especially at higher temperatures⁸, it was necessary to investigate whether and to what extent such an exchange had taken place in the preparations of phenol-t and lonol-t. The possible transition of tritium from the hydroxylic group to the benzene ring should of course give too small tritium activities in the hydrocarbons evolved with the Grignard compounds.

The check of this exchange proceeded in the same manner as described by Kukhtenko⁹. Tritium in the hydroxylic group of the ordinary phenol was washed off by dissolving the phenol in a large volume of 2 % aqueous sodium hydroxide. The phenolate solution was acidified and the phenol was extracted by benzene. The extract was dried with anhydrous calcium chloride and distilled for isolation of phenol free from tritium in the hydroxylic group. In the case of lonol-t, which is not soluble in sodium hydroxide, the method was modified. The tritiated lonol was dissolved in 96 % ethanol, after which ordinary water was added in portions while shaking the mixture until lonol began to precipitate. The precipitated crystals were carefully washed with much water and dried.

The phenols free from hydroxylic tritium were burned over cupric oxide like the initial tritiated phenols, and the radioactivity of the combustion water after reduction to hydrogen was determined by means of a Geiger-Müller counter. The activities thus obtained indicate that the tritiated phenols are practically free from tritium in the benzene rings.

The technique of the Grignard decompositions was the same as the one used earlier, *i. e.* the Grignard reagent in *n*-butyl ether solution was added by means of an injection syringe to a solution of the phenol in the same solvent. The phenols were present in excess over the Grignard compounds.

The tritiated phenols and the hydrocarbons formed in the decompositions were burned over cupric oxide and the radioactivity of the combustion water was determined (after reduction to hydrogen) in the same manner as in the case of the detritiated phenols.

The ratios k_T/k_H in the tables have not been corrected for the change in the isotopic composition of the phenols taking place during the reaction.

3. Assarsson, L. O. *Acta Chem. Scand.* **11** (1957) 1283.
4. Assarsson, L. O. *Acta Chem. Scand.* **12** (1958) 1547.
5. v. Braun, J. and Kirschbaum, G. *Chem. Ber.* **52** (1919) 1725.
6. Stillson, G. H., Sawyer, D. W. and Hunt, C. K. *J. Am. Chem. Soc.* **67** (1945) 303.
7. Wiberg, K. B. *J. Am. Chem. Soc.* **77** (1955) 5987.
8. Ingold, C. K., Raisin, C. G. and Wilson, C. L. *J. Chem. Soc.* **1936** 1637.
9. Kukhtenko, I. I. *Doklady Akad. Nauk. SSSR* **93** (1953) 487.

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Isotope Effect in the Methanolysis of *n*-Butylmagnesium Bromide.

A Reinvestigation

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In a previous preliminary paper¹ measurements of the hydrogen isotope effect in the methanolysis of *n*-butylmagnesium bromide have been reported. The ratios k_T/k_H obtained in those experiments diverge considerably, the ratio obtained with the freshly prepared Grignard reagent being larger than those obtained with an

Table 1. Results in the decomposition of *n*-butylmagnesium bromide with methanol in *n*-butyl ether at 20°C.

k_T/k_H	Number of parallel determinations of tritium in combustion water	Mean value (including error in determination of tritium in combustion water from the methanol)

1. Assarsson, L. O. *Acta Chem. Scand.* **9** (1955) 1399.
2. Assarsson, L. O. *Acta Chem. Scand.* **10** (1956) 1509.

1.014	1	1.00 ± 0.03
1.002	1	
1.006	2	
0.978	1	

older reagent. This fact was supposed to be due to small amounts of moisture gradually entering the flask containing the Grignard reagent and forming inactive butane. This "false" butane, staying dissolved in the solvent, possibly might also be supposed to be formed by other reactions of the Grignard reagent.

In order to eliminate the "false" butane, part of the solvent *n*-butyl ether was distilled off in vacuum immediately prior to every methanolysis. Owing to the high volatility of butane, its absence then seems warranted. The ratios k_T/k_H obtained in the present experiments show very good reproducibility.

As k_T/k_H is equal to unity the isotopic composition of the methanol does not change during the reaction and hence no correction of the ratio is necessary.

It is interesting to note that the inverse isotope effect obtained by Wiberg² has not been confirmed by the present experiments, using tritium instead of deuterium.

1. Assarsson, L. O. *Acta Chem. Scand.* **11** (1957) 1283.
2. Wiberg, K. B. *J. Am. Chem. Soc.* **77** (1955) 5987.

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