

a 2% potassium hydroxide solution (c , 1.425). Hockett¹⁹ recorded $[\alpha]^{24D} -29.7$ in a 2% sodium hydroxide solution and Reichstein²² gave $[\alpha]^{22D} -32.8^\circ$ in a 2% potassium solution.

Summary

1. The "2,3-monoacetone galactosedibenzylmercaptal" of Pacsu and Löb was found to be a mixture of two isomeric monoacetone derivatives.

2. The chemical structure of the higher rotating isomer was investigated and it was proved that the isopropylidene group was attached on carbon atoms 4 and 5.

3. This conclusion was drawn from the results of a series of transformations in which the substance was first converted into the 4,5-monoace-

tone galactosedimethylacetal. On methylation the latter gave rise to the 2,3,6-trimethyl derivative which on hydrolysis and subsequent oxidation yielded crystalline 2,3,6-trimethyl γ -galactonolactone.

4. Oxidation by periodic acid of the monoacetone galactosedimethylacetal gave glyoxal and 2,3-acetone *d*-threose, which scission products could form only if the starting material had the isopropylidene group at carbon atoms 4 and 5.

5. The glyoxal was isolated as *bis*-phenylhydrazone, the 2,3-acetone threose was converted into *d*-threonic acid from which the acid potassium salt of *l*-tartaric acid was prepared.

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[CONTRIBUTION NO. 168 FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, THE UNIVERSITY OF TEXAS]

Acidic Constituents of a California Straight-run Gasoline Distillate

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The acidic constituents of petroleum from various regions have been a source of rather extensive investigation. The isolation and identification of numerous individuals of the acyclic series have been reported. Among these are: formic and oxalic acids from Grosny distillates by Schidkoff²; palmitic, stearic, myristic, and arachidic acids from Ishikari distillates by Tanaka and Kuwata³; isoamylacetic and diethylpropionic acids from Baku petroleum by Chichibabin⁴; isovaleric, *n*-heptylic, *n*-octylic, and *n*-nonylic acids and ethyl mercaptan from a West Texas pressure distillate by Williams and Richter⁵; *n*-butyric and *n*-valeric acids and dimethylmaleic anhydride from a Texas distillate by Schutze⁶; and isocaproic acid from Rumanian petroleum by Nenitzescu and co-workers.⁷

As to the phenolic constituents, phenol, the three cresols, and several of the xylenols have been isolated.^{5,7,8}

(1) This paper represents part of a dissertation submitted to the Graduate School of The University of Texas in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Schidkoff, *J. Soc. Chem. Ind.*, **18**, 360 (1899).

(3) Tanaka and Kuwata, *J. Faculty Eng. Tokyo Imp. Univ.*, **17**, 293 (1928).

(4) Chichibabin, *et al.*, *Chimie et industrie*, Special No., 306 (March, 1932).

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

(6) H. G. Schutze, Ph.D. Dissertation, The University of Texas, June, 1938, to be published elsewhere.

(7) Nenitzescu, Isăcescu and Volrap, *Ber.*, **71B**, 2056 (1938).

(8) (a) Tanaka and Kobayashi, *J. Faculty Eng. Tokyo Imp. Univ.*, **17**, 127 (1927); (b) Holzmann and von Pilat, *Brennstoff-Chem.*, **11**, 409 (1930).

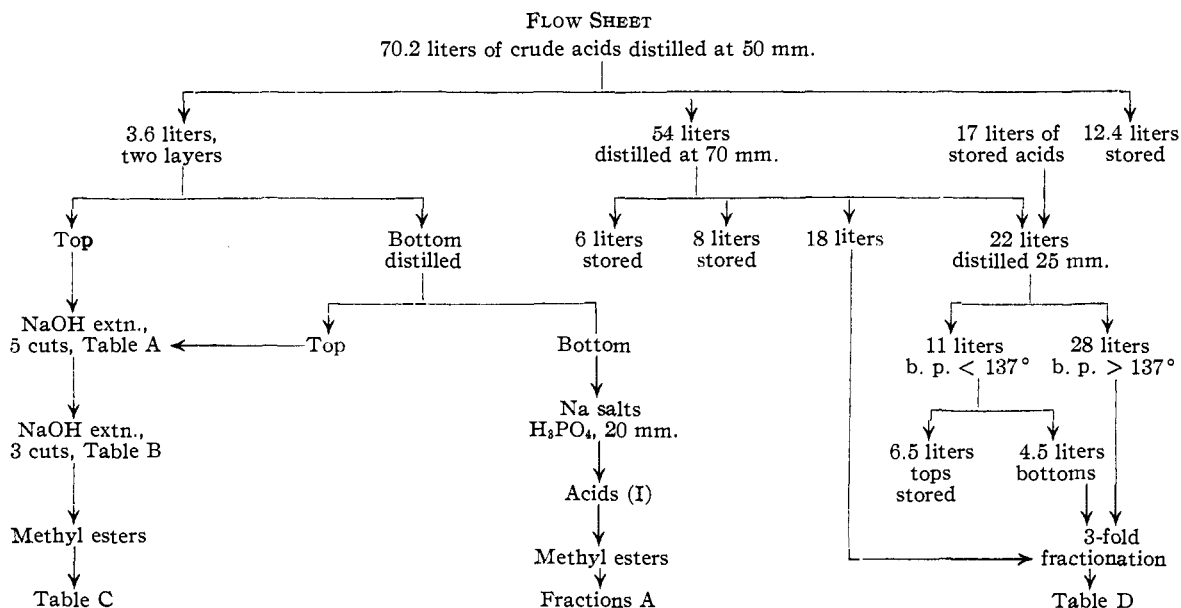
The isolation of numerous naphthenic acids, varying in complexity from cyclopentanecarboxylic acid to pentacosan-naphthenic acid, has been reported. Later investigation has proved that the majority of these acids were mixtures. Von Braun and co-workers⁹ are given credit for the isolation of the first homogeneous naphthenic acid. These investigators isolated 3,3,4-trimethylcyclopentanone from the degradation products from mixtures of decanaphthenic acids from various sources. This ketone was then reconverted to 3,3,4-trimethylcyclopentylacetic acid.

Very recently Nenitzescu and co-workers⁷ have reported the isolation, through selective amide formation, and identification of cyclopentanecarboxylic, cyclopentylacetic, and 3-methylcyclopentylacetic acids from Rumanian petroleum.

The material investigated in the present study was a complex mixture of crude petroleum acids from the sodium carbonate wash of Signal Hill straight-run gasoline.¹⁰ The objectives of the investigation were: (1) to study and to improve methods of separation of acid mixtures, (2) to attempt to develop new methods of separation, (3) to attempt the isolation and identification of all of the aliphatic acids from formic through the pentanoic acids, and (4) to study the fractions in

(9) Von Braun, Mannes and Reuter, *Ber.*, **66B**, 1499 (1933).

(10) These crude acids were kindly donated by the MacMillan Petroleum Corporation of Long Beach, California.



the region of the nonanoic acids with a view to the isolation and identification of some of the individuals. The fractions in the region of the hexanoic, heptanoic, and octanoic acids are being investigated by another student in this Laboratory. The general procedure for the partial separation of this mixture is shown in the accompanying Flow Sheet.

In two runs, 70 l. of crude acids was distilled under reflux at 50 mm. from a 15-gallon steel still with a 110 cm. \times 12 cm. column. Natural gas was used in the capillary in this case and in all subsequent vacuum distillations. The three fractions shown on the Flow Sheet were obtained. The two layers in the first fraction were separated, the top layer amounting to 2840 cc. and the bottom layer 760 cc.

By a series of distillations the 760-cc. portion was separated into 20 cc. of acids and 740 cc. of water solution of acids. The 20-cc. portion was returned to the top layer obtained originally. In this manner, the majority of dissolved acids of higher molecular weight than propionic acid were removed.

The 740-cc. portion was neutralized with 115 cc. of 3 *N* sodium carbonate, and an excess of 25 cc. was added. The basic solution was evaporated to dryness on a steam cone. The residue was pulverized and dried thoroughly at 20 mm. to obtain 29.1 g. of powder. One-half of this powder was distilled at 20 mm. with 25 cc. of phosphoric acid¹¹ (dried for twenty-four hours at 150–160° and 20 mm. with a capillary leak) to obtain 4.5 g. of acids.

Formic Acid.—Small portions of this mixture (I on Flow Sheet) reduced silver nitrate and mercuric chloride solutions.

The balance of the 4.5-g. portion was distilled with 23 cc. of methyl *n*-caproate¹² and 0.6 cc. of 18 *N* sulfuric

acid to obtain 3.0 g. of dry methyl esters. The esters were fractionated under a high reflux ratio through a 70 cm. \times 5 mm. column containing a spiral of chromel wire to obtain several fractions with n_D^{20} values: A1, 1.3560; A2, 1.3572; A3, 1.3609; A4, 1.3765; A5, 1.3780; residue, not detd.

Acetic Acid.—The n_D^{20} value reported for methyl acetate is 1.3619.¹³ Fraction A3 yielded, after saponification, Duclaux values of 7.0, 7.5, and 8.0, respectively, for the first three 10% distillates. The Duclaux values for acetic acid given by Kamm¹⁴ are: 6.8, 7.1, and 7.4.

The combined top layers (2860 cc.) amounted to 14.8 equivalents. A consideration of the differences in solubility and in K_a values for the lower acids expected in this mixture indicated the possibility of separation through fractional extraction with sodium hydroxide. The two experimental difficulties recognized were: loss of lower acids as a result of water solubility and solubility of the sodium salts in the free acid layer. The following procedure was designed to lower these factors to a minimum.

The whole portion (2860 cc.) was stirred effectively for six hours with 3 liters of normal sodium hydroxide. The top layer was stirred thoroughly for thirty minutes with three 500-cc. portions of water. The washes were combined with the bottom layer and the combination distilled to small volume. The residue was steam distilled until the distillate became neutral to litmus. All distillates were combined, made slightly basic with sodium hydroxide, evaporated to small volume, and the concentrated solution mixed with the top layer. The residue was concentrated further and an excess of 18 *N* sulfuric acid was added with cooling. The freed acids were separated and the heavy layer extracted three times with petroleum ether (30–60°). The solvent was removed and the acids dried at 100° and 20 mm.

(13) "International Critical Tables," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1926, p. 276.

(11) Curtius and Franzen, *Ann.*, **404**, 109 (1914).

(12) Geo. D. Graves (to E. I. du Pont de Nemours and Co.), U. S. 1,852,808, Oct. 18, 1932.

(14) Kamm, "Qualitative Organic Analysis," 2d ed., John Wiley and Sons, Inc., New York, N. Y., 1938, p. 153.

This procedure was repeated four times, beginning each time with the mixture of the top layer and the combination of basic distillates which had been concentrated by evaporation. A stubborn emulsion resulted during the fourth extraction. This emulsion was broken through: (1) addition of water and extraction with petroleum ether (30–60°), and (2) steam distillation of the raffinate. This treatment yielded a fraction listed as 4a in Table A. After the fifth extraction, a small portion, insoluble in an excess of sodium hydroxide, was discarded.

TABLE A

	Wt., g.	n_{20}^D	Equiv. wt.
1	284.0	1.4139	104.5
2	297.3	1.4204	115.6
3	342.7	1.4286	127.9
4	555.5	1.4367	144.3
4a	178.1	1.4410	159.0
5	252.8	1.4407	156.8

Fractions 1 and 2 (Table A) were extracted separately with three equal portions of normal sodium hydroxide as described above. No appreciable emulsion formation occurred in these cases due to the transfer of the weak, emulsifying acids to fractions 4, 4a, and 5 by the previous extraction.

TABLE B

	Wt., g.	n_{20}^D	Equiv. wt.
1a	67.5	1.4155	90.6
1b	83.1	1.4103	98.0
1c	77.1	1.4147	109.0
2a	79.8	1.4135	107.0
2b	97.4	1.4181	113.1
2c	97.8	1.4273	126.5

Fractions 1a, 1b, 1c, and 2a (Table B) were converted separately to the methyl esters by refluxing for three hours with an equal volume of methanol containing 2% hydrogen chloride. The unchanged acids were recovered and esterified as before. The two portions of esters were combined. This general procedure was followed in all subsequent esterifications, except that in some cases the unchanged acids after the second operation were recovered and esterified as before to yield a third portion of esters. The yields in grams from fractions 1a, 1b, 1c, and 2a were: 57.9, 74.3, 79.8, and 77.8 (one esterification), respectively.

Dimethylmaleic Anhydride.⁶—A solid crystallized out when the unchanged acids recovered after the first esterification of 1a (Table B) were cooled with an ice-salt mixture. This solid melted at 94–95° after two recrystallizations from petroleum ether (60–68°). Treatment with resorcinol and sulfuric acid, followed by neutralization with sodium hydroxide, gave a yellow-green fluorescence.¹⁵ This reaction is given by the anhydride ring group of phthalic anhydride. This same group is present in dimethylmaleic anhydride. The mixed melting point of the isolated acid with synthetic dimethylmaleic anhydride showed no depression. All of this anhydride had been concentrated in the fraction from which it was isolated. Schutze found the same substance in eight different fractions in his investigation of Texas petroleum acids.

(15) Mulliken, "The Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1st ed., Vol. I, 1905, p. 84.

The methyl esters of fractions 1a, 1b, 1c, and 2a were fractionated separately, under good reflux, from a 200-cc. still with a 130 cm. × 8 mm. (i. d.) column containing a spiral of chromel wire. The fractions obtained were combined on the basis of boiling points and indices of refraction. The combinations were subjected to four-fold refractionation and recombination, the esters with boiling points above that of methyl *n*-valerate being set aside each time. For the smaller combinations a 30-cc. still with a 75 cm. × 5 mm. (i. d.) column containing a spiral of small glass rod was used.

TABLE C

	Wt., g.	n_{20}^D	B. p., °C.
1	0.35	1.3728	< 79
2	2.54	1.3792	79–80
3	1.2	1.3831	80–91
4	7.44	1.3843	91–92
5	5.0	1.3862	92–101
6	3.95	1.3885	101–102
7	8.7	1.3923	102–115
8	57.2	1.3942	115–116
9	11.9	1.3962	116–126
10	12.8	1.3983	126–127
11	165.0	> 127

Propionic, Isobutyric, *n*-Butyric, Isovaleric, and *n*-Valeric Acids.—Small portions of fractions 2, 4, 6, 8, and 10 (Table C) were saponified and the 2-alkylbenzimidazoles¹⁶ of the recovered acids were prepared.

TABLE C-1

No.	B. p. of acid, °C.	n_{20}^D of acid	M. p. of 2-alkylbenzimidazole, °C.		
			Synthetic	Isolated	Mixed
2	141–142	1.3872	174.5	178.5	176
4	153–154	1.3948	234	233.5	234
6	162–163	1.3982	159	158	158
8	175–176	1.4050	190.5	190	190
10	185–186	1.4090	154	153	153

The *p*-phenylphenacyl esters¹⁷ of the acid from fraction 2 (Table C) and of propionic acid were also prepared: m. p., synthetic, 103°; isolated, 100.5°; mixed, 102°.

Attempts to isolate methylethylacetic and trimethylacetic acids were unsuccessful; in fact, there was very little indication, if any, of their presence in the mixture investigated.

In two runs, the 54-liter fraction (Flow Sheet) was distilled under reflux at 70 mm. from the 15-gallon still to obtain the four fractions shown on the Flow Sheet. The top fraction (22 liters) was combined with a similar fraction of 17 liters from an earlier distillation of 30 liters of crude acids. This combination was topped to 137° at 25 mm. from Claisen flasks. The tops were retopped to 137° at 25 mm. in the same manner. This procedure yielded the 11-liter and 28-liter fractions shown on the Flow Sheet.

The 28-liter fraction was combined with the 18-liter fraction (Flow Sheet) and the combination (1500-cc. charges) subjected to two-fold fractionation at 3 mm. under a high reflux ratio from a 2-liter still with a 145 cm. × 3.5 cm. (i. d.) glass marble-(7 mm. diam.)-filled column.

(16) Pool, Harwood and Ralston, *THIS JOURNAL*, **59**, 178 (1937).

(17) Drake and Bronitsky, *ibid.*, **52**, 3715 (1930).

After each fractionation similar fractions were combined on the basis of boiling points and indices of refraction. The combinations after the second fractionation were combined with similar fractions obtained from the two-fold fractionation (3 mm.) through the 145-cm. column of the 11-liter portion (b. p. < 137° at 25 mm.). These final combinations were then fractionated a third time through the 145-cm. column to obtain the following fractions.

TABLE D

Vol., cc.		n_D^{20}	Vol., cc.		n_D^{20}
Tops	7	665	1.4415
1	275	1.4349	8	585	1.4426
2	2265	1.4374	9	175	1.4437
3	1865	1.4384	10	1300	1.4450
4	8650	1.4390	11	1250	1.4480
5	1752	1.4398	Bottoms
6	1005	1.4405			

Menschutkin¹⁸ has shown that primary, secondary, and tertiary aliphatic acids differ greatly in their velocities of esterification. His results suggested the possibility of separation of petroleum acids through fractional esterification.

Two liters of fraction 4 (Table D) was fractionated at 3 mm. through the 145-cm. column to obtain a main fraction of 1614 cc.—the tops and bottoms were combined with similar fractions from the previous fractionation. The main fraction was fractionally esterified by refluxing each time for twelve hours with one-fourth of the calculated amount of methanol-2% hydrochloric acid. After each step the mixture of acids and esters was washed, dried and then fractionated at 25 mm. through the 145-cm. column until the distilling temperature rose abruptly. Corresponding fractions from the four series obtained showed very little difference in physical properties. Possibly, interchange between the acids and esters¹² may have occurred during the fractionation, although a detailed study of this type of reaction in this Laboratory with synthetic acids and esters indicated that the reaction would not occur except in the presence of a catalyst.

Fractionation of the unchanged acids remaining after the fourth step yielded a solid acid, m. p. 194–195° from dilute alcohol.

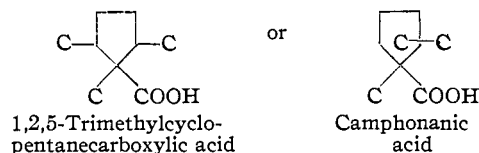
The balance of fraction 4 (Table D) was subjected to three-fold esterification. More of the solid acid was recovered from the unchanged acids remaining after the third esterification. A similar procedure with fraction 5 (Table D) yielded additional solid to total 62.5 g.

Data Determined on this Solid Acid.—(a) Qualitative analysis: negative for sulfur, nitrogen, and halogen. (b) M. p. 194–195° from dilute alcohol. (c) Equivalent weight: calcd. for $C_9H_{16}O_2$, 156.21; found, 156.33. (d) C and H. Calcd. for $C_9H_{16}O_2$: C, 69.20; H, 10.32. Found: C, 69.41; H, 10.02. (e) Unsaturation tests: negative. (f) 0.1047 g. of acid in 1.0021 g. of camphor melted at 177°, while camphor alone melted at 174°. (g) An electrometric titration proved that the acid is monobasic.

The behavior of the compound in the Rast molecular weight determination and the high melting point led us to suspect a tertiary acid

(18) Menschutkin, *Ann. chim. phys.*, [5] **23**, 14 (1881).

closely related to camphor. A search of the literature on known $C_9H_{16}O_2$ acids and homologs of near the same molecular weight led us to predict that the isolated acid was either



The former is unknown but Appel¹⁹ in 1933 prepared camphononic acid. Although his degradation from *d*-camphoric acid yields the dextrorotatory acid while the isolated acid is inactive or slightly levorotatory, his synthesis was repeated since only *d*-camphoric acid was available at the time. The constants of the acid obtained agreed with those of Appel's acid with the exception of the m. p., which was found to be 192–193° instead of 190–191°. In agreement with Appel, esterification by methanol and hydrochloric acid failed. The *p*-bromoanilides and *p*-toluidides of the *d*-camphononic acid and of the isolated acid were prepared according to Kuehn and McElvain.²⁰ The melting points of the acids and of their derivatives are tabulated.

	<i>dl</i> -Camphononic	Isolated	Mixed
Acid	192–193	194–194.5	193–194
<i>p</i> -Bromoanilide	102–103	119–120	111–115
<i>p</i> -Toluidide	114–115	110–111	111–112

Since none of the mixed melting points showed a depression, it appeared that the isolated acid was either pure *dl*-camphononic acid and the slight rotation due to an error, or that the rotation was due to a small amount of an active acid. The *dl*-acid was then prepared from *dl*-camphor.

dl-Camphoric acid was prepared from *dl*-camphor according to Noyes.²¹ The dibasic acid was degraded to *dl*-camphononic acid by Appel's procedure. The *p*-bromoanilide and the *p*-toluidide were prepared as described above.

	<i>dl</i> -Camphononic	Isolated	Mixed
Acid	193–194	194–194.5	193.5–194
<i>p</i> -Bromoanilide	119–120	119–120	119–120
<i>p</i> -Toluidide	110–111	110–111	110–111

This proves definitely that the isolated acid is *dl*-camphononic acid—the first naphthenic acid isolated from American petroleum.

(19) Appel, *Z. physiol. Chem.*, **218**, 202 (1933).

(20) Kuehn and McElvain, *THIS JOURNAL*, **53**, 1173 (1931).

(21) Noyes, *Am. Chem. J.*, **16**, 501 (1894).

Summary

1. A mixture of crude petroleum acids has been partially separated through fractionation as acids, fractional extraction with sodium hydroxide, fractionation as methyl esters, and through differences in tendencies to esterify.

2. The separation of aliphatic acids of low molecular weight through systematic fractional extraction with sodium hydroxide is effective.

3. Fractional esterification of a particular mixture of acids by a batch procedure yielded very little separation.

4. Isolation of peculiar individual substances

from the mixture of unchanged acids recovered after esterification has proved to be relatively simple.

5. Formic acid has been identified through qualitative tests. Dimethylmaleic anhydride and acetic, propionic, isobutyric, *n*-butyric, isovaleric, and *n*-valeric acids have been isolated and identified. Of these eight substances, acetic, propionic, and isobutyric acids have not been reported previously.

6. *dl*-Camphonic acid has been isolated and identified as the first American naphthenic acid.

AUSTIN, TEXAS

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF KENTUCKY]

The Use of *n*-Butyl Chlorosulfonate and *n*-Butyl Chlorosulfite in the Friedel-Crafts Reaction

BY CHAS. BARKENBUS, RALPH L. HOPKINS AND J. FORREST ALLEN

Alkyl halides have been used for many years in the Friedel-Crafts reaction as a means of introducing alkyl groups into aromatic nuclei. More recently efforts to extend the scope of this reaction to permit use of a wider variety of alkylating agents have resulted in the use of many types of esters, both organic and inorganic, with widely varying results. Besides the esters of the fatty acids such inorganic derivatives as alkyl sulfates, orthosilicates, phosphates, hypochlorites,¹ borates,² and sulfites³ have been used.

In a search for a more direct method of making alkyl benzenesulfonates, an investigation was made of the method described by Frèrejacque,⁴ who claimed to have prepared the methyl sulfonates of benzene, toluene, naphthalene, and chlorobenzene by the action of methyl chlorosulfonate on the above compound. Using *n*-butyl chlorosulfonate and benzene no butylbenzene sulfonate could be obtained. However, a reaction took place at 60° with evolution of hydrogen chloride, and from the reaction mixture a small hydrocarbon residue was obtained, although most of the product was converted into an unworkable tar. All methods used in attempting to show that some sulfonates were produced failed. The addition of anhydrous aluminum chloride caused

the ester to react extremely vigorously even at 0° with copious evolution of hydrogen chloride.

A study of this reaction under the most favorable conditions showed it to be principally one of alkylation with production of *s*-butylbenzene and *m*-di-*s*-butylbenzene. Chlorination also takes place, and chlorobenzene was recovered in quantity. Alkylation of toluene under similar conditions yielded *m*- and *p*-*s*-butyltoluenes and *o*-chlorotoluene along with smaller amounts of *p*-chlorotoluene and various side-chain chlorinated products. In both cases higher boiling hydrocarbon fractions were obtained.

The alkylating action of *n*-butyl chlorosulfite on benzene in the presence of anhydrous aluminum chloride was also investigated. Less high-boiling material is produced by this ester than was observed with the *n*-butyl chlorosulfonate, and chlorination does not take place, but an unstable sulfur compound of undetermined nature is produced, and unfavorably affects the quality of the yield.

Experimental

Reactions of *n*-Butyl Chlorosulfonate

Benzene.—A series of experiments was carried out to determine the most suitable reacting conditions and the proper proportions of reactants necessary for the maximum yield of *s*-butylbenzene. From these it was concluded that the temperature is best maintained between 0 and 5°. The most efficient proportion of aluminum chloride to ester is 2:1. The use of 9 moles of benzene with the

(1) Kane and Lowy, *THIS JOURNAL*, **58**, 2605 (1936).

(2) Kaufman, German Patent 555,403; French Patent 720,034.

(3) Bowden, *THIS JOURNAL*, **60**, 645 (1938).

(4) Frèrejacque, *Compt. rend.*, **183**, 807 (1926).