

Cyanoethylation of Hydroxy Derivatives of Fats

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Abstract

Mono-, di-, and trihydroxy derivatives of fats have been cyanoethylated in high yields by use of excess acrylonitrile as solvent and aqueous benzyltrimethylammonium hydroxide as catalyst. Reaction variables of the cyanoethylation in excess acrylonitrile have been examined with methyl 12-hydroxystearate as the model compound. At moderate reaction temperatures the cyanoethylation reaction is 93% complete before the competing polymerization of the acrylonitrile consumes the catalyst.

Introduction

THE CYANOETHYLATION of hydroxy compounds has been widely investigated in the laboratory (1) and applied commercially (2). Yet there are few reports in which the reaction has been carried out successfully on alcohols derived from fatty materials. Bruson (1) found that esters of hydroxy acids resist cyanoethylation by standard procedures, but 10 years later DuPuy (3) successfully applied this reaction to derivatives of ricinoleic acid by using a modified standard procedure. The successful reaction with acrylonitrile of esters of hydroxylated fatty acids, or their derivatives, has not been reported.

The purpose of this work was to study the cyanoethylation of hydroxy derivatives of fats and to investigate the properties and reactions of the resulting β -cyanoethyl ethers. The preparative aspects concerned the application of conventional cyanoethylation procedures, and of modified procedures, to methyl *threo*-9,10-dihydroxystearate, the preparation of several mono-, di-, and tri- β -cyanoethoxy derivatives of stearic acid and the investigation of the effect of processing variables in the cyanoethylation of methyl 12-hydroxystearate by the use of excess acrylonitrile as solvent.

Experimental Section

Materials Used

Methyl 12-Hydroxystearate. Technical grade (Eastman) 12-hydroxystearic acid was methylated, and the resulting ester was chromatographed on a Florisil column. The product was eluted with benzene. Mp 57.5–58°C. Lit. (4): mp 58.0–58.2°C.

Methyl threo-9,10-Dihydroxystearate. Methyl 9,10-epoxystearate was hydrated (5). Mp 69.0–70.0°C. Lit. (6): mp 70.0°C.

Methyl erythro-9,10-Dihydroxystearate. Oleic acid was oxidized with alkaline potassium permanganate (7), and the resulting dihydroxy acid was methylated. The purified product melted at 102.0–103.0°C. Lit. (6): mp 103.0°C.

Methyl 9,10,12-Trihydroxystearate. Methyl ricinoleate was epoxidized (8), and the product was hydrated with aqueous fluoboric acid (5). The purified product melted at 67.0–69.0°C.

1,9,10-Trihydroxyoctadecane. Methyl *threo*-9,10-dihydroxystearate was reduced with sodium in ethanol-toluene (9) mp 80.0–81.0°C. Lit. (10): 81.0–82.0°C.

Hydrated Epoxidized Soybean Oil. Commercial (Flexol Plasticizer EPO) epoxidized soybean oil was hydrated (5), and the product containing 7.3% hydroxyl groups was used without further purification.

Monostearin. Glycidyl stearate was hydrated with aqueous sulfuric acid (1). Thin-layer chromatography (TLC) on silica gel saturated with boric acid indicated, upon development with a chloroform-acetone-methanol (70:27:3) mixture, that the product contained approximately 90% monostearin.

Acrylonitrile. Practical-grade acrylonitrile (Eastman) was used, as received, for most cyanoethylations. For some experiments the acrylonitrile was redistilled, and the fraction boiling at 77°C was used.

Benzyltrimethylammonium Hydroxide (BTAH). A 40% aqueous solution (Eastern Chemical Corporation) was used as received.

Procedures

Analytical Procedures. Gas-liquid chromatography (GLC) was carried out with 4-ft \times 1/4-in. stainless steel columns, packed with 4% XE-60 on Gas-Chrom Z. The temperature was programmed at 6° per minute from 200–400°C. The helium gas flow was 60 ml per minute. Analytical and preparatory thin-layer chromatographic (TLC) plates were coated with silica gel containing 10% binder (Adsorbosil 1). Monocycanoethoxylated derivatives were developed in 95% benzene, 5% ether mixtures, but polycycanoethoxylated compounds required mixtures containing 79% benzene, 20% ether, and 1% methanol. Analytical plates were charred after spraying with a solution of potassium dichromate in aqueous sulfuric acid. After development, preparatory plates were sprayed with an alcoholic solution of 2', 7'-dichlorofluorescein, and the bands were located under UV light. Infrared (IR) spectra were determined with a Perkin-Elmer Model 237B spectrophotometer.

Methyl threo-9,10-Di-(2-cyanoethoxy)-octadecanoate. Methyl *threo*-9,10-dihydroxystearate (5.0 g, 0.015 mole), dissolved in 40 ml of acrylonitrile (0.60 mole), was placed in an air-cooled, 500-ml, round-bottom flask equipped with magnetic stirrer. To this solution at room temperature 1 ml of benzyltrimethylammonium hydroxide (BTAH) (0.0025 mole catalyst) was added rapidly with stirring. The temperature of the reaction mixture rose rapidly to about 75°C (reflux) after addition of the base. The mixture was stirred for one hour while it cooled to room temperature. Water (50 ml) and acetone (100 ml) were added in succession, and the resulting mixture was neutralized with dilute HCl and extracted with three 200-ml portions of ether. The combined extracts were washed with water, dried over anhydrous sodium sulfate, and evaporated to an oily residue. The latter was redissolved in a mixture containing 79% benzene, 20% ether, and 1% methanol, then passed through a short column of Florisil. Removal of the solvent from the eluate left 6.6 g of colorless oil (theory 6.6 g). GLC analysis indicated that the oil contained 95% of the desired product, 4.1% methyl 9(10)-hydroxy-10(9)-(2-cyanoethoxy)-octadecanoate, and traces of unreacted starting-material. A sample was purified for analysis by preparatory TLC. The IR spectrum

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was consistent with the proposed structure. Anal. Calc'd for $C_{25}H_{44}O_4N_2$: C, 68.77; H, 10.16; N, 6.41. Found: C, 68.68; H, 10.35; N, 6.20.

Methyl erythro-9,10-Di-(2-cyanoethoxy)-octadecanoate. Methyl erythro-9,10-dihydroxystearate (2.0 g, 0.006 mole), dissolved in 15 ml (0.27 mole) of acrylonitrile, was treated with 0.6 ml of BTAH solution (0.0015 mole catalyst), and the product was isolated as described above for the *threo* analog to obtain 2.64 g of colorless oil (theory 2.64 g). GLC analysis indicated that the oil contained 97% of the desired product, 2.5% of the monocyanoethoxy derivative, and a trace amount of unreacted starting material. TLC and IR analyses were consistent with this composition. A sample was purified for analysis by preparatory TLC. Anal. Calc'd for $C_{25}H_{44}O_4N_2$: C, 68.77; H, 10.16; N, 6.41. Found: C, 69.06; H, 10.33; N, 6.66.

Methyl 12-(2-Cyanoethoxy)-octadecanoate. Methyl 12-hydroxystearate (1.1 g, 0.0035 mole), dissolved in 4.0 g (0.075 mole) of acrylonitrile, was treated with 0.2 ml of BTAH solution (0.00050 mole catalyst) as before, and the product was isolated as described for methyl *threo*-9,10-di-(2-cyanoethoxy)-octadecanoate. GLC analysis of the 1.27 g of colorless oil (theory 1.28 g) showed it to contain 98% of the desired product with traces of unreacted starting-material and by-products. The IR spectrum was consistent with the proposed structure. Mass spectroscopy gave a parent peak of m/e 367 (theory 367.6). Anal. Calc'd for $C_{22}H_{41}O_3N$: C, 71.88; H, 11.24; N, 3.81. Found: C, 71.89; H, 11.12; N, 3.80.

Methyl 9,10,12-Tri-(2-cyanoethoxy)-octadecanoate. Methyl 9,10,12-trihydroxystearate (1.0 g, 0.003 mole), dissolved in 15 ml (0.27 mole) of acrylonitrile, was treated with 0.6 ml BTAH solution (0.0015 mole catalyst), and the product, 1.36 g of colorless oil (theory 1.45 g), was isolated as described for methyl *threo*-9,10-di-(2-cyanoethoxy)-octadecanoate. The content of the oil included 85% of the desired product as determined by preparatory TLC. Anal. Calc'd for $C_{28}H_{47}O_5N_3$: C, 66.50; H, 9.37; N, 8.31. Found: C, 66.42; H, 9.02; N, 8.20.

2,3-Di-(2-cyanoethoxy)-propyl octadecanoate. Glycerol monostearate (0.20 g, 0.00056 mole), dissolved in 10 ml (0.15 mole) of acrylonitrile, was treated with 0.4 ml of BTAH solution (0.0010 mole catalyst), and the product was extracted as described for the preparation of methyl *threo*-9,10-di-(2-cyanoethoxy)-octadecanoate. The yellow oily material which was obtained (0.92 g) was crystallized from ether and from hexane and was further purified by preparatory TLC to obtain 0.22 g of essentially pure oil (theory: 0.26 g). Anal. Calc'd for $C_{27}H_{48}O_4N_2$: C, 69.78; H, 10.41; N, 6.03. Found: C, 69.78; H, 11.22; N, 6.19.

1,9,10-Tri-(2-cyanoethoxy)-octadecane. To a solution of 1,9,10-octadecanetriol (0.12 g, 0.0004 mole) in 1 ml (0.015 mole) of acrylonitrile at 60C was added 0.1 ml of BTAH solution (0.00025 mole catalyst). After 1 hr the reaction mixture was worked up as in previous experiments. The crude oil obtained weighed 0.205 g (theory 0.183 g). The desired product, which constituted 50% of the oil, gave an IR spectrum consistent with the expected structure. Anal. Calc'd for $C_{27}H_{47}O_3N_3$: C, 70.24; H, 10.26; N, 9.10. Found: C, 70.14; H, 10.04; N, 8.76.

Cyanoethylated Soybean Oil. To a solution of 0.25 g hydrated epoxidized soybean oil in 5 ml of acrylonitrile was added 0.2 ml of BTAH solution. After 3 hr of stirring at room temperature, the reaction product was isolated as described for the prepara-

tion of methyl *threo*-9,10-di-(2-cyanoethoxy)-octadecanoate to give 0.32 g of yellow oil (theory 0.31 g). The IR spectrum showed the essential disappearance of hydroxyl bands, the presence of nitrile bands, and the presence of bands associated with soluble acrylonitrile polymers (see discussion). Percentage OH, 0.24 (7.3% before cyanoethylation); percentage nitrogen, 7.35 (expected 4.9%, based on hydroxyl content of starting material, which contained no nitrogen).

Methyl 9(10)-(2-cyanoethoxy)-10(9)-hydroxyoctadecanoate. Methyl *threo*-9,10-dihydroxystearate (1.0 g, 0.0003 mole) was dissolved in 3 ml of pyridine containing 0.004 g KOH. To this solution at room temperature was added slowly 0.4 ml (0.0060 mole) of acrylonitrile. The mixture was stirred for 2 hr, two additional portions of 0.4 ml acrylonitrile were then added at 15-min intervals, and the mixture was stirred for 1 hr more. The reaction product was isolated as described for previous experiments to obtain 1.2 g of colorless oil (theory for monocyanoethylation 1.16 g). GLC analysis showed that the oil had the following composition: methyl *threo*-9,10-di-(2-cyanoethoxy)-octadecanoate, 15%; methyl 9(10)-(2-cyanoethoxy)-10(9)-hydroxyoctadecanoate, 65%; unreacted starting material, 20%. The monocyanoethylated product was isolated by preparatory TLC. Anal. Calc'd for $C_{22}H_{41}O_4N$: C, 68.89; H, 10.77; N, 3.65. Found: C, 68.96; H, 10.82; N, 3.47.

The following series of experiments were carried out in order to explore the effect of varying reaction conditions upon product yield. The cyanoethylation of the model compound, methyl 12-hydroxystearate, was carried out on a small scale by the representative procedure described. Variations to this procedure are illustrated below.

Cyanoethylation of Methyl 12-Hydroxystearate. A solution of methyl 12-hydroxystearate (0.5 g, 0.0016 mole) in 4.0 g (0.075 mole) of acrylonitrile was placed in a 250-ml, round-bottom flask, which was equipped with a magnetic stirrer and with a reflux condenser. The temperature of the reaction mixture was controlled by means of a water bath maintained at 26.0 ± 0.5 C. To the mixture at 26C was added rapidly 0.1 ml of BTAH solution containing 0.00025 moles catalyst. Sixty seconds after the addition of the base, acrylonitrile polymerization to an ether-insoluble polymer was observed by an almost instantaneous darkening of the solution, accompanied by the evolution of heat. The 60-sec induction period was reproducible within ± 5 sec in duplicate experiments. After 1 hr of stirring at 26C, the mixture was diluted with 3 ml of water, and 6 ml of acetone were added. The resulting mixture was neutralized with dilute HCl and extracted with three 20-ml portions of ether. The insoluble polymers were filtered out of the water layer, and dried to give 0.71 g of yellow solid. The combined ether extracts were washed with water, dried over sodium sulfate, and concentrated to give 0.61 g of a semisolid (theory: 0.58 g). GLC analysis indicated that 88.1% of the total amount of starting material which was recovered was in the form of the cyanoethylated product.

Variation of Reaction Temperature. The cyanoethylation of methyl 12-hydroxystearate, as described in the sample procedure, was carried out at various temperatures in the range of 15–60C. Results are shown in Table I.

Variation of Amount of Catalyst. The cyanoethylation of methyl 12-hydroxystearate, as described in

TABLE I
Cyanoethylation of Methyl 12-Hydroxystearate. Effect of
Variation in Reaction Temperature

Tempera- ture	Product ^a			Induc- tion period, sec
	Weight, g	Degree of cyano- ethyla- tion ^b	Insoluble polymer weight, g	
15	0.59	94.2	0.60	129
26	0.61	88.1	0.71	40
35	0.56	86.3	0.61	13
45	0.54	75.1	0.60	3
60	0.52	51.4	0.68	<1

^a Starting mixture: 0.5 g methyl 12-hydroxystearate, 4.0 g acrylonitrile, 0.1 ml BTAH solution.

^b Percentage of recovered, cyanoethylated starting material, as measured by GLC.

the sample procedure, was carried out at 26C at various catalyst concentration levels. Results are shown in Table II.

Effect of Nonreactive Diluent. The cyanoethylation of methyl 12-hydroxystearate was carried out, as described in the sample procedure, except that pyridine was added to the mixture at various dilution levels prior to the addition of catalyst. Results are listed in Table III.

Effect of Water and Aqueous Ammonia on the Progress of the Cyanoethylation Reaction. The cyanoethylation of methyl 12-hydroxystearate was carried out as described in the sample procedure except that 0.4 ml of BTAH was used instead of 0.1 ml. Immediately after addition of the catalyst and at periodic intervals thereafter, samples containing 1.6 mg of fatty ester were withdrawn, quenched by injection into acidified (HCl) water, and extracted with ether. At the end of one hour the remaining reaction mixture was worked up as usual.

The above experiment was repeated twice. In one experiment 0.1 ml of water was added to the acrylonitrile before the catalyst was introduced, and in the other 0.1 ml of aqueous concentrated ammonium hydroxide was added. The data of all three experiments are plotted in Fig. 1.

Discussion

It is generally recognized that compounds with high equivalent weights per hydroxyl groups are cyanoethylated with greater difficulty than those with lower equivalent weights. Previous workers have attempted to overcome this obstacle by raising the reaction temperature, but the results have not been altogether satisfactory. An explanation of the remaining limitations follows from the results of the present work.

The cyanoethylation of hydroxy compounds is generally carried out in the presence of a strong base.

TABLE II
Cyanoethylation of Methyl 12-Hydroxystearate. Effect of
Variation in the Amount of Catalyst

Catalyst ^a		Product ^c			Induc- tion period, sec
Volume, ml	Mole ratio ^b	Weight, g	Degree of cyano- ethyla- tion ^d	Insoluble polymer weight, g	
0.005	125.0	0.49	2.9	0.01	60
0.010	62.5	0.52	27.7	0.05	60
0.050	12.5	0.57	76.7	0.40	35
0.100	6.3	0.61	88.1	0.71	40
0.200	3.1	0.61	92.9	0.89	34
0.400	1.6	0.82	97.3	1.20	113
0.600	1.0	0.90	97.2	1.40	150

^a Benzyltrimethylammonium hydroxide as 40% aqueous solution.

^b Ratio: moles of methyl 12-hydroxystearate/moles of catalyst.

^c Starting mixture: 0.5 g methyl 12-hydroxystearate, 4.0 g acrylonitrile, catalyst as specified, temp. 26C.

^d Percentage of recovered, cyanoethylated starting material, as measured by GLC.

TABLE III
Cyanoethylation of Methyl 12-Hydroxystearate. Effect of Addition
of Pyridine as Diluent

Acrylonitrile Pyridine	Product ^a		Insoluble polymer weight, g
	Weight, g	Degree of cyanoethyla- tion ^b	
10/1	0.58	86.0	0.93
4/1	0.51	83.0	0.90
2/1	0.55	59.0	0.94
1/1	0.54	39.0	0.80

^a Starting mixture: 0.5 g methyl 12-hydroxystearate, 4.0 g acrylonitrile, 0.2 ml BTAH solution, pyridine, temp. 26C.

^b Percentage of recovered, cyanoethylated starting material, as measured by GLC.

Presumably the first step in this reaction is the abstraction of a hydroxyl proton from the compound to be cyanoethylated. A competing reaction is the base-initiated homo-reaction of acrylonitrile. This self-condensation, which leads to ether-insoluble polymers as well as to soluble products and which will henceforth simply be referred to as polymerization reaction, competes with the cyanoethylation reaction since it consumes both acrylonitrile and base. It is strongly exothermic and occurs with considerable violence (2). For this reason the addition of a strong base to acrylonitrile has generally been deemed inadvisable.

Cyanoethylation of hydroxylated materials is typically carried out by dissolving the alcohol and a strong base catalyst in an inert solvent, e.g., dioxane, pyridine, and acrylonitrile slowly added at 20–80C. Attempts to cyanoethylate methyl 12-hydroxystearate under these conditions by use of dioxane as solvent and aqueous benzyltrimethylammonium hydroxide (BTAH) solution as base gave less than 5% conversion to the desired product. Treatment of methyl *threo*-9,10-dihydroxystearate by a similar procedure and with dioxane, pyridine, or benzene as the solvent and with potassium hydroxide, aqueous BTAH, or sodium carbonate as the base also gave poor conversions. The best results were obtained by the addition of pyridine as the solvent and aqueous BTAH as the catalyst and by the addition of fresh amounts of acrylonitrile and catalyst over a period of 5 days to obtain about 70% conversion to the dicyanoethoxy ester. However, excessive amounts of by-products which were formed during this prolonged period were difficult to separate from the product.

By contrast, the cyanoethylation of methyl 12-hydroxystearate occurs easily and in high yield when excess acrylonitrile is used as solvent. The reaction

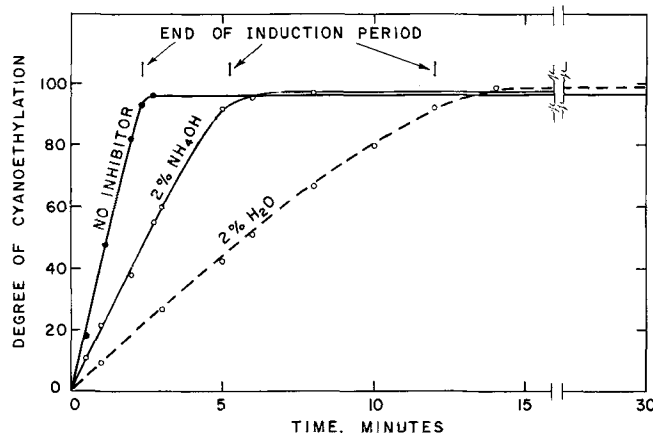


Fig. 1. Cyanoethylation of methyl 12-hydroxystearate; progress of the reaction in the presence and absence of inhibitors.

is carried out by placing a small amount of the solution (e.g., approximately 6 ml) in a flask of relatively large volume (e.g., 250 ml) and immersing the flask in a water bath, the temperature of which is controlled closely. Efficient stirring spreads a large portion of the solution over the walls of the flask and permits efficient heat transfer. The temperature dependence of the reaction is evident from the data of Table I. Addition of the catalyst is followed by an induction period (for the polymerization reaction), during which there is no visual evidence of reaction. It will be shown later that during this period cyanoethylation is actually progressing and in some reactions exceeds 90% completion.

The end of the induction period is signalled by momentary warming of the mixture and by the appearance of coloration. The symptoms are more severe and appear more abruptly at elevated onset temperatures. When the reaction is carried out at 60°C, polymerization occurs almost at the instant at which the base is added, and the mixture reaches reflux temperature (77°C) momentarily. The polymerization of acrylonitrile gives rise to two groups of products: ether-insoluble polymers which are readily separated from the mixture and ether-soluble products which are not readily separable. The presence of the latter can be detected on IR spectra and on TLC plates, but they are not measured by GLC analysis. The latter, when applied to the crude sample, measures only the amounts of recovered starting-material and of the cyanoethylated product which is present. The inability to analyze the crude samples completely is reflected in the term "degree of cyanoethylation," which is equal to the amount of cyanoethylation product, divided by the sum of the product and the recovered starting-alcohol, the quotient multiplied by 100. The ether-soluble self-condensation products of acrylonitrile can be separated by passage through Florisil. This has been done in the preparatory-scale experiments. This experience indicates that the amount of this type of impurity rarely exceeds 5% of the crude sample.

Both the degree of cyanoethylation and the induction period decreased with the increasing reaction-temperature. The amount of insoluble polymer which was formed remained essentially constant and is believed to be a function of the amount of catalyst (initiator) used.

Variations in the amount of catalyst also affect the course of the reaction (Table II). At low catalyst concentration there was essentially no reaction during the 1-hr period. Increasing amounts of catalyst increased both the degree of cyanoethylation and the amount of insoluble polymer which was formed but had little effect upon the induction period. At high catalyst levels, however, the induction period increased considerably, probably because of the inhibiting effect of the water added with the catalyst.

In order to test this inhibiting effect upon the polymerization reaction, a series of experiments was carried out in which the base was added to redistilled acrylonitrile (no hydroxy compound present) in the presence and absence of varying amounts of water and concentrated aqueous ammonia as inhibitors. Addition of 2% by volume of water increased the induction period of redistilled acrylonitrile from 28 sec to 8 min while 2% concentrated aqueous ammonia prolonged the period to about 6 min. The inhibitors also had the effect of modifying the extent of heat evolution and decreasing the amount of insoluble

polymer which was formed, i.e., decreasing the average polymer chain-length.

The inhibiting effect can also be seen from Fig. 1, which compares the progress of the cyanoethylation of methyl 12-hydroxystearate in the presence and absence of 2% water and 2% concentrated aqueous ammonia. At the end of the polymerization induction period, the yield of product was the same in all experiments, about 93%. The inhibitors had no effect upon final product yield (97%). Apparently they slow both the cyanoethylation and the polymerization reaction.

Yet an inert solvent which was used as diluent appeared to affect the cyanoethylation reaction much more severely than the polymerization. The use of co-solvents is sometimes desirable because of the poor solubility of some polyhydroxy compounds in acrylonitrile. It is quite apparent from the data of Table III however that it is important to keep the amount of co-solvent to a minimum in order to obtain satisfactory yields in cyanoethylation reactions. Although the data illustrate the use of pyridine as diluent, 1,4-dioxane at the 4/1 level gave identical results. Dimethyl sulfoxide, as a co-solvent, caused an almost instantaneous, violent reaction to take place when the catalyst was added.

With slight modifications, as indicated in the Experimental Section, the cyanoethylations of methyl *erythro*- and *threo*-9,10-dihydroxystearate, methyl 9,10,12-trihydroxystearate, 1,9,10-octadecantriol, monostearin, and hydroxylated soybean oil were carried out. Methyl 9(10)-hydroxy-10(9)-cyanoethoxystearate was prepared by the cyanoethylation of the dihydroxy ester with pyridine as the solvent and potassium hydroxide as the catalyst.

Cyanoethylated soybean oil and 1,9,10-tricyanoethoxyoctadecane could not be analyzed by GLC since they decomposed on the column. The other cyanoethylated compounds were analyzed without difficulty.

The IR spectra of the reaction products were consistent with the expected structures. All fully cyanoethylated products had bands at 2250 cm^{-1} ($\text{C}\equiv\text{N}$ stretching) and at 1100–1110 cm^{-1} ($\text{C}-\text{O}-\text{C}$ stretching). The intensity of these peaks varied qualitatively as the number of nitrile and ether links per molecule. The increasing absorptions, together with the decreasing intensity and disappearance of the hydroxyl bands in the 3500 cm^{-1} region, gave a crude method of following the reaction in those experiments where GLC could not be used.

Infrared spectra of the ether-soluble polymers show a strong 2250 cm^{-1} peak with a minor peak at 2225 cm^{-1} . The strong 2250 cm^{-1} peak in the polycyanoethylated compounds mask the polymer absorption there, but the small peak at 2225 cm^{-1} indicates the presence of polymer.

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