Dimer Acid Esters by Simultaneous Dehydration and Polymerization of Technical Methyl Ricinoleate

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Abstract

Filtrol 13 may be used to dehydrate methyl ricinoleate with simultaneous dimerization and polymerization of the linoleate esters formed. Hydrolysis of the ester group is avoided by the use of xylene as an azeotroping solvent and the preferred method of reaction is the dropwise addition of the ester to a stirred suspension of catalyst in xylene. Products prepared by this technique had a dimer/polymer ratio of about 5 when the yield was 50%. The acid value of the polymer was 7 and of the recovered monomer 3–4.

Introduction

Though the dehydration of castor oil has been extensively studied (e.g., 1,5) much of the published information, while reporting on the different isomers of linoleic esters produced, gives little indication of the extent of polymerization which can occur at the same time and which consumes some of the dienoic esters as they are formed. Elsewhere (9) we have reported on the rapid polymerization of conjugated dienoic acids induced by acid clay catalysts and we wished to extend our studies of this heterogeneous system to see if we could thereby dehydrate methyl ricinoleate. This technique might produce a different ratio of the geometrical isomers of linoleic esters from that obtained by other means and might also give dimerized esters directly under more vigorous conditions. We hoped to avoid hydrolysis of the ester group by use of azeotroping toluene or xylene to remove water rapidly from the system.

Dehydration by clays is reported in (6) and (11) while polymer formation in castor oil using activated clays is the basis of a patent (12). The use of ion exchange resins is described (4) but the only reference to the use of azeotroping solvents in connection with castor oil dehydration appears to be in a Russian patent (10). Of particular relevance, also, was the work of Body and Shorland (2) on dehydration of methyl ricinoleate by $KHSO_4$.

Experimental

Materials

Technical Methyl Ricinoleate was prepared by methanolysis of castor oil. Typical gas-liquid chromatography (GLC) analysis of the distilled product was

	%		%
Unidentified	0.2	Nonconj. linoleic	4.4
Palmitic	1.1	Conj. linoleic	Trace
Stearic	0.6	Ricinoleic	90.7
Oleic	3.1		

Hydroxyl value = 163.0

Filtrol 13 (a product of the Filtrol Corporation) was dried, either by heating to 150C overnight or by azeotroping with xylene. Weights of catalyst reported are always dry weight.

Method

Azeotropic Dehydrations were carried out in a heated round-bottomed flask fitted with stirrer, Dean and Starke distillation head, thermometer, dropping funnel and (in certain cases) nitrogen inlet. In earlier experiments all ingredients were mixed at the start but in later experiments (see Tables) the catalyst was stirred with xylene at reflux temperature and the ester added dropwise as fast as water of dehydration was removed. With a hydroxyl value of 163 about 5.3 g of water per 100 g ester was expected. In some cases 6–6.5 g was produced possibly due to side reactions, e.g., formation of methanol on partial hydrolysis.

Illustrative of the process is experiment No. 9.

Dried Filtrol 13 (100 g) was stirred in refluxing xylene (200 cc) and methyl ricinoleate (500 g) added at such a rate that water of dehydration was collected as rapidly as possible. The addition took 53 min at the outset of which the temperature of the reaction mixture was 140C and at the end of which it was 184C. After a further 5 min, when a total of 27 cc of water had been collected, the reaction mixture was rapidly cooled. After filtration to remove catalyst and washing of the filter cake with xylene, solvent was removed in vacuo and monomeric esters distilled until the temperature in the distillation flask was 270C at 0.2 mm mercury pressure.

The monomer weighed 226.5 g and had A.V. 3.8. The residue (A.V. 7.1, S.V. 184.8) weighed 244.0 g and had the composition: monomer, 10.9%; dimer, 75.6%; polymer, 13.5%.

TABLE I

Dehydration/Polymerization of Methyl Ricinoleate by Filtrol 13;
All Ingredients Mixed at Start

No.	% Cat.[a]	Temp, C	Time, Min	Water collected, cc	Wt. % residue	Residue analysis							Monomer anal.	
						A.V.	S.V.	Hydroxyl value	M.	D.	P.	D/P	A.V.	Hydroxyl value
1	5	180	60	5.4	34.3	4.2	195	6.3	3.4	75.7	20.9	3.6	2.3	4.8
2	5	180	120	6.0	34.3	4.6	....	....	11.7	70.7	17.6	4.0	2.1	....
3[b]	5	140–150	120	5.0	25.5	.	.....	...	.....	......	......	....	1.3	....
4	10	160–180	20	6.2	35.3	5.2	182.7	2.4	12.1	68.1	19.8	3.4	3.0	0.4
5	10	180	60	6.8	48.4	7.9	175.9	0	12.4	69.8	17.8	3.9	4.4	0
6	20	180	10	6.0	41.7	6.3	....	...	10.3	73.4	16.3	4.5[c]	3.4	....

[a] % ge. catalyst is weight % on the ester.
[b] All experiments used 100 g ester and 50 cc of xylene except No. 3 where 150 cc of xylene was used.
[c] Analysis of an unreesterified sample which tends to show high D/P value.

TABLE II

Dehydration/Polymerization of Methyl Ricinoleate by Filtrol 13
Addition of Ester to Catalyst + Solvent under Reflux

No.	Weight of ester g	Vol. of xylene, cc	Wt. of catalyst, g	Temp, C	Time (min)		Water collected, cc	Residue analysis				Monomer A.V.
					Of addition	After addition		Wt. %	A.V.	S.V.	D/P	
7	100	50	20	140–194	20	10	6.4	45.6[a]	7.4	....	5.6	4.6
8	500	200	100	140–184	53	5	27.0	49.6	7.2	....	4.6	3.4
9	500	200	100	140–184	53	5	27.0	51.8	7.1	184.8	5.6	3.8
10	100	50	10	140–180	20	10	4.5[b]	41.0	4.7	209.8	5.9[d]	2.3
11	100	50	5	150–185	20	25	4.5[c]	29.4	2.7	....	8.2[d]	1.2
12	100	50	10	145–185	20	340	5.7	45.5	4.3	189.1	4.3	1.9
13	100*	50	10	140–180	20	10	5.7	65.0	25.5	179.6	4.2	18.4

* Then solvent removed and heated under nitrogen for 4 hours at 250C.
[a] Residue hydroxyl value = 0.
[b] Incomplete water removal.
[c] Incomplete water removal hydroxyl value of monomer = 3.5.
[d] Result suspect where reaction is incomplete.

Analysis. Dimer and polymer were analyzed by the method of Paschke et al. (8) after reesterification of the sample.

GLC of monomers was carried out as reported in Reference 3.

Hydroxyl values were measured according to British Standard Spec. 684 (1958) Method 1, p. 58.

Results

Preliminary experiments established that a rapid reaction occurred in the presence of 10–20% of catalyst giving a high degree of dehydration always accompanied by polymer formation. Since the polymerized residue had good color, low hydroxyl value and reasonably low acid value, experiments were designed to enhance dimer formation.

Table I illustrates the earlier experiments when ingredients were mixed together; Table II shows the more readily controllable modified conditions which appear to give a higher dimer/polymer ratio.

The use of large volumes of xylene (experiment 3), or toluene as an alternative solvent led to slow or incomplete reaction. Lesser amounts of catalyst (5%) required prolonged reaction time. A marked difference between the conditions of experiments 1–6 and 7–13 was that whereas the former were at constant temperature the latter group began at the temperature of the refluxing solvent and ended at that of the solution (about 40C higher).

In some experiments where water removal had been incomplete (e.g., experiments 10 and 11) apparently high dimer/polymer ratios were obtained. Since the composition of the distillation residue is in these cases uncertain such dimer/polymer values are suspect and only where the water of reaction approached the theoretically required figure and the dimer portion of the product had negligible hydroxyl value have we accepted the analyses as correct.

Prolonged reaction (experiment 12) gave no improvement in yield but removal of solvent after the dehydration stage and heating under nitrogen at more elevated temperature (250C) for several hours (experiment 13) raised the yield to 65%, though high A.V. resulted in both residue and monomer, possibly due to pyrolysis of the methyl groups or hydrolysis resulting from release of "bound water" in the clay. The low saponifications value suggests that some decarboxylation could also have occurred.

Composition of Recovered Monomer

GLC of monomer showed only small amounts of conjugated linoleic ester to be present but with a fair amount of nonconjugated isomer. Typical analysis is that of the distilled monomer from experiment 9.

	%			%
Unidentified low mol wt	ca. 11.3	Nonconj. linoleic		57.6
		Conjugated linoleic	c/t	1.1
Palmitic	2.4			
Unidentified 2	0.4		c/c	0.0
Stearic	2.8			
Oleic	19.4		t/t	4.8

A comparison of the analysis with that of the starting material shows that an apparent increase in weight of oleic acid has occurred (corresponding in this experiment to the formation of 6.8 g of oleic or *iso*-oleic per 100 g of starting material). Some low molecular weight materials also result from pyrolysis. A materials balance for experiment 9 is shown in Table III.

Other Catalysts

Acid catalysts such as sodium or potassium bisulfate of sulfuric acid also gave rapid dehydration but produced a polymeric product of poor color and with a low dimer/ polymer ratio. Amberlite IR-120 (10%) gave incomplete reactions and low yield while an alkaline earth ("Surrey Powder") proved reactive but was slower than Filtrol 13.

Re-use of Filtrol 13

Catalyst recovered from the reaction could be reused at least twice though increased reaction time was required for complete dehydration (about 150 min when used for the third time) and yields of product fell slightly.

Dehydration of Castor Oil

Castor oil could be dehydrated by the same technique though reaction was much slower and solvent had to be progressively removed to raise the reflux

TABLE III

Materials Balance for Experiment 9

Feedstock	Wt. of monomer		500 g
	% linoleic		Ca. 4
	% Ricinoleic		90.7
	% Oleic		Ca. 3
	Total potential wt. of linoleic after dehydration	(A)	445.7 g
	Wt. of oleic		Ca. 15 g
Recovered monomer	Wt. of monomer recovered		252.8 g
	% linoleic (all forms)		63.5
	% Oleic		19.4
	% low M.W. esters		11.3
	Wt. of linoleic (all forms)	(a)	160.6 g
	Wt. of oleic		49.0 g
	Wt. of low M.W. fragments	(b)	28.6 g
	Water produced		26.5 g
	Wt. of polymer	(c)	217.7 g
	Wt. increase in oleic	(d)	34.0 g
	Experimental loss (by diff.)		3.0 g
	(a) + (b) + (c) + (d)		440.9 g
	Approx. equal to (A)		445.7 g

temperature to 228C. After a total reaction time of 2 hr 25 min, a bodied dehydrated castor oil was obtained with an hydroxyl value of 6.2, acid value 25.5 and viscosity 7.2 stokes (at 25C).

Discussion

Formation of dimerized and polymerized linoleic esters appears to be mainly from the conjugated dienoic esters formed during the dehydration and since conversion of the nonconjugated diene is so very much slower the yield of product is limited at temperatures below 200C. Elevation of the temperature (as in experiment 13) results in conversion of some of the nonconjugated linoleic esters with improved yield. This is in agreement with the work reported on dienoic acids (9) as is the formation of oleic (or *iso*-oleic acid) by a hydrogen transfer mechanism which is known to occur even in the absence of catalysts (7).

Whereas the treatment of conjugated dienoic acids with Filtrol 13 leads to products of low dimer/polymer ratio even in the presence of a solvent (9) it is remarkable that much improved yields of dimer ester are produced using the technique described here.

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