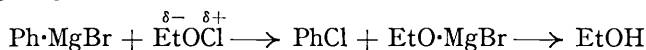


### 150. Further Instances of the Formation of Chlorobenzene from Phenylmagnesium Bromide and Chlorinated Substances.

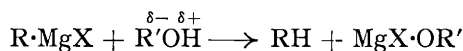
By RAYMOND J. W. LE FÈVRE and PETER J. MARKHAM.

THE formation of chlorobenzene from *N*-chloro-compounds and phenylmagnesium bromide has been recorded (J., 1932, 1745), and the reactions of this Grignard compound with chlorine-containing substances of three other types are now described.

(i) Addition of an ethereal solution of ethyl hypochlorite (Bloomfield and Farmer, J., 1932, 2062) to phenylmagnesium bromide under the standard conditions for a Grignard reaction led to the isolation of chlorobenzene in yields of about 60%, the only detectable by-product being ethyl alcohol :



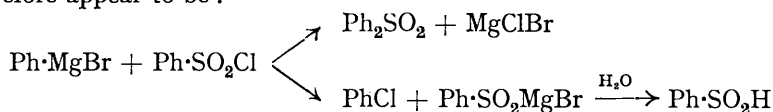
The apparently complete exclusion of phenetole from the product is in accord with other reactions of alkyl hypochlorites (*e.g.*, the formation from olefins of chloroalkoxy-addition compounds; Goldschmidt, *Ber.*, 1925, **58**, 572) which show that these esters enter a reaction either polarised, or predisposed to polarise, in the sense  $\overset{\delta-}{\text{RO}}-\overset{\delta+}{\text{Cl}}$ . The result obtained above is therefore strictly comparable with the familiar reaction between hydroxylic compounds and Grignard reagents :



(ii) The interaction between phenylmagnesium bromide and iodobenzene dichloride yields, according to Hepworth (J., 1921, **119**, 1244), mainly iodobenzene and diphenyl; since chlorobenzene might have been overlooked, we have repeated his experimental directions on as large a scale as possible. Chlorobenzene, however, is not formed. Some chlorination of the ether occurs (giving difficultly separable mixtures of chloroethyl ethers)—an interesting observation, since iodobenzene dichloride and ether have been found not to react in the absence of the Grignard reagent.

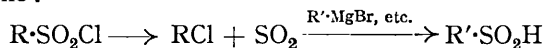
(iii) According to Hepworth and Clapham (J., 1921, **119**, 1188; compare, however, Wedekind and Schenk, *Ber.*, 1921, **54**, 1604) the interactions of phenylmagnesium bromide with benzene- and *p*-toluene-sulphonyl chlorides yield chiefly diphenyl- and phenyl-*p*-tolylsulphones respectively. Since, however, chlorobenzene has been isolated from the mixture formed when phenylmagnesium bromide acts on sulphuryl chloride (Oddo, *Atti R. Accad. Lincei*, 1905, [v], **14**, i, 169), some of these experiments have been repeated. We find that chlorobenzene is formed in both preparations, the yields (calculated on the bromobenzene taken) being about 25% for the reaction  $\text{Ph}\cdot\text{MgBr} + \text{Ph}\cdot\text{SO}_2\text{Cl}$  and slightly less

in the corresponding instance of *p*-toluenesulphonyl chloride. In the first case a small quantity of benzenesulphonic acid was easily isolated along with the diphenylsulphone mentioned by the above authors; the simultaneous reactions predominantly occurring would therefore appear to be :



Essentially similar results were obtained when ethylmagnesium bromide was used.

Some sulphonyl halides (notably camphor-10-sulphonyl chloride and bromide) lose sulphur dioxide remarkably smoothly and form the corresponding halogeno-derivatives (*e.g.*,  $\beta$ -chloro- and  $\beta$ -bromo-camphors in the instance cited), but the isolation in our experiments of chlorobenzene in the cases where R is either *p*-tolyl or ethyl indicates the improbability that the results reported above had their origin in any such decomposition or involved the interaction of sulphur dioxide with the Grignard reagent in the manner required by the scheme :



#### EXPERIMENTAL.

*Interaction of Phenylmagnesium Bromide and Ethyl Hypochlorite.*—An ice-cold solution of ethyl hypochlorite in anhydrous ether (150 c.c. of about 5% strength) was added slowly to phenylmagnesium bromide (from bromobenzene, 17 g., magnesium, 2.5 g., and ether, 200 c.c., *i.e.*, a slight excess of the Grignard reagent), and the mixture kept at room temperature for 9 hours. Water and ice were then added. Distillation of the dried (sodium sulphate) ethereal layer gave two main fractions, b. p. 70—80° and 120—135° (8 g.). The former contained ethyl alcohol (iodoform test) and benzene; the latter was evidently chlorobenzene (Found : C, 64.4; H, 4.6. Calc. : C, 64.0; H, 4.4%) and gave 1-chloro-2 : 4-dinitrobenzene, m. p. and mixed m. p. 52°, on nitration.

*Interaction of Phenylmagnesium Bromide and Iodobenzene Dichloride.*—To a Grignard solution prepared from magnesium (8.2 g.), bromobenzene (53.8 g.), and ether (200 c.c.), was added slowly iodobenzene dichloride (94 g.; ice-salt cooling). When the violent reaction had ceased, the mixture was refluxed for a short while and kept for 24 hours at the ordinary temperature. Addition of water then caused only a very slight reaction (*i.e.*, hardly any excess of the Grignard reagent was present); the ethereal layer was therefore removed, shaken with dilute aqueous sodium hydroxide, dried (sodium sulphate), and evaporated. The residual liquid on distillation gave, in addition to iodobenzene (4.4 g.) and a residue (21 g.), a number of ill-defined fractions which were evidently mixtures (Found : Cl, 39.7—52.9%).

*Interaction of Phenylmagnesium Bromide and Benzenesulphonyl Chloride.*—The Grignard solution prepared from bromobenzene (70 g.), magnesium (10 g.), and ether (200 c.c.) was treated slowly with benzenesulphonyl chloride (25 g., in ether, 100 c.c.). After 12 hours, the solution was decomposed with dilute sulphuric acid and ice, the ethereal layer washed with aqueous sodium hydroxide and dried, and the mass remaining after distillation of the ether steam-distilled; the volatile oils were extracted from the distillate with light petroleum, dried, and fractionated, leaving a few g. of residue consisting of diphenyl, m. p. and mixed m. p. 69—70° after crystallisation from alcohol (charcoal). The first fraction, b. p. 125—133° (16 g.), was identified as chlorobenzene by analysis and dinitration; the second fraction, b. p. 134—160° (6 g.), appeared to be mainly unused bromobenzene.

The alkaline washings on acidification with dilute sulphuric acid and ether extraction gave, after drying (sodium sulphate) and distillation, a mass of crystals, m. p. 80—81° (not depressed by admixture with benzenesulphonic acid, m. p. 83°). The residue in the flask after steam distillation crystallised from alcohol (charcoal) in white plates of diphenylsulphone, m. p. and mixed m. p. 126—128° (Found : C, 66.2; H, 4.7%).

*Interaction of Phenylmagnesium Bromide and p-Toluenesulphonyl Chloride.*—This was performed exactly as above, bromobenzene (85 g.), magnesium (13 g.), ether (200 c.c.), and *p*-toluenesulphonyl chloride (34 g., in ether, 150 c.c.) being used. The chlorobenzene fraction, b. p. 126—132°, weighed 12 g. and was formally identified as before.

*Interaction of Ethylmagnesium Bromide and p-Toluenesulphonyl Chloride.*—The reaction

between magnesium (33 g.), ethyl bromide (148 g.), ether (300 c.c.), and *p*-toluenesulphonyl chloride (65 g., in ether, 250 c.c.) was carried out as described by Wedekind and Schenk (*loc. cit.*), except that the reflux condenser was joined to the top of a vertical helical condenser through which ice-cold brine was circulating. During the ebullition accompanying the vigorous reaction a condensate (about 30 g.) was collected in a cooled receiver. It smelt strongly of ethyl chloride, burned with a green-edged flame, and boiled below 18°. Its aqueous solution was neutral to litmus, although during combustion hydrogen chloride was produced. It thus appeared to be ethyl chloride, contaminated possibly with a trace of ether.

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