ethylene chloride, trimethylene bromide, or tetramethylene chloride in 100 ml. of anhydrous ether, and the stirring continued for 35–40 min. In the experiment with methylene chloride, the reaction mixture was still deeply colored (cherry red) after this time but in the experiments with the other three halides the red color faded and a yellow or tan suspension was produced within a few minutes. The liquid ammonia was evaporated on the steam bath as an equal volume of ether was added. The resulting ethereal suspension was cooled and shaken with water. The two layers were separated. The aqueous layer was extracted with ether and the ethereal extract combined with the original ethereal layer. The ethereal solution was dried over Drierite, and the solvent removed. The residue was recrystallized from appropriate solvents to give the hydrocarbons I–IV. The data for these compounds are summarized in Table I. The molecular weights were estimated by boiling point elevations in chloroform solution.[13]

Benzylation of sodium triphenylmethide. This reagent (0.1 mole) was prepared as described below, and its alkylation with a molecular equivalent of benzyl chloride was effected essentially as described recently[2] for the corresponding alkylation of sodium diphenylmethide. There was obtained a 99% yield of 1,1,1,2-tetraphenylethane (V), m.p. 143–144° after recrystallization from benzene and petroleum ether. The reported melting point for this hydrocarbon is 144°.[8]

Twofold alkylations of sodium triphenylmethide with methylene halides. To a stirred suspension of 0.1 mole of sodium amide in 300–400 ml. of liquid ammonia[12] was added 24.4 g. (0.1 mole) of triphenylmethane in 50–100 ml. of anhydrous ether. The resulting dark red solution was stirred for 10 min. To this stirred reagent was added 0.05 mole of ethylene chloride, trimethylene bromide, or tetramethylene chloride in 50–100 ml. of anhydrous ether, and the stirring continued for 50–90 min. (Dry Ice condenser). The red color of the reagent was discharged within 15–45 min. The reaction mixture was worked up as described above for the experiments with sodium diphenylmethide. The results are summarized in Table II.

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[13] We are indebted to Mr. W. F. Owens, Jr., of Wake Forest College for these determinations.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND THE ENGINEERING EXPERIMENT STATION,
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Synthesis of Some Octenoic Acids

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Received October 18, 1958

The preparation and properties of *trans*-4- and -6- and of *cis*-3-, -4-, and -6-octenoic acids are reported in this paper. The previously reported isomers, *trans*-3- and *cis*-2-octenoic acids, are also reported in this paper. The *cis* acids were prepared by the catalytic semihydrogenation of the corresponding octynoic acids. The *trans* acids were obtained either directly or indirectly starting with a *trans* alkenoic acid obtained by a Knoevenagel condensation. Physical properties, including infrared spectra, were determined for all of the acids and most of the intermediates. The infrared spectra of the *trans* compounds showed strong absorption in the region of 10.2–10.35 microns. None of the *cis* compounds showed absorption in this region.

The isomeric unbranched octenoic acids were needed in a study of the ionization constants of unsaturated fatty acids. Of the eleven isomers, the following acids are reported in the literature: *trans*-2-,[2,3] *trans*-3-,[4] *trans*-5-,[5] *cis*-2,[2] *cis*-5-[5] and 7-octenoic acid.[6,7] The preparation and properties of the unreported isomers, *trans*-4- and -6- and *cis*-3-, -4-, and -6-octenoic acids, are presented in this paper. Due to the method of preparation of *trans*-3-octenoic acid and the lack of agreement of physical constants for *cis*-2-octenoic acid, the preparation and properties of these acids are also included. The physical properties of the acids are given in Table I.

The *cis* octenoic acids were prepared by catalytic semihydrogenation of the corresponding octynoic acids. Hydrogenation of acetylenic compounds in the presence of catalytic substances is reported to give predominantly *cis* ethylenic compounds.[8–11] This method has been used to prepare unsaturated acids[5,6] and hydrocarbons[12] having a *cis* configuration. In this work, W-5 Raney nickel[13] which had been aged five to six months was used as the catalyst, and dry thiophene-free benzene was found to be the most suitable solvent. In previous studies[5,14] a sharp decrease in the rate of hydrogenation was reported to occur after one molar equivalent of hydrogen had been absorbed. In

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[1] Abstracted in part from the M.S. thesis of James H. Diamond. Present address: Hastings Chemical Division, Minnesota Mining and Manufacturing Company, Saint Paul, Minn.

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TABLE I

PHYSICAL PROPERTIES OF OCTENOIC ACIDS

Octenoic Acid	Boiling Point, °C.	Melting Point, °C.	n_D^{20}	Density, 20°	Molar Refraction	Analyses, Found Carbon	Hydrogen
cis-2-[a]	89 (0.9 mm.)	−6	1.4441	0.9234	40.91[b]	67.1[c]	9.75
cis-3-	96 (0.5 mm.)	−25	1.4433	0.9352	40.33	67.4	9.82
cis-4-	96 (0.8 mm.)	−35	1.4417	0.9301	40.43	67.3	9.84
cis-6-	88 (0.8 mm.)	−17	1.4441	0.9378	40.29	67.2	9.70
trans-3-[d]	92 (1.4 mm.)	1	1.4452	0.9378	40.37	67.0	9.82
trans-4-	93 (1.5 mm.)	−4	1.4441	0.9313	40.57	67.5	9.89
trans-6-	90 (1.2 mm.)	6	1.4454	0.9422	40.20	67.3	9.93

[a] Bourguel, *Bull. soc. chim. France*, **45**, 1067 (1929), reported for *cis*-2-octenoic acid, b.p. 127° at 15 mm., n_D^{20} 1.456, density 0.940 at 15°. [b] Calculated molar refraction of octenoic acid, 40.26. The atomic and multiple bond refraction constants were taken from A. Weissberger, *Physical Methods of Organic Chemistry*, Vol. I, Interscience Publishers, Inc., New York, N. Y., 1945, pp. 672–80. [c] Calculated for octenoic acid: C, 67.6; H, 9.92. Microanalyses by Weiler and Strauss, Microanalytical Laboratory, 164 Banbury Road, Oxford, England. [d] Delaby and Lecomte, *Bull. soc. chim. France*, **4**, 1007 (1937), reported for *trans*-3-octenoic acid, b.p. 142° at 19 mm., n_D^{20} 1.4456, density 0.942 at 20°.

this work there was in no instance a sharp break in the rate of hydrogenation. After the approximate theoretical volume of hydrogen was absorbed, there was observed a gradual decrease in the rate of hydrogenation. Therefore, the most likely impurities in the *cis*-octenoic acids prepared in this manner are the parent acetylenic acid and octanoic acid.

Catalytic semihydrogenation of 2-octynoic acid gave the *cis*-2-octenoic acid.

cis-3-Octenoic acid was prepared by the semihydrogenation of 3-octynoic acid which was synthesized by the following route rather than by a published method[15] since use of the latter gave an impure product. The 3-octyn-1-ol which had been obtained in 21% yield by Newman and Wotiz[15] from 1-hexynylsodium and ethylene oxide in liquid ammonia, and in 25% yield in the present investigation from 1-hexynylmagnesium bromide and ethylene oxide in ethyl ether, was obtained in markedly improved yield, 81%, by carrying out the Grignard reaction in benzene. The use of benzene in place of ether allows a higher reflux temperature thus enabling the thermal rearrangement of the first formed, weakly bound oxonium complex[16] to take place. Oxidation of normal C_4, C_5, and C_6 acetylenic primary alcohols has been reported[17,18] to give the corresponding acetylenic acids in yields of 11 to 50%. Oxidation of the 3-octyn-1-ol gave a 21% yield of 3-octynoic acid when a mixed solvent of water and acetone was used, whereas with water alone the yield was only 2.3%.

$$C_4H_9C{\equiv}CH \xrightarrow{C_2H_5MgBr} C_4H_9C{\equiv}CMgBr \xrightarrow[(2)\ H_2O,\ H+]{(1)\ (CH_2)_2O}$$

$$C_4H_9C{\equiv}CCH_2CH_2OH \xrightarrow{CrO_3,\ H_2SO_4} C_4H_9C{\equiv}CCH_2COOH$$

cis-4- and *cis*-6-Octenoic acids were prepared by catalytic semihydrogenation of the corresponding octynoic acids, prepared as previously reported.[15]

The *trans*-octenoic acids were prepared by utilizing the Knoevenagel condensation. Evidence that the acids produced by a Knoevenagel condensation, as well as the alcohols and bromides obtained from these acids, have a *trans* configuration is supported by the strong infrared absorption of these compounds in the 10.3-micron region.[19] The Knoevenagel condensation in the presence of pyridine yields the *trans*-2-alkenoic acid whereas in the presence of triethanolamine, the *trans*-3-alkenoic acid is formed.[20]

The reported preparation of *trans*-3-octenoic acid[4] involved an allylic rearrangement of 1-hepten-3-ol to 1-bromo-2-heptene during bromination of the alcohol with phosphorus tribromide. In view of the fact that the conversion of secondary allylic alcohols to bromides with phosphorus tri-

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bromide is reported[21] to give, under ordinary preparative conditions, an equilibrium mixture containing mainly the primary bromide along with 10 to 20% of the secondary bromide, it seems likely that the previously reported *trans*-3-octenoic acid contained isomeric impurities. *trans*-3-Octenoic acid was prepared by the condensation of *n*-hexaldehyde and malonic acid in triethanolamine.

trans-4-Octenoic acid was prepared by the following series of reactions:

$$\mathrm{C_4H_9CHO} \xrightarrow[\text{Triethanolamine}]{\mathrm{CH_2(COOH)_2}}$$

$$\mathrm{C_3H_7CH{=}CHCH_2COOH} \xrightarrow[\text{(2) PBr}_3]{\text{(1) LiAlH}_4}$$

$$\mathrm{C_3H_7CH{=}CHCH_2CH_2Br} \xrightarrow[\text{(3) H}_2\text{O, H}^+]{\text{(1) Mg; (2) CO}_2}$$

$$\mathrm{C_3H_7CH{=}CHCH_2CH_2COOH}$$

trans-6-Octenoic acid was synthesized by the following series of reactions:

$$\mathrm{CH_3CH_2CHO} \xrightarrow[\text{Triethanolamine}]{\mathrm{CH_2(COOH)_2}}$$

$$\mathrm{CH_3CH{=}CHCH_2COOH} \xrightarrow[\text{(2) PBr}_3]{\text{(1) LiAlH}_4}$$

$$\mathrm{CH_3CH{=}CHCH_2CH_2Br} \xrightarrow[\text{(3) H}_2\text{O, H}^+]{\text{(1) Mg; (2) (CH}_2)_2\text{O}}$$

$$\mathrm{CH_3CH{=}CHCH_2CH_2CH_2CH_2OH} \xrightarrow{\mathrm{PBr_3}}$$

$$\mathrm{CH_3CH{=}CH(CH_2)_4Br} \xrightarrow[\text{(3) H}_2\text{O, H}^+]{\text{(1) Mg; (2) CO}_2}$$

$$\mathrm{CH_3CH{=}CH(CH_2)_4COOH}$$

EXPERIMENTAL

Boiling points and melting points are uncorrected.

cis-2-Octenoic acid.[2] 2-Octynoic acid,[22] b.p. 101° at 1 mm., was prepared in 58% yield by the carbonation of the Grignard reagent of 1-heptyne.

A 16.2-g. (0.12 mole) sample of 2-octynoic acid was semihydrogenated catalytically using 5 g. of W-5 Raney nickel,[13] aged for 5 to 6 months, and 100 ml. of benzene. The reaction was allowed to proceed until a 10% excess of hydrogen was taken up. After removal of the catalyst and benzene, rectification of the crude acid gave a 61% yield of *cis*-2-octenoic acid.

cis-3-Octenoic acid. 3-Octyn-1-ol. The Grignard reagent from 2.51 moles of ethyl bromide, using 2.66 g.-atoms of magnesium and 700 ml. of dry ether, was prepared in the usual manner. Seven hundred milliliters of dry, thiophene-free benzene was added to the ethereal solution of the Grignard reagent, and then a total of 700 ml. of solvent (mostly ether) was removed by distillation. The Grignard reagent was cooled to 10°, and a solution of 2.0 moles of 1-hexyne in 35 ml. of benzene was added over a period of 95 min. The reaction mixture, after refluxing for 5 hr., was a smooth grayish suspension. Ethylene oxide (2.82 moles) was passed onto the surface of the stirred 1-hexynylmagnesium bromide, which was cooled in an ice bath. The reaction mixture, after standing overnight, was refluxed for 4 hr. Six hundred milliliters of solvent was removed by distillation, and after cooling, the addition complex was decomposed by adding cold water and then cold 20% sulfuric acid. The organic layer was separated, dried over magnesium sulfate, and rectified The yield of 3-octyn-1-ol, b.p. 87° at 9 mm., n_{D}^{20} 1.4541, was 81%. Reported values of 3-octyn-1-ol are b.p. 97° at 15 mm. and n_{D}^{25} 1.4542.[23]

3-Octynoic acid. An oxidizing solution was prepared by dissolving 1.23 moles of chromium trioxide in 370 g. of conc. sulfuric acid and diluting with water to give 770 ml. of solution. A mixture of 110 g. (0.86 mole) of 3-octyn-1-ol, 160 ml. of water, and 350 ml. of acetone was cooled in an ice bath, and the oxidizing solution was added over a period of 4 hr. After stirring for an additional 4 hr. at 0°, the organic material was extracted with ether. The crude acid was freed of neutral impurities by extraction of the acid from the ethereal solution using potassium hydroxide solution. The free acid, recovered by acidification of basic solution, was dried over magnesium sulfate and then rectified. The acid was colorless when freshly distilled but turned yellow upon standing overnight. A yield of 21% of 3-octynoic acid, b.p. 85° at 0.4 mm., m.p. 19°, n_{D}^{20} 1.4573, was obtained. Recorded values for 3-octynoic acid are b.p. 110° at 2 mm., m.p. 18°, and n_{D}^{25} 1.4577.[15]

cis-3-Octenoic acid was prepared by semihydrogenating 21.5 g. (0.15 mole) of 3-octynoic acid using 16 g. of W-5 Raney nickel, aged for 5 to 6 months, and 70 ml. of benzene. After the theoretical quantity of hydrogen was taken up, the catalyst and solvent were removed, and an 82% yield of *cis*-3-octenoic acid was obtained upon fractional distillation of the crude acid.

cis-4-Octenoic acid. In essentially the same manner as described by Newman and Wotiz,[15] 4-octynoic acid, m.p. 49°, was prepared starting with 1-pentyne. Semihydrogenation of 0.096 mole of 4-octynoic acid using 7 g. of W-5 Raney nickel, aged 5 to 6 months, and 100 ml. of benzene gave a 69% yield of *cis*-4-octenoic acid.

cis-6-Octenoic acid. 6-Octynoic acid was prepared according to the procedure described by Newman and Wotiz.[15] The crude acid, purified by recrystallization from diethyl ether, had a m.p. of 44° whereas the reported value is 37°. A 0.143-mole sample of 6-octynoic acid was semihydrogenated using 13 g. of W-5 Raney nickel, aged 5 to 6 months, and 100 ml. of benzene. After the removal of the catalyst and benzene, the crude acid was rectified, giving a 71% yield of *cis*-6-octenoic acid.

trans-3-Octenoic acid. trans-3-Octenoic acid was prepared in a 35% yield by the condensation of *n*-hexaldehyde with malonic acid in the presence of triethanolamine in a manner similar to that described by Linstead and Noble[24] for the preparation of *trans*-3-hexenoic acid.

trans-4-Octenoic acid. trans-3-Heptenoic acid[25] was prepared by condensing 0.77 mole of 1-pentanal with 0.8 mole of malonic acid in the presence of 0.8 mole of triethanolamine. The yield was 18%; b.p. 77° at 0.5 mm., n_{D}^{20} 1.4410.

trans-3-Hepten-1-ol was prepared by the reduction of *trans*-3-heptenoic acid using lithium aluminum hydride.[26,27] The yield of the alcohol, b.p. 66° at 9 mm., n_{D}^{20} 1.4393, was 83%.

1-Bromo-*trans*-3-heptene was prepared, using the procedure of Crombie and Harper,[27] in a 59% yield. The product had a b.p. of 66° at 20 mm. and n_{D}^{20} 1.4687.

trans-4-Octenoic acid was prepared in a 38% yield by carbonation of the Grignard reagent from 26.1 g. (0.15 mole) of 1-bromo-3-heptene.

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trans-6-Octenoic acid. trans-3-Pentenoic acid[24] was prepared by condensing 5.20 moles of freshly distilled propionaldehyde with 5.20 moles of malonic acid in 5.20 moles of triethanolamine. The acid, obtained in a 13% yield, had a b.p. of 54° at 1 mm. and n_D^{20} 1.4357.

trans-3-Penten-1-ol[28] was prepared by the reduction of 1.28 moles of *trans*-3-pentenoic acid using 1.71 moles of lithium aluminum hydride. The alcohol, yield 81%, had a b.p. of 47° at 13 mm. and n_D^{20} 1.4334.

1-Bromo-*trans*-3-pentene was prepared in a 71% yield using 1.00 mole of *trans*-3-penten-1-ol, 0.41 mole of phosphorus tribromide, and 0.36 mole of dry pyridine in 75 ml. of carbon tetrachloride. The bromide, obtained in a 71% yield, had a b.p. of 80° at 152 mm. and n_D^{20} 1.4686.

trans-5-Hepten-1-ol was prepared by the reaction of the Grignard reagent from 0.70 mole of 1-bromo-*trans*-3-pentene and 0.94 mole of ethylene oxide. The procedure used was similar to that described by Huston and D'Arcy.[29] The alcohol was obtained in a 49% yield and had the following properties: b.p. 77° at 11 mm., n_D^{20} 1.4437, density 0.8536 g./ml. at 20°, m.p. of α-naphthylurethan, 79–80°.

Anal. Calcd. for $C_{13}H_{21}O_2N$: N, 4.95. Found: N, 4.98.

1-Bromo-*trans*-5-heptene was prepared in a 56% yield using 36.5 g. (0.32 mole) of *trans*-5-hepten-1-ol, 0.12 mole of pyridine, and 0.15 mole of phosphorus tribromide in 66 ml. of carbon tetrachloride. The bromide had a b.p. of 85° at 34 mm. and n_D^{20} 1.4691.

trans-6-Octenoic acid was prepared in a 52% yield by the carbonation of the Grignard reagent obtained from 30.1 g. (0.17 mole) of 1-bromo-*trans*-5-heptene.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF DELAWARE]

β-Cyano-α-hydroxycinnamates from the Xylenes

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Received October 20, 1958

This paper describes the synthesis, separation, and characterization of β-cyano-α-hydroxycinnamates from the xylenes. The separated isomers from *o*-xylene and *m*-xylene have been used to obtain pure hydrolytic cleavage products.

It has been shown in previous reports[1] that isomeric monoalkylphenylacetonitriles could be separated through the intermediate β-cyano-α-hydroxycinnamates. We have accordingly applied this process to the nitriles from the xylenes and have also characterized the products.

The mixture of monochloromethylation products from *o*-xylene led to a mixture of ethyl β-cyanodimethyl-α-hydroxycinnamates. The lower melting isomer I was best separated from the mixture by crystallization from ethyl acetate. The less abundant higher melting isomer II could then be obtained from the non-volatile residue of the filtrate by crystallization from toluene. The relative amounts of I and II that have been isolated are in the ratio 9:4.

Mild alkaline hydrolysis[1] of I gave the pure nitrile which was further hydrolyzed to 3,4-dimethylphenylacetic acid and a small amount of the amide. 3,4-Dimethylacetophenone[2a,b] synthesized from *o*-xylene was converted successively to 3,4-dimethylbenzoic acid, the acid chloride, the diazoketone and the identical 3,4-dimethylphenylacetic acid, thus establishing that I is ethyl β-cyano-3,4-dimethyl-α-hydroxycinnamate, and that the methyl groups in this series are in positions 3 and 4.

The nitrile from II was found to be a solid which by similar refluxing with alkali gave almost entirely the corresponding amide. This was converted to the acid by saponification in diethylene glycol. The structure of the acid was established by oxidation[3] to hemimellitic acid. This was converted to trimethyl hemimellitate which was identical with an authentic sample.[4] These facts show that in this series the methyl groups are in the 2,3-positions and that II is ethyl β-cyano-2,3-dimethyl-α-hydroxycinnamate.

Likewise the ethyl β-cyanodimethyl-α-hydroxycinnamates expected from the chloromethylation products of *m*-xylene (III,IV) and *p*-xylene (V) have been isolated. The separation of the esters derived from *m*-xylene was tedious due to the small amount of IV. Some simplification was attained by the fact that the sodium salt of III crystallized well from the alcohol medium and IV could be obtained from the filtrate. The mild alkaline hydrolysis of III gave the nitrile. More vigorous hydrolysis of III gave the amide and the acid. This acid was oxidized to trimellitic acid which shows that the methyl groups in III and its degradation products are in positions 2 and 4. Similarly the structure of the 2,6-isomer (IV) was shown by hydrolysis to the amide and acid followed by oxidation of the acid to hemimellitic acid. The identity of the single

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[4] We are indebted to Professor Lee Irvin Smith, University of Minnesota, for this sample.