

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

THE ABSENCE OF REARRANGEMENT OF THE ISOBUTYL GROUP DURING THE FORMATION OF ISOBUTYLMAGNESIUM BROMIDE AND ITS RELATION TO THE THEORY OF REARRANGEMENTS¹

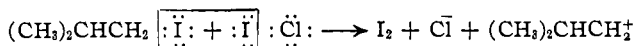
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The ready change of isobutyl compounds to tertiary butyl compounds has long been known. The interconversion of the bromides has been thoroughly studied.² The results of these studies indicate that (1) rearrangement of isobutyl bromide to tertiary butyl bromide at high temperatures in the *vapor phase* may occur by way of dissociation and addition of hydrogen bromide (Brunel) but (2) this rearrangement takes place more readily in the liquid phase and at temperatures at which there is no dissociation into hydrogen bromide and olefin. Heating the *vapor* of isobutyl bromide at 140° for fourteen hours produces no rearrangement while heating the *liquid* at the same temperature for *one* hour gives a 55% conversion to the tertiary bromide (Michael). The isobutyl "ions" readily rearrange by the transfer of an electron pair and its proton.³

Other isobutyl compounds undergo similar rearrangements. Isobutyl iodide reacts with silver acetate in the absence of a solvent to give isobutyl acetate while the presence of acetic acid as a solvent makes tertiary butyl acetate the chief product.⁴ Similar results are obtained with silver cyanate.⁵ With silver oxide in the presence of acetic acid, isobutyl bromide yields tertiary butyl alcohol and tertiary butyl acetate (Linnemann). An even more interesting example of this transformation is the conversion of isobutyl iodide to tertiary butyl chloride by the action of iodine monochloride (Linnemann). This reaction apparently occurs as follows



The two ions left are peculiar in that each is the result of a "chemical reaction" rather than of an ordinary "ionization." Each is present only in

¹ Presented by Albert R. Lux in partial fulfilment of the requirements for the Ph.D. degree at the Pennsylvania State College. See p. 3274.

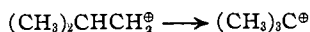
² Elketoff, *Ber.*, **6**, 1258 (1873); Meyer and Pond, *ibid.*, **18**, 1623 (1885); Faworsky, *Ann.*, **354**, 327 (1907); Michael and Leupold, *ibid.*, **379**, 263 (1911); Brunel, *Ber.*, **44**, 1000 (1911); *Ann.*, **384**, 245 (1911); *THIS JOURNAL*, **39**, 1978 (1917); Michael and Zeidler, *Ann.*, **393**, 81 (1912); Michael Scharf and Voight, *THIS JOURNAL*, **38**, 653 (1916); Meerwein and van Emster, *Ber.*, **55**, 2520 (1922); W. Hüchel, "Theoretische Grundlagen der organischen Chemie," Leipzig, 1931, Vol. I, pp. 205-207.

³ See p. 3278.

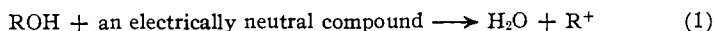
⁴ Linnemann, *Ann.*, **162**, 12 (1872).

⁵ Brauner, *Ber.*, **12**, 1874 (1879).

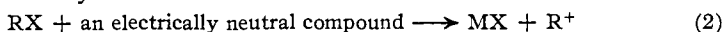
small concentrations. This apparently favors the monomolecular rearrangement.



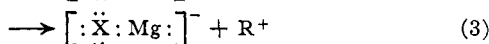
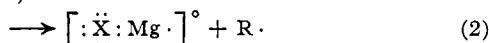
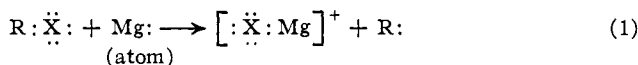
The literature contains no definite indication regarding a rearrangement of the isobutyl group during the formation or reaction of the Grignard reagent.⁶ This reaction was interesting to us because of the following relations:



If the hydroxyl is removed with the octet of the oxygen complete, the carbon to which it was attached must at some instant have only six electrons.⁷ Similarly



In each case the R^+ may undergo rearrangement before combining with a negative ion from the reaction mixture. (3) On the other hand, if RX is treated with an electrically neutral *element* such as magnesium or sodium, the possible intermediate products are more varied. Thus



In each case the pictured intermediate products can combine to form RMgX . A consideration of the three possible processes in detail is instructive. The first could give no rearrangement, since the organic radical has its full complement of electrons. Since there is no source of protons present, it can only combine with the MgX^+ . The free $\text{R} \cdot$ radicals formed according to (2) might combine to give $\text{R} : \text{R}$ or might disproportionate.



The R^+ could merely lose a proton to the $\text{R} :$ or it could first rearrange and then lose a proton. In all cases studied to date, these two possible processes give the same product. Cases in which different products could be formed are being studied in this Laboratory in connection with both the Grignard and Wurtz reactions. If the third picture is correct, the R^+ should rearrange at least in part and the rearranged product could then give the corresponding Grignard reagent.

⁶ Gilman and Heck, *Bull. soc. chim.*, [4] **45**, 1095 (1929). Other rearrangements involving the Grignard reagent are recorded in the literature as follows: Richard, *Ann., chim. phys.*, [8] **21**, 342 (1908); Tiffeneau and Delange, *Compt. rend.*, **139**, 573 (1903); Gilman and Kirby, *THIS JOURNAL*, **51**, 3475 (1929); **54**, 345 (1932); Gilman and Harris, *ibid.*, **53**, 3541 (1931); Austin and Johnson, *ibid.*, **54**, 647 (1932).

⁷ This is on the simple assumption that the subtraction of eight electrons from the fourteen electrons originally associated with the carbon and its attached oxygen leaves only six with the carbon.

In the present study isobutyl bromide (5 moles) containing less than 0.5% of tertiary bromide was converted to 3.7 moles of Grignard reagent and 0.8 mole of gas consisting mainly of isobutylene and isobutane.⁸ The Grignard solution was diluted with dry ether and treated with oxygen at 0°. The resulting ROMgBr product was decomposed by ammonium sulfate solution and the resulting alcohol was fractionally distilled through special columns and tested for tertiary butyl alcohol by procedures found effective with mixtures containing 2% of tertiary butyl alcohol in isobutyl alcohol. No tertiary butyl alcohol was detected. When the Grignard solution from tertiary butyl chloride was similarly treated, an 80% yield of the alcohol was obtained.

These experiments practically eliminate process (3) from consideration. This study is being continued.

Experimental

Preparation of Isobutyl Bromide.—In a 3-liter three-necked flask provided with an efficient stirrer, a thermometer and a dropping funnel, was placed 1036 g. (14 moles) of isobutyl alcohol, b. p. 107–108°. After cooling to -4° , 1390 g. (5.1 moles) of phosphorus tribromide was added during six hours, with vigorous stirring and below -1° at all times. The cooling bath was removed and the mixture was allowed to stand for twelve hours. The mixture was then distilled through a short column using the vacuum of a water pump. The bromide was not heated above 50° . Much hydrogen bromide was evolved during the distillation. The crude bromide was shaken with 50 g. of anhydrous potassium carbonate and allowed to stand for two days with 25 g. of freshly calcined potassium carbonate. The latter was removed and the bromide was distilled under reduced pressure through an 85×2 cm. packed column of the total condensation, adjustable take-off type (Fig. 1). The isobutyl bromide was collected at $41.5\text{--}42.2^{\circ}$ (137 mm.), yield 1060 g. (55% of the theoretical amount).

Analysis of Isobutyl Bromide for Tertiary Butyl Bromide.—The method of Michael and Leupold² was used. It depends on the fact that cold distilled water will hydrolyze *tert.*-butyl bromide but will not react with the isobutyl compound. The hydrogen bromide formed is conveniently determined by the Volhard method.

The isobutyl bromide prepared above was found to contain about 0.6% of tertiary bromide.

Further Purification of Isobutyl Bromide.—About 1 kg. of this isobutyl bromide was stirred with 300 cc. of distilled water for five hours. After washing with a fresh portion of distilled water, the bromide layer was dried over potassium carbonate and fractionated through the 85×2 cm. column. Over 80% of the bromide was recovered at $41.8\text{--}42.5^{\circ}$ (135 mm.); d_4^{20} 1.266, n_D^{20} 1.4363.

Anal. Calcd. for C_4H_9Br : Br, 58.3. Found: Br, 58.5, 58.2; tertiary bromide, 0.37, 0.29%.

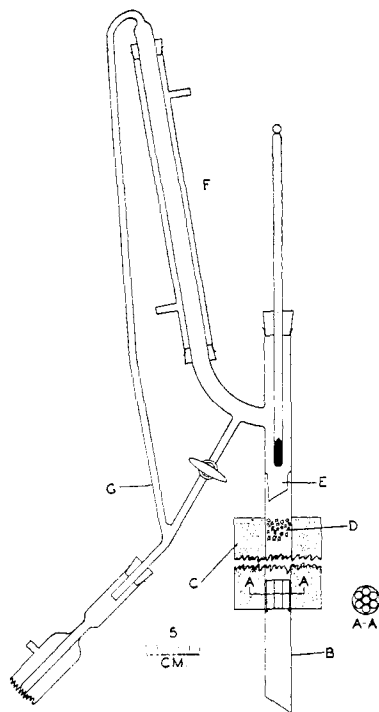
Preparation of Isobutylmagnesium Bromide.—A 2-liter three-necked flask was fitted with a mercury-sealed stirrer; a thermometer, an efficient reflux condenser and a 500-cc. dropping funnel. The condenser was connected to two traps, the first cooled with ice and the second with solid carbon dioxide and acetone.

To 120 g. of magnesium turnings and a crystal of iodine was added a small amount

⁸ The exact composition of this gas and the effect of varying conditions on its composition are being studied in relation to the theory of the Grignard reaction.

of the purified isobutyl bromide in dry ether. As soon as the reaction started, 250 cc. of dry ether was added and the rest of a solution of 685 g. (5 moles) of the highly purified isobutyl bromide in 625 cc. of dry ether was added as follows. Half of the solution was added during seven and a half hours. Then the remaining half was diluted with 375 cc. of dry ether and added during six and a half hours. The temperature of the reaction mixture was at all times below 50° . The trapped material amounted to 46 g. (0.8 mole) and was mainly isobutane and isobutylene. Titration of an aliquot part of the clear Grignard solution with standard acid showed that 3.7 moles of butylmagnesium bromide had been formed.

Fig. 1.—Several columns of this type were used in this study and in the researches described in the accompanying papers. A, A mat for holding up the packing in the column. It is made of several short pieces of glass tubing fused together, and rests on small indentations in the column. B, The column, of 20 mm. inside diameter Pyrex tubing measuring 100 cm. from the bottom to E, and about 115 cm. over-all. C, Magnesias pipe insulation. In some of the columns this was supplemented or replaced by electric heating coils (see Fig. 2). D, Packing made from 6-mm. glass tubing cut in 6-mm. lengths. This was kindly supplied by the du Pont Co. at cost. E, Drip indicator made by sealing a 15-mm. tube inside the column. F, Condenser made of 15-mm. Pyrex tubing with a jacket 25 cm. long. In some columns an internal condenser was used. In these, the drip indicator, E, was usually omitted as the reflux ratio could be calculated by counting the drops from the tip of the internal condenser instead of from E. G, Pyrex tubing 8 mm. in diameter with a stopcock having a 2-mm. bore. The take-off is adjusted by this stopcock. The tube G makes possible the use of the column under reduced pressure. Thus the ordinary disadvantages of distillations from Claisen flasks under reduced pressures are avoided.



Treatment of the Grignard Solution with Oxygen.—The solution was filtered through glass wool into a 5-liter flask equipped with a mercury-sealed stirrer, a thermometer, an inlet tube and an efficient reflux condenser attached to a mercury trap having a head of about 2.5 cm. of mercury.

The solution was diluted with 2250 cc. of ether, the inlet tube was adjusted to reach to about 2 cm. above the solution and stirring was started. After the solution had been cooled to -2° by an ice-salt mixture, dry oxygen was passed over the stirred cold solution at such a rate that none escaped through the mercury trap. The temperature was kept below 0° at all times. After about eight hours, the temperature dropped sharply and oxygen bubbled through the mercury trap. The treatment with oxygen at 0° or lower was continued for three hours.

The solution was added to a mixture of 1.5 kg. of cracked ice and 1.3 kg. of ammonium sulfate. The ether layer was separated and washed twice with 500-cc. portions of water which was added to the water layer. The water layer was extracted 10 times with 300-cc. portions of ether. The combined ether extracts were washed with water. The ether solutions were dried with 500 g. of anhydrous potassium carbonate. The ether was then removed by distillation through the 85×2 cm. column using a high reflux ratio. The residue was then carefully fractionated through a similar 38×1.8 cm. packed column as follows.

Fraction	Bar., mm.	B. p., °C.	Reflux ratio	Wt., g.
A1	742	60-67	15:1	0.7
2		67-81	8:1	2.5
3		85-90	60:1	13.0
4	745	90-95	60:1	17.0
5		95-100	60:1	2.0
6		100-106	60:1	2.5
7		106-107.2	60:1	7.0
8	742	107.2-107.4	60:1	78.5
9		107.4-107.8	60:1	90.5
10		107.8-107.9	60:1	21.0
11		Residue		8.5

Fractions A7-9 represent a 74% yield of isobutyl alcohol based on the Grignard reagent used. Fractions A2-4 were redistilled through a 55×0.8 cm. Vigreux column, bar. 743 mm.

Fraction	B. p., °C.	Reflux ratio	Wt., g.
Starting with fractions A2, 3			
B1	60-79	2:1	0.5
2	79-85	2:1	1.0
3	85-89	5:1	
Fraction A4 added			
	85.5-87	5:1	23.5
4	87-90	5:1	0.5
5	Residue		4.0

Fractions A5, 6, 7 and B2, 3, 4 were combined and distilled through a 90×1.2 cm. adiabatic column of the *partial* condensation type (Fig. 2), bar., 729-731 mm.

Fraction	B. p., °C.	Reflux ratio	Wt., g.	n_D^{20}
C1	84.6-85	46:1	0.5	
2	85-87	12:1	2.5	
3	87-89	20:1	12.0	1.4214

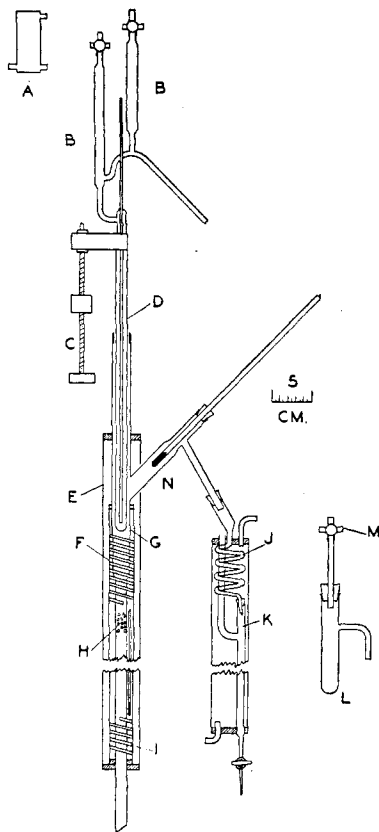
At this point it was found that the distillate contained halogen (Beilstein test and sodium ethylate test). The distillation was then completed in the small Vigreux column.

3a	90-96	2:1	2.5	1.4032
4	96-105	2:1	1.5	
5	105-106.2	20:1	7.5	

Fractions C3, 3a were redistilled through the Vigreux column. Bar., 734 mm.

Fig. 2.—This column was designed by M. R. Fenske and constructed by Franklin Johnston for the separation of smaller amounts of liquids than those which can be separated by means of columns of the total condensation, partial take-off type (Fig. 1).

A, A one-gallon can arranged to supply a constant head of water to the inside tube of the condenser D. The outlet of the condenser is connected to the drop indicator L and the flow of water through the condenser is regulated by the screw clamp M. B, Air traps to take air bubbles out of the line leading from the condenser to the drop indicator. If these traps are omitted, air bubbles prevent the accurate adjustment of the flow of condenser water which is necessary in careful separations. C, A brass screw 15 cm. long arranged to make possible the accurate raising and lowering of the condenser within the enlarged top of the column. D, Condenser 39 × 1 cm. The cooling water from the constant level device enters the middle tube of the condenser. The condenser can be raised or lowered inside the column by means of the screw C. At the start of a distillation, the condenser is lowered until no vapor passes through the side arm N. After the column has reached equilibrium, the condenser is raised to allow a slow stream of vapor to pass through N to the condenser J. If this stream of vapor is very slow, the readings of the thermometer are not significant. The course of the distillation is then followed by taking the refractive indices of the fractions. E, An insulating jacket consisting of a Pyrex tube 123 cm. long and 4.3 cm. inside diameter. F, A Pyrex tube, 115 cm. long and 2.7 cm. inside diameter, carrying the heating ribbon I. G, Column consisting of a Pyrex tube 29 cm. long and 2.1 cm. inside diameter sealed to the top of a Pyrex tube 113 × 1.2 cm. H, Packing consisting of Lessing rings, 5 × 5 mm., made of 50-mesh copper screen. Packed space, 90 cm. long. I, Heating ribbon. The jacket F is wrapped with 42 ft. (125 turns) of Chromel resistance ribbon, $\frac{1}{16} \times 0.005$ in., having a resistance of 1.68 ohms per ft.; total resistance, 70 ohms. A fixed outside resistance of 61 ohms and a variable resistance of 45 ohms with a capacity of 3.1 amp. are arranged to give the maximum flexibility in heating the column. The temperature of the column is given by a thermometer between the tubes F and G. J, A copper condenser consisting of 45 cm. of tubing 5 mm. outside diameter. K, A 10-cc. buret connected to the copper condenser. The buret and condenser are in a glass jacket through which cold water runs. L, Drop indicator connected to the outlet from the condenser D. This is used to measure the flow of cooling water through this condenser. M, Screw clamp used to regulate the flow of cooling water. By proper adjustment of the flow of water and the height of the condenser D in the column, the flow of vapor through N can be very accurately controlled. N, Side arm of column to convey the vapors which pass the partial condenser D to the total condenser J. The distance from the column to the second side arm is 9 cm.



D1	86.5-87	8:1	2.5	
2	87-89	8:1	7.0	1.4200
3	89-89.5	6:1	2.5	
4	Residue		1.0	

Analysis of Fraction D2.⁹ Calcd. for C₄H₉Br: Br, 58.3. Found: Br, 45.3, 44.5; tertiary bromide, 0.3. No fraction corresponding to *tert.*-butyl alcohol was detected.

Separation of a Known Mixture Containing 98% Isobutyl Alcohol and 2% Tertiary Butyl Alcohol.—A mixture of 4 g. of *tert.*-butyl alcohol (m. p. 25°) and 196 g. of isobutyl alcohol (b. p. 107-108°) was fractionated through a 38 × 1.8 cm. packed column with total condenser and variable take-off.

Fraction	B. p., °C.	Reflux ratio	Wt., g.
E1	99.9-101	60:1	12
2	101-105.5	60:1	11.5
3	105.5-107	60:1	14
4	Residue		160

Fractions E1, 2, 3 were combined and fractionated through the 90 × 1.2 cm. partial condensation column (Fig. 2).

Fraction	B. p., °C.	Reflux ratio	Wt., g.
F1	78	26:1	1.3
2	81.2-85.8	26:1	1.5

Fraction F1 did not freeze at -10° but F2 had a m. p. of +6°. The two fractions were mixed with concentrated hydrochloric acid (16 cc.) and an oily layer separated. This was dried with potassium carbonate and then had the correct b. p. for tertiary butyl chloride, 50-50.5°.

Preparation of Tertiary Butyl Alcohol from Tertiary Butylmagnesium Chloride.—The Grignard reagent was prepared from one mole each of tertiary butyl chloride and magnesium in the usual way, yield 60%. The solution was diluted with more ether, making a total of 600 cc. of ether, and treated with oxygen below 0°. The mixture was poured on ice. The ether layer was distilled in the usual way, the alcohol fractions being distilled through the 38 × 1.4 cm. column.

Fraction	B. p., °C.	Reflux ratio	Wt., g.	M. p., °C.
G1	62-78	30:1	6	- 8
2	78-81.8	30:1	24	+ 8
3	Residue		4	+21

Summary

1. No rearrangement to tertiary butyl compounds is found when pure isobutyl bromide is converted to the Grignard compound and then to isobutyl alcohol by the action of oxygen.

2. The possible relation of these facts to the theoretical consideration of rearrangements and of the Grignard reaction is indicated.

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⁹ Cf. Meisenheimer and Schlichenmaier, *Ber.*, **61**, 2029 (1928).