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Gordon, Maxwell

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Anomalous Reactions of Phenetole Halides. A New Type of Ether Splitting

Maxwell Gordon

June 22, 1950

Berkeley, California

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ANOMALOUS REACTIONS OF PHENETOLE HALIDES. A NEW TYPE OF ETHER SPLITTING¹

Maxwell Gordon^{2,3}

Radiation Laboratory and Department of Chemistry
University of California, Berkeley

June 22, 1950

In an effort to prepare β -C¹⁴-labeled phenoxypropionic acid for some mechanism studies we attempted to form the Grignard of β -bromo and β -chloroethyl phenyl ether with both simultaneous and subsequent carbonation. We also tried the cyanide reaction, and our efforts met with failure in all cases.

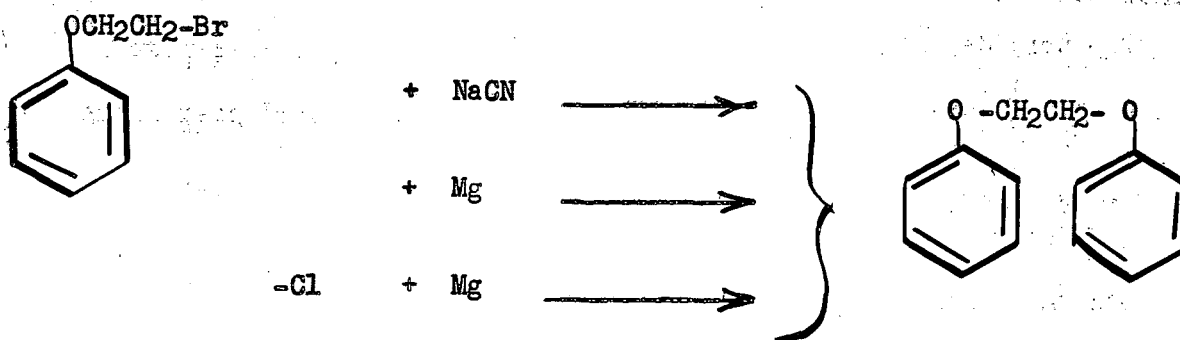
The results obtained in the Grignard reactions were not unexpected in view of the fact that Grignard⁴ obtained ethylene and phoxymagnesium bromide on reacting β -bromoethyl phenyl ether with magnesium in ether. Gilman⁵ reported a 35.5% yield of Grignard from β -chloroethyl phenyl ether based on titration of the product. However, in view of the results of Grignard⁴, Gilman stated that the formation of the Grignard should not be accepted until it had been used in a synthetic procedure. This we attempted to do without success in the carbonation reaction. Hence it must be con-

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- 1 The work described in this paper was sponsored by the Atomic Energy Commission.
 - 2 Atomic Energy Commission Postdoctorate Research Fellow in the Physical Sciences of the National Research Council, 1949-1950.
 - 3 Present Address: Organic Chemistry Department, Imperial College of Science and Technology, London S.W. 7, England.
 - 4 Grignard, Compt. rend., 138, 1048 (1904).
 - 5 Gilman and McCracken, Rec. trav. chim., 46, 469 (1927).
-

cluded that the compound titrated by Gilman was phenoxymagnesium chloride, and not β -phenoxyethyl magnesium chloride, since the acid-base titration procedure would not distinguish between these two compounds.

As a result of our efforts to react β -bromoethyl phenyl ether with sodium cyanide we isolated a 30% yield of 1,2-diphenoxyethane, identified by its crystal form, melting point, mixed melting point with an authentic sample, analysis and infrared spectrum.

The reaction of β -chloroethyl phenyl ether with magnesium, in our hands, resulted in the formation of some phenoxymagnesium chloride and ethylene, but no phenoxypropionic acid after carbonation. We also isolated approximately a 20% yield of 1,2-diphenoxyethane, identified as before. Grignard⁴, starting with the β -bromophenole, reported the isolation of a small amount of a compound, m.p. 98°, which he identified as 1,4-diphenoxybutane. In view of our results, and the fact that this melting point is identical with that of 1,2-diphenoxyethane, it is possible that the compound isolated by Grignard could have been 1,2-diphenoxyethane. If this is the case it would appear that all three reactions, the Grignard with β -chloro and β -bromophenole and the cyanide reaction, give the identical anomalous product.



These reactions are being investigated further to determine what other products may be formed and to determine whether the same mechanism applies in all cases.

It is curious that γ -phenoxypropyl bromide reacts normally with cyanide to give γ -phenoxybutyronitrile⁶. The labile nature of alkyl-oxygen bonds in alkyl-aryl ethers has been noted many times before⁷, but the reagents involved are usually strong acids and the products are usually alkyl phenols and olefins. In view of these considerations the isolation of 1,2-diphenoxyethane is of interest.

6 Marvel and Tanenbaum, J. Am. Chem. Soc., 44, 2645 (1922).

7 Wheland, "Advanced Organic Chemistry," John Wiley and Sons, New York (1949), pps. 555-561.
