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Factors Determining the Course and Mechanism of Grignard Reactions. XIV. Replacement of Halogen Atoms of Aromatic Halides with Hydrogen Atoms by the Action of Grignard Reagents and Cobaltous Chloride

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It is well established that aliphatic and aromatic Grignard reagents do not react, even at elevated temperatures, with monohalogenated and dihalogenated aromatic compounds. However, an energetic reaction occurs when cobaltous chloride is added to such a reaction mixture. Thus, butylmagnesium bromide reacts with phenyl bromide in the presence of 5 mole per cent. of cobaltous chloride to yield the following compounds:

Compound	Yields in % of amount calculated
Benzene	44
Butane and butylene	83
Butylbenzene	3
Biphenyl	3
Polyphenyls	11[1]

In order to ascertain the scope and general utility of this reaction, a number of dihalogenated aromatic compounds and monohalogenated polycyclic compounds were treated with Grignard reagents in the presence of cobaltous chloride. The results obtained with the dihalogenated aromatic compounds are summarized in Table I; those obtained with the monohalogenated polycyclic derivatives, in Table II.

TABLE I

REACTION OF GRIGNARD REAGENTS WITH ORGANIC HALIDES IN THE PRESENCE OF COBALTOUS CHLORIDE[a]

Grignard reagent[b]	Aromatic halide	Reaction,[c] %	Products identified[d] in %	
C_6H_5MgBr	o-$C_6H_4Cl_2$	48	C_6H_5Cl	12
	m-$C_6H_4Cl_2$	53	C_6H_5Cl	29
	p-$C_6H_4Cl_2$	30	C_6H_5Cl	10
	m-$C_6H_4Br_2$	81	C_6H_5Br	40
	p-$C_6H_4Br_2$	84	C_6H_5Br	45
CH_3MgBr	p-$C_6H_4Br_2$[e]	63	C_6H_5Br	37
	2,2′-$(C_6H_4Br_2)_2$[f]	66	$(C_6H_5)_2$	60
	2,2′-$(C_6H_4Br_2)_2$[g]	48	$(C_6H_5)_2$	20
			o-$C_6H_5C_6H_4Br$	8
C_6H_5MgBr	o-$C_6H_4Cl_2$	26	C_6H_5Cl	6
	m-$C_6H_4Br_2$	65	C_6H_5Br	44
	p-$C_6H_4Br_2$	87	C_6H_5Br	55
	2,4-$CH_3OC_6H_3Br_2$[h]	62	Anisole	10
			o- and p-bromoanisole	40
	o-$CH_3C_6H_4Br$	59	$C_6H_5CH_3$	33

[a] Five mole per cent. of cobalt chloride calculated on the basis of the organic halide used. [b] Five per cent. excess of Grignard reagent used. [c] These values are calculated from the halide ion titration of the aqueous solution (*cf.* ref. 1). [d] In all cases, some unreacted material and residue of polymeric substances were obtained. [e] An excess (130%) of the Grignard reagent was used. [f] Halide added to tenfold excess of Grignard reagent and 50 mole per cent. of cobalt chloride. [g] Tenfold excess of Grignard reagent and 11 mole per cent. cobalt chloride used. [h] Excess (150%) of Grignard reagent used.

TABLE II

REACTION OF GRIGNARD REAGENTS WITH POLYCYCLIC AROMATIC HALIDES IN THE PRESENCE OF COBALTOUS CHLORIDE

Grignard reagent	Mole % $CoCl_2$	Aromatic halide	% Reaction by aqueous layer titration	Products identified, %
n-BuMgBr	0	p-Bromobiphenyl	0	Biphenyl (52)
n-BuMgBr	5		65	Bixenyl (1.3)
PhMgBr	0	p-Bromobiphenyl	11	
PhMgBr	5		70	Biphenyl (52)
n-BuMgBr	0	2-Bromonaphthalene	0	
n-BuMgBr	5		60	Naphthalene (44)
PhMgBr	0	2-Bromonaphthalene	1	
PhMgBr	5		70	Naphthalene (47) Biphenyl (57)
n-BuMgBr	0	1-Bromonaphthalene	17	
n-BuMgBr	5		76	Naphthalene (62)
n-BuMgBr	0	9-Bromophenanthrene	5	
n-BuMgBr	5		71	Phenanthrene (54)
PhMgBr	5		96	Phenanthrene (55) Biphenyl (73)
n-BuMgBr	0	9-Bromoanthracene	1	
n-BuMgBr	5		53	Anthracene (49)
n-BuMgBr	0	2-Bromofluorene	0	
n-BuMgBr	5		50	Fluorene (50)
n-BuMgBr	0	3-Bromoacenaphthene	0	
n-BuMgBr	5		47	Acenaphthene (54)

Discussion

The results summarized in Tables I and II indicate that, although Grignard reagents do not react with aromatic halides (monohalogenated and dihalogenated hydrocarbons), a reaction leading to the replacement of a halogen atom by a hydrogen atom takes place in the presence of cobaltous chloride. The wide applicability of this method is indicated by the variety of halogenated substances which react as indicated. Thus, bromobenzene, p-bromobiphenyl, 1- and 2-bromonaphthalenes, 9-bromophenanthrene, 9-bromoanthracene, 2-bromofluorene, and 3-bromoacenaphthene give the corresponding hydrocarbons when treated with Grignard reagents in the presence of cobaltous chloride. Furthermore, ortho-, para- and meta-dichloro- and dibromobenzenes, 2,2′-dibromobiphenyl and 2,4-dibromoanisole give the corresponding monohalogen derivatives, or, if an excess of Grignard reagent is used, the corresponding hydrocarbons. The yields (40–55%) reported in the tables are not necessarily those that could be obtained under optimum experi-

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[1] (a) Kharasch, Lewis and Reynolds, THIS JOURNAL, 65, 498 (1943); (b) Kharasch and Fields, *ibid.*, 63, 2316 (1941).

mental conditions; hence, no significance should be attached to slight variations in the figures recorded. However, the differences noted between dichloro- and dibromobenzenes are probably real; they indicate a greater resistance of the chloro compounds to reduction.

The replacement of the halogen atom by a hydrogen atom probably proceeds by a free radical chain mechanism in which the cobalt subhalide acts as the chain carrier.

R = Aliphatic radical; R′ = Aromatic radical

(a) $RMgX + CoCl_2 \longrightarrow RCoCl + MgXCl$
(b) $RCoCl \longrightarrow R\cdot + CoCl\cdot$
(c) $R'\cdot Br + CoCl\cdot \longrightarrow R'\cdot + CoClBr$
(d) $R'\cdot + C_2H_5OC_2H_5 \longrightarrow R'H$

The compounds formed from the aliphatic free radical R (produced in reaction b) and those formed from the ether molecule (reaction d) have already been discussed.[1a] Of interest, although fully expected, was the non-selective replacement of a halogen atom in 2,4-dibromoanisole by a hydrogen atom.

The dimerization of some aromatic radicals by the action of alkyl or aryl halides and cobaltous chloride on the Grignard reagents of these radicals has already been reported.[1b] It has now been found that *p*-biphenylmagnesium bromide,[2] and 9-phenanthrylmagnesium bromide, when treated with ethyl bromide and 5 mole per cent. of cobaltous chloride, give quantitative yields of bixenyl and biphenanthryl, respectively. These results taken in conjunction with those reported in Tables I and II substantiate a previous statement[1b] that the dimers of aromatic radicals are not formed in ether solution (or for that matter in other solvents) by the combination of the two free aromatic radicals; they are formed by some other mechanism which we hope to discuss in the near future. On the other hand, free radicals formed from weakly electronegative radicals do dimerize in ether solution.[3]

Experimental

Hydrocarbons.—The hydrocarbons used were purchased from the Eastman Kodak Company. They were purified by fractional distillation under reduced pressure and by crystallization from suitable solvents.

Bromohydrocarbons.—1-Bromonaphthalene and 2-bromonaphthalene were prepared in the usual manner. *p*-Bromobiphenyl was obtained from the Eastman Kodak Company. Phenanthrene dibromide was prepared by the procedure of Austin.[4] It was converted by heat into the 9-bromophenanthrene; this compound was purified first by distillation (b. p. 237-242° under 22 mm. pressure) and then by crystallization from ligroin (m. p. 63°). A similar procedure applied to anthracene yielded the 9-bromoanthracene (m. p. 100°). 2-Bromofluorene was prepared by the method of Clarkson and Gomberg.[5] 3-Bromoacenaphthene was prepared by the method of Compton and Walter.[6] 2,2′-Dibromobiphenyl was prepared according to the method of Schwechten.[7]

Reaction of Aryl Grignard Reagents with Ethyl Bromide in the Presence of Cobaltous Chloride; Preparation of Bixenyl and Biphenanthryl.—To 0.05 of a mole of the aryl Grignard reagent kept at 5°, five mole per cent. of cobaltous chloride was added. To this mixture, ethyl bromide (0.1 mole) dissolved in a small amount of ether, was slowly added in one and one-half to two hours. The reaction mixture was decomposed by ice and acidulated water (acetic acid), and then worked up in the usual way. Halide ion titrations of the water solution indicated 38% and 40% reactions, respectively. The yield of bixenyl (m. p. 302° after crystallization from nitrobenzene) calculated on the basis of the amount of Grignard reagent used was 60%. However, if this yield is corrected for the bixenyl (20%) present in the Grignard reagent, it is quantitative (40%). The yield of biphenanthryl (40%) was quantitative if calculated on the basis of the Grignard reagent that had reacted. The biphenanthryl thus obtained melted at 180° after crystallization from a mixture of chloroform and methanol.

Reaction of Grignard Reagents with Polycyclic Aromatic Halides in the Presence of Cobaltous Chloride (Table II).—The experimental technique was the same as described in previous papers.[1b] The cobaltous chloride (5 mole per cent.) was added to the Grignard reagent (0.05 mole) at low temperatures; then a solution of the organic halide (0.05 mole) in ether was added at a rate sufficient to maintain a gentle refluxing of the ether solution. The mixture was thoroughly agitated throughout the addition. After the addition was complete, the reaction mixture was refluxed for two hours on a water-bath; it was allowed to stand overnight, and was worked up in the usual way by pouring it onto ice, and extracting the mixture with ether. The aqueous layer was made up to 250 cc. volume; aliquot parts were withdrawn for halide ion titration. The ether solution was evaporated and worked up in the usual way. The results are recorded in Table II.

Reaction of Grignard Reagents with Dihalo Aromatic Compounds (Table I).—The Grignard reagents were prepared from ordinary magnesium turnings. In all cases, except where noted in Table I, the Grignard reagent was added to the halide in ether solution containing half of the total amount of the cobaltous chloride used in the experiment. After half of the Grignard reagent had been added, the other half of the cobalt chloride was added to the reaction mixture. Vigorous stirring and refluxing was maintained throughout the period of addition and for one hour thereafter. The reaction mixture was then treated in the usual manner; the products were separated by fractional distillation, or by crystallization from appropriate solvents.

Summary

1. In the presence of cobaltous chloride (5 mole per cent.), Grignard reagents reduce (a) dihalogenated aromatic compounds to the monohalogenated derivatives, (b) *o*-bromotoluene to toluene, (c) polycyclic aromatic halides to the corresponding hydrocarbons. In all cases some polymeric materials are obtained.

2. A mechanism for the replacement of the halogen atom by a hydrogen atom is suggested.

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[2] This reagent, as commonly prepared, contains about 20% bixenyl.

[3] For a fuller discussion, see Kharasch, Engelmann and Urry, THIS JOURNAL, **66**, 365 (1944).

[4] Austin, *Trans. Chem. Soc.*, **93**, 1763 (1908).

[5] Clarkson and Gomberg, THIS JOURNAL, **52**, 2886 (1930).

[6] Compton and Walter, *Trans. Chem. Soc.*, **101**, 958 (1912).

[7] Schwechten, *Ber.*, **65**, 1605 (1932).