

scribed above for the production of allyl acrylate. Data obtained in the pyrolysis of methallyl α -acetoxypropionate are given in Table III.

TABLE III
PYROLYSIS OF METHALLYL ACETOXYPROPIONATE

Temp., °C.	Feed rate, drops/min.	Yield of acrylic ester, per cent. of theoretical	Loss as gas, per cent. by weight	Unchanged material, %
475	10	15	19	35
550	10	13	44	10
525	15	28	20	17
516	30	41	13	35
545	60	41	10	25

The pyrolysis of 152.9 g. of methallyl acetoxypropionate at 540–550° and a contact time of 4.9 seconds resulted in 137.1 g. of a liquid product. This was washed with water and with sodium carbonate solution to remove acetic acid, after which it was dried and fractionated. Methallyl acrylate (32 g.) was thus obtained. It distilled at 54–56° under 25 mm. pressure. Methallyl acetoxypropionate (38.5 g.) was collected at 100–110° under 20 mm. pressure. The yield of methallyl acrylate was 41.4% of the theoretical.

Methallyl acrylate is a clear, colorless, mobile liquid with

a mild, not unpleasant odor. Its physical properties are given in Table I. In its behavior toward light, heat, and polymerization catalysts, it is similar to allyl acrylate. When it is copolymerized with methyl acrylate or vinyl acetate, its modifying effect is also similar to that of allyl acrylate, but somewhat less pronounced.

Summary

1. Allyl and methallyl lactates were prepared by direct esterification of lactic acid with the alcohols and by alcoholysis of poly(lactyl)lactic acid.
2. Allyl and methallyl acetoxypropionates were prepared from the corresponding lactates by acetylation with acetic anhydride.
3. Allyl and methallyl acrylates were obtained in moderate yields in the pyrolysis of the corresponding acetoxypropionates.
4. These acrylic esters can be used to prepare polymers and interpolymers which, by virtue of cross-linkages, are less soluble, less fusible, and harder than polymers obtained by polymerizing methyl acrylate or vinyl acetate alone.

PHILADELPHIA, PA.

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Petroleum Acids. V. Aliphatic Acids from California Petroleum

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Hancock and Lochte³ reported on preliminary separations performed on 70 liters of petroleum acids from the Signal Hill, California, fields⁴ and on the isolation and identification of aliphatic acids with less than six carbon atoms. The higher boiling complex mixture of acids not studied at that time was carefully fractionated through 6-foot packed columns and thus divided into two series of fractions, those boiling below and those boiling above 223°—the boiling point of *n*-heptanoic acid. To remove hydrocarbons and phenolic compounds and any possible tertiary or otherwise hindered acids, the various acid fractions were recombined on the basis of boiling point and index of refraction into convenient-sized batches and individually esterified by refluxing for twenty-four hours with dry methanol containing 2% by weight of dry hydrogen chloride.

(1) From the Ph.D. Theses of W. A. Quebedeaux (1940), George Wash (1941), W. O. Ney (1942), and W. W. Crouch (1942), University of Texas.

(2) Research Assistant, University Research Institute, Project No. 49.

(3) Hancock and Lochte, *THIS JOURNAL*, **61**, 2448 (1939).

(4) Donated by the MacMillan Petroleum Corporation of Long Beach.

Each batch was cooled, diluted with an equal volume of water, and the ester layer separated. The esters were washed with water, three or four times with 0.7 *N* sodium carbonate, and finally with 0.1 *N* sodium hydroxide solution. Each washing was done by thorough mechanical stirring for two hours at room temperature. The esters were then dried over anhydrous sodium sulfate while the unesterified acids were recovered and again subjected to the esterification procedure just described. Any acids not esterified by two such treatments were fractionated and studied by other workers.^{3,5}

Each batch of esters was then saponified, the acids liberated, dried, and re-esterified as before to remove all hydrocarbons and phenolic compounds.

A total of 41.0 liters of acids yielded 39.44 liters of esters and 4 liters and unesterified acids which, on second treatment, yielded an additional 2.23 liters of esters and left a residue of 2.03 liters of unesterified acids.

(5) Shive, Horeczy, Wash and Lochte, *THIS JOURNAL*, **64**, 385 (1942).

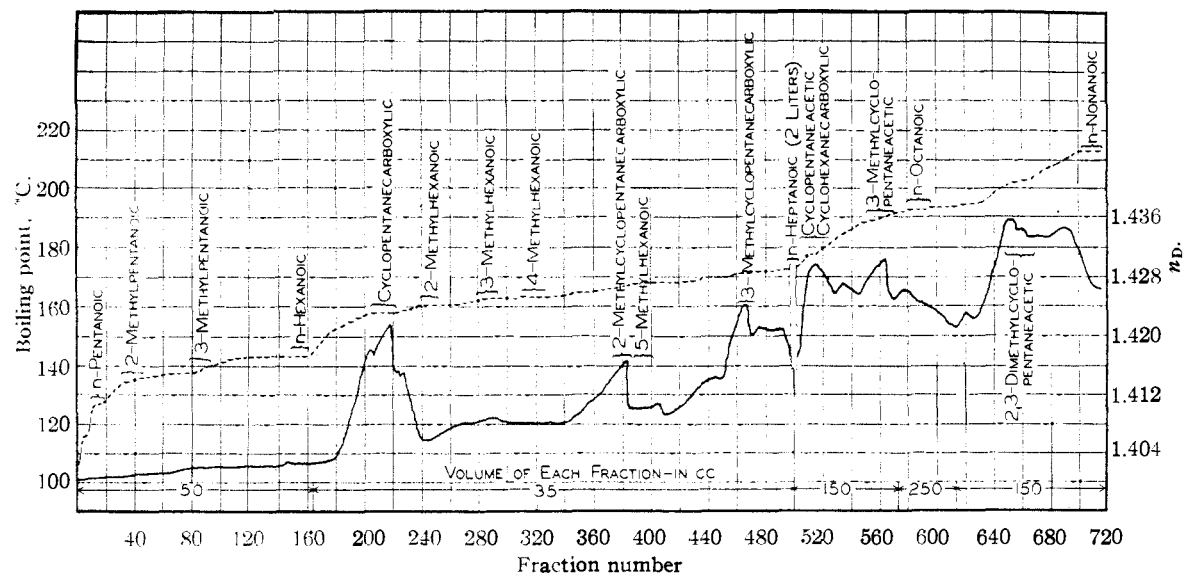


Fig. 1.—Ester fractions.

The batches of esters obtained were fractionated in order of boiling point through a 12-foot steel column packed with 0.5-in. Berl saddles and operated at 10:1 reflux at 20–30 mm. pressure. Distillate was removed continuously at a rate of 5–6 cc. per minute and material of slightly higher boiling point than the distillate added continuously as required. This fractionation was repeated on all of the esters, dividing the esters like the acids into two series separated by methyl heptanoate boiling at 173°. Two liters of this ester was obtained as residue from the lower series and as first fractions of the higher.

The total volume of methyl esters boiling below 173° was only about 2 liters, while approximately 37 liters boiled above methyl heptanoate.

A plot of ester fraction number against atmospheric boiling point and against index of refraction was now prepared and recombinations and refractionations done on the basis of the information obtained from the curves. The lower boiling series was now refractionated through a 6-ft. Stedman column (250 cones) with, however, only moderate additional separation. The higher fractions were refractionated through the steel column one or more additional times depending on the physical data obtained. Detailed data were plotted on large scale curves from which data on 720 methyl ester fractions are shown as Fig. 1, to which reference will be made frequently in this and future communications.

By a systematic study of series of fractions showing essentially constant boiling points and

low index of refraction, the following aliphatic acids have been isolated and identified from this series of 720 fractions: 2- and 3-methylpentanoic acid and *n*-hexanoic acid; 2-, 3-, 4-, and 5-methylhexanoic acids and *n*-heptanoic acid; and *n*-octanoic and *n*-nonanoic acids. In case of the lower members of the series it was often possible to identify the aliphatic acids by simply saponifying the ester and then preparing solid derivatives and identifying by comparison with known acids synthesized in this project. Usually, however, a more elaborate series of fractional neutralization or liberation processes had to be employed on the highly fractionated material before solid derivatives could be obtained or, if obtained, could be purified by recrystallization.

In case the melting point of a derivative on purification approached that of an acid previously isolated in this work a mixed melting point with the known derivative was made. This practice avoided waste of time involved in purification of a compound previously identified, but it may have resulted in failure to identify a new acid in case the melting point of this particular derivative was not depressed on mixing with this derivative of the known acid.

Only methyl substituted aliphatic acids have been isolated and of these none had more than one methyl group. Since any method of separation now known would probably fail to isolate acids found in only small amounts this failure to find other types of aliphatic acids may merely indicate that other acids are not present in large

amounts. In a few cases promising ester series yielded mixtures that could not be separated. Some of these may contain considerable amounts of missing acids.

Unless future developments should make the isolation of some particular aliphatic acid of vital interest it is not planned to study eight carbon and higher aliphatic acids because of the slight interest in these and because of difficulties involved in identifying such acids.

Experimental

Search for 2,2-Dimethylpropanoic and 2-Methylbutanoic Acids.—Hancock was not able to isolate either trimethylacetic or methylethylacetic acid in his study of these California acids. Since more efficient fractionating columns were now available, all methyl esters boiling between 90 and 130° were refractionated. "Plateaus" were obtained at 115.0–115.6° and at 126.2–126.4°. The ester of the tertiary acid boils at 102° so was evidently absent, but the methyl ester of 2-methylbutanoic acid boils at 115° and that of 3-methylbutanoic acid at 116.7°. A mixed melting point of synthetic 3-methylbutanoic and of petroleum *o*-phenylenediamine derivatives showed no depression and since Hancock,³ in a careful study of esters with identical boiling points, was able to identify only 3-methylbutanoic acid, no further search for 2-methylbutanoic acid was made.

2-Methylpentanoic Acid.—Fractions 30–55, Fig. 1, were converted to the *p*-toluidide over the chloride and this derivative recrystallized to a constant melting point at 81°. The *p*-toluidide (11 g.) was hydrolyzed by heating in a sealed tube for twenty-four hours at 140–150° with concentrated hydrochloric acid to yield 3 g. of acid, b. p. 193–194°, n_D^{20} 1.4140, d_4^{20} 0.9219, n. d. 1.300,⁶ neutralization equivalent 116. This was converted to the acid chloride, b. p. 140°, n_D^{27} 1.4330, which was changed to the amide, m. p. 76–78°; and to the *p*-phenylphenacyl ester, m. p. 62.5–63.0°. For 2-methylpentanoic, Hommelen⁷ reported b. p. 192–194°, d_4^{20} 0.9230, n_D^{20} 1.4136; for the acid chloride, b. p. 140–141°; for the amide, m. p. 79.6°. Mixed melting points, of these and the corresponding derivatives of the acid synthesized by the malonic ester synthesis alkylating first with *n*-propyl iodide, were not depressed.

3-Methylpentanoic Acid.—Ester fractions 80–85, Fig. 1, converted to the acid, b. p. 196°, n_D^{20} 1.4146, d_4^{20} 0.9192; to the acid chloride, and finally to the *p*-toluidide, m. p. 74°, indicated that the acid was probably 3-methylpentanoic acid reported by Hommelen⁷ to yield a *p*-toluidide melting at 74.8°. This acid was prepared from 2-methylbutanol through the bromide and the Grignard acid synthesis. The synthetic acid, b. p. 197°, n_D^{20} 1.4150, was converted to its *p*-toluidide, m. p. 73.2°, mixed m. p. 73–74°.

***n*-Hexanoic Acid.**—Ester fractions 155–160, Fig. 1, and the acid obtained from them agreed closely in physical properties, b. p. 203°, n_D^{20} 1.4152, d_4^{20} 0.9227, with values

reported for *n*-hexanoic acid. The relatively large volume of material in adjacent fractions with properties similar to these further indicated that this was probably the ester of a normal aliphatic acid. A comparison of synthetic and petroleum acid *p*-toluidides showed that both, and a mixture, melted at 74°.

2-Methylhexanoic Acid.—Ester fractions 248–249, Fig. 1, out of the "plateau" at fractions 240–260 were saponified and the acids distilled, b. p. 206°, n_D^{20} 1.4193. The amide melted at 70–71° and the *p*-toluidide at 82.5–83.0°.

Anal. of *p*-toluidide. Calcd. for $C_{14}H_{21}ON$: N, 6.39. Found: N, 6.23.

These properties agree with those for 2-methylhexanoic, so this acid was synthesized by the malonic ester synthesis alkylating first with *n*-butyl bromide. The acid, b. p. 208–211°, n_D^{20} 1.4205, d_4^{20} 0.9162, n. d. 1.292, was converted to the amide, m. p. 69–70°, mixed m. p. 69–70°; and to the *p*-toluidide, m. p. 82–83°, mixed m. p. 82–83°.

3-Methylhexanoic Acid.—Ester fractions 285–290, Fig. 1, were combined and saponified, and the acids liberated and fractionated. The main fraction, b. p. 210°, n_D^{20} 1.4200, d_4^{20} 0.9158, was changed to the amide, m. p. 99°; and the *p*-toluidide, m. p. 71–73°.

Anal. of *p*-toluidide. Calcd. for $C_{14}H_{21}ON$: N, 6.39. Found: N, 6.44.

3-Methylhexanoic acid was synthesized by the malonic ester synthesis alkylating with 2-bromopentane. The acid, b. p. 215–216°, n_D^{20} 1.4227, d_4^{20} 0.9182, n. d. 1.306, was converted to its amide, m. p. 99–100°, mixed m. p. 99°; its *p*-toluidide, m. p. 73–74°, mixed m. p. 71–73°; and its *p*-phenylphenacyl ester, m. p. 61–62°.

4-Methylhexanoic Acid.—Ester fractions 300–340, Fig. 1, appeared to be practically uniform and fractions 313–314 were combined, b. p. 162°, n_D^{20} 1.4080. The acid obtained, b. p. 212°, n_D^{20} 1.4232, was converted to the amide, m. p. 102–103°; and the *p*-toluidide, m. p. 82°.

Anal. of *p*-toluidide. Calcd. for $C_{14}H_{21}ON$: N, 6.39. Found: N, 6.33.

4-Methylhexanoic acid was suspected and synthesized by the malonic ester synthesis alkylating with 2-methyl-1-bromobutane. The acid, b. p. 214–217°, n_D^{20} 1.4227, d_4^{20} 0.9215, was changed to its amide, m. p. 103–104°, mixed m. p. 103°; and its *p*-toluidide, m. p. 82°, mixed m. p. 82°.

5-Methylhexanoic Acid.—Ester fractions 392–393, Fig. 1, were selected from the series 388–402 to determine the acid present just below 2-methylcyclopentane carboxylic acid. The combined sample boiled at 167° and had n_D^{20} 1.4097. Saponification yielded the acid, b. p. 210°, n_D^{20} 1.4220, from which the amide, m. p. 101–103°; and the *p*-toluidide, m. p. 73°, were prepared.

Anal. of *p*-toluidide. Calcd. for $C_{14}H_{21}ON$: N, 6.39. Found: N, 6.22.

These properties indicated that the acid might be 5-methylhexanoic acid previously isolated from Baku petroleum by Tchitchibabine⁸ and by Neutzescu⁹ from Roumanian petroleum. It was prepared using isoamylbromide as alkylating agent in the malonic ester synthesis. The acid obtained, b. p. 216–222°, n_D^{20} 1.4210, d_4^{20} 0.9140,

(6) Schutze, Shive and Lochte, *Ind. Eng. Chem., Anal. Ed.*, **12**, 262 (1940).

(7) Hommelen, *Bull. soc. chim. Belg.*, **42**, 243 (1933).

(8) Tchitchibabine, *Chimie & industrie*, Sp. Number 306–318, March (1932).

(9) Neutzescu, Isacescu and Volrap, *Ber.*, **71B**, 2056 (1938).

n. d. 1.300, was converted to its amide, m. p. 102-104°, mixed m. p. 101-103°; and to its *p*-toluidide, m. p. 74°, mixed m. p. 73-74°.

***n*-Heptanoic Acid.**—Early in the separation procedures the presence of large amounts of *n*-heptanoic acid had been indicated by the boiling point of the acid, and particularly that of the methyl ester, since methyl esters in mixture appear to boil close to their true boiling points, and this acid and its methyl ester were used as convenient dividing points between the lower and the higher series of acids and esters. Williams and Richter¹⁰ had previously isolated this acid (*n*-octanoic, and *n*-nonanoic) from Texas pressure distillate. The amide was prepared in our work by treating the methyl ester with an equal volume of concentrated ammonium hydroxide and leaving the mixture for a week in a stoppered flask before filtering off the amide formed. After five recrystallizations the melting point was 94.5-95.0° and a mixed melting point with an authentic sample was 95.0°; *o*-phenylenediamine derivative, m. p. 136° mixed m. p. 136°.

***n*-Octanoic Acid.**—One liter of acids obtained from ester fractions 580-590, Fig. 1, was dissolved in 8 liters of petroleum ether (b. p. 65-80°) and stirred vigorously for two hours with 350 cc. of 10% sodium hydroxide solution. The layers were separated and an attempt made to remove another fraction of acids in the same way, but emulsification prevented further use of this method at this stage without extensive further dilution of the petroleum ether as well as the aqueous solution; so the remaining acids were neutralized in one step, dried, and fractionated, b. p. 236-238°, n_D^{20} 1.4327, d_4^{20} 0.9185, n. d. 1.317. The n. d.

(10) Williams and Richter, *THIS JOURNAL*, **57**, 1686 (1935).

value indicated that the acid was practically all aliphatic in nature and the large volume of this series available and physical properties indicated *n*-octanoic acid. The amide melted at 105-106° and there was no depression in a mixed melting point with the amide of authentic *n*-octanoic acid.

***n*-Nonanoic Acid.**—Ester fraction 710, Fig. 1, b. p. 213°, n_D^{20} 1.4257, yielded an amide melting at 99°. Mixed with the amide of known *n*-nonanoic acid the melting point was unchanged. This with the large volume available and physical properties showed the presence of this acid, b. p. 254-256.5°, n_D^{20} 1.4379.

Summary

By careful and extensive fractionation of certain California petroleum acids and their esters a series of 720 fractions of esters was obtained. Curves of ester fraction number plotted against boiling point and against index of refraction are presented as Fig. 1.

By studying various series of ester fractions with low index of refraction and with essentially constant boiling point the following aliphatic acids were isolated and identified: 2- and 3-methylpentanoic and *n*-hexanoic acids; 2-, 3-, 4-, and 5-methylhexanoic and *n*-heptanoic acids, and *n*-octanoic and *n*-nonanoic acids.

No evidence for the presence of 2,2-dimethylpropanoic or 2-methylbutanoic acid could be found.

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Petroleum Acids. VI. Naphthenic Acids from California Petroleum

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All except the last of the series of naphthenic acids reported in this paper were isolated from the series of 720 fractions of methyl esters of petroleum acids shown in Fig. 1 of the preceding paper of this series³ (hereafter referred to as Fig. 1).

Preliminary experiments had shown that procedures used at the refinery and supplemented here had removed phenolic compounds from these acids. This made it possible to decide which of the 720 fractions of esters were derived from naphthenic acids by noting the index of refraction of the fraction. The first 180 fractions consisted almost entirely of esters of aliphatic acids,

but "peaks" in the refractive index curve showed an accumulation of naphthenic acids at fractions 210-220, 370-380, 460-470, 510-520, 530-540, 560-565, 650-660 and 680-690 with possibly minor concentrations at various other series of fractions. The curve did not indicate, however, whether any particular "peak" was due to a single naphthenic acid or to several; and the boiling point curve showed that, in all cases, fractions consisted of mixtures of esters of both aliphatic and naphthenic acids. The isolation and identification of aliphatic acids from this mixture was relatively simple in those cases in which a single main acid of this type was present since partial neutralization in practically all cases removed naphthenic acids to a sufficient extent to permit preparation of solid derivatives of the aliphatic

(1) From theses submitted in partial fulfillment of requirements for the Degree of Doctor of Philosophy, University of Texas, 1942.

(2) General Aniline and Film Corporation Fellow, 1942.

(3) Quebedeaux, Wash. Ney, Crouch and Lochte, *THIS JOURNAL*, **65**, 767 (1943).