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Reduction of Polymers Using Complex Metal Hydrides. II

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A study of the reaction between acylating and alkylating agents and the reaction mixtures obtained from the reduction of simple ketones and esters with complex metal hydrides is described. Pure poly(allyl alcohol) was prepared by the reduction of poly(methyl acrylate) with lithium aluminum hydride using sodium potassium tartrate in the isolation procedure. A number of other ester-containing vinyl polymers were also reduced with lithium aluminum hydride, acetylated directly, and then hydrolyzed to the pure hydroxyl-containing polymers. These polymers were also reduced with lithium borohydride. In these cases, acetylation was not required for product isolation.

Although a number of articles in recent years have described the reduction of polymers containing pendant ester groups, no general, simple method to achieve this end has as yet appeared. Rånby[1] reported the reduction of poly(butylacrylate), but has not yet published his experimental details. Houel reported the reduction of both poly(methyl acrylate)[2] and poly(methyl methacrylate),[3] using a solution of lithium aluminum hydride in tetrahydrofuran. After hydrolysis of the reaction mixture with water, the precipitated solids were stirred with hot *m*-cresol and the resulting slurry was extracted with dilute hydrochloric acid to remove the suspended inorganic solids. It was claimed that the poly(allyl alcohol) so obtained was insoluble in all organic solvents except pyridine and *m*-cresol. Shulz and co-workers[4] have also reported the reduction of poly(methyl acrylate) with lithium aluminum hydride in tetrahydrofuran. Their method of isolation was not given, but they report their higher molecular weight products to be soluble only in mixtures of hydrochloric acid with methanol, dioxane, or tetrahydrofuran. No analyses were given. Marvel and co-workers reported the reduction of a butadiene–methyl acrylate copolymer[5] and of poly(dimethyl itaconate)[6] with lithium aluminum hydride in tetrahydrofuran, using ethyl acetate to decompose the excess hydride, followed by 2*N* sulfuric acid to dissolve the inorganic solids. Almost complete (93%) reaction was claimed for the poly(dimethyl itaconate) reduction. The product was soluble in a water–dioxane mixture, although it contained some ash. A patent granted to Imperial Chemical Industries, Ltd.[7] claimed the reduction of poly(methyl acrylate) and poly(methyl methacrylate) with lithium aluminum hydride in tetrahydrofuran. After hydrolysis of the reaction mixture with water, the product was isolated by treatment of the precipitated solids with dilute hydrochloric acid. The poly(allyl alcohol) was reported to be insoluble in all solvents. Poly(methyl methacrylate), on the other hand, has presented no difficulties, its reduced product being soluble in a 1:1 methanol–tetrahydrofuran mixture.

In a continuation of the work at these Laboratories on the reduction of polymers with complex metal hydrides,[8] the problem of ester reduction was reinvestigated to see whether a general, reproducible method for the reduction of polymeric esters to the corresponding hydroxylated polymers could be found. From the results obtained by the previous investigators, and concurrently here, it became apparent that complete reduction of poly(methyl acrylate) could be accomplished by lithium aluminum hydride in tetrahydrofuran, the dimethyl ether of diethylene glycol (diglyme) or *N*-methylmorpholine. Difficulty arose, however, in the isolation of the product. The hydroxylated polymer was easily rendered insoluble by intermolecular etherification in acid media.[6] It also formed a strong complex with aluminum hydroxide, which made isolation of an ash-free polymer very difficult. It was found, for example, that the procedure given in Belgian Patent 571,019[7] gave a product, containing an appreciable amount of ash, soluble in a methanol–dilute hydrochloric acid mixture. All attempts to remove the aluminum hydroxide by *p*H control, precipitation, or dialysis were futile. Treatment with sodium hydroxide solution at a *p*H of 12 to remove the aluminum as the soluble aluminate reprecipitated the aluminum-containing polymer. Dialysis of the methanol–hydrochloric acid solution did not effect purification, since the aluminum ion would not pass through the cellophane membrane. The method reported by Marvel and co-workers[6] and by Houel[2] also gave samples of poly(allyl alcohol) containing some aluminum which could not be removed by the methods just mentioned.

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[1] B. G. Rånby, Makromdec. Chem., 42, 1 (1960).

[2] B. Houel, *Compt. rend.*, 246, 2488 (1958).

[3] J. Petit and B. Houel, *Compt. rend.*, 246, 1427 (1958).

[4] R. C. Shulz, P. Elzer, and W. Kern, *Chimia*, (Switz.) 13, 237 (1959)

[5] C. S. Marvel, R. M. Potts, and C. King, *J. Am. Chem. Soc.*, 77, 177 (1955).

[6] C. S. Marvel and J. H. Shepherd, *J. Org. Chem.*, 24, 599 (1959).

[7] Belgian Patent 571,019, Imperial Chemical Industries, Ltd. (1958).

[8] H. L. Cohen and L. M. Minsk, *J. Org. Chem.*, 24, 1404 (1959).

Potassium sodium tartrate complexes strongly with aluminum ions and an aqueous solution of this reagent has been used to hydrolyze lithium aluminum hydride reduction mixtures. The aluminum and lithium salts dissolve in the aqueous phase, leaving the reduced organic product in the organic solvent. Addition of a concentrated solution of potassium sodium tartrate to the poly(methyl acrylate) reduction mixture in *N*-methylmorpholine caused precipitation of the inorganic salts as a hydrated solid, while the reduced polymer dissolved in the aqueous *N*-methylmorpholine which resulted from the addition of the tartrate solution. The pure reduced product could then be isolated by conventional means. It was soluble in methanol or in pyridine, each containing at least 5% of water, and remained in solution on further addition of water until about a 1:1 mixture resulted. Substitution of diethyleneglycol dimethyl ether or tetrahydrofuran for *N*-methylmorpholine necessitated dilution of the reduction mixture with an equal volume of methanol prior to the addition of the aqueous tartrate solution. The use of *N*-methylmorpholine was, therefore, simpler and preferable.

An ethylene–diethyl maleate copolymer was also successfully reduced by lithium aluminum hydride in *N*-methylmorpholine using the tartrate method for isolation. On the other hand, the products from the reductions of poly(acetoxymethyl vinyl ketone), poly(butyl acetoxyacrylate) and the methyl acrylate–maleic anhydride copolymer precipitated with the inorganic salts on addition of the tartrate solution, and therefore could not be isolated in an ash-free state.

In an attempt to find a general procedure for the reduction of ester polymers and the subsequent isolation of soluble products, acetylation of the reduced polymers was tried next. Treatment of the dried solids, precipitated by the addition of water to a reduction mixture, with acetyl chloride in the presence or absence of pyridine usually gave insoluble products. When the precipitated solids were heated at high temperatures (140°) with acetic anhydride, dark, soluble products could sometimes be isolated; usually, however, separation of the polymer solution from the aluminum salts could not be achieved.

One would expect that the addition of an excess of acylating reagent to the unhydrolyzed reaction mixture from a lithium aluminum hydride reduction of a ketone or an ester would acylate the reduced compound. No reports, however, concerning this type of reaction could be found in the literature. Cautious addition of an excess of acetyl chloride or acetic anhydride to the reduction mixtures from ethyl valerate and pentanone-3 did, indeed, give good yields of *n*-amyl acetate and 3-pentyl acetate, respectively. Addition of these acylating reagents to the mixture obtained from the reduction of ethyl valerate with the sodium borohydride–aluminum chloride complex also gave amyl acetate, but in lower yield. Sodium borohydride reduction of 3-pentanone, followed by reaction with an excess of acetic anhydride, gave a moderate yield of 3-pentyl acetate. The addition of isopropyl acetate, or, preferably, isopropenyl acetate,[9] to an unhydrolyzed lithium aluminum hydride reduction mixture of ethyl valerate, followed by distillation of the volatile constituents, also gave, *via* the ester interchange reaction, amyl acetate in moderate yield. A similar *trans*-esterification has recently been reported by Stapp and Rabjohn.[10]

Methyl amyl ether and methyl 3-pentyl ether, respectively, were obtained in moderate yield by the addition of excess methyl sulfate to the lithium aluminum hydride reduction mixture of ethyl valerate and 3-pentanone. Methyl *p*-toluenesulfonate and hexyl bromide, on the other hand, did not alkylate the reduced products. Alkylation attempts with methyl sulfate on reduction mixtures, obtained when sodium borohydride was used on ketones, or when the sodium borohydride–aluminum chloride complex was used on esters, were also unsuccessful. All of these reactions with simple organic compounds were run in diethyleneglycol dimethyl ether.

The addition of an excess of acetic anhydride to a poly(methyl acrylate) reduction mixture in diethyleneglycol dimethyl ether gave a gel, which broke up on heating to higher temperatures (110–140°) with stirring, and precipitated a fine white powder. The supernatant liquid was a solution of the soluble poly(allyl acetate) which was almost free from inorganic salts. The acetate could be isolated by conventional means and freed from any residual inorganic matter by extraction of a chloroform solution with dilute hydrochloric acid. By using this procedure, poly(methyl acrylate), poly(acetoxymethyl vinyl ketone), poly(butyl acetoxyacrylate), and a maleic anhydride–methyl acrylate copolymer were converted completely to the acetates of the corresponding reduced polymers which could be saponified with sodium hydroxide, preferably in methoxy ethanol solution. The acylated polymers and their hydrolyzed derivatives were usually colored.

Tetrahydrofuran could also serve as the solvent for the reduction, although when used, it had to be removed by distillation, after the addition of acetic anhydride, in order to attain temperatures high enough to effect acetylation. *N*-Methylmorpholine, on the other hand, could not be used. At low temperatures, no acetylation resulted, while at higher temperatures, cross-linked, insoluble

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(9) H. J. Hagemeyer and D. C. Hull, *Ind. Eng. Chem.*, **41**, 2920 (1949).

(10) P. Stapp and N. Rabjohn, *J. Org. Chem.*, **24**, 1798 (1959).

products were formed. With all of these solvents, acetyl chloride gave insoluble products.

While the acetylation procedure described was a general method for the isolation of the reduced polymers, it was tedious and usually gave colored products. Work was therefore continued toward a simpler method. It was found that lithium borohydride in diethyleneglycol dimethyl ether solution reduced polymeric esters, anhydrides, and lactones at temperatures above 100°. Following reduction, the cooled reaction mixture was poured into dilute aqueous acetic acid. Poly(allyl alcohol), from poly(ethyl acrylate) precipitated in relatively pure form. The products derived from the reduction of poly(acetoxymethyl vinyl ketone), poly(butyl acetoxyacrylate) and the methyl acrylate–maleic anhydride copolymer dissolved. Dialysis removed the inorganic materials completely so that the polymeric derivative could be isolated by evaporation of the water. The products in all cases were colorless.

The acetylated polymers, when free from aluminum salts, were soluble in acetone, chloroform, dioxane, tetrahydrofuran and dimethylformamide. They were insoluble in methanol, ether and water. The poly(allyl alcohol) prepared was soluble in methanol, acetone and pyridine containing 10–45% of water. No pure solvent for this material could be found. The other hydroxyl polymers were soluble in water and water–methanol mixtures containing up to 40% of methanol. They were insoluble in dimethylformamide and dimethyl sulfoxide.

Infrared analysis of the hydroxyl polymers indicated that reduction was complete.

The viscosities of the original and reduced polymers are included in Table II. Although an exact comparison of relative degree of polymerization cannot be made from the respective viscosities of different types of polymers, run in different solvent systems, the much lower viscosities of some of the reduced polymers would appear to indicate that some degradation had taken place. This is because hydroxyl-containing polymers usually have higher viscosities than the esters derived from them.

It may be concluded from the work described in this and the preceding paper[8] that the complex metal hydrides are as useful for the reduction of polymeric materials as they are for simple organic compounds. The difficulties encountered due to the lower reactivities and limited solubilities of most polymers can usually be overcome by the proper choice of hydride, solvent, reaction conditions and isolation procedures.

EXPERIMENTAL

Starting materials. *N*-Methylmorpholine, diethyleneglycol dimethyl ether and tetrahydrofuran were purified by refluxing over sodium, then fractionating through a glass, helix-packed column. Lithium aluminum hydride, sodium borohydride, lithium borohydride (Metal Hydrides, Inc.), and aluminum chloride (Merck Analytical Grade) were used as purchased. The other reagents were Eastman Kodak White Label Grade, fractionated before use.

A methyl acrylate–maleic anhydride copolymer was made by copolymerizing the ingredients in acetone solution. It contained 72 mole % of methyl acrylate. The ethylene–diethyl maleate copolymer was made by the reaction of an ethylene–maleic anhydride copolymer (Monsanto Chemicals) with ethanol in the presence of sulfuric acid and benzene. Analysis showed esterification was not complete, the composition being calculated at about 40% diester and 60% monoester. This derived polymer was soluble in *N*-methylmorpholine, while the original polymer was not.

Reactions. To conserve printing space, only representative reactions are given. Data for the simple organic compounds are given in Table I. Data for the polymer reactions are given in Table II. Method B is identical with the procedure described in the previous paper.[8]

TABLE I

REDUCTION AND ACYLATION OF SIMPLE COMPOUNDS

Compound Reduced	Reducing Agent	Acylating or Alkylating Agent	Yield, %
3-Pentanone	[a]	[d]	65[m]
3-Pentanone	[b]	[e]	57
3-Pentanone	[b]	[d]	70
3-Pentanone	[b]	[f]	15
3-Pentanone	[b]	[g]	30
3-Pentanone	[b]	[h]	78
3-Pentanone	[b]	[i]	60
3-Pentanone	[a]	[i]	0
3-Pentanone	[b]	[j]	0
3-Pentanone	[b]	[l]	0
3-Pentanone	[b]	[k]	0
Ethyl valerate	[b]	[d]	90
Ethyl valerate	[c]	[d]	70
Ethyl valerate	[b]	[g]	75
Ethyl valerate	[b]	[i]	78[p]
Ethyl valerate	[c]	[i]	0
Ethyl valerate	[b]	[j]	0

[a] Sodium borohydride. [b] Lithium aluminum hydride. [c] Sodium borohydride–aluminum chloride. [d] Acetyl chloride. [e] Acetic anhydride. [f] Ethyl acetate. [g] Isopropyl acetate. [h] Isopropenyl acetate. [i] Methyl sulfate. [j] Hexyl bromide. [k] Methyl *p*-toluenesulfonate. [l] Benzyl chloride. [m] B.p. 131–132°. *Anal.* Calcd. for $C_7H_{14}O_2$: C, 64.7; H, 10.75; acetyl, 33.1. Found: C, 65.0; H, 11.1; acetyl, 33.5. [p] B.p. 99.5–100.5°, n_D^{20} 1.3870. *Anal.* Calcd. for $C_6H_{14}O$: C, 70.5; H, 13.7. Found: C, 70.5; H, 13.3.

Analytical values given in Table II are the averages of at least two determinations, each of which agreed within 0.4 unit. Yields given for the simple organic compounds are of pure products boiling in the range given in Table I and the Experimental. In most cases, they represent the results of only one experiment, and especially in the case of the ethers, can probably be increased by better isolation procedures.

Reduction of ethyl valerate by lithium aluminum hydride, followed by acetylation with acetyl chloride. A solution of 39 g. (0.3 mole) of ethyl valerate in 100 ml. of diethyleneglycol dimethyl ether was added, dropwise, with stirring, to a solution of 7.6 g. (0.2 mole) of lithium aluminum hydride in 150 ml. of diethyleneglycol dimethyl ether. Following addition, the mixture was heated 0.5 hr. on a steam bath, then cooled. Acetyl chloride (80 g.) (1.0 mole) was added, dropwise, giving an exothermic reaction. Following addition, the mixture was refluxed for an additional hour on a steam bath, then distilled up to 155°. The distillate was washed with

TABLE II

Original Polymer and Viscosity	Reducing Agent	Method of Isolation	Analysis			Yield, %	Hydrolysis			Yield, %
				Calcd.	Found			Calcd.	Found	
Methyl acrylate	$LiAlH_4$	A	C	62.2	61.9	85				
$\eta = 0.60$[a]			H	10.3	10.2					
			Methoxyl	0	<1					
			η	—	0.76[b]					
Methyl acrylate	$NaBH_4 \cdot AlCl_3$	A	C	62.2	61.8	80				
			H	10.3	10.2					
			Methoxyl	0	<1					
Methyl acrylate	$LiAlH_4$	C	C	60.0	59.9	70	C	62.2	61.5	48
			H	8.0	7.8		H	10.3	10.3	
			Acetyl	43.0	41.3		Acetyl	0	1.0	
			Methoxyl	0	<1					
			Ash	0	0.1					
Methyl acrylate	$LiAlH_4$	D	C	60.0	56.0	50	C	62.2	61.2	75
			H	8.0	8.1		H	10.3	10.1	
			Acetyl	43.0	44.3		Acetyl	0	0.5	
Methyl acrylate	$LiBH_4$	E	C	62.2	61.7	85				
$\eta = 0.60$[a]			H	10.3	10.1					
			Methoxyl	0	<1					
			η	—	0.65					
Methyl methacrylate	$LiAlH_4$	B	C	66.8	65.9	70				
			H	11.0	11.0					
			Methoxyl	0	<1					
			Ash	0	0.1					
Ethylene-diethyl maleate	$LiAlH_4$	A	C	62.0	61.5	75				
			H	10.3	10.1					
			Ethoxyl	0	0.0					
			Ash	0	0.0					
Acetoxymethyl vinyl ketone	$LiAlH_4$	C	C	55.8	55.8	90	C	54.6	54.3	85
			H	7.0	7.2		H	9.1	9.1	
			Acetyl	50.0	46.5		Acetyl	0	<1	
Acetoxymethyl vinyl ketone	$LiBH_4$	E	C	54.8	55.1	85				
			H	9.1	8.9					
$\eta = 0.43$[a]			Acetyl	0	0.5					
			η	—	0.26[e]					
Methyl acrylate-maleic anhydride[c]	$LiAlH_4$	C	C	58.8	58.4	65	C	59.5	58.7	40
			H	7.7	7.6		H	9.9	9.8	
			Acetyl	43.0	44.2		Acetyl	0	0.6	
Ethyl acrylate-maleic anhydride[d]	$LiBH_4$	E	C	58.1	57.1	85				
			H	9.6	10.0					
$\eta = 0.26$[a]			Ethoxyl	—	0.5					
			η	—	0.58[e]					
Butyl α-acetoxyacrylate	$LiAlH_4$	C	C	53.1	52.3	50	C	48.8	49.1	52
			H	6.4	6.6		H	8.1	7.7	
			Acetyl	54.5	52.3		Acetyl	0	<1	
Butyl α-acetoxyacrylate	$LiBH_4$	E	C	48.8	49.3	85				
			H	8.1	7.6					
$\eta = 0.64$[a]			η		0.12[e]					

[a] In acetone. [b] In 80% v/v aqueous methanol. [c] 72 Mole % methyl acrylate. [d] 64 Mole % ethyl acrylate. [e] In water.

water and redistilled, giving a fraction, b.p. 148.5–149.0°, n_D^{20} 1.4014, weighing 35 g. (90%).

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.7; H, 11.75. Found: C, 64.6; H, 11.5.

Reduction of 3-pentanone, followed by reaction with methyl sulfate. A solution of 52 g. (0.6 mole) of 3-pentanone in 200 ml. of diethyleneglycol dimethyl ether was reduced with a solution of 7.6 g. (0.2 mole) of lithium aluminum hydride in 200 ml. of diethyleneglycol dimethyl ether. A solution of 80 g. (0.67 mole) of distilled dimethyl sulfate was then added, dropwise, with stirring. Following addition, the mixture was heated 3 hr. on a steam bath. The complex was decomposed by the cautious addition of 100 ml. of 2*N* sulfuric acid and the mixture steam distilled. The distillate was extracted with ether, dried over sodium sulfate and distilled, giving 36 g. (60%) of product, b.p. 88.5–89.0°, n_D^{20} 1.3864.

Anal. Calcd. for $C_6H_{14}O$: C, 70.6; H, 13.7. Found: C, 71.0; H, 13.9.

Reduction of 3-pentanone, followed by reaction with isopropenyl acetate. A solution of 43 g. (0.5 mole) of 3-pentanone in 100 ml. of diethyleneglycol dimethyl ether was reduced by 5.6 g. (0.15 mole) of lithium aluminum hydride in 150 ml. of diethyleneglycol dimethyl ether. Isopropenyl acetate (100 g., 1 mole) was then added. The stirred mixture was slowly distilled on a steam bath until no more acetone came over. The reaction complex was treated with 1 l. of water and then steam distilled. The distillate was extracted with ether, dried and distilled; yield, 50 g. (77%), b.p. 131–132°.

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.7; H, 10.75; acetyl, 33.1. Found: C, 64.7; H, 11.0; acetyl, 32.5.

Reduction of poly(methyl acrylate) with lithium aluminum hydride. Method A. To a refluxing, stirred suspension of 3.8 g. (0.1 mole) of lithium aluminum hydride in 200 ml. of purified *N*-methylmorpholine, under nitrogen, was added, dropwise, over a period of 2 hr., a solution of 8.6 g. (0.1 mole) of poly(methyl acrylate) ($\{\eta\}$ = 0.60, 0.25 g./100 ml. in acetone) in 100 ml. of *N*-methylmorpholine. After addition, the mixture was stirred under reflux for an additional 3 hr. Then, while still hot, a solution of 30 g. of potassium sodium tartrate in 150 ml. of water was added, dropwise, and very cautiously, until the excess hydride had been decomposed. Following addition of all the tartrate solution, the mixture was stirred hot for an additional hour and allowed to cool.

The filtered solution was evaporated to dryness on a steam bath under vacuum, leaving a soft residue. This was stirred with a mixture of 90 ml. of methanol and 10 ml. of water for 3 hr. Most of the solid dissolved, giving a viscous solution. Some granular powder remained and was centrifuged off. The polymer was precipitated in acetone. The purification process was repeated, giving 5 g. (85%) of a tough resin after vacuum drying over phosphorus pentoxide.

Anal. Calcd. for C_3H_6O: C, 62.2; H, 10.3; methoxyl, 0. Found: C, 61.9; H, 10.3; methoxyl, <1; ash, 0.3; $\{\eta\}$ = 0.76.

Reduction of poly(methyl acrylate), acetylation with acetic anhydride and hydrolysis. Preparation of poly(allyl acetate). Method C. A solution of 8.6 g. (0.1 mole) of poly(methyl acrylate) in 100 ml. of tetrahydrofuran was added, dropwise, under nitrogen, to a refluxing solution of 3.8 g. (0.1 mole) of lithium aluminum hydride in 200 ml. of tetrahydrofuran over a period of 1 hr. Following addition, the mixture was refluxed and stirred for an additional 2 hr., then cooled.

Acetic anhydride (250 ml.) was added, dropwise, to the mixture, cautiously at first, until all the excess lithium aluminum hydride had reacted. The mixture was then heated slowly with stirring, and the tetrahydrofuran was allowed to distill until the internal temperature reached 110°. The mixture became exceedingly thick. After stirring at 110° for 1 hr., the mixture became much more fluid and a fine, white precipitate was left. Heating was continued for a total of 3 hr.

The cooled mixture was filtered, the filter cake being washed with acetone. The combined washings were evaporated to dryness on a steam bath under vacuum. The residue, after solution in acetone, was precipitated in ether. This procedure was repeated twice to give an analytical sample; yield, 7 g. of a soft polymer which hardened somewhat on vacuum drying.

Anal. Calcd. for $C_5H_8O_2$: C, 60.0; H, 8.0; acetyl, 43. Found: C, 60.0; H, 7.9; acetyl, 41.4; methoxyl, >2; ash, 0.1.

Reduction of poly(methyl acrylate), followed by reaction with isopropenyl acetate. Method D. A solution of 8.6 g. of poly(methyl acrylate) in 100 ml. of diethyleneglycol dimethyl ether was added, dropwise, under nitrogen, with heating over a period of 1 hr. to a stirred solution of 3.8 g. (0.1 mole) of lithium aluminum hydride in 100 ml. of diethyleneglycol dimethyl ether. Following addition, the mixture was heated and stirred at 110° for 3 hr.

Isopropenyl acetate (100 g.) was then added, dropwise, with stirring. Following addition, the temperature was raised to 135° for 2 hr., 20 ml. of material being allowed to distill. The mixture was then cooled and decomposed by the addition of a solution of 20 g. of sodium potassium tartrate in 100 ml. of water. After the stirred mixture had been heated to boiling and allowed to cool, the mixture was centrifuged. The supernatant liquid was evaporated to dryness on a steam bath under vacuum, dissolved in a mixture of acetone, and methanol, and precipitated in ether, giving 5 g. of a soft, amber solid after drying.

Anal. Calcd. for $C_5H_{10}O_2$: C, 60.0; H, 8.0; acetyl, 43. Found: C, 56.1; H, 8.1; acetyl, 44.4.

Hydrolysis of this product gave 2.3 g. of a tan solid.

Anal. Calcd. for C_3H_6O: C, 62.2; H, 10.3. Found: C, 61.2; H, 10.1; acetyl, 0.5.

Reduction of poly(butyl α-acetoxyacrylate) with lithium borohydride. Method E. A solution of 9.3 g. (0.05 mole) of poly(butyl α-acetoxyacrylate) in 100 ml. of diethyleneglycol dimethyl ether was added dropwise over a period of 1 hr. to a stirred solution of 2.5 g. of lithium borohydride in 200 ml. of diethyleneglycol dimethyl ether kept at 100° under nitrogen. Following addition, the mixture was heated to 115° for an additional 2 hr., then allowed to cool to room temperature.

The reaction mixture was then poured slowly into 1 l. of water containing 50 ml. of acetic acid, giving a clear solution which was dialyzed overnight. The undialyzed material was filtered, then evaporated to dryness on a steam bath under vacuum. The residue was dissolved in 20 ml. of distilled water giving a clear viscous solution which was precipitated into acetone to give a white powder. The product was vacuum dried; yield, 3.3 g., soluble in water, but insoluble in methanol, acetone and ether.

Anal. Calcd. for $C_3H_6O_2$: C, 48.8; H, 8.1. Found: C, 49.2, 49.4; H, 7.5, 7.7; N, 0.12.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE ARMOUR INDUSTRIAL CHEMICAL COMPANY]

Phase Properties of Mixtures of 9- and 10-Oxo-octadecanoic Acids and of 9- and 10-Hydroxyoctadecanoic Acids[1]

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Pure homolog-free samples of 9- and 10-oxo- and the corresponding hydroxyoctadecanoic acids have been prepared and phase diagrams for mixtures of the isomers have been established. That for the oxo acids is a simple eutectic system; that for the hydroxy acids shows compound formation at a 1:1 ratio of the components. On the basis of these diagrams the identity of various preparations of the four compounds reported in the literature is discussed. Evidence for preferential reactivity at the 9- or 10-position of the eighteen-carbon fatty-acid molecule which is based upon conclusions regarding the identity of the oxo or hydroxy acids is invalidated.

A number of reports in the literature present evidence for a directive influence during reactions of unsaturated or epoxy eighteen-carbon fatty acids which results in preferential reactivity at the 9- or 10-position of the molecule. For the most part, this evidence is based on isolation of a preponderance of a substance identified as 9- or 10-oxo- or 10-hydroxyoctadecanoic acid.

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[1] Presented in part before the Division of Organic Chemistry at the 138th Meeting of the American Chemical Society, New York, September, 1960.

[2] Address communications to this author.