[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE REACTION BETWEEN ORGANOMAGNESIUM HALIDES AND THE ARYL ESTERS OF BORIC, CARBONIC, SILICIC AND PHOSPHORIC ACIDS

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RECEIVED JANUARY 15, 1926 PUBLISHED APRIL 5, 1926

Introduction

Aryl esters of sulfonic acids react quite differently towards a number of reagents, particularly the Grignard reagent, from the alkyl esters of sulfonic acids. With alkyl esters[1] the following alkylating action takes place.

$$2RSO_2O\text{—Alkyl} + 2RMgX \longrightarrow 2R\text{—Alkyl} + (RSO_2O)_2Mg + MgX_2 \quad (1)$$

No arylating action occurs with aryl esters,[2] instead the -OAryl group is removed to form sulfones as follows.

$$RSO_2\text{—O—Aryl} + R'MgX \longrightarrow RSO_2R' + \text{Aryl—OMgX} \quad (2)$$

The ready alkylating action of sulfonic esters can be correlated with that of halogen esters (the alkyl halides), but it appears to be highly unique in the sense that no other alkyl esters of oxygen and sulfur acids behave in a like manner towards organomagnesium halides and several other classes of compounds. A single exception is the work reported by Khotinsky and Melamed.[3] They described the formation of toluene as a result of the reaction between methyl borate and phenylmagnesium bromide (I). This prompted a study of the reaction of the aryl esters of boric, carbonic, silicic and phosphoric acids with typical Grignard reagents The reaction in all cases takes place according to (II): that is, the -O-Aryl group is removed, as is the case with all aryl esters so far studied.[4]

Inasmuch as the alkylating action of alkyl sulfonates is smooth and very satisfactory for many synthetic purposes,[1] it was considered advisable to check the formation of toluene reported by Khotinsky and Melamed[3] from the reaction between methyl borate and phenylmagnesium bromide. A very careful search failed to reveal any toluene. Accordingly the alkylating action of esters of oxygen acids towards Grignard reagents is confined exclusively, at present, to alkyl sulfonates. All other alkyl esters of oxygen acids undergo a reaction like that in (2) where the -OAlkyl and not the alkyl alone is removed.

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[1] Gilman and Beaber, THIS JOURNAL, **47**, 518 (1925). References to all earlier work on this reaction are contained in this article or in the papers to which it refers. Subsequent to this reference is some work by Bert, *Bull. soc. chim.*, **37**, 1252 (1925).

[2] Gilman, Beaber and Meyers, *ibid.*, **47**, 2047 (1925).

[3] Khotinsky and Melamed, *Ber.*, **42**, 3090 (1909).

[4] Aryl halides, which may be considered as aryl esters of halogen acids, react with R'MgX compounds to give R—R' compounds. However, the ease of this arylating action is decidedly inferior to that of alkyl halides.

Experimental Part

In general, the ester was added to an ether solution of the Grignard reagent and after boiling under a reflux condenser the mixture was hydrolyzed and both the ether and aqueous layers examined for reaction products. Where reactions were carried out at higher temperatures most of the ether was distilled from a water-bath, after the RMgX compound in ether had been prepared and an equivalent amount of dry benzene or toluene added. In some of the experiments with boric esters, the reaction mixture was distilled prior to hydrolysis in order to collect the very sensitive alkyl borides. A careful study was made of those fractions that might contain hydrocarbons formed as a result of any *arylating* action after the manner of the alkylating action of alkyl sulfonates (see Reaction 1). Several experiments under various conditions were made with each ester. However, only a selected run which was generally checked is given.

Triphenyl Borate.—Khotinsky and Melamed[3] observed the following reaction between alkyl borates and either alkyl- or arylmagnesium halides.

$$B(OR)_3 + R'MgX \longrightarrow R'B(OR)_2 + MgX(OR) \qquad (3)$$

The boric esters so formed give substituted boric acids ($R'B(OH)_2$) on hydrolysis.

Triphenyl borate[5] with three equivalents of *n*-butylmagnesium bromide gave an 80% yield of phenol and a small amount of a yellow compound that sputtered and fumed in the air and was probably *n*-butyl boride. Since this boride is not described in the literature, corresponding runs were made with *n*-propylmagnesium bromide. Again using 0.1 mole of triphenyl borate, there were obtained 56% of phenol and about 7% of *n*-propyl boride. Distillation was carried out in an atmosphere of nitrogen, and the propyl boride agreed in its properties with those described by Krause.[6]

The reaction between 0.1 mole of triphenyl borate and four equivalents of phenylmagnesium bromide in ether solution gave 40% of phenol, 16.5% of phenylboric acid, $C_6H_5B(OH)_2$ and a small amount of diphenyl (1.3%) that corresponds with that generally obtained in the preparation of phenylmagnesium bromide.[7]

Trimethyl Borate.—The conditions described by Khotinsky and Melamed[3] were closely followed in three experiments with methyl borate and phenylmagnesium bromide. Using 0.25 mole of methyl borate,[8] an 86% yield of phenyl boric acid was obtained. With 0.64 mole of methyl borate, 58% of phenylboric acid and 30% of benzene was obtained. In both these experiments methyl alcohol was identified as a reaction product. In a one-mole run of methyl borate a very careful search failed to reveal any toluene. The benzene, formed as a result of the hydrolysis of phenylmagnesium bromide, was identified by preparing *m*-dinitrobenzene from it.

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[5] Prepared according to the method of Pictet and Geleznoff, *Ber.*, **36,** 2219 (1903).

[6] Krause, *Ber.*, **54B,** 2784 (1921).

[7] Porter and Steele, This Journal, **42,** 2650 (1920).

[8] From Kahlbaum.

Diphenyl Carbonate.—Chichibabin,[9] in a study of the reaction of diethyl carbonate and the ethyl ester of orthocarbonic acid ($C(OC_2H_5)_4$) with various Grignard reagents, obtained esters in good yield (as high as 80%) as well as small amounts of ketones and tertiary alcohols. The same type of reaction was observed in this work when diphenyl carbonate was used.

A vigorous reaction took place when 0.1 mole of diphenyl carbonate was added to 0.25 mole of phenylmagnesium bromide. The products obtained were: triphenyl carbinol (69 and 41%); phenyl benzoate (6 and 21%), and phenol (45 and 61%). The absence of any appreciable amount of diphenyl showed that no phenylating reaction had occurred. In the small amount of liquid that remained after removing phenyl benzoate there may have been some benzophenone.

Ethylmagnesium iodide with diphenyl carbonate gave no ethyl benzene. The phenol fraction yielded a very small amount of an unidentified compound melting at 27°. In this run some benzene was obtained and its identity was confirmed by the preparation of *m*-dinitrobenzene. There is no ready explanation for the highly unexpected presence of benzene. A duplicate run with reagents from the same stock bottles gave no benzene.

Tetra-*p*-Cresyl Silicate.—Khotinsky and Seregenkoff[10] found that tetraethyl silicate reacts with the Grignard reagent as does ethyl orthocarbonate[9] in the sense that only one $-OC_2H_5$ group is removed, even when an excess of RMgX compound is used.

$$Si(OC_2H_5)_4 + RMgX \longrightarrow RSi(OC_2H_5)_3 + MgX(OC_2H_5) \qquad (4)$$

Hydrolysis gave silicic acids (RSiOOH); however, when the reaction mixture was warmed for a long time prior to hydrolysis complex, insoluble silicon compounds were formed by condensation reactions.

Because of a slow reaction in ether, the mixture of equivalent quantities (0.5 mole) of tetracresyl silicate and phenylmagnesium bromide was refluxed for four hours at 104° in an ether-toluene solution. In addition to 17.5% unchanged ester, there was obtained 46.5% of *p*-cresol and about 7.5 g. of a complex silicon compound, undoubtedly formed by a condensation reaction as a result of the protracted heating.

With benzylmagnesium chloride, under corresponding conditions, 0.5 mole of ester gave 30% of *p*-cresol and 4 g. of a complex silicon compound. It is probable that reaction took place to only a limited extent, because of the vigorous reaction on hydrolysis. The *p*-cresol may owe its formation, in part, to the known ready hydrolysis of the ester into *p*-cresol and silicic acid.[11]

Triphenyl and Tri-*p*-Cresyl Phosphates.—Michaelis and Wegner[12] have shown that in the reaction between monophenoxy phosphorous oxy-

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[9] Chichibabin, *Ber.*, **38,** 561 (1905).

[10] Khotinsky and Seregenkoff, *Ber.*, **41,** 2946 (1908).

[11] Hertkorn, *Ber.*, **18,** 1679 (1885).

[12] Michaelis and Wegner, *Ber.*, **48,** 316 (1915). Apparently no study has been made of the reaction between alkyl phosphates and organomagnesium halides. Several typical alkyl phosphates are to be investigated in connection with other alkyl esters of oxygen acids to determine whether alkyl sulfonates are unlike all other esters in their behavior towards the Grignard reagent. An alkyl nitrate was studied by Moureu [*Compt. rend.*, **132,** 837 (1901)], but no alkylating action was reported.

chloride ($(C_6H_5O)POCl_2$) and phenylmagnesium bromide that both the halogens and the phenoxy group are replaced to give triphenyl-phosphine oxide, $(C_6H_5)_3P{=}O$. The same type of replacement of -OR group by the R of RMgX (2) was observed in this study of triaryl phosphates.

From the reaction between 0.1 mole of triphenyl phosphate and four equivalents of phenylmagnesium bromide there was obtained 17% of triphenyl phosphine oxide and 49% of phenol. No reaction took place between triphenyl phosphate and *n*-propylmagnesium bromide when the mixture was refluxed in ether for six hours. However, when 0.1 mole of ester was refluxed for 12 hours at 95° in an ether-toluene solution of 0.4 mole of *n*-propylmagnesium bromide, there resulted 49% of phenol and 5 g. of a compound that boiled at 280–282° and melted at 36°. This phosphorus-containing liquid may have been tri-*n*-propyl-phosphine oxide that melts at 38°, but attempts to characterize it by the chloro-aurate were unsuccessful.[13] The triphenyl-phosphine oxide was identified, however, by the preparation of the corresponding chloroaurate.

In several runs of the reaction between tri-*p*-cresyl phosphate and benzylmagnesium chloride it was shown that no arylating action took place. When 0.1 mole of ester was refluxed with 0.4 mole of benzylmagnesium chloride at 95° for ten hours, 28% of *p*-cresol and 15.5 g. of a compound melting at 148° were obtained. This unidentified phosphorus organic compound was not tribenzyl-phosphine oxide which has been described and melts at 216°.[14] The tricresyl phosphate when refluxed with phenylmagnesium bromide at 106° for five hours gave 50% of triphenyl-phosphine oxide and 54% of *p*-cresol.

The absence of tribenzyl-phosphine oxide in the benzylmagnesium chloride experiment indicated that this Grignard reagent may have reduced the oxide.[15] Accordingly, 14 g. of triphenyl-phosphine oxide was refluxed with six equivalents of phenylmagnesium bromide for 15 hours at 104° and after working up in the customary manner 10 g. or 71.5% of the oxide was recovered. When a corresponding experiment was carried out with ethylmagnesium iodide, 7 g. or 50% of the oxide was covered. In neither run was there any evidence of triphenyl phosphine.

Triphenyl Phosphite.—The reaction between triphenyl phosphite[16] ($(C_6H_5O)_3P$) and phenylmagnesium bromide is unusually smooth, and proceeds after the manner of all other aryl esters (2). From 0.1 mole of the ester and 0.4 mole of phenylmagnesium bromide there was obtained 60% of triphenyl phosphine and 68% of phenol.

Summary

Trimethyl borate, contrary to experiments of others, has been found to have no methylating action towards phenylmagnesium bromide. All aryl esters of oxygen acids thus far studied show no arylating action with Grignard reagents, instead the -OAryl group is replaced.

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[13] Pickard and Kenyon, *J. Chem. Soc.*, **89**, 262 (1906).

[14] Sauvage, *Compt. rend.*, **139**, 674 (1904).

[15] Gilman and Pickens, THIS JOURNAL, **47**, 2406 (1925). See Footnote 19 for other references to the reducing action of some Grignard reagents.

[16] Prepared according to the method of Noak, *Ann.*, **218**, 85 (1883). Also, Conant, Wallingford and Gandheker, THIS JOURNAL, **45**, 767 (1923).