

PALLADIUM- AND RHODIUM-CATALYZED SYNTHESIS OF ESTERS BY REACTION OF BUTADIENE, CARBON DIOXIDE, AND OXIRANES

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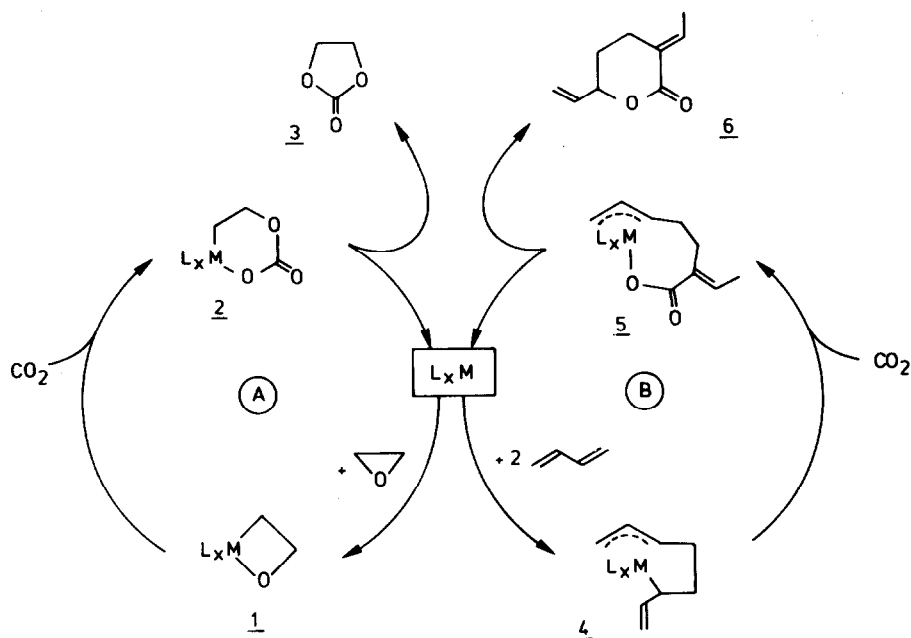
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Summary

Butadiene, carbon dioxide and ethylene oxide interact in the presence of palladium or rhodium catalysts to give (2'-hydroxyethyl)2-ethylidene-4,6-heptadienoate in a "one pot" reaction. When propylene oxide was used, two related isomeric esters with an additional methyl group in the alcohol part of the ester were obtained, in yields of up to 24%. Kinetic investigations suggest that the reaction occurs via the lactone 2-ethylidene-6-hepten-5-olide. The products are accounted for in terms of a mechanism involving the coordination of the oxirane to an allylic transition metal carboxylate complex and insertion of the oxirane to give an allylic alkoxy complex. Elimination of the products occurs via a hydrogen migration step.

Introduction

A variety of syntheses using carbon dioxide as a building block are used to give both industrial bulk chemicals and fine organic products [1], and in recent years use of transition metal catalyzed reactions has led to novel developments in CO₂ chemistry [2]. One typical example is the reaction of ethylene oxide with carbon dioxide to give ethylene carbonate, **3**, a useful solvent in the production of fibers and varnishes. This reaction was discovered by "IG Farben" in 1943, and since then a very large number of catalysts has been investigated. Several transition metal catalysts permit very mild conditions and give high yields and selectivities for this reaction. In 1973 De Pasquale reported the excellent activity of coordinatively unsaturated nickel (0) phosphine catalysts and proposed the mechanism outlined in cycle A of Scheme 1. In an oxidative addition step ethylene oxide coordinates to the nickel center yielding the metallaoxacyclobutane **1**; carbon dioxide then inserts into the metal–oxygen bond forming the intermediate **2**, from which the product **3** separates in a reductive elimination [3].

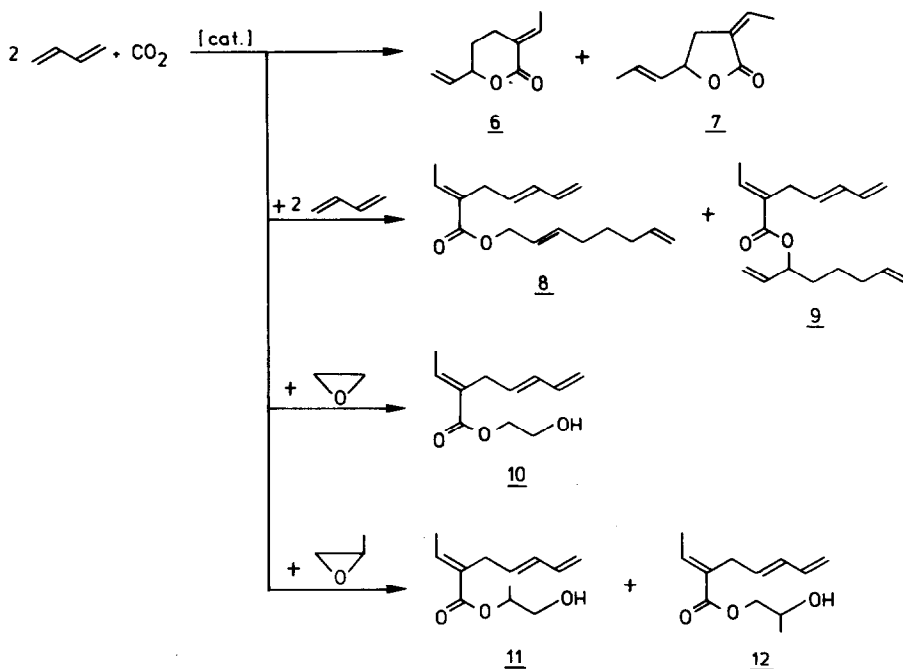


SCHEME 1

Compounds of chromium, manganese, iron and cobalt in the presence of organic halides also catalyze the carboxylation of epoxides [4], and halides of ruthenium or rhodium increase the reaction rate [5]. Kisch found catalysts which are active even at room temperature and under ordinary pressure [6] but even his most effective catalyst, a mixture of molybdenum pentachloride and triphenylphosphine, needs a fairly long reaction time. Fujinami recently reported that low valent palladium compounds are particularly effective in catalysis of the reaction of oxiranes with carbon dioxide; for example, butadiene monoxide reacted with CO_2 at 1 atm and at $0^\circ C$ to give an almost quantitative yield of the corresponding carbonate. With $Pd(PPh_3)_4$ as catalyst a reaction time of only 15 min was necessary [7].

Another interesting reaction is the palladium-catalyzed synthesis of lactone **6** starting from butadiene and carbon dioxide [8–12] (see cycle B in Scheme 1). Initially two molecules of butadiene add to the catalyst to give the η^1, η^3 -bisallyl complex **4**. Upon insertion of carbon dioxide into the metal–carbon bond the carboxylate complex **5** is formed, and the δ -lactone **6** separates from this in a cyclization process. Lactone **6** was obtained in yields of $> 50\%$ and in selectivities $> 95\%$.

Oxiranes and butadiene proved to be highly active partners in reactions with carbon dioxide. The question arose as to which route in Scheme 1 is preferred if both molecules brought into reaction with CO_2 at the same time. Both the oxidative addition of the oxirane forming complex **1** and the addition of butadiene yielding complex **4** seemed to be possible initial steps leading to higher-membered ring lactones or longer chain esters. We therefore extended our investigations of the transition metal initiated activation of carbon dioxide to the three-component co-reaction of butadiene, oxiranes, and CO_2 .



SCHEME 2

Results and discussion

Butadiene, carbon dioxide and ethylene oxide react together in the presence of palladium catalysts to give the novel glycol ester **10** of 2-ethylidene-4,6-heptadienoic acid in a "one pot" reaction. The analogous synthesis, involving three components, could be carried out with propylene oxide; the presence of the additional methyl group of the propylene oxide causing the formation of two isomers, the esters **11** and **12** (Scheme 2).

Side reactions give products derived from butadiene and CO_2 , namely the lactones **6** and **7** and, by further addition of butadiene, the octadienyl esters **8** and **9**. It is noteworthy that the octadienyl esters **8** and **9** and the novel hydroxyesters **10**, **11** and **12** are derivatives of the same 2-ethylidene-4,6-heptadienoic acid, demonstrating that the mechanistic pathways are closely related to one another. It must also be emphasized that in the reaction of butadiene, CO_2 and oxiranes, no carbonates, neither the ethylene carbonate **3** nor the corresponding propylene carbonate, could be detected as by-products.

In order to optimize the reaction and to obtain more details of the mechanism, the influence of the reaction parameters on the formation of the ester **11** and **12** was studied. A systematic variation of the palladium catalyst was carried out using as catalyst precursor palladiumbis(acetylacetonate) modified by various ligands, especially by mono- and bidentate phosphines. Table 1 shows the yields of the glycol esters **11** and **12** and of the by-products **6**–**9**, and the selectivities for these products.

Trialkylphosphines with linear substituents, mono- and bidentate phosphines containing phenyl groups, and 2,2'-bipyridine yield only small amounts of the main

TABLE 1
EFFECTS OF VARIATION OF THE LIGANDS ^a

Ligand ^b	Yields (mol%)		Selectivities (mol%)		
	Products 11 + 12	By-products 6-9	11 + 12	6-9	Dimers
PBu ₃ ⁿ	2	3	16	13	70
bipy	3	3	16	32	52
PEt ₃	3	1	31	3	66
PPh ₃	5	1	21	4	75
dppe	6	1	46	8	46
dcpe	8	17	35	50	15
PCy ₃	10	17	28	33	39
PPR ₃	22	3	62	5	33

^a 0.5 mmol Pd(acac)₂; 1.5 mmol ligand, 100 mmol butadiene; 150 mmol CO₂; 100 mmol propylene oxide; 10 ml CH₃CN; 20 h; 90°C. ^b bipy = 2,2'-bipyridine; dppe = 1,2-bis(diphenylphosphino)ethane; dcpe = 1,2-bis(dicyclohexylphosphino)ethane.

products and the by-products 6-9. Use of phosphines containing cyclohexyl groups, 1,2-bis(dicyclohexylphosphino)ethane and tricyclohexylphosphine, leads to increased formation (8-10%) of the glycol esters, but the yield of the by-products also rises to 17%. The only exception in this comparison is with triisopropylphosphine as ligand; in this case a yield of 22% of the glycol esters can be reached and only small amounts of the butadiene/CO₂-by-products are formed. The selectivity data in Table 1 show that in all experiments some butadiene dimers are also produced.

Not only the type of ligand, but also the amount of it used relative to the metal

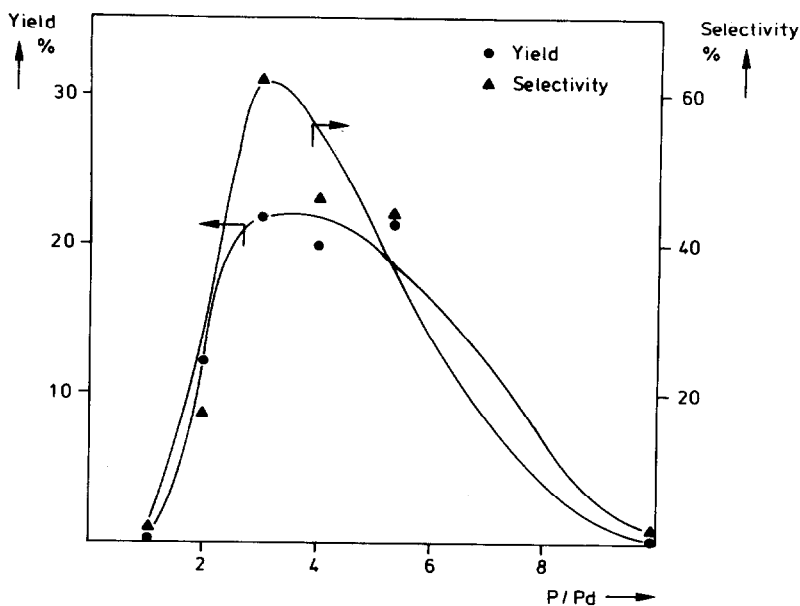


Fig. 1. Influence of the phosphine/palladium ratio on the yield and selectivity of the esters 11 and 12.

TABLE 2

EFFECTS OF VARIATION OF CATALYST CONCENTRATION AND OF THE RATIOS OF THE STARTING MATERIALS ^a

Pd(acac) ₂	Butadiene/CO ₂ / propylene oxide	Yields (mol%)		Selectivities (mol%)		
		11 + 12	6-9	11 + 12	6-9	Dimers
0.16	1/1.5/1	3	24	10	63	27
0.32	1/1.5/1	13	15	33	30	37
0.50	1/1.5/1	22	3	62	5	33
1.00	1/1.5/1	10	1	55	1	44
0.50	1/0.7/1	15	18	31	28	41
0.50	1/1.0/1	21	7	42	11	47
0.50	1/2.0/1	18	10	60	24	16
0.50	1/3.7/1	13	15	21	17	62
0.50	1/1.5/0.5	15	15	19	27	54
0.50	1/1.5/1.5	24	2	31	1	68
0.50	1/1.5/2.0	14	1	28	1	71
0.50	1/1.5/3.0	18	11	39	17	44

^a Ligand: triisopropylphosphine; all other data as given in Table 1.

has a great influence on catalysis. As shown in Fig. 1, the best yields of the glycol esters are obtained with phosphine/palladium ratios between 3/1 and 5/1; by far the best selectivity, 62%, is obtained at a 3/1 ratio.

The catalyst concentration, the butadiene/CO₂ ratio, and the butadiene/propylene oxide ratio also have an important influence on the ester formation. Some typical data are given in Table 2. At lower catalyst concentrations (0.16 mmol) the formation of by-products 6-9 predominates, but at higher catalyst concentrations (0.5 mmol) the esters 11 and 12 are the main products.

The optimum ratio of butadiene to carbon dioxide is 1/1.5; decrease or increase in the quantity of CO₂ reduces the yield of the glycol esters and enhances the formation of the by-products 6-9. Another important parameter influencing the reaction is the amount of propylene oxide. Best results are obtained with a butadiene/CO₂/propylene oxide ratio of 1/1.5/1.5, which leads to a 24% yield of the glycol esters 11 and 12. Only nitriles such as acetonitrile or benzonitrile can be used as solvents. Use of other polar or non-polar solvents resulted in only small amounts of glycol esters.

The yield of the glycol esters is very sensitive to the reaction temperature. As can be seen from Fig. 2, only in the small range of 85-95°C were reasonable yields and selectivities obtained.

The optimum yield of the products 11 and 12 is reached after 20-25 h (Fig. 3). With longer reaction times the yield is lower, indicating decomposition of the primary products. All the investigations described so far were carried out with palladiumbis(acetylacetonate) as the catalyst precursor. As shown in Table 3, this compound is one of the best catalysts, and its effectiveness is exceeded, and then only slightly, by tris(palladiumbisacetate). Cationic palladium complexes also provide catalysis leading to the glycol esters in yields of 14-20%. It is noteworthy that the esters are also formed when the rhodium complexes tris(rhodiumbisacetate) or (bisethylene)rhodiumacetylacetonate as catalysts are used, but the yields are very low.

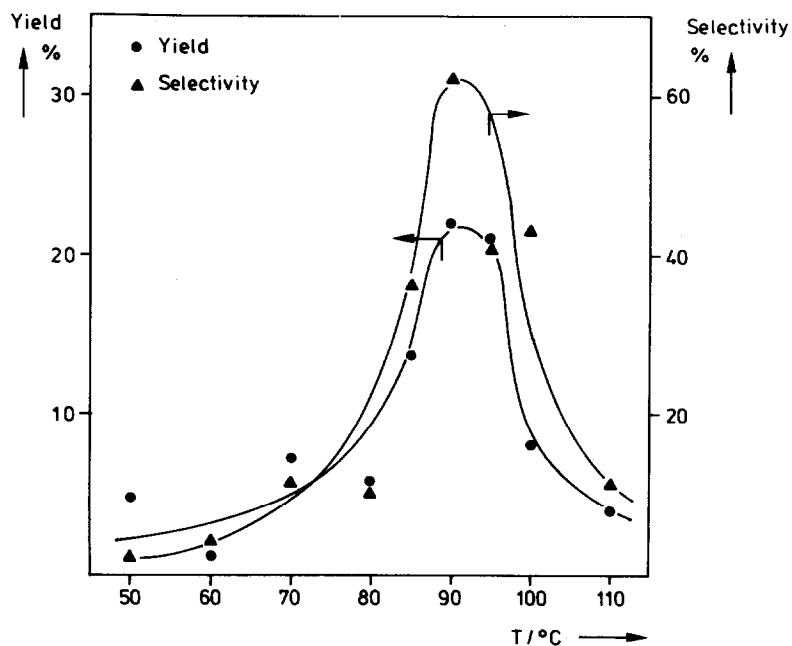


Fig. 2. Influence of the reaction temperature on the yield and selectivity of the esters **11** and **12**.

The proposed mechanism of the reaction with ethylene oxide is shown in Scheme 3. The first step is evidently the addition of butadiene and carbon dioxide to the catalyst to give the carboxylate complex **5**. As a result of our investigations the

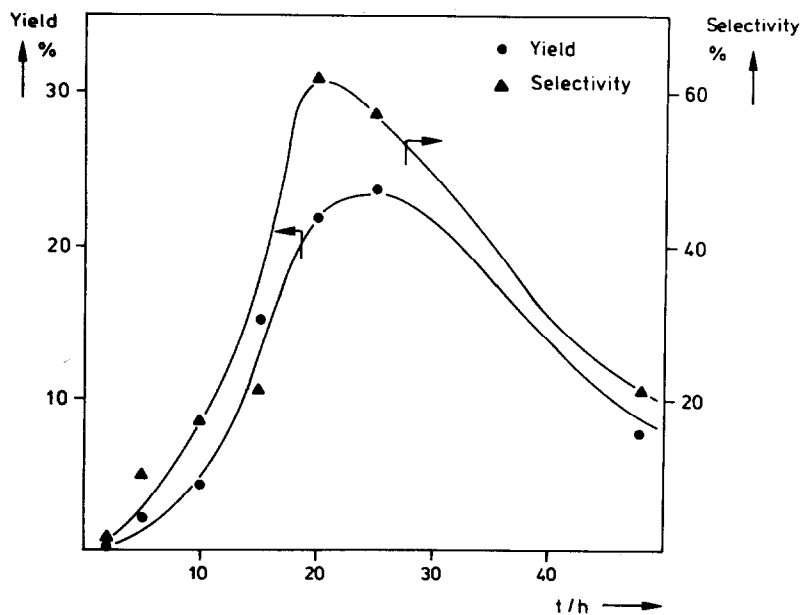


Fig. 3. Influence of the reaction time on yield and selectivity of the esters **11** and **12**.

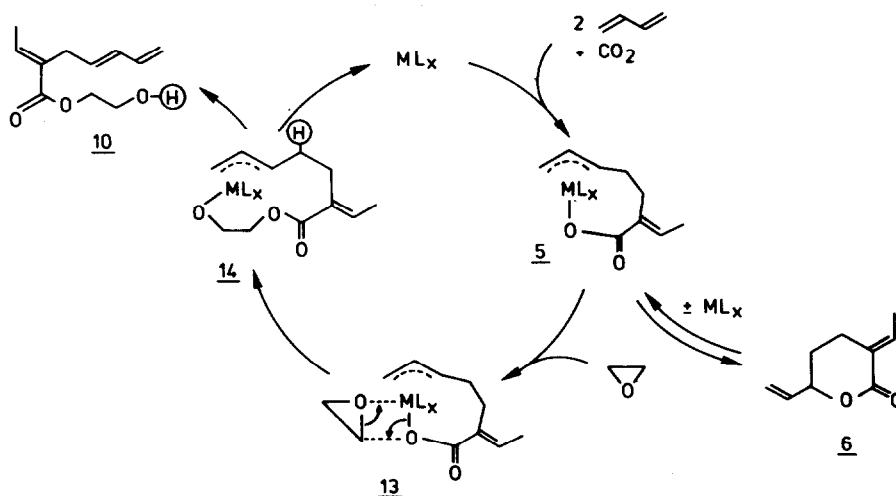
TABLE 3
EFFECTS OF VARIATION OF THE TRANSITION METAL CATALYST PRECURSOR ^a

Metal compound	Yields (mol%)		Selectivities (mol%)		
	11 + 12	6-9	11 + 12	6-9	Dimers
Pd(dba) ₂	9	22	29	49	22
Pd(acac) ₂	22	3	62	5	33
[Pd(OAc) ₂] ₃	24	3	48	4	48
[(cod)Pd(Cp)]BF ₄	14	1	30	2	68
[η^3 -C ₃ H ₅ Pd(CH ₃ CN) ₂]BF ₄	20	4	45	7	48
[Rh(OAc) ₂] ₃ ^b	3	1	51	5	44
(C ₂ H ₄) ₂ Rh(acac) ^b	1	5	25	10	65

^a Ligand: PPr₃; all other data as given in Table 1. ^b Ligand: PEt₃.

coordination of the oxirane by the carboxylate complex to form the intermediate **13** is very sensitive to a change in reaction conditions. In a synchronous process the oxirane ring opens and inserts into the existing metal-oxygen bond. A carbon-oxygen and a new metal-oxygen bond are formed, giving the (alkoxy)(allyl) complex **14** which then releases the glycol ester **10** with re-formation of the catalyst ML_x. The release of the ester must be accompanied by a hydrogen-shift from the acid chain to the oxygen of the first oxirane, thus producing a hydroxy group. This migration of hydrogen from the position α to the allyl group results in formation of the 1,3-diene structure.

The formation of the δ -lactone **6** by an elimination from complex **5** seems to compete with the production of ester **10**. Kinetic investigations revealed that at reaction times up to 10 h the δ -lactone predominates, and upon more prolonged reaction the δ -lactone disappears almost quantitatively from the reaction mixture, resulting in an optimum yield of the glycol esters after about 25 h. This observation



SCHEME 3

suggests that the ester **10** is formed from the lactone **6**. An experiment involving the optimum palladium catalyst $\text{Pd}(\text{acac})_2/\text{PPr}_3^i$, propylene oxide and a pure sample of the isolated lactone **6** led to the same yield (24%) of esters as is obtained by starting from butadiene and carbon dioxide. Comparative investigations showed that this coupling of the δ -lactone **6** and the oxirane occurs in transition metal catalyzed processes, since no ester was formed in thermal or base (PPr_3^i) catalyzed reactions.

Experimental

All experiments were performed under argon dried with 4 Å molecular sieve. The solvents were dried and distilled under argon. Analysis of the product mixtures was by GLC using a Sichromat 3 apparatus with a OV 1701 glass capillary and a temperature program from 70–250°C (6 min isothermal; rate of heating: 7°C/min). The isolation of the esters was by preparative GLC (Hupe APG 402). The products were identified by IR (Perkin–Elmer 782), ^1H and ^{13}C NMR (Bruker CXP 200) spectroscopy and by GLC/MS (Varian MAT 112 S). In ^{13}C NMR analysis the degree of substitution of the carbon atoms (p = primary, s = secondary, t = tertiary, q = quaternary) was determined by the Spin Echo Fourier Transform (SEFT) method.

Product identification

(2'-Hydroxyethyl)2-ethylidene-4,6-heptadienoate (**10**)

^1H NMR (200 MHz, DMSO): δ 6.88 (q, 1H, $\text{CH}_3\text{CH=}$); 6.27 (dt, 1H, $\text{CH}_2=\text{CHCH=}$); 6.02 (dd, 1H, $=\text{CHCH=CH}$); 5.68 (dt, 1H, CH=CHCH=CH_2); 5.03 (dd, 1H, $\text{CH}_2=\text{CH}$); 4.80 (s, 1H, OH); 4.07 (t, 2H, $\text{OCH}_2\text{CH}_2\text{OH}$); 3.59 (t, 2H, CH_2OH); 3.06 (d, 2H, $\text{CCH}_2\text{CH=}$); 1.78 (d, 3H, CH_3) ppm.

^{13}C NMR (50.3 MHz, DMSO): δ 166.4 (q, OC=O); 138.6 (t, $\text{CH}_3\text{CH=}$); 136.9 (t, $\text{CH}_2=\text{CH}$); 131.6 (t, $\text{CH}_2\text{CH=}$); 131.3 (t, CH=CHCH=); 130.3 (q, $=\text{C}$); 115.7 (s, $\text{CH}_2=$); 65.9 (s, CH_2OH); 59.0 (s, $\text{OCH}_2\text{CH}_2\text{OH}$); 28.8 (s, $=\text{CCH}_2\text{CH=}$); 14.0 (p, CH_3) ppm.

IR: ν 3450, 3045, 2962, 2930, 2880, 1715, 1650, 1455, 1390, 1280, 1210, 695 cm^{-1} .

Mass spectrum: $m/e = 196$ (M^+ , 5%), 134 (82), 119 (21), 107 (44), 91 (100), 79 (48), 45 (41), 41 (45).

Mixture of (1'-methyl-2'-hydroxyethyl)2-ethylidene-4,6-heptadienoate (**11**) and (2'-methyl-2'-hydroxyethyl)2-ethylidene-4,6-heptadienoate (**12**)

^1H NMR (200 MHz, DMSO): δ 6.87 (q, 1H, $\text{CH}_3\text{CH=}$); 6.27 (dt, 1H, $\text{CH}_2\text{CHCH=}$); 6.01 (dd, 1H, $=\text{CHCH=CH}$); 5.67 (dt, 1H, CH=CHCH=CH_2); 5.02 (dd, 2H, $\text{CH}_2=\text{CH}$); 4.75 (m, 1H, OH); 3.79–3.95 (m, 1, OCHCH_3); 3.32–3.50 (m, 2H, OCH_2CH); 3.05 (d, 2H, $\text{CCH}_2\text{CH=}$); 1.77/1.78 (d, 3H, $\text{CH}_3\text{CH=}$); 1.08 (t, 3H, CH_3CH) ppm.

^{13}C NMR (50.3 MHz, DMSO): δ 166.2 (q, OC=O); 138.5 (t, CH=CH_2); 136.8 (t, CH_3CH); 131.5 and 131.4 (t, CH=CH); 130.3 (q, $=\text{C}$); 115.6 (s, $=\text{CH}_2$); 71.3 and 63.8 (t, OCHCH_3); 69.1 (s, OCH_2); 28.8 (s, $=\text{CCH}_2\text{CH=}$); 16.3 and 19.9 (p, CH_3CH); 14.0 (p, $\text{CH}_3\text{CH=}$) ppm.

IR: ν 3450, 3045, 2962, 2930, 2880, 1715, 1650, 1455, 1390, 1280, 1210 cm^{-1} .

Mass spectrum: $m/e = 210$ (M^+ , 30%), 134 (70), 119 (68), 107 (92), 91 (100), 79 (44).

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