The Alkylation of Benzene in the Presence of Acid Catalysts

By Robert L. Burwell, Jr., and S. Archer

Partial elucidation of the mechanism of the alkylation of benzene by alcohols in the presence of appropriate catalysts may be expected from a study in which an optically active alcohol is employed. The extent of such elucidation should be increased where data on the effect of the catalyst on the alcohol alone are available.

Price and Lund[1] have reported such an investigation employing aluminum chloride and boron trifluoride with optically active s-butyl alcohol and benzene. The resulting s-butylbenzene was completely racemized in the first case and somewhat over 99% racemized in the second. Of the effect of the catalyst on the alcohol alone it is known only that polymers were produced.

Burwell[2] has studied, under a variety of conditions, the action of hydrofluoric, sulfuric and phosphoric acids on optically active s-butyl alcohol. An investigation of the alkylation of benzene by these catalysts with the same alcohol is reported in this paper. l-s-Butyl alcohol was employed save in the experiments with phosphoric acid in which case the dextrorotatory alcohol was used.

The observed rotations (1-dm. tube) of the s-butylbenzenes corrected to a fully resolved[3] s-butyl alcohol were: hydrogen fluoride, 0.17°; sulfuric acid, 0.08°; phosphoric acid, 0.15°; and boron trifluoride, 0.17°. The last value is in good agreement with that of Price and Lund[1] for the boron trifluoride catalyst. The signs of the rotations were in all cases opposite those of the original alcohols.

The maximum observed rotation of d-s-butylbenzene is +23.60°.[4] Thus, the fractional maintenance of configuration is: hydrogen fluoride, 0.0072; sulfuric acid, 0.0034; phosphoric acid, 0.0064; and boron trifluoride, 0.0072.

The s-butylbenzenes after isolation were fractionated in a 25-plate column without significant change in rotation. d-s-Butyl alcohol gave a dextrorotatory solution in dl-s-butylbenzene, thus eliminating small quantities of alcohol as the

source of the rotations. Thus the rotations are apparently genuine.

With a 4.7 molar ratio of phosphoric acid to alcohol, a 12% yield of s-butylbenzene was obtained at 70° in two hours. With phosphoric acid and alcohol alone, molar ratio 1.37, 5.3% of the alcohol was decomposed to butylene in twenty minutes.[2] In two hours 32% would have decomposed had the same rate of gas evolution continued. Allowing a factor of eight for the 30° difference in temperature, one observes that the rates of alkylation and dehydration are of the same order of magnitude. The greater proportion of phosphoric acid employed in the alkylation reaction ensures that the rate of alkylation cannot much exceed that of the rate of dehydration. It would appear probable that the rate-determining step in both reactions is the formation of the same intermediate, but that the intermediate reacts more rapidly with benzene than it does to form butylene. The alcohol could not have been racemized before it reacted since, in the experiment with alcohol alone, the recovered alcohol had the same rotation as the initial.

If the mechanism of the alkylation is to involve an intermediate incapable of protracted maintenance of configuration, then the average time interval between the formation of the intermediate and its reaction with benzene should not be very much larger than the period in which the intermediate would invert in configuration. In particular, if the intermediate is to be[5]

$$CH_3-\overset{+}{\underset{H}{C}}-C_2H_5$$
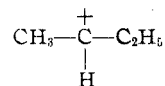
then the average life should be not many times the period of one molecular vibration. A small proportion of the ions would then react so soon after formation as to give a final product with a slight excess of one configuration.

With hydrogen fluoride as the alkylating catalyst, yields were low with a catalyst–alcohol ratio of 5 and good with a ratio of 10. With the alcohol alone a ratio of 4.6 gave a recovered alcohol 23% racemized[2]; a ratio of 5 produced a little polymer and a ratio of 10, considerable. It is then appar-

(1) Price and Lund, THIS JOURNAL, 62, 3105 (1940).

(2) Burwell, ibid., 64, 1025 (1942).

(3) Calculated on the basis of the maximum $\alpha^{20}D$ 11.07°; cf. Viditz, Biochem. Z., 259, 294 (1933).

(4) Harrison, Kenyon and Shepherd, J. Chem. Soc., 658 (1926); Levene and Marker, J. Biol. Chem., 100, 684 (1933).

(5) Price and Ciskowski, THIS JOURNAL, 60, 2500 (1938).

ent that some racemization of the alcohol must be expected before alkylation could occur.

In alkylation with 95.8% sulfuric acid, a catalyst–alcohol ratio of 1.10 was employed with a reaction time of three hours at 53°. At 40° with a ratio of 1.03 the alcohol alone was half racemized in thirty minutes.[2] From the formal activation energy of the racemization, 21,000 cal., the period of half-racemization at 53° would be $30/4.7 = 6.4$ minutes. One should, therefore, expect the alcohol to be extensively racemized before it could react. These considerations are reflected in the lower rotation of the s-butylbenzene prepared by sulfuric acid.

Wohl and Wertyporoch[6] have reported that boron trifluoride will not catalyze the alkylation of benzene by alkyl chlorides. We have obtained a similar result with cyclohexyl bromide and toluene. However, boron trifluoride will vigorously catalyze alkylation when the corresponding fluoride is substituted for the bromide. This contrast would appear to result from a decrease in the driving force of the reaction occasioned by the much greater stability of the resulting BF_4^- ion as contrasted with BF_3Br^- ion or the BF_3Cl^- ion.

Experimental

The preparation of the materials employed in this research is described by Burwell.[2]

It was observed that the rotation of 0.234 g. of d-s-butyl alcohol ($\alpha^{26}D$ +5.75°) dissolved in 2.445 g. of dl-s-butylbenzene was $\alpha^{25}D$ +0.62°.

Phosphoric Acid as the Alkylating Agent.—l-s-Butyl alcohol (0.162 mole, $\alpha^{20}D$ −4.14°) was added slowly to a rapidly stirred mixture of 0.73 mole of dry thiophene-free benzene and 0.786 mole of 100% phosphoric acid. The mixture was maintained at 70° for two hours and then at 25° for two more hours. The contents of the flask were poured into ice water. The organic layer was washed successively with water, sodium carbonate solution and water again. After drying, the solution was distilled from a small modified Claisen flask to yield 0.019 mole of s-butylbenzene boiling at 61–62° (16 mm.), $n^{20}D$ 1.4885, $\alpha^{22}D$ +0.055° (1-dm. tube). The yield was 12% of the theoretical. When the reaction temperature was 50°, no detectable alkyl benzene was produced.

Sulfuric Acid as the Alkylating Agent.—The procedure with 95.8% sulfuric acid was similar to that described above: 18.4 g. of catalyst (0.180 mole of 100% acid) was employed and the reaction was run at 53° for three hours. There was obtained 0.060 mole of s-butylbenzene boiling at 65–67° (20 mm.), $n^{20}D$ 1.4885, $\alpha^{22}D$ +0.03°, and 0.032 mole of di-s-butylbenzene boiling at 111–115° (15 mm.). The yields were 37 and 40% of the theoretical. Distillation of the first product through a 25-plate column[2] raised $n^{20}D$ to 1.4894 without change in the rotation.

Boron Trifluoride as the Alkylating Agent.—Upon saturation of the alcohol–benzene mixture with boron trifluoride followed by a twelve-hour reaction period at 20°, there was obtained a 51% yield of the monosubstituted product, b. p. 63–64° (15–16 mm.), $n^{20}D$ 1.4885, $\alpha^{22}D$ +0.13° (2-dm. tube) and a 20% yield of the disubstituted benzene boiling at 110–112° (15 mm.). Distillation of the s-butylbenzene through a 25-plate column raised $n^{20}D$ to 1.4895 without altering the rotation.

Hydrogen Fluoride as the Alkylating Agent.—1.62 moles of liquid anhydrous hydrogen fluoride at 0° was poured cautiously into a mixture of 0.162 mole of d-s-butyl alcohol ($\alpha^{22}D$ +5.75°) and 0.80 mole of benzene kept in ice throughout the addition. After standing unstirred at 16° for five hours, the mixture was poured onto ice and neutralized with potassium carbonate. The aqueous layer was extracted with ether and the latter combined with the benzene solution. After drying and distillation from the Claisen flask, 0.049 mole of s-butylbenzene was obtained, b. p. 71–73° (24 mm.), $n^{20}D$ 1.4892, $\alpha^{24}D$ −0.16° (2-dm. tube), and also 0.022 mole of di-s-butylbenzene, b. p. 120–125° (24 mm.). The yields were 30 and 27%, respectively; after distillation in the 25-plate column, $n^{20}D$ 1.4895, $\alpha^{24}D$ −0.18°.

In a preliminary experiment with inactive alcohol similar to the above, the hydrogen fluoride at 0° was added to the alcohol–benzene mixture at 16°. Immediately after the addition vigorous boiling occurred. The yields were distinctly higher, 55 and 26%.

In an experiment similar to the one immediately above but employing a molar ratio of catalyst to alcohol of but 5, the yields were but 17 and 8%, respectively.

Cyclohexyl Fluoride.—0.0137 mole of cyclohexyl fluoride[7] was dissolved in 0.707 mole of dry toluene. The resulting mixture was treated with boron trifluoride. After a short induction period a violent reaction occurred in which much of the material was ejected from the reaction vessel. After fourteen hours at room temperature, the material was worked up as described in the experiments with hydrogen fluoride. Distillation afforded 8 g. of p-cyclohexyltoluene, b. p. 136–138° (23 mm.), $n^{20}D$ 1.5233.

Cyclohexyl Bromide.—0.092 mole of cyclohexyl bromide was dissolved in 0.66 mole of dry toluene. The solution was treated with boron trifluoride. There was no sign of reaction. After five hours at room temperature the mixture, which had developed a light orange color, was processed as described above. Thirteen grams of cyclohexyl bromide was recovered.

Summary

1. Alkylation of benzene by optically active s-butyl alcohol in the presence of hydrofluoric, sulfuric and phosphoric acids produces s-butylbenzene with a definite but very small rotation.

2. With sulfuric acid, which is known to catalyze the racemization of s-butyl alcohol, the rotation was the least.

3. With phosphoric acid, the rate of alkylation

(6) Wohl and Wertyporoch, Ber., **64**, 1360 (1931).

(7) We are indebted to Professor J. H. Simons who kindly furnished this sample of cyclohexyl fluoride.

is approximately equal to the rate of dehydration to butylene in the absence of benzene.

4. Boron trifluoride catalyzes the alkylation

of toluene by cyclohexyl fluoride but not by cyclohexyl bromide.

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The Heat Capacity and Vapor Pressure Hysteresis in Liquid Isopentane. Isomers Due to Hindered Rotation

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The appearance of apparent hysteresis in the heat capacity of liquid ethylene dichloride[1] has been attributed by Railing to hindered rotation but the interpretation has been questioned by Pitzer somewhat arbitrarily.[2] The presence of isomers due to hindered rotation will manifest itself when the minima are unequal and the barrier height large due to any of the possible causes. In most aliphatic compounds the barriers will be small enough for equilibrium to be attained at ordinary temperatures. The equilibria, as lower temperatures are approached, will be characterized by decreasing proportions of the isomers of highest energy. Rapid cooling, therefore, will yield a liquid which will approach equilibrium from the side of excess of the isomer of higher energy. The isomer of higher energy will have a configuration of greater repulsive forces (assuming the barriers to be due to repulsion). Such a configuration corresponds to higher force constants and therefore higher frequencies, and, other things being equal, will lead to lower heat capacities than those of the form of lower energy. The non-equilibrium mixture obtained by rapid cooling, therefore, should have lower heat capacities than the equilibrium mixture. A rapidly heated equilibrium mixture will approach equilibrium from the side of excess of the form of *lower* energy. Thus, more heat will be taken up for the heating than required by the equilibrium mixture, and this heat would be re-emitted as equilibrium was reached, producing warmer drifts of a calorimeter accompanying heat capacities *higher* than normal.

A non-equilibrium mixture, as identified by its heat capacity, might be expected to manifest differences in vapor pressure from those of the equilibrium mixture. *We have been able to demonstrate such a hysteresis in the vapor pressure*

of liquid isopentane and have proved it to be experimentally real.

Heat Capacity Hysteresis.—Figure 1 is a graph of heat capacities obtained on the liquid in adiabatic calorimeter, B. The legend to the points in Fig. 1 also gives a complete history of the cooling of each. The diameter of the circles and the length of side of the squares is five times the experimental precision (0.06%).[3] Figure 1 shows a general agreement with the above predictions about the heat capacities of non-equilibrium mixtures of isomers due to restricted rotation. One particular feature of Fig. 1 requires comment. Series B, D and H were taken on a sample after it had been distilled into the calorimeter sufficiently slowly to produce equilibrium conditions as shown by the subsequent behavior, while Q and T were slowly cooled and are therefore also on a mixture which has reached equilibrium. At the lower temperatures these points approximate those of non-equilibrium mixtures, but rapidly deviate from the non-equilibrium curve as the temperature increases. Series H goes to the lowest temperatures and one might assume that its heat capacity curve merges into that of the *non-equilibrium* mixture due to some phenomenon characteristic of the degrees of freedom involved. It is then necessary to explain why all the other series (B, D, Q, and T) have a different temperature at which the divergence occurs. It is to be noted that, in general, the series which has spent longest at lower temperatures branches off at lower temperatures than in the case of any other run. We believe that this is due to the fact that the series was rapidly heated to the sensitive region prior to taking heat capacities. In this way a mixture was produced which was superheated, thereby keeping the low temperature ratio of isomers which is

(1) Railing, THIS JOURNAL, **61**, 3349 (1939).
(2) Pitzer, *ibid.*, **62**, 331 (1940).
(3) Aston and Eidinoff, *ibid.*, **61**, 1533 (1939).