methylbenzoyl)benzoic acid (II).—A mixture of 5 g. of 3,6-dimethoxy-phthalic anhydride and 25 cc. of *m*-cresol methyl ether was condensed in the same manner as the *o*- and *p*-cresol methyl ethers with the exception of a few details. The mixture was heated up to 75° during the course of 1.5 hours, and maintained at that temperature for 7 hours. When worked up in the manner previously described, no alkali-insoluble product was obtained but merely 4.9 g. (65%) of a dimethyl ether, probably 3-hydroxy-6-methoxy-2-(4-methoxy-1-methylbenzoyl)benzoic acid (II). This was purified by crystallization from methyl alcohol, forming colorless prisms melting at 194–195°. It was dried to constant weight before it was analyzed.

Analyses. Subs., 0.0766: CO_2, 0.1806; H_2O, 0.0342. Calc. for $C_{17}H_{16}O_6$: C, 64.56; H, 5.06. Found: C, 64.30; H, 4.67.

Summary

1. 3,6-Dimethoxy-phthalic anhydride was condensed with *o*-, *m*- and *p*-cresol methyl ethers.

2. The benzoyl-benzoic acids formed from the *o*- and *p*-cresol methyl ethers were condensed by means of sulfuric acid to the corresponding trihydroxy-methyl-anthraquinones or their methyl ethers. By varying the conditions of condensation it was possible either to obtain partial demethylation or complete demethylation during this reaction.

3. The structures of the benzoyl-benzoic acids obtained were established: first, by comparison with the isomeric substances obtained by the condensation of 3,6-dimethoxy-phthalic anhydride with cresols; and second, by direct proof.

4. It has been established that the entering group takes the *para* position to the methoxyl groups in the *o*- and *m*-cresol ethers and the *ortho* position to the methoxyl in the *p*-cresol methyl ether.

5. The structure of the anthraquinones obtained from the benzoyl-benzoic acids was determined.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

THE YIELDS OF SOME GRIGNARD REAGENTS

BY HENRY GILMAN AND ROY McCRACKEN[1]

RECEIVED JULY 31, 1923

Introduction

In connection with a series of studies involving the Grignard reagent, it was necessary to determine the approximate yield in the preparation of a number of typical RMgX compounds. A knowledge of such yields is quite indispensable in certain studies. In particular is this true of reactions involving an excess of some compound treated with the Grignard reagent, and when the interpretation of mechanism of such a reaction

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[1] This paper is an abstract of a thesis presented by Roy McCracken in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at Iowa State College.

is in no small way determined by the yields of products. Apart from these immediate considerations, the study is not without some interest in such general problems as steric hindrance and the order of activity of halogens in organic compounds.

The method used for the quantitative estimation of the various compounds was that previously described.[2] Although no optimum condition was determined for the formation of any of the reagents described in this paper, advantage was taken of the opportunity to incorporate where possible those factors which were found earlier[3] to give a maximum yield of ethylmagnesium iodide. It is quite probable that although the quantity of organic halide used was only that which would react theoretically with 1.15 g. of magnesium, the yields determined are such as may be expected, in larger runs made under comparable conditions. In this connection a quantitative study of yields, when the commonly used solvent (ether) is replaced in large part by other more desirable solvents such as benzene, is in progress. Here the method of analysis by titration will be checked in part by the preparation of standard compounds in fairly large quantities.

Procedure

The technique was essentially identical with that previously described in determining the best conditions for the preparation of ethylmagnesium iodide.[3] In each run 1.25 g. of magnesium turnings was used, and the weight of halide taken was approximately that which would theoretically react with 1.15 g. of magnesium. A small crystal of iodine was added in each run as a catalyst; the halide in ether was added over a 45-minute period, and stirring was used throughout.

With a few of the compounds (the bromotoluenes, β-bromostyrene, and α-bromonaphthalene) which react with magnesium rather sluggishly at first, a minor alteration in procedure was made. Instead of adding 25 cc. of ether to the magnesium before the addition of the halide, only about 3 cc. was run in and then about 2 cc. of the ether solution of halide. This mixture was warmed until the reaction set in, and then the remainder of the ether solution of halide was added over 45 minutes.

Duplicate runs were made on each compound, and from each run two samples were removed for analysis. The yields given in the following table are, therefore, average yields for at least 4 analyses. Because of the apparently unusual results observed with some of the compounds, repeated check determinations were made up to 12 and 16 analyses. The agreement in results was of the order already noted:[3] very few of the analyses varied from the average by more than 1%, and practically all were within 0.5% of the average.

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[2] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

[3] Gilman and Meyers, *ibid.*, **45**, 159 (1923).

TABLE I
RESULTS

Halide used	Av. % yield of corres. organomagn. hal.	Halide used	Av. % yield of corres. organomagn. hal.	Halide used	Av. % yield of corres. organomagn. hal.
n-Propyl iodide..	79.35	*n*-Butyl bromide...	91.23	*o*-Bromotoluene......	86.65
n-Butyl iodide...	65.23	*iso*-Butyl bromide..	78.23	*m*-Bromotoluene.....	84.75
n-Amyl iodide...	75.76	*sec*-Butyl bromide..	68.26	*p*-Bromotoluene.....	88.16
n-Hexyl iodide...	59.50	*tert*-Butyl bromide..	20.62	Benzyl chloride......	94.28
n-Heptyl iodide..	64.27	*n*-Butyl chloride...	87.38	α-Bromonaphthalene.	70.50
n-Octyl iodide...	44.22	Bromobenzene......	94.37	Bromocyclohexane...	68.32
Lauryl bromide..	73.70	Iodobenzene.......	84.58	β-Bromostyrene.....	47.59

With *n*-butyl iodide a first pair of duplicate runs gave an average percentage yield of 78.24. Because it was felt early in the work that the yield should have been nearer to those with *n*-butyl bromide and *n*-butyl chloride, a check determination was made on a more highly purified sample. This second pair of duplicate runs averaged more than 10% lower. This necessitated another determination, and to avoid any uncertainty a third and a fourth pair of duplicate runs were made. The second, third and fourth runs agreed quite closely and the average of these three runs (12 analyses) is that given, 65.23%. Although the percentage obtained in the first determination fits in admirably with the drop in yield with increasing length of carbon chain, it should be discarded.

In the cases of *n*-hexyl iodide, lauryl bromide and bromocyclohexane a pair of duplicate runs was made and the result for each is the average of 8 analyses.

n-Butyl chloride showed no evidence of a reaction with magnesium until after three hours of stirring. In sequence, each reaction mixture was stirred for 4 hours, then allowed to stand for 8 hours, and finally stirred for 4 hours.

The percentage listed for benzyl chloride is an average of a pair of duplicate runs. In another determination, where the benzyl chloride was used directly without special purification by drying and by distillation, the yield was 4% less.

All halides were purified at least by a combination of drying and distillation, with the exception of the butyl bromides, butyl chloride, and the bromotoluenes. These were used directly from small stock bottles, and were of the regular high grade quality to be had from American houses.

Discussion

The yields of organomagnesium halides prepared from normal alkyl iodides confirm in large part several observations to be found in the literature. It has long been known that the yield of Grignard reagent drops with the increasing length of the carbon chain, and that probably the concurrent Wurtz reaction becomes more prominent.

Two interruptions to an orderly decrease, however, are to be noted with *n*-butyl and *n*-hexyl iodides. Several check analyses with highly and freshly purified samples failed to alter appreciably the average percentages indicated. If an explanation for this apparent irregularity is sought in the phenomenon of alternating properties of even and odd numbered members of an homologous series, it must be remembered that the yield of ethylmagnesium iodide, determined scores of times, has always been considerably higher than that of *n*-propylmagnesium iodide.

The yields of the 4 butylmagnesium bromides indicate in a striking fashion that the increasing complexity of branching of an alkyl group runs parallel with a decrease in yield of the corresponding organomagnesium halides.

The three bromotoluenes show comparatively small differences.

A comparison of yields of several of the compounds reveals the desirability of using bromides instead of iodides where the bromides are not too volatile and where there is not too much difficulty in initiating a reaction with magnesium. First, *n*-butyl bromide gives a decidedly larger yield of the corresponding organomagnesium compound than does *n*-butyl iodide. Second, the yield of phenylmagnesium bromide is significantly larger than that of phenylmagnesium iodide. Third, it is quite obvious that if the regular decrease in yield with normal alkyl halides extends to the higher members of a series, the yield of laurylmagnesium bromide far exceeds what one might expect for laurylmagnesium iodide.

In this connection the yield of *n*-butylmagnesium chloride is noteworthy. It is considerably larger than that of *n*-butylmagnesium iodide and only slightly smaller than that of the corresponding bromide. There is a possibility that it might exceed the yield of bromide if the reaction with magnesium could be made to start more easily.[4] This point is to be tested in connection with some studies on the activation of reagents used in the preparation of organomagnesium compounds. There is undoubtedly a limiting factor here when one compares the halogen attached to like radicals, because work recently published[5] and studies now being carried on in this Laboratory point strongly to decidedly poor yields of organomagnesium fluorides, whenever it is possible to prepare them at all.

The yield of benzylmagnesium chloride is surprisingly high. For this reason it was checked and re-checked. The literature contains many references to the rather large quantity of dibenzyl formed by the usual Wurtz-Fittig reaction which apparently accompanies all preparations of the Grignard reagent. It is highly probable, therefore, that the conditions for an optimum yield of ethylmagnesium iodide which have been extended to the compounds mentioned in this study might, for the present, be advantageously used in the preparation of all Grignard reagents.

The yields of the last three compounds listed were determined because they are typical of some classes of substances frequently used in synthetic work.

Summary

The yields of a number of typical Grignard reagents have been determined, and attention has been directed to some apparent regular-

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[4] The observations on chlorides should be restricted to alkyl chlorides, for although it is possible to prepare phenylmagnesium chloride directly the reaction is unusually sluggish and the yield such as to make the preparation essentially without value.

[5] Swarts, *Bull. soc. chim. Belg.*, **30**, 306 (1921).

ities underlying the correlation of yield with the kind of organic halide used.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

THE FORMATION OF FREE RADICALS BY REDUCTION WITH VANADOUS CHLORIDE

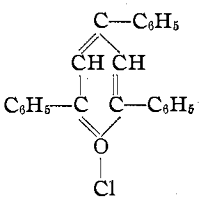
Preliminary Paper

BY J. B. CONANT AND A. W. SLOAN

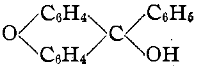
RECEIVED AUGUST 3, 1923

The addition of vanadous chloride to a solution of triphenylpyrylium chloride (I) causes the formation of a reddish precipitate which can be obtained in a fairly pure condition by filtering in an atmosphere of carbon dioxide. This colored, insoluble substance behaves like a free radical; a chloroform solution of it is bright red and the color disappears when the solution is shaken with air. The substance is reoxidized to the pyrylium salt by ferric chloride; if this process is carried out quantitatively in the absence of oxygen a maximum of one molecule of ferric chloride is required. Considerably less than this amount suffices to oxidize a precipitate which has stood for some hours even in an atmosphere of carbon dioxide; the compound is apparently unstable.

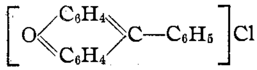
While these facts clearly indicated that we were dealing with a free radical, we desired to obtain still more positive evidence. We, therefore, investigated the reduction of the salts of phenylxanthenol (II) from the chloride of which Gomberg[1] obtained the free radical phenylxanthyl by the action of metals in benzene solution. Phenylxanthenol dissolves to a slight extent in concd. hydrochloric acid, producing an orange-colored solution. This solution presumably contains a chloride for which the oxonium formula (III) can be written. This salt is much more readily hydrolyzed than the pyrylium salt, so that it is necessary to work with concd. hydrochloric acid solutions. When such a solution of phenylxanthylium chloride is treated with vanadous chloride a brown precipitate



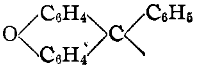
(I)



(II)



(III)



(IV)

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[1] Gomberg and Cone, *Ann.*, **370**, 154 (1909).