tertiary hydroxyl regardless of whether the amino group is primary, secondary, or tertiary. The results obtained in these condensations are summarized in Table I; the last two phenethylamine derivatives are new compounds. These were converted into their hydrochlorides which were analyzed. The other hydrochlorides correspond in properties to those obtained from the phenethylamines prepared by condensing benzene and an unsaturated amine[3a] or from the action of formamide on an alkylated phenylacetone.[3b]

TABLE I

CONDENSATION OF BENZENE AND AMINO ALCOHOLS

Amino alcohol	Phenethylamine derivative Yield, %	B. p., °C.	(Mm.)	M. p., HCl salt, °C.
$(CH_3)_2C(OH)CH_2NH_2$	87	87–89	10	....
$(CH_3)_2C(OH)CH_2NHCH_3$	78	92–92.5	11	....
$(CH_3)_2C(OH)CH_2NHC_2H_5$	86	96–98	11	191.5–192.5
$(CH_3)_2C(OH)CH(NH_2)CH_3$	63	100–102	10	214–215
$(CH_3)_2C(OH)CH(NHCH_3)CH_3$	63	99–100.5	9	230–231[a]
$(CH_3)_2C(OH)C(NH_2)(CH_3)_2$	73	123–126	14	207–210[b]

[a] *Anal.* Calcd. for $C_{12}H_{20}NCl$: Cl, 16.59. Found: Cl, 16.63. [b] *Anal.* Calcd. for $C_{12}H_{20}NCl$: Cl, 16.59. Found: Cl, 16.39.

Experimental

Amino Alcohols.—The amino alcohols were prepared by the action of ammonia or an amine upon the proper ethylene oxides. A sample of 1-amino-2-methyl-2-propanol was also obtained from the Shell Development Company.[4] 3-Methylamino-2-methyl-2-butanol is apparently a new compound. It was obtained in 85% yield by heating 160 g. (1.6 moles) of 33% methylamine and 34.5 g. (0.4 mole) of trimethylethylene oxide in a pressure bottle at 100° for three hours. It distilled at 152–155° (750 mm.), n^{20}_D 1.4394, d^{20}_4 0.9018.

Anal. Calcd. for $C_6H_{15}ON$: N, 11.91. Found: N, 11.97.

Condensation Reactions.—A typical reaction is described. To a cooled well-stirred mixture of 80 g. (0.6 mole) of anhydrous aluminum chloride and 78 g. (1 mole) of benzene was added 17.8 g. (0.2 mole) of 1-amino-2-methyl-2-propanol. Much heat was evolved. The mixture was then stirred and refluxed for three hours, allowed to stand overnight, and poured on ice. The benzene layer was extracted with dilute hydrochloric acid and this extract combined with the aqueous layer which was then made strongly alkaline. The amine which separated was taken up in ether and the ether solution was dried and distilled. The fraction distilling at 87–90° (10 mm.) weighed 26 g. corresponding to 87% of the theoretical amount of β,β-dimethylphenethylamine. The phenylthiourea of the amine melted at 106–106.5°.

An attempt to condense 1-amino-2-propanol with benzene under the conditions just described gave about 1% of β-methylphenethylamine.

Summary

Amino alcohols containing a tertiary hydroxyl group condense with benzene in the presence of excess aluminum chloride to give β,β-dialkylphenethylamine derivatives.

EVANSTON, ILLINOIS RECEIVED FEBRUARY 10, 1943

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[3] (a) Weston, Ruddy and Suter, THIS JOURNAL, 65, 674 (1943); (b) Suter and Weston, *ibid.*, 64, 533 (1942).

[4] We wish to express our thanks for the gift of this material.

[CONTRIBUTION FROM EASTERN REGIONAL RESEARCH LABORATORY, BUREAU OF AGRICULTURAL CHEMISTRY AND ENGINEERING, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

Pyrolysis of Lactic Acid Derivatives. Preparation of Allyl and Methallyl Acrylates[1]

BY C. H. FISHER, CHESSIE E. REHBERG AND LEE T. SMITH

In recent years considerable attention[2–6] has been devoted to the pyrogenic conversion of various lactic acid derivatives into acrylic esters, which have become well known as intermediates used in the production of certain acrylic resins[7] and synthetic rubber.[8] Several of these investigations[2,3,6] were concerned with methyl α-acetoxypropionate, a lactic acid derivative which decomposes smoothly and readily when pyrolyzed, yielding methyl acrylate and acetic acid

$$CH_3COOCH(CH_3)COOCH_3 \xrightarrow{500°C.} CH_2{=}CHCOOCH_3 + CH_3COOH$$

In view of the fact that high yields of methyl acrylate are obtained when methyl acetoxypropio-

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[1] Presented before the Division of Organic Chemistry at the 104th meeting of the American Chemical Society at Buffalo, New York, September 7–11, 1942. Not copyrighted.

[2] Burns, Jones and Ritchie, *J. Chem. Soc.*, 400, 714, 1054 (1935); U. S. Patent 2,265,814, Dec. 9, 1941.

[3] Smith and Claborn, *Ind. Eng. Chem., News Ed.*, 17, 370, 641 (1939).

[4] Stearn, Makower and Groggins, *Ind. Eng. Chem.*, 32, 1335 (1940).

[5] Claborn, U. S. Patent 2,229,997, Jan. 28, 1941.

[6] Smith, Fisher, Ratchford and Fein, *Ind. Eng. Chem.*, 34, 473 (1942).

[7] Neher, *ibid.*, 28, 267 (1936).

[8] Ziegler, *Chem.-Ztg.*, 62, [14] 125 (1938); *Rubber Chem. and Technology*, 11, 501 (1938); I. G. Farbenindustrie A.-G., British Patent 360,822, Oct. 30, 1931; Anderson, Hill and Morgan, British Patent 514,912, Nov. 21, 1939; Starkweather and Collins, U. S. Patent 2,218,362, Oct. 15, 1940; Clifford, U. S. Patent 2,279,293, Apr. 14, 1942.

nate is pyrolyzed, attempts[2] have been made to produce other acrylic esters by pyrolyzing the ethyl and *n*-butyl esters of α-acetoxypropionic acid. Poor yields of ethyl and butyl acrylate were obtained, however, owing to a competitive reaction, which presumably would occur in the thermal decomposition of all the higher *n*-alkyl α-acetoxypropionates, yielding acetoxypropionic acid and olefins

$$CH_3COOCH(CH_3)COOCH_2CH_2R \longrightarrow CH_3COOCH(CH_3)COOH + CH_2{=}CHR$$

In view of the work of Van Pelt and Wibaut,[9] who observed that acetates of primary and secondary alcohols decompose at 500–525° and 450°, respectively, secondary- and tertiary-alkyl acetoxypropionates would be expected to decompose more readily than the ethyl and *n*-butyl acetoxypropionates pyrolyzed by Burns, Jones and Ritchie.[2]

The present investigation was undertaken because it appeared likely that the undesired decomposition into acetoxypropionic acid and olefin described above might not occur to a serious extent with allyl and methallyl α-acetoxypropionates (I).

$$\underset{\text{I}}{CH_3COOCH(CH_3)COOCH_2CR{=}CH_2} \quad (\text{I, } R = H \text{ or } CH_3)$$

Hydrogen on the beta-carbon atom, which presumably facilitates the undesired side reaction, is lacking in the methallyl ester (I, R = CH_3), and only one such hydrogen atom is present in the allyl ester (I, R = H). The expectation that moderate yields of allyl and methallyl acrylates would result from the pyrolysis of allyl and methallyl acetoxypropionates (I) was realized. These results are not necessarily at variance with those of Hill and Isaacs,[10] who indicated that on pyrolysis α-methylallyl acetate (II) decomposes readily into butadiene and acetic acid. That α-methylallyl esters (II) and β-methylallyl esters (I, R = CH_3) behave differently when pyrolyzed can be attributed to the presence of four β-hydrogen atoms in α-methylallyl esters and the absence of β-hydrogen atoms in esters of type I.

$$\underset{\text{II}}{CH_3COOCH(CH_3)CH{=}CH_2} \longrightarrow CH_3COOH + CH_2{=}CHCH{=}CH_2$$

Our interest in the preparation of allyl and methallyl acrylates was aroused also because these esters possess two olefinic linkages, and hence on polymerization should be capable of yielding cross-linked polymers and interpolymers. Such polymers, by virtue of their cross-linkages, are generally harder, less soluble, and less fusible than related linear polymers.[11,12]

The allyl and methallyl acetoxypropionates were prepared from 100% lactic acid that had been produced by the hydrolysis of methyl lactate.[3] The difficulties usually met in esterifying lactic acid were experienced. Probably the competition of the allyl or methallyl alcohol with the alcoholic hydroxyl group of lactic acid was largely responsible for the relatively low esterification yields. The yields of allyl and methallyl lactates were increased by (a) using large excesses of alcohol; (b) repeatedly treating the residue (presumably condensation polymers of lactic acid) from the distillation of the esterification mixture with additional quantities of alcohol; and (c), in the case of allyl lactate, converting lactic acid into its condensation polymer and subsequently allowing this polymer to react with an excess of allyl alcohol.

On acetylation with acetic anhydride, both allyl and methallyl lactates reacted readily to form allyl and methallyl α-acetoxypropionates (I) in high yields. On the basis of earlier work, it would be expected that these acetylations could also be effected satisfactorily with ketene[13] and with acetyl chloride.[14]

When passed through a glass tube at temperatures ranging from 475 to 575°, allyl and methallyl acetoxypropionates (I) decomposed into allyl and methallyl acrylates, respectively, yields of approximately 40% of the theoretical being obtained.

The principal liquid by-product obtained in the pyrolysis experiments was acetaldehyde, which probably was formed by decomposition of the allyl acetoxypropionates into α-acetoxypropionic acid, followed by decomposition of the latter into acetaldehyde, carbon monoxide and acetic acid. A small amount of yellow liquid, as yet unidentified, was collected by distillation at approximately 90°. The principal gaseous products of the pyrolysis experiments, listed in order of

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[9] Van Pelt and Wibaut, *Rec. trav. chim.*, **60**, 55 (1941).

[10] Hill and Isaacs, U. S. Patent 2,224,912, Dec. 17, 1940.

[11] H. Mark and R. Raff, "High Polymeric Reactions. Their Theory and Practice," Interscience Publishers, Inc., New York, N. Y., 1941, 476 pp.

[12] Pollack, Muskat and Strain, U. S. Patent 2,273,891, Feb. 24, 1942; Patnode, U. S. Patent 2,181,739, Nov. 28, 1939; Rutovskiĭ and Zabrodini, *Org. Chem. Ind.* (U. S. S. R.), **7**, 441 (1940).

[13] Claborn and Smith, This Journal, **61**, 2727 (1939).

[14] Patterson and Forsyth, *J. Chem. Soc.*, **103**, 2263 (1913).

decreasing yields, were carbon monoxide, carbon dioxide, olefins, paraffins and hydrogen.

It was observed that increasing the rate of feed (which decreases the contact time) lowered the conversion per pass, increased the yield of acrylic ester, and decreased the yield of gaseous products. Raising the reaction temperature increased the conversion per pass but also the yield of gases. Temperatures of approximately 550° and a contact time of six seconds appeared to be most suitable. Probably further study of the variables involved would reveal more satisfactory conditions, under which higher yields of the acrylic esters could be obtained.

Although the acetyl derivatives of allyl and methallyl lactates were pyrolyzed in the present investigation, from previous work[2] it would be expected that propionyl, benzoyl and other acyl derivatives could be used satisfactorily. From the standpoint of convenience, an ester of molecular weight higher than that of the acetate would have been more satisfactory than allyl acetoxypropionate (I). The two pyrolysis products, allyl acrylate and acetic acid, have boiling points of 122 and 118° and hence are not readily separated by distillation. Obviously, it would be easier to separate allyl acrylate from the less volatile organic acids that would be obtained in the pyrolysis of lactic esters such as allyl α-benzoyloxypropionate.

It was considered likely from earlier work[2,9] that allyl and methallyl methacrylates might be obtained more satisfactorily than the acrylates by pyrogenic methods. Preliminary experiments, in which approximately 75% yields of the two methacrylates were obtained from the acetoxyisobutyrates, have confirmed this view.

The mechanism of the thermal decomposition of alkyl α-acetoxypropionates has been discussed briefly by Smith and co-workers.[6]

Polymerization Experiments.—That allyl and methallyl acrylates, even when constituting low proportions of a mixture of acrylates, are capable of modifying the solubility and other properties of the polymers obtained was demonstrated by simple experiments. Several ethyl acetate solutions of individual and mixed acrylates containing 20% of the monomer or monomers, together with benzoyl peroxide (0.3% of the monomer), were heated at 65° for twenty-four hours. The solution consisting of 20% methyl acrylate and 80% ethyl acetate was transformed into a viscous solution of the polymer. However, the solutions containing 80% ethyl acetate and 0.2, 1.0, 2.0 and 4.0% allyl acrylate, together with 19.8, 19.0, 18.0 and 16.0% methyl acrylate, respectively, gave firm, elastic, solid gels, which were insoluble in the common solvents and which, when dried, were much harder and tougher than polymeric methyl acrylate.

The mass or bulk polymerization of methyl acrylate solutions containing 1% allyl acrylate or 1% methallyl acrylate yielded polymers which were insoluble and distinctly harder than polymeric methyl acrylate. Similar results were obtained in the mass polymerization of vinyl acetate containing 1% allyl acrylate or 1% methallyl acrylate.

The authors are grateful to the Analytical and Physical Chemistry Division for analytical data and to other members of the Carbohydrate Division who assisted in the experimental work.

Experimental

Allyl Lactate.—The direct esterification of lactic acid with allyl alcohol, in which benzene was used to remove water by azeotropic distillation, was not satisfactory because only moderate yields of allyl lactate (25 to 35%) were obtained. The use of acid catalysts, such as sulfuric or *p*-toluenesulfonic acid, appeared to be of little or no value. The polylactyllactic acid residue left from the distillation of the ester could be used in a subsequent experiment, thus increasing the over-all yield. From four moles (360 g.) of 100% lactic acid and 4.4 moles (256 g.) of allyl alcohol, a total of 268 g. of allyl lactate was obtained. This represents a total conversion of 51.5% of the lactic acid to ester. After the third treatment of the acid with allyl alcohol, a residue of 150 g. of polylactyllactic acid remained. Further treatment with allyl alcohol undoubtedly would have increased the conversion into ester.

Higher conversions of lactic acid into allyl lactate were obtained by removing as much water as possible from lactic acid by refluxing with benzene before addition of the allyl alcohol. Thus, from 2 moles (180 g.) of 100% acid 34 g. of water was removed. To the lactic acid polymer thus obtained 6 moles (348 g.) of allyl alcohol was added. After this mixture was refluxed for four hours, the products were fractionated. Only 45 g. (17.5% of the theoretical) of allyl lactate was obtained. However, by heating the recovered alcohol again with the polylactyllactic acid residue, to which 1 to 2 g. of *p*-toluenesulfonic acid had been added, an additional 159 g. of ester was obtained. The total yield in the two steps was 204 g., or 78% of the theoretical. It is noteworthy that although the presence of an acid catalyst had little effect on the yield of ester from lactic acid, it increased the yield from polylactyllactic acid almost four-fold.

Allyl lactate is a clear, colorless, mobile liquid with a mild odor. Its physical properties and analytical data are recorded in Table I.

TABLE I

PHYSICAL PROPERTIES OF ESTERS

Ester	B. p., °C.	Press., mm.	n^{20}_D	d^{20}_4	Molecular refraction Calcd.	Molecular refraction Found	Saponification equivalent Calcd.	Saponification equivalent Found
Allyl lactate	79	25	1.4369	1.0452	32.62	32.61	130.1	133.5
Methallyl lactate	78	11	1.4389	1.0181	37.24	37.23	144.2	150.2
Allyl acetoxypropionate	98	20	1.4270	1.0544	41.98	41.93	86.1	88.0
Methallyl acetoxypropionate	95	10	1.4314	1.0330	46.60	46.70	93.1	95.5
Allyl acrylate	122	760	1.4295	0.9410	30.63	30.75	...	...
Methallyl acrylate	72	50	1.4385	.9275	35.25	35.74	126.1	128.3

Methallyl Lactate.—Five moles (450 g.) of 100% lactic acid, 5.5 moles (396 g.) of methallyl alcohol, and 300 cc. of benzene were refluxed with continuous removal of water until no more water was produced. Fractionation of the mixture gave 212 g. of ester. The recovered alcohol was returned to the flask containing the polylactyllactic acid residue and again refluxed for several hours, thus producing an additional 115 g. of ester. The recovered alcohol was heated with the acid residue five times more, additional alcohol being added three times. Also, the addition of a small quantity of *p*-toluenesulfonic acid in one of the later stages was helpful. The total yield of ester thus obtained was 460 g., or 64.6%. The use of strong acid catalysts with methallyl alcohol is inadvisable because of their tendency to cause the rearrangement of the alcohol to form isobutyraldehyde.

Methallyl lactate was prepared also in rather low yields by heating methallyl chloride and 64% aqueous sodium lactate in a closed vessel at 110–250°. Methallyl lactate is clear, colorless, and mobile, and has a mild, pleasant odor (see Table I for physical properties).

Allyl α-Acetoxypropionate.—Allyl lactate (1.5 moles, 195 g.) was acetylated by adding, with stirring, 168 g. (1.65 moles, 10% excess) of acetic anhydride. One gram of phosphoric acid was added, and the mixture was maintained at 60–100° during the addition of acetic anhydride. After standing for one-half hour the mixture was fractionated under reduced pressure. Two hundred and thirty grams of the acetoxypropionate was obtained. This was 89% of the theoretical. The product was a clear, colorless, limpid liquid with a faint, pleasant odor. Its physical properties are recorded in Table I.

Methallyl α-Acetoxypropionate.—The procedure for the preparation of methallyl acetoxypropionate from methallyl lactate was similar to that described above for the allyl ester. A yield of 93% was obtained. It was a clear, colorless, mobile liquid having a faint odor. The physical properties are given in Table I.

Allyl Acrylate.—Allyl acetoxypropionate was pyrolyzed by passing its vapors through a Pyrex glass tube containing short lengths of Pyrex tubing as contact material. The temperature and contact time ranged from 500 to 575° and six to fifteen seconds, respectively. The pyrolysis equipment was essentially the same as that previously described.[6] Best results were obtained with temperatures of approximately 550° and a contact time of six seconds. From the experimental results it seems likely that higher yields might be obtained with lower contact times.

To illustrate the effect of varying the temperature and contact time in the pyrolyses, the results of several experiments are given in Table II.

TABLE II

PYROLYSIS OF ALLYL ACETOXYPROPIONATE

Temp., °C.	Feed rate, drops/min.	Yield of acrylic ester, per cent. of theoretical	Loss as gas, per cent. by weight	Unchanged material, %
525	25	36	18	26
525	40	38	14	36
525	60	38	13	45
546	60	43	18	29
572	60	31	31	9
550	15	20	30	7

Table II shows that increasing the feed rate (decreasing the contact time) produces higher yields of acrylate, causes less loss as gaseous by-products, and lowers the conversion per pass. Raising the temperature increases the conversion but also increases the amount of gaseous by-products.

By the pyrolysis of 134.8 g. of allyl acetoxypropionate at 546°, with a contact time of 5.9 seconds, 111.2 g. of liquid and 9.1 liters of gaseous by-products were obtained. Orsat analysis indicated that the latter consisted of 3.06 liters of carbon dioxide, 4.08 liters of carbon monoxide, 1.55 liters of olefins, 0.18 liter of paraffins, 0.13 liter of oxygen, and 0.08 liter of hydrogen.

Fractionation of the liquid product yielded 60.0 cc. of material boiling at 40–60° at 50 mm. pressure, which consisted essentially of acetic acid and allyl acrylate. A second fraction boiling at 90–110° at 27 mm. pressure was virtually pure allyl acetoxypropionate. The first fraction was washed with water, then with aqueous sodium carbonate solution, and finally with water again. After the fraction was dried with sodium sulfate and a little hydroquinone was added to inhibit polymerization, the material was again distilled. The product was 26.6 g. (42.6% of theoretical) allyl acrylate, boiling at 45–50° at 40 mm. pressure. Its boiling point at atmospheric pressure was 122°. Caspary and Tollens[15] reported the boiling point of allyl acrylate as 119–124° and the color as yellow. Our product was clear and colorless and had a characteristic, somewhat unpleasant odor. Its physical properties are recorded in Table I.

Allyl acrylate of the purity obtained in our experiments may be stored at room temperature without polymerization, provided that it is not exposed to strong direct light. Heating at 50° or higher in the absence of an inhibitor results in polymerization, the final product being a hard, brittle, transparent, insoluble, and infusible resin.

Methallyl Acrylate.—The equipment and general procedure used in this preparation were the same as that de-

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(15) Caspary and Tollens, *Ann.*, **167**, 247 (1873).

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 polylactyllactic 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. RECEIVED NOVEMBER 27, 1942

[CONTRIBUTION NO. 311 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

Petroleum Acids. V. Aliphatic Acids from California Petroleum

BY W. A. QUEBEDEAUX,[1] GEORGE WASH,[1] W. O. NEY,[1] W. W. CROUCH[1,2] AND H. L. LOCHTE

Hancock and Lochte[3] reported on preliminary separations performed on 70 liters of petroleum acids from the Signal Hill, California, fields[4] 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. 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.

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(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.

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