action of the acid on isoparaffins is marked at room temperature,[10] are indicative of another type of mechanism for "isomerization" during alkylation. The same may be said for boron fluoride catalyzed alkylation. Grosse and Ipatieff's explanation for the large amounts of 2,3-dimethylbutane formed from ethylene and *i*-butane[11] is a thermodynamic impossibility.[12]

Boron fluoride has been reported as an isomerization catalyst.[13] However, Ipatieff and Grosse[14] obtained no isomerization of *i*-butane when it was subjected to boron fluoride, water, and nickel. While the validity of some of the patent claims may be doubtful, it would not be surprising if complexes formed by interaction of boron fluoride with the solid additives presumably present had catalytic properties.

At higher temperatures zinc chloride, ferric chloride, and stannic chloride are reported to be catalysts[15]; here the halides certainly have the desired acidic properties.

The mechanism presented leads to an important prediction, namely, that if the catalyst used is $RAlX_4$, *alkylation should be observed along with isomerization.* If the RX added splits out HX in the presence of Al_2X_6, then it is not possible to test the prediction by this method, for olefins will alkylate isoparaffins in the presence of promoted aluminum halides. However, certain aliphatic halides such as methyl bromide, methylene bromide, and ethyl bromide are apparently stable in the presence of aluminum bromide and can be used in critical experiments to test the prediction.

There is an indication that alkylation did occur in the experiment with methylene bromide in the preceding paper,[3] but the small amount of high-boiling material could not be identified. The expected pentane fraction in the methyl bromide experiment in the preceding paper would be so small as to be lost as column holdup in the fractionation analysis.

In the following paper are given the results of experiments with relatively large amounts of methyl and ethyl bromide, performed primarily as a test of the mechanism presented here.

Acknowledgments.—Many of the ideas presented in this paper were formulated and developed in discussions with members of the Chemistry staff of the University of California, among whom may be particularly mentioned, Professors M. Calvin, H. S. Frank, G. N. Lewis, K. S. Pitzer, the author's National Research Fellowship sponsor, the late S. Ruben, and T. D. Stewart.

Summary

A mechanism for the aluminum halide catalyzed isomerization of paraffin hydrocarbons has been presented. The striking feature of the mechanism is that aluminum in AlX_4^- is still acidic. The mechanism accounts for the known facts of paraffin isomerization.

It is predicted as a consequence of the postulated mechanism that methyl bromide and ethyl bromide should alkylate paraffin hydrocarbons in the presence of aluminum bromide.

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(10) Whitmore and Johnson, THIS JOURNAL, **63**, 1481 (1941).

(11) Grosse and Ipatieff, *J. Org. Chem.*, **8**, 438 (1943).

(12) *Cf.* the equilibrium concentrations of the hexanes, Rossini, Prosen and Pitzer, *J. Res. Natl. Bur. Stds.*, **27**, 529 (1941).

(13) Dutch Patent 48,596; U. S. Patents 2,257,896; 2,271,043.

(14) Ipatieff and Grosse, THIS JOURNAL, **57**, 1616 (1935).

(15) See ref. 4, Appendix III.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Aliphatic Friedel–Crafts Reactions. I. The Alkylation of Butanes by Methyl and Ethyl Bromide

BY JULIUS D. HELDMAN[1]

In the preceding paper,[2] a mechanism for the promoted aluminum halide catalyzed isomerization of paraffin hydrocarbons was presented.

The mechanism leads to the prediction that under certain conditions, when the promoter is methyl bromide or possibly ethyl bromide, and with a relatively light paraffin, such as a butane, alkylation should be observed along with isomerization of the paraffin. In short, a purely aliphatic Friedel–Crafts alkylation should occur.

The experiments here reported were conceived and carried out as a test of the proposed mechanism. Even small amounts of pentanes resulting from reaction in the systems *n*- or *i*-butane–methyl bromide–aluminum bromide would have been a positive test,[3] but actually it was found that substantial yields of *i*-pentane can be obtained in this manner as well as the isomer of the butane charge.

The pressure of other work has made it necessary to discontinue this line of work before a detailed study of the experimental conditions conducive to high yields of alkylate could be completed. However, the experiments presented unequivocally establish the occurrence of an aliphatic alkylation of the classical Friedel–Crafts type and are hence separately reported.

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(1) National Research Fellow in Chemistry, 1942–43.

(2) Heldman, THIS JOURNAL, **66**, 1789 (1944).

(3) The amount of pentanes in the absence of methyl bromide is negligible at relatively low temperatures; see Leighton and Heldman, THIS JOURNAL, **65**, 2276 (1943).

In the alkylation of butanes with methyl bromide, small amounts of higher paraffins, resulting from further alkylation of the primary products, are observed. There is no indication of the formation of neopentane; the negative result here also is predicted by the previously proposed mechanism. *n*-Pentane would be expected as about ten per cent. of the pentane fraction at room temperature if the *n*–*i*-pentane equilibrium were reached.[4] From this work it is not possible to state conclusively that *n*-pentane is a product (although it would certainly be expected from isomerization of the *i*-pentane formed), for the small amounts produced would appear as holdup in the fractionation analysis along with the higher alkylates.

After the reaction has proceeded for some time, a typical viscous lower layer, at first yellow and gradually turning to deep red, appears. This is undoubtedly due to the cracking of the pentanes formed. The phenomenon and its correlation with the cracking reaction have been pointed out by Glasebrook, Phillips and Lovell.[5]

Ethyl bromide, which apparently does not split out hydrogen bromide in the presence of aluminum bromide,[6] also alkylates butanes to produce a mixture of hexanes and presumably higher alkylates. Since the ease of cracking of paraffins increases with increasing molecular weight, the typical lower layer appears quite early in the course of this reaction. Concomitant with the formation of the lower layer are observed large amounts of ethane[7] and some propane and *i*-pentane.

Under conditions where the alkylations above proceed at a measurable rate, no reactions were observed in preliminary studies of the systems propane–methyl bromide–aluminum bromide and *n*-butane–methyl chloride–aluminum chloride. In the latter case, upon removal of the volatile substances from the reaction mixture, a low melting solid complex of methyl chloride and aluminum chloride was produced.

The fact that no isomerization occurred in the latter, homogeneous system indicates that the greater activity of aluminum bromide as compared to aluminum chloride[8] is not due to the greater solubility of the bromide, as had been previously suggested.[7]

With the exception of patents,[9] upon the validity of which some doubt has been cast,[10] the results here reported are apparently the first successful completely aliphatic Friedel–Crafts alkylations. Alkylation of isoparaffins by olefins is now a well known reaction, but in this case dehydrobromination of methyl bromide to produce an olefin cannot occur. Previous attempts, always made with higher paraffins, which are easily cracked, and higher alkyl halides, which almost instantaneously undergo complicated reactions in the presence of aluminum halides,[11] have always given such a variety of products that the occurrence of the alkylation reaction *per se* has been an open question.

Experimental

The general experimental methods have all been previously outlined. Extraneous moisture and hydrogen bromide were strictly excluded. In most of the experiments capsules of aluminum bromide were used.

After reaction, the volatile products were distilled into ethanolamine to remove the methyl or ethyl bromide (and hydrogen bromide formed from the alkylation reaction). The hydrocarbon layer in most instances was then fractionated in a micro precision 3 mm. i. d. unpacked Podbielniak type R column, manually operated. In one case the products were distilled after passage through potassium hydroxide pellets and the *n*-butane calculated from the amount of *n*-butane–methyl bromide azeotrope.[12]

In the following table are given the charges, experimental variables, and yields of hydrocarbon boiling higher than the initial butane.[a] Since the experiments were designed primarily to test for alkylation, the butane cut was carefully analyzed in only a few runs. The one result in which practically no alkylation was observed is at present inexplicable.

TABLE I

SUMMARY OF ALKYLATION EXPERIMENTS

n-C_4H_{10}, moles × 10^4	Al_2Br_6, moles × 10^4	CH_3Br, moles × 10^4	Temp., deg. °C.	Time, hr.	Alkylate moles × 10^4
753	18.3	390	78 ± 2	64.8[a]	130[b]
750	15.8	392	25 ± 3	120[c]	52[d]
250	18.1	392	25.0	96	33[e]
500	34.2	392	25 ± 3	68.8[c]	83[f]
500	14.3	392	25.0	95.8	<7.5[g]
494[h]	16.9	580	50 ± 1	47.8	62[i]
520[h]	14.2	392	25 ± 3	283	58[j]
230[k]	16.7	392	25 ± 3	*ca.* 120	0
500	29.2[l]	860[m]	25 ± 3	90	0[n]
500	25.2	262[o]	25 ± 3	42[p]	150[q]
250	6.38	183[o]	25.0	72[r]	52[s]
741[h]	31.0	642[o]	50 ± 1	47.8[r,t]	95[u]

[a] Yellow layer formed after 20 hr.; *ca.* 0.7 cc. red lower layer at end. [b] 1.5 cc. hydrocarbon residue boiling above

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[4] Rossini, Prosen and Pitzer, *J. Res. Natl. Bur. Stds.*, **27**, 529 (1941).

[5] Glasebrook, Phillips and Lovell, THIS JOURNAL, **58**, 1944 (1936).

[6] All the solutions of aluminum bromide in ethyl bromide that have been prepared by the author are light yellow. Wertyporoch, *Ber.*, **64B**, 1369 (1931), states in a footnote on p. 1373 that such a solution was "schwach gelb"; yet in the last paragraph of the same page he speaks of "die farblose Lösung" of aluminum bromide in ethyl bromide.

[7] Nenitzescu and Dragan, *Ber.*, **66B**, 1892 (1932), found large amounts of the paraffin corresponding to the alkyl halide added in attempting to alkylate heptane with ethyl, propyl, and butyl chlorides.

[8] Leighton and Heldman, THIS JOURNAL, **65**, 2276 (1943).

[9] British Patent 327,411; French Patent 669,739.

[10] Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Corporation, New York, N. Y., 1941, p. 737.

[11] Nenitzescu and Ionescu, *Ann.*, **491**, 189 (1931).

[12] Heldman, THIS JOURNAL, **66**, 661 (1944).

10°, micro b. p. 26–27°, $n^{20}\text{D}$ 1.3569. [c] Traces of yellow lower layer formed. [d] 0.6 cc. hydrocarbon residue boiling above 10°, micro b. p. 29°, $n^{20}\text{D}$ 1.3610. [e] $n^{20}\text{D}$ 1.3575. [f] Traces of permanent gases formed. [g] 20.6% of total *n*-butane charge isomerized to *i*-butane. [h] *i*-Butane charge. [i] The heart cut of this fraction was 30 × 10^{-4} mole, $n^{20}\text{D}$ 1.3548. [j] The complete column analysis was 9 × 10^{-4} mole low boiling material, 410 × 10^{-4} mole *i*-C_4H_{10}, 62 × 10^{-4} mole *n*-C_4H_{10}, 34 × 10^{-4} mole *i*-pentane, 24 × 10^{-4} mole boiling higher than *i*-pentane. [k] Propane. [l] Aluminum chloride. [m] Methyl chloride. [n] No *i*-butane; no alkylate. After removal of volatile products, 0.920 g. of a white to light amber solid remained, m. p. 24°, stable to pumping at 10^{-5} mm. [o] Ethyl bromide. [p] Light yellow solution. *Ca.* 0.3 cc. light orange lower layer developed at end of run. [q] Total distillate boiling above *n*-butane, $n^{20}\text{D}$ 1.3800. Traces of low boiling material. [r] Light yellow solution. [s] Traces of low boiling material; butane fraction 47.7% isomerized. [t] *Ca.* 0.5 cc. deep red lower layer formed. [u] The complete analysis was as follows: traces of CH_4, 140 × 10^{-4} mole C_2H_6, 80 × 10^{-4} mole C_3H_8, 82 × 10^{-4} mole *n*-C_4H_{10}, 185 × 10^{-4} mole *i*-C_4H_{10}, 130 × 10^{-4} mole *i*-C_5H_{12}, 95 × 10^{-4} mole C_6H_{14} and higher, $n^{20}\text{D}$ 1.3779.

Summary

In the presence of aluminum bromide, methyl and ethyl bromide will alkylate butanes to give substantial yields of pentanes and hexanes, respectively, as well as some higher paraffins. The occurrence of the alkylation reaction substantiates a prediction based on the mechanism of paraffin isomerization previously presented.

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NOTES

Trimethylchlorosilane

BY W. F. GILLIAM AND ROBERT O. SAUER

Taylor and Walden[1] have recently reported the successful preparation of trimethylchlorosilane by direct chlorination of trimethylsilane. We obtained this chlorosilane in January, 1941, by the reaction of methylmagnesium chloride with a mixture of methylchlorosilanes[2] in ether solution.

Experimental

429.5 g. of a methylchlorosilane mixture[3] (b. p. 68.0–70.1°; 57.8% Cl; 2.75 moles dimethyldichlorosilane and 0.50 mole of methyltrichlorosilane) was dissolved in one liter of anhydrous ether and added to a 5-liter, three-neck flask fitted with a stirrer, an addition funnel, and a condenser cooled by a bath of acetone and solid carbon dioxide. To this solution was slowly added 500 cc. of a 4.1 *M* solution of methylmagnesium chloride in ether; the magnesium chloride precipitated as a fine sludge. The ether solution was separated and the ether removed by distillation; fractional distillation of the residue in a column of 40 theoretical plates gave five fractions totaling 38.7 g. (0.35 mole) of trimethylchlorosilane. The higher boiling constituents contained 159.2 g. (1.23 moles) of dimethyldichlorosilane, and 30.8 g. of an intermediate fraction. These materials were analyzed by the hydrolysis of approximately 1-g. samples and the titration of the liberated acid with *N*/2 sodium hydroxide. A sample of trimethylchlorosilane collected at 57.0° (748 mm.) gave 32.5, 32.6% Cl (calcd., 32.64% Cl). The dimethyldichlorosilane distilled at 70.0° (757 mm.) and gave 54.8, 54.8% Cl (calcd., 54.95% Cl).

Another sample of trimethylchlorosilane[3] upon careful fractional distillation in a column of 50 theoretical plates gave three consecutive fractions having the following properties: (a) b. p. 57.6–57.7° (760 mm.); d^{27}_{27} 0.8538; % Cl, 32.58, 32.59, 32.59; (b) b. p. 57.7° (760 mm.)-57.3° (749 mm.); d^{27}_{27} 0.8536; % Cl, 32.57, 32.56, 32.57; (c) b. p. 57.7° (760 mm.); d^{27}_{27} 0.8536, 0.8538; % Cl, 32.55, 32.57.

The vapor density of trimethylchlorosilane indicates this compound to be slightly associated at 100°. The result obtained by the Dumas method was 5.091 g./l. (S. T. P.) corresponding to a molecular weight of 114 (calcd., 108.6).

The molecular weight of this compound was also determined cryoscopically in cyclohexane (determined freezing point constant, 207). The following results show trimethylchlorosilane to exist as the dimer in this solvent at 6° (maximum concentration of solute, 0.3%): mol. wt., 223, 205, 216, 212 (calcd. for the dimer, 217.2).

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[1] Taylor and Walden, THIS JOURNAL, **66**, 842 (1944).

[2] Gilliam, Liebhafsky and Winslow, *ibid.*, **63**, 801 (1941).

[3] Mr. W. J. Scheiber of this Laboratory kindly provided and distilled these materials.

The Solubility of Potassium Iodide in Sodium Hydroxide Solutions at 20°

BY H. DARWIN KIRSCHMAN[1] AND RICHARD POMEROY[1]

In former articles[2] we have presented the results of studies on the solubility of potassium iodide in potassium hydroxide solutions and of sodium iodide in sodium hydroxide solutions at 20°. The present paper extends these studies to the iodide of potassium in solutions of sodium hydroxide from 0 to 16.5 *N*.

The results of our measurements are presented in Table I and Fig. 1.

Experimental

The solutions were equilibrated and analyzed as previously described except that the concentration of iodide was determined by titration with standard silver nitrate solution using eosine as an adsorption indicator. Equilibrium was more rapidly established than in the case of sodium iodide in sodium hydroxide solutions but less

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[1] 117 East Colorado St., Pasadena 1, Calif.

[2] (a) Kirschman and Pomeroy, THIS JOURNAL, **65**, 1695 (1943); (b) Pomeroy and Kirschman, *ibid.*, **66**, 178 (1944).