Application of the Prins Reaction on Oleic Acid

TORSTEIN ARTUN,[1] Norwegian Defense Research Establishment, Kjeller, Norway

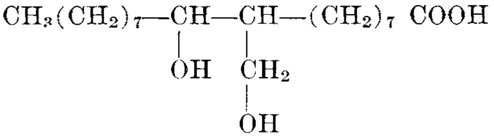
Abstract

The probable structure of the various components of oleic acid-formaldehyde adducts is discussed. The adducts are reduced to alcohols by high pressure hydrogenation with copper chromite as a catalyst. The new alcohols are distilled, analyzed and used for the preparation of various esters with carboxylic acids. The esters were evaluated as low temperature lubricant base stocks and low temperature plasticizers.

Introduction

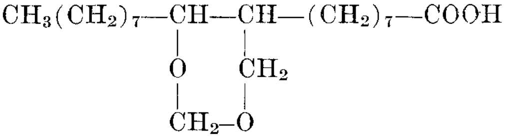
THE FIRST COMPREHENSIVE study of the reactions of formaldehyde with ethylenic hydrocarbons was published by Prins (1). Since the early work of Prins, several groups of investigators have studied the mechanism of the Prins reaction with cyclohexene (2–10).

Our work with oleic acid was also guided by the study of LeBel et al. with *cis-* and *trans-*4-octene (11). According to the present knowledge the following products from formaldehyde and oleic acid are most likely to be formed.

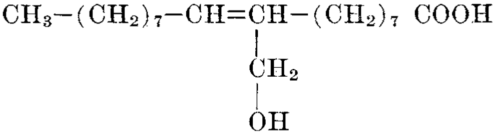


$$CH_3(CH_2)_7{-}CH(OH){-}CH(CH_2OH){-}(CH_2)_7\ COOH$$

I

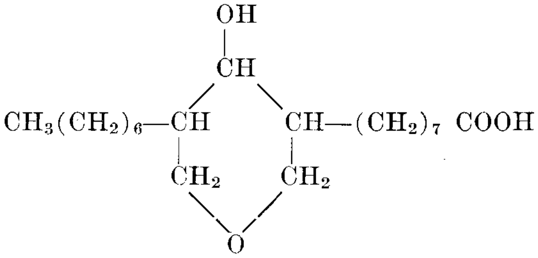


II

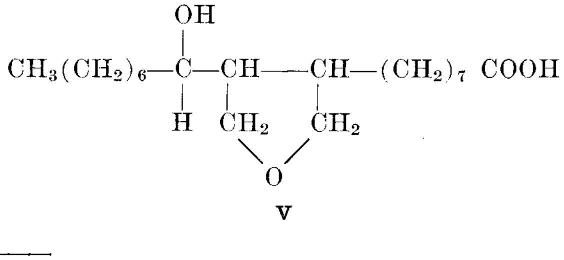


$$CH_3{-}(CH_2)_7{-}CH{=}C(CH_2OH){-}(CH_2)_7\ COOH$$

III



IV



V

These formulas are given for a primary attack of a protonized formaldehyde molecule at the No. 9 carbon atom of the chain.

With a primary attack at the 10 position it is easily seen how the formulas I, II and III have to be changed. In formula IV the position of the ring system will be one carbon atom closer to the carboxyl group and in formula V the hydroxyl group will move to the 7 position of the chain.

The compound I is a 1,3 diol resulting from addition of one molecule of formaldehyde and one molecule of water to the oleic acid. The compound II with a m-dioxane ring results from the addition of 2 molecules of formaldehyde. The compound III may arise from I by dehydration or may be formed directly under anhydrous conditions. The reaction mechanisms leading to I, II and III were studied by Baker (12), Price (13) and Yang et al. (14). Also the compounds IV and V may arise from the addition of two molecules of formaldehyde. The mechanisms of the additions leading to IV and V are newly explained for cyclohexene by Dolby et al. (10).

From the oleic acid formaldehyde adducts, with the exception of compound II, it would be possible to prepare diesters by introducing an alcohol at the carboxyl group and an acid at the hydroxyl group. This would be an inconvenient procedure with the esterification being performed in two steps. Therefore, in this work, the oleic acid formaldehyde adducts were hydrogenolized to dialcohols which afterwards were esterified to diesters.

The hydrogenolysis was performed by using the well-known method of reducing fatty acids to fatty alcohols at high temperatures and high pressures of hydrogen. Early accounts of this method are given by Normann (15) and Adkins and Folkers (16,17). An investigation of the hydrogenolysis of methyl laurate to lauryl alcohol is reported by Church et al. (18). Today processes based both on fatty acid methyl esters and the fatty acids themselves as starting materials are used in commercial production. Further, for the oleic acid formaldehyde adducts both methods have been useful when tried on laboratory and pilot plant scale.

The alcohols prepared by hydrogenolysis of the oleic acid formaldehyde adducts have been fractionated and examined. Both the original mixture of alcohols and fractions of them have been used to prepare esters with potentialities as low temperature lubricants and plasticizers.

Oleic Acid Formaldehyde Adducts

The reaction between oleic acid and formaldehyde in acetic acid solution with sulfuric acid as a catalyst was easily performed at temperatures in the region of 50–115C. The velocity of the reaction was followed by observing the decrease with time of the iodine values of the ether extractable mixture. Increasing the concentration of olefin, formaldehyde or sulfuric acid in the system or the temperature would increase the reaction velocity. In this system there may also be some addition of acetic acid at the double bond. This competing reaction is easily avoided by adding a few per cents of water to the system or using acetic acid of not more than 95% concentration.

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[1] Oslo Tekniske Skole, Oslo, Norway.

TABLE I

Distillation Analysis of Methyl Esters of Oleic Acid Formaldehyde Adducts

Fraction No.	Distillation temperature at 0.5 mm Hg C	Quantity g	Quantity %	S.V.	OH V.	CH_2O after splitting, %	I.V.
1	131–181	35.2	11.1	222	0	0.23	2
2	181–200	18.2	5.7	217	10	1.84	18
3	200–207	93.3	29.6	174	50	1.97	10
4	207–250	42.3	13.4	171	111	0.41	6
5	250–285	19.3	6.1	171	105	0	14
6	285–310[a]	50.5	15.9	172	43	0	30
Residue		52.2	16.5		4	0	
Loss		5.4	1.7				
Total		316.4	100.0			0.78[b]	

[a] Upper limit uncertain.

[b] This value arises as the sum when the values above are multiplied with the quantities of the respective fractions, in per cent.

When using more than 2½ mole formaldehyde per mole of oleic acid the addition will proceed to iodine values below 5 for the addition products. Table I gives a distillation analysis of such adducts after complete saponification followed by methylation of the acids set free from the soaps. The composition of the technical oleic acid used was: saturated acids, 12.9%; palmitoleic acid, 24.0%; oleic acid, 50.1%; polyunsaturated acids 13.0%: total, 100.0%.

In Table I are also given the saponification values (S.V.), OH values (OH V.) and iodine values (I.V.) for the various fractions. The column for the CH_2O content represents formaldehyde split from the dioxane compounds by sulfuric acid in acetic acid and benzene under anhydrous conditions. The formaldehyde is distilled off together with benzene and determined by the sodium sulfite method. In our experiments this procedure yielded 85% of the formaldehyde from authentic material and the values given in Table I have been adjusted to 100%.

Except for the fraction 1, the iodine values were higher than for the starting materials. This is probably due to dehydration during the distillation.

The fractions 1 and 2, Table I, contained saturated fatty acids originating from the technical oleic acid together with increasing amounts of formaldehyde adducts, indicated by the CH_2O split-off, and the OH values. The fractions 3–6 are all formaldehyde adducts.

Dioxane compounds, as indicated by the CH_2O determined after splitting, are found in the four lowest boiling fractions. The highest content was found in fraction 3. The amount of 1.97% of formaldehyde as found in this fraction corresponds to 23.4% of dioxane compounds as dioxane stearic acid methyl ester. The total of 0.78% formaldehyde in the adducts corresponds to 9.3% of dioxane compounds.

The higher boiling fractions 4 and 5 had the highest content of alcohols as indicated by the OH values 111 and 105, respectively. In fraction 6 the OH value was lower probably due to the splitting off of OH groups by dehydration at the higher distillation temperatures. The iodine value of 30 supports this conclusion. The OH values found are lower than would be expected from the survey given in the introduction where only dioxane compounds and various alcohols are considered. The higher boiling fractions containing no dioxane compounds should give OH values of about 153 if they consisted of terahydrofuran or -pyran derivatives with one hydroxyl group. Perhaps the Kaufmann method may give too low OH values for such compounds, but no reasonable explanation is found for the discrepancy.

TABLE II

Distillation Analysis of Hydrogenated Oleic Acid Formaldehyde Adducts

Fraction No.	Distillation temperature at 0.5 mm Hg, C	Quantity g	Quantity %	N_D^{20}	OH V.	CH_2O split off %
1	70–130	18.0	8.4	1.4447	317	0.14
2	130–163	24.3	11.4	1.4534[a]	249	0.20
3	163–185	36.0	16.7	1.4636[a]	220	0.61
4	185–191	35.3	16.5	1.4675	218	1.56
5	190–195	30.8	14.4	1.4692	211	2.11
6	195–220	44.7	20.9	1.4776[a]	264	0.40
Residue		20.4	9.5	1.4918		
Loss		4.5	2.2			
Total		214.0	100.0			0.809

[a] Measured at 50C and 60C and corrigated to 20C.

Experimental

Preparation of Oleic Acid Formaldehyde Addition Products

Commercial oleic acid		100	parts by weight
Paraformaldehyde,	97%	33	parts by weight
Acetic acid,	98%	93	parts by weight
Sulfuric acid,	98%	6.1	parts by weight

The paraformaldehyde was dissolved in the acetic acid-sulfuric acid by heating to 105C. After cooling to 85C the fatty acid was added in portions in the course of 15 min at 82–86C. After addition of all the fatty acid the temperature rose to 110C because of the reaction heat evolved. After cooling the temperature of the charge was held at 90–100C for 2 hr.

The addition products were washed with water and analysis gave:

S.V. 220, A.V. 143, I.V. 4.3, OH V. 18

Analysis of the addition products after saponification, acidification washing and evaluation gave:

S.V. 170, A.V. 161, I.V. 5.6, OH V. 80.

OH groups bound as acetate esters in the crude product are set free by the saponification and therefore the OH V. is higher in the refined product.

Determination of the Dioxane Compounds

The addition products (5–10 g) were refluxed for 10 hr with 150 ml of 100% acetic acid, 100 ml benzene and 0.4 ml of concentrated sulfuric acid. The formaldehyde and water evolved were collected under the benzene layer in a trap connected to the condenser. The formaldehyde in the water layer was determined by the sodium sulfite method (20). If crystals of paraformaldehyde had separated these were dissolved in water regulated to pH about 9 by adding portions of 0.5 N NaOH.

Applied on 4-phenyl-1.3-dioxane the method produced 85% of the theoretical amount of formaldehyde. The same value was also found by boiling with butyric acid and xylene using *p*-toluenesulfonic acid as a catalyst.

Hydrogenolysis of the Oleic Acid Formaldehyde Adducts to Alcohols

Before the hydrogenation it is important to clean the addition products from acetic and sulfuric acid bound as esters during the formaldehyde addition process. Both acetic acid and traces of sulfuric acid will contaminate the hydrogenation catalyst, leading to incomplete reduction of the carboxyl group. The ester splitting may be performed in a conventional way by means of water under pressure using ZnO as a catalyst.

For convenience the adducts were saponified with an excess of caustic soda, the soaps split with a slight

TABLE III

Viscosity Properties and Pour Points of Normal Carboxylic Acid Esters of a Middle Fraction of Alcohols Containing Ring Systems and of 2-Ethylhexyl-Sebacate

Compound	Viscosity in centistokes at						VI (D D)	Pour point C
	98.9C	37.8C	0C	−20C	−40C	−53.9C		
Acetic acid (C_2) esters	3.75	16.46	95	430			136	−56
Propionic acid (C_3) esters	3.60	14.40	73.9	295	1950	16000	154	−60
Butyric acid (C_4) esters	3.84	15.57	81.9	310	2150	12000	162	−64
Caproic acid (C_6) esters	4.35	17.88	93.6	350	2600		174	−50
Caprylic acid (C_8) esters	4.90	21.72	119.9	460			162	−34
Capric acid (C_{10}) esters	5.70	26.67	153.5				157	−21
Lauric acid (C_{12}) esters	6.75	33.30	206.3				153	−10
Myristic acid (C_{14}) esters	7.85	39.53					152	0
2-Ethylhexyl-Sebacate	3.32	12.6	60.9	210	1410	9000	154	−55

excess of sulfuric acid and the fatty acids thoroughly washed free from sulfuric acid with warm water. The water was at last removed from the fatty material under vacuum.

The adducts have been hydrogenated both as free acids and as methyl esters in a laboratory scale. In pilot plant scale 550 kg acids were hydrogenated to alcohols in good yield. A continuous Lurgi plant in West Germany with a feeding capacity of about 8 kg/hr was used. A stream of hydrogen gas of 320 kg/cm^2 pressure was forced through the oil-catalyst suspension in the reactor. Volatile reaction products as water and traces of methanol and low molecular oil products were continuously separated from the gas phase in special condensers before the hydrogen was led back to the reactor again. After leaving the reactor the oil and catalyst were separated by filtration in a filter press.

The main products from the reactor contained no free acids and had saponification values of about 3, corresponding to a yield of over 98% of transformed carboxylic acids.

In Table II is given a distillation analysis of the alcohols together with the refraction indices, OH values and quantities of formaldehyde split off from the various fractions.

The first fraction and also much of fraction 2 are mixtures composed to a great extent of monoalcohols originating from the low molecular saturated fatty acids in the raw materials used. Also low molecular compounds formed by splitting of the hydrocarbon chain during the hydrogenation process may give rise to the high OH V. found for these fractions.

The fraction 3 is a mixture of such monoalcohols and alcohols from the formaldehyde adducts. Fractions 1, 4 and 5 are fluids at room temperature and fractions 2, 3 and 6 are solid.

Dialcohols originating from the addition products of constitutions IV and V would exhibit OH values of 340. The corresponding monoalcohols with only one OH group less would exhibit OH values of 179. The OH values of all the fractions in the table are lying between these numbers. The fraction 6 with the OH value 264 have the highest content of dialcohols. After repeated (6 times) crystallisations from acetone this fraction gave a crystalline product with mp = 90.5C and OH value 298 (Kaufmann) and 330 (Fritz) (19). It is believed that the method of Fritz will produce too high values due to a splitting of the tetrahydropyran or -furan systems. Analysis C = 72.64, H = 12.12, O = 14.44. Calculated for $C_{20}H_{40}O_3$ (the alcohol from adduct IV or V) C = 73.12, H = 12.27, O = 14.61.

As seen from the formaldehyde values in Table II all the fractions contain dioxane compounds. The highest contents were found in the fluid fractions 4 and 5. Formaldehyde (2.11%) as found in fraction 5 correspond to 23.2% of dioxanestearyl alcohol in this fraction. This is the alcohol originating from the adduct with structure II. It was surprising that the high-pressure hydrogenation did not split the dioxane structure of this type. From the values of total CH_2O split off from the addition products and the hydrogenated adducts, no reduction of the contents of dioxane compounds can be concluded. Only the small amounts of methanol in the water phase of the condensate from the hydrogenation procedure suggest that a slight splitting of the dioxane compound may have occurred.

The present hydrogenation method was previously applied by Emerson et al. (21) to 4-phenyl-1,3-dioxane. Using much lower temperatures and hydrogen pressures than in this investigation they noted a splitting of the dioxane ring and obtained 3-phenyl-1-propanol in 85% yield.

It was therefore astonishing to observe how resistant to hydrogenolysis were the dioxane compounds with structure II. Obviously the explanation lies in the difference of the electronic configuration of the substituents of the dioxane compounds in the two cases.

Experimental

The 551 kg adducts were hydrogenated in a continuous Lurgi plant as mentioned before. The amount of 41.85 kg copper chromite catalyst promoted with Ba was used. The amount obtained was 555 kg alcohols with catalyst and 58.7 kg condensed vapours, composed of water and volatile alcohols. The main product gave the analytical data: S.V., 3.1; I.V., 2.5; A.V., 0; and OH V. 251.5.

The alcohols were distilled in vacuum using a packed column with low pressure drop.

Esters of Alcohols from Oleic Acid Formaldehyde Adducts

Both fractions and the whole mixture of alcohols have been used for preparing esters with carboxylic acids. The purpose of this investigation was search-

TABLE IV

Viscosity Properties, Pour Points and Cold Flex of the New Esters as PVC Plasticizers in Comparison with Dioctyl-Phtalate and -Sebacate

Components		Viscosity in centistokes		Pour point C	Cold flex C
		37.8C	98.9C		
Alcohols [a]	Propionic acid esters	15.05	3.52	−12	−24.5
Alcohols [b]	Propionic acid esters	19.45	4.14	−14	−24.0
Alcohols [c]	Propionic acid esters	21.60	4.35	−41	−21.3
2-Ethyl-hexanol	Pthalic acid ester	30.0	4.36		−16.0
2-Ethyl-hexanol	Sebacic acid ester	12.6	3.32	−55	−38.5

[a] Hydrogenated oleic acid formaldehyde adducts without any fractionation.

[b] Alcohols a minus a forerun of 11.9%.

[c] Alcohols a minus a forerun of 11.9% and a distillation residue of 14.0%.

ing for ester compositions with potentialities as low temperature lubricant base stocks, especially with higher viscosity indices and lower pour points than those of the 2-ethylhexyl-sebacate, and with just as good thermal stability. Also, the purpose was to find new plasticizers for PVC products intended for use at low temperatures. The esters with the best properties were obtained using a middle fraction boiling at 210C at 2 mm Hg. This fraction was prepared in a continuous pilot distillation plant with two columns with 13 theoretical plates each. The quantity of the fraction represents 20% of the original alcohol mixture.

However, this middle fraction is also a mixture of alcohols containing dioxane- and other ring systems. The OH V. is 232. A series of esters were prepared from it, using the normal carboxylic acids with even numbers of carbon atoms from C_2 to C_{14}. In Table III are listed viscosity properties and pour points of these esters.

As seen from Table III the propionic, butyric and capronic acid esters have excellent viscosity properties and low pour points. But only the butyric acid esters also give a sufficient low viscosity at 53.9C to meet the military specifications (22) to a jet engine lubricating oil as to these properties. The four first esters listed in the table, having pour points of −50 to 64 C should have potentialities as special plasticizers for PVC formulas intended for use at low temperatures.

The butyric acid esters were also exposed to the military thermal oxidation stability test (22). Phenothiazine as an antioxidant had to be added. With 1.0% phenothiazine the ester was stable but not with 0.5%.

During the present work it was hoped to find a method of regulating either the formaldehyde addition procedure or the hydrogenation procedure or both to produce only alcohols with the promising properties of the middle fraction. However, all experiments in this direction have failed. Therefore esters were finally prepared from the whole mixture of alcohols, from the mixture where a forerun of 11.9% containing the solid monoalcohols had been removed and also of the mixture minus a forerun and a distillation residue. Viscosity properties and cold flex of test sheets of PVC blends were these esters are used as plasticizers are listed in Table IV. Corresponding data obtained with dioctyl-phthalate and -sebacate are also given.

As seen from Table IV the fractionation of the alcohols has little influence on the utility of the esters as plasticizer with respect to cold flex of the test sheets. The propionic esters of the total alcohol mixture have the highest pour point but produce PVC formulas with the lowest cold flex. With respect to the cold flex all three ester types are superior to dioctylphtalate but inferior to dioctylsebacate. Therefore, the potentialities of these esters as plasticizers seems to be a matter of their price in comparison with competing esters for special low temperature PVC formulas.

Experimental

The esters of Table III were prepared by alcoholysis using 100% excess of the methyl esters of the respective acids. $NaOCH_3$ was added as a catalyst in amounts equal to 0.7% of the mixture and the methanol removed at the top of the column during reflux.

The esters of Table IV were prepared using a direct method of esterification with ZnO as a catalyst.

The test sheets for determining the cold flex were prepared according to the recipe: PVC, 100 parts by weight; plasticizer, esters, 47 parts; epoxy plasticizer, 3 parts; stabilisation agent and lubricant, 2.5 parts.

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