BRANCHED-CHAIN FATTY ACIDS. XXV. METHODS OF SYNTHESIS OF 2-ALKENOIC ACIDS[1]

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In the preceding paper (1) in this series there was described the synthesis of 2-alkenoic acids containing a 2-methyl substituent, and in an earlier report (2) there was described the synthesis of a 3-methyl-2-alkenoic acid. Since 2-alkenoic acids not substituted at the double bond are desired for examination of their infrared and ultraviolet spectra, as well as other properties, an investigation of methods of synthesis of such acids is described in the present report.

The Reformatsky reaction with a methyl ketone provides a satisfactory entry (2) to synthesis of 3-methyl-2-alkenoic acids, but the yield of normal 2-alkenoic acid was very poor when an aldehyde was used. Since Linstead and co-workers (3, 4) have shown that the Doebner condensation gives a high ratio of 2-alkenoic acid when the reaction is carried out in pyridine with piperidine as catalyst, the utility of this method has been examined. Unfortunately, the effectiveness of this approach, in the cases presently studied, is severely limited by the pronounced tendency of higher straight-chain aldehydes to polymerize. Thus, this approach to 2-alkenoic acids has been abandoned, for the present, but the method has furnished a sufficient sample of 2-hexacosenoic acid for biological testing (5).

There was also obtained, *via* the Doebner condensation, a small sample of 5-methyl-2-hendecenoic acid (I), which possesses physical properties very similar

$$C_6H_{11}CHCH_2CH{=}CHCO_2H \qquad\qquad C_9H_{19}CH{=}CHCO_2H$$
$$|$$
$$CH_3$$

$$\text{I} \qquad\qquad\qquad\qquad \text{II}$$

to those of the 2-alkenoic acid obtained by dehydrohalogenation of 2-bromo-5-methylhendecanoic acid. Furthermore, our 2-dodecenoic acid (II) from dehydrohalogenation exhibited a melting point near that reported (6) for a sample of this acid prepared by the Doebner reaction. Since the Doebner reaction has yielded (7) crotonic acid, known to be *trans*, it seems established that the dehydrohalogenation reaction gives the *trans*-2-alkenoic acids. Myers (8) has reached this same conclusion on the basis of other evidence. It would be expected from the concerted nature of the base-catalyzed elimination reaction (9) that the *trans* isomer would result from the occurrence of elimination with the molecule in the least hindered conformation. In the case of the 2-methyl-2-alkenoic acids (1), however, the question arises as to whether the methyl or carboxyl will present less hindrance; so definite evidence on the geometrical isomerism of this type must await further investigation.

Although the literature contains numerous reports of syntheses of 2-alkenoic acids by dehydrohalogenation of 2-bromo acids with potassium hydroxide in methanol, our yields of pure 2-alkenoic acid were always low, and difficult, if at all possible, to separate from the other products of the reaction (2-methoxy and 2-hydroxy acids). Results were not improved significantly by use of ethanol or propanol as solvent. Myers (8) has recently reported that the 2-iodo acid gives better results, but his over-all yield of 2-alkenoic acid from stearic acid was 25 %, and about an equal amount of α-hydroxystearic acid was obtained.

The more serious side reactions encountered when n-alkoxides or alkali hydroxides are used for the dehydrohalogenation are eliminated by the use of potassium tert-butoxide in tert-butyl alcohol, and this method appears the most satisfactory one for obtaining 2-alkenoic acids from the saturated acids via the 2-bromo acids. Since α-halogenation of the higher fatty acids is slow and difficult to carry to completion, some saturated acid usually remains in the unsaturated acid, but this is readily removed by the method of partial esterification applied extensively by Linstead (10). Saturated ester may be readily separated from 2-bromo ester by fractional distillation, but attempted dehydrohalogenation of methyl 2-bromododecanoate with tert-butoxide, followed by saponification, yielded 2-methoxydodecanoic acid. Although the trans-esterification equilibrium is displaced almost entirely in favor of methyl ester, the low concentration of methoxide apparently competed successfully in displacement of the halogen.

In a previous paper (2), it was reported that saponification of pure 2-alkenoic or 3-alkenoic esters with 10 % potassium hydroxide gave a mixture of the respective 2- and 3-alkenoic acids. This was unexpected since Linstead (11) had reported that, in a case studied carefully by him, the 2- and 3-alkenoic acids were not equilibrated at an appreciable rate under these conditions. These apparently inconsistent results have now been correlated by the observation that our 5-methyl-2-hendecenoic acid also is not equilibrated in this way. Although saponification of an unhindered ester is rapid, it seems necessary to assume that very rapid equilibration occurs prior to saponification by way of the resonating enolate ion of the ester:

$$\overset{\ominus}{R}CHCH{=}CHCO_2C_2H_5 \leftrightarrow RCH{=}CH\overset{\ominus}{C}HCO_2C_2H_5$$
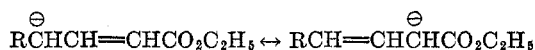
The ultraviolet spectra of the 2-alkenoic acids prepared in this investigation were determined in 95 % ethanol, and maxima were found in the region of 208–210 mμ, in agreement with the finding (2) reported for 2-nonenoic acid. For 2-dodecenoic acid, 5-methyl-2-hendecenoic acid, and 2-hexacosenoic acid respectively, the values determined for ϵ were 13,480; 13,520; and 13,850. It is of interest that these values are about 1,500 above that reported (2) for a 3-methyl-2-enoic acid, and more than 2,000 above the value (1) for a 2-methyl-2-enoic acid. Also, the methyl ester of 2-hexacosenoic acid showed an extinction coefficient identical (within experimental error) with that for the acid, whereas the esters of both types of methyl-substituted 2-enoic acids showed significantly

stronger absorption than did the acids. Although these differences might be ascribed to variable purity of the samples or unreliability of absorption data at these short wavelengths, an effort has been made to obtain pure compounds in all instances. Some evidence of purity of the compounds and reliability of the data are afforded by the consistent values cited above (also *cf.* Experimental and ref. 1) for the unsubstituted 2-enoic acids; also, the solid methyl 2-hexacosenoate showed nearly the same extinction coefficient as previously reported (2) for ethyl 2-nonenoate. These consistent values for ultraviolet absorption are in marked contrast to the variable ones recently reported by Jocelyn and Polgar (12).

EXPERIMENTAL[2]

n-Tetracosanoic acid. Methyl 6-ketotetracosanoate was prepared essentially as has been described for methyl 3,3-dimethyl-5-ketooctadecanoate (13). From 0.3 mole of magnesium, 0.3 mole of octadecyl bromide [fractionated, b.p. 178° (2 mm.), n_D^{25} 1.4607], 0.018 mole of anhydrous cadmium chloride, and 0.2 mole of δ-carbethoxyvaleryl chloride,[3] there was obtained 110 g. of crude keto ester, which was not distilled but subjected directly to the modified Wolff-Kishner reduction (14). The crude acid obtained from the reduction mixture was esterified with 20 equivalents of commercial absolute ethanol containing 10% by weight of concentrated sulfuric acid. Fractionation yielded two principal fractions: (a) wt. 20.5 g., b.p. 160° (3 mm.), m.p. 25–27° (presumably octadecane containing a little octadecene, carried through from the cadmium reaction); (b) ethyl tetracosanoate, wt. 43.3 g. (54.5%, based on ester acid chloride), b.p. 228–229.5° (2.0 mm.), m.p. 51–54°; lit. (15) b.p. 198–199° (0.24 mm.), m.p. 54.8°. There was 20 g. of residue.

The ester was saponified with alcoholic potassium hydroxide, and the tetracosanoic acid, obtained directly by dilution and acidification of the reaction mixture, was used for the preparation of tetracosanal. A sample of this acid, crystallized once from acetone, gave a 90% recovery of material of m.p. 82.5–84.0° (lit. (16) m.p. 84.15°).

n-Tetracosanal. The reagents and conditions used for the Rosenmund reduction (17) were validated by preparation of the bisulfite addition compound of octadecanal in 61% yield (over-all, from stearic acid). This bisulfite compound gave mostly the polymer of octadecanal (m.p. of product, 55–70°) when heated under reflux for 1 hour with 10% sodium carbonate solution, but was cleaved to the aldehyde after stirring for 16 hours at room temperature with 10% carbonate solution.

n-Tetracosanoic acid (38.5 g.) was converted to the acid chloride with 19 ml. of thionyl chloride in 75 ml. of dry benzene (30–40° for 2 hours, to prevent crystallization of acid), then overnight at room temperature). After excess thionyl chloride had been thoroughly removed by distillation at reduced pressure, followed by distillation similarly of two 50-ml. portions of dry benzene, the residual acid chloride was reduced by the procedure described (17), using 5 g. of commercial 5% palladium-on-barium sulfate catalyst, 0.8 ml. of quinolinesulfur regulator, and 200 ml. of xylene. After catalyst had been removed by filtration with charcoal and Supercel, the xylene solution was diluted with 600 ml. of peroxide-free ether

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[2] All melting points are corrected unless otherwise specified, all boiling points are uncorrected. All distillations, except as otherwise specified, were through a 2-ft. column of the simple Podbielniak type (Cason and Rapoport, *Laboratory Text in Organic Chemistry*, Prentice-Hall, Inc., New York, 1950, p. 237). Microanalyses are by the Microanalytical Division, Dept. of Chemistry, University of California. Ultraviolet spectra were determined on a Beckman Model DU quartz spectrophotometer, in 95% ethanol solution, at concentrations such that optical densities were in the range 0.15–1.5.

[3] Prepared *via* the half ester, as in previous work: *cf.* Cason and Prout, *J. Am. Chem. Soc.*, **66**, 46 (1944).

and stirred overnight with 500 ml. of saturated sodium bisulfite solution. The addition compound, removed by filtration from the organic layer in which it was suspended, weighed 24.6 g. (57.5%).

The pulverized bisulfite compound was stirred for 48 hours with 12% potassium carbonate solution (more concentrated solution gave slower reaction) and 250 ml. of peroxide-free ether. At this point, 8.9 g. of solid was filtered from the two-phase solution and 10.1 g. of aldehyde, m.p. 57.5–62°, was recovered from the ether. After the solid had been stirred an additional 6 days with a similar two-phase mixture, 2.8 g. of solid was removed by filtration, and an additional 4.3 g. of aldehyde, m.p. 57–62°, was recovered. Various attempts to obtain a pure sample of aldehyde by crystallization from benzene, benzene-ether, or benzene-acetone, gave material melting in the range 80–86° (largely polymer, presumably). Sublimation gave material of m.p. 57–65°.

The *oxime* was prepared by heating for 3 hours a mixture of 1.87 g. of crude aldehyde, 25 ml. of absolute ethanol, 10 ml. of benzene, 5.5 ml. of pyridine, and 3.0 g. of hydroxylamine hydrochloride. The reaction mixture was diluted with water and the organic layer was worked up to yield 1.04 g. of yellow solid, m.p. 84–108°. After considerable manipulation including 14 crystallizations from benzene-ether and benzene-acetone, there was obtained 30 mg. of reasonably pure oxime, m.p. 112–113.5° (after 12th crystallization, m.p. 110–113.5°).

Anal. Calc'd for $C_{24}H_{49}NO$: N, 3.82. Found: N, 3.29.

2-Hexacosenoic acid was prepared by a Doebner reaction which used 9.7 g. of crude *n*-tetracosanal, 2.9 g. of malonic acid, 25 ml. of dry pyridine, and 0.25 ml. of piperidine. The mixture was heated at 60° for 4 hours, then raised gradually over a period of 3 hours to 125°. After the reaction mixture had been shaken out with a mixture of 200 ml. of 6 N sulfuric acid, 600 ml. of ether, 150 ml. of chloroform, and 170 ml. of benzene, 0.6 g. of solid was removed from the two-phase solution by filtration and discarded, and then the organic phase was stirred overnight with 250 ml. of saturated aqueous bisulfite. A small precipitate was filtered and discarded, then the acid obtained from the organic phase was crystallized from benzene-acetone (95 ml.: 50 ml.) to give 6.9 g. of brown solid, m.p. 63–72°. After two additional crystallizations (wt. 3.76 g., m.p. 66–76°), purification (13) by use of the Amberlite IRA-400 strong anion exchange resin (wt. 2.1 g., m.p. 75–78°), two crystallizations from ether (wt. 0.9 g., m.p. 77–80°), a second pass through Amberlite IRA-400, and three crystallizations from benzene-ether, there was obtained 0.45 g. of 2-hexacosenoic acid believed to be essentially pure; m.p. 79.4–80.2°, λ_{max} 210 mμ, ϵ_{max} 13,850 [single clearly defined band, of the usual form (1)].

Anal. Calc'd for $C_{26}H_{50}O_2$: Eq. wt., 395. Found: Eq. wt., 401.

Methyl 2-hexacosenoate was prepared by allowing 200 mg. of the purified acid to stand for three hours at room temperature with excess of diazomethane. After three crystallizations from acetone, the sample had m.p. 55–57°, and the ultraviolet spectrum showed two bands, ϵ_{210} 10,810 (max), ϵ_{295} 2,675 (max). Since it was suspected that the impurity was the pyrazoline arising from addition of diazomethane to the double bond, 120 mg. of ester was slowly sublimed at 140° (0.3 mm.), and the first 80 mg. collected was resublimed. The first 40 mg. collected from the second sublimation is regarded as pure ester, m.p. 54.3–57.6°, re-m.p. 55.8° (crystallized sample also melts completely when placed in a pre-heated bath at 55.8°; thus polymorphism is indicated), λ_{max} 210 mμ, ϵ_{max} 13,600 (single clearly defined band).

Anal. Calc'd for $C_{27}H_{52}O_2$: C, 79.35; H, 12.83.
          Found: C, 80.33; H, 12.29.

2-Bromo acids and esters. Of the numerous procedures examined for preparation of 2-bromoacids, the most satisfactory in our hands was a modification of the procedure of Clarke and Taylor (18), as described in the preceding paper (1) for preparation of 2-bromo-2-methyldodecanoic acid. Without a 2-substituent, the reaction was usually nearly complete in 10–12 hours, but an excess of bromine was necessary to accelerate the reaction and to compensate for losses in the stream of hydrogen bromide evolved. Complete elimination

of starting acid was difficult, but conversion to ester and distillation of bromo ester indicated yields of bromoacid of the order of 90%.

A method similar to that of Mendel and Coops (19) was regarded as most convenient for preparation of small lots of bromo ester. To a stirred mixture of 10 g. of dodecanoic acid [purified by distillation of the ester, b.p. 117–118° (5 mm.)] and 1.05 equiv. of phosphorus tribromide, heated on a steam-bath, there was added rapidly 1.05 mole-equiv. of bromine (conversion of tribromide to pentabromide), then an additional 1.10 mole-equiv. of bromine was added during about 15 mins. After the mixture had been heated with stirring for 4 hours, it was cooled to room temperature and 8 mole-equiv. of methanol was added. The mixture was stirred at room temperature for 30 mins. and under reflux for one hour, then worked up and fractionated to yield 90–95% of methyl 2-bromododecanoate, b.p. 141.5–143° (5 mm.), n_D^{25} 1.4585; lit. (20) b.p. 135–137° (3 mm.), n_D^{25} 1.4572.

Examination of procedures for dehydrohalogenation utilized 2-bromododecanoic acid or its ester. In some runs, the isomeric 5-methylhendecanoic acid was used with similar results. Representative runs are described.

A. Potassium hydroxide in methanol. A solution of 0.025 mole (7.3 g.) of methyl 2-bromododecanoate in 20 ml. of dry methanol was added to a solution of 8 equiv. (11.2 g.) of potassium hydroxide in 50 ml. of methanol. After this mixture had been heated under reflux for 90 mins. it was diluted with water and neutral material was removed by extraction with hexane. Acids were recovered from the aqueous phase after acidification, and distilled in a Claisen flask to yield 4.5 g. of product. Since pure bromo ester was used as starting material, acids expected from this procedure would be 2-dodecenoic acid, 2-hydroxydodecanoic acid, and 2-methoxydodecanoic acid. Percentages of these substances, respectively, may be estimated as 16%, 68%, and 16% from the following analytical data: n_D^{25} 1.4444, ϵ_{208} 2,160, eq. wt. 214. Efforts to separate pure 2-alkenoic acid by fractional distillation or countercurrent extraction were unsuccessful.

B. Potassium hydroxide in ethanol. Results were similar to those in *A* except that a fraction of 0.8 g. boiling slightly above the impure 2-alkenoic acid appeared to be principally *2-ethoxydodecanoic acid*, b.p. 166–168° (4 mm.), n_D^{25} 1.4420, m.p. 25–27° (uncorr.).

Anal. Calc'd for $C_{14}H_{28}O_3$: Eq. wt. 244. Found: Eq. wt. 245.

C. Potassium hydroxide in 1-propanol. From a 0.05-mole run, there was isolated by crystallization from 30 ml. of hexane 1.38 g. of 2-hydroxydodecanoic acid, m.p. 64–70°. After recrystallization, the m.p. was 73–74°, lit. (21), m.p. 73–74°. Fractionation of the material from the filtrate from the above crystallization, at 2 mm. pressure, yielded three fractions: (a) wt. 1.7 g., b.p. 145–150.5°, n_D^{25} 1.4527; (b) wt. 2.1 g., b.p. 150.5–156.2°, n_D^{25} 1.4464; (c) wt. 4.5 g., b.p. 156.2–157.3°, n_D^{25} 1.4394. The index of refraction indicates that Frac. (a) is about 75% 2-alkenoic acid, and a low yield of pure 2-alkenoic acid could no doubt be obtained by this method. Frac. (c) is largely *2-n-propoxydodecanoic acid*, which was purified by use of Amberlite IRA-400 and refractionation to yield 2.14 g., b.p. 166.5–167.5° (3 mm.), n_D^{25} 1.4412.

Anal. Calc'd for $C_{15}H_{30}O_3$: Eq. wt. 258. Found: Eq. wt. 262.

D. Potassium tert-butoxide with methyl 2-bromododecanoate. A solution of 15 g. (0.05 mole) of the bromo ester in 200 ml. of dry *tert*-butyl alcohol containing 0.25 mole of potassium *tert*-butoxide was heated under reflux for 2 hours. Water was added to the hot solution, and the cooled acidified solution was extracted with hexane. Concentration of the extract to 25 ml. and cooling to room temperature deposited a 60% yield of crystalline 2-methoxydodecanoic acid, m.p. 54.2–55.1°. Two additional crystallizations gave colorless needles, m.p. 55.0–55.9°; lit. (22) m.p. 52°.

Anal. Calc'd for $C_{13}H_{26}O_3$: C, 67.78; H, 11.37; Eq. wt., 230.
        Found: C, 67.87; H, 11.22; Eq. wt., 233.

2-Dodecenoic acid. The bromo acid was prepared from 10 g. of pure *n*-dodecanoic acid as described under preparation of bromo acids, and the crude bromo acid was added to 3 equivalents of potassium *tert*-butoxide solution (10 g. of potassium per 200 g. of dry *tert*-butyl alcohol) and heated under reflux for 4 hours. After a usual work-up involving dilution

with water, acidification, and extraction with hexane, the product was distilled at 4 mm. pressure to yield four fractions: (a) wt. 0.5 g., b.p. 86–153°; (b) wt. 1.76 g., b.p. 153–157.5°, n_D^{25} 1.4550; (c) wt. 3.63 g., b.p. 157.5–158.0°, n_D^{25} 1.4588, ϵ_{208} 10,910 (max); (d) wt. 1.98 g., b.p. 158.0–162.0°, n_D^{25} 1.4609, ϵ_{209} 10,980 (max). Total yield, fracs. (b–d), 74%.

To obtain the pure 2-alkenoic acid, 4.81 g. of fracs. (b) and (c) was partially esterified by allowing it to stand at 20° for 2 hours with 30 ml. of commercial absolute ethanol containing 2% of its weight of concentrated sulfuric acid. Separation of neutral and acidic material by use of Amberlite IRA-400, followed by distillation in a Claisen flask, yielded 2.75 g. of pure 2-dodecenoic acid, b.p. 148–150° (3 mm.), m.p. 16–19° (uncorr.), n_D^{25} 1.4580, ϵ_{208} 13,480 (max); lit. (6) b.p. 172–174° (8 mm.), m.p. 17°.

Methyl 5-keto-3-methylnonanoate was prepared from di-*n*-butylcadmium and β-methyl-γ-carbomethoxybutyryl chloride in the usual manner.[4] There was used 1.8 moles of *n*-butyl bromide per mole of ester acid chloride. In three runs of 0.5–2 moles, yields of ester, based on acid chloride, were 90–91%, b.p. 118–119° (7 mm.), n_D^{25} 1.4514.

Anal. Calc'd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.07.

Found: C, 66.07; H, 10.04.

3-Methylnonanoic acid was obtained from the above keto ester by the modified Wolff-Kishner reduction (14); yields 89–94%; b.p. 136–137° (7.5 mm.), n_D^{25} 1.4335; lit. (23) b.p. 133° (8 mm.), n_D^{25} 1.4339.

5-Methylhendecanoic acid was prepared in 89% yield from 1-bromo-4-methyldecane (24) and potassium cyanide according to the procedure of Ruhoff (25), except that the acid was directly fractionated, b.p. 153–154° (6 mm.), n_D^{25} 1.4393.

Anal. Calc'd for $C_{12}H_{24}O_2$: Eq. wt., 200.3. Found: Eq. wt., 199.3.

For the *methyl ester*, b.p. 116–117° (6.5 mm.), n_D^{25} 1.4304.

5-Methyl-2-hendecenoic acid. A. By the Doebner reaction. The Rosenmund reduction of 38.9 g. of 3-methylnonanoyl chloride, carried out as described for the reduction of *n*-tetracosanoyl chloride, yielded no pure aldehyde; 8.6 g. of impure aldehyde, b.p. 64–65° (4 mm.), n_D^{20} 1.4343, was obtained by cracking a polymer at 190–200°. There has been a previous report (26) of failure of the Rosenmund reduction with an acid chloride substituted by alkyls at the 2- and 3-positions.

When 16.4 g. of crude 3-methylnonanal was used in the Doebner condensation, essentially as described for the preparation of 2-hexacosenoic acid, distillation of the product at 9 mm. pressure yielded two principal fractions: (a) 3-methylnonanoic acid, wt. 4.7 g., b.p. 142–143°, n_D^{25} 1.4328; (b) 5-methyl-2-hendecenoic acid, wt. 3.4 g., b.p. 169–170°, n_D^{25} 1.4576. The latter fraction was purified by separation from neutral material by use of Amberlite IRA-400 strong anion exchange resin, and distillation. For the pure acid, wt. 2.38 g., b.p. 162–163° (7 mm.), n_D^{25} 1.4596, λ_{max} 210 mμ, ϵ 13,160.

Anal. Calc'd for $C_{12}H_{22}O_2$: Eq. wt., 198. Found: Eq. wt., 195.

B. By dehydrohalogenation. A 21-g. sample of 5-methylhendecanoic acid was converted to the unsaturated acid essentially as in the synthesis of 2-dodecenoic acid, except that heating with potassium *tert*-butoxide solution was for only 2 hours, and the partial esterification was repeated three times. The final yield of pure acid was 3.90 g. (19%), b.p. in a Claisen flask 158–161° (5 mm.), n_D^{25} 1.4587, λ_{max} 209 mμ, ϵ 13,520, Eq. wt., 206.

A 1-g. sample of this acid was heated under reflux for 75 mins. with a solution of 0.71 g. of potassium hydroxide in 12 ml. of 95% ethanol. The acid recovered from this treatment had unaltered physical constants, n_D^{25} 1.4587, ϵ_{209} 13,140 (max).

SUMMARY

trans-2-Alkenoic acids not substituted at the double bone may be conveniently prepared from the corresponding saturated acids by α-bromination with bromine, followed by dehydrohalogenation with potassium *tert*-butoxide. The Doebner

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[4] For references on this procedure and preparation of this ester acid chloride: *cf.* ref. 1.

synthesis of such unsaturated acids is limited by the difficulty of accessibility and instability sometimes encountered in higher aliphatic aldehydes.

Although heating a 2-alkenoic acid with 10% potassium hydroxide solution does not cause rapid equilibration with the 3-alkenoic acid, saponification of a pure 2-alkenoic ester under the same conditions does cause such equilibration.

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