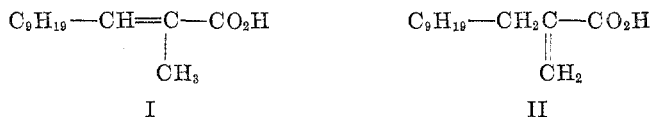# BRANCHED-CHAIN FATTY ACIDS. XXIV. SYNTHESIS OF 2-METHYL-2-DODECENOIC ACID AND OF 2-METHYLENEDODECANOIC ACID[1]

JAMES CASON, NORMAN L. ALLINGER, AND DAVID E. WILLIAMS

Recent publications (1, 2) from this laboratory have shown that C_{27}-phthienoic acid, the physiologically active (3) acid isolated from the lipids of the tubercle bacillus, is a 2-methyl-2-alkenoic acid. In view of this finding, synthetic acids of this type are desired for biological testing and for use in model degradative studies, and the present report deals with an investigation of methods suitable for preparation of such acids, which appear not to have been investigated previously.

Since 2-bromo acids not having a 2-alkyl substituent may be efficiently dehydrohalogenated (4) by use of potassium *tert*-butoxide in *tert*-butyl alcohol, this method was applied to 2-bromo-2-methyldodecanoic acid prepared by the Hell-Volhard-Zelinsky reaction. There was obtained, not the 2-methyl-2-alkenoic acid (I), but a mixture of 2-methylene acid (II) and conjugated dienoic acid.

$$C_9H_{19}-CH\!\!=\!\!C-CO_2H \qquad\qquad C_9H_{19}-CH_2C-CO_2H$$
$$\underset{\displaystyle CH_3}{|} \qquad\qquad\qquad\qquad\quad \underset{\displaystyle CH_2}{||}$$
$$\text{I} \qquad\qquad\qquad\qquad\qquad \text{II}$$

Although no effort was made to isolate the dienoic acid, its presence to the extent of about 18% was indicated by an absorption maximum in the ultraviolet spectrum (Fig. 1, Curve III) at about 270 mμ. Furthermore, when the mixture of unsaturated acids was subjected to the Diels-Alder reaction with maleic anhydride, and the tricarboxylic acid removed by extraction from hexane with aqueous methanol, the unsaturated acid recovered from the hexane phase gave a spectrum (Fig. 1) in which the band at 270 mμ was entirely absent.

It will be noted that the 2-methylene acid (Curve IV) has its absorption maximum at about 208 mμ, approximately the same wavelength as that of a 2-alkenoic acid (Curve I) having no substituents in the 2- or 3-positions, but the molar extinction coefficient of the 2-methylene acid is much lower. The similar positions of these maxima follow from the fact that in both compounds there are two substituents on the double bond. With a third substituent, as in the 2-methyl-2-alkenoic acid (Curve II), the maximum is shifted to longer wavelengths by about 10 mμ. The structures assigned to the acids whose spectra are represented by curves II and IV (Fig. 1) seem reasonable, from the methods of synthesis and from the ultraviolet spectra; however, they were further confirmed by subjecting each acid to analysis for terminal methyl. Whereas the 2-methyl acid yielded 1.55

moles of acetic acid per mole [normal for two terminal methyl groups in the molecule (1)], the 2-methylene acid yielded only 1.05 moles of acetic acid per mole (some rearrangement prior to oxidation, in the strongly acidic medium, would be expected). These data verify the position of the double bond in C_{27}-phthienoic acid (1) as in the chain, not to a methylene group.

The 2-methylene acid, II, would be expected as the principal product from dehydrohalogenation of 2-bromo-2-methyldodecanoic acid with base, for the electron density at the hydrogens on the methyl group is lower than at those on the adjacent methylene group. Once formed in this position, the double bond does not isomerize in base under the mild conditions used, for the acid has no α-hydrogen and no vinylogous α-hydrogen; hence the enolate ion cannot form and
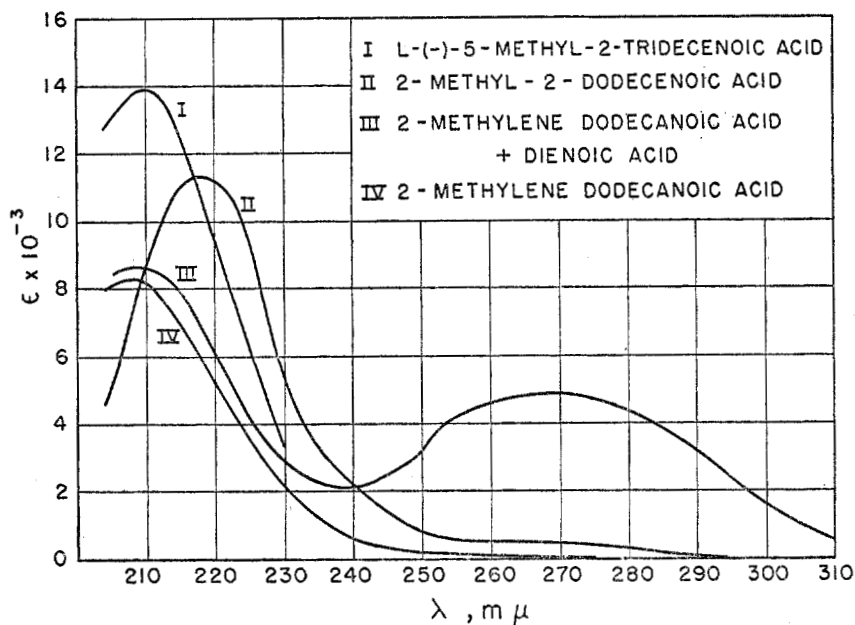

FIG. 1. ULTRAVIOLET SPECTRA OF UNSATURATED ACIDS

serve as a means of equilibration of the double bond. The presence of the dienoic acid may be satisfactorily explained if it be assumed that some loss of hydrogen bromide from the tertiary bromide occurs during the slow α-substitution of bromine. Since this loss occurs under acidic conditions, the reaction would be unimolecular, the Saytzeff rule (5) would be expected to hold, and the most highly branched alkene would be the principal product. This 2-alkenoic acid, I, (which adds bromine very slowly) would then brominate in the 4-position, by the principle of vinylogy, and subsequent dehydrohalogenation with base would yield the dienoic acid.

In order to obtain the 2-methyl-2-alkenoic acid, methyl 2-methyldodecanoate was brominated with N-bromosuccinimide, and the bromo ester was dehydro-

halogenated by heating with quinoline to 150°. The α,β-unsaturated ester was separated from other esters by careful fractional distillation, and the 2-alkenoic acid obtained by saponification. The ultraviolet spectrum (Fig. 1) shows the absence of significant quantities of the methylene acid. The method of bromination and the results with the 2,5-dimethyl ester (*cf.* below) would suggest the probability of some random bromination down the chain, which would lead to unconjugated dienoic acid. For the carefully purified sample shown in Figure 1, however, the steep positive slope of the curve below 215 mμ and the equally steep negative slope of the lower curve in Figure 2 indicate absence of significant amounts of such acids.

Formation of the 2-methyl-2-alkenoic ester by heating the α-bromo ester with quinoline might be attributed to loss of halogen acid by the unimolecular route; however, it seems more likely that there would occur, in part at least, the second order reaction involving attack of the base on a *beta* hydrogen. If the latter is the fact, then it must be assumed that the hydrogen ion concentration in the reaction medium, consisting of quinoline hydrobromide in quinoline, is sufficient to give a carbonium ion rearrangement of the double bond from methylene to the position of lower energy in the chain. This route is suggested by the observation that pure samples of 2-methyl-2-alkenoic ester were not obtained when dehydrohalogenation was conducted at lower temperatures with pyridine or picoline. Occurrence of rearrangement under the conditions of dehydrohalogenation was demonstrated by heating a sample of methyl 2-methylenedodecanoate (ester of II) with a solution of quinoline hydrobromide in quinoline of the concentration resulting in dehydrohalogenation. Whereas the methylene ester had λ_{max} at 210 mμ, the recovered ester has λ_{max} at 218 mμ, and there is no observable hump on the shoulder at 210 mμ.

Although the above-described procedure, involving α-bromination with N-bromosuccinimide, furnished a sample of 2-alkenoic acid sufficient for comparison of its absorption spectrum with that of the 2-methylene acid, the method has not proved to be of general synthetic utility. When the procedure was applied to conversion of methyl 2,5-dimethylheptadecanoate to the corresponding unsaturated ester, the fraction of α,β-unsaturated ester contained about 20% of conjugated dienoic ester, as shown by the ultraviolet absorption spectrum (Fig. 2). Failure of the absorption curve to drop steeply below 220 mμ also indicates presence of some non-conjugated unsaturated ester in this fraction. This was verified by absorption of 1.77 moles of hydrogen per mole of unsaturated ester. Furthermore, a lower-boiling fraction (containing saturated ester and esters in which the unsaturation is not conjugated with the carbonyl) gave an ultraviolet spectrum (Fig. 2) showing the presence of considerable non-conjugated unsaturated ester; so some product was obtained in which there had been attack at the 5-position (or possibly some other more remote position) and not at the 2-position.

Various experimental conditions failed to improve the results with the 2,5-disubstituted ester. When bromination with N-bromosuccinimide was attempted in carbon tetrachloride with ethanol as catalyst, no reaction had occurred after

two hours under reflux. Bromination also failed to occur in acetic acid solution, at temperatures of 23–50°, with no catalyst, with potassium bromide, or with benzoyl peroxide. Reaction was followed by determination of positive bromine volumetrically.

Since no more than a trace of conjugated dienoate was present in the 2-methyl ester and its absorption curve drops steeply below 218 mμ (Fig. 1), it appears that tertiary hydrogens are selectively attacked in the peroxide-catalyzed bromination with N-bromosuccinimide, regardless of whether such hydrogen is on a carbon *alpha* to a carbonyl. Barnes and Buckwalter (6) have recently reported the selective attack by N-bromosuccinimide on the tertiary hydrogen in *p*-cymene, and have attributed this to the relative stability of the tertiary alkyl radical formed in the process.
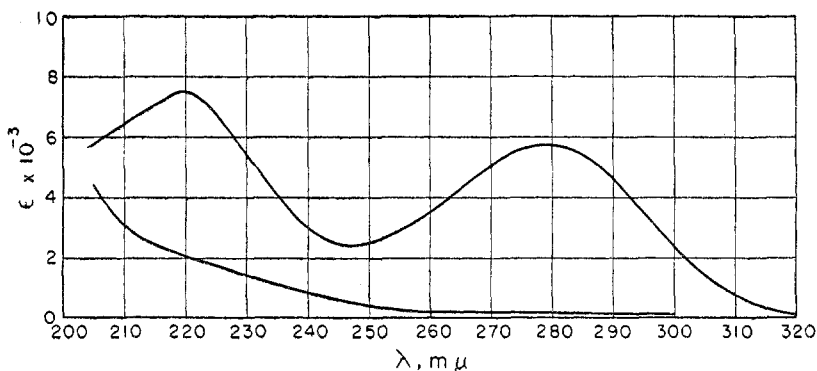

FIG. 2. ULTRAVIOLET SPECTRA OF FRACTIONS OBTAINED BY BROMINATION AND DEHYDROHALOGENATION OF METHYL 2,5-DIMETHYLHEPTADECANOATE. Lower curve, Frac. 1; upper curve, Frac. 5 (*cf.* experimental).

EXPERIMENTAL[2]

2-Methyldodecanoic acid was prepared by alkylation of diethyl methylmalonate (from decarbonylation of the oxalpropionate) with *n*-decyl bromide, in the presence of sodium ethoxide. In 0.5-mole runs, yields of diethyl methyl-*n*-decylmalonate were in the range 76–81%; b.p. 152–153° (2 mm.). Conversion of the substituted malonic ester to the desired acid was in 94% yield; b.p. 159.5–160.5° (5.5 mm.), n_D^{25} 1.4401, m.p. 24° (uncorr.).

Anal. Calc'd for $C_{13}H_{26}O_2$: Eq. wt., 214.3. Found: Eq. wt., 211.7.

The *methyl ester*, obtained in 89% yield by esterification with 20 mole-equivalents of methanol containing 10% by weight of concentrated sulfuric acid, had b.p. 123–124° (5.5 mm.), n_D^{25} 1.4298.

2-Methylenedodecanoic acid. To a mixture of 10 g. (0.047 mole) of 2-methyldodecanoic acid and 0.2 g. of phosphorus trichloride, stirred at 90–95°, there was added during about 15

mins. 9 g. (0.056 mole) of bromine. If the reaction had not started after addition of about 1 g. of bromine, the remainder of the addition was delayed until reaction had begun (occasionally additional phosphorus trichloride was required). After the mixture had been stirred for 4 hours at the same temperature an additional 7.5 g. (0.047 mole) of bromine was added and stirring and heating were continued for an additional 18 hours. The reaction appeared much slower than when acids with no *alpha* substituent were brominated (4).

The crude bromo acid, dissolved in carbon tetrachloride, was washed twice with water, then solvent and excess bromine were removed at reduced pressure on the steam-bath. The crude acid was added to a solution of 3 equivalents of potassium *tert*-butoxide in *tert*-butyl alcohol (5 g. of potassium per 100 ml. of *tert*-butyl alcohol distilled from sodium), and the mixture was heated under reflux for 1 hour. After the mixture had been worked up by dilution with water, acidification, and extraction with hexane, the product was distilled in a Claisen flask to yield 8.12 g. of crude unsaturated acid, b.p. 148–172°, n_D^{25} 1.4511. This acid was partially esterified by allowing it to stand at 20° for 2 hours with 50 ml. of commercial absolute ethanol containing 10% by weight of concentrated sulfuric acid [modified from the procedure of Eccott and Linstead (7)]. Separation of neutral material by use of the Amberlite IRA-400 strong anion exchange resin (8) and distillation of the acid in a Claisen flask yielded 4.13 g. of unsaturated acid with n_D^{25} 1.4584. The ultraviolet spectrum of this sample (Fig. 1, Curve III) shows two maxima, with the following extinction coefficients: ϵ_{210} 8,640; ϵ_{270} 4,870.

For separation of the dienoic acid, the mixed unsaturated acids were heated under reflux with two mole-equivalents of maleic anhydride in 30 cc. of dry benzene for 60 hours. The cooled mixture was passed through a four-stage Kies (9) extraction. This procedure has proved more convenient than use of the ion exchange resin. Each of the first two tubes contained 36 ml. of methanol, 32 ml. of 6 N sodium hydroxide, and 53 ml. of water. The last two tubes contained 30% aqueous methanol. After the solution had been passed through the tubes it was followed by 250 ml. of benzene. The aqueous phases from the tubes, containing acid free of neutral material, were combined, acidified, and extracted with three 150-ml. portions of hexane. These separate extracts were washed in series with three 100-ml. portions of water and 100 ml. of saturated sodium chloride solution. Removal of solvent and distillation in a Claisen flask gave 3.35 g. of acid, n_D^{25} 1.4590. There was only one maximum in the spectrum, λ_{max} 210 mμ, ϵ 8,850, and ϵ_{270} was 47. On fractional distillation at 5 mm. pressure, three fractions were collected, whose n_D^{25} were respectively 1.4579, 1.4579, 1.4580. The center fraction, weighing 1.23 g., b.p. 163–163.5° (5 mm.), ϵ_{208} 8,150 (max), was used for the ultraviolet spectrum (Fig. 1, Curve IV) and for analysis. On long standing, it crystallized, m.p. 30° (uncorr.).

Anal. Calc'd for $C_{13}H_{24}O_2$: Eq. wt., 212.3. Found: Eq. wt., 211.0.

Terminal methyl analysis, according to the procedure used in this laboratory for high molecular weight aliphatic compounds (1), gave in duplicate runs 1.02, 1.08 moles of acetic acid per mole of unsaturated acid.

When the center fraction, above, was again subjected to partial esterification, the acid recovered after separation of neutral material had essentially unchanged properties: n_D^{25} 1.4582, ϵ_{208} 8,180 (max). A second preparation of this acid, processed similarly, had b.p. 162.5–163° (4.5 mm.), n_D^{25} 1.4572, ϵ_{208} 7,550 (max), ϵ_{219} 4,990.

Isomerization with quinoline hydrobromide. A sample (0.39 g.) of 2-methylenedodecanoic acid was esterified by allowing it to stand for 30 minutes in ether solution at 0° with excess diazomethane. Distillation in a Claisen flask gave 0.36 g. of colorless ester, λ_{max} 210 mμ, ϵ 6,270 (no effort was made to highly purify the ester), ϵ_{220} 5,000. This sample of ester was heated at 152–157° for 2 hours with 2 ml. of a solution consisting of 1 equivalent of anhydrous hydrogen bromide and 5 equivalents of quinoline (the ratio resulting in dehydrohalogenation; *cf.* preparation of methyl 2-methyl-2-dodecenoate). After dilution with water and extraction with ether, the extract was washed with dilute hydrochloric acid, water, and a saturated solution of sodium chloride, then distilled in a Claisen flask to

yield 0.28 g. of ester λ_{max} 218 mμ, ϵ 8,560, ϵ_{210} 7,700. Both the shift in maximum and increase in extinction coefficient are expected if the double bond shifts from methylene to chain.

Methyl 2-methyl-2-dodecenoate. A mixture of 12.68 g. (0.056 mole) of methyl 2-methyl-dodecanoate, 29.69 g. (0.167 mole) of commercial N-bromosuccinimide,[3] and 0.66 g. of benzoyl peroxide[3] in 150 ml. of carbon tetrachloride was heated under reflux for 45 minutes, at which time all the N-bromosuccinimide had been consumed. After removal of succinimide by filtration, the solution was washed with 5% aqueous potassium hydroxide then with water until the washings were neutral. After solvent had been removed at reduced pressure and a bath temperature below 45°, the residue was heated with 33 ml. of quinoline for 40 minutes at 100°, then for 2 hours at 140–160°. The tarry mixture was shaken out with ether and water, then washed with 4 portions of 1 N hydrochloric acid and with saturated sodium chloride solution. The residue obtained from the ether solution was fractionally distilled at 5.5 mm. pressure to give three fractions: (a) b.p. 129–133°, n_D^{25} 1.4574, wt. 0.82 g.; (b) b.p. 133–134°, n_D^{25} 1.4597, wt. 4.96 g.; (c) b.p. 134–146°, n_D^{25} 1.4705, wt. 0.5 g.; residue, 4.5 g. Although Frac. (b) is a nearly pure sample of unsaturated ester (λ_{max} 219 mμ, ϵ 12,200), Fracs. (a) and (b) were combined and distilled through a 1.5-meter Podbielniak type column (10) at 5.2 mm. pressure. Of the seven arbitrary fractions in which the distillate was collected, fractions five and six (wt. 1.87 g.) had identical physical properties: b.p. 135°, n_D^{25} 1.4574, λ_{max} 219 mμ, ϵ 12,200.

Anal. Calc'd for $C_{14}H_{26}O_2$: C, 74.28; H, 11.58.

Found: C, 74.07; H, 11.18.

2-Methyl-2-dodecenoic acid was obtained by saponification of 1.5 g. of its ester (Fracs. 5 and 6, above) with 10% alcoholic potassium hydroxide. Rapid distillation in a Claisen flask gave 1.29 g. of acid, m.p. 33° (uncorr.), n_D^{25} 1.4698, λ_{max} 218 mμ, ϵ 11,330 (complete curve in Fig. 1). The ratio of this extinction coefficient to that of the ester indicates little, if any, equilibration (11) with the 3-alkenoic acid on saponification.

Anal. Calc'd for $C_{13}H_{24}O_2$: Eq. wt. 212.3; Found: Eq. wt., 214.0.

Terminal methyl analysis (1) gave, in duplicate runs, 1.54, 1.57 moles of acetic acid per mole of unsaturated acid.

Methyl 3-methyl-5-ketopentadecanoate. β-Methylglutaric anhydride was prepared by the excellent method of Ställberg-Stenhagen (12). This was converted in 89% yield to methyl hydrogen β-methylglutarate, b.p. 147–149° (11 mm.), by the method described for the succinic half ester (13), except that the product was purified by fractional distillation. The half ester was converted to the ester acid chloride, b.p. 103–104° (13.5 mm.), in 90% yield by the method previously described (13).

Following procedures previously reported (8, 14) for carrying out a keto ester synthesis by use of an organocadmium reagent, a Grignard reagent was formed from 884 g. (4 moles) of n-decyl bromide (purified by fractional distillation) and 97.3 g. (4 moles) of magnesium. This was converted to the cadmium reagent with 350 g. of anhydrous cadmium chloride, and in boiling benzene solution the cadmium reagent was allowed to react with 357 g. (2 moles) of the ester acid chloride from β-methylglutaric acid. Fractional distillation yielded 464 g. (82%) of keto ester, b.p. 185–188° (7 mm.).

The ester was characterized by saponification to *3-methyl-5-ketopentadecanoic acid* which was purified by removal of neutral material from the salt in a Kies (9) extractor, sublimation, and crystallization from acetone; m.p. 44.6–45.2°.

Anal. Calc'd for $C_{16}H_{30}O_3$: Eq. wt. 270.4. Found: Eq. wt., 272.0.

Methyl 3-methylpentadecanoate. The above keto ester (463 g., 1.63 moles) was reduced by the modified Wolff-Kishner method (15), using 312 g. of potassium hydroxide, 253 ml. of 85% hydrazine hydrate, and 2 liters of diethylene glycol. The crude acid obtained on dilution and acidification of the reaction mixture was dried and esterified by heating for 2 hours under reflux with 1350 ml. of methanol and 105 g. of concentrated sulfuric acid.

---

[3] When a lower ratio of N-bromosuccinimide was used, saturated ester was recovered. No reaction occurred in boiling carbon tetrachloride when benzoyl peroxide was omitted.

Work-up of the reaction mixture and fractionation yielded 330 g. (75%) of the desired ester, b.p. 170–174° (8 mm.).

The ester was characterized by saponification to *3-methylpentadecanoic acid*, purified by removal of neutral material from the salt in a Kies (9) extractor and crystallization from acetone; m.p. 37.2–37.6°.

Anal. Calc'd for $C_{16}H_{32}O_2$: Eq. wt., 256.4. Found: Eq. wt., 259.0.

3-Methylpentadecanol was prepared by hydrogenation of 329 g. of the above ester, in the presence of 19.4 g. of copper chromite catalyst (16), at an initial cold pressure of 2780 lbs. p.s.i. and a maximum pressure at 250° of 4400 lbs. p.s.i.; time 8 hours. Fractionation yielded 269.5 g. (91%) of the desired alcohol, b.p. 171–174° (9 mm.),n_D^{25} 1.4473.

Anal. Calc'd for $C_{16}H_{34}O$: C, 79.26; H, 14.14.

Found: C, 79.64; H, 13.92.

3-Methylpentadecyl bromide was prepared from the alcohol (268.5 g.) with anhydrous hydrogen bromide taken from a cylinder, following the published procedure (17). Fractionation yielded 300 g. (89%), b.p. 175–180° (9 mm). A center cut, used for analysis, had n_D^{25} 1.4589.

Anal. Calc'd for $C_{16}H_{33}Br$: Br, 26.17. Found: Br, 26.78.

Methyl 2,5-dimethylheptadecanoate. Diethyl methylmalonate (204.6 g., 1.18 moles), prepared by decarbonylation of the oxalpropionate, in 700 ml. of ethanol (dried with sodium and diethyl phthalate) was metalated with 23.7 g. (1.03 moles) of sodium, then alkylated with 299 g. (0.98 mole) of 3-methylpentadecyl bromide. Heating under reflux with stirring was continued for 8 hours; titration of aliquots showed no additional consumption of alkali after 7 hours. After neutralization with acetic acid, distillation of most of the alcohol, and dilution with 500 ml. of water, the product was extracted with benzene. After the benzene had been removed at reduced pressure, all material volatile at 100° and 6 mm. pressure was removed, then the residue was saponified by heating under reflux with stirring for 4 hours with a solution of 7.84 moles of potassium hydroxide in 1200 ml. of 95% ethanol. Alcohol was distilled at reduced pressure, then the residue was shaken out with aqueous sulfuric acid and ether. The extract was washed until washings were neutral, solvent was distilled, and the residue was decarboxylated by heating at 200° for 4 hours. The residual monocarboxylic acid was esterified with 20 moles of methanol containing 63 g. of concentrated sulfuric acid. Work-up of the reaction mixture and distillation yielded 238 g. (78%) of ester, b.p. 186–186.5° (6.5 mm.), n_D^{25} 1.4391.

Anal. Calc'd for $C_{20}H_{40}O_2$: C, 76.86; H, 12.90.

Found: C, 77.12; H, 12.66.

2,5-Dimethylheptadecanoic acid was obtained by saponification of the ester and distilled, b.p. 210–210.5° (6 mm.), n_D^{25} 1.4472. The mixture of stereoisomers began to crystallize on cooling to −20°, but melted on warming up, and isolation of crystalline material by low temperature crystallization from acetone was difficult. The liquid distillate was titrated.

Anal. Calc'd for $C_{19}H_{38}O_2$: Eq. wt., 298.5. Found: Eq. wt., 300.

Unsaturated esters from methyl 2,5-dimethylheptadecanoate.[4] The dimethyl ester was treated with N-bromosuccinimide as described for methyl 2-methyldodecanoate, except that only two mole-equivalents of N-bromosuccinimide were used. The reaction mixture was worked up as described for the monosubstituted ester, except that the product was first distilled in a Claisen flask to give a crude yield of 72%, b.p. 175–201° (3 mm.), then this distillate was fractionated through the 1.5-meter column (10) at 5.0 mm. pressure to give the following fractions:

FRAC. NO.	B.P., °C.	WT., g.	n_D^{25}
1	175.0–183.6	3.91	1.4506
2	183.6–185.0	7.22	1.4537
3	185.0–187.0	1.89	1.4580
4	187.0–191.0	1.66	1.4596
5	191.0–193.0	2.69	1.4625

[4] A part of the experiments reported in this section are by Dr. C. Freeman Allen, of this laboratory.

Ultraviolet spectra were taken for Fracs. 1 and 5, and the complete curves are shown in Fig. 2. For Frac. 1, the shape of the curve at about 220 mμ shows presence of only a trace of 2-alkenoate, and the steep rise below 210 mμ is presumed to be the edge of the band for an isolated double bond having a maximum below 200 mμ. For Frac. 5, containing 2-alkenoate and conjugated dienoate, ϵ_{219} 7,420 (max), ϵ_{230} 5,790 (max).

SUMMARY

Dehydrohalogenation of 2-bromo-2-methyldodecanoic acid by means of potassium *tert*-butoxide yields 2-methylenedodecanoic acid, whereas use of quinoline with the corresponding ester leads to the 2-methyl-2-dodecenoate.

N-Bromosuccinimide is not of general utility for α-bromination of saturated esters, for there appears to be selective attack on tertiary hydrogens at other sites in the molecule.

BERKELEY 4, CALIF.

REFERENCES

(1) CASON AND SUMRELL, *J. Biol. Chem.*, **192**, 405 (1951).
(2) CASON, FREEMAN, AND SUMRELL, *J. Biol. Chem.*, **192**, 415 (1951).
(3) HUSSEINI AND ELBERG, *Am. Rev. Tuberc.*, **65**, 655 (1952).
(4) CASON, ALLINGER, AND SUMRELL, *J. Org. Chem.*, following paper.
(5) DHAR, HUGHES, INGOLD, MANDOUR, MAW, AND WOOLF, *J. Chem. Soc.*, 2093 (1948).
(6) BARNES AND BUCKWALTER, *J. Am. Chem. Soc.*, **73**, 3858 (1951).
(7) ECCOTT AND LINSTEAD, *J. Chem. Soc.*, 2153 (1929).
(8) CASON, SUMRELL, AND MITCHELL, *J. Org. Chem.*, **15**, 850 (1950).
(9) KIES AND DAVIS, *J. Biol. Chem.*, **189**, 637 (1951).
(10) CASON, ALLINGER, SUMRELL, AND WILLIAMS, *J. Org. Chem.*, **16**, 1172 (1951).
(11) CASON AND SUMRELL, *J. Org. Chem.*, **16**, 1181 (1951).
(12) STÄLLBERG-STENHAGEN, *Arkiv Kemi, Mineral. Geol.* **25A**, No. 10 (1947).
(13) CASON, *Org. Syntheses*, **25**, 19 (1945).
(14) CASON AND PROUT, *Org. Syntheses*, **28**, 75 (1948).
(15) HUANG-MINLON, *J. Am. Chem. Soc.*, **68**, 2487 (1946).
(16) ADKINS, *Org. Syntheses*, Coll. Vol. II, 144 (1943).
(17) REID, RUHOFF, AND BURNETT, *Org. Syntheses*, Coll. Vol. II, 246 (1943).