

yielded a fraction distilling at 195–205°C at less than 1 mm pressure from which a small amount of DHP was crystallized by dissolving the fraction in warm carbon tetrachloride.

It should be possible to form 5,5,5-trimethylol valeric acid from adipaldehydic acid, the other fragment resulting from the reductive ozonization of petroselinic acid, when the mixed aldehydes are reacted with formaldehyde and alkali. The authors were not successful in isolating from the complex reaction mixture a fraction which could be proven to be pure trimethylol valeric acid. After acidifying the alkaline water solution from the reaction mixture it was evaporated to dryness. The residue was then extracted with hot absolute ethanol. From the ethanol solution, the acids were absorbed on a Dowex 1 ion exchange resin column in the hydroxyl form, the column rinsed to neutrality, and the acids eluted with normal hydrochloric acid. Evaporation of the eluate gave a very viscous almost colorless liquid. This had an infrared spectra similar to that expected of trimethylol valeric acid with high absorption for hydroxyl and carboxyl groups and which readily polymerized on standing.

ACKNOWLEDGMENT

Analyses and molecular weight by L. E. Brown and A. F. Cucullu; infrared spectra by G. J. Boudreaux and S. H. Miles.

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[Received May 17, 1965—Accepted June 7, 1965]

Instrumental Study of Aldehyde Oils and Their Reaction with Selected Amines¹

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Abstract

Unsaturated aldehyde oils prepared by partial ozonization of soybean oil gave infrared and nuclear magnetic resonance spectra in qualitative accord with the structures expected. Infrared spectra indicated that the unsaturation present was in the *trans* form. Reactions of dialdehyde oil with various amines proceeded with surprising ease at room temperatures to give facticelike, crosslinked products.

Introduction

THE PREPARATION of aldehyde oils by ozonization of soybean oil has been reported previously (2–4). Complete ozonization of soybean oil gave a product that contains up to an average of 2.5 aldehyde groups per molecule after removal of nonester fragments. This product is highly reactive and can undergo a number of resin-forming reactions. Partial ozonization of soybean oil may be controlled to give products having an average of one or two aldehyde groups per molecule (2,4). These "monoaldehyde" and "dialdehyde" oils have varying degrees of residual unsaturation depending upon the method used for reducing the ozonolysis products. Reduction by zinc and acetic acid has no effect on residual unsaturation. Neither does catalytic hydrogenation in the presence of pyridine, but without pyridine the residual double bonds are at least partially saturated to give a heterogeneous mixture of solid and oil. Also in the absence of pyridine, the use of a catalyst causes

relatively large amounts of carboxylic ester to be formed and results in lower yields of aldehydic products.

Partial ozonization of soybean oil to give mono- or dialdehyde oils has the advantages of giving a product of lesser and more controllable reactivity, of economic use of ozone, and of producing lesser amounts of byproduct caproaldehyde, pelargonaldehyde, and malonaldehyde than does complete ozonization. Residual unsaturation, particularly in monoaldehyde oil, furthermore offers the possibility of acting as an additional reaction site.

Infrared (IR) and nuclear magnetic resonance (NMR) spectra of some aldehyde oils as well as reactions of dialdehyde oil with selected diamines are discussed in this paper.

Experimental

Instrumental Analyses

IR spectra were obtained with a Perkin-Elmer 221-G spectrophotometer (5). The spectra of liquid oil samples were obtained from thin films on sodium chloride plates. The solid derivatives were incorporated in potassium bromide pellets for IR absorption analysis.

NMR spectra were obtained with a Varian HR-60 spectrometer equipped with an electronic integrator. NMR samples were dissolved in a deuterated chloroform solution.

Preparation of Aldehyde Oils

Various aldehyde oils were prepared in the pilot-plant facilities of the Northern Laboratory by methods described previously (2–4): monoaldehyde oil, by hydrogenation over Pd/CaCO₃ of soybean oil ozonolysis products (25 parts) in ethyl acetate (60 parts)

¹ Presented before the Division of Organic Coatings and Plastics Chemistry, American Chemical Society, March 1962. A partial report of work done under contract with the USDA and supervised by the Northern Division of the Agricultural Research Service.

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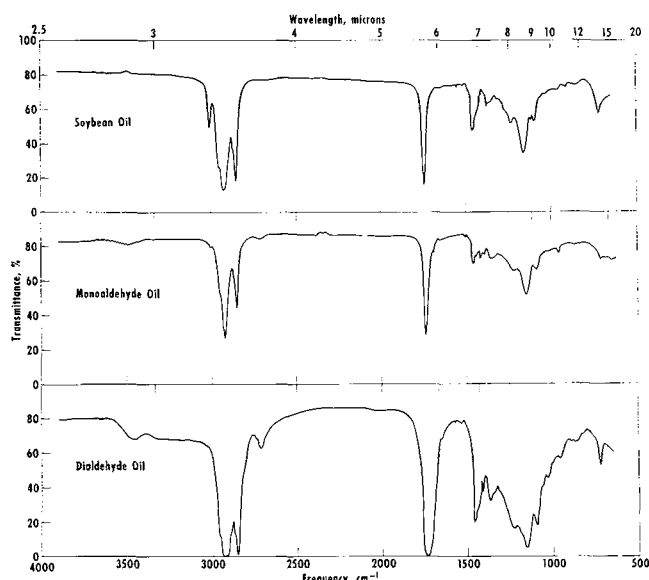


FIG. 1. Infrared spectra of soybean oil and of monoaldehyde and dialdehyde oils.

and methanol (30 parts); dialdehyde oil, by hydrogenation over Pd/CaCO₃ poisoned with lead acetate of margarine oil (partially hydrogenated soybean oil) ozonolysis products 12.5 parts in ethanol (100 parts)-pyridine (5 parts); and trialdehyde oil, by reduction of soybean oil ozonolysis products (7.5 parts) with zinc and acetic acid in ethyl acetate (22.5 parts)-methanol (11.25 parts). The aldehyde oils had the following characteristics after removal of the nonester fragments:

Oil	Molecular weight	Carbonyl value, meq/gm	Aldehyde groups/molecule
Monoaldehyde	746	1.36	1.01
Dialdehyde	865 ^a	2.13	1.84
Trialdehyde	700	3.79	2.66

^a High molecular weight caused by some condensation of the aldehyde molecules.

Reactions of Dialdehyde Oil

Reactions with the diamines were carried out on a 50 mM (43.3 g) scale, usually at room temperature. Solubilities of the products were tested in CP grade acetone, chloroform, carbon tetrachloride, ethyl acetate, ethyl alcohol, benzene, ether, and xylene and in technical grade dimethyl formamide and hexane.

Hydrazine (anhydrous) with equimolar amounts of dialdehyde oil in ethanol solution gave, in 10-15 min, an amber, rubbery material that showed slight solubility in only chloroform, xylene, and benzene.

p-Phenylenediamine with equimolar amounts of dialdehyde oil gave a bulky resilient mass formed before all the diamine was added. With a 1:2 molar ratio of diamine and dialdehyde oil, a similar resilient mass was formed. After this solid was removed, ground in a food blender, and filtered, the filtrate did not react further with additional *p*-phenylenediamine. After an ethanol wash the filter cake was dried under vacuum. The dried cake was dark brown and resilient but broke easily when slight tension was applied. The relative insolubility of this material indicated that crosslinking had taken place, and its poor tensile strength indicated low molecular weight. The product swelled in chloroform, carbon tetrachloride,

benzene, xylene, and dimethyl formamide but was insoluble in other solvents.

The reaction conditions were varied in an attempt to form a polymer with a greater chain length and consequently greater tensile strength. Usually, solid *p*-phenylenediamine was added to an ethanol solution of the dialdehyde oil, but the product was essentially the same if an ethanol solution of *p*-phenylenediamine was added with vigorous agitation. A fivefold increase in the proportion of the ethanol used as the reaction medium also showed no apparent effect on the product obtained. Because the reaction proceeded with such ease and rapidity at room temperature, it was felt that lowering the reaction temperature might result in a decreased reaction rate and consequently promote the formation of a polymer of greater chain length. At 0°C in ethanol the reaction proceeded similarly, and the product was indistinguishable from that obtained at room temperature. When the reactants were cooled to -70°C, no reaction took place, so the temperature was allowed to rise slowly. About -5 to 0°C the compounds became sufficiently soluble to react, but the product was essentially the same as that obtained at room temperature.

m-Phenylenediamine in 1:2 molar ratio with dialdehyde oil gave a yellow, solid reaction product; the resilient filter cake easily crumbled. It was insoluble in organic solvents, but swelled in chloroform and xylene.

o-Phenylenediamine in 1:2 molar ratio gave a dark, viscous, sticky mass that was partially soluble in acetone, chloroform, benzene, and xylene. It swelled in carbon tetrachloride and dimethyl formamide, was insoluble in other solvents, and in contrast to the other products was fusible.

Ethylenediamine in 1:2 molar ratio gave a yellow, granular, and resilient filter cake. The product became swollen in chloroform, benzene, and xylene and was insoluble in other solvents.

1,6-Hexanediamine in 1:2 molar ratio gave a filter cake that on standing became a semisolid mass quite similar to art gum but darker in color. The product was insoluble in the solvents tested.

Piperidine (1.2 mM) and aldehyde oil (10.6 mM of carbonyl) when mixed at room temperature gave a transparent, rubbery gel within 30 min.

Melamine (30 mM) and dialdehyde oil (50 mM) gave no reaction in ethanol at room temperature. The reaction mixture was refluxed for 2 hr. On cooling, a white solid amounting to about one-third of the starting melamine was filtered off. After standing for several days, the filtrate separated into two layers. The upper layer could be decanted; the lower layer was a tough gelatinous material. After drying the latter in a vacuum oven, a dark-amber resilient material resembling art gum was obtained. The product swelled in chloroform and benzene, was partially soluble in carbon tetrachloride, and was insoluble in other solvents.

Urea in equimolar mixture with dialdehyde oil gave no reaction in ethanol at room temperature. The reaction mixture was refluxed for 6 hr with a small amount of concentrated hydrochloric acid. After removal of the ethanol, a highly viscous liquid was recovered.

Results and Discussion

IR Absorption of Aldehyde Oils

The IR spectrum of the starting soybean oil compared to the spectra of the mono- and dialdehyde oil

TABLE I
 Nuclear Magnetic Resonance Data

Proton associated with	Soybean oil		Monoaldehyde oil		Dialdehyde oil		Trialdehyde oil	
	NMR	Theoretical	NMR	Theoretical	NMR	Theoretical	NMR	Theoretical
-CHO	0	0	0.7	1	0.7	1.9	1.1	2.7
-CH=CH-	8	8-10 ^a	1.7	6-8 ^a	1.9	2-4 ^a	0.4	0 ^a
-CH ₂ -O	4	4	4	4	4	4	4	4
HC-O	1	1	1	1	1	1	1	1
=C-CH ₂ -C=	3	2-4	0	2-4	0	0-2	0	0
-CH ₂ -, -CH ₃ , α-CH ₂ -	82	81-87	62	64-70	51	53-59	44	42

^a Soybean oil contains up to 15% of saturated acids, not taken into account in these figures.

showed the differences expected in molecular structure (Fig. 1). However the differences involved were relatively small in large molecules as only slight variations were observed. [In all three spectra.] The aldehyde function in the aldehyde oils was evident as well as the olefinic unsaturation in all three spectra. The soybean oil exhibited an ester function at 1740, 1150, and 1230 cm⁻¹. Evidence of the long-chain fatty acids was observed at 720, 1460, 2850, and 2920 cm⁻¹. Olefinic unsaturation was indicated by the absorption at 3010 cm⁻¹, and the absence of absorption at 960 cm⁻¹ indicated that this unsaturation was *cis*. The aldehyde oils showed the same evidence for ester and long fatty-acid chains as the soybean oil, although absorption appeared in these spectra at 2720 cm⁻¹ characteristic of an aldehyde function. In the aldehyde oils unsaturation appears to be essentially *trans* based on weak absorption at 3010 cm⁻¹ and the presence of the band at 960 cm⁻¹. The latter is much stronger in the monoaldehyde oil. The *cis,trans* isomerization undoubtedly resulted from the hydrogenation of the ozonolysis products over palladium catalysts.

Nuclear Magnetic Resonance

The NMR spectral peaks observed for the starting soybean oil were associated with the expected groups (Table I). The areas of these peaks were in proportions that gave good agreement with the theoretical structure for soybean oil.

The spectra of the aldehyde oils exhibited peaks corresponding to the protons associated with the -CHO groups in addition to the groups of the original soybean oil. In addition, two prominent peaks unidentified were in positions that corresponded to NMR peaks of some of the solvents used in processing the oils.

Integration of NMR peaks and comparison of areas under these peaks with those due to the protons associated with the secondary hydrogen atoms of the glycerine portion of the molecule gave ratios of pro-

tons as shown in Table I. Johnson and Shoolery (1) reported on work that showed that the tertiary hydrogen of the glyceride portion of the molecule did not appear in the same NMR position as the secondary hydrogen, but did appear in a position that coincided with the position of the protons associated with olefinic unsaturation. This effect has been taken into account in developing the ratios in Table I. A range of values is given for some theoretical structures as variations could occur depending on the site of ozonization and reduction. In soybean oil and aldehyde oils the presence of some saturated fatty acids (up to 10-15%) could also account for values of olefinic unsaturation lower than those given.

The aldehydic content in di- or trialdehyde oils, as evidenced by the NMR data, was considerably lower than that shown by carbonyl determinations (1.9 and 2.7 aldehyde groups per molecule, respectively). In monoaldehyde oil, the olefinic unsaturation by NMR was lower than theoretical. In carbonyl determinations (by the hydroxylamine hydrochloride method) any acetal present in the sample would probably hydrolyze to the aldehyde and measure as such. NMR determinations, however, would show only aldehyde protons in their assigned positions. Further, any additional reaction of the samples (for example, oxidation or aldol condensation) that might occur would undoubtedly limit the accuracy of NMR determinations since all data reported in Table I are based on the premise that each molecule contains 4 (and only 4) -CH₂O- protons. Oxidation or aldol condensation would probably introduce extraneous absorptions in the same spectral region in which the glyceryl -CH₂O- groups absorb and, accordingly, would introduce an error in all the calculated values for any given sample. The presence of solvents in the processed oils might also interfere with NMR results for glyceride protons if the solvent impurities appear in the -CH₂O- region of the spectra.

This NMR study was not carried out in detail

 TABLE II
 Infrared Absorption of Dialdehyde Oil Derivatives

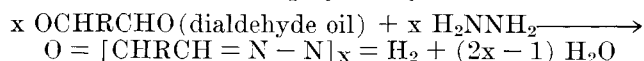
Functionality associated with infrared frequency	Frequency, cm ⁻¹	Relative strength of absorption peaks ^a						
		Dialdehyde oil	Derivative					
			Hydrazine	<i>p</i> -Phenylene-diamine	Melamine	1,6-Hexane-diamine	<i>m</i> -Phenylene-diamine	Ethylene-diamine
-CH ₂ -	2920	S	S	S	S	S	S	S
-CH ₂ -	2850	S	S	S	S	S	S	S
CH in CHO	2720	W
C=O in CHO and O -C-O-CH ₂	1740	S	S	S	S	S	S	S
-C=N-	1610-40	...	W	W	W(Br)	MW	W	W
	1560-70	...	W	...	WM(Br)	MW	VW	W
	1520	M	M	W
-CH ₂ -	1460	M	M	M	M	M	MW	M
-C-CH ₃	1370	W	W	W	W	W	W	W
Ester C=O	1230	S	S	S	S	S	S	S
	1150	S	S	S	S	S	S	S
CH deformation in -CH=CH-(<i>trans</i>)	960	VW	?	?	?	?
-CH ₂ -(CH ₂) ₂ -CH ₂	720	W	W	W	W	W	W	W

^a S = strong, M = medium, W = weak, ? = possible, and Br = broad.

since it was intended mainly to serve as a background for the investigation of the general area of reactions of aldehyde oils. Applying NMR spectroscopy to the rather complex molecular structure of oils has been relatively recent. Although a more comprehensive NMR study would be necessary to define the structures of these materials precisely, the evidence obtained does confirm the formation of aldehydic function by ozonization and reduction of soybean oil. Further, it demonstrates that reduction of the ozonide to the aldehyde takes place without reduction of the residual unsaturation of the fatty acid portion of the triglyceride molecule.

Reactions of Dialdehyde Oil

Aldehydes, in general, react with substituted hydrazines to form hydrazones and with other primary amines to form Schiff bases or anils. It was postulated that anhydrous hydrazine and dialdehyde oil could produce a linear polymer by the reaction:



Also, an aldol condensation could occur under the basic conditions inherent in the amines.

The reaction of dialdehyde oil and some amines took place with surprising ease. The apparent condensation proceeded rapidly under mild conditions—room temperature and without catalysts. However the highly insoluble nature of the product indicated that a nonlinear cross-linked polymer was formed. The extreme insolubility of the product in the reaction media may have provided the driving force for rapid completion of the reaction.

The amines tested that gave rapid reaction included hydrazine; *p*-, *o*-, and *m*-phenylenediamine; and ethylene and hexamethylenediamine. The products obtained were generally insoluble and infusible facticelike solids indicating their crosslinked nature and low molecular weight. Variations in conditions, including lower temperature, dilution, and different order of mixing, had no effect on the reaction between *p*-phenylenediamine and dialdehyde oil.

IR Spectra of Products

Since the products of the reaction of dialdehyde oil with diamines were insoluble in most solvents, NMR data for these materials were unobtainable. IR absorption spectra of these compounds were obtained, however, by incorporating the solids in potassium bromide pellets. These spectra are compared with the spectrum of the dialdehyde oil (obtained from a film on a sodium chloride plate) in Table II.

The aldehyde function with an absorption peak at 2720 cm^{-1} is discernible only in the spectrum of the aldehyde oil. The spectra of all the samples show absorption peaks associated with esters, long aliphatic chains and, usually, *trans* unsaturation. All the reaction products show at least two weak absorption peaks in the 1520 to 1640- cm^{-1} range. In this area IR absorption is indicative of $-\text{C}=\text{N}-$ structure and other structures, especially $\text{C}=\text{C}$ of benzene rings. There is no significant amount of hydroxyl function in these materials. The melamine derivative showed absorption at 810 cm^{-1} that is not present in the other compounds but does appear on the reference spectrum for melamine resins.

Reaction Paths

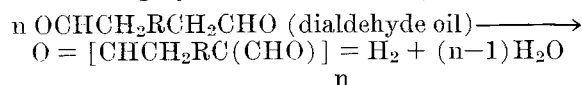
The IR data indicate that the aldehyde and amine functions probably condense to form a Schiff-base

type of compound, since the appearance of peaks associated with $-\text{C}=\text{N}-$ structure were observed. From these data no explanation for the consumption of one-half mole of diamine for each mole of dialdehyde oil is apparent.

One possible explanation for this apparent reduced functionality of the dialdehyde oil is the formation of an amine-catalyzed aldol condensation of the aldehyde oil before condensation of the aldehyde function with the amines or simultaneously with the condensation. To determine whether the diamine acted as a catalyst, 50 mM (43.3 g) of dialdehyde oil were reacted with 2.5 mM (0.27 g) of *m*-phenylenediamine in ethanol at room temperature. A small amount of rubbery material was filtered off. When dried, this weighed 2.46 g, approximately the theoretical weight (2.39 g) for an equimolar reaction product. In a similar experiment, the filtrate was stripped of ethanol and a fluorescent oil was recovered. After standing 24 hr, a factice was formed that had a carbonyl value of 1.64 mM/g , compared with 2.03 for the starting dialdehyde oil. The molecular weight of the product, soluble in the same solvents as the dialdehyde oil, was 1100 compared with approximately 900 for the starting dialdehyde oil (determined by boiling-point elevation of benzene).

This approximate rise of 20% in molecular weight plus the change in physical state of the filtrate, as compared to the starting material, indicates that competing reactions are occurring. One such reaction might be a catalyzed aldol condensation. This theory is substantiated by the observations that only about one-half of the stoichiometric amount of aromatic diamine reacted with the dialdehyde oil and that piperidine catalyzed gelation of the oil as described in the Experimental section. Complete disappearance of the aldehyde from the IR spectra of the diamine derivative indicates that dialdehyde oil is not merely entrained in precipitated product. The reaction of 50 mM of dialdehyde oil and 0.25 mM of *m*-phenylenediamine resulted in a fluorescent oil.

Aldol condensation followed by dehydration could give a linear polymer with a dialdehyde oil:



The condensation could occur at the active methylene group *alpha* to either the aldehyde or ester group but is illustrated only at the methylene *alpha* to the aldehyde. Such a product would still have a number ($n+1$) of aldehyde groups available for further reaction. Reaction with either an active methylene group or with a diamine could produce crosslinked polymers of short-chain length. The unsaturation in conjugation with carbonyl would account for the fluorescence of the materials described.

ACKNOWLEDGMENTS

R. J. Jakobsen, T. F. Page, Jr., and E. J. Brewer of the Instrumental Analysis Laboratories of Battelle Memorial Institute gave IR and NMR data and assistance in interpretation. R. E. Beal prepared the aldehyde oil samples.

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[Received August 31, 1964—Accepted June 14, 1965]