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Some Abnormal Reactions of Organomagnesium Halides

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tetrabromo derivative of diphenyl ether obtained some years ago by Cook [J. Am. Chem. Soc., 32, 1286 (1910)] by direct bromination. A number of derivatives of this product have been obtained, but there is still some doubt as to the exact structure of the compound. Negative results are due in part to the stability of diphenyl ether derivatives, which makes it difficult to "split" the compounds in such a way as to recognize the character of the radicals present.

STATE UNIVERSITY,
IOWA CITY, IOWA.

ORGANO-LEAD COMPOUNDS IN THE TREATMENT OF CANCER

HENRY GILMAN AND JACK ROBINSON

New organo-lead compounds have been prepared by means of the Grignard reagent. These compounds are being tested in cancer studies, as anti-knock agents, and as reagents to combat some plant diseases. Grignard reagents are being prepared from tetra-*p*-bromophenyl-lead, diphenyl-di-*p*-bromophenyl-lead, and halogeno-alkyl lead types by reaction with the special magnesium-copper alloy using mercuric salts as catalysts. Solubilizing groups like dialkylamino, diethyl-aminoethyl, and various carboxylic acid groups are being attached to the R groups which in turn are attached to lead.

For allied purposes the same types are being prepared where the lead has been replaced by tin, antimony, selenium and tellurium.

IOWA STATE COLLEGE,
AMES, IOWA.

SOME ABNORMAL REACTIONS OF ORGANOMAGNE- SIUM HALIDES

HENRY GILMAN, J. E. KIRBY, R. E. FOTHERGILL AND
S. A. HARRIS

Nitro and nitroso groups react with methylmagnesium halides (and other RMgX compounds) to give methane and some ethane. The gases so evolved make it necessary to correct for the ordinary determination of active hydrogen by means of the Zerewitinoff method. Accordingly, the new hydroxy structure proposed for

o-nitrobenzaldehyde finds no support on the basis of gas evolved when treated with alkylmagnesium halides.

Benzylmagnesium halides, and related RMgX compounds like α -naphthylmethylmagnesium chloride (where the -MgX group is attached to a carbon that is attached in turn to an unsaturated carbon) have been found to give rearrangement products with new compounds like ethyl chlorocarbonate and ethylene oxide. In some cases (with benzylmagnesium chloride) rearrangement takes place to the para position. A study is in progress of the mechanism of such rearrangements.

In connection with the proof of the *non*-addition of RMgX compounds to an ethylenic linkage, it has been shown that cinnamyl chloride when treated with magnesium gives largely a Grignard reagent which when treated with carbon dioxide gives methyl atropic acid. The three other cases in the literature that have been offered as apparent proofs for the addition of RMgX compounds to an ethylenic linkage are also being investigated.

IOWA STATE COLLEGE,
AMES, IOWA.

THE ACTION OF THE ALKYL CHLORIDES IN THE WURTZ REACTION

HARRY F. LEWIS

At the last meeting of the Iowa Academy, a report was made on the mechanism of the Wurtz reaction using butyl and isobutyl bromides. The preparation of octane in this manner is costly and an attempt has been made to replace the bromide by the chloride. This report covers such experiments. Either in the presence or absence of ether as a solvent, the reaction is difficult to control. Yields of octane up to 20% based on the butyl chloride have been obtained. An extremely inflammable by-product is produced and it is difficult to complete a preparation without at least one fire. Using octane itself as a solvent, several bad explosions resulted.

STERIC HINDRANCE IN THE BEHAVIOR OF PHENYL ALKYL ETHER AND DERIVATIVES

L. CHAS. RAIFORD AND D. M. BIROSEL

It is known that phenyl alkyl ethers substitute in the phenyl radical less easily than phenol; nevertheless, phenetol will give a