[CONTRIBUTION FROM THE MEDICAL SCHOOL, UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

# UNSATURATED FATTY ACIDS. II.<sup>1</sup> SYNTHESIS OF cis- AND trans-5-OCTENOIC ACIDS<sup>2</sup>

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A program was recently initiated in these laboratories with the intention of elucidating some of the features of the metabolism of straight-chain fatty acids having carbon-carbon unsaturation. In connection with these studies (2) it became necessary to have several octenoic acids of high purity and established structure.

The present publication reports the synthesis and characterization of two new members of the series of eleven theoretically possible octenoic acids, only four of which have been described previously (3).

By suitable combination and application of the chloroalkyne synthesis of Henne and Greenlee (4) and stereospecific catalytic semihydrogenation (5), Strong and his associates (6) have recently provided a straight-forward general method for the preparation of straight-chain *cis*-mono-enoic fatty acids. As shown in the following diagram, this procedure has now been applied successfully to the synthesis of *cis*-5-octenoic acid (III):



Trimethylene iodochloride was condensed with sodium butynide in a liquid ammonia medium to give 1-chloroheptyne-4 (I). The chloro group of this intermediate was then replaced by cyano, using sodium cyanide, and the resulting nitrile (which was not isolated) hydrolyzed directly to II, m.p.  $8^{\circ}$ .<sup>3</sup> The overall yield of II from trimethylene iodochloride was 30%. That II has the expected structure was shown by catalytic hydrogenation, in which process two

<sup>1</sup> Paper I of this series, entitled "A Total Synthesis of Linoleic Acid," was published recently elsewhere (1).

<sup>2</sup> This paper is based on work performed under Contract AT-04-1-GEN-12 between the Atomic Energy Commission and the University of California at Los Angeles.

<sup>3</sup> The preparation of 5-octynoic acid (II) by a procedure essentially the same as that employed in these laboratories was reported by Newman and Wotiz (7) while the present work was in progress. Completion of the synthesis of all the octynoic acids by Newman and Wotiz, together with the stereospecific semireduction methods revealed here and elsewhere (6) makes the full series of octenoic acids potentially available. molecular equivalents of hydrogen were absorbed and caprylic acid was formed; and by permanganate oxidation to propionic acid, in agreement with the location of the triple bond depicted in II.

Addition of one mole-equivalent of hydrogen to II in the presence of Raney nickel at room temperature and atmospheric pressure gave a product identified as cis-5-octenoic acid (III) on the basis of the following criteria: In experiments in which the catalytic hydrogenation of II was permitted to proceed to completion, a sharp decrease in rate of hydrogen-uptake was noted at the point of 50%-saturation; this manifestation of the fact that the rate of hydrogenation of II to III is much greater than that of the conversion of III to caprylic (octanoic) acid augurs well for the fact that the olefinic acid prepared under these conditions will be essentially free of II and caprylic acid. Confirmation of the homogeneity of this product was furnished by observations made during the preparation of solid derivatives from it (see Experimental). The cis-configuration of III is clearly indicated by its infrared absorption spectrum (Fig. 1, Curve B), most strikingly by the absence of the intense narrow  $10.3-\mu$  band so characteristic of trans-disubstituted olefins (8), and also by the presence of the weak broad band centered at ca. 13-14  $\mu$  which has been ascribed (8) to the *cis*-disubstituted ethylene group. In agreement with the classical generalization regarding the comparative melting points of *cis-trans* isomers, the *p*-phenylphenacylate of III (m.p. 47°) melted several degrees lower than that of its trans-counterpart (m.p. 56°).

Although the catalytic semihydrogenation of the corresponding acetylenic acids provides a method generally applicable to the preparation of *cis*-enoic straight-chain fatty acids (6) essentially uncontaminated by isomeric substances, no equally attractive general synthesis of the corresponding *trans*acids has been developed. Ahmad, Bumpus, and Strong (6) have obtained a *trans*-acid of this type by selenium-isomerization (elaidinization) of the *cis*isomer, but this procedure is obviously limited to cases in which some property (such as high melting-point) permits facile separation of the desired compound from greater or lesser amounts of unchanged precursor remaining in the resulting equilibrium mixture. The production of mixtures (particularly serious in the case of higher fatty acids, whose minor differences in physical properties and propensity for solid-solution formation make clean separations exceedingly difficult) evokes adverse evaluation also of other procedures (9) devised in the past for the synthesis of *trans*-olefinic fatty acids.

Although the conversion of symmetrically disubstituted acetylenes to *trans*olefins through the mediation of a solution of metallic sodium in liquid ammonia apparently had not been applied previously to a compound containing the carboxyl function, the high stereospecificity of this method of semireduction (5) and the availability of the requisite 5-octynoic acid (II) were strong factors favoring an attempt to prepare *trans*-5-octenoic acid (IV) by this procedure. In order to increase its compatability with the sodium-liquid ammonia solution, II was first converted to its sodium salt.



The product of this reaction, which was obtained in high yield, was shown to be IV on the basis of the following observations: first, its properties and those of its derivatives differed from those of the starting material (II) and of its *cis*-isomer (III); and second, its infrared absorption spectrum (see Fig. 1, Curve D) exhibited the intense  $10.3-\mu$  peak characteristic of the *trans*-disubstituted ethylene group (8), in contradistinction to the spectra of II (Curve E), III (Curve B), and caprylic acid (Curve A).



FIGURE 1. INFRARED ABSORPTION SPECTRA OF A: octanoic (caprylic) acid; B: cis-5octenoic acid (III); C: trans-5-octenoic acid (IV) from IX; D: same from sodium-liquidammonia reduction of II; E: 5-octynoic acid (II); and F: trans-3-hexenoic acid (V). All curves were run using 0.1-mm. cells and 5 weight-% solutions in carbon tetrachloride; because of the strong absorption of this solvent in the 12.5-13.2- $\mu$  region, features in this wavelength range are probably non-characteristic.

Additional confirmation of the identity of the product (IV) of the novel sodium-liquid ammonia semireduction of II was afforded by the synthesis of the same substance by a modification of a more conventional procedure employed earlier (10) in the preparation of a homolog of IV.

$$\begin{array}{c} C_{2}H_{5}CH=\!\!\!CHCH_{2}COOH \rightarrow C_{2}H_{5}CH=\!\!\!CHCH_{2}CH_{2}OH \rightarrow C_{2}H_{5}CH=\!\!\!CHCH_{2}CH_{2}Br \rightarrow \\ V & VI \\ C_{2}H_{5}CH=\!\!\!CHCH_{2}CH_{2}CH_{2}CH(COOC_{2}H_{5})_{2} \rightarrow C_{2}H_{5}CH=\!\!CHCH_{2}CH_{2}CH_{2}CH(COOH)_{2} \rightarrow IV \\ VIII & IX \end{array}$$

trans-3-Hexenoic acid (V), prepared (11) by the Knoevenagel reaction of *n*-butyraldehyde with malonic acid in the presence of triethanolamine, was reduced to trans-3-hexenol-1 (VI) via lithium aluminum hydride [cf. Crombie and Harper (8)]. The action of phosphorus tribromide and pyridine on VI gave the bromide (VII), which, on reaction with sodiomalonic ester, gave ethyl trans-3hexenylmalonate (VIII). The corresponding free acid (IX), obtained by saponification of VIII, was readily decarboxylated by heating, giving IV. Evidence that the double bond in the hexenoic acid used as a starting material in this synthesis has the trans-configuration has been summarized by Crombie and Harper (8); further substantiation of this important fact is afforded by the presence of the 10.3- $\mu$  spike in the infrared absorption spectrum (Fig. 1, Curve F) of the substance. None of the operations employed in converting V to IV was of a type which would be expected to alter the geometric configuration of the double-bond; the homogeneity of the crystalline intermediate malonic acid (IX) attested the fact that no such isomerization had occurred.

Identity of samples of *trans*-5-octenoic acid prepared by the two methods was established on bases of physical constants, mixed melting points of the free acids and of their p-phenylphenacyl esters, and infrared spectra (that of IV prepared *via* the malonic ester synthesis is shown in Fig. 1, Curve C).

The studies reported here have demonstrated that *trans*-5-octenoic acid of high stereoisomeric purity can be prepared simply and in excellent yield by the action of liquid-ammonia solutions of metallic sodium on the corresponding acetylenic acid (II). At the present time, however, claims for general applicability of the method cannot be made without reservation in view of reported failures (12) of this reagent to effect reduction of certain octadecynoic acids; these failures have been ascribed provisionally to poor solubility relationships which are probably of less importance in application of the reduction to lower homologs.

#### EXPERIMENTAL PART

All melting points are corrected and were determined in an apparatus of the Hershberg type, heated electrically in such a way that the rate of heating at the reported melting point was 0.5°/min.; numbers reported as melting points of substances melting below room temperature represent the temperature at which the last visible particle of solid in the melt liquifies [see Experimental, ref.(1)]. Microanalyses were performed by Dr. A. Elek of the Elek Microanalytical Laboratories, Los Angeles; and infrared absorption spectroscopy by Dr. Ralph Nusbaum of the Spectroscopy Section of this project. A Baird Model B Infrared Spectrophotometer fitted with a sodium chloride prism was employed.

Trimethylene iodochloride was prepared essentially as described by Hass and Huffman

(13), by the action of an acetone solution of sodium iodide on trimethylene chloride (Eastman), although the yield (53%) reported by them could not be duplicated. One-mole runs gave 34-39% yields of the desired product, b.p.  $90-95^{\circ}$  at 45 mm.

1-Chloroheptyne-4 (I) was obtained by the interaction of sodamide, 1-butyne (Farchan), and trimethylene iodochloride in liquid ammonia solution employing conditions resembling closely those used by Strong and coworkers (6) in the preparation of analogous compounds. The yield of I, b.p. 74-75° at 31 mm.,  $n_2^{20}$  1.4517, Emich micro-b.p. 168° at 755 mm., was 38.6%. Although this material gave analytical results somewhat at variance with theory, it was of adequate purity to serve as the precursor of II (see below).

Anal. Cale'd for C<sub>7</sub>H<sub>11</sub>Cl: C, 64.36; H, 8.49; Cl, 27.15.

Found: C, 65.10; H, 8.40; Cl, 26.45.

Newman and Wotiz (7), who employed trimethylene bromochloride (instead of the iodochloride) to obtain I (yield, 30%), have indicated that I prepared in this way is not spectroscopically pure; a sample prepared by them in another way and subjected to careful purification showed  $n_D^{25}$  1.4540 and b.p. 164° at 1 atm.

5-Octynoic acid (II). The action of sodium cyanide on I, followed by alkaline hydrolysis of the resulting crude acetylenic nitrile [analogous reactions have been described in detail by Strong and his associates (6)] gave a 77% yield of II, b.p. 95-96.5° at 0.3 mm.,  $n_{2}^{55}$  1.4555,  $d_{2}^{77}$  0.9787, M<sub>p</sub> 38.7 (Calc'd 38.7). This product, which decolorized alkaline permanganate rapidly, solidified on cooling (micaceous colorless flakes) and had m.p. 7.6°; Newman and Wotiz (7) give b.p. 111° at 2 mm.,  $n_{2}^{25}$  1.4540, and m.p. 8°.

Anal. Calc'd for C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>: C, 68.54; H, 8.63; Neut. equiv., 140.

Found: C, 68.44; H, 8.58; Neut. equiv., 141, 140.

The methyl ester of II was prepared in 92% yield (0.02-mole run) by refluxing the acid overnight in methanol containing a small amount of p-toluenesulfonic acid (7); the product was a colorless oil of mixed esterish and acetylenic odor, b.p. 60° at about 2 mm.,  $n_{2}^{\frac{15}{2}}$  1.4425 [lit. (7), b.p. 64° at 2 mm.,  $n_{2}^{\frac{15}{2}}$  1.4421]. An attempt was made to convert this ester to the amide, which was to be compared with that described by Newman and Wotiz (7), m.p. 105°; however, a solution of 0.12 g. of the ester in about 2 ml. of liquid ammonia left over the weekend in a sealed tube at room temperature yielded only a trace of crystalline material. Subsequently, there came to our attention work of Roe, Scanlan, and Swern (14) indicating that temperatures in the neighborhood of 175° are necessary in order to convert fatty acid esters to amides with undiluted ammonia; use of a concentrated methanol solution of ammonia seems to have been more effective in the conversion of methyl caprylate to caprylamide (see below).

The *p*-bromophenacyl ester of II, prepared in the usual way (15), was recrystallized from methanol or from  $60-70^{\circ}$  petroleum ether-benzene, glistening white plates, m.p.  $63.3-64.3^{\circ}$ , mixed m.p. with the corresponding derivative of caprylic acid (see below)  $49-56^{\circ}$ .

Recrystallization of the *p-phenylphenacyl ester of II* from methanol gave clusters of irregular colorless blades, m.p. 75.1-75.5°.

Anal. Cale'd for  $C_{22}H_{22}O_3$ : C, 79.01; H, 6.63.

Found: C, 79.08; H, 6.65.

Cooling and scratching an equimolar mixture of II and benzylamine (16) gave a crystalline solid which, by seeding, could be recrystallized from a small amount of ethyl acetate at  $-15^{\circ}$ , white flaky solid, m.p. 45-46°, whose hygroscopic nature and poor crystallizing power made it ill-suited for characterization or analysis.

Permanganate oxidation of II. Compound II (0.70 g., 0.005 mole) was dissolved in 10 ml. of 10% aqueous sodium bicarbonate and, with stirring and ice-cooling, was treated with slightly more than two molecular equivalents of potassium permanganate in 3% aqueous solution, added at a rate approximating that at which the reagent was decolorized. Solids were filtered from the reaction mixture with the aid of Celite and the filtrate concentrated to about 10 ml. Then 50% aqueous sulfuric acid (10 ml.) was added and about 10 ml. of the resulting acidic mixture distilled off through a short bead-packed column. Titration of this distillate with aqueous sodium hydroxide showed it to contain 0.00176 mole of free acid.

Treatment of the titrated aqueous solution with 0.40 g. (theoretical mole-equiv., 0.49 g.) of *p*-bromophenacyl bromide in the usual way (15) gave 0.35 g. of a pale yellow, flaky solid, crude m.p. about 50–60°. Recrystallization of this material from 60–70° petroleum ether gave clusters of large colorless plates, m.p.  $61.4-62.4^\circ$ , identified as the *p*-bromophenacyl ester of propionic acid by mixed m.p.  $(61.6-62.6^\circ)$  with an authentic sample.

Complete hydrogenation of II. A mixture of 0.4 g. of II, about 0.5 ml. of an ethanol paste of W-5 Raney nickel catalyst (17), and 25 ml. of absolute ethanol was shaken with moist hydrogen at room temperature and atmospheric pressure; the acid was added after the solvent and catalyst had been saturated with hydrogen. One molecular equivalent of hydrogen was taken up in about ten minutes, while absorption of the second required about four hours longer. These observations are in qualitative agreement with those of Adkins and Billica (17) in connection with the hydrogenation of stearolic acid under similar conditions. Removal of catalyst and solvent left 0.37 g. of residual oil, a sample of which, after distillation in a highly-evacuated Emich microfractionating tube (18), melted at 14.1°; after admixture with an approximately equal amount of authentic caprylic acid (m.p. 16.0°), a melting point of 15.0° was observed. Another sample of the reduction product was converted to the p-bromophenacyl ester, m.p. 65.2-66.6°, unaffected by admixture with authentic caprylic acid p-bromophenacylate.

Although the following observation was unconfirmed, it may be of interest that in the hydrogenation of a 1.40-g. sample of the methyl ester of II under essentially the same conditions, no break in the hydrogen uptake rate occurred. Two molecular equivalents of the gas were absorbed, yielding 1.39 g. (theory 1.44 g.) of fragrant colorless oil, b.p. 58.8-58.9° at 2 mm. A small amount (0.15 g.) of this oil was dissolved in 3 ml. of a 17% solution of anhydrous ammonia in absolute methanol and allowed to remain, tightly stoppered, at room temperature for three days. Removal of volatile material in a stream of dry air left a residue whose odor indicated the presence of some unchanged ester; this was removed by applying a 5-mm. vacuum for some time, leaving 0.06 g. of white flakes, m.p. 105.2-105.9°, raised by recrystallization from benzene to 105.4-106.0°, in good agreement with that reported for caprylamide by Hofmann (19).

Controlled hydrogenation of II. cis-5-Octenoic acid (III). The conversion of II to III was easily carried out as indicated above, except that the shaking with hydrogen was discontinued when the sharp decrease in hydrogen uptake rate was noted, or, if the quantitative nature of the hydrogenation apparatus permitted, when one molecular equivalent of hydrogen had been absorbed. As soon as possible after the completion of the reaction had been noted in either of these ways, the catalyst was centrifuged from the reaction mixture. The yields of III were, aside from mechanical losses, essentially quantitative. III is a colorless oil of typical unsaturated-fatty-acid odor; it exhibited the following physical properties: b.p. 88.5° at 0.4 mm.,  $n_p^{a}$  1.4434,  $n_p^{38}$  1.4422,  $d_1^{24}$  0.9604.

Anal. Calc'd for C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>: C, 67.56; H, 9.92; Neut. equiv. 142.

Found: C, 67.48; H, 9.92; Neut. equiv. 141.5, 142.

A 1.17-g. sample of this material on treatment with diazomethane in the usual way gave 0.95 g. (74%) of the corresponding *methyl ester*, a fragrant, colorless oil, b.p. 63° at 5.5 mm.

The *p*-bromophenacyl ester of III crystallized from 60-70° petroleum ether as fine colorless needles, m.p. 47.2-48.0° with some prior sintering.

Anal. Calc'd for C16H19BrO3: C, 56.65; H, 5.65.

Found: C, 56.56; H, 5.74.

The *p*-phenylphenacyl ester, recrystallized from petroleum ether, melted at 46.8-47.2°.

Anal. Calc'd for C<sub>22</sub>H<sub>24</sub>O<sub>3</sub>: C, 78.54; H, 7.19.

Found: C, 78.58; H, 7.30.

An adduct of III with 2,4-dinitrobenzenesulfenyl chloride (kindly supplied by Prof. N. Kharash, University of Southern California) was prepared by heating 0.20 g. each of the acid and the reagent in 5 ml. of glacial acetic acid on a steam-bath for 25 minutes. Pouring the resulting solution into ice-water gave a very viscous clear yellow oil which crystallized on standing. The adduct, which formed supersaturated solutions readily in benzene and

emerged therefrom slowly even after seeding, formed clusters of tiny light-yellow needles, m.p. 148.2-149.6°.

Anal. Calc'd for C<sub>14</sub>H<sub>17</sub>ClN<sub>2</sub>O<sub>6</sub>S: C, 44.62; H, 4.55.

Found: C, 44.66; H, 4.56.

trans-3-Hexenoic acid (V), prepared according to the directions of Linstead, Noble, and Boorman (11), was obtained in 31% yield; it boiled at  $106.5-108^{\circ}$  at 18 mm. and melted at  $13.4^{\circ}$ . A sample freed of traces of oil by centrifugal filtration at  $10^{\circ}$  melted at  $14.6^{\circ}$  [Linstead and co-workers (11) gave m.p.  $12^{\circ}$ ], but inasmuch as the infrared absorption spectrum (see Fig. 1, Curve F)<sup>4</sup> was not changed appreciably by this treatment, the crude material was used in the following step.

trans-3-Hexenol-1 (VI). Reduction of 29.8 g. (0.258 mole) of V with 12.3 g. (0.323 mole) = 25% excess) of lithium aluminum hydride gave 21.0 g. (81%) of VI, b.p. 53° at 9 mm., in agreement with Crombie and Harper (8).

1-Bromo-trans-3-hexene (VII). Four groups of investigators have reported preparing 1-bromo-3-hexenes within the recent past, but the materials described in three of these communications (21) must be presumed to have the *cis*-configuration, at least predominantly, since they were prepared from the so-called "leaf alcohol", a naturally-occurring 3-hexenol-1 shown recently by Crombie and Harper and by Sondheimer (8) to have the *cis*-structure. More recently Normant (22) has described a bromide whose immediate precursor was a 3-hexenol-1 synthesized by a procedure shown in studies of analogous reactions in these laboratories (23) and elsewhere (24) to yield products of greatly predominant *trans*-configuration.

Following a procedure outlined by Goering, Cristol, and Dittmer (25) for the preparation of the next lower homolog of VII, 21.0 g. (0.21 mole) of VI gave 14 g. (41%) of VII, b.p. 72° at 44 mm.,  $n_2^{24}$  1.4671,  $d^{27}$  1.203, M<sub>p</sub> 37.54 (Calc'd 37.21); Normant's product (22) had b.p. 44-45° at 12 mm. and  $d^{15}$  1.212.

Anal. Calc'd for C<sub>6</sub>H<sub>11</sub>Br: C, 44.19; H, 6.80.

Found: C, 44.23; H, 6.88.

The infrared absorption spectrum of VII (5 weight-% in carbon tetrachloride; 0.1-mm. cell) shows the "trans-olefin" peak strongly (at 10.3 $\mu$ , 31.5% transmission); this material is essentially transparent in the 2-16 $\mu$  range with the exception of the peak mentioned above, the C—H groups at *ca*. 3.4 and 6.9 $\mu$ , and two unidentified sharp spikes at 7.88 $\mu$  (59% T) and 8.26 $\mu$  (54% T).

Ethyl trans-3-hexenylmalonate (VIII). To a solution of 1.97 g. (0.086 mole) of sodium in 150 ml. of absolute ethanol (26) was added 13.7 g. (0.086 mole) of freshly-redistilled ethyl malonate. Then 14 g. (0.086 mole) of VII was added over a period of 25 minutes. The resulting mixture, after refluxing for two hours and standing overnight at room temperature, was freed of most of its ethanol by heating on a steam-bath; the residue was cooled and treated with ice-water and the product extracted with ether. Dried and distilled, these extracts yielded 13.5 g. (65%) of VIII, b.p. 104–105° at 0.4 mm.,  $n_{\rm p}^{27}$  1.4362,  $d^{29.5}$  0.9719,  $M_{\rm p}$  65.09 (Calc'd 65.12).

Anal. Cale'd for C<sub>18</sub>H<sub>22</sub>O<sub>4</sub>: C, 64.43; H, 9.15.

Found: C, 64.34; H, 9.20.

trans-3-Hexenylmalonic acid (IX) was obtained by treating 5.0 g. (0.021 mole) of the ester (VIII) with a solution of 2.4 g. of potassium hydroxide in 2.7 ml. of water. Stirred magnetically, the mixture, after an induction period of about 15 minutes, heated spontaneously to 75° and became homogeneous. After standing overnight at room temperature and then washing with ether, the aqueous solution was acidified with 6 N hydrochloric acid and the product extracted with three 10-ml. portions of ether. Dried over magnesium sulfate and

<sup>&</sup>lt;sup>4</sup> The infrared absorption spectrum of V was reported in 1937 by Delaby and LeComte (20); with due respect for improvements in infrared spectroscopy which have been forthcoming in the interim, it is of interest that the absorption maxima reported by these authors bear little resemblance in position or intensity to those found in the present work.

freed of solvent, these extracts yielded a crystalline residue of IX weighing 4.0 g. (theory 3.9 g.) and melting at  $91.5-92.8^{\circ}$ . A small sample recrystallized from  $60-70^{\circ}$  petroleum ether-benzene melted at  $92.5-92.7^{\circ}$ .

Anal. Cale'd for  $C_9H_{14}O_4$ : C, 58.05; H, 7.58.

Found: C, 58.51; H, 7.66.

trans-5-Octenoic acid (IV). A. From the hexenylmalonic acid (IX). A small Claisen flask was charged with 2.4 g. (0.013 mole) of recrystallized IX (m.p. 91.8-92.6°) and the system evacuated to such an extent that the product (IV) would distill into the receiver (cooled in Dry-Ice) at the decarboxylation temperature of its precursor. Redistillation of the crude product (1.7 g.) gave 1.5 g. (80%) of IV, b.p. 85-87° at 0.2 mm.,  $n_2^{24}$  1.4431,  $d^{26}$  0.9339, M<sub>b</sub> 40.42 (Calc'd 40.22). On standing at -15° overnight, IV crystallized; it melted at -9°. The infrared absorption spectrum of this product is shown in Fig. 1, Curve C.

B. From 5-octynoic acid (II). A solution of 2.8 g. (0.02 mole) of II in a small amount of aqueous methanol was neutralized (against phenolphthalein) by the dropwise addition of dilute sodium hydroxide and freed of solvent. After the residual sodium 5-octynoate was dried by leaving it for several days in a vacuum-desiccator over concentrated sulfuric acid. it was slowly added with stirring to 1.4 g. (0.06 gram-atom) of sodium in 500 ml. of liquid ammonia. The ammonia was then allowed to evaporate overnight, a small stream of nitrogen being passed through the apparatus to prevent ingress of air. With the reaction vessel immersed in an ice-bath, the residual greyish solid was treated with 100 ml. of methanol (cautiously at first), then with 100 ml. of water. After acidification with 6 N hydrochloric acid, the liberated acid was taken up in three 25-ml. portions of 60-70° petroleum ether. These extracts were dried and freed of solvent and the residual oil distilled, giving 2.4 g. (85%) of IV, b.p. 75-80° at 0.15 mm.,  $n_{\rm p}^{20}$  1.4438,  $d^{23}$  0.9307, m.p. -12°, mixed m.p. with sample prepared by Method A (see above)  $-11^{\circ}$ . The identity of these two products was further substantiated by comparison of their infrared spectra (see Fig. 1, Curves C and D) and of the p-phenylphenacylates prepared from them (see below). Another sample of IV prepared by Method B (b.p. 84° at 0.5 mm.,  $n_{D}^{25}$  1.4440) was analyzed:

Anal. Calc'd for C<sub>8</sub>H<sub>14</sub>O<sub>2</sub>: C, 67.57; H, 9.92.

Found: C, 67.61; H, 9.99.

The *p*-phenylphenacylate of IV (prepared by Method B) formed clusters of jagged colorless plates from 60-70° petroleum ether, m.p. 53.2-54.1°; that from Method-A IV melted at 56.2-56.5°; a mixture of the two materials melted at 53.3-55.0°.

Anal. Calc'd for C<sub>22</sub>H<sub>24</sub>O<sub>8</sub>: C, 78.54; H, 7.19.

Found: C, 78.58; H, 7.26.

After some effort, it was possible to obtain the *benzylamine salt of IV* in a crystalline condition; however, the hygroscopicity and extraordinary solubility of this derivative in solvents of both polar and non-polar nature make it of doubtful utility for characterization. The salt dissolves readily in a small amount of  $60-70^{\circ}$  petroleum ether at room temperature; upon cooling such a solution to  $-15^{\circ}$  and seeding, the derivative is obtained as white plates, m.p.  $41.5-43.5^{\circ}$ 

#### SUMMARY

Two new octenoic acids have been synthesized and characterized. cis-5-Octenoic acid was obtained by catalytic semihydrogenation of 5-octynoic acid. trans-5-Octenoic acid was prepared by two methods: (1) a classical two-carbon elaboration of trans-3-hexenoic acid via the malonic ester synthesis and (2) a novel sodium-liquid-ammonia semireduction of the corresponding acetylenic acid.

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