[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

A STUDY OF THE POSSIBLE INTERCHANGE OF RADICALS ON HEATING A MIXTURE OF AN R'X AND AN RMgX COMPOUND

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Introduction

In connection with studies on the comparative reactivity of RX compounds toward magnesium in ether, combinations of two RX compounds have been allowed to compete for a quantity of magnesium insufficient to react with both halides.[1] It would be necessary to assume in such studies that there is no interchange of radicals, as follows

$$RX + Mg \longrightarrow RMgX \qquad (I)$$
$$R'X + RMgX \longrightarrow R'MgX + RX \qquad (II)$$

Obviously, if an interchange of radicals as illustrated in Reaction II occurred then the quantity of R'MgX compound formed would not be solely a measure of the rate of reaction between the R'X compound and Mg, but also a measure of any R'MgX compound that might have formed in accordance with Reaction II.

The assumption of no interchange of radicals appeared altogether reasonable prior to some studies by Gilman and Fothergill[2] on the probable dissociation of some Grignard reagents. Accordingly, the present study was undertaken to determine definitely whether the interchange pictured in Reaction II actually takes place under our particular experimental conditions. We have found that no such interchange of radicals occurs.[3]

The method used was to add carbon dioxide to a mixture of R'X and RMgX compounds subsequent to refluxing in an ether–toluene or ether–benzene mixture for a few hours. If no interchange took place, the acid formed after carbonation should be pure RCOOH. If some interchange occurred, then some R'COOH and RCOOH would result. In each of the several cases studied only one acid was obtained, namely, the acid corresponding with the RMgX initially present.

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[1] The results of another aspect of this problem have already been reported by Gilman and Van der Wal, *Bull. soc. chim.*, **45** (1929). See, also, Rudd and Turner, *J. Chem. Soc.*, 687 (1928), and Gilman and Zoellner, THIS JOURNAL, **50**, 2520 (1928).

[2] Gilman and Fothergill, *ibid.*, **51** (1929). An account of this investigation was presented at the May, 1929, meeting of the American Chemical Society held at Columbus, Ohio.

[3] We mean this statement to be confined to the specific combinations used in this study. We consider it likely that special combinations like triphenylmethylmagnesium chloride and bromotriphenylchloromethane will show an interchange. Studies of such combinations of R'X and RMgX compounds, each of which has a tendency to dissociate, are in progress.

Depending on the lability of the halogen in the R′X compound, a reaction takes place between the halide and the RMgX compound, as follows

$$R'X + RMgX \longrightarrow R'R + MgX_2 \qquad \text{(III)}$$

With some R′X compound, Reaction III goes to completion.[4] In order to have some RMgX present at the end of the preliminary refluxing with R′X, an insufficient quantity of the latter was used. The chief products obtained, therefore, were the RCOOH from the RMgX, and the RR coupling product. However, in the reaction between triphenylchloromethane, $(C_6H_5)_3CCl$, and phenylmagnesium bromide a very unusual product resulted, in addition to a small quantity of tetraphenylmethane, $(C_6H_5)_4C$, which would be expected in accordance with Reaction III. This unexpected product was obtained in a 47.4% yield and was identified as *p*-phenyl-triphenylmethane, *p*-$C_6H_5C_6H_4C(H)(C_6H_5)_2$. This compound was unexpected because it was not reported by a number of other investigators[5] of this particular reaction between triphenylchloromethane and phenylmagnesium halides. A study is in progress of this and related reactions concerned with the rearrangement of halides and organomagnesium halides,[6] and free radicals formed from them.[7]

Experimental Part

With the exception of triphenylmethylmagnesium chloride,[8] the Grignard reagents were taken from stock solutions of known titration value. The RMgX solutions were free from magnesium. After refluxing the ether–toluene or ether–benzene mixtures of RMgX and R′X compounds for about three hours and at a temperature of about 60°, the cooled mixture was treated with carbon dioxide after the procedure of Gilman and Parker.[9]

Subsequent to hydrolysis the acids were extracted with dilute alkali and then recovered in a customary manner by acidification. None of the acids was purified by crystallization. Instead the "crude acid" obtained directly on acidification (after carefully extracting the alkaline solution with ether to remove all non-acidic compounds) was dried to constant weight. With the acid obtained in this manner a melting-point

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[4] See Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1929); Gomberg and Cone, *Ber.*, **39**, 1461 (1906); Späth, *Monatsh.*, **34**, 1965 (1913). Together with Reaction III another coupling reaction can occur: $2RX + 2R'MgX \longrightarrow R{\cdot}R + R'{\cdot}R' + 2MgX_2$. This reaction has been discussed in detail by Fuson, THIS JOURNAL, **48**, 830, 2681, 2937 (1926).

[5] Gomberg and Cone, *Ber.*, **39**, 1461 (1906); Freund, *ibid.*, **39**, 2237 (1906); Schmidlin, *ibid.*, **43**, 1137 (1910); Meyer, *J. prakt. Chem.*, **82**, 521 (1910); Gomberg and Kamm, THIS JOURNAL, **39**, 2009 (1917); Gomberg and Forrester, *ibid.*, **47**, 2374 (1925).

[6] Gilman and Harris, *ibid.*, **49**, 1825 (1927); Gilman and Kirby, *ibid.*, **51**, 1571 (1929).

[7] Gilman and Fothergill, *ibid.*, **50**, 3334 (1928); *ibid.*, **51** (1929); Gilman and Kirby, *ibid.*, **51**, 1571 (1929).

[8] Prepared in practically quantitative yields by the method of Gilman and Zoellner, *Rec. trav. chim.*, **48** (1929).

[9] Gilman and Parker, THIS JOURNAL, **46**, 2816 (1924).

determination, a mixed melting-point determination with an authentic specimen and a neutralization equivalent were made.

Where the possible mixtures of acids were benzoic and phenylacetic acids (see the first two experiments in Table I) the method of mixed melting points is highly accurate. This was established by the melting-point determinations of a series of authentic mixtures of these two acids. From these preliminary melting-point determinations it was shown that *less* than 0.5% of either acid mixed with the other acid would give an unmistakable softening and depression of the melting point. This method of melting point of mixtures is not sufficiently sensitive with acids whose melting points are considerably removed from each other. An illustration is the third experiment given in Table I. In this case a distinctly high percentage of benzoic acid is required to depress the melting point of triphenylacetic acid. For this reason the purity of triphenylacetic acid was measured by the neutralization equivalent. Neutralization equivalents were also made of the acids in the fourth and fifth experiments (see Table I).

The non-acidic products were recovered in the usual manner from the ether–toluene or ether–benzene layer after alkaline extraction. These products were less carefully examined in this preliminary study because our chief interest was with the acids. Some details concerning the several experiments are given in the footnotes accompanying Table I.

TABLE I

REACTION BETWEEN R'X AND RMGX COMPOUNDS

		R'X								
		Used		Recovered						
		G.	Mole	G.	%	RMgX	Mole	RCOOH	G.	%
1	C_6H_5Br[a]	23.5	0.15	19.0	80	$C_6H_6CH_2MgCl$	0.25	$C_6H_5CH_2COOH$	15.2	44.7
2	$C_6H_5CH_2Cl$[b]	20.0	.15	14.0	70	C_6H_5MgBr	.25	C_6H_6COOH	10.6	34.7
3	C_6H_6Br[c]	4.0	.025	3.3	82.5	$(C_6H_5)_3CMgCl$	.04	$(C_6H_5)_3CCOOH$	6.1	51.2
4	$(C_6H_6)_3CCl$[d]	27.8	.1	..	..	$C_6H_5CH_2MgCl$	.25	$C_6H_5CH_2COOH$	3.2	9.4
5	$(C_6H_6)_3CCl$[e]	20	.072	..	..	C_6H_5MgBr	.25	C_6H_5COOH	11.6	38

[a] The phenylacetic acid obtained in this experiment melted at 77°, and a mixed melting-point determination with an authentic specimen of phenylacetic acid which melted at 77° showed no depression.

[b] The temperature during the three-hour period of heating was 64°. The benzoic acid obtained here melted at 121° and showed no depression in a mixed melting-point determination with an authentic specimen.

[c] This is the only experiment in which an ether–benzene mixture was used. In all others an ether–toluene mixture was used. Refluxing for three and one-half hours was carried out in an inert atmosphere by means of the special apparatus of Gilman and Hewlett, *Rec. trav. chim.*, **48** (1929). The neutralization equivalent of the triphenylacetic acid was 289; the calculated value is 288. There were also obtained 0.3 g. of triphenylcarbinol and 0.4 g. of triphenylmethane.

[d] A flocculent orange-colored precipitate formed on the addition of the Grignard solution, and the stirred and refluxed mixture later assumed an opaque light yellow color. The phenylacetic acid showed no depression in a mixed melting-point determination with an authentic specimen. Its neutralization equivalent was 137.6, whereas the calculated value is 136. There was also obtained 25.1 g. or a 75.2% yield of 1,1,1,2-tetraphenylethane, $(C_6H_5)_3CCH_2C_6H_5$.

[e] On the addition of the Grignard reagent the solution assumed a deep cherry-red color. The benzoic acid showed no depression in a mixed melting-point determination with an authentic specimen. Its neutralization equivalent was 120.1, whereas the calculated value is 122.

In addition there was obtained 0.2 g. or a 0.63% yield of tetraphenylmethane, the identity of which was confirmed by a mixed melting-point determination with an authentic specimen.

The non-acidic fractions also gave 10.9 g. or a 47.4% yield of *p*-phenyltriphenylmethane which after several crystallizations from hot absolute alcohol melted at 111°.

Anal. Calcd. for $C_{25}H_{20}$: C, 93.69; H, 6.31. Found: C, 93.20; H, 6.48. Mol. wt.: calcd., 320; found, 311.4.

The identity of this hydrocarbon was confirmed by a mixed melting-point determination with an authentic specimen melting at 111–112° and prepared in accordance with the directions of Schlenck, Weickel and Herzenstein, *Ann.*, **372**, 18 (1909).

Summary

In connection with rate studies, series of mixtures containing an R′X and an RMgX compound have been heated to determine whether there is an interchange of radicals. No such interchange was observed. In the reaction between triphenylchloromethane and phenylmagnesium bromide an unusual product, *p*-phenyl-triphenylmethane, was obtained in a 47% yield.

AMES, IOWA

NEW BOOKS

Introductory Theoretical Chemistry. BY G. H. CARTLEDGE, Associate Professor of Chemistry, The Johns Hopkins University. Ginn and Company, 15 Ashburton Place, Boston, Massachusetts, 1929. xiv + 523 pp. 71 figs. 14 × 21 cm. Price, $3.60.

In the order of treatment, the author has followed the plan of his earlier "Inorganic Physical Chemistry."

Part I, pp. 1–202, The Nature of Matter, gives an interesting résumé of the historical development of the various laws relating to the gaseous, solid and liquid states. The kinetic theory, Avogadro's law, the determination of atomic weights, radioactivity, atomic structure and surface tension are carefully treated. Numerous examples and references are given to classical experiments, such as Black's quantitative study of chalk and lime, and Landolt's research into the conservation of mass. An abstract (7 pages) from "A Revision of the Atomic Weights of Sodium and Chlorine," Richards and Wells, serves to stimulate interest in original work.

Part II, pp. 203–294, deals with the nature of solutions. Here also the historical development is emphasized. Perfect solutions and Raoult's law are illustrated by the method of vapor pressure lowering. The molecular weight of dissolved substances is determined in accordance with the older ideas (van't Hoff factor *i*) instead of by application of modern thermodynamic methods. A whole chapter (16 pages) is devoted to osmotic pressure. The electrical properties of solutions are given 38 pages with emphasis upon the Arrhenius theory and the degree of ionization. Colloidal solutions are treated in 10 pages.

Part III, pp. 295–466, deals with the nature of reactions. The author first devotes a chapter to the speed of reactions. The equilibrium constant