

Free Radical Additions to Esters of Unsaturated Fatty Acids. Preparation of Dicarboxylic Acids and Other Polyfunctional Products¹

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Abstract

Peroxide initiated free radical addition of acetic acid, acetic anhydride and ethyl cyanoacetate to methyl undecylenate and methyl oleate gives interesting and important derivatives in fair to excellent yields. Of these, the most important are the dicarboxylic acids, brassylic and carboxymethylstearic acids.

Acetic acid and acetic anhydride both give the same ultimate products but because of the greater amount of by-product in the methyl undecylenate reaction with acetic acid and the need for pressure in the reaction of acetic acid with methyl oleate, acetic anhydride is the preferred addendum for preparing the dicarboxylic acids. There is very little by-product formed in addition of acetic anhydride to methyl undecylenate and methyl oleate.

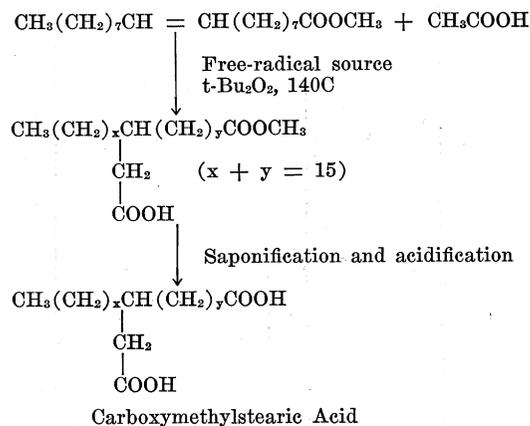
Ethyl cyanoacetate adds readily to both methyl undecylenate and methyl oleate; however, ethyl cyanoacetate is difficult to remove completely from the reaction products. Hydrolysis to destroy it also causes some hydrolysis of the addition products. On the other hand, it is very difficult to hydrolyze completely and subsequently decarboxylate the ethyl cyanoacetate addition products of methyl undecylenate and methyl oleate to obtain dicarboxylic acids.

THE PREPARATION of dicarboxylic acids from unsaturated fatty acids is extremely important both practically and fundamentally. Although various preparative methods are available, most methods have serious drawbacks. The direct introduction of the carboxyl group is an intriguing research area and some work along this line has been conducted in our laboratory (1, 2) and elsewhere. For example, Nikishin et al. (3) found that esters of α -alkyldicarboxylic acids could be obtained by free radical addition of certain monobasic acids or their esters to terminally unsaturated acids or their esters. Allen et al. (4) have reported the addition of acetic acid and its derivatives to 1-olefins. A vast literature is available on additions of numerous active hydrogen compounds (aldehydes, ketones; alcohols, etc.) to terminal olefins, but little work has been published on nonterminal olefins (5).

The free radical initiated addition of acetic acid, acetic anhydride and other active hydrogen compounds to the relatively unreactive unsaturated center of methyl oleate was therefore investigated. Experiments using methyl undecylenate were carried out concurrently to determine if the reactions were at all

feasible and also because of the important end-products which would be obtained.

Ethyl cyanoacetate was chosen as the third addendum to extend the scope of free radical reaction with fatty acid esters and because the ethyl cyanoacetate addition product theoretically could be hydrolyzed and decarboxylated to give the same dicarboxylic acids as would be obtained by addition of acetic acid or anhydride (see later discussion). The general reaction investigated is shown schematically below, using acetic acid as a typical addendum and methyl oleate as the substrate.



From methyl undecylenate, brassylic acid would be the anticipated reaction product. Addition of acetic anhydride should produce intermediate anhydride adducts readily hydrolyzable to dicarboxylic acids.

Experimental

Starting Materials

Methyl oleate (94.5%) essentially free of polyunsaturates was obtained from Monomer-Polymer Laboratories, Bordon Co., Chemical Division. Methyl undecylenate (> 99%) was prepared from undecylenic acid, obtained from Baker Castor Oil Co., by esterification and distillation. The addenda were best obtainable grades; they were dried and distilled before use. Di-*t*-butyl peroxide was obtained from Monomer-Polymer Laboratories and was used as received. Silica Gel dessicant, activated 100-200 mesh, used in column chromatography was obtained from Davison Chemical Division, W. R. Grace Co.

Experiments were carried out in thoroughly dried glass apparatus. Nitrogen was bubbled through the reaction mixture to provide agitation and to insure an inert atmosphere. In pressure reactions the apparatus was purged with nitrogen before sealing.

Gas-Liquid Chromatography (GLC)

A dual column programmed temp gas chromato-

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TABLE I
Free Radical Additions to Methyl Oleate

Exp. no.	Mole ratio per mole methyl oleate		Temp C	Time, Hr	% Reaction	
	Addendum	Di-t-butyl peroxide			Total	Main product
3	Acetic acid, 400	0.9	140	90 ^a	79	70
5	Acetic anhydride, 50	0.3	140	72	78	78
8	Ethyl cyanoacetate, 400	0.14	130-135	48	65	> 64
9	Ethyl cyanoacetate, 50	0.14	135-140	20	88	83
10	Ethyl cyanoacetate, 50	0.15	135-140	16	48	~ 48
10	Ethyl cyanoacetate, 50	0.16	135-140	24	97	92

^a Approx 2 atm.

graph with a four-filament thermal conductivity detector cell was used. The columns, 2 ft long by 0.25 in. O.D., and 0.18 in. I.D., were of stainless steel and packed with 60-80 mesh Diatoport P (diatomaceous earth) coated with 10% silicone gum rubber (methyl) G.E. SE-30. The columns were operated isothermally at 200C for the methyl esters of the acetic acid and hydrolyzed acetic anhydride addition products of methyl undecylenate, and at 220C for the ethyl cyanoacetate addition product of methyl undecylenate. They were operated isothermally at 250C for all derivatives of methyl oleate. In each case, the columns were programmed up to 300C after the main products came off. A flow rate of 50 ml of helium per minute was maintained at the column exit. Sample sizes were from 0.5 to 2.0 μ l. An automatic attenuator/integrator was used in conjunction with the recorder. Some uncertainty exists in the composition of some of the reaction products because model compounds, especially dimers, were not available to calibrate peak areas with composition.

Experiment 1: Addition of Acetic Acid to Methyl Undecylenate (100:1 mole ratio). A mixture of 3.97 g (0.02 mole) of methyl undecylenate (99+%), 120.1 g (2.00 mole) of acetic acid, and 0.219 g (0.0015 mole) of di-t-butyl peroxide was refluxed under a nitrogen atm for 23 hr. The course of the reaction was followed by disappearance of methyl undecylenate (gas-liquid chromatography). After 16-20 hr, 68-70% of the methyl undecylenate had disappeared. The reaction mixture was poured into water and extracted with ether. The dried product was converted to methyl esters by acid-catalyzed methanolysis. Analysis by gas-liquid chromatography (GLC) showed that the product consisted of 29% unreacted methyl undecylenate, 40% dimethyl brassylate, and 31% other products, two-thirds of which had a long retention time and was a dimer. Column chromatography of 2.5 g of this esterified reaction mixture on 120 g of Florisil, eluting with 100% Skellysolve B followed by mixtures containing 25, 50 and 100% ether, yielded unreacted methyl undecylenate, dimethyl brassylate and telomer. Mol wts corresponding to dimer, trimer and higher telomers were found. Mol wt calculated: 470.7, 669.0, 867.3 and 1065.0. Mol wt found: 485, 669, 916.

Experiment 2. See Table II.

Experiment 3: Addition of Acetic Acid to Methyl Oleate (400:1 mole ratio: approx 2 atm). A mixture of 1.48 g (0.005 mole) of methyl oleate (94.5%), 120.1 g (2.00 mole) of acetic acid and 0.1097 g (0.00075 mole) of di-t-butyl peroxide was heated in a glass pressure bottle (No-Sol-Vit) to 140C for 18 hr. A small sample was then removed for GLC analysis and an additional 0.1097 g of di-t-butyl peroxide was added to the reaction vessel using a small amt of acetic acid to transfer the catalyst. The reaction was continued for 108 hr longer, removing samples and add-

ing 0.1097 g portions of catalyst at 18 hr intervals. A total of 0.6582 g (0.0045 mole) of di-t-butyl peroxide was used.

GLC analyses showed that the reaction was approx 26% complete after 18 hr, and 79% complete after 90 hr, based on unreacted methyl oleate. No further addition took place after 90 hr. The product was converted to methyl esters by refluxing with 20 ml of anhydrous methanol and 2 ml of dimethyl sulfate for 36 hr. The reaction mixture was worked up by slowly pouring it into ice-cold aqueous sodium carbonate solution, extracting with ether and washing with water until neutral. GLC analyses showed 70% main product and 3% dimer.

Experiment 4: Addition of Acetic Anhydride to Methyl Undecylenate (400:1 mole ratio). After refluxing a mixture of 1.98 g (0.01 mole) of methyl undecylenate, 408.4 g (4.00 mole) of acetic anhydride and 0.206 g (0.0014 mole) of di-t-butyl peroxide for 48 hr, most of the acetic anhydride was removed by distillation. To the remaining product was added 50 ml of 2N NaOH and the mixture refluxed for 4 hr, after which it was poured into an excess of 2N HCl, extracted with ether and water-washed. Evaporation of ether yielded 2.3 g of a white solid, mp 103-105C, iodine number 3.0 and acid number, 456, indicating approximately 98% conversion to brassylic acid. GLC analyses of the methyl esters of this product showed that it contained 95% brassylic acid and 2% dimer.

Two crystallizations of the methyl esters from methanol (5 ml/g) at -26C yielded a white crystalline material, mp 33C (lit. 36C) (7). Analysis calculated for $C_{15}H_{28}O_4$; C, 66.1; H, 10.3. Found: C, 66.5; H, 10.5. The X-ray powder diffraction pattern of this material was identical with that of an authentic sample of dimethyl brassylate. GLC analyses of this material showed it to be >99% pure.

Experiment 5. Addition of Acetic Anhydride to Methyl Oleate (50:1 mole ratio). To a mixture of 59.3 g (0.2 mole) of methyl oleate (94.5%) and 1021 g (10.0 moles) of acetic anhydride was added 17.56 g (0.12 mole) of di-t-butyl peroxide in four equal portions of 4.39 g (0.03 mole). After each addition the mixture was refluxed for 18 hr (total 72 hr). Samples were removed at 18 hr intervals and the amt of unreacted methyl oleate remaining in the reaction mixture was determined by GLC. The extent of reaction was 18 hr, 30.6%; 36 hr, 60.0%; 54 hr, 71.7%; 72 hr, 77.7%.

The saponified, acidified product had an acid number of 300 (calculated 342). Esterification of 59 g by the procedure of Experiment 3 yielded 58.6 g of crude methyl esters with an acid number of 6.0. GLC analysis showed an over-all reaction of 89% of which the main product was 74%. Two closely related peaks may be isomers in which case the main product would amount to 82%.

TABLE II
Free Radical Additions to Methyl Undecylenate

Exp. no.	Mole ratio per mole methyl undecylenate		Temp C	Time, Hr	% Reaction	
	Addendum	Di-t-butyl peroxide			Total	Main product
1.....	Acetic acid, 100	0.75	118	16	68	...
1.....	Acetic acid, 100	0.75	118	23	71	40
1.....	Acetic acid, 100	0.15 ^a	118	16	70	44
1.....	Acetic acid, 100	0.15 ^a	118	23	72	45
2.....	Acetic acid, 400	0.15	118	16	92	66
4.....	Acetic anhydride, 400	0.15	140	24	79	...
4.....	Acetic anhydride, 400	0.15	140	48	98	> 95
6.....	Ethyl cyanoacetate, 50	0.14	135-140	24	95	88
7.....	Ethyl cyanoacetate, 400	0.14	130-135	24	98	> 82
similar to 9.....	Diethyl malonate 50	0.14	135-140	20	> 97	~ 60

^a Similar to Exp. 1, but twice the amt of catalyst.

Distillation of 50.8 g of methyl esters using a micro Vigreux column yielded six fractions totalling 29.3 g, distilling from 153 to 242C at 0.3 to 1.0 mm. Distillation was discontinued because of decomposition; GLC analysis of the residue showed it to be polymeric. A small middle fraction, 9.3 g of colorless liquid distilling from 190 to 195C at 0.3 mm was 86% methyl carbomethoxymethylstearate, based on GLC analysis, and 11.7% of two closely related peaks which are presumable isomers. Analysis calculated for methyl carbomethoxymethylstearate, C₂₂H₄₂O₄: C, 71.3; H, 11.4; saponification number, 303; molar refractivity, 107.4. Found: C, 71.2; H, 11.3; saponification number, 302; molar refractivity, 107.5.

Experiment 6: Addition of Ethyl Cyanoacetate to Methyl Undecylenate (50:1 mole ratio). Ten equal portions of a mixture of 3.97 g (0.02 mole) of methyl undecylenate, 4.52 g (0.04 mole) of ethyl cyanoacetate, and 0.412 g (0.0028 mole) of di-t-butyl peroxide were added at 2 hr intervals to 108.6 g (0.96 mole) of ethyl cyanoacetate at 135-140C. After 20 hr, the ethyl cyanoacetate was distilled off under reduced pressure. The remaining product, 5.8 g, contaminated with some ethyl cyanoacetate, showed 95% addition by GLC analysis. Attempts to crystallize this material were unsuccessful. Column chromatography of 5.8 g of the reaction mixture on 174 g of silica gel using a mixture of 25% Skellysolve B and 75% benzene and then 100% benzene yielded 4.1 g of material, when combined, which consisted of approximately 88% main product, 5.6% ethyl cyanoacetate, and 6.4% by-product. (Fractions were combined on the basis of IR spectra and GLC).

Two crystallizations of 4.1 g of the chromatographed material from methanol, (3 ml/g) at -26C yielded 3.0 g of a white solid, mp 26.5-27C, which was approximately 99% pure by GLC. Analysis calculated for C₁₇H₂₉NO₄: C, 65.6; H, 9.39; N, 4.50. Found: C, 66.0; H, 9.60; N, 4.35. The nuclear magnetic resonance (NMR) spectrum had all the characteristic proton bands expected for methyl (cyanocarboethoxymethyl) bethoxymethyl) undecylate.

Hydrolysis

To 1.9 g of the above crystallized product was added 85 ml of 6N HCl and the mixture was refluxed for 106 hr. The product was extracted with ether and washed free of HCl. The dried product had 1.47% nitrogen showing incomplete hydrolysis. To 0.9 g of the incompletely hydrolyzed product was added 100 ml of 20% aqueous NaOH and the mixture was refluxed for 24 hr using a small amt of methanol to control foaming. The neutralized product was extracted with ether and washed free of hydrochloric

acid. Esterification of the dried product was carried out by conventional acid-catalyzed methanolysis. Analysis by GLC showed 95% diester. Crystallization of 0.8 g from methanol (5 ml/g) at -26C yielded 0.5 g of a white crystalline material, mp 32.0-32.5C. The x-ray powder diffraction pattern of this material was identical with an authentic sample of dimethyl brassylate.

Experiment 7. See Table II.

Experiment 8. See Table I.

Experiment 9: Addition of Ethyl Cyanoacetate to Methyl Oleate (50:1 mole ratio). Ten equal portions of a mixture of 2.97 g (0.01 mole) of methyl oleate, 2.26 g (0.02 mole) of ethyl cyanoacetate, and 0.206 g (0.0014 mole) of di-t-butyl peroxide were added at 2 hr intervals to 54.3 g (0.48 mole) of ethyl cyanoacetate at 135-140C.

Experiment 10: Addition of Ethyl Cyanoacetate to Methyl Oleate (50:1 mole ratio). To 848 g (7.5 moles) of ethyl cyanoacetate at 135-140C, a mixture of 44.5 g (0.15 mole) of methyl oleate and 3.29 g (0.0225 mole) of di-t-butyl peroxide was added dropwise over a 16 hr period. Analysis of the mixture by GLC showed 48-50% reaction. By adding 0.219 g (0.0015 mole) of di-t-butyl peroxide dissolved in 3 ml of ethyl cyanoacetate over an additional 8 hr period the extent of the reaction was increased to 97%.

After removal of most of the ethyl cyanoacetate by vacuum distillation, 64.2 g remained, consisting of 6% ethyl cyanoacetate, 4% methyl oleate, 4% side product, and 86% main product. Distillation of this product through a micro Vigreux column yielded 31 g of pale yellow liquid in four main fractions, distilling at 211 to 212C at 0.3 mm. GLC analyses of these fractions showed them to be from 84 to 87% methyl (cyanocarboethoxymethyl)-stearate.

Redistillation of 30.6 g of the combined main fractions through a molecular still at 100 to 160C at 1 to 5 μ in eight passes, yielded five main fractions. On the basis of GLC analysis the fourth and fifth fractions, amounting to 12.4 g, were combined for further separation by column chromatography. The remaining three fractions, 5.9 g, showed from 82-89% main product (a value as high as 97% is obtained if closely related GLC peaks are considered to be isomers). The ultimate analysis of these combined fractions gave unusually good results. Analysis calculated for C₂₄H₄₃NO₄: C, 70.4; H, 10.58; N, 3.42. Found: C, 70.9; H, 10.85; N, 3.44. The NMR spectrum had all the characteristic proton bands expected for methyl (cyanocarboethoxymethyl)stearate.

Column chromatography of combined fractions 4 and 5 of the distilled portion (86-89% main product)

TABLE III

Effect of Amount of Catalyst and Time on By-Product Formation; Addition of Acetic Acid to Methyl Undecylenate (100:1)^a

	0.075 Mole Di-t-butyl peroxide/mole Methyl Undecylenate		0.15 Mole Di-t-butyl peroxide/mole Methyl Undecylenate	
	16 hr	23 hr	16 hr	23 hr
% Unreacted.....	32	29	30	28
% Dimethyl brassylate.....	40	44	45
% Dimer.....	21	17	19
% Other products (~ 5)	10	9	8

^a At 400:1, a 66% conversion to main product and 21% conversion to dimer was obtained (Exp. 2, Table II).

was carried out using 50 g of silica gel per gram of product. Elution was accomplished by using 100% Skellysolve B followed by 95% Skellysolve B: 5% ether. Fractions having from 90 to 92% of main product were rechromatographed obtaining fractions having 95 to 96% main product by GLC. Analysis calculated for $C_{24}H_{43}NO_4$: C, 70.4; H, 10.58; N, 3.42. Found: C, 70.2; H, 10.54; N, 3.82. The NMR spectrum had all the characteristic proton bands expected for methyl (cyanocarbethoxymethyl)stearate. GLC showed the presence of a trace of ethyl cyanoacetate which would account for the slightly high nitrogen.

Experiment 11: Hydrolysis of Methyl Oleate-Ethyl Cyanoacetate Addition Products. Decarboxylation and Column Chromatography. A reaction mixture containing 76.2% methyl (cyanocarbethoxymethyl)stearate, 7.0% ethyl cyanoacetate, 14.7% starting material and 2.1% by-products, as determined by GLC, was divided into two portions. One portion (2.9 g) was refluxed for 72 hr with 30 ml of 20% aqueous sodium hydroxide. A small amt of methanol was used to control foaming. The neutralized product was extracted with ether and washed free of hydrochloric acid. After drying over sodium sulfate, the ether was removed yielding 2.7 g of a brown liquid; acid number 312.

The other portion (3.0 g) was refluxed with constant boiling hydrochloric acid for 72 hr. This portion after extracting with ether and washing, yielded 2.5 g of brown liquid; acid number 226. Because the low acid number indicated incomplete hydrolysis it was subjected to alkaline hydrolysis as on the previous portion.

Esterification of the combined hydrolyzed portions by the dimethyl sulfate method already described, yielded a product which, on GLC analysis, revealed three main peaks which were identified as methyl oleate, methyl-(carbomethoxymethyl)stearate, and presumably a triester.

Three grams of the esterified product were chromatographed, using 90 g of silica gel and eluting with benzene. A fraction was obtained which had the same retention time on GLC as the methyl esters of the product obtained from the reaction of methyl oleate and acetic acid or the hydrolyzed and reesterized product from the acetic anhydride reaction. It contained >97% methyl (carbomethoxymethyl)stearate; its identity was confirmed by NMR.

The remaining methyl ester portion from above was hydrolyzed. The acid number was found to be 323. Heating the product 11 hr on the steam bath to decarboxylate, reduced the acid number to 311. Further heating at 180C/10 mm for 2 hr, reduced the acid number to 268. An analysis for nitrogen gave 0.41% showing that hydrolysis had been incomplete, therefore decarboxylation was discontinued.

Results and Discussion

Acetic acid adds to methyl oleate (400:1 mole ratio) with 0.9 mole of di-t-butyl peroxide as initiator at 140C and approximately 2 atm to give 70% conversion to the 1:1 adduct, methyl (carboxymethyl)stearate (Exp. 3, Table I). With 50 moles of acetic anhydride (Exp. 5) to one of methyl oleate and 0.3 mole of di-t-butyl peroxide at 140C and atmospheric pressure, from 75 to 80% of the desired 1:1 addition occurs. Ethyl cyanoacetate (Exps. 9, 10) gives from 80–90% of 1:1 addition product with methyl oleate at a 50:1 mole ratio with from 0.14 to 0.16 mole of di-t-butyl peroxide at 140C.

Methyl undecylenate is a more reactive substrate (Table II) than methyl oleate. Acetic acid adds readily to methyl undecylenate (400:1) at atmospheric pressure and 118C with 0.15 mole of di-t-butyl peroxide as initiator (Exp. 2) to give about 66% 1:1 adduct, which is hydrolyzed readily to brassylic acid. Acetic anhydride adds essentially quantitatively to methyl undecylenate (400:1) at 135 to 140C (Exp. 4) as does ethyl cyanoacetate (Exp. 6, 7) to give high yields of 1:1 adduct.

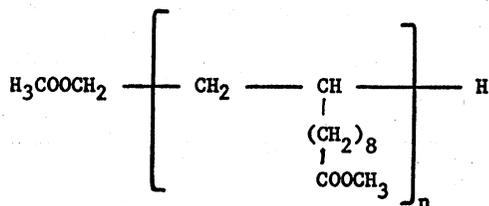
GLC analysis of the methyl esters of the reaction product obtained by free radical initiated addition of acetic acid to methyl undecylenate (Exp. 2, Table II) shows the formation of a large amt of product having a considerably greater retention time than the main product, dimethyl brassylate. This is a dimer. In the case of acetic acid addition to methyl oleate (Exp. 3, Table I) the amt of a similar material was found to be relatively small, only about 3%. Only a small amt of this material (<3%) was found in the addition product of acetic anhydride to methyl undecylenate and none was found in the addition product of acetic anhydride to methyl oleate (Exp. 5, Table I).

One explanation for the difference in behavior of acetic acid and acetic anhydride might be that the chain transfer step of the reaction with acetic acid may be sufficiently endothermic (slow) to permit chain termination by dimerization. On the other hand, in the acetic anhydride additions, 1:1 adduct formation may be more exothermic and fast compared to the chain termination, telomerization or dimerization processes (5,6). Also, the polymerization of terminal olefinic compounds is more rapid than that of non-terminal ones.

Neither time nor the amt of catalyst appear to affect appreciably the amount of byproduct formation in the addition of acetic acid to methyl undecylenate (Table III).

Acetic anhydride was preferred to acetic acid as an addendum. In addition to methyl undecylenate, the acetic anhydride addition product was relatively free of dimer. With methyl oleate, pressure was required to add acetic acid whereas reactions with acetic anhydride could be carried out at atmospheric pressure.

Programmed GLC analysis of dimethyl brassylate obtained by methanolysis of the product from the reaction of acetic acid with methyl undecylenate shows a considerable amount, 20% or more, of material of much greater retention time than dimethyl brassylate. On the other hand, only about 2% of this material is present in the dimethyl brassylate obtained from the hydrolyzed and esterified product from the reaction of acetic anhydride with methyl undecylenate. Column chromatography of the esterified reaction product (Exp. 1) showed not only dimer, but higher telomers. The mol wts found are consistent with a telomer



of the formula above (6). Dimethyl brassylate, containing 2% dimer, has the same X-ray diffraction pattern as that of authentic dimethyl brassylate. The melting point is slightly lower than that reported in the literature (7).

In reactions of acetic acid and acetic anhydride with methyl undecylenate and methyl oleate small amounts of side products other than dimer and telomers are formed. In these cases, however, we were able to remove these side products on purification.

Addition products obtained by reaction of ethyl cyanoacetate with methyl undecylenate have side products with similar retention times to the main peak in GLC analysis. Traces of these peaks still remain after column chromatography and crystallization. No unexpected proton bands are observed in the NMR spectra of this material and the C, H, and N analyses are not noticeably affected.

Analyses by GLC of the reaction products of methyl oleate with ethyl cyanoacetate gave results which appear anomalous. In Experiment 10, Table I, for example, analysis of the reaction product after distilling off most of the ethyl cyanoacetate, showed an overall reaction of 97% of which 86% was main product. Distillation of the product improved the appearance considerably; a pale yellow liquid was obtained from a dark brown mixture. On the other hand distillation did not appreciably change the composition. Ultimate analysis and NMR, however, agreed rather well for methyl (cyanocarbethoxymethyl)stearate. The conclusion is that the byproducts are closely related to the main product and some of them, at least, are probably isomers.

Although TLC appeared to separate ethyl cyanoacetate from the products of the reaction and suggested column chromatography should be a means of purifying the methyl (cyanocarbethoxymethyl)stearate, it was found that ethyl cyanoacetate remained in the material even after two separations by column chromatography of redistilled material. Attempts to hydrolyze the small amount of ethyl cyanoacetate remaining in the distilled reaction mixture with dilute hydrochloric acid caused some hydrolysis of the methyl (cyanocarbethoxymethyl)stearate.

From this one might expect that methyl (cyanocarbethoxymethyl)stearate could be hydrolyzed to a tricarboxylic acid which in turn could be decarboxylated to a dicarboxylic acid, carboxymethylstearic acid, the same dicarboxylic acid obtained after hydrolysis of the free radical addition product of acetic acid to methyl oleate or the product obtained by hydrolysis of the anhydride obtained by the addition of acetic anhydride to methyl oleate. Hydrolysis of methyl (cyanocarbethoxymethyl)stearate with dilute hydrochloric acid (Exp. 8) was only partially complete, however. The use of more concentrated acid, hydrochloric or sulfuric, did not prove successful.

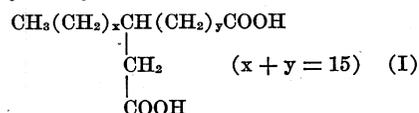
Although alkaline hydrolysis (Exp. 11) of methyl (cyanocarbethoxymethyl)stearate was also incomplete

we were able to isolate a small fraction of methyl (carbomethoxymethyl)stearate by column chromatography of the re-esterified hydrolyzed product.

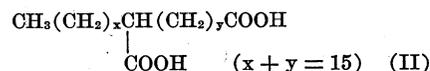
Hydrolysis of methyl (cyanocarbethoxymethyl)undecylenate, the product obtained by the reaction of ethyl cyanoacetate with methyl undecylenate, was exceedingly slow with dilute hydrochloric acid. Because of this, alkaline hydrolysis was employed as above (Exp. 6, Table II). The esterified product was found to be dimethyl brassylate, the compound expected.

Experiments in which diethyl malonate was the addendum were carried out with methyl undecylenate and methyl oleate in a manner similar to Experiment 9. Analysis by GLC of the reaction product from methyl undecylenate (Table II) showed over 97% reaction but there were at least eight peaks with the major one amounting to approx 60%. Addition to methyl oleate was less than 5% and showed five peaks. Due to the complex nature of the reaction mixtures, the small amount of reaction obtained with methyl oleate and the fact that the ultimate products would be the same as those obtained by the addition of acetic anhydride to methyl undecylenate and methyl oleate, no further work was done using this addendum.

Carboxymethylstearic acid:



obtained by the methods described in this paper differs from carboxystearic acid:



the product obtained by the carboxylation of oleic acid with carbon monoxide (4,5) by a methylene group between the branched carboxyl group and the main chain. The presence of this methylene group changes the properties, as might be expected. For example, while the rate of esterification of the carboxyl group on the side chain of carboxymethylstearic acid (I) is slow compared to that of its terminal carboxyl group, it is four to five times faster than esterification of the nonterminal carboxyl group in carboxystearic acid (II), as measured by reduction in acid number. Moreover, the saponification number of the methyl ester of carboxymethylstearic acid (I) could be determined by a conventional method, whereas the results were low for the methyl ester of carboxystearic acid (II), even with more concentrated solutions of base, longer periods of time and elevated temperature.

Extension of the free radical reactions of acetic acid, acetic anhydride, and ethyl cyanoacetate to unsaturated fatty acid esters, should greatly extend the scope of this reaction to produce useful products.

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