ORGANIC DEUTERIUM COMPOUNDS

XIX. SYNTHESIS OF SOME DEUTERATED LAURIC ACIDS AND THEIR METHYL ESTERS¹

M. ELAINE ISABELLE AND L. C. LEITCH

ABSTRACT

The synthesis of lauric acids deuterated in the carboxyl, the terminal methyl, and the a-methylene groups and in various combinations of these is described. The methyl and methyl- d_3 esters of each of the acids were also prepared. Two further examples of homolytic halide addition to olefins are reported. The reaction between alkyl halides and silver acetylides is described. A mechanism involving

a new type of free radical is postulated.

In connection with studies by Jones and co-workers (9) on the infrared spectra of aliphatic fatty acids and their methyl esters it became necessary to prepare a number of deuterated lauric acids and methyl laurates. The series of compounds synthesized in this work are shown below.

$CH_3(CH_2)_{10}CO_2R$		$CH_3(CH_2)_9CD_2CO_2R$
(I)		(III)
$CD_3(CH_2)_{10}CO_2R$		$\mathrm{CD}_3(\mathrm{CH}_2)_9\mathrm{CD}_2\mathrm{CO}_2\mathrm{R}$
	$(R = H, D, CH_3, CD_3)$	

The compounds in the first group presented no particular problem. Lauric acid-dwas obtained by decomposing lauroyl chloride with deuterium oxide. Methyl-d₃ laurate was obtained in excellent yield by heating silver laurate with methyl- d_3 bromide (14).

The synthesis of the key compound in the second series, lauric acid labelled on the terminal carbon atom of the chain, proved more difficult. Since methyl- d_3 iodide of high isotopic purity is now readily available, the preparation of the deuterolauric acid in question was attempted by the reactions shown below:

$$CD_{3}I + NaC \equiv C(CH_{2})_{8}CO_{2}CH_{3} \rightarrow CD_{3}C \equiv C(CH_{2})_{8}CO_{2}CH_{3} + NaI,$$
$$CD_{3}C \equiv C(CH_{2})_{8}CO_{2}CH_{3} \rightarrow CD_{3}(CH_{2})_{10}CO_{2}CH_{3}.$$

In pilot experiments with methyl iodide, however, we were unable to methylate the sodium derivative of methyl 10-undecynoate in liquid ammonia. This observation is in agreement with that of Taylor and Strong (20), who found that the alkynes $CH_3(CH_2)_mC \equiv CH$ did not condense in sodamide – liquid ammonia with $I(CH_2)_nCl$ where m < 10 or n < 3. Attempts to alkylate by this method were therefore abandoned.

The reaction of deuterated alkyl iodides (and even bromides) with the silver salts of aliphatic acids is a very convenient reaction for the synthesis of deuterated esters (13)and was used above to prepare methyl- d_3 laurate. There was a possibility that silver acetylides would also react under suitable conditions, at least with methyl iodide, to give alkylacetylenes. Observations in the literature (6) relating to the inertness of silver acetylides to alkyl halides were ignored, and the silver derivative of methyl 10-undecynoate was heated to 75° C. for several hours with an excess of methyl iodide. It was an agreeable surprise to isolate methyl 10-dodecynoate although in only 40 to 50%yields. The new ester was identified by its infrared spectrum, which showed no absorption

¹Manuscript received August 26, 1957.

Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 4610.

Can. J. Chem. Vol. 36 (1958)

for acetylenic hydrogen, and by the melting point of the acid; it was evidently methyl 10-dodecynoate. A similar reaction was found to take place with ethyl iodide to give methyl 10-tridecynoate. It therefore appears that silver acetylides will react with certain alkyl halides. The synthesis is particularly valuable with labelled halides owing to the ease with which unreacted halide may be recovered.*

In order to avoid using a large excess of labelled methyl iodide an experiment was next carried out in ether as a solvent. The product isolated from the reaction was not pure methyl 10-dodecynoate; its index of refraction was low, the melting point of the 10-dodecynoic acid was also low, and the ester gave a precipitate of the silver acetylide when shaken with ammoniacal silver nitrate in alcohol. The product seemed to be a mixture of methyl 10-undecynoate and 10-dodecynoate.

Several other runs were made in ether or benzene as solvent and in one case, in the absence of methyl iodide. The results of these experiments, which show the yield of ester, its index of refraction, and the melting point of the acid obtained on hydrolysis, are given in Table I.

Wt. of silver derivative (g.)	Vol. of methyl iodide (ml.)	Solvent (ml.)	Yield (ml.)	$n_{ m D}^{20}$	M.p. of acid (°C.)
12.7	10.0	None	4.0	1.4529	51
13.7	10.0	10 ml. ether	5.4	1.4510	47
10.0	4.0	10 ml. ether	0.5	1.4500	-
6.0	5.0	10 ml. C₅H₅	1.0	1.4480	-
6.0	5.0	None	-	1.4516	50 - 51
6.0	None	10 ml. ether	1.0	1.4460	42 - 43

TABLE I INFLUENCE OF SOLVENT ON THE YIELD AND PURITY OF THE METHYL 10-DODECYNOATE

The formation of methyl 10-undecynoate in the presence of ether may well take place by a free radical mechanism. According to this view the silver acetylide would produce the radical $CH_3OOC(CH_2)_8C \equiv C$ mentioned in reference 11, which could then give rise to the acetylenic ester by abstraction of a hydrogen atom from the solvent or from the ester itself:

$CH_{3}OOC(CH_{2})_{8}C \equiv CAg \rightarrow CH_{3}OOC(CH_{2})_{8}C \equiv \dot{C} + Ag,$

$CH_{3}OOC(CH_{2})_{8}C \equiv \dot{C} + C_{2}H_{5}OC_{2}H_{5} \rightarrow CH_{3}OOC(CH_{2})_{8}C \equiv CH + \dot{C}_{2}H_{4}OC_{2}H_{5}.$

The following observations are submitted as evidence in favor of this mechanism. When the silver derivative of methyl 10-undecynoate was heated alone in a sealed tube, a silver mirror was formed and a small yield of methyl 10-undecynoate was obtained. Much polymeric material was found. Moreover, when the acetylide was heated in benzene- d_6 , a product was isolated which had a small band in the region of the acetylenic deuterium vibration. Waters (23) is inclined to believe that silver derivatives ought to participate readily in free radical reactions because of the weak electropositive character of silver. Also, Glockling (5) has shown that the heterogeneous decomposition of iso-1-butenyl silver gives rise to iso-1-butenyl radicals, $(CH_3)_2C=\dot{C}H$. On the basis of all this evidence we submit that a $CH_3OOC(CH_2)_8C=\dot{C}$ radical is involved in the present reactions and that the formation of methyl 10-undecynoate in the presence of ether takes place by abstraction of hydrogen from the solvent or from the ester itself.

*After this work was completed Davis and Schreiber (3) reported the synthesis of acetylenic ketones by reaction of the silver derivatives of 1-hexyne and 1-octyne with acid chlorides in CCl_4 .

CANADIAN JOURNAL OF CHEMISTRY, VOL. 36, 1958

Regarding the alkylation of the silver acetylide by methyl and ethyl iodides, one is tempted to invoke a free radical mechanism and represent the reaction by the steps shown below:

$$CH_{3}OOC(CH_{2})_{8}C \equiv CAg \rightarrow CH_{3}OOC(CH_{2})_{8}C \equiv C + Ag,$$

$$CH_3I + Ag \rightarrow \dot{C}H_3 + AgI$$
,

$$CH_3 + CH_3OOC(CH_2)_8C \equiv C \rightarrow CH_3OOC(CH_2)_8C \equiv CCH_3.$$

However, the formation of methane by abstraction of hydrogen from the solvent or of ethane by dimerization, which are normal reactions of free radicals, has not been observed in these experiments.

In view of the comparative stability of the ions $R.C \equiv C^-$, it is possible that the alkylation takes place by a "push-pull" mechanism via the transition state shown below:

$$R_{\cdot}C \equiv C^{-} + CH_{3}I \xrightarrow{Ag} R_{\cdot}C \equiv C - CH_{3} - I \rightarrow R_{\cdot}C \equiv CCH_{3} + AgI_{\cdot}$$

With methyl- d_3 iodide, methyl 10-dodecynoate deuterated on the terminal carbon atom of the chain was obtained. Reduction in an alkaline medium by the method of Schwenk *et al.* (19) gave lauric-12- d_3 acid from which methyl laurate-12- d_3 was obtained on esterification. There was no evidence of α -deuteration as judged from the infrared spectra of the acid or ester.

Lauric-12- d_3 acid was also synthesized by an alternative method. Jensen, Kharasch, and Urry have reported the peroxide induced addition of polyhalogenomethanes to olefins (7). It has now been found that addition of chloroform to methyl undecylenate gives a mediocre yield of methyl 12-trichlorolaurate. Dechlorination of the ester by means of zinc and acetic acid-d gave an 80% yield of methyl laurate-12- d_3 . Deuterium oxide – dioxane mixtures can also be employed for the dehalogenation, and thus the necessity of preparing acetic acid-d can be avoided. Infrared spectra gave no evidence of α -deuteration in the acid or ester. The other members of this series of deuterated lauric acids were prepared by methods already described for lauric acid itself (7).

The third series of compounds involved the preparation of lauric acid deuterated on the α -methylene group. Interest was focused first on α -dibromolauric acid as a starting material. Textbooks on organic chemistry often make the general statement that further bromination of an α -bromo acid chloride by the Hell-Volhard method leads to the α -dibromo acid chloride. However, there are few references to these acids or their derivatives in the literature to substantiate this statement. α,α -Dibromoheptanoic acid has been reported but it was prepared from *n*-heptaldehyde diacetal (2), not from the acid. α,α -Dibromobutyric acid was supposedly formed when α -bromobutyric acid was heated with excess bromine in a sealed tube (15). Bromination of lauric acid beyond the α'' -bromo stage in sealed tubes was completely unsuccessful in our hands in that inseparable mixtures of polybromobutyric acids seemed to be formed.

The required methyl ester was synthesized by making use of another peroxide induced addition to olefins. Methyl dichloroacetate was found to add readily to 1-decene to give a mediocre yield of methyl 2,2-dichlorolaurate. Dechlorination with deuterium oxide in dioxane and zinc dust gave an excellent yield of methyl laurate-2,2- d_2 (III; R=CH₃). The other members of this series were obtained as already described for the normal acid.

The final series of deuterated lauric acids and their esters (IV) were prepared from methyl laurate- $12-d_3$ by the following route:

Can. J. Chem. Downloaded from www.nrcresearchpress.com by TPE/MAIN LIBRARY on 04/11/14 For personal use only.

ISABELLE AND LEITCH: ORGANIC DEUTERATED COMPOUNDS, XIX

$$\begin{split} (\mathrm{CO}_2\mathrm{C}_2\mathrm{H}_{\mathfrak{b}})_2 &+ \mathrm{CD}_{\mathfrak{z}}(\mathrm{CH}_2)_{10}\mathrm{CO}_2\mathrm{CH}_{\mathfrak{z}} \xrightarrow{\mathbf{C}_2\mathrm{H}_{\mathfrak{b}}\mathrm{OK}} \mathrm{CD}_{\mathfrak{z}}(\mathrm{CH}_2)_{\mathfrak{g}}\mathrm{CH}(\mathrm{CO}_2\mathrm{CH}_{\mathfrak{z}})_2 \\ &\xrightarrow{-\mathrm{OD}} \mathrm{CD}_{\mathfrak{z}}(\mathrm{CH}_2)_{\mathfrak{g}}\mathrm{CH}(\mathrm{CO}_2\mathrm{CH}_{\mathfrak{z}})_2 \xrightarrow{-\mathrm{OD}} \mathrm{CD}_{\mathfrak{z}}(\mathrm{CH}_2)_{\mathfrak{g}}\mathrm{CD}(\mathrm{CO}_2\mathrm{D})_2 \\ &\xrightarrow{\mathrm{CD}_{\mathfrak{z}}(\mathrm{CH}_2)_{\mathfrak{g}}\mathrm{CD}(\mathrm{CO}_2\mathrm{D})_2 \longrightarrow \mathrm{CD}_{\mathfrak{z}}(\mathrm{CH}_2)_{\mathfrak{g}}\mathrm{CD}_2\mathrm{CO}_2\mathrm{O}_2\mathrm{D} + \mathrm{CO}_2. \end{split}$$

The reactions were first carried out with the normal ester. The Claisen condensation with methyl laurate to *n*-decyl malonic ester took place readily and the yields from there on were nearly quantitative (17, 18). Similar syntheses were then carried out with the terminally labelled ester; thus lauric acid labelled on both the α -methylene and the terminal carbon atom of the chain was obtained.

An interesting observation relative to the 1420 cm.⁻¹ band of fatty acids in the infrared came to light on comparison of the spectra of the acids in carbon tetrachloride solution. Jones (8) has attributed the 1420 cm.⁻¹ band to the scissoring vibrations of the α -methylene group in R.CH₂CO₂CH₃. When the spectrum of α -deuterated lauric acid was examined it still showed a band of medium intensity at 1417 cm.⁻¹. It seemed most unlikely that deuterium would have been lost by exchange in the α -position during hydrolysis of the ester. The band was also present but of reduced intensity in the acid after exchange with deuterium oxide. However, it was entirely absent from the spectrum of the α -deuterated acid chloride. It was likewise absent from the spectrum of methyl 2,2-dichlorolaurate and 2,2-dichlorolauroyl chloride. It was present, however, in the spectrum of lauroyl chloride and lauronitrile. The absorption in the 1420 cm.⁻¹ region is therefore not due solely to the α -methylene but also to the hydroxyl group. The spectrum of lauric acids labelled in the methyl group showed no absorption in the 1380 cm.⁻¹ region. Quantitative studies on the spectra of these acids by Jones and co-workers now in progress will be reported by them in detail elsewhere.

EXPERIMENTAL

Lauroyl Chloride

Can. J. Chem. Downloaded from www.nrcresearchpress.com by TPE/MAIN LIBRARY on 04/11/14 For personal use only.

Lauric acid (1.0 g.) was warmed on the steam bath with 1 ml. of thionyl chloride (purified by distillation over quinoline and linseed oil). After 4 hours' heating, excess thionyl chloride and hydrogen chloride were pumped off. The residue was then twice distilled on the vacuum line in a Späth bulb. Yields: 0.8 ml., n_D^{20} 1.4455. Its infrared spectrum showed no absorption in the 3000–3600 cm.⁻¹ region and the band at 1407 cm.⁻¹ was reduced to one-half of its intensity in the spectrum of lauric acid where it appears at 1417 cm.⁻¹.

Lauric Acid-d

Lauroyl chloride was warmed on the steam bath for 1 hour with 2.0 ml. of deuterium oxide. After hydrolysis the lauric acid-d was extracted with pentane. After one recrystallization from pentane, 0.8 g. of acid was obtained. Since the acid still showed some absorption in the 3000–3400 cm.⁻¹ region in the infrared, it was exchanged by being heated with 10 ml. of deuterium oxide on the steam bath overnight. The equilibrated product was worked up as already described. There was little if any change in its spectrum by this treatment. The intensity of the band at 1417 cm.⁻¹ was the same as that in lauroyl chloride; part of it was masked by the absorption in the 1325–1410 cm.⁻¹ region. There was slight absorption in the 3000–3600 cm.⁻¹ region due to the presence of residual OH.

Methyl-d₃ Laurate, CH₃(CH₂)₁₀CO₂CD₃

Silver laurate was prepared as described in reference 12 by adding at the same rate

443

CANADIAN JOURNAL OF CHEMISTRY, VOL. 36, 1958

equivalent amounts of aqueous silver nitrate and potassium laurate to hot water, with stirring. The precipitate was filtered off, washed with water, and then acetone, and dried under vacuum in the dark.

Six grams of thoroughly dry silver laurate was placed in a tube (2 cm.×15 cm.) fitted with a ground glass joint. After the tube was constricted to facilitate sealing later, 15 ml. of anhydrous ether and 1.85 g. of methyl- d_3 bromide (13) were distilled into the tube, which was then frozen in liquid nitrogen, evacuated, and sealed. The reactants were heated to 85° C. in a rocking furnace for 20 hours.

Silver iodide was filtered off and washed with anhydrous ether. The residue, after removal of the ether, was distilled in a Späth bulb placed in an air furnace at 100° C. The yield of methyl- d_3 laurate was 3.5 g. (85.7%). It was a colorless liquid melting at + 10° C., $n_{\rm D}^{20}$ 1.4329.

For ordinary methyl laurate prepared in the same manner $n_{\rm p}^{20}$ was 1.4329.

Methyl 10-Undecynoate, HC=C(CH₂)₈CO₂CH₃

10-Undecynoic acid was prepared as described in reference 10. Thirty grams of the acid were esterified with methanol and a trace of sulphuric acid under reflux for 4 hours. The ester had b.p. 69–71° at 1 mm., $n_{\rm p}^{20}$ 1.4465. Yield: 32 g.

Methyl 10-Dodecynoate, CH₃C=C(CH₂)₈CO₂CH₃

The silver derivative of methyl 10-undecynoate was prepared by shaking overnight 10.0 g. of the ester with 170 ml. of ammoniacal silver nitrate solution (prepared by dissolving 8.5 g. of the salt in 100 ml. of water and adding ammonium hydroxide until the precipitate of silver oxide initially formed had just dissolved). Yield: 13.2 g. of product, m.p. 76-78° C. Calc. for $C_{12}H_{19}O_2Ag$, % Ag 35.6. Found: 35.2%.

The silver derivative (12.7 g.) was heated at 75° C. in a sealed tube overnight with 10.0 ml. of methyl iodide. The solids were filtered off in a gravity funnel and washed with ether. The residue, after removal of the ether by distillation, was distilled under vacuum from a Späth bulb in an air furnace at 85° C. Yield of product $n_{\rm D}^{20}$ 1.4529 was 4.0 ml. (45% of the theoretical).

10-Undecynoic Acid, CH₃C=C(CH₂)₈COOH

The methyl ester was hydrolyzed by being heated on the steam bath for a few minutes with a slight excess of alkali in 50% ethanol-water. The solution was diluted with water and acidified at 0° C. with dilute hydrochloric acid. After one recrystallization from petroleum ether the acid melted at 51° C. Neutralization equivalent, calc. for $C_{12}H_{20}O_2$: 196; found: 198.

Methyl 10-Tridecynoate, $C_2H_5C \equiv C(CH_2)_8CO_2CH_3$

Eight grams of the silver derivative of methyl 10-undecynoate was heated with 4.0 ml. of ethyl iodide in a sealed tube overnight at 80° C. The reaction product was worked up and purified as described for the lower homologue. Yield: 1.2 g., $n_{\rm p}^{20}$ 1.4504.

Methyl 10-Decynoate-12-d₃, CD₃C=C(CH₂)₈CO₂CH₃

The silver derivative of methyl 10-undecynoate was heated in a sealed tube with 6.7 ml. of methyl- d_3 iodide (13) overnight at 65° C. The product was isolated and purified as already described. Yield: 1.8 g. (50% of the theoretical) of ester, $n_{\rm D}^{20}$ 1.4514.

Methyl 12-Trichlorolaurate, CCl₃(CH₂)₁₀CO₂CH₃

A solution of 45 ml. of methyl 10-undecylenate in 75 ml. of chloroform containing 0.5 g. of dissolved dibenzoyl peroxide was heated in a pressure bottle for 4 hours at

444

445

110° C. in an oven; a further 0.5 g. of peroxide was added at the end of this time and heating was resumed overnight or for another 12 to 15 hours. The bulk of the chloroform was removed on the steam bath and the residue was distilled in a Vigreux column under reduced pressure (0.5 mm.). After collection of the unchanged methyl undecenoate at 65° C. the boiling point rose rapidly to 128–130° C. at 0.5 mm. and the trichloroester began to distill. Yield: 12.0 ml., n_{10}^{20} 1.4695.

Methyl Laurate-12-d₃, CD₃(CH₂)₁₀CO₂CH₃

(a) By reduction of 10-dodecynoic acid with Raney nickel.—10-Dodecynoic acid (1.0 g.) was dissolved in 200 ml. of 2% sodium hydroxide in water, and Raney nickel alloy (10.0 g.) was added in small portions over a period of 1 hour while the mixture was being heated on the steam bath. The hot solution was then filtered and the filtrate was acidified with dilute hydrochloric acid. The melting point of the acid which was filtered off was $42-43^{\circ}$ C. The acid was converted into the methyl ester by heating the silver salt with methyl bromide as described above.

(b) By zinc dust – deuterium oxide dechlorination.—To a suspension of 14.0 g. of zinc dust (50% excess) in 150 ml. of anhydrous dioxane containing 30 ml. of deuterium oxide was added dropwise, with stirring, 15 g. of methyl trichlorolaurate. The reaction mixture was stirred overnight at 90° C. and under reflux for 4 hours. The reaction mixture was filtered and freed of dioxane by distillation under reduced pressure. The residue was taken up in ether and filtered from suspended solids. The filtrate was freed of ether and distilled in a Späth bulb yielding 8.2 g. (80.3% yield) of methyl laurate-12- d_3 , $n_{\rm D}^{20}$ 1.4332.

The trichloro ester can also be dehalogenated with acetic acid-d and zinc dust with slightly higher yield but at the expense of preparing acetic acid-d.

Lauric-12-d₃ A cid, CD₃(CH₂)₁₀COOH

The acid was obtained by hydrolysis of the ester in nearly quantitative yield. Its infrared spectrum did not show the presence of a band for the CH_3 group at 1383 cm.⁻¹.

Lauric-12- d_3 Acid-d, CD₃(CH₂)₁₀CO₂D

This acid was prepared from the previous acid through the acid chloride.

Methyl-d₃ Laurate-12-d₃, CD₃(CH₂)₁₀CO₂CD₃

Silver laurate-12- d_3 prepared as described for the normal acid was heated with excess methyl- d_3 bromide in a sealed tube and the product was isolated as described in the case of methyl- d_3 laurate. The yield of distilled product, $n_{\rm p}^{20}$ 1.4337, was 92%.

Bromination of Lauric Acid

Attempts to brominate lauric acid under reflux in the presence of small amounts of phosphorus trichloride always resulted in the formation of α -bromolauric acid. No evidence of the presence of α -dibromolauric acid was ever found.

Brominations carried out at 140° C. in sealed tubes as described by Otto (15) likewise were unsatisfactory. Vast quantities of hydrogen bromide were evolved when the tubes were opened but the product boiled over a wide temperature range. Mixtures of dibrominated lauric acids were probably formed under these conditions. It is apparently not possible to introduce two bromine atoms in the α -position by this means.

Methyl 2,2-Dichlorolaurate, CH₃(CH₂)₉CCl₂CO₂CH₃

1-Decene (115 ml.), methyl dichloroacetate (177 g.), and 4.0 g. of dibenzoyl peroxide were heated for 15 hours on the steam bath. Unreacted decene and dichloroacetate ester were distilled off under 50 mm. pressure. After collection of a fraction (7.5 ml.) between

CANADIAN JOURNAL OF CHEMISTRY, VOL, 36, 1958

86° and 90° C. at 0.1 mm., methyl dichlorolaurate distilled over between 92° and 94° C. at 0.1 mm., n_D^{20} 1.4594, n_D^{23} 1.4584. The yield was only 28–30% but is offset by the ease of preparation of the ester.

Methyl Laurate-2,2-d₂, CH₃(CH₂)₉CD₂CO₂CH₃

Acetic acid-d was prepared as already described from acetyl chloride and deuterium oxide (16). To the acetic acid-d obtained from 26 ml. of acetyl chloride was added 6 g. of zinc dust and 5 ml. of methyl 2,2-dichlorolaurate. After the mixture had been stirred at room temperature overnight the zinc had nearly all turned white. The reaction mixture was poured into ice-water and extracted with 40 ml. of pentane. The residue, after removal of the pentane by distillation, was distilled in a Späth bulb. Yield: 3-6 g. of product, $n_{\rm p}^{22}$ 1.4342.

Reduction with deuterium oxide instead of acetic acid-*d* resulted in an impure product which showed unsaturation.

Lauric-2,2-d₂ Acid, CH₃(CH₂)₉CD₂COOH

The ester was hydrolyzed, isolated, and purified as described for lauric-12- d_3 acid. The yield was 2.9 g.

Lauric-2,2-d2 Acid-d

Can. J. Chem. Downloaded from www.nrcresearchpress.com by TPE/MAIN LIBRARY on 04/11/14 For personal use only.

446

This acid was prepared from lauric- $2, 2-d_2$ acid via the chloride.

2,2-Dichlorolauroyl Chloride, CH₃(CH₂)₉CCl₂COCl

Dichloroacetyl chloride was prepared as described by Brown (1). The acid chloride (180 g.), decene-1 (53 ml.), and dibenzoyl peroxide (2.0 g.) were heated on the steam bath overnight. The reaction mixture was fractionated in a short Vigreux column under 0.06 mm. pressure. Unreacted decene and dichloroacetyl chloride were collected up to 80° C. 2,2-Dichlorolauroyl chloride then distilled at 82–83° C. Yield: 6.0 ml., n_p^{20} 1.4629.

The amide was prepared by treating a sample of the chloride with ammonia and dilute ethanol. After one recrystallization from ethanol the amide melted at 62–64° C.

2,2-Dichlorolauric Acid, CH₃(CH₂)₉CCl₂COOH

A mixture of 1 ml. of 2,2-dichlorolauroyl chloride and 5 ml. of water was stirred overnight at room temperature and extracted with ether. The ether solution was dried over anhydrous sodium sulphate and distilled. The residue which remained was distilled in a Späth bulb. The distillate was a colorless liquid with an odor of lauric acid. Its neutralization equivalent was somewhat low.

Methyl-d₃ Laurate-2,2-d₂, CH₃(CH₂)₉CD₂CO₂CD₃

The silver salt was prepared as has already been described for ordinary lauric acid and lauric- $12-d_3$ acid. Methyl- d_3 laurate- $2,2-d_2$ was prepared from the silver salt and methyl- d_3 bromide as described above.

Diethyl n-Decylmalonate, $CH_3(CH_2)_9CH(CO_2C_2H_5)_2$

"Molecular" potassium (2.0 g.) was prepared in xylene dried over sodium (21), and washed three times by decantation with absolute ether. It was then covered with 40 ml. of absolute ether and anhydrous ethanol (2.8 ml., dried by distillation over magnesium ribbon) was added. The reaction mixture was heated for 4 hours under reflux. Diethyl oxalate (9.4 ml.) and methyl laurate (9.2 ml.) were added to the ice-cold suspension of potassium ethoxide in ether. After 25 hours' stirring the reaction mixture was poured into ice-water containing a little hydrochloric acid. The ether was separated, washed

three times with water, and dried over anhydrous sodium sulphate. The ether was removed at the ordinary pressure and the residue decarboxylated by heating under vacuum at 150° C. until no further evolution of gas took place. The product began to reflux as the pressure fell to 0.5 mm. The yield of product, n_D^{20} 1.4364, b.p. 120–124° C., was 9.0 ml.

Floyd and Miller (4) report b.p. 155–158° C. at 3 mm. and $n_{\rm D}^{25}$ 1.4353 for *n*-decylmalonic ester.

n-Decylmalonic-2-d Acid-d2, CH3(CH2)9CD(CO2D)2

Sodium deuteroxide was prepared by adding 7.0 g. of clean sodium in small portions to 50 ml. of deuterium oxide stirred under an atmosphere of dry nitrogen. n-Decylmalonic ester was then added and the reaction mixture was stirred overnight just below the boiling point. The solution was acidified by addition of deuterium sulphate until strongly acid, and extracted with ether. On evaporation of the ether, 6.1 g. of white solid melting at 111-113° C. was obtained. According to Wallingford (22) n-decylmalonic acid melts at 118-119°. Recrystallization of the acid from chloroform raised its melting point to 116° C. The deuterated acid could be expected to melt at a lower temperature than the normal one (24).

Heating above its melting point converted the *n*-decylmalonic- d_2 acid- d_2 into lauric- $2, 2-d_2$ acid-d.

Diethyl n-Decylmalonate-10- d_3 , CD₃(CH₂)₉CH(CO₂C₂H₅)₂

A Claisen condensation between diethyl oxalate and methyl laurate- $12-d_3$ was carried out exactly as just described. From 9.3 g. of laurate ester there was obtained 9.3 ml. of malonic ester, $n_{\rm D}^{20}$ 1.4373. Hydrolysis gave 6.1 g. of acid, m.p. 111–113° C.

Lauric-2,2,12,12,12,12-d₅ Acid-d, CD₃(CH₂)₉CD₂CO₂D

Can. J. Chem. Downloaded from www.nrcresearchpress.com by TPE/MAIN LIBRARY on 04/11/14 For personal use only.

This acid was obtained by decarboxylating the corresponding malonic acid in a glycerine bath at 140° C.

Methyl Laurate-2,2,12,12,12-d₅, CD₃(CH₂)₉CD₂CO₂CH₃

Silver laurate-2-2,12,12,12, d_{5} was prepared as already described for the normal acid. It was converted into the ester by heating with methyl iodide, also as described above.

Methyl-d₃ Laurate-2,2,12,12,12,-d₅, CD₃(CH₂)₉CD₂CO₂CD₃

This ester was prepared by the methods described above.

ACKNOWLEDGMENTS

The authors wish to thank Dr. R. N. Jones for helpful discussions and Mr. R. Lauzon for the infrared spectra of several compounds.

REFERENCES

- BROWN, H. C. J. Am. Chem. Soc. 60, 1325 (1938).
 CHANCEL, P. Bull. soc. chim. (France), 714 (1950).
 DAVIS, R. B. and SCHREIBER, D. H. J. Am. Chem. Soc. 78, 1675 (1956).
 FLOYD, D. E. and MILLER, S. E. J. Am. Chem. Soc. 69, 2354 (1947).
 GLOCKLING, F. J. Chem. Soc. 3640 (1956).
 JACOBS, T. L. Organic reactions. Vol. V. John Wiley & Sons, Inc., New J. LARASCH. M. S. and ULDY, W. H. L. Am. Chem. Soc.

- JACOBS, T. L. Organic reactions. Vol. V. John Wiley & Sons, Inc., New York. 1949. p. 45.
 JENSEN, E. V., KHARASCH, M. S., and URRY, W. H. J. Am. Chem. Soc. 69, 1100 (1947).
 JONES, R. N. and SANDORFY, C. Chemical applications of spectroscopy. *Edited by* W. West. Interscience Publishers, Inc., New York. 1956. Chap. IV, p. 505.
 - To be published. Jones, R. N.
- 10. KHAN, N. A. Organic syntheses. Vol. 32. John Wiley & Sons, Inc., New York. 1952. p. 104.

- ,-

448

- LEITCH, L. C. N.R.C. Review, p. 66 (1954).
 LÜTRINGHAUS, A. and SCHADE, D. Ber. 74, 1566 (1941).
 NOLIN, B. Can. J. Chem. 32, 1 (1954).
 NOLIN, B. and LEITCH, L. C. Can. J. Chem. 31, 153 (1953).
 OTTO, R. Ann. 239, 275 (1887).
 RENAUD, R. and LEITCH, L. C. Can. J. Chem. 34, 98 (1956).
 ROTHNERFORD, K. G. and NEWMAN, M. S. J. Am. Chem. Soc. 79, 213 (1957).
 SCHWENK, E., PAPA, D., WHITMAN, B., and GINSBERG, H. F. J. Org. Chem. 9, 175 (1944).
 VOGEL, A. Practical organic chemistry. 3rd ed. Longmans, Green & Co. Inc., New York. 1956. Chap. II, Sect. 50, p. 193.
 WALLINGFORD, V. H., HOMEYER, A. H., and JONES, D. M. J. Am. Chem. Soc. 63, 2056 (1941).
 WALERS, W. A. Chemistry of free radicals in solution. Oxford University Press, London. 1948. p. 210.
 WILSON, C. L. J. Chem. Soc. 492 (1935).