Light-induced Reactions of Unsaturated Fatty Acid Methyl Esters. III.

Photo-dimerization Reactions of Conjugated Fatty Acid Methyl Esters

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Abstract

The photochemical reactions of conjugated fatty acid methyl esters, that is, methyl α -eleostearate, methyl *cis*-9, *trans*-11-and *trans*-9, *trans*-11-octadecadienoates, under various conditions were studied. The formation of dimers was rapid from these conjugated fatty esters in either CCl_4 or CHCl_3 . However, the dimers produced were found to be chlorinated. Accordingly, the photo-dimerization in halomethanes was recognized to be a kind of telomerization, where the halomethane itself took part in the reaction.

In the greater part of the photochemical reactions in organic solvents other than halomethanes, the *cis-trans* isomerization reaction was observed. Especially, the *cis, trans*-conjugated fatty ester was converted into only *trans, trans*-conjugated isomer in heptane without forming the dimer. Then, both the photo-dimerization and the isomerization of the conjugated fatty esters in heptane were suggested to be carried out by the conversion of the conjugated fatty esters into their electronically excited molecules by irradiation.

Futhermore, the effective wave length of light on the photochemical reactions of the conjugated esters was also examined by monochromatic radiation.

1 Introduction

It is well known that unsaturated fatty acids are thermally converted to dimers plus higher polymers and that the products are used as dimer acids for industrial purposes. Many studies have already been carried out on the thermal polymerization reactions and on the structures of the dimers of unsaturated fatty acids or esters^{1)~4)}. However, the photo-dimerization of unsaturated fatty acids have hardly been studied. Therefore, we have studied the photo-dimerization reaction as a new method for the dimerization of unsaturated fatty esters.

Methyl β eleostearate was previously observed to form dimers in heptane, CCl_4 and CHCl_3 by irradiation with light of a high pressure mercury lamp (100 W)^{5), 6)}. However, the feature of the photo-dimerization of methyl β eleostearate in heptane was found to be quite different from that in either CCl_4 or CHCl_3 from the analyses of the structures

of the produced dimers in each solvent. The photo-dimerization in heptane was considered to proceed via the electronically excited molecule of the eleostearate by direct absorption of photons.

On the other hand, the photochemical reaction of the eleostearate in CCl_4 was recognized to be a kind of telomerization, in which CCl_4 directly takes part in the reaction as Cl and CCl_3 radicals formed by irradiation.

In the present work, we have further examined the photo-dimerization reactions carried out in solution on the conjugated fatty acid methyl esters which readily dimerize thermally. The conjugated fatty esters used are as follows: methyl α eleostearate, methyl *cis*-9, *trans*-11- and *trans*-9, *trans*-11-octadecadienoates.

2 Experimental

2.1 Materials

2.1.1 Methyl α Eleostearate

The ester was prepared from tung oil by the method described by O'Connor *et al.*¹⁾ After saponification of tung oil, the fatty acid were liberated by adding diluted sulfuric acid. The α eleostearic acid was separated by crystallization from 95% aqueous ethanol and then from petroleum ether. The product was esterified in N_2 atmosphere, and refined by adsorption chromatography on alumina column, using petroleum ether as an eluent. The ester obtained was found to be 92.1% pure including methyl β eleostearate as impurities.

2.1.2 Methyl *cis*-9, *trans*-11-octadecadienoate

The commercial dehydrated castor oil fatty acids containing 49.0% of *cis*, *trans*-conjugated octadecadienoic acid, which is formed by the dehydration of ricinoleic acid, were converted to methyl esters by refluxing for 1 hr with methanol containing about 1% of *p*-toluenesulfonic acid. Methyl *cis*-9, *trans*-11-octadecadienoate was separated from the methyl esters by the urea-adduct method, and it was purified by solvent crystallization at -60°C , using a mixture of methyl alcohol and acetone⁸⁾. The ester separated was further refined by adsorption chromatography by a similar method to that used for the methyl α eleostearate. The product was analyzed by GLC and proved to be 90.5% pure including methyl linoleate and *trans*, *trans*-conjugated octadecadienoate as impurities.

2.1.3 Methyl *trans*-9, *trans*-11-octadecadienoate

Ricinelaic acid was dehydrated by heating at 235°C under vacuum for 3 hr and the crude dehydrated acid were obtained by vacuum distillation. *Trans*-9, *trans*-11-octadecadienoic acid was obtained by crystallization from aqueous ethanol solution of crude acids at -15°C ⁹⁾. The methyl ester of the acid was analyzed by GLC and proved to be 91.3% pure with methyl stearate and trace of *cis*, *trans*-conjugated octadecadienoate.

2.2 Photochemical Reactions

2.2.1 Photochemical reactions with high pressure mercury lamp

Twenty grams of conjugated fatty ester was dissolved in 300 ml of organic solvent with 2 g of methyl stearate as a internal reference. The photochemical reactions were carried out under the nitrogen atmosphere at $25 \pm 2^\circ\text{C}$ by irradiation with light of high pressure mercury lamp (100 W) in a water cooled quartz well placed in the solution.

2.2.2 Photochemical reactions with low pressure mercury lamp

Five grams of conjugated ester was dissolved in 300 ml of solvent with 0.5 g of methyl stearate. The photochemical reactions were carried out at $35 \pm 2^\circ\text{C}$ by irradiation with light of low pressure mercury lamp (30 W).

2.2.3 Photochemical reactions with monochromatic irradiation

Irradiation was carried out with monochromatic irradiation apparatus JASCO CRM-50 equipped with 2 kW xenon lamp, the light of which was dispersed to the monochromatic light by diffraction grating. The solutions of the esters prepared with a similar procedure to the reactions with the low pressure mercury lamp were irradiated under the nitrogen atmosphere in quartz tubes of 5 mm internal diameter arranged in the tube holder, where the each tube was illuminated with the different monochromatic light.

2.3 Separation of Photo-dimerization Product

The dimers were separated from the photochemical products by column chromatography using a 2 : 1 mixture of silica gel and alumina gel as an absorbent and benzene as an eluent. The effluent was collected in ten gram fractions in sample tubes using a fraction collector. The % transmittance of each fraction was measured at $2,925\text{ cm}^{-1}$ by an IR spectrometer and plotted as a chromatogram. On the basis on this graph, the monomer and the dimer were fractionated.

2.4 Analysis of Monomer Fraction

The analysis of monomer fractions was performed by Gas Liquid Chromatography using a 2 m by 3 mm, 15% butanediol succinate column at 210°C . The quantities of the various components in the chromatogram were determined by the internal standard.

2.5 Analysis of Photochemical Products

2.5.1 Thin layer chromatography

The fractions separated were analyzed by thin layer chromatography on 4 : 1 mixture of alumina gel and silica gel with benzene as the ascending developing solvent. The degree of separation of the dimer was determined.

2.5.2 Gas liquid chromatography

The temperature programming GLC was employed for the quantitative analysis of the dimer. Chromatography was carried out using 1 m stainless steel column of 3 mm internal diameter. The packing used was 1.5% silicon gum rubber on 60~

80 mesh chromosorb W. Temperature : 200~330°C. Prog. : 10°C/min. Flow rate : 40 ml/min.

2.5.3 Measurement of molecular weight

Mean molecular weights of the dimers were measured by a vapor pressure osmometer (Mechrolab Model 301 A) using CCl_4 as a solvent.

2.5.4 IR spectra

IR spectra were measured with Hitachi EP 1-S₂ spectrometer using the method of liquid film.

2.5.5 Mass spectra

Mass spectra were measured by a Consolidated Electrokinetics Model CEC 21-110 high resolution mass spectrometer.

2.6 Determination of Chlorine

The amounts of chlorine were determined by semimicro higher alcohol-metallic sodium method⁽¹⁰⁾.

3 Results and discussion

3.1 Photochemical Reaction of Conjugated Fatty Acid Methyl Esters

The photochemical reactions of conjugated fatty esters under various conditions are summarized in Table-1. In this table, the results of the photo-

dimerization of methyl β eleostearate are quoted for reference from our previous studies^{(5), (6)}. It should be noted that the concentration of fatty esters is about 0.2 M in the case of the photoreactions with the light of high pressure mercury lamp, while it is about 0.05 M in the reactions by irradiation with the light of low pressure mercury lamp. Hence, neither the rates of dimerization nor the yields of the dimers is comparable between the photo-reactions with high and low pressure mercury lamp. And, the photo-reactions under the same conditions other than irradiation lamp are found to be somewhat different with one another on account of the different distribution of wave length of light source. The results of the different photo-reactions depending on the wave length of irradiated light will be discussed later in detail.

From Table-1, it is seen that every photochemical reaction in CCl_4 or CHCl_3 forms the dimers in short reaction time without regard to the structures of the conjugated fatty esters, and that the yields of dimers in CCl_4 are relatively high as compared with those in CHCl_3 . On the other hand, the photo-

Table-1 Photo-dimerization products of conjugated fatty acid methyl esters.

No.	Fatty ester	Lamp (W)	Time (hr)	Solvent	Dimer				
					Yield (wt%)	Cl (wt%)	Mean mol. weight	I.V.	n_D^{25}
1 ^a	β -Eleostearate	H 100 ^c	2.0	CCl_4	48.9	20.5	733.9	84.3	1.5050
2 ^a		H 100	4.0	CHCl_3	40.4	16.8	666.0	89.5	1.5018
3 ^b		H 100	6.0	Heptane	32.8		545.9	149.8	1.4842
4		L 30 ^d	2.0	Heptane	61.2				
5	α -Eleostearate	H 100	4.0	CCl_4	51.1	20.4	715.4		1.5076
6		L 30	2.0	CCl_4	37.5				
7		L 30	4.0	CHCl_3	27.8				
8		L 30	4.0	Heptane	18.4				
9		L 30	4.0	EtOH	25.4				
10		L 30	4.0	Benzene	14.7				
11	<i>cis</i> -9, <i>trans</i> -11-Octadecadienoate	H 100	4.0	CCl_4	58.3	20.1	671.9		1.4911
12		H 100	6.0	CHCl_3	34.3	11.9	694.3	53.8	1.4864
13		L 30	1.0	CCl_4	58.5				
14		L 30	1.5	CHCl_3	40.6				
15		L 30	5.0	Heptane	Tr.				
16		L 30	5.0	EtOH	16.0				
17		L 30	5.0	Benzene	8.1				
18		L 30	5.0	Acetone	Tr.				
19	<i>trans</i> -9, <i>trans</i> -11-Octadecadienoate	H 100	4.0	CCl_4	49.2	25.4	729.9	79.8	1.4883
20		H 100	6.0	CHCl_3	26.5	12.7	665.5	104.4	1.4895
21		H 100	6.0	Heptane	11.7		545.0	142.8	1.4826
22		L 30	2.0	Heptane	38.6				

a; Reference⁽⁶⁾, b; Reference⁽⁵⁾

c; Concentration of fatty esters : ca 0.2 M

d; Concentration of fatty esters : ca 0.05 M

dimerization is a main process in heptane for methyl β eleostearate and methyl *trans*-9, *trans*-11-octadecadienoate, especially by irradiating with the light of low pressure mercury lamp. The photo-dimerization of α eleostearate was performed only in heptane and ethyl alcohol and the yields of dimers are not so high.

The photo-reaction processes of methyl *cis*-9, *trans*-11-octadecadienoate in organic solvents other than halomethanes (Experiment No. 15~18 in Table-1) are shown in Fig.-1. From this figure and the results in Table-1, the decrease of the *cis*, *trans* conjugated fatty ester is contributed only by its conversion to *trans*, *trans* conjugated isomer particularly in heptane and in acetone. The isomerization reactions are also observed on α eleostearate in both heptane and benzene.

Moreover, the photochemical reaction processes of methyl *trans*-9, *trans*-11-octadecadienoate in heptane with high and low pressure mercury lamps (Exp. Nos. 21 and 22) are shown in Figs.-2 and 3, respectively. These figures show that the reactions have different features depending on the light source. Namely, the photo-isomerization of esters such as *trans*, *trans* conjugated ester to *cis*, *trans*

conjugated isomers prevails over the dimerization reaction by irradiation with the light of high pressure mercury lamp, while by irradiation with the light of low pressure mercury lamp the photo-dimerization reaction is a main process and the isomerization scarcely occurs. From the results mentioned above, it is assumed that the yields of the products are different on account of the different intensity of the distributed wave length of light source, that is, photo-dimerization proceeded faster than photo-isomerization when the intensity of light is high.

As for the examination of the wave length of light, the reaction of α eleostearate in CCl_4 with

Fig.-1 Photo-isomerization reactions of methyl *cis*-9, *trans*-11-octadecadienoate.

Fig.-2 Photochemical reaction of methyl *trans*-9, *trans*-11-octadecadienoate in heptane by irradiation with high pressure mercury lamp (100 W).

Fig.-3 Photochemical reaction of methyl *trans*-9, *trans*-11-octadecadienoate in heptane by irradiation with low pressure mercury lamp (30 W).

the monochromatic irradiation is shown in **Fig.-4**, and those of methyl *cis*-9, *trans*-11-octadecadienoate in CCl_4 and in heptane are also shown in **Fig.-5** and **6**, respectively. From these figures, the photo-dimerization of α eleostearate is found to proceed faster with the light of longer wave length as compared with that of *cis*, *trans* conjugated fatty ester even in the same solvent.

As the *cis*, *trans* conjugated fatty ester has already

Fig.-4 Photo-dimerization of methyl α eleostearate in CCl_4 by diffraction grating monochromatic radiation.

Fig.-5 Photochemical reaction of methyl *cis*-9, *trans*-11-octadecadienoate in CCl_4 by diffraction grating monochromatic radiation.

Fig.-6 Photochemical reaction of methyl *cis*-9, *trans*-11-octadecadienoate in heptane by diffraction grating monochromatic radiation.

been noticed to form dimers in halomethanes and to be converted into *trans*, *trans* conjugated isomer in organic solvent other than halomethanes by irradiating, the results of monochromatic irradiation in **Fig.-5** and **6** clearly show the difference between the photo-reaction in CCl_4 and that in heptane. Practically, the photo-dimerization of *cis*, *trans* conjugated ester in CCl_4 is carried out mainly with the light of 275 nm wave length, while the photo-isomerization in heptane goes with the neighboring light of 230 nm.

Above all, from the photo-reaction experiment with monochromatic radiation, it is observed as theoretically well known that the irradiation with the light of wave length which the conjugated fatty esters absorb is necessary for the photo-reaction.

3.2 The Photo-dimerization Products of Conjugated Fatty Acid Methyl Esters

The properties of main photo-reaction dimers of conjugated fatty esters are listed in **Table-1**. It is interesting that every photo-reaction dimer in CCl_4 and CHCl_3 is chlorinated, and that the amounts of chlorine in the dimers produced in CCl_4 are relatively high with 20% level as compared with those in CHCl_3 with 10% level. The chlorinated dimers are found to have reasonable mean molecular weights, but low iodine values and high refractive indexes. Meanwhile, the photo-reaction dimers in heptane have reasonable mean molecular weight and iodine values as ordinary dimers of fatty ester.

Furthermore, the photo-reaction dimers in CCl_4

Fig-7 IR spectra of fractions of the photochemical product of methyl *cis*-9, *trans*-11-octadecadienoate in CCl_4 .

a : Monomer fraction
b : Dimer fraction

and heptane were examined in detail. To begin with, the results concerning the dimer of methyl *cis*-9, *trans*-11-octadecadienoate in CCl_4 (Exp. No. 11 in **Table-1**) is discussed as the model of the chlorinated dimer.

The IR spectrum of the dimer is shown in **Fig-7** together with that of monomer fraction. The absorption bands at 984 and 948 cm^{-1} , are observed in *cis*, *trans* conjugated fatty esters, disappeared and the absorption band at 968 cm^{-1} corresponding to an isolated *trans* double bond appeared. Moreover, the absorption band at 770 cm^{-1} , characteristic of C-Cl bond, is also observed. The data in **Fig-7** show that the photo-dimerization is carried out at the conjugated double bonds and that the produced dimers are chlorinated.

The high resolution mass spectral analysis is shown in **Table-2**. In this table, the parent peak M_1 is found at mass number 704.4133, for which the molecular formula is $\text{C}_{39}\text{H}_{67}\text{O}_4\text{Cl}_3$. This molecular formula is supposed to be the structure in which one H atom of the dimer of the conjugated ester is substituted by CCl_3 group. At the mass number 622.4683, the parent peak M_2 corresponding to a molecular formula $\text{C}_{38}\text{H}_{67}\text{O}_4\text{Cl}$ is also measured, where one H atom of the dimer molecule is substituted by a Cl atoms. Then, the plain dimer of the conjugated ester is certainly observed

at mass number 588.5065. Moreover, giving the consideration to the mean molecular weights and the amounts of chlorine shown in **Table-1**, the dimer of a molecular formula $\text{C}_{39}\text{H}_{66}\text{O}_4\text{Cl}_4$, where two H atoms of the dimer molecule are substituted by a Cl atom and CCl_3 group, is presumed to exist in the dimer fraction, even though the fragment ions are not identified in the mass spectral analysis.

Accordingly, it is considered that the photo-reaction dimers produced in CCl_4 are the mixture of those molecules mentioned above. Then, it is obvious that CCl_4 directly takes part in the photo-dimerization of the conjugated esters. The same results have also been obtained in the photo-reac-

Table-2-1 The high resolution mass spectral analysis of the photo-dimerization products of methyl *cis*-9, *trans*-11-octadecadienoate in CCl_4 .

Relative intensity	Mass detemd.	Mass calcd.	Fragment ion	Chemical formula of fragment ion
62.3	706.4121	706.4252 706.3876	M_1	$\text{C}_{39}\text{H}_{69}\text{O}_4^{85}\text{Cl}_3$ $\text{C}_{39}\text{H}_{67}\text{O}_4^{85}\text{Cl}_2^{87}\text{Cl}$ $\text{C}_{39}\text{H}_{66}\text{O}_4^{85}\text{Cl}_3$ $\text{C}_{39}\text{H}_{66}\text{O}_4^{85}\text{Cl}_2^{87}\text{Cl}$ $\text{C}_{39}\text{H}_{67}\text{O}_4^{85}\text{Cl}_3$ $\text{C}_{39}\text{H}_{66}\text{O}_4^{85}\text{Cl}_3$ $\text{C}_{39}\text{H}_{65}\text{O}_4^{85}\text{Cl}_3$
48.3	705.4108	705.4174 705.3798		
65.8	704.4133	704.4096		
27.3	703.4099	703.4018		
32.0	702.4009	702.3940		
8.2	670.4369	670.4484		
8.7	669.4333	669.4406		
18.1	634.4716	634.4716	$M_1 - ^{85}\text{Cl}$	$\text{C}_{39}\text{H}_{67}\text{O}_4^{85}\text{Cl}_2$
6.4	633.4634	633.4588	$M_1 - ^{85}\text{Cl}_2$	$\text{C}_{39}\text{H}_{67}\text{O}_4^{85}\text{Cl}$
13.4	633.3202	633.3238	$M_1 - (\text{CH}_2)_4\text{CH}_3$	$\text{C}_{34}\text{H}_{56}\text{O}_4^{85}\text{Cl}_3$
13.4	632.4491	632.4510		

Table-2-2

Relative intensity	Mass detemd.	Mass calcd.	Fragment ion	Chemical formula of fragment ion
7.6	623.4769	623.4794	M_2	$\text{C}_{38}\text{H}_{66}\text{O}_4^{85}\text{Cl}$
26.2	622.4683	622.4716		$\text{C}_{38}\text{H}_{67}\text{O}_4^{85}\text{Cl}$
25.0	621.4587	621.4638		$\text{C}_{38}\text{H}_{66}\text{O}_4^{85}\text{Cl}$
15.7	621.3110	621.3238	$M_1 - \text{CH}=\text{CH}(\text{CH}_2)_3\text{CH}_3$	$\text{C}_{38}\text{H}_{66}\text{O}_4^{85}\text{Cl}_3$
29.7	620.4573	620.4560	$M_1 - (\text{CH}_2)_5\text{CH}_3$	$\text{C}_{33}\text{H}_{52}\text{O}_4^{85}\text{Cl}_3$
15.7	619.2985	619.3082		
11.1	608.2913	608.3160		
34.4	607.2850	607.3082	$M_1 - \text{CH}=\text{CH}(\text{CH}_2)_4\text{CH}_3$	$\text{C}_{32}\text{H}_{54}\text{O}_4^{85}\text{Cl}_3$
7.6	606.2871	606.3004	$M_1 - (\text{CH}_2)_6\text{CH}_3$	$\text{C}_{32}\text{H}_{52}\text{O}_4^{85}\text{Cl}_3$
36.7	605.2937	605.2926		
26.6	595.2613	595.3082		
15.1	593.2885	593.2926	$M_1 - \text{CH}=\text{CH}(\text{CH}_2)_5\text{CH}_3$	$\text{C}_{31}\text{H}_{52}\text{O}_4^{85}\text{Cl}_3$
55.4	588.5065	588.5104	M_3	$\text{C}_{38}\text{H}_{66}\text{O}_4$
97.1	587.5009	587.5026		$\text{C}_{38}\text{H}_{67}\text{O}_4$
100.0	586.4947	586.4948		$\text{C}_{38}\text{H}_{66}\text{O}_4$
65.5	585.4872	585.4870		$\text{C}_{38}\text{H}_{65}\text{O}_4$
55.4	584.4842	584.4792

Fig.-8 IR spectra of fractions of the photochemical product of methyl *trans*-9, *trans*-11-octadecadienoate in heptane.
a : Monomer fraction, b : Dimer fraction

tions in CHCl_3 . Therefore, the photo-dimerization of the conjugated fatty esters in halomethanes are recognized as previously studied⁶⁾ to be a kind of telomerization, in which the halomethane itself forms Cl and CCl_3 radicals upon the irradiation of light.

Finally, the photo-reaction dimer of methyl *trans*-9, *trans*-11-octadecadienoate in heptane (Exp. No. 21 in Table-1) was studied. In Fig.-8 the IR spectrum of the dimer is shown together with the monomer fraction.

This figure shows that the absorption band at 968 cm^{-1} corresponding to an isolated *trans* double bond appeared in while the absorption band of *trans, trans* conjugated double bonds at 988 cm^{-1} became small.

Thinking about the high iodine values as compared with the thermal reaction dimers of the conjugated esters and the existence of the absorp-

tion band of *trans, trans* conjugated double bonds and also absence of that of a cyclic structure in the IR spectrum, the dimer produced in heptane is considered to be predominantly a noncyclic linked dimer formed by a coupling of the conjugated ester rather than the Diels-Alder addition cyclic dimer which is mainly found in the thermal dimerization products. Moreover, from the kinetic examination, the decrease of the conjugated esters is known to be in nearest agreement with a first order reaction. Therefore, it is suggested that the photo-dimerization in heptane proceeds by the conversion of the conjugated fatty esters into their excited molecules by irradiation.

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