Nonvolatile α-Branched Chain Fatty Acid Derivatives: III. Addition of Acid Chlorides, Anhydrides and Amides to Terminal Olefins[1]

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Abstract

A *t*-butyl peroxide initiated free radical reaction was employed for the preparation of α-branched fatty acid chlorides, which were then converted in situ to methyl esters. Similarly prepared were an α-branched fatty acid amide and an α-branched acid anhydride. The latter was converted to the methyl ester. The use of the acid chloride and acid anhydride permitted reduction in the molar ratio of reactants to half or less than that used in the addition of esters to terminal olefins without affecting the yield. The resulting increase of α-branched product concentration in the reaction mixture also made isolation of the product easier. The direct addition of a variety of stearic acid derivatives to 1-decene under the same conditions (20:4:1.2 molar ratio of reactants at 160 C) gave the following olefin based yield order: stearoyl chloride > stearic anhydride > stearamide and methyl stearate > stearic acid.

Introduction

CONSIDERABLE ATTENTION has been devoted in recent years to the preparation of α-branched fatty acid derivatives for a variety of purposes. The stability, extended liquid state range, and other desirable qualities of these α-branched fatty acid derivatives made their synthesis of great practical interest. The *t*-butyl peroxide initiated free radical addition of fatty acids to terminal olefins described by Petrov et al. (1) was the procedure followed in most of the subsequent preparations of 2-alkyl fatty acid derivatives.

Ault et al. (2,3) prepared several 18 to 21 carbon 2-alkyl fatty acids in this manner, converted them to sulfonated derivatives and evaluated their surface active properties. Maerker et al. (4) synthesized a series of 28 to 38 carbon esters of 2-alkyl fatty acids, studied various purification methods, established the structure of methyl 2-decyloctadecanoate, and investigated the nature of byproducts formed. Ault et al. (5,6) prepared a variety of α-branched fatty esters directly and some others by alcoholysis of methyl 2-decyl stearate, characterized the products, and made bench scale evaluations of their lubricant properties. Another report (7) dealt with the preparation and lubricant qualities of α-branched esters that have aryl and alkyl substituents on the α-branch and one ester in which the α-branch was on the alcohol portion of the ester. In all these studies a 40:4:1 molar ratio of fatty derivative to terminal olefin to *t*-butyl peroxide and a reaction temperature of 140 to 160 C were used. The low yields and failures met in the attempted preparation of certain α-branched fatty acid esters of potential value as lubricant additives prompted the search for other routes to their synthesis. The well-known facility with which acid chlorides and, to a lesser extent, acid anhydrides can be converted to hard-to-prepare esters or other desirable derivatives, suggested their use for this purpose. This paper describes the results obtained in the *t*-butyl peroxide initiated free-radical addition of stearoyl chloride to 1-decene under varying conditions and the conversion of the resulting products to the methyl esters. Comparison of results obtained from the direct addition to 1-decene of stearoyl chloride, stearic anhydride, stearic acid, stearamide and methyl stearate under the same conditions is presented, and an accounting for the olefin used in one of the runs is also included.

Materials and Data

Materials

Stearoyl Chloride. The acid chlorides used in the 40:4:1 and 20:4:1 runs were cuts obtained from distillation of commercial stearoyl chloride. The boiling points were 164–172 C @ 1.5 mm and 164–167 C @ 1.0 mm, respectively. The stearoyl chloride used in later runs was prepared by the reaction of hystrene stearic acid (97%) with PCl_5 or PCl_3 (8,9) and was purified by molecular distillation between 130 and 140 C at less than 25μ Hg pressure.

1-Decene. A complimentary sample from Gulf Oil Corp. was redistilled, the cut collected at 170 C, 98% pure by GLC, was used in all runs.

Di-t-butyl Peroxide. The peroxide purchased from Monomer-Polymer Corporation, Philadelphia, was used as received.

Methanol, *t*-butyl alcohol, phenol and pyridine were all reagent grade or better and were used as received.

Stearic acid of 99.1% purity by GLC (mp 69.2–69.4 C), stearamide (mp 107.6–108 C), stearic anhydride (mp 69.5–69.9 C) and methyl stearate of 97% purity by GLC were used in the direct addition runs.

Experimental Procedures

Analytical Procedures

Analytical TLC plates were coated with silica gel containing 10% binder (Adsorbosil 1) and were charred after spraying with a solution of potassium dichromate in aqueous sulfuric acid. Preparative TLC plates of 2.0 mm thickness (purchased from Brinkmann Instruments, Inc.) or coated with 0.75 mm Adsorbosil 1 were sprayed, after development, with an alcoholic 0.2% solution of 2′,7′-dichlorofluorescein, and the bands were located under UV light. Infrared (IR) spectra were determined with a Perkin-Elmer Model 237 spectrophotometer. GLC determinations were carried out as reported prevoiusly (4).

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[1] Presented at the AOCS Meeting, Chicago, October 1967.
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Preparation of Methyl 2-Decylstearate Via Stearoyl Chloride Addition to 1-Decene

The following typical procedure, except for variations in molar ratio of reactants, was used in the peroxide initiated free radical addition of stearoylchloride to 1-decene. The molar ratio of stearoyl chloride to 1-decene to di-*t*-butyl peroxide employed in this run was 20:4:1.2. To 37.9 g (0.125 mole) of stearoyl chloride stirred and maintained at 160 C under anhydrous conditions a mixture of 4.7 g (0.0335 mole) of 1-decene and 1.45 g (0.0099 mole) of di-*t*-butyl peroxide diluted with 12.6 g (0.0416 mole) stearoyl chloride was added dropwise over a period of 80 min. The resulting reaction mass was stirred for 4 hr 20 min longer at 160 C and then allowed to cool to room temperature. To the stirred, amber-colored, semi-solid reaction mixture a mixture of 5.87 g (0.183 mole) methanol and 13.2 g (0.167 mole) pyridine was added dropwise over a 30 min period. Slow addition was required to avoid elevation of reaction mass temperature more than a few degrees above the boiling point of methanol by the exothermic reaction. The resulting mixture was stirred for 3.5 hr longer at reflux temperature and was then allowed to cool. The mixture was dissolved in 200 ml Skellysolve B, 100 ml water was added, the pH of the solution was adjusted to 3.0 with dilute HCl, and the pyridine hydrochloride containing aqueous layer was drawn off and discarded. The organic layer was washed with two 100 ml portions of water, was dried over anhydrous $CaSO_4$, and was then filtered. The filtrate was concentrated in a rotary vacuum evaporator until the pressure dropped to 0.7 mm at 55 C. The resulting amber-colored residue weighed 52.9 g (theory = 55.3 g). The residue contained only a minor amount of free carboxylic acid as judged by IR. Analytical TLC indicated, upon elution with a 30:70 benzene, Skellysolve B mixture, that methyl stearate and methyl 2-decylstearate were the principal components. Minor amounts of by-products were also present.

Fractionation was carried out on 160 mg of the crude product by preparatory TLC (4), followed by re-esterification of a small amount of polar material (see below), and GLC analysis of the α-branched material containing fractions. This gave a methyl 2-decylstearate content of 18.7% (66.7% yield based on 1-decene) and a *t*-butyl 2-decylstearate content of 0.5% (1.6% yield based on olefin).

Additions of stearoyl chloride to 1-decene, carried out at four different ratios of acyl halide to olefin to initiator are compared in Table I. For the 40:4:1 experiment, the yield determined by preparative TLC was verified by vacuum distillation of the reaction mixture.

TABLE I

Addition of Stearoyl Chloride to 1-Decene
Effect of Change in Reagent Ratio on Olefin Conversion

Product Reagent Ratio[a]	Yield, Per cent[b]			
	40:4:1	20:4:1.2	10:4:1	10:4:0.5
Methyl 2-decylstearate	64.5	66.7	25.5	18.9
t-Butyl 2-decylstearate	1.2	1.6	4.4	1.1
Hydrocarbon calculated as olefin polymer[c]	19.3	26.3	23.8	15.3
Telomer[d]	1.4	1.9	1.7	1.3
Total olefin products	86.4	96.5	54.0	55.1

[a] Molar ratio of stearoyl chloride:1-decene:*t*-butyl peroxide.
[b] Based on olefin.
[c] Estimated except in 20:4:1.2 experiment.
[d] Estimated to be formed from two molecules of olefin and one molecule of stearoyl chloride.

Addition of Other Fatty Derivatives to 1-Decene

The peroxide initiated addition of a variety of fatty derivatives to 1-decene was effected in the manner described for the 20:4:1.2 acid chloride run. The results from these experiments are compared in Table II. The need for keeping the addition mixtures liquid in these runs involving materials which are normally solids at room temperature was met by heating each mixture near the melting point of the diluent being used (38 C for methyl stearate, 70 C for stearic acid and stearic anhydride, and 108 C for stearamide). The reaction mixtures from the acid and the anhydride runs were esterified with methanol containing p-toluene sulfonic acid catalyst. The stearamide product mixture was assayed as such by analytical TLC using 2% and 5% methanol in benzene mixtures as developing solvents and was fractionated by preparative TLC with 10% methanol in benzene mixture.

Olefin Accountability

The crude product mixture from the addition of stearoyl chloride to 1-decene (reagent ratio 20:4:1.2) was re-examined by column chromatography and preparative TLC to determine the fate of the olefin which did not form α-branched product.

A column of Florisil (25.4 g), prepared in hexane, was charged with total crude mixture (1.504 g) and the column was eluted with hexane in 15 ml fractions. The residue from the first two fractions (A, 5.1 mg) was set aside, and the residues from the following 10 fractions were combined (117 mg) and placed on a second Florisil (23.5 g) column. Elution of the second column with hexane gave 35.2 mg of material which, by IR and TLC behavior was judged to be hydrocarbon in nature, probably olefin polymer. This amount, translated to original crude product, represents 26.3% of the olefin used in the experiment. Residue A (5.1 mg) of front-running material from the first column was judged by the criteria set previously (4) to be a combination of two molecules of olefin with one molecule of stearoyl chloride. This material represented 1.9% of the starting olefin.

In a separate experiment total crude mixture (600 mg) was streaked on a 2.0 mm preparative TLC plate which had been pre-washed with developing solvent. The plate was developed with benzene-hexane (35:65) and the most polar band was scraped and extracted. The extraction residue was esterified with 20% BF_3-etherate in methanol, and the reaction product (77 mg) was chromatographed on a Florisil (11.5 g) column. Elution with hexane and 5% methylene chloride in hexane gave a mixture (29.1 mg) containing an estimated (from analytical TLC) 10.1 mg of methyl 2-decylstearate. This amount of branched ester represented 6.1% of the olefin used as starting material.

TABLE II

Fatty Derivative Additions to 1-Decene[a]

α-Branched Products in Reaction Mixture	Fatty Derivatives				
	Stearoyl chloride	Stearic anhydride	Stearic acid	Methyl stearate	Stearamide[b]
Concentration (%)	18.3	16.2	7.4	11.9	12.1
Yield[c] (%)	68.3	58.7	27.1	44.0	44.8

[a] Fatty derivative:1-decene:*t*-butyl peroxide ratio (20:4:1) nominally; runs were made at 160 C.
[b] Addition product mixture not converted to ester.
[c] Based on olefin.

Results and Discussion

The preparation of alkyl 2-decylstearates from stearoyl chloride and 1-decene requires fairly pure acyl halide for good conversions. Failure to remove phosphorus compounds during the preparation of stearoyl chloride (9) prevented α-addition, while the presence of free fatty acids or anhydrides gave low conversions in the esterification step. Washing of the crude acyl halide (8), followed by short-path distillation, gave an excellent grade stearoyl chloride in good yield. This method can also be applied to the recovery for recycle of the unreacted acyl halide from reaction mixtures.

The addition of fatty acids and their derivatives is usually carried out with a large excess of fatty material present to act as solvent. This procedure has the disadvantage that the crude product has to be subjected to a tedious, sometimes difficult, and always expensive separation procedure. Since lower dilution ratios are in the interest of ease of operation and of economy, a study was made to determine the effect of the variation of reagent ratio on product yield. From the results, summarized in Table I, it is clear that while a 50% reduction of stearoyl chloride to olefin ratio from 40:4 to 20:4 could be tolerated, much greater reduction in this ratio led to serious yield losses. For the purpose of analysis, the reaction mixture after completion of the addition step was treated with methanol. As a result, the bulk of the α-branched product was isolated as the methyl ester. A portion of the branched product and of the unbranched material, appeared as the *t*-butyl ester. The latter arose from the combination of acyl halide with tertiary butanol derived from the initiator.

There are two routes by which the branched *t*-butyl ester may be formed, since esterification might precede or follow the addition reaction. However, it is believed that prior esterification followed by addition of the ester to 1-decene is the path which probably predominates, especially when the reaction is carried out at the higher dilutions. At any rate, only about 20–30% of the potentially available *t*-butyl alcohol was trapped in this manner. The balance escaped at the high reaction temperature.

In all the acyl halide addition experiments carried out at 160 C a nonpolar fraction was formed, which was attributable partly to high molecular weight hydrocarbons and partly to a combination of two or perhaps more molecules of olefin with one molecule of acyl halide (4). The yield of the desired branched product decreased with increasing olefin concentration beyond the 20:4 ratio and, at constant acyl halide to olefin ratio, with decreasing catalyst concentration. It is also evident from the data of Table I that the drastic reductions in yield at the 10:4 acyl halide to olefin ratio are primarily due to failure of olefin to react at all and only secondarily due to consumption of olefin in by-product formation.

Because of the method of work-up unreacted olefin would have been removed in the work-up of the ester if it were still present at this time. It is therefore only possible to speculate whether olefin failed to react because it escaped during the reflux periods, or whether it failed to react for other reasons. Escape of the olefin seems unlikely. Failure to react then may have been due to a decrease in the concentration (stability?) of acyl halide radicals. The latter view was strengthened by the results of an experiment at the 20:4:1.2 ratio in which reaction temperature was decreased to 145 C and the reaction time after addition was increased from 4.3 hr to 7 hr. Under these conditions which lowered the *t*-butoxy radical concentration at any one time, the yield of the desired branched product was 37%. The data in Table II permit comparison of yields from the addition of a variety of fatty acid derivatives to 1-decene under same conditions. Product mixtures from these runs, except that from the amide run, were converted to the methyl ester before determination of their compositions by preparatory TLC. The yield order in these direct additions was as follows: stearoyl chloride > stearic anhydride > stearamide and methyl stearate > stearic acid. The additional and main advantage of the acid chloride addition reaction is that its product can be readily converted to a wide variety of α-branched derivatives that cannot be prepared directly or in good yield.

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[Received July 1, 1968]