[Contribution from the Chemical Laboratory of the University of California]

BRANCHED-CHAIN FATTY ACIDS. XIX. CHEMICAL PROPERTIES AND ULTRAVIOLET ABSORPTION SPECTRA OF 2- AND 3-ALKENOIC ACIDS AND ESTERS[1]

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The original objective of this investigation was to study the ultraviolet absorption spectra of α,β- and β,γ-unsaturated acids, in connection with the study of unsaturated acids from the tubercle bacillus (1). During the preparation of suitable pure compounds, however, it developed that some study was required of the chemical properties of these compounds.

Ethyl 2-nonenoate was prepared by dehydration of the β-hydroxy ester obtained from a Reformatsky reaction between ethyl bromoacetate and *n*-heptaldehyde. None of the 3-nonenoate could be isolated from the product so obtained. Ethyl 3-hydroxy-3-methylnonanoate was also prepared by a Reformatsky reaction in the manner previously described (2), but dehydration of this hydroxy ester by either iodine or thionyl chloride and pyridine gave a mixture containing about two parts of the 3-nonenoate to one part of the 2-nonenoate. Since these esters boil about 10° apart at 5 mm., they were separated by fractional distillation. Although Linstead and co-workers (3) have made extensive studies of the equilibration of α,β- and β,γ-unsaturated acids there appears to have been no report of the heat stability of the isomeric unsaturated esters. Thus, each of the ethyl 3-methylnonenoates was heated in an atmosphere of nitrogen for 24 hours at 225°. In neither case did any equilibration between the esters occur, thus fractional distillation is a feasible and useful method of obtaining such isomeric esters in a pure condition.

The ultraviolet absorption spectra of these three esters are shown in Figure 1, together with that of methyl palmitate for comparison. It will be noted, for the α,β-unsaturated esters, that the substituent methyl on the doubly-bonded carbon shifts the $\lambda_{\max}$ towards the red by about 10 mμ. This shift is analogous to that noted for α,β-unsaturated ketones. In the β,γ-unsaturated ester, the band for the carbon—carbon double bond remains in its normal position below 200 mμ, and the ester band appears as a hump on the shoulder of the alkene band. Since ϵ_{219} for the α,β-unsaturated ester is about 14,000 and ϵ_{219} for the β,γ-unsaturated ester (or other monounsaturated ester) is only about 1,100, the absorption in this region furnishes a rapid and accurate method for analyzing such esters, which appears much superior to the previously-used chemical methods (4).

Linstead has studied the equilibration of 2- and 3-alkenoic acids by heating with alkali, and on the basis of data obtained with cyclohexylideneacetic acid has stated (5) that boiling with 10% alcoholic alkali for several hours should give very little equilibration. Thus, it was assumed by us that alkaline hydrolysis of

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the above-described pure esters for one hour with 5% alkali would yield the pure unsaturated acids, and the 3-methyl-2-nonenoic acid obtained in this way has

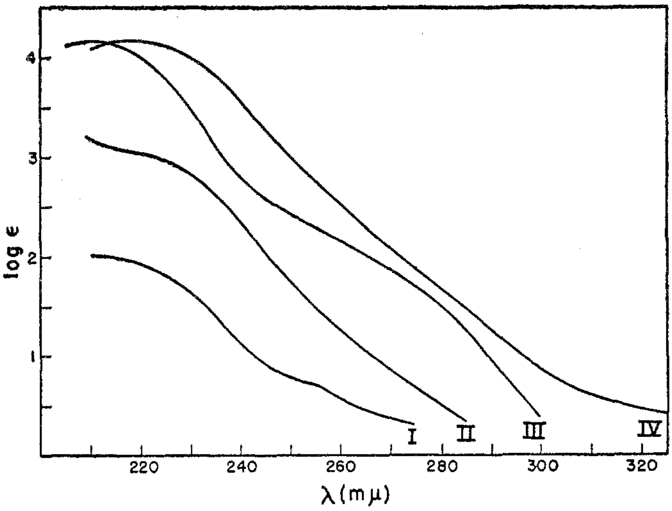

Figure 1. Ultraviolet Absorption Spectra of Pure Unsaturated Esters. I, methyl palmitate (for reference); II, methyl 3-methyl-3-nonenoate; III, methyl 2-nonenoate; IV, methyl 3-methyl-2-nonenoate.

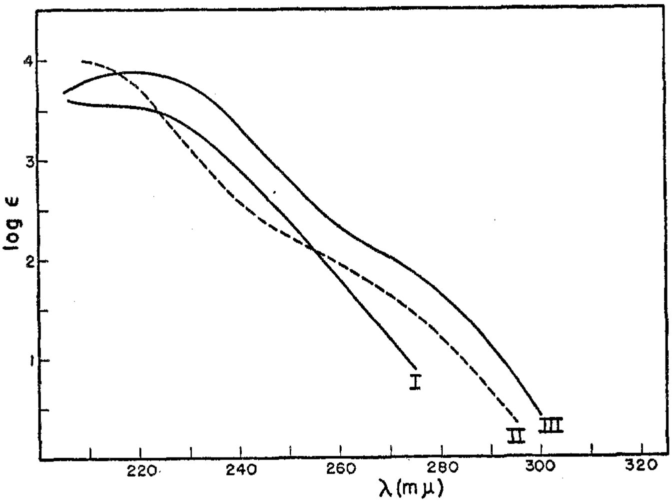

Figure 2. Ultraviolet Absorption Spectra of Unsaturated Acids Obtained by Saponification of Pure Unsaturated Esters. I, 3-methyl-3-nonenoic acid; II, 2-nonenoic acid; III, 3-methyl-2-nonenoic acid.

been described by us (1) as "pure", but this has now been found to be incorrect. In Figure 2 are shown the spectra for the three acids obtained by alkaline hydrolysis of the corresponding pure esters. It will be noted that 2-nonenoic acid has a considerably higher extinction coefficient than the 3-methyl-2-nonenoic acid, also that the ratio of the extinction coefficients of the 3-methylnonenoic acids is smaller than that of the esters (Figure 1).

The equilibration of the α,β- and β,γ-unsaturated acids on mild alkaline hydrolysis of the esters has been verified by several independent experiments. A sample of the pure 3-nonenoate was saponified and the resultant acid re-esterified with diazomethane. The resultant methyl ester boiled over the range 87–94° (5.0 mm.), and was collected in six fractions. The lowest-boiling fraction had ϵ_{219} 1,650 (not a maximum), while the last had λ_{max} at 219, ϵ_{max} 11,140. Further, when a sample of 3-methyl-2-nonenoic acid, whose spectrum is shown in Figure 2, was esterified with ethanol and sulfuric acid, the unesterified portion of acid had λ_{max} at 219, ϵ_{max} 12,000. The curve was parallel to that in Figure 2 but higher by the amount indicated. This sample of 3-methyl-2-nonenoic acid is regarded as pure. Since it has ϵ_{max} considerably higher than the acid obtained by saponification of pure ethyl 2-nonenoate, it follows that pure α,β-unsaturated aliphatic acids cannot generally be obtained by saponification of the corresponding esters. The most hopeful case would be a 2-methyl-2-alkenoic acid. The synthesis of such acids, presently being investigated in this laboratory, is complicated by their ease of polymerization.

TABLE I

EQUILIBRATION OF 3-METHYLNONENOIC ACIDS BY HEATING

ACID	HEATING PERIOD	n_D^{25}	ϵ_{219}
3-Methyl-2-nonenoic	none	1.4588	7,970 (max)
	2 hours at 160–190°	1.4602	9,640 (max)
3-Methyl-3-nonenoic	none	1.4522	3,420
	3 hours at 175°	1.4527	4,560
	24 hours at 200°	1.4578	7,360[a]

[a] ϵ_{max} of 7,480 occurred at 217 mμ.

The few previous reports of the ultraviolet absorption spectra of α,β-unsaturated acids agree on the occurrence of a maximum in the region 210–220 mμ, but there is considerable discrepancy in the extinction coefficient. Lauer, Gensler, and Miller (6) report ϵ_{max} about 25,000 for 2-pentadecenoic acid and 2-heptadecenoic acid. These values appear far too high, and Burr and Miller (7), using a sample of 2-pentadecenoic acid supplied by Lauer, report ϵ_{max} of about 15,800. The latter figure is closer to ours, but apparently too high since it is above our values for the pure α,β-unsaturated esters shown in Figure 1, and esters absorb slightly more strongly than acids. Ungnade and Morriss (8) report ϵ_{max} for octahydro-1-naphthoic acid as about 9,300. Van der Hulst (9) did not extend his curve below 220 mμ, while Caliezi and Schinz (10) do not report the value for ϵ_{max}.

Since the unsaturated acids described above were always isolated by rapid distillation in a Claisen flask it seems reasonable to assume that the equilibration occurred during the alkaline hydrolysis, not during the brief heating for distillation. This assumption has been justified by heating samples of the two acids, with the results shown in Table I. It is seen that heating shifts the equilibrium slowly, and actually more in favor of the α,β-unsaturated isomer, away from the equilibrium position attained by brief heating of 3-methyl-2-nonenoic acid with alkali.

Since heating shifts the equilibrium in favor of the α,β-unsaturated isomer, it was hoped that 2,3,4-trimethyl-2-hexadecenoic acid could be obtained by heat equilibration of the unsaturated acid obtained by ring-opening of 2,3,4-trimethyl-1,4-hexadecanolide. The synthesis of this unsaturated acid has been described in an earlier paper (11). This attempt failed, apparently because the γ-substituted β,γ-unsaturated acid equilibrated with the lactone rather than with the α,β-unsaturated acid. Heating of the unsaturated acids not bearing a γ-substituent resulted in formation of little, if any, lactone. These findings are consistent with those of Arnold, Elmer, and Dodson (12).

No effort has been made, in these studies, to establish the position of equilibrium at complete equilibration under the various conditions, for it is not regarded as germane to the present investigation which is directed towards establishing what conditions are suitable for the obtaining of pure isomers.

EXPERIMENTAL

All boiling points are corrected. All distillations, unless otherwise specified, were through the 1.5-meter column previously described (11). Ultraviolet absorption spectra were determined with a Beckman Model DU quartz spectrophotometer in the manner described in the preceding paper of this series.

Ethyl 3-methylnonenoates were prepared as has been described (2). In one run, the product (72 g.) was distilled without dehydration to yield 30 g. of material boiling below 115° (5.0 mm.) and 40.8 g. of *ethyl 3-methyl-3-hydroxynonanoate*, b.p. 115–115.5° (5.0 mm.), n_D^{25} 1.4343. Fieser and co-workers (13) prepared the ester similarly and reported b.p. 100–101° (1 mm.), n_D^{25} 1.4343. This distilled ester could not be dehydrated with iodine as described (2) for the crude ester; it was dehydrated with thionyl chloride and pyridine, according to Linstead and Millidge (14), to give a 77% yield of a mixture of unsaturated esters which was of essentially the same composition as obtained by iodine dehydration of the crude ester.

In a representative separation of the unsaturated esters, a 60-g. lot was fractionated at 5.0 mm. pressure to yield: (a) 3.1 g., b.p. 93–94°; (b) 14.8 g. of *ethyl 3-methyl-3-nonenoate*, b.p. 94–94.5°; (c) 19.6 g., b.p. 94.5–97°; (d) 9.4 g., b.p. 97–104°; (e) 12 g. of *ethyl 3-methyl-2 nonenoate*, b.p. 104–105°. Fractions (b) and (e) were collected in several sub-fractions with nearly identical indices of refraction. For the 3-nonenoate, n_D^{25} 1.4357, ϵ_{219} 1,140. For the 2-nonenoate, n_D^{25} 1.4490, λ_{max} 219 mμ, ϵ_{max} 14,500. The sample of the 2-nonenoate described in the literature (13), b.p. 83–88° (0.5 mm.), n_D^{25} 1.4411 apparently contained considerable of the 3-nonenoate.

3-Methyl-3-nonenoic acid, prepared by heating under reflux for one hour a mixture of 9.46 g. of ethyl ester and 148 ml. of 5% alcoholic potassium hydroxide (2 equiv. of alkali), gave the spectrum in Figure 2, which indicates equilibration with the α,β-unsaturated isomer. Any ester or other neutral material was removed, before rapid distillation in a Claisen flask, by use of a column of Amberlite IRA-400 (a strong anion exchange resin). Since elution from the column involves brief contact, at room temperature, with dilute hydrochloric acid, in one run this treatment was substituted by orthodox extraction of neutral material from aqueous solution of the salt. As expected, there was no change in the extent of equilibration. This acid had b.p. 109–111° (1.5 mm., distilled in Claisen flask), n_D^{25} 1.4522, ϵ_{219} 3,420. The sample of this acid described in the literature (13), b.p. 103–104° (0.3 mm.), n_D^{25} 1.4512, appears to be only slightly richer in the 3-isomer than our sample.

A sample of this acid, esterified in 89% yield with diazomethane, gave an ester of b.p 87–94° (5.0 mm.). Of the six fractions collected in this range, the first fraction had n_D^{25} 1.4376, ϵ_{219} 1,650, ϵ still increasing at 205 mμ. The highest-boiling fraction had n_D^{25} 1.4458, λ_{max} 219 mμ, ϵ_{max} 11,140.

The data in Table 1 were obtained by heating another sample of this acid in an atmosphere of nitrogen and distilling in a Claisen flask before determination of physical constants.

3-Methyl-2-nonenoic acid was obtained from the ester, as described above for the isomer. The sample which gave the spectrum in Figure 1 had b.p. 113–115° (1 mm.), n_D^{25} 1.4588, λ_{max} 219 mμ, ϵ_{max} 7,970. A pure sample of this acid was obtained by partial esterification, consisting of heating for one hour under reflux a mixture of 2.7 g. of acid and 30 equivalents of ethanol containing 10% by weight of concentrated sulfuric acid. There was recovered 485 mg. of acid, b.p. 113–114° (1.0 mm.), n_D^{25} 1.4648, λ_{max} 219 mμ, ϵ_{max} 12,070. The sample reported in the literature (13) had n_D^{25} 1.4636, in fairly good agreement with our sample.

The ester (1.90 g.) recovered from this esterification had b.p. 94–105° (5.0 mm.), n_D^{25} 1.4412, indicating about 41% of the α,β-unsaturated isomer. Some equilibration would be expected during the esterification with acid catalyst (15).

A sample of acid obtained directly from saponification was used for heating in an atmosphere of nitrogen to yield the data in Table 1.

Ethyl 2-nonenoate. Ethyl 3-hydroxynonanoate was prepared as described (2) for the 3-methyl-3-hydroxynonanoate except that the ratio of ethyl bromoacetate to zinc to freshly distilled heptaldehyde was 1:1.2:1.4. The chloro ester, obtained with thionyl chloride in pyridine, was not dehydrohalogenated by heating under reflux with pyridine, but halogen acid was lost on heating under reflux for two hours with 5 equivalents of 2,4,6-collidine. The yield was only 20%. Fractionation at 5.0 mm. pressure gave 1.8 g., b.p. 99.5–102°, n_D^{25} 1.4394, followed by 7.5 g., b.p. 102°, n_D^{25} 1.4404, λ_{max} 210 mμ, ϵ_{max} 14,250. From the literature (16), b.p. 118–120° (12 mm.), n_D^{25} 1.439.

2-Nonenoic acid, obtained by saponification of the ester as described above, had b.p. 136–139° (5.0 mm.), n_D^{25} 1.4526, λ_{max} 210 mμ, ϵ_{max} 9,550. The sample of this acid described in the literature (17), b.p. 135–138° (5 mm.), n_D^{25} 1.4561, would appear considerably more homogeneous than that obtained by us by saponification of the pure ester.

Heat treatment of 2,3,4-trimethylhexadecenoic acid. Ethyl 2,3,4-trimethylhexadecenoate was prepared as described previously (11), the acid was heated at 190–200° for 60 hours in an atmosphere of nitrogen, then the ester was prepared with diazomethane and fractionated at 5.0 mm. pressure to yield the following fractions:

FRACTION	WT., G.	B.P., °C.	n_D^{25}
1	2.2	150–181.5	1.4493
2–6	20.9	181.5–184	1.4520
7	1.5	184–186.5	1.4528
8	0.5	186.5–188	1.4539
9	0.8	188–205	1.4565
10, 11	4.7	205–207	1.4555

Fraction 6 gave ϵ_{220} 750, ϵ still increasing at 205 mμ, thus no appreciable amount of α,β-unsaturated ester was formed by heating. Fractions 10 and 11 are probably 2,3,4-trimethyl-1,4-hexadecanolide.

SUMMARY

Fractional distillation may be used to separate α,β- and β,γ-unsaturated esters, and the ultraviolet absorption spectra is a convenient and accurate method for determining purity of such esters.

Saponification with 5% alcoholic potassium hydroxide causes rather rapid equilibration of the double bond between the α,β- and β,γ-positions. Heating of the unsaturated acids to 170–190° causes equilibration to shift more towards α,β-unsaturation than does heating with alcoholic potassium hydroxide.

Heating of a 4-alkyl-3-alkenoic acid failed to give equilibration with the 2-alkenoic acid, on account of lactone formation. In absence of the 4-alkyl substituent, there is little, if any, lactone formation.

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