

### 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

RECEIVED JUNE 26, 1939

[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,<sup>1</sup> borates,<sup>2</sup> and sulfites<sup>3</sup> 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,<sup>4</sup> 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).

above ratio increases the total yield and greatly facilitates stirring.

From the results of the foregoing conclusions two large-scale runs were made in each of which 3 moles of crude *n*-butyl chlorosulfonate prepared according to Barkenbus and Owen<sup>5</sup> and used without distillation was added slowly to 27 moles (2106 g.) of benzene (dried over sodium) and 6 moles (800 g.) of anhydrous aluminum chloride (technical) with stirring at 0–5°. After the elapse of three hours the mixture was poured onto 5 kg. of cracked ice, washed with concentrated hydrochloric acid and water and allowed to stand overnight with concentrated ammonium hydroxide, which readily removed labile chlorine compounds. The benzene was then washed repeatedly with 80% sulfuric acid until the acid no longer developed a color. This treatment removed unsaturated material, which has a tendency to decompose in distillation. No sulfonates could be isolated from this fraction. After washing with sodium hydroxide, drying over calcium chloride, and distillation of the excess benzene, a total residue of 652 g. remained.

Preliminary fractionation in a short column removed about 60 g. of chlorobenzene which boiled at 128–130° and was identified as *p*-nitrochlorobenzene by nitration. Much chlorine still remained and was removed by heating with sodium. Fractionation of the mixture on a large column similar to that described by Tongberg, Quiggle, and Fenske<sup>6</sup> was performed at 3 mm. and many small fractions were collected. By taking the index of refraction of each fraction and plotting against the amount distilled two main fractions of constant index were obtained. The first main fraction weighing 83 g. was identified as *s*-butylbenzene by the method of Reilly and Hickenbottom:<sup>7</sup> m. p. of acetamino derivative 124–125°; listed m. p. 125–126°;  $n_D^{20}$  1.4910. Ipatieff<sup>8</sup> gives 1.4902. The second fraction weighing 165 g. was characterized as *m*-di-*s*-butylbenzene by oxidation to isophthalic acid and

conversion of the latter to its methyl ester (m. p. 67–68°);  $n_D^{20}$  1.4890; b. p. 88–92° at 3 mm. This fraction contained a trace of the ortho isomer as shown by the fluorescein test: yields, *s*-butylbenzene, 19%; *m*-di-*s*-butylbenzene 26.6%; chlorobenzene 11.2%.

**Toluene.**—Six moles of *n*-butyl chlorosulfonate was allowed to react with 12 moles of aluminum chloride and 54 moles (4968 g.) of toluene for three hours after addition of the ester at –2°. The product was washed and fractionated in a manner analogous to that used for benzene. The following products were separated and identified: *m*-*s*-butyltoluene 290 g. (32.4%); b. p. 193–197°;  $n_D^{20}$  1.4957. This fraction was completely soluble in concd. sulfuric acid; *p*-*s*-butyltoluene 174 g. (19.6%); b. p. 201–202°;  $n_D^{20}$  1.4950. Only a trace of this fraction was soluble in cold concd. sulfuric acid; *o*-chlorotoluene 83 g. (21.8%). The *o*-chlorotoluene and *p*-chlorotoluene fractions were not pure but were contaminated slightly with each other, due to the closeness of their boiling points. They were of sufficient purity to obtain readily *o*-chlorobenzoic and *p*-chlorobenzoic acid by oxidation of the respective fractions: *p*-chlorotoluene 23.5 g. (6.2%). A high boiling hydrocarbon residue of 170 g. also was obtained but the components were not identified. Considerable benzoic acid, probably derived from benzotrichloride, resulted from the sodium treatment and smaller amounts of other side-chain chlorinated products were present.

### Summary

The action of *n*-butyl chlorosulfonate on benzene and toluene in the presence of anhydrous aluminum chloride has been investigated. The principal effect is one of alkylation accompanied by nuclear and side-chain chlorination.

*n*-Butyl chlorosulfite reacts with benzene and aluminum chloride to produce *s*-butylbenzene. The reaction is not accompanied by chlorination, but sulfur derivatives are produced.

LEXINGTON, KENTUCKY

RECEIVED MAY 27, 1939

(5) Barkenbus and Owen, *THIS JOURNAL*, **56**, 1206 (1934).

(6) Tongberg, Quiggle and Fenske, *Ind. Eng. Chem.*, [11] **26**, 1212 (1934).

(7) Reilly and Hickenbottom, *J. Chem. Soc.*, **117**, 120 (1920).

(8) Ipatieff, Corson and Pines, *THIS JOURNAL*, **58**, 919 (1936).

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO]

## Fractionation of the Hydrogen Isotopes in the Distillation of Ethyl Alcohol

BY ALEX H. WIDIGER AND WELDON G. BROWN

During the course of some experiments on hydrogen exchange reactions in deuterio-alcohol in which it was necessary to recover the alcohol from the mixtures, for deuterium analysis, by careful fractional distillation under reduced pressure, using small laboratory columns, we had occasion to suspect that serious errors were being introduced as a result of fractionation of the hydrogen isotopes during the distillations. In view of the small mass difference between  $C_2H_5OD$  and

$C_2H_5OH$ , and the difficulty of accomplishing the desired separations (*e. g.*, phenylacetylene and alcohol) with our columns, the possibility of accounting for our results on this basis was not considered seriously until after a number of more obvious possible sources of error had been eliminated. It was nevertheless possible to show, by distillations of alcohol alone, that the degree of isotopic separation is fully capable of accounting for our results.