reacted ferrocene (3.9 g.; 11% of the original amount). Distillation of the ferrocene-free residue gave III (34.7 g.; 32% yield) which was collected as an orange-red oil within the temperature range of 180–198° (0.17–0.25 mm.). This material was subsequently column-chromatographed on 1000 g. of Woelm, nonalkaline, Grade I alumina. The product, III, was eluted from the column with a benzene-ethanol mixture (35 parts of benzene and 1 part of ethanol) after the column was developed with benzene. The material was chromatographically homogeneous; n_D^{25} 1.5202.

Anal. Calcd. for $C_{23}H_{48}FeSi$: C, 71.76; H, 10.32; Fe, 11.92. Found: C, 71.96; H, 10.30; Fe, 11.85.

The residue obtained from the distillation of the crude reaction product was column-chromatographed on 800 g. of alumina. Development and elution were carried out with benzene, and IV (29.8 g.; 35% yield) was obtained from the eluate. A portion of the product was rechromatographed for analysis; n_D^{25} 1.5054.

Anal. Calcd. for $C_{46}H_{86}FeSi_2$: C, 73.55; H, 11.54; Fe, 7.43. Found: C, 73.23; H, 11.36; Fe, 7.24.

B. III and IV *via* sodiation of ferrocene.[6] Ferrocene (23.3 g.; 0.125 mole), dissolved in toluene, was treated with phenylsodium[12] (0.25 mole) at room temperature during 24 hr.; and at 75–80° for an additional 7 hr. Tri-*n*-hexylbromosilane (90.8 g.; 0.25 mole) was rapidly added (mild exothermic reaction), and the mixture stirred at room temperature overnight; then heated at 70–80° for 24 hr. The reaction mixture, cooled to 10°, was passed through a bed of "Filter-Aid," and the filtrate (500 ml.) was heated on a steam bath *in vacuo* (20 min.) to sublime the unreacted ferrocene (17.9 g.; 77% of the initial amount). The residue was then heated under distillation conditions, and material which was collected up to 100° (0.04 mm.) was not investigated. The undistilled portion (28.2 g. of a dark fluid) was chromatographed on 400 g. of alumina. The chromatogram was developed with cyclohexane and eluted with benzene. Two bright orange-colored bands were successively eluted. The slower-moving band yielded III (580 mg., 0.5% yield) which when rechromatographed was obtained analytically pure; n_D^{25} 1.5202.

Elution of the faster-moving band gave IV (5.63 g., 8% yield); n_D^{25} 1.5054.

C. IV *via* tri-*n*-hexylsilylcyclopentadiene (X). Freshly distilled cyclopentadiene (13.7 g.; 0.21 mole) was added to sodium shot (2.34 g.; 0.10 mole) over a 15-min. period. Evolvement of hydrogen ceased 45 min. after the addition was completed. The reaction mixture was cooled to 5°, and tri-*n*-hexylbromosilane (36.5 g.; 0.10 mole), dissolved in 20 ml. of THF was added with stirring during a 1-hr. period. The mixture was allowed to reach room temperature while the stirring was continued for an additional 2 hr. After the reaction mixture was subsequently heated under reflux during 24 hr., it was cooled to room temperature and passed through a bed of Filter-Aid to remove the white precipitate (NaBr) which was present. The filtrate was evaporated on a steam bath *in vacuo*, and the residue distilled.

Infrared analysis of a fraction collected at 140–160° (0.5–0.7 mm.), n_D^{25} 1.4750–1.4743, indicated the presence of a substituted cyclopentadiene compound. A portion of this material (3.5 g.; 0.01 mole based on the presence of pure X) was dissolved in benzene and treated with *n*-butyllithium (9 ml. of a 0.18*M* ethereal solution), and then heated under reflux during 1 hr. Iron(II) chloride (3.5 g.; 0.02 mole) was added as a slurry in THF, and the reaction mixture heated under reflux for 3 hr.; then stirred at room temperature during an additional 24 hr. After the mixture was poured onto 200 ml. of water-crushed ice and phase-separated, ether extracts of the aqueous phase were combined with the bulk organic portion. The presence of the ferrocene nucleus in this solution was indicated by means of a paper chromatography test.[13] Evaporation of the solvent yielded a dark fluid which was heated to 250° (0.1 mm.) until no further distillate was obtained. The undistilled portion was chromatographed on 30 g. of alumina, and the compound, IV (56 mg., 4% yield), n_D^{25} 1.5056, was obtained from the benzene eluate.

The infrared spectrum of the product was found to be identical to those of the disubstituted compounds (both IV) prepared *via* the 2 metalation procedures.

Acknowledgment. The authors wish to express their appreciation to Mr. F. F. Bentley and associates of this laboratory for the infrared spectra cited in this work.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DE PAUL UNIVERSITY]

The Active 12-Methyloctadecanoic Acids

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Received September 29, 1958

The (+)- and (−)-12-methyloctadecanoic acids have been prepared from (+)- and (−)-2-octanols by the procedure pioneered by Prout, Cason, and Ingersoll.[2] The active acids have higher melting points than the DL-acid.

The preparation of the active 12-methyloctadecanoic acids represents an extension of earlier work[2,3] and the scheme is given in the chart.

The (+)- and (−)-2-octanols[4] (I) were converted to the antipodally pure (−)- and (+)-3-methylnonanoic acids (V) by a four-step procedure in which optical purity was assured by fractional crystallization of the (−)- and (+)-2-octylmalonic acids (IV). The active forms of IV (m.p. 106–108°) were obtained readily by crystallization from hexane; however, the DL-form (m.p. 80–82°) did

(1) This work was abstracted from the Master of Science theses submitted to the faculty at De Paul University by Donald E. Dickson (1952) and Robert J. Klimkowski (1958).

(2) F. S. Prout, J. Cason, and A. W. Ingersoll, *J. Am. Chem. Soc.*, **70**, 298 (1948).

(3) J. Cason and R. A. Coad, *J. Am. Chem. Soc.*, **72**, 4695 (1950).

(4) J. Kenyon, *Org. Syntheses*, **Coll. Vol. I**, 2nd ed., 418–21 (1941).

not crystallize except when equal amounts of the two purified antipodes were mixed.

The active 3-methylnonanoic acids[5] ($[\alpha]_D \mp 4.5°$) (V) which resulted from decarboxylation of the (−)- and (+)-2-octylmalonic acids (IV) were esterified and reduced catalytically over copper chromite. The yields of (−)- and (+)-3-methyl-1-nonanol (VII) were low, presumably because conditions for reduction were too severe and gave hydrocarbon (3-methylnonane). Action of hydrogen bromide gave the (+)- and (−)-1-bromo-3-methylnonanes (VIII). These bromides were lengthened to the ethyl (±)-12-methyl-9-oxo-octadecanoate (IX) and the keto esters were reduced[6] to give (±)-12-methyloctadecanoic acid (XI). The properties of these acids and their derivatives are summarized in Table I.

EXPERIMENTAL

All melting points and boiling points were uncorrected. Most products were fractionated through a 60-cm., heated Vigreux column. Density is reported in absolute units (g./cc.). The expression "hexane" refers to Skellysolve B, a ligroin fraction, b.p. 60–70°, supplied by the Skelly Oil Company, Kansas City, Mo. All rotations were observed in a Rudolph Universal High Precision polarimeter through a two-decimeter tube unless otherwise noted. The elemental analyses were performed by Abbott Laboratories, North Chicago, Ill., by Micro-Tech Laboratories, Skokie, Ill. or by Drs. Strauss and Weiler, Oxford, England.

2-Octanol (I) was resolved by the method of Kenyon.[4] The alcohols used had specific activities of $[\alpha]^{26}_D$ +7.92° to +9.19° and $[\alpha]^{26}_D$ −5.91° to −9.07°. Pickard and Kenyon[8] reported maximum values $[\alpha]_D$ ±9.9°. Highly purified alcohol was not required because the very efficient crystallization of antipodal 2-octylmalonic acids (below) effected separation of pure antipodal 2-octylmalonic acid where the excess of one form was small.

The *2-bromo-octanes* (II) were prepared in 50–80% yields using the basic procedure of Hseuh and Marvel:[9] DL-form, b.p. 110–115° (90 mm.), d^{23} 1.111; (−)-form, b.p. 105–108° (60 mm.), d^{25} 1.105, $[\alpha]^{26}_D$ −35.3° (homogeneous); (+)-form, b.p. 95–97° (13 mm.), d^{24} 1.10, $[\alpha]^{25}_D$

TABLE I

MELTING POINTS OF 12-METHYLOCTADECANOIC ACID AND DERIVATIVES

	Acid, °C.	Acid, α^{27a}_D	Amide, °C.	Tri-bromo-anilide, °C.
DL-	26–27		84–86	93–94
	27.6–28.2[b]		86–88.2[b]	94.2–95.2[b]
(+)	37–38	+0.09°	74–75	89–91
(−)	36–37	−0.10°	72–75	90–92

[a] Rotation is homogeneous, 2 d. tube. [b] Ref. 7.

Scheme for Synthesis of 12-Methyloctadecanoic Acid[a]

$C_6H_{13}CH(CH_3)\text{—}OH$ (+9.19[b], −9.07) I $\xrightarrow{79\text{–}80\%}$ $C_6H_{13}CH(CH_3)\text{—}Br$ (−35.3, +30.8) II $\xrightarrow{71\text{–}83\%}$ $C_6H_{13}CH(CH_3)\text{—}CH\text{—}(COOC_4H_9)_2$ (0.0, 0.0) III $\xrightarrow{69\text{–}70\%}$

$C_6H_{13}CH(CH_3)\text{—}CH\text{—}(COOH)_2$ (−8.33, +8.18) IV $\xrightarrow{92\%}$ $C_6H_{13}CH(CH_3)\text{—}CH_2COOH$ (−4.51, +4.44) V $\xrightarrow{92\text{–}98\%}$ $C_6H_{13}CH(CH_3)\text{—}CH_2COOC_2H_5$ (−0.59, +0.59) VI $\xrightarrow{37\text{–}67\%}$

$C_6H_{13}CH(CH_3)\text{—}CH_2CH_2OH$ (−0.37, +0.38) VII $\xrightarrow{80\text{–}82\%}$ $C_6H_{13}CH(CH_3)\text{—}CH_2\text{—}CH_2Br$ (+1.15, −1.17) VIII $\xrightarrow{43\text{–}52\%}$

$C_6H_{13}CH(CH_3)\text{—}CH_2\text{—}CH_2\text{—}C(=O)(CH_2)_7COOC_2H_5$ (+0.11, —) IX $\xrightarrow{60\text{–}73\%}$ $C_6H_{13}CH(CH_3)\text{—}(CH_2)_{10}\text{—}COOC_2H_5$ (+0.15, −0.14) X $\xrightarrow{59\text{–}92\%}$

$C_6H_{13}CH(CH_3)\text{—}(CH_2)_{10}COOH$ (+0.09 (2d), −0.10 (2d)) XI

[a] The yields refer to those obtained with the active antipodes. [b] These numbers are the specific rotation in degrees (except for XI, an "observed" rotation) for the two forms using the light of the sodium D-line. The first rotation listed throughout is the optical activity of the compound ultimately prepared from (+)-2-octanol; the rotation below the first is the activity of the compund derived from (−)-2-octanol.

(5) This acid was resolved previously by P. A. Levine and R. E. Marker who reported $[\alpha]_D$ +0.78°, *J. Biol. Chem.*, **91**, 98 (1931).

(6) Huang-Minlon, *J. Am. Chem. Soc.*, **68**, 2487 (1946).

(7) J. Cason, E. L. Pippen, P. B. Taylor, and W. R. Winans, *J. Org. Chem.*, **15**, 135 (1950).

(8) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **99**, 49 (1911).

(9) C.-M. Hseuh and C. S. Marvel, *J. Am. Chem. Soc.*, **50**, 855 (1928).

+30.8° (homogeneous). The maximum optical activity is ±38.9°.[10]

Butyl 2-octylmalonates (III) were prepared by adaptation of the malonic ester procedure in 1-butanol of Reid and Ruhoff.[2,11] Thus 21 g. of DL-2-bromo-octane and 27 g. of ethyl malonate were condensed to furnish 33 g. (92%) of butyl DL-2-octylmalonate; b.p. 160–210° (3 mm.); d^{20} 0.932; n_D^{25} 1.4361

The (+)-form[12] was prepared from 27.4 g. of (−)-2-bromo-octane ($[\alpha]_D^{26}$ −35.3°). The yield of ester was 39.0 g. (83%); b.p. 131–134° (0.3 mm.); n_D^{25} 1.4360; d^{25} 0.925; $[\alpha]_D^{26}$ +0.0° (homogeneous).

The (−)-form[12] was prepared in 71% yield (140 g.) from 116 g. of (+)-2-bromo-octane ($[\alpha]_D^{26}$ +29.3°): b.p. 131–134° (0.3 mm.); n_D^{25} 1.4360; d^{25} 0.925; $[\alpha]_D^{26}$ −0.0° (homogeneous).

Anal. Calcd. for $C_{19}H_{36}O_4$: C, 69.46; H, 10.88; sapon. equiv., 164. Found: C, 68.97; H, 11.05; sapon. equiv., 169 (DL), 159 (+), 161 (−).

DL-*2-Octylmalonic acid* (IV). Butyl DL-2-octylmalonate (33 g.) was heated under reflux for an hour in a solution of 23 g. of potassium hydroxide, 150 ml. of 95% ethyl alcohol, and 6 ml. of water. After extraction the solvent was removed furnishing 17 g. (78%) of crude acid as an oil.

DL-2-Octylmalonic acid failed to crystallize directly. However, the DL-acid made from mixing the two forms had a melting point of 80–82° after two crystallizations from hexane.

(−)-*2-Octylmalonic acid* was prepared from 145 g. of butyl (+)-2-octylmalonate[12] and furnished 120 g. (126%) of crude acid. The acid was systematically crystallized from hexane to give 66 g. (69%) of pure (−)-2-octylmalonic acid; m.p. 106–108° (apparently polymorphic); $[\alpha]_D^{26}$ −8.3° (0.901 g. dissolved up to 10 ml. in 95% ethanol, α_D^{26} −0.75°, 1 d. tube).

Anal. Calcd. for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32; equiv. wt., 108.1. Found: C, 61.30; H, 9.27; equiv. wt., 107.2.

(+)-2-*Octylmalonic acid* was prepared in 130% (120 g.) crude yield by saponifying 140 g. of the butyl (−)-2-octylmalonate.[12] Systematic crystallization from hexane gave 64 g. (70%) of pure (+)-2-octylmalonic acid: m.p. 106–108° (probably polymorphic); $[\alpha]_D^{26}$ +8.2° (0.882 g. of acid dissolved up to 10 ml. in 95% ethanol, α_D^{26} +0.72°, 1 d. tube); equiv. wt., 108.6 (calcd. for $C_{11}H_{20}O_4$: 108.1).

DL-*3-Methylnonanoic acid* (V). Seventeen g. of DL-2-octylmalonic acid was heated at 165–170° for an hour. The product was distilled: b.p. 122–125° (3 mm.); 10 g. (76%); n_D^{23} 1.4318; d^{23} 0.888; equiv. wt., 174.1 (calcd. for $C_{10}H_{20}O_2$: 172.3).

The *p-bromoanilide*[13] was prepared in 83% yield and crystallized twice from methanol, m.p. 93–94°.

Anal. Calcd. for $C_{16}H_{23}BrNO$: N, 4.31. Found: N, 4.39.

The *amide*[2] was prepared in 93% yield. Three crystallizations from acetone gave a waxy solid, m.p. 85–86°.

Anal. Calcd. for $C_{10}H_{21}NO$: N, 8.18. Found: N, 8.48.

(−)-*3-Methylnonanoic acid* was prepared from 59.5 g. of (−)-2-octylmalonic acid ($[\alpha]_D^{26}$ −8.3°): b.p. 140–141° (11 mm.); 43.5 g. (92.2%); n_D^{25} 1.4326; d^{24} 0.899; $[\alpha]_D^{26}$ −4.51° (homogeneous, 1 dm.); equiv. wt., 169.6 (calcd. for $C_{10}H_{20}O_2$: 172.3).

The *p-bromoanilide* had m.p. 109–109.5° after two crystallizations. The *amide* had m.p. 86.5–88°.

(10) W. Gerrard, *J. Chem. Soc.*, 848 (1945).

(11) E. E. Reid and J. Ruhoff, *Org. Syntheses*, **Coll. Vol. II**, 474–5 (1943).

(12) The plus or negative sign here is arbitrary because the optical activity is zero. The sign corresponds to the sign observed by Prout, Cason, and Ingersoll (Ref. 2) for the active butyl 2-decylmalonates.

(13) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, New York, N. Y. (1956), p. 200.

(+)-*3-Methylnonanoic acid* was prepared from 72 g. of (+)-2-octylmalonic acid ($[\alpha]_D^{25}$ +8.3°) in 92% yield (52.5 g.): b.p. 131–133° (9 mm.); n_D^{25} 1.4323; d^{24} 0.898; $[\alpha]_D^{26}$ +4.44° (homogeneous, 1 dm.); equiv. wt., 174.5 (calcd. for $C_{10}H_{20}O_2$: 172.3).

The *p-bromoanilide* melted at 109–110°. The *amide* melted at 86–88°.

Ethyl DL-*3-methylnonanoate* (VI). DL-3-Methylnonanoic acid (96.9 g.) was esterified with ethanol in the usual way to give 100.9 g. (92.1%); b.p. 108–109° (16 mm.); n_D^{25} 1.4240; d^{25} 0.864.

Anal. Calcd. for $C_{12}H_{24}O_2$: C, 71.95; H, 12.08. Found: C, 71.70; H, 11.98.

Ethyl (−)-*3-methylnonanoate* was prepared from 41.5 g. of (−)-3-methylnonanoic acid ($[\alpha]_D^{26}$ −4.51°) in 91.9% yield: 44.2 g.; b.p. 108–109° (16 mm.); n_D^{25} 1.4238; α_D^{33} −1.02° (homogeneous); $[\alpha]_D^{33}$ −0.59°.

Ethyl (+)-*3-methylnonanoate*, prepared from 32.5 g. of (+)-3-methylnonanoic acid ($[\alpha]_D^{30}$ +4.54°), was obtained in 98.1% yield: 36.9 g.; b.p. 101–102° (1 mm.); n_D^{25} 1.4238; α_D^{33} +1.02° (homogeneous); $[\alpha]_D^{33}$ +0.59°.

DL-*3-Methyl-1-nonanol* (VII). A mixture of 100.9 g. of ethyl DL-3-methylnonanoate and 8 g. of copper chromite[14] in a bomb was charged with hydrogen at 1575 p.s.i. at 30°. The mixture was then heated and shaken at 285° for 3 hr. Upon fractionation two products were obtained: (1) 16.7 g., b.p. 48–84° (1 mm.), n_D^{25} 1.4536; and (2) 43.0 g. (55.8%), b.p. 95–97° (1 mm.), d^{25} 0.847, n_D^{25} 1.4355. Fraction 1 was insoluble in concentrated sulfuric acid and presumably is DL-3-methylnonane. The literature[7] reports b.p. 108–109° (11 mm.).

Anal. Calcd. for $C_{10}H_{22}O$: C, 75.88; H, 14.01. Found: C, 75.29; H, 13.86.

(−)-*3-Methyl-1-nonanol* was prepared from 39.1 g. of ethyl (−)-3-methylnonanoate ($[\alpha]_D^{31}$ −0.59°). Fractionation gave two fractions: (1) 7.2 g., probably hydrocarbon; b.p. 62–73° (30 mm.); n_D^{25} 1.4326; and (2) 21.1 g. (67.4%) of alcohol; b.p. 125–126° (30 mm.); n_D^{25} 1.4353; α_D^{35} −0.63° (homogeneous); $[\alpha]_D^{35}$ −0.37°.

(+)-*3-Methyl-1-nonanol* was prepared from 36.2 g. of ethyl (+)-3-methylnonanoate ($[\alpha]_D^{33}$ +0.59°). Distillation gave 14.6 g. of forerun; b.p. 43–65° (1 mm.); n_D^{25} 1.4330 and 13.0 g. (37.2%) of alcohol; b.p. 96–97° (1 mm.); n_D^{25} 1.4356; α_D^{35} +0.64° (homogeneous), $[\alpha]_D^{35}$ +0.38°.

DL-*1-Bromo-3-methylnonane* (VIII). DL-3-Methyl-1-nonanol (43.0 g.) was treated at 100° with hydrogen bromide.[15] The reaction mixture, dissolved in benzene, was washed with cold concentrated sulfuric acid, water, and saturated sodium chloride solution. After drying over potassium carbonate the bromide was distilled: 45.0 g. (74.8%); b.p. 92–94° (1 mm.); n_D^{25} 1.4553; d^{25} 1.060.

Anal. Calcd. for $C_{10}H_{21}Br$: C, 54.30; H, 9.57; Br, 36.13. Found: C, 54.63; H, 9.60; Br, 35.87.

The literature gives b.p. 121–122° (25 mm.).[7]

(+)-*1-Bromo-3-methylnonane* was prepared in 81.8% yield from 19.8 g. of (−)-3-methyl-1-nonanol ($[\alpha]_D^{35}$ −0.37°). Distillation gave 22.5 g. of bromide; b.p. 92–94° (1 mm.); n_D^{25} 1.4550; α_D^{27} +2.43° (homogeneous); $[\alpha]_D^{27}$ +1.15°.

(−)-*1-Bromo-3-methylnonane* was prepared in 80.3% yield from 13.0 g. of (+)-3-methyl-1-nonanol ($[\alpha]_D^{35}$ +0.38°). Distillation furnished 14.6 g. of bromide; b.p. 92–94° (1 mm.); n_D^{25} 1.4552; α_D^{27} −2.48° (homogeneous); $[\alpha]_D^{27}$ −1.17°.

Ethyl DL-*9-oxo-12-methyloctadecanoate* (IX). Di-(DL-3-methylnonyl-)cadmium[16] was made using 2.70 g. of magnesium, 24.2 g. of DL-1-bromo-3-methylnonane and 12.1 g. of cadmium chloride. After the solvent had been changed to benzene, 20.7 g. of ω-carbethoxycaprylyl chloride [b.p.

(14) W. A. Lazier and H. R. Arnold, *Org. Syntheses*, **Coll. Vol. II**, 142–5 (1943).

(15) E. E. Reid, J. Ruhoff, and R. Burnett, *Org. Syntheses*, **Coll. Vol. II**, 246–8 (1943).

(16) J. Cason and F. S. Prout, *Org. Syntheses*, **Coll. Vol. III**, 601–605 (1955).

148–152° (3 mm.)][17] was added. After the usual work-up the product was fractionated to give 17.8 g. (47.7%) of keto ester; b.p. 195–230° (1 mm.); n_D^{25} 1.4482; d^{25} 0.864. Two carbon-hydrogen analyses indicated that the keto ester was contaminated with ethyl azelate: C, 72.44, 72.54; H, 11.56, 11.65 (calcd. for $C_{21}H_{40}O_3$: C, 74.06; H, 11.87). Cason *et al.*[7] report a 43% yield, b.p. 216–220° (5 mm.).

Ethyl (+)-9-oxo-12-methyloctadecanoate. This ester was prepared using 18.6 g. of (+)-1-bromo-3-methylnonane ($[\alpha]_D^{27}$ +1.15°), 2.02 g. of magnesium, 9.3 g. of cadmium chloride, and 15.9 g. of ω-carbethoxycaprylyl chloride. Distillation gave 14.8 g. (51.9%); b.p. 198–225° (1 mm.); n_D^{25} 1.4481; α_D^{28} +0.10° (homogeneous, 1 dm. tube); $[\alpha]_D^{28}$ +0.11°.

Ethyl (−)-9-oxo-12-methyloctadecanoate. The levorotatory ester was made from 14.4 g. of (−)-1-bromo-3-methylnonane ($[\alpha]_D^{27}$ −1.17°), 1.60 g. of magnesium, 7.16 g. of cadmium chloride, and 12.2 g. of ω-carbethoxycaprylyl chloride. The yield was 9.4 g. (43%); b.p. 191–212° (1 mm.); n_D^{25} 1.4479.

Ethyl DL-*12-methyloctadecanoate* (X). Ethyl DL-9-oxo-12-methyloctadecanoate (17.0 g.), 9.5 g. of potassium hydroxide, 8.5 ml. of 85% hydrazine hydrate, and 85 ml. of diethylene glycol was heated under reflux for 1.5 hr.[6] The mixture was concentrated until the temperature of the solution was 195°, then reflux was continued 4 hr. The reaction mixture was worked up to furnish the acid. The crude acid was esterified with absolute ethanol and sulfuric acid. The ester was ultimately distilled to give 12.3 g. (75.4%) of ethyl DL-12-methyloctadecanoate; b.p. 205–212° (1 mm.); n_D^{25} 1.4425; d^{25} 0.824; sapon. equiv., 319 (calcd. for $C_{21}H_{42}O_2$: 327). Cason *et al.*[7] report b.p. 183–185° (2 mm.), n_D^{25} 1.4463.

Ethyl (+)-12-methyloctadecanoate was prepared by the procedure used above with 14.8 g. of ethyl (+)-9-oxo-12-methyloctadecanoate ($[\alpha]_D^{28}$ −0.10°). After extraction and esterification 10.5 g. (73.1%) of (+)-ester was obtained; b.p. 191–204° (0.5 mm.); n_D^{25} 1.4428; α_D^{28} +0.23° (homogeneous); $[\alpha]_D^{28}$ +0.15°; sapon. equiv., 322 (calcd. for $C_{21}H_{42}O_2$: 327).

(17) F. S. Prout and J. Cason, *J. Org. Chem.*, **14**, 132 (1949); *cf.* also H. McKennis, Jr., and V. du Vigneaud, *J. Am. Chem. Soc.*, **68**, 832 (1946).

Ethyl (−)-12-methyloctadecanoate was prepared by reduction of 9.4 g. (ethyl (−)-9-oxo-12-methyloctadecanoate. After the work-up 5.4 g. (60%) reduced (−)-ester was obtained; b.p. 190–198° (0.5 mm.); n_D^{25} 1.4429; α_D^{30} −0.22° (homogeneous); $[\alpha]_D^{30}$ −0.14°; sapon. equiv., 325 (calcd. for $C_{21}H_{42}O_2$: 327).

DL-*12-Methyloctadecanoic acid* (XI). Ethyl DL-12-methyloctadecanoate (5.2 g.) was heated under reflux for 1 hr. with 3.6 g. of potassium hydroxide in 100 ml. of 95% ethanol. The mixture was diluted with water and extracted with ether. The aqueous phase was acidified with hydrochloric acid and the acid was extracted with benzene. Removal of the solvent and crystallization of the acid from acetone-water mixtures furnished 3.7 g. (78%), m.p. 26–27°, equiv. wt., 299.1 (calcd. for $C_{19}H_{38}O_2$: 298.5). The literature[7] reports m.p. 27.6–28.2°.

The *amide*[2] after 5 crystallizations from methanol-water melted at 84–86°. A mixture containing equal amounts of the (+)- and (−)-amides melted at 76–78°.

The *tribromoanilide*[18] after 5 crystallizations from methanol-water melted at 93–94°. A mixture of equal amounts of (+)- and (−)-forms melted at 91–92°.

(+)-12-Methyloctadecanoic acid was prepared in 92% yield using 5.8 g. of ethyl (+)-12-methyloctadecanoate. Two crystallizations from acetone-water gave 4.9 g. of the (+)-acid; m.p. 37–38°; α_D^{27} +0.09° (homogeneous, 2 dm., tube); equiv. wt., 298.9 (calcd. for $C_{19}H_{38}O_2$: 298.5).

The *amide*[2] after 5 crystallizations melted at 74–75°.

The *tribromoanilide*[18] after 5 crystallizations melted at 89–91°.

(−)-12-Methyloctadecanoic acid was prepared like the other two forms using 5.4 g. of ethyl (−)-12-methyloctadecanoate. Two crystallizations from acetone-water furnished 2.9 g. (59%) of (−)-acid, m.p. 36–37°, α_D^{27} −0.10° (homogeneous, 2 dm. tube); equiv. wt., 299.4 (calcd. for $C_{19}H_{38}O_2$: 298.5).

The *amide*[2] after 5 crystallizations melted at 72–74°.

The *tribromoanilide*[18] melted at 90–92° after 5 crystallizations.

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[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT DIVISION OF HUMBLE OIL AND REFINING CO.]

Ozonolysis of Norbornylene

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Received November 12, 1958

Ozonolysis of norbornylene in methanol, a "reacting" solvent, gave a mixture of an aldehydic methoxyhydroperoxide and its condensation products, whereas "inert" solvents afforded a polymeric, active oxygen-containing substance tentatively characterized as a polymeric ozonide. The nature and modes of formation of these materials are discussed. Conversion of both products to *cis*-cyclopentane-1,3-dicarboxylic acid was effected in high yield.

In a course of study concerned with the preparation of carboxylic acids from olefins employing ozone as an oxidant, the conversion of norbornylene to cyclopentane-1,3-dicarboxylic acid was investigated. Since the literature does not reveal any reports of ozonolysis studies utilizing this olefin, it was of interest to characterize the intermediate, or active oxygen-containing, products formed prior to oxidative decomposition to the desired acid.

Criegee and co-workers have shown[1] that, in general, the ozonolysis of olefins in hydroxylic or "reacting" solvents gives rise to hydroperoxides

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