Production of Vinylic Unsaturation by Partial Dehydrobromination of Vicinal Dibromo Fatty Derivatives[1]

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Abstract

The reaction of methyl dibromostearate with metal cyanates in dimethyl formamide or dimethyl sulfoxide results in the disappearance of the peak at 548 cm^{-1} in the IR spectrum due to the –C–Br group. Chemical analysis of the products reveals the presence of residual bromine. Gas liquid chromatography and nuclear magnetic resonance examination of the products shows the presence of olefinic unsaturation and this indicates that partial dehydrobromination has occurred. The result is a double bond with one carbon atom attached to a bromine atom. This structure has some vinylic characteristics. The application of this process to partially brominated linseed oil yields a dehydrobrominated linseed oil, with residual bromine. This oil has drying properties very similar to raw linseed and safflower oils.

Introduction

Active methylene groups and *cis* unsaturation in linoleic and linolenic acids of safflower, soybean and linseed oils are responsible for their drying properties. Polymerization occurs by free radical attack at the active methylene groups and is essentially of the linear additive type with cross-linking, which may occur through peroxide bridges (–O–O–) or directly as carbon to carbon (–C–C–) linkages (1). Synthetic resins obtained by polymerization of other functionalities as in the classes of vinyls, acrylates, acrylonitriles, isocyanates and epoxides have invaded the coatings field and have caused a shrinkage in the market for all oil-based paints and linseed oil types in particular. In a program of study to introduce more reactive groups into linseed oil, an exploratory study was initiated. In one phase of this work, methyl dibromostearate was treated with metal cyanates to ascertain whether isocyanate groups could be incorporated into the fatty chain by substitution. Instead, evidence for the occurrence of partial dehydrobromination was obtained in all these experiments; this paper reports the results.

Experimental Procedure

Brominated Oleate

Technical grade oleic acid (Emery) was converted into methyl ester by refluxing with methanol and 2% sulfuric acid. The methyl ester was analyzed

TABLE I
Reaction of Brominated Oleate and Brominated Linseed Oil with Metal Cyanates

Expl. no.	Reactants	Reaction conditions				Product analyses			
		Temp. °C	Time hr	Solvent	Cyanate excess, %	Iodine value	Bromine content	Bu amine consump.[a]	Absorption at 548–550 cm^{-1}
	Brominated oleate	....	....	....	......	......	33.8	....	Sharp peak of medium size
1	Brominated oleate + potassium cyanate	38	48	DMF	125	30.2	19.3	None	No peak
2	Brominated oleate + potassium cyanate	60–65	4	DMF	100	22.5	24.7	None	Sm. peak
3	Brominated oleate + potassium cyanate	92–94	72	DMF	25	45.7	18.7	None	No peak
4	Brominated oleate + potassium cyanate	92–94	48	DMF	125	51.2	18.1	None	No peak
5	Brominated oleate + potassium cyanate	92–94	6	DMF	50	40.8	17.2	None	No peak
6	Brominated oleate + sodium cyanate	92–94	6	DMF	50	36.0	18.9	None	No peak
7	Brominated oleate + lead cyanate	92–94	24	DMF	50	8.6	21.1	None	Sharp peak of medium size
8	Brominated oleate ± potassium cyanate	38–40	24	DMSO	50	28.0	17.9	None	No peak
9	Brominated oleate ± potassium cyanate	88–92	6	DMSO	50	37.9	17.6	None	No peak
10	Brominated oleate + sodium cyanate	24–34	24	DMSO	50	14.0	29.1	None	Sharp peak of medium size
11	Brominated oleate + sodium cyanate	88–92	6	DMSO	50	41.3	18.1	None	No peak
12	Brominated oleate + lead cyanate	88–92	65	DMSO	50	27.9	15.4	0.6 Ml	Very sm.
13	Brominated oleate + lead cyanate	92–94	7	DMSO	50	30.6	17.0	2.0 Ml	Very sm.
14	Brominated oleate ± sodium hydroxide	At reflux	4	Methanol	100	29.7	18.3	None	None
	Brominated linseed oil	....	....	....	......	132.7	17.6	....	Very small peak
15	Brominated linseed oil + sodium cyanate	92–94	15	DMF	0	143.2	5.4	None	No peak
16	Brominated linseed oil + sodium cyanate	92–94	4	DMF	0	133.6	5.9	None	No peak

[a] Two-milliliter aliquot was reacted with 10 ml of butyl amine in dioxane (25 g/liter) for about 18 hr and the excess titrated with 0.1 N HCl with methyl red indicator. A blank for 10 ml butylamine was conducted at the same time (4). Values recorded are the differences between blank and sample readings.

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by gas-liquid chromatography (2). Results are as follows: Myristate, 3.2%; palmitate, 4.2%; palmitoleate, 7.4%; oleate, 75.2%; linoleate, 6.8% unidentified, 3.2% (as three peaks); and IV, 86.2.

This technical grade methyl ester was brominated in ice-cold ether solution until the yellow color of bromine persisted. Excess bromine was removed with sulfur dioxide. The ether solution was washed with water, dried over anhydrous sodium sulfate, and ether was distilled. Last traces were removed in a rotary evaporator under vacuum over a steam bath. Analysis is given in Table I.

Linseed Oil

An alkali refined grade, Cargill's Supreme, was used with the following analysis (2): SV, 194; IV, 185; palmitate, 6.3%; stearate, 3.8%; oleate, 20.6%; linoleate, 16.3% and linolenate, 53.0%.

Partial Bromination of Linseed Oil

Mean molecular weight of this linseed oil is 867.0 and the number of double bonds per mole is: $1.85 \times 867.6/254 = 6.32$. Bromine required to add to one double bond in 100 g of oil is: $185 \times 80/6.32 \times 127 = 18.44$ g. Linseed oil, 100 g, was dissolved in 200 ml of hexane and cooled in an ice bath. A solution was prepared by dissolving 6 ml of bromine in 200 ml of hexane. The bromine solution previously cooled in an ice bath was added in small aliquots to the cold linseed oil solution over a period of 3 hr. It was observed that under these conditions, addition of bromine to the unsaturation of the oil was slow, since the yellow color of the bromine did not disappear immediately. Enough time was allowed between each addition for the color to change. After all the bromine solution had been added, the solution was kept in the bath for an additional hour and then warmed to room temperature. Some solid material deposited and this was redissolved by addition of chloroform. The solution was washed with water to remove any acidity due to HBr formation. The washings required 75.7 ml of 0.077 N NaOH equivalent to 0.5% bromine. The water-washed hexane solution was dried over anhydrous sodium sulfate and the solvent distilled off. The last traces were removed by heating over a steam bath in a rotary evaporator under vacuum. Analysis of the brominated linseed oil is recorded in Table I.

Reaction of the Brominated Methyl Oleate With Metal Cyanates in Dimethyl Formamide

The best laboratory grades of potassium and sodium cyanates were used. Lead cyanate was prepared by precipitation from lead nitrate and potassium cyanate. A 250 ml three-necked flask was provided with a stirrer and a thermometer. This was charged with 4.56 g (0.01 mole) of dibromostearate. To this, 100 ml of dimethyl formamide, DMF, were added followed by heating and stirring on a steam bath. When the desired temperature was reached (see Table I) 2.43 g (0.03 mole + 50% excess) potassium cyanate were added and the reaction was conducted for the desired period of time. Reactions with sodium and lead cyanates were conducted similarly. To follow the reaction, aliquots of 2.5 ml were removed periodically and treated with *n*-butyl amine, (4) as mentioned below. The hot reaction mixture was transferred to a separatory funnel, cooled somewhat, and extracted several times with hexane. Recovery of esters was about 90% of the theoretical.

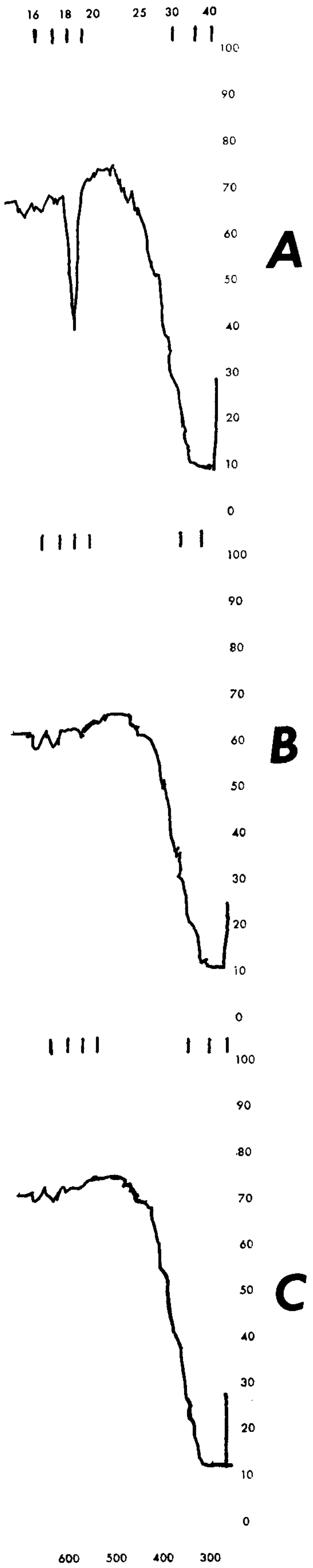

FIG. 1. Infrared spectra in the region 600–300 cm^{-1} of: (A) Brominated methyl oleate. (B) Products of recreation between brominated oleate and potassium cyanate in dimethyl formamide. (C). Product of reaction between brominated oleate and sodium hydroxide in methanol.

Reactions at room temperature were performed in a 250 ml Erlenmeyer flask with a magnetic stirrer.

Reaction of Brominated Linseed Oil With Sodium Cyanate in Dimethyl Formamide

A 500 ml DMF solution which contained 114 g brominated linseed oil was heated on a steam bath with stirring and then 14.5 g of sodium cyanate were added. After 4 hr, the mixture was transferred to a separatory funnel and extracted with hexane. About 1200 ml of hexane extracts were obtained from which the dehydrobrominated oil was recovered after distillation of the solvent. The last traces of solvent were removed under vacuum in a rotary evaporator on a steam bath. The specific gravity of the product was 0.9557 (25 C) and that of linseed oil was 0.9007 (25 C). Other properties are recorded in Table I.

Analytical Procedures

Bromine contents of different products were determined according to the method of Vogel (3). The presence of isocyanate groups was determined with *n*-butyl amine in dioxane (4).

Infrared analyses were run in potassium bromide cells with a 0.025 mm spacing on a Beckman IR-10 spectrophotometer. Absorption for –C–Br grouping occurs at 548–550 cm^{-1} (5). Typical spectra with different products are shown in Figure 1. Gas liquid chromatography determinations were made with a Barber-Colman, Model 5000 chromatograph equipped with a flame ionization detector and temperature programmer. Nitrogen was used as a carrier gas. Quantitative analyses of methyl oleate and linseed methyl esters were run on a 12% DEGS/Anakrom 6 ft glass column, ¼ in. OD, programmed at 140–190 C at 2C/min.

For brominated esters and cyanate reaction products, a higher temperature was required. These were analyzed on a 4 ft column ¼ in. O.D. packed with 10% Dow-Corning 200 on Gas Chrom Q. These were programmed at 10C/min between 160–240 C. Typical chromatographs are shown in Figure 3.

Typical NMR spectra are shown in Figure 4. A Varian 60 Mc instrument was used.

Results and Discussion

Selection of a suitable solvent for the reaction of the brominated methyl oleate and potassium cyanate was important. The mixture was treated with potassium cyanate in ethyl ether, acetone, tetrahydrofuran and acetonitrile at reflux temperatures and with dioxane at steam bath temperatures (92–94 C) under continuous stirring for 18–24 hr. Neither the reaction mixture during or after the reaction, nor the recovered products reacted with butyl amine. This was indicative of the absence of the –NCO group. The products had the typical peak for –C–Br of the same magnitude as that of the parent compound (Fig.

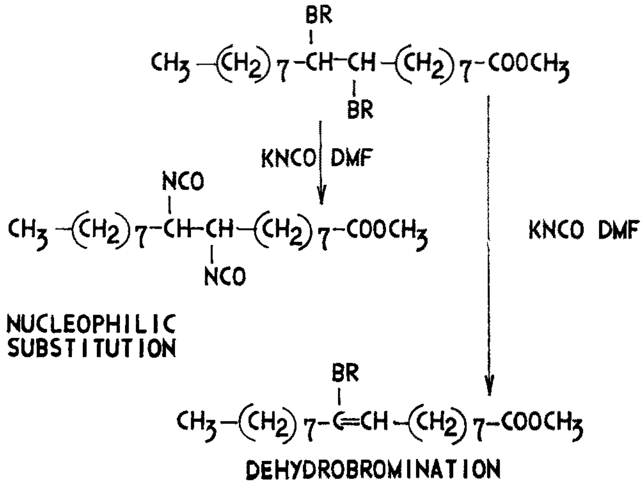

FIG. 2. Possible reactions between potassium cyanate and brominated oleate.

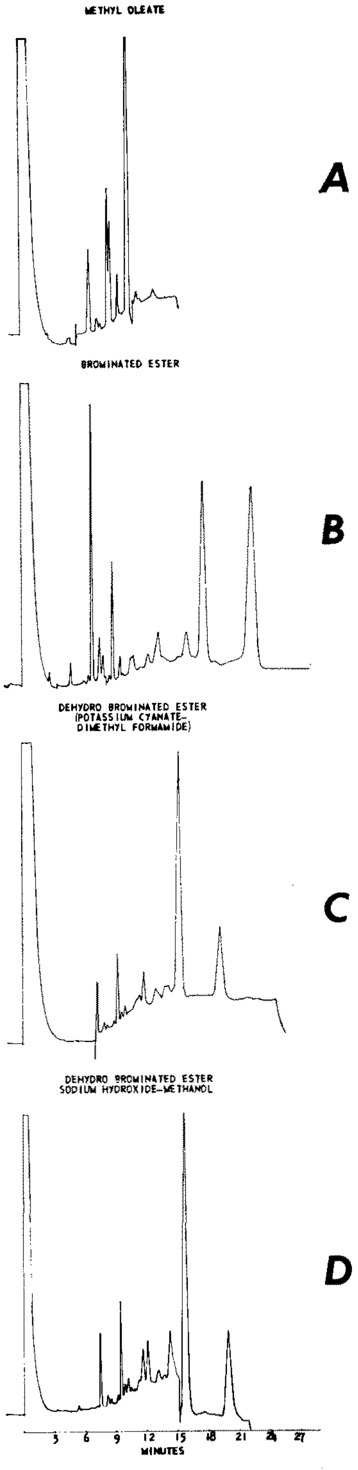

FIG. 3. Gas liquid chromatograms on a Dow-Corning Silicone Column (DC-200) of: (A) Methyl oleate, (B) Brominated oleate, (C) Brominated oleate-potassium cyanate- DMF reaction product. (D) Brominated oleate–sodium hydroxide–methanol reaction product.

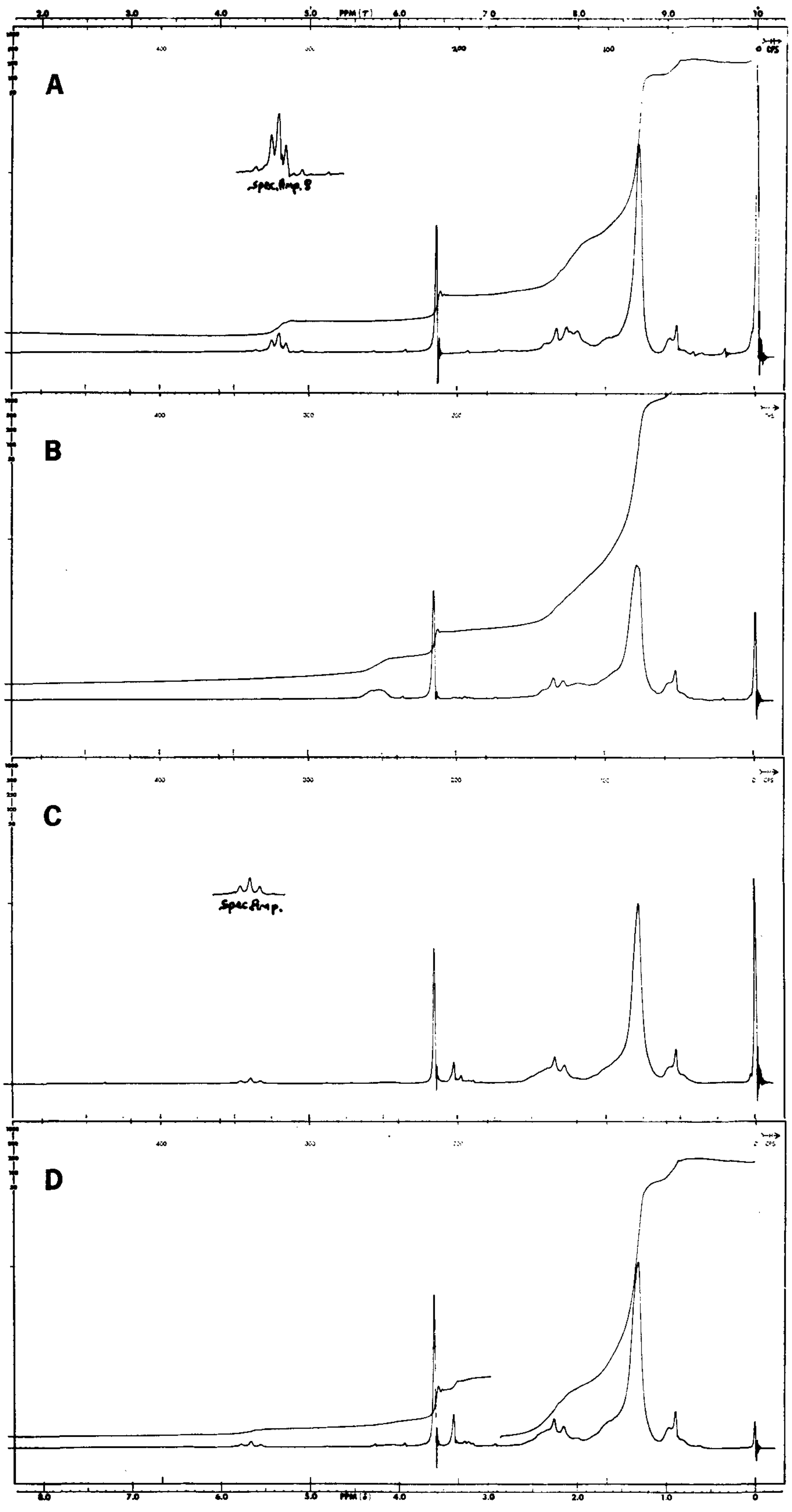

FIG. 4. NMR spectra of: (A) Methyl oleate. (B) Brominated oleate. (C) Brominated oleate-sodium cyanate-DMF reaction. (D) Brominated oleate-sodium hydroxide-methanol reaction.

1A). When the reaction was performed in dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) this peak disappeared in the products which did not react with butyl amine, Figure 1B. Further, no peaks characteristics of the $-N=C=O$ appeared at 2200–2600 cm^{-1} (6) even with products from experiments in which the reaction mixture did react with butyl amine.

Two possible reactions of vicinal dibromides are nucleophillic substitution, to give a diisocyanate (7) and partial dehydrobromination to give a bromoolefin (8,9). These are as shown in Figure 2. The formation of diisocyanate is ruled out because of inertness to butyl amine, the presence of bromine in the product, and the absence of the peak at 2200–2600 cm^{-1} characteristic of the $-N=C=O$. Confirmatory evidence for this is obtained in the GLC analysis shown in Figure 3. The dibromostearate has two strong peaks (Fig. 3B) which are away from the point where methyl oleate (Fig. 3A) elutes under identical conditions. Alcoholic sodium hydroxide causes partial dehydrohalogenation with vicinal dihalides (8,9). The product of reaction of the brominated oleate with sodium hydroxide in methanol has no peak at 548–530 cm^{-1} (Fig. 1C) but has residual bromine (see Table I, Expt. 14). Its gas chromatogram (Fig. 3D) is very similar to the cyanate-reacted products (Fig. 3C). It is therefore concluded that the cyanate ion acts as a weak base in DMF and DMSO and causes partial dehydrobromination of the vicinal dibromides.

Further confirmation of this was obtained in the NMR spectra shown in Figure 4. In the brominated oleate (Fig. 4B) the triplet at 4.5–4.7 ppm (τ) due to the olefinic hydrogens (10) of methyl oleate has disappeared and a broad doublet appeared at 5.6–5.8 ppm (τ). The latter is due to the hydrogens on the carbon atoms bearing the bromine atoms.

In the NMR spectrum of the sodium hydroxide reaction product Figure 4D, and that from the sodium cyanate Figure 4C, this peak also disappears, but the triplet at 4.5–4.7 ppm (τ) is partly restored. This is because the dehydrobrominated product has only one olefinic hydrogen which is also influenced by the bromine atom attached to the other carbon of the double bond. In these products a new peak appears at 7.4 ppm (τ), perhaps due to the $-CH_2-$ group adjacent to the bromine atom. It should be pointed out that the bromine atom attached to the olefinic carbon atom imparts the vinylic character to the double bond and thus this double bond can be expected to behave differently from the normal *cis* double bond.

It is of further interest to learn whether a modified linseed oil with a vinylic double bond will have altered drying properties. The dehydrobrominated linseed oil was studied for its film-forming properties in comparison with alkali-refined linseed and safflower oils. Films 3 mil thick which contained driers as Pb 5%, Ca 0.2%, Mn 0.05%, Co 0.05% were cast. In common with the other oils, the dehydrobrominated oil had a touch dry time of about 6 hr. In the Gardner wheel tester none of these films dried tack free in 12 hr. The thermal gelation time of the dehydrobrominated oil as compared to that of tung oil is much slower but the bodying rate was comparable to linseed oil.

Evidence presented in this paper indicates that fat-derived vicinal dibromide compounds may partially dehydrobrominate with the isocyanates of several metals to yield vinylic monobromine derivatives rather than isocyanate substitution products. Since the monobromides yield dried films similar to those produced from linseed oil, they might be used in flame resistant compositions.

ACKNOWLEDGMENT

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