residue. After adding ether to the alcoholic solution a small amount of a colorless solid separated. This air-dried solid began to melt at 130°, resolidified, softened again at 154° with the formation of gas bubbles. The ether–alcohol mother liquor was evaporated to a clear liquid which solidified on standing for one day at room temperature. Ether was added, the solid filtered, and recrystallized from water; m.p. 131–134° (Fuson and Cole reported a melting point of 139° for *cis*-cyclopentane-1,2-dicarboxylic acid[17]); neut. equiv., calcd. 79.1; found neut. equiv., 81.9.

The acid was converted to its N-phenylimide by the method of Tingle and Cram.[18] After two recrystallizations from water–ethanol (1:1) it melted at 87.5–88.5° (m.p. 89° reported by Fuson and Cole[17]). The acid was converted to its anhydride by heating in a test-tube with a free flame until it distilled on the side of the tube. After cooling the solid residue was recrystallized twice from petroleum ether (b.p. 40–50°); m.p. 68–71° (Fuson and Cole reported a melting point of 73.5–74°[17]).

Bicyclo[3.2.0]2-heptene (VIII).—This olefin was formed from I or II by a modification of the Wolff–Kishner reduction.[8] From 8.4 g. (0.078 mole) of I or II, 4.9 g. (70%) of VIII, b.p. 101.5–103°, was obtained. On redistillation this gave 3.4 g.; b.p. 102.5–103°; n^{20}_{D} 1.4646; d^{20}_{4} 0.8703; M_D 29.88 (calcd. M_D 30.17).

Anal. Calcd. for C_7H_{10}: C, 89.29; H, 10.71. Found: C, 89.10; H, 10.71.

On microhydrogenation of a 253-mg. sample over 25 mg. of pre-reduced platinum oxide catalyst in 10 cc. of 95% ethanol, 98.1% of one molar equivalent of hydrogen was absorbed.

Bicyclo[3.2.0]heptane (IX).—To the above hydrogenation mixture was added an additional 2.97 g. of VIII and this also was reduced. After removal of the platinum, 20 cc. of water was added to the alcoholic solution. The hydrocarbon layer was dried over anhydrous magnesium sulfate and distilled over sodium to give 2.5 g. (76%) of IX, b.p. 105–110°. The main fraction (2.1 g.) boiled at 109–109.5°; n^{20}_{D} 1.4532; d^{20}_{4} 0.8522; M_D 30.52 (calcd. M_D 30.64).

Bicyclo[4.2.0]-?-octen-7-one (X or XI).—This was prepared by a method similar to that used for I or II. A mixture of 80 cc. of toluene, 22 g. (0.27 mole) of 1,3-cyclohexadiene, and 0.34 mole of ketene was heated in a bomb at 100° for four hours and yielded 2.2 g. of crude ketone, b.p. 97–137° (92 mm.). This crude ketone gave 2.3 g. of its semicarbazone, m.p. 194.5–198.5° which was recrystallized from methanol–water (3:1), m.p. 200.5–201°.

Anal. Calcd. for $C_9H_{13}N_3O$: C, 60.31; H, 7.31; N, 23.45. Found: C, 60.36; H, 7.06; N, 23.56.

On hydrolysis, 2.22 g. of the semicarbazone afforded 1.00 g. (66%) of bicyclo[4.2.0]-?-octen-7-one; b.p: 190.5–192°; n^{20}_{D} 1.4950; d^{20}_{4} 1.024; M_D 34.79 (calcd. M_D 34.80).

On microhydrogenation of a 310-mg. sample over 30 mg. of pre-reduced platinum oxide catalyst in 10 cc. of 95% ethanol, 99.6% of one molar equivalent of hydrogen was absorbed.

Bicyclo[4.2.0]octan-7-one Semicarbazone.—To the above hydrogenation mixture was added an additional 0.624 g. of X or XI (total 0.934 g.) which was also reduced. After filtering the platinum the alcohol was removed by distillation under diminished pressure. The residue could not be distilled because of foaming and it was converted directly to its semicarbazone. After two recrystallizations from methanol–water (2:1), 0.6 g. (43.3%) of XII semicarbazone was obtained, m.p. 164–166°.

Anal. Calcd. for $C_9H_{15}N_3O$: C, 59.64; H, 8.34; N, 23.19. Found: C, 59.47; H, 8.31; N, 23.14.

Bicyclo[4.2.0]-2-octene (XIII).—This was obtained from X or XI semicarbazone, m.p. 185–191°, without purification of the intermediate ketone. From 6.2 g. (0.0346 mole) of the semicarbazone 4.1 g. (97%) of crude ketone was obtained. This was reduced by the modified Wolff–Kishner method[8] to give 1.5 g. (41.5%) of XIII; b.p. 137–139°; n^{20}_{D} 1.4810; d^{20}_{4} 0.8948; M_D 34.40 (calcd. M_D 34.79). On microhydrogenation it absorbed 94.6% of one molar equivalent of hydrogen.

Bicyclo[4.2.0]octane (XIV).—To the above mixture obtained in microhydrogenation was added an additional 0.93 g. of XIII which was also reduced. After isolating the hydrocarbon in the usual way there was obtained 0.72 g. (59.4%) of XIV; b.p. 136–137.5°; n^{20}_{D} 1.436; d^{20}_{4} 0.866; M_D 35.08 (calcd. M_D 35.26). For this compound Reppe[10] has reported b.p. 136°, n^{20}_{D} 1.4613; d^{20}_{4} 0.8573.

Anal. Calcd. for C_8H_{14}: C, 87.19; H, 12.81. Found: C, 87.20; H, 12.71.

ITHACA, N. Y. RECEIVED OCTOBER 21, 1950

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[17] R. C. Fuson and W. Cole, THIS JOURNAL, **60**, 1238 (1938).

[18] J. B. Tingle and M. P. Cram, *ibid.*, **37**, 598 (1907).

[CONTRIBUTION FROM THE DEPARTMENT OF BIOCHEMISTRY, QUEEN'S UNIVERSITY]

2-Octadecenoic Acid. I. Preparation and Some Reactions of the *cis* and *trans* Isomers

BY GORDON S. MYERS[1]

The *trans* configuration for the 2-octadenoic acid melting at 58.5°, which has been proposed previously by other workers, is now further substantiated by the preparation of the *cis*-2-octadecenoic acid isomer (m.p. 50.5–51°). The configuration assigned to each isomer is based on the comparison of some of their physical and chemical properties. A comparison is made of some of the reactions and properties of the isomeric 2-octadecenoic acids with those of oleic and elaidic acid (*cis*- and *trans*-9-octadecenoic acid, respectively). It has been found that hydroxylation of *trans*-2-octadecenoic acid with peracetic acid and with alkaline potassium permanganate, gives the low-melting and high-melting dihydroxy acid, respectively. *trans*-9-Octadecenoic acid, on the other hand, gives the high-melting 9,10-dihydroxystearic acid on treatment with peracetic acid, and the low-melting isomer on hydroxylation with alkaline permanganate. An improved preparation of *trans*-2-octadecenoic acid, by dehydrohalogenation of 2-iodostearic acid with alcoholic alkali, is reported; and the following new compounds are described: 2,3-dibromostearic acid (m.p. 57°), 2,3-dihydroxystearic acid (m.p. 106–107°) and three 2,3(3,2)-bromoacetoxystearic acids.

Some 2-octadecenoic acid was required as an intermediate in the duplication of some naturally occurring lipids. Le Sueur[2] prepared one of the two possible geometric isomers, along with a by-product of 2-hydroxystearic acid, by dehydrohalogenation of 2-bromostearic acid. Ponzio[3] increased the yield somewhat by using 2-iodostearic acid and alkali. As far as the author is aware, the other isomeric 2-octadecenoic acid has not been described.

The known 2-octadecenoic acid (m.p. 58.5°) is reported to have the *trans* configuration. This is based on its similarity to elaidic acid (*trans*-9-octadecenoic acid) in (1) the melting point depression on mixing with stearic acid[4]; (2) parachor[5];

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[1] Research Laboratories, Ayerst, McKenna and Harrison Ltd., Montreal.

[2] Le Sueur, *J. Chem. Soc.*, **85**, 1708 (1904).

[3] Ponzio, *Gazz. chim. ital.*, **34**, II, 77 (1904).

[4] Semeria, *ibid.*, **55**, 79 (1925).

[5] Semeria and Ribotti-Lissone, *ibid.*, **60**, 862 (1930).

and (3) the detergent action of their soaps.[6] No similarity to brassidic (*trans*-13-docosenoic acid) and elaidic acids was found, however, on comparing the melting points of the two diastereoisomeric dihydroxy acids which are obtained from each acid by hydroxylation with alkaline potassium permanganate and with peracetic acid. Elaidic and brassidic acids on treatment with alkaline permanganate give the low-melting isomer of 9,10-dihydroxystearic acid (m.p. 95°) and 13,14-dihydroxybehenic acid (m.p. 98–100°)[7] and on treatment with peracetic acid give the high-melting dihydroxy acids (m.p. 132° and 131–133°, respectively). In contrast, the known 2-octadecenoic acid gave with alkaline permanganate a 2,3-dihydroxystearic acid melting at 126°, and one melting at 107°, with peracetic acid. To help elucidate further the configuration of this 2-octadecenoic acid, it seemed advisable to attempt to prepare the *cis* form. A compound believed to be *cis*-2-octadecenoic acid (m.p. 50.5°) has been prepared and an improved laboratory preparation of the *trans* acid is reported.

2-Octadecenoic acid melting at 58.5° (I) was hydroxylated with alkaline permanganate, using the procedure outlined by Ponzio,[3] and the 2,3-dihydroxystearic acid melting at 126° (II) was isolated in 17% yield. All attempts to increase this yield were unsuccessful. Hydroxylation of I with a mixture of peracetic acid and a catalytic amount of sulfuric acid, followed by saponification to hydrolyze any acetoxy groups, gave the isomeric 2,3-dihydroxystearic acid melting at 107° (III) in 37% yield. When hydroxylation with peracetic acid was carried out in the presence of a catalytic amount of osmium tetroxide by the method of Butenandt,[8] II was obtained as expected (yield 8%). In each case, the yields of dihydroxystearic acids were low in comparison with those obtained on hydroxylation of 9-octadecenoic[9,10] and 13-docosenoic[7] acids. This difference, due, undoubtedly, to the proximity of the carbon–carbon double bond to the carboxyl group, was demonstrated also when 2-octadecenoic acid (I) failed to be hydroxylated with performic acid (used so successfully by Swern and co-workers[10] on the 9-octadecenoic acids). It was recovered unchanged, also, after treatment with peracetic acid under conditions that Findley, Swern and Scanlan[11] found suitable for converting the 9-octadecenoic acids to the epoxides.

2-Octadecenoic acid (I) was brominated by a modification of the method used by Ponzio,[3] to obtain 2,3-dibromostearic acid melting at 71° (IV). Debromination of IV with zinc gave relatively pure I. Hunsdiecker[12] used an acetic acid solution of hydrogen bromide to convert hydroxy acids to bromo acids. When 2,3-dihydroxystearic acid melting at 126° was treated with hydrogen bromide under similar conditions, a bromoacetoxystearic acid melting at 57° (V) was obtained instead. The 2,3-dihydroxystearic acid isomer melting at 107° gave a mixture of two bromoacetoxystearic acids; one melting at 49° (VI) and the other at 84.5° (VII). The bromoacetoxy structures for these compounds are indicated by elemental analysis and their failure to acetylate further, on treatment with acetyl chloride. The reaction of V with zinc gave a good yield of relatively pure *trans*-2-octadecenoic acid (I), while VI on similar treatment gave a mixture of acids which was separated chromatographically on a column of silicic acid:Celite into *trans*-2-octadecenoic acid (yield 63%), together with a small amount (16% yield) of *cis*-2-octadecenoic acid melting at 50.5° (VIII). The identity of VIII was established by its (1) oxidation to palmitic acid with an acetone solution of potassium permanganate, (2) hydroxylation to the 2,3-dihydroxystearic acids melting at 107 and 126° with alkaline permanganate and with peracetic acid, respectively, (3) hydrogenation to stearic acid, and (4) bromination to 2,3-dibromostearic acid melting at 57° (IX). *cis*-2-Octadecenoic acid could be isomerized to the *trans* form (I) with boiling 25% alcoholic potassium hydroxide, in 38% yield (aqueous nitrous acid was ineffective). No unchanged *cis* acid could be recovered. The amount of *trans* isomer actually formed was probably much larger, since it is itself slowly decomposed in hot concentrated alcoholic alkali. In fact, treatment of the *trans* form for three hours with boiling 25% alcoholic potassium hydroxide gave no *cis* acid, and only 41% of the starting material could be recovered unchanged. The remainder of the product may have been 3-octadecenoic acid since alkali is known to convert 2-hexenoic acid to an equilibrium mixture of 2- and 3-hexenoic acids.[13] It has been found, however, that both *cis* and *trans*-2-octadecenoic acids are relatively stable toward hot dilute alkali. This finding has resulted in the development of an improved procedure for the preparation of *trans*-2-octadecenoic acid, whereby 2-iodostearic acid is dehydrohalogenated by refluxing for a short time with 10% alcoholic potassium hydroxide.

The infrared absorption spectra of the isomeric 2-octadecenoic acids have been measured both by Dr. G. Papineau-Couture[14] and by Dr. R. N. Jones[15] and will be published shortly.[16] They report that the C═C stretching band of the *trans* compound is at a higher frequency than that of the *cis* compound (values of 1653 and 1640 cm.$^{-1}$, respectively; measured in carbon disulfide solution). This difference is analogous to that found by Murty and Seshadri in their Raman spectra studies of the frequency of the ethylenic double bond in unsaturated carbonyl compounds[17] and is in accord with the configurations postulated for the 2-octadecenoic acids. The latter investigators report, for example, that the C═C frequency of the

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(6) Bertram and Kipperman, *Chem. Weekblad*, **32**, 624 (1935).

(7) Dorée and Pepper, *J. Chem. Soc.*, 477 (1942).

(8) Butenandt, Schmidt-Thomé and Paul, *Ber.*, **72**, 1116 (1939).

(9) McKay and Bader, *J. Org. Chem.*, **13**, 75 (1948).

(10) Swern, Billen, Findley and Scanlan, THIS JOURNAL, **67**, 1786 (1945); Swern, *ibid.*, **70**, 1235 (1948).

(11) Findley, Swern and Scanlan, *ibid.*, **67**, 412 (1945).

(12) Hunsdiecker, *Ber.*, **77B**, 185 (1944).

(13) Linstead and Goldberg, *J. Chem. Soc.*, 2343 (1928).

(14) Research Chemist, Research Laboratories of Ayerst, McKenna and Harrison Ltd., Montreal.

(15) Division of Chemistry, National Research Council, Ottawa.

(16) Sinclair, McKay, Myers and Jones, in preparation.

(17) Murty and Seshadri, *C. A.*, **34**, 7744 (1940).

cis and *trans* isomers of ethyl crotonate occurs at 1644 and 1653 cm.$^{-1}$, respectively.

Measurements of the ultraviolet absorption spectra of the isomeric 2-octadecenoic acids are indicated in Fig. 1. The absorption maximum in each case is at about 2130 Å. and agrees very well with that reported for 2-heptadecenoic acid.[18]

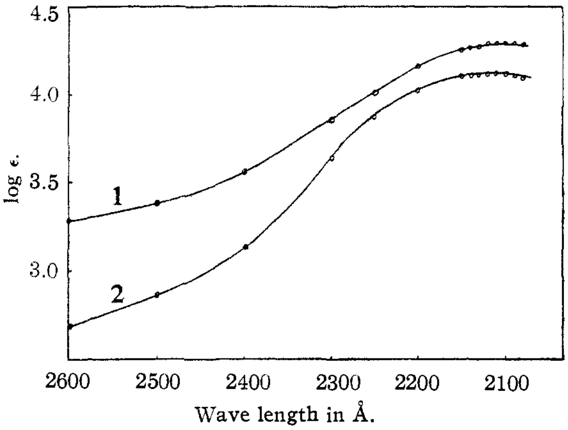


Fig. 1.—Ultraviolet absorption spectra of the *cis*- and *trans*-2-octadecenoic acids: (1) *trans*-2-octadecenoic acid, (2) *cis*-2-octadecenoic acid.

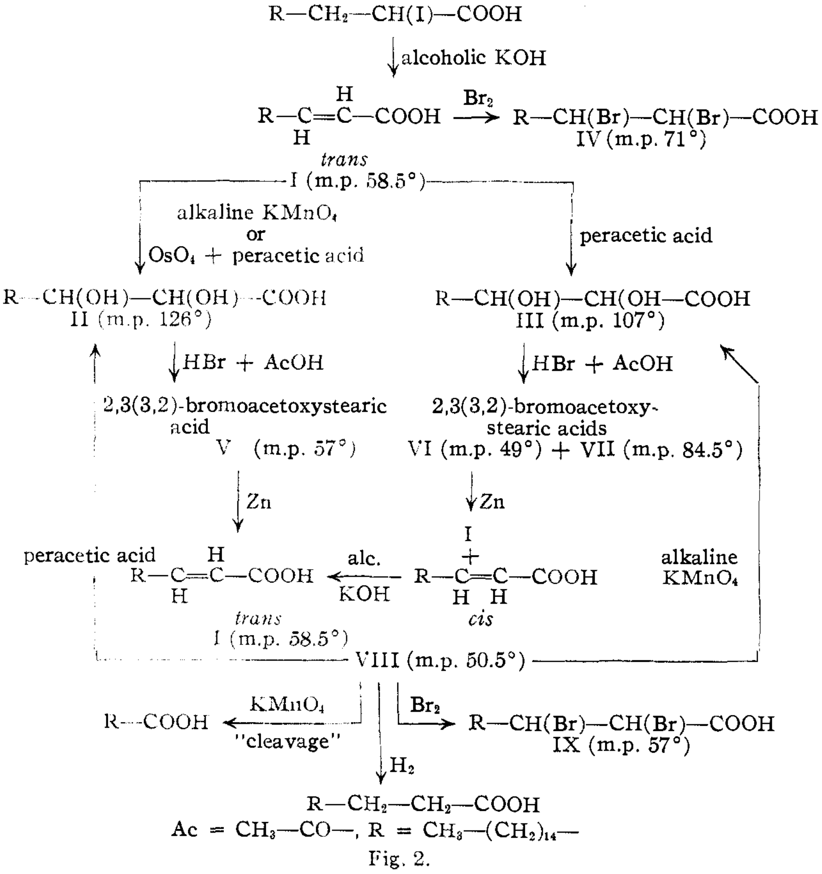
From a consideration of the melting points, solubilities, isomerization properties and the infrared spectra of the 2-octadecenoic acids, it is most probable that the one melting at 58.5° (I) is the *trans* form, while the one melting at 50.5° (VIII) is the *cis* isomer. A summary of their methods of preparation, together with some of their reactions, are indicated in Fig. 2.

Experimental

Preparation of *trans*-2-Octadecenoic Acid (I).—To a solution of 8 g. (0.143 mole) of potassium hydroxide in 100 cc. of alcohol was added 15 g. (0.0366 mole) of 2-iodostearic acid and the mixture was warmed immediately and refluxed for one hour. The solution was diluted with water, acidified and extracted with ether. The ether extract was water-washed and the solvent evaporated to give 10.63 g. of residue, m.p. 48–72°. This residue was suspended in 50 cc. of boiling petroleum ether (b.p. 30–60°) and the insoluble 2-hydroxystearic acid was filtered. A second crop of the latter separated on cooling to room temperature; total wt. 1.4 g. (13% yield), m.p. 80–88°. The filtrate contained largely *trans*-2-octadecenoic acid, which was recrystallized several times from petroleum ether and alcohol to give 4.4 g. (43% yield), m.p. 58–58.5°, and 0.54 g. (5% yield), m.p. 56–57°. All attempts to find *cis*-2-octadecenoic acid in the crystallization liquors, either by fractional crystallization or by chromatographic adsorption on a column of 4:1 silicic acid: Celite, were unsuccessful. The latter technique yielded only further amounts of the *trans* acid and 2-hydroxystearic acid, together with a small amount of an unidentified material, m.p. 48–52°.

The following procedure, starting with stearic acid, was used for the preparation of larger amounts of *trans*-2-octadecenoic acid: Phosphorus trichloride (15 g.) was added to 426 g. (1.5 moles) of stearic acid (Eastman Kodak Co., practical grade) and the mixture was warmed under a reflux condenser until molten. Bromine (300 g., 1.87 moles) was then added carefully to the melt over a period of 15 minutes and the contents were digested on a steam-bath for 18 hours. An additional 180 g. (1.13 moles) of bromine was then added and the heating was continued for another eight hours. The reaction mixture was cooled, diluted with water and the excess bromine destroyed with sodium sulfite. The product was extracted with ether (1 l.) and the ether extract was washed with water and dried with magnesium sulfate. The ether was evaporated and the crude 2-bromostearic acid (m.p. 52–56°) was dissolved in 3500 cc. of alcohol and converted to 2-iodostearic acid by refluxing for six hours with 290 g. (1.75 moles) of finely ground potassium iodide. This mixture was cooled, 280 g. (5 moles) of potassium hydroxide was added and the slurry was refluxed for one hour and then poured into 8 l. of water containing 550 cc. of concentrated hydrochloric acid. The precipitate was filtered, dissolved in ether (1.5 l.) and the ether extract washed with water and then cooled for several hours at 4°. The 2-hydroxystearic acid which separated was filtered, and washed with petroleum ether. The filtrate and washes were concentrated and the residue recrystallized from petroleum ether and alcohol to give 106 g. of *trans*-2-octadecenoic acid, m.p. 57–57.5° (25% yield from stearic acid). Weight of crude 2-hydroxystearic acid was 97 g. (21% yield), m.p. 79–82°.

Preparation of the Isomeric 2,3-Dihydroxystearic Acids.—The preparation of the high-melting isomer (II), m.p. 126°, by alkaline permanganate oxidation of *trans*-2-octadecenoic acid, was briefly described by Ponzio.[3] No yields were reported. The details of its preparation from both *cis*- and *trans*-2-octadecenoic acids are given here.



Ac = CH_3—CO—, R = CH_3—$(CH_2)_{14}$—

Fig. 2.

trans-2-Octadecenoic acid (I) (6 g., 0.0213 mole) was

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(18) Rusoff, Platt, Klevens and Burr, This Journal, **67**, 673 (1945).

dissolved in 500 cc. of water containing 8.4 g. (0.15 mole) of potassium hydroxide, by warming to 60°. The solution was cooled to 5° by the addition of 700 cc. of ice-water mixture and stirred for an hour with a cold solution of 3.6 g. (0.0228 mole) of potassium permanganate in 100 cc. of water. The excess permanganate was then destroyed with an acidified solution of sodium sulfite and the precipitate was filtered and dissolved in ether (400 cc.). The ether solution was concentrated and the residue was washed with warm petroleum ether and crystallized from alcohol (15 cc.) to give 1.15 g. (17% yield), m.p. 124–124.5°. Further crystallizations from alcohol raised the melting point to 125.5–126°.

Treatment of a solution of *trans*-2-octadecenoic acid (2.82 g.) and osmium tetroxide (0.1 g.) in acetic acid (50 cc.) with portionwise addition of 10 cc. of 30% hydrogen peroxide solution over a period of three hours, on a steam-bath (a modification of the procedure used by Dorée and Pepper on erucic acid[7]), gave 2.78 g. of waxy product. This material was crystallized from petroleum ether and alcohol to give 0.24 g. of 2,3-dihydroxystearic acid, m.p. 124–124.5° (7% yield).

A solution of *cis*-2-octadecenoic acid (0.1 g.) in 3 cc. of acetic acid containing a drop of concentrated sulfuric acid, was treated on a steam-bath with portionwise addition of 0.5 cc. of 30% hydrogen peroxide solution over a period of six hours. The product was precipitated with water and filtered. This material was washed with warm petroleum ether and the insoluble 2,3-dihydroxystearic acid, wt. 0.062 g. (55% yield), m.p. 123–124°, was crystallized from alcohol to melt at 125–125.5°.

The low-melting 2,3-dihydroxystearic acid isomer (III), m.p. 106–107°, was obtained in yields of 28–37% by treatment of *trans*-2-octadecenoic acid with peracetic acid, and only in traces by hydroxylation of the *cis* acid with alkaline permanganate.

A solution of 34.2 g. of *trans*-2-octadecenoic acid in 175 cc. of acetic acid containing 1.5 cc. of concentrated sulfuric acid was treated at 100° with portionwise addition of 70 cc. of 30% hydrogen peroxide solution over a period of five hours. This reaction mixture was diluted with water and the precipitate was digested on the steam-bath with 150 cc. of 30% aqueous potassium hydroxide to saponify any acetylated dihydroxystearic acid. The hydrolysate was acidified and extracted with ether. The extract was concentrated and the residue was digested with warm petroleum ether (75 cc.) and filtered. Weight of 2,3-dihydroxystearic acid was 10.5 g. (28% yield), m.p. 105–106°. Further crystallizations from alcohol raised the melting point to 106–107°.

Anal. Calcd. for $C_{18}H_{36}O_4$: C, 68.3; H, 11.5. Found: C, 68.6; H, 11.0.

Treatment of a solution of 0.15 g. (0.00053 mole) of *cis*-2-octadecenoic acid in 15 cc. of 1% aqueous potassium hydroxide with 20 cc. of 1% potassium permanganate (0.00127 mole) for five minutes, gave 0.153 g. of product. This material was washed with petroleum ether and the insoluble 2,3-dihydroxystearic acid (0.008 g., 5% yield; m.p. 98–100°) was crystallized from acetone to melt at 101–102°. The melting point of this material was not depressed on admixture with the low-melting dihydroxystearic acid obtained above. When 0.1 g. of 2,3-dihydroxystearic acid (III) was treated under the same conditions, for 30 minutes with the same amount of 1% aqueous potassium permanganate and alkali, only 45% was recovered unoxidized.

Preparation of the Isomeric 2,3(3,2)-Bromoacetoxystearic Acids.—Three of the four possible 2,3- and 3,2-bromoacetoxystearic acids have been isolated from the reaction of the isomeric 2,3-dihydroxystearic acids with hydrogen bromide in acetic acid. The results of experiments now in progress, to assist in assigning a definite structure to each isomer, will be reported shortly.

The high-melting 2,3-dihydroxystearic acid (II) (6.32 g.), was digested at 80–88° for five hours with a solution of 33.8 g. of 48% hydrobromic acid in 100.4 cc. of acetic anhydride. The reaction mixture was concentrated under reduced pressure and the oily residue was dissolved in ether and washed with water. Evaporation of the dried ether solution gave 8.12 g. of liquid residue which was purified by several low-temperature crystallizations from petroleum ether to give 4.12 g. (49% yield) of 2,3(3,2)-bromoacetoxystearic acid (V), m.p. 53–55°. Further recrystallization of this material at 4°, from acetone and petroleum ether (30–60°), gave a product which melted at either 46.5–47° or 57°, depending on which polymorphic form crystallized out. The low-melting form could be converted to the higher one by heating it above the m.p. and allowing it to solidify slowly. The low-melting form crystallized in small, fuzzy, elongated rods which dissolved readily in petroleum ether at room temperature. The high-melting form, a microcrystalline solid, was slowly soluble in petroleum ether at room temperature and once it was dissolved, the solution showed little tendency to deposit crystals until cooled quite considerably (4°).

Anal. Calcd. for $C_{20}H_{37}O_4Br$: C, 57.0; H, 8.86; Br, 19.0. Found: C, 57.2; H, 8.65; Br, 18.7.

The low-melting 2,3-dihydroxystearic acid (III) (12.64 g.), was treated similarly at 80° for six hours with a solution of 67.6 g. of 48% hydrobromic acid in 200 g. of acetic anhydride, to give a mixture of two bromoacetoxystearic acids (17.2 g.), which was separated by fractional recrystallizations from petroleum ether. The more insoluble one weighed 1.22 g. (7% yield); m.p. 80–82°. This was recrystallized further from a mixture of acetone and petroleum ether to give a white crystalline 2,3-(3,2)-bromoacetoxystearic acid (VII), melting at 84.5–85°.

Anal. Calcd. for $C_{20}H_{37}O_4Br$: C, 57.0; H, 8.86; Br, 19.0. Found: C, 57.2; H, 8.78; Br, 19.4.

The crude yield of the more soluble bromoacetoxy acid was 8.6 g. (51% yield); m.p. 44–47°. This was recrystallized from petroleum ether to give 5.58 g. of 2,3(3,2)-bromoacetoxystearic acid (VI), m.p. 49°.

Anal. Calcd. for $C_{20}H_{37}O_4Br$: C, 57.0; H, 8.86; Br, 19.0. Found: C, 57.4; H, 8.82; Br, 19.5.

The absence of a free hydroxyl group in compounds V, VI and VII was demonstrated by refluxing each for several hours with acetyl chloride. In each case the starting material was recovered unchanged. Treatment with acetyl chloride in pyridine was ineffective also.

***trans*-2-Octadecenoic Acid from 2,3(3,2)-Bromoacetoxystearic Acid (V).**—Practically pure *trans*-2-octadecenoic acid was obtained when V (0.3 g.) was refluxed for eight hours with 0.9 g. of zinc dust in 5 cc. of acetone. The reaction mixture was acidified and the product extracted with ether. Evaporation of the ether left 0.16 g. (79% yield) of the acid; m.p. 55–56°. Crystallization from alcohol raised the m.p. to 58–58.5°.

***cis*- and *trans*-2-Octadecenoic Acids from 2,3(3,2)-Bromoacetoxystearic Acid (VI).**—Zinc dust (100 g.) was added portionwise over a period of 30 minutes to a solution of 95.5 g. of 2,3(3,2)-bromoacetoxystearic acid (VI) in 400 cc. of acetone, and the contents were refluxed for 16 hours. The reaction mixture was acidified, extracted with ether and the ether extract was washed with water and concentrated under reduced pressure to leave a solid residue of 2-octadecenoic acids (62 g., 97% yield); m.p. 46–54°. This crude product was recrystallized several times from petroleum ether and from alcohol to give 40.8 g. (64% yield) of *trans*-2-octadecenoic acid (I), m.p. 57.5–58°. The mother liquors were separated into an additional 6.17 g. (10% yield) of I, together with 11.4 g. (18% yield) of crude *cis*-2-octadecenoic acid (VIII), m.p. 48–49°, by chromatographing twice from a 4:1 silicic acid:Celite column. Pure VIII was obtained as a white micro-crystalline solid melting at 50.5–51° after three further purifications from petroleum ether.

Anal. Calcd. for $C_{18}H_{34}O_2$: C, 76.6; H, 12.16. Found: C, 76.4; H, 12.0.

Oxidation of *cis*-2-Octadecenoic Acid to Palmitic Acid.—Powdered potassium permanganate (1.1 g.) was added over a period of one hour to a boiling solution of 0.2 g. of *cis*-2-octadecenoic acid (VIII) in 7 cc. of acetone. This mixture was refluxed for another hour and then decolorized with an acid solution of sodium sulfite and extracted with ether. The ether extract contained 0.186 g. of sticky solid which was crystallized from acetone and from alcohol to give 0.051 g. (28% yield) of crude palmitic acid, m.p. 55–57°. Further purification gave palmitic acid melting at 60–61°. No depression was observed on admixture with an authentic sample (m.p. 61–62°).

Hydrogenation of the Isomeric 2-Octadecenoic Acids.—A solution of 1.128 g. (0.004 mole) of *cis*-2-octadecenoic acid (VIII), m.p. 50.5–51°, in 75 cc. of methanol was shaken with hydrogen and 0.1 g. of Adams platinum oxide catalyst at atmospheric pressure until absorption was complete (24 hours). The acid absorbed 0.0042 ± 0.0002 mole of hydrogen to give a quantitative yield of stearic acid (1.13 g.; m.p. 68–69°).

trans-2-Octadecenoic acid (1.128 g., 0.004 mole) (I), m.p. 58.2–58.5°, was hydrogenated similarly and 0.0038 ± 0.0002 mole of hydrogen was absorbed to give a quantitative yield of stearic acid (1.13 g., m.p. 68–69°).

Isomerization of *cis*-2-Octadecenoic Acid to the *trans* Form.—Attempts to effect this isomerization with warm aqueous nitrous acid (conditions suitable for conversion of oleic to elaidic acid) were unsuccessful. Although VIII is relatively stable in 10% alcoholic potassium hydroxide solution, it can be converted to I with more concentrated alkaline solutions.

cis-2-Octadecenoic acid (0.3 g.) and 1 g. of potassium hydroxide in 4 cc. of alcohol were refluxed for three hours and then acidified and extracted with ether. The ether extract was concentrated and the residue (0.319 g., m.p. 47–52°) was purified by chromatographing from a 4:1 silicic acid:Celite column to give 0.114 g. (38% yield) of *trans*-2-octadecenoic acid, m.p. 57–58°. No unchanged VIII was recovered.

When I was treated similarly, only 41% was recovered unchanged and no *cis*-2-octadecenoic acid was found.

Preparation of the Isomeric 2,3-Dibromostearic Acids.—The high-melting dibromide was prepared by a modification of the procedure used by Ponzio.[3] *trans*-2-Octadecenoic acid (16.92 g., 0.06 mole) was added to a cold solution of 14.4 g. (0.09 mole) of bromine in 45 cc. of dry, alcohol-free chloroform. The solution so obtained was allowed to stand at room temperature for several hours, and then warmed to 50° for 12 hours. The reaction mixture was dissolved in ether and the excess bromine was destroyed with aqueous sodium sulfite. Evaporation of the ether gave 26.5 g. of crude 2,3-dibromostearic acid, m.p. 68–69°. Two crystallizations from petroleum ether raised the m.p. to 71–72° (78% yield).

cis-2-Octadecenoic acid (0.1 g., 0.000355 mole) was treated with 0.3 g. (0.0019 mole) of bromine in 2 cc. of alcohol-free chloroform. After standing for three days, the reaction mixture was processed to give 0.156 g. of crude low-melting 2,3-dibromostearic acid isomer; m.p. 52–54°. This was recrystallized several times from petroleum ether to give 0.095 g. (61% yield) of 2,3-dibromostearic acid (IX), m.p. 57–57.2°.

Anal. Calcd. for $C_{18}H_{34}O_2Br_2$: C, 48.9; H, 7.76; Br, 36.15. Found: C, 49.4; H, 8.13; Br, 35.9.

Ultraviolet Spectra.—Hexane was used as the solvent for each acid. It was purified by agitating four times with fuming sulfuric acid and was finally washed with water, dried over sodium sulfate and distilled.

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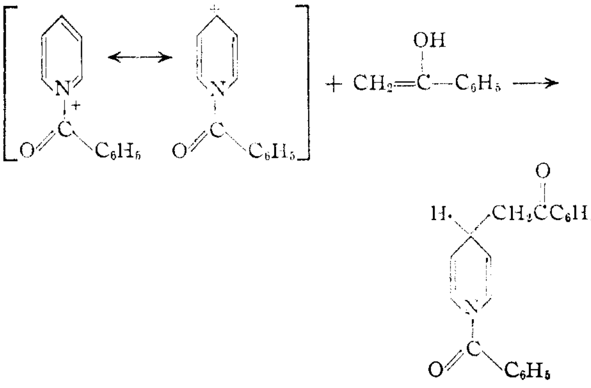
[Contribution from the Chandler Laboratory, Columbia University]

Condensation of Ketones with Acylpyridinium Salts[1]

By W. von E. Doering and William Edwin McEwen[2]

Claisen's product, $C_{20}H_{17}NO_2$, of the reaction of pyridine, benzoyl chloride and acetophenone has been shown to be 1-benzoyl-4-phenacyl-1,4-dihydropyridine. The product from pyridine, acetic anhydride and acenaphthenone does not have the structure assigned to it by E. Ghigi but rather is 1-acetoxy-2-(1′-acetyl-1′,4′-dihydro-4′-pyridyl)-acenaphthylene. These interesting reactions of acylpyridinium salts at the γ-position of pyridine have been extended to the condensation with propiophenone and cyclohexanone, where the same type of product is produced.

Claisen and Haase[3] have reported the formation of a yellow, crystalline compound (I), $C_{20}H_{17}NO_2$, from the reaction of acetophenone, benzoyl chloride and pyridine for six weeks. For this uninvestigated molecule we have hypothesized the structure I on the mechanistic grounds that an intermediate acylpyridinium salt,[4] electron deficient in the α and γ positions, react with the electron-donating, enolic tautomer of acetophenone.[5] Hydrolysis of I with dilute sulfuric acid, effected by Claisen and Haase,[3] reformed the starting fragments, acetophenone, pyridine and benzoic acid, but did not permit a structural assignment.



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(1) Taken from a dissertation submitted May 23, 1947, in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Faculty of Pure Science of Columbia University.

(2) E. I. du Pont Fellow, 1946–1947.

(3) L. Claisen and E. Haase, *Ber.*, **36**, 3674 (1903).

(4) Although V. Prey, *ibid.*, **75**, 537 (1942), has failed to isolate benzoylpyridinium chloride, the existence of this compound in equilibrium is very likely in view of Prey's successful isolation of acetylpyridinium chloride and *p*-nitrobenzoylpyridinium chloride. This latter salt has also been isolated by B. M. Bogoslovskii, *J. Gen. Chem.* (*U. S. S. R.*), **7**, 255 (1937); *C. A*, **31**, 4319 (1937).

(5) The few reactions in the literature support the contention that acylpyridinium salts are substituted at the γ-position in contrast to alkylpyridinium salts which react generally at the α-position: E. Koenigs and E. Ruppelt, *Ann.*, **509**, 142 (1934), obtained 4-(*p*-dimethylaminophenyl)-pyridine and benzaldehyde from dimethylaniline, benzoyl chloride and pyridine; O. Dimroth and R. Heene, *Ber.*, **54**, 2934 (1921), reduced pyridine and acetic anhydride with zinc dust to 1,1′-diacetyltetrahydro-4,4′-dipyridyl, a reaction in which 4-ethylpyridine was also produced [M. Dohrn and H. Horsters, German Patent 390,333; *Frdl.*, **14**, 517 (1926)], by way of 1,4-diacetyl-1,4-dihydropyridine as intermediate [J. P. Wibaut and J. F. Arens, *Rec. trav. chim.*, **60**, 119 (1941)]