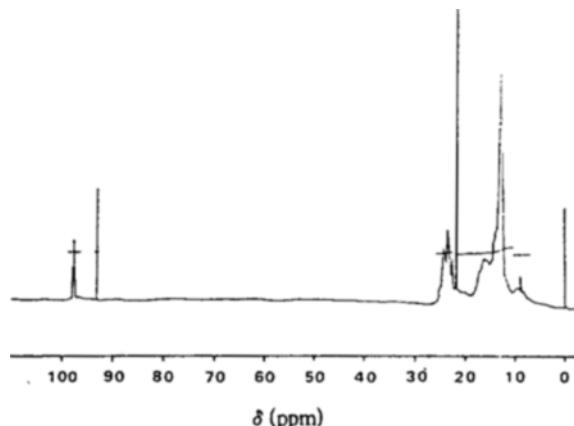


Fig. 6. $^1\text{H-NMR}$ Spectrum (80 MHz, CDCl_3/TMS) of extracts after acidifying water layer treated in aqueous NaHCO_3 solution of raw products obtained from the ozonolysis of cyclododecene in the presence of equimolar pyridine in CH_2Cl_2 at 0°C .

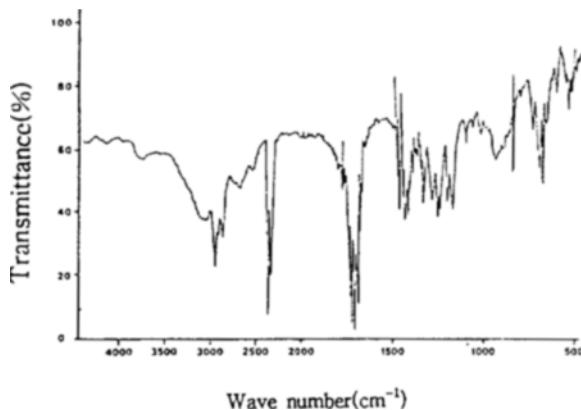


Fig. 7. IR Spectrum of extracts after acidifying water layer treated in aqueous NaHCO_3 solution of raw products obtained from the ozonolysis of cyclododecene in the presence of equimolar pyridine in CH_2Cl_2 at 0°C .

band at ca. $2980\text{-}3600\text{ cm}^{-1}$ and carbonyl at ca. 1725 cm^{-1} and C-H of aldehyde group at ca. 2700 cm^{-1} .

From the ozonolysis in the presence of pyridine, the polymeric ozonide, 1,12-dodecanedicarboxylic acid, 1,12-dodecanedialdehyde, and 12-oxododecanoic acid were obtained and the yields were 10.25%, 26.31%, 26.72%, and 36.72%, respectively.

3. Effects of Reaction Temperature

The 2.41 g (14.5 mmole) of cyclododecene was used in the presence of equimolar pyridine on the basis of olefin and 100 ml of MC at various temperature, that is -78°C , -15°C , 0°C , 20°C . As shown in Fig. 8, the yields of 1,12-dodecanedialdehyde decreased with temperature, whereas that of 1,12-dodecanedicarboxylic acid increased. In other words, the α,ω -dialdehyde (1,12-dodecanedialdehyde) and α,ω -dicarboxylic acid (1,12-dodecanedicarboxylic acid) are competitive, and their relative yields are sensitive to the reaction temperature.

4. Effects of Solvent

The 2.41 g (14.5 mmole) of cyclododecene and equimolar pyridine catalyst were used in 100 ml of solvents such as EE, EA, and MC at 0°C . The dipole moments of EE, EA, and MC are 1.15D, 1.78D, and 1.65D, respectively. In a higher polar solvent,

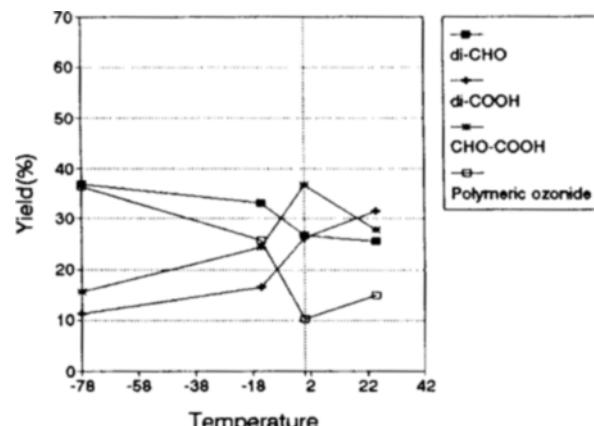


Fig. 8. Effects of reaction temperature on the yields of products obtained from ozonolysis of cyclododecene in the presence of equimolar pyridine in CH_2Cl_2 (based on the $^1\text{H-NMR}$ analysis).

the yield of polymeric ozonide decreased and that of 12-oxododecanoic acid increased. Especially the yield of 12-oxododecanoic acid was maximized in MC (Fig. 9). Even though the dipole moment of MC is smaller than EA, the practical polarity of MC is larger than EA due to the relatively larger dielectric constant of MC compared to that of EA [16].

Conclusively, in case of the larger carbon number of ring, the zwitterion and aldehyde moiety obtained from the ozonolysis had their increased steric hindrance, and thus the rearrangement to the ω -formyl carboxylic acid decreased and the recombination to the polymeric ozonide increased. Of these conditions, the better yield of ω -formyl carboxylic acid (12-oxododecanoic acid) was obtained in the presence of pyridine catalyst, in MC solvent, and at 0°C .

CONCLUSION

The ω -formyl carboxylic acid (12-oxododecanoic acid) was produced by ozonolysis of cyclododecene. In this study, the effects of the presence of pyridine, temperature, and kinds of solvent on the product yields were examined. The following results were obtained.

1. The optimum condition for a maximum yield of ω -formyl carboxylic acid (12-oxododecanoic acid) was determined to be under equimolar presence of pyridine based on cycloolefin (cyclododecene) and in methylene chloride solvent at 0°C . The best yield for 12-oxododecanoic acid was 36.72%, and those of polymeric ozonide, 1,12-dodecanedialdehyde, 1,12-dodecanedicarboxylic acid were 10.25%, 26.72%, and 26.31%, respectively.

2. The yields of undesirable polymeric ozonide were 86% in the absence of pyridine catalyst, whereas only 10.25% was measured in the presence of the catalyst.

3. As the temperature increased, the yield of α,ω -dialdehyde decreased but the yield of α,ω -dicarboxylic acid increased.

4. In a higher polar solvent, the yield of polymeric ozonide decreased and that of ω -formyl carboxylic acid (12-oxododecanoic acid) increased.

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