[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

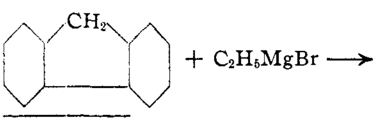
The Higher Benzenoid Hydrocarbons. Syntheses with the Aid of Metallo Derivatives[1]

BY HARRY F. MILLER AND G. BRYANT BACHMAN

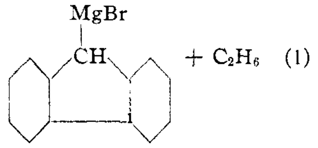
In recent years certain of the more complex hydrocarbons present in coal tar have been made available in commercial quantities. Because of the meager development of the fundamental chemistry of these substances, however, many of their simple mono-substituted derivatives are as yet unknown. For this reason it was decided to study one of the more important synthetic intermediates, the Grignard reagent, in regard to its usefulness for synthesis in this field. In the work reported, the preparations of the Grignard reagents of the most readily available bromo derivatives of anthracene, phenanthrene, fluorene and acenaphthene have been studied. We were successful in preparing and determining the yields of the Grignard reagents from 9-bromophenanthrene and from fluorene hydrocarbon. The general usefulness of these reagents has been tested by reaction with alkyl halides, acetyl chloride and ethyl orthoformate. Several new derivatives of fluorene and phenanthrene have been synthesized.[2]

The preparation of the lithium compounds corresponding to the Grignard reagents has also been undertaken in some cases and certain syntheses effected thereby which could not be carried out with the Grignard reagent. The 9-lithium derivative of fluorene was found to be a much more useful reagent than the corresponding Grignard reagent.

Some of the most interesting results were obtained with fluorene hydrocarbons. Courtot[3] has reported the preparation of 9-fluorylmagnesium bromide by means of the reaction

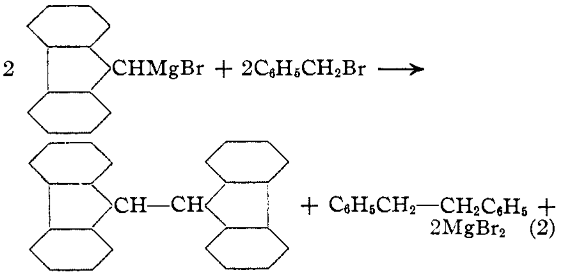


$+ C_2H_5MgBr \longrightarrow$



$+ C_2H_6$ (1)

We found it impossible to duplicate this preparation with good yields. Invariably about 65% of the original fluorene was recovered unchanged, and the amount of ethane evolved corresponded to only 32% reaction according to the above equation. Furthermore, the products of the reactions of fluorenylmagnesium bromide with other substances were always contaminated with large amounts of unchanged fluorene and in some cases were difficult to purify. This difficulty could be overcome in part through the fact that fluorylmagnesium bromide is insoluble in cold xylene. This enabled us to separate it from unchanged fluorene and ethylmagnesium bromide and to carry out reactions with it successfully. These reactions did not always proceed in the expected manner. For example butyl bromide did not react even on long continued boiling. Benzyl bromide on the other hand reacted as follows



(2)

This result is interesting because it represents a double coupling reaction.[4] No trace of benzylfluorene was found. With acetyl chloride reaction was normal, and 9-acetylfluorene resulted in good yields. Ethyl orthoformate appeared to react normally, but from the reaction mixture only a polymerized amorphous solid with no definite melting point could be isolated.

Much simpler in its preparation and more normal in its behavior is 9-fluoryllithium.[5] An improved method of preparing this substance has been used. With the aid of this reagent and alkyl

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[1] Read before the Organic Section of the American Chemical Society at the Cleveland Meeting in September, 1934.

[2] When this work was about completed a very interesting paper by W. E. Bachmann appeared [THIS JOURNAL, **56**, 1363 (1934)], which contained the results of a study of 9-phenanthrylmagnesium bromide. Fortunately there was but little overlapping of his experimental work with ours. We concur with this author in every respect, including the wide applicability and usefulness of this reagent.

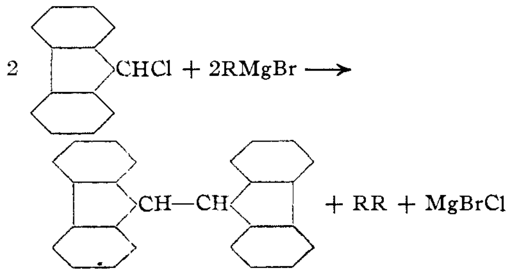
[3] Courtot, *Ann. chim.*, [9] **4**, 84 (1915). It is significant perhaps that in a later résumé of fluorene chemistry, *ibid.*, [10] **14**, 141 (1930), Courtot fails to discuss the usefulness of fluorenylmagnesium bromide as a synthetic reagent.

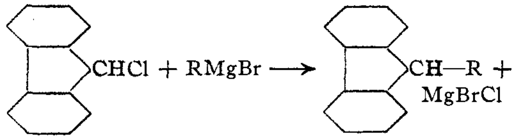
[4] *Cf.* Fuson, THIS JOURNAL, **48**, 830, 2681 (1926); **55**, 720 (1933).

[5] Schlenk and Bergmann, *Ann.*, **465**, 188 (1928).

bromides or chlorides fluorene homologs were prepared in good yields. Acetyl chloride also reacted normally to give 9-acetylfluorene.

The value of 9-chlorofluorene for synthetic purposes was likewise investigated. With this reagent two types of reactions with alkyl magnesium halides were found to occur.


(3)


(4)

At first we were able to observe only the occurrence of reaction (3). With phenyl, *n*-amyl, *n*-butyl and cyclohexyl magnesium bromides the principal product containing the fluorene nucleus was bisdiphenylenethane. On one occasion, however, the reaction of cyclohexylmagnesium bromide with 9-chlorofluorene was carried out in benzene solution with the ether removed. In this case a 25% yield of a new compound, cyclohexylfluorene, resulted. These results may be explained if it is assumed (a) that RMgX compounds tend to react normally with alkyl halides while R_2Mg tends to produce coupling, and (b) that various solvents influence the equilibrium

$$2RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (5)$$

probably on the basis of relative solubilities. Evidently benzene favors the formation of RMgX, which reacts normally with 9-chlorofluorene to give substituted alkyl fluorenes. The R_2Mg present to the greater extent in the ether solution is responsible for the coupling which occurs in that solvent. Bert[6] and others have already pointed out the effect of different solvents on the yields of normal substitution products. Schlenk[7] has shown that RMgX is less soluble than R_2Mg in benzene. This factor may be responsible for shifting the equilibrium in (5) to the left.

It seemed desirable to test our theory of this reaction by treating 9-chlorofluorene in ether solution with a Grignard reagent which is known to exist predominantly in the form RMgX. In such a case coupling should occur to a limited extent only, and the principal reaction should correspond to (4). The Grignard reagent from ethyl iodide has been shown by Johnson and Adkins[8] to contain only 4.2–9.6% of diethylmagnesium in ether solution under normal conditions. When this reagent was treated with 9-chlorofluorene, we were able to isolate 9-ethylfluorene in 65% yields. Coupling occurred only to the extent of about 20%. Our investigation of the effect of solvents on the equilibrium (5) is being continued.

The patent literature states that fluorene will react with metallic sodium, sodium amide or sodium hydroxide at high temperatures and under pressure. Evidently an autoclave is necessary, for no appreciable reaction seems to occur when fluorene and sodium metal or sodium amide are heated together in boiling xylene over considerable periods of time.

Very little success attended the attempts to prepare metallo-organic derivatives from 9-bromoanthracene, 2-bromofluorene, and 3-bromoacenaphthene. The first of these did not react appreciably with magnesium and ether even in sealed tubes at 200°. The second and third did not react with activated magnesium or lithium in either ether or boiling xylene. The preparation of 2-acenaphthylmagnesium bromide has been reported,[9] but we were unable to repeat this work although many attempts using magnesium activated in several different ways were made. An effort to form a Grignard reagent from 9,10-dihydroanthracene by reaction with ethylmagnesium bromide was likewise unsuccessful although there is a close formal relationship of this hydrocarbon to fluorene. The 9,10-dihydroanthracene was synthesized in excellent yields by the reduction of anthracene with sodium in liquid ammonia.

Experimental

Hydrocarbons.—Except for a part of the phenanthrene,[10] all of the hydrocarbons were purchased from the Eastman Kodak Company. They were purified by fractional distillation under diminished pressure and repeated recrystallization from suitable solvents. For purposes of distillation under diminished pressure a simple piece of apparatus (shown diagrammatically in the figure) was constructed from two 2-liter flasks. This was especially

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[6] Bert, *Compt. rend.*, **186**, 587 (1928).

[7] W. Schlenk, Jr., *Ber.*, **64**, 734, 739 (1931).

[8] Johnson and Adkins, THIS JOURNAL, **54**, 1943 (1932).

[9] Grignard, Bellet and Courtot, *Ann. chim.*, [9] **4**, 52 (1915).

[10] The authors are indebted to the Republic Creosoting Company of Indianapolis for a generous sample of phenanthrene.

convenient in the distillation of anthracene, which tends to clog the delivery tube of an ordinary distilling flask because of its high melting point. The carbazole present as an impurity in the anthracene was effectively removed by distilling in the presence of sodium or potassium hydroxide or a mixture of both.[11] Subsequent and repeated recrystallization from benzene yielded a pure product, m. p. 216.5°. Phenanthrene was purified by the method of Cohen and Cormier,[12] except that the distillation following the treatment with nitric acid was carried out under diminished pressure. The danger of explosion was thereby eliminated and the yields somewhat improved. Fluorene and acenaphthene were distilled and then recrystallized from 95% alcohol. In the case of acenaphthene it was found advantageous not to cool the solution below 35° before filtering. If this is done the isomeric ethyl naphthalenes do not precipitate. The ability to form large crystals does not indicate high purity in acenaphthene. In some cases crystals 3–5 cm. long were obtained which melted several degrees too low.

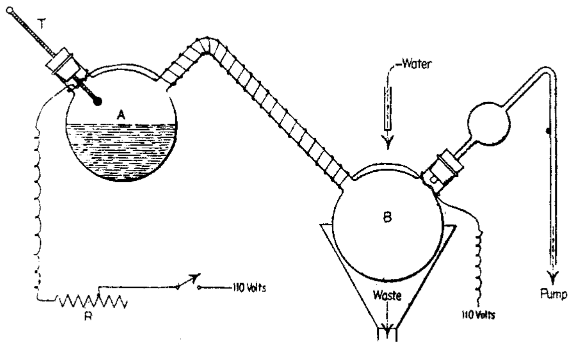

Fig. 1.

Dihydroanthracene.—Anthracene (17.8 g.) was suspended in liquid ammonia (200 cc.) and clean metallic sodium (4.6 g.) was added in small pieces with vigorous stirring during the course of half an hour. The liquid became dirty green and then almost black at first, but finally assumed a reddish-brown color. After standing another half an hour the mixture was neutralized with solid ammonium nitrate and allowed to evaporate. The residue was extracted with water and then boiled with 200 cc. of 75% alcohol. A little anthracene remained undissolved. The alcoholic solution deposited pure dihydroanthracene, m. p. 104–105°, on cooling; yield 13.5 g. (76%).

Bromohydrocarbons.—Phenanthrene dibromide was prepared by the procedure of Austin[13] and converted by heating into 9-bromophenanthrene. This was purified by distillation, b. p. 238–241° (22 mm.), 360° (760 mm.), and recrystallization from alcohol, m. p. 63°; yield 50%. A similar procedure starting with anthracene yielded 9-bromoanthracene, m. p. 100°, in 55% yields. 2-Bromofluorene, m. p. 110°, was prepared in 85% yields as directed by Clarkson and Gomberg.[14] The procedure of Crompton and Walker[15] gave a 40% yield of 3-bromoacenaphthene, b. p. 204–209° (30 mm.), 327–332° (760 mm.) and m. p. 52°.

The Grignard Reagents.—Magnesium in ether suspension reacts readily with 9-bromo-phenanthrene to form the Grignard reagent in 92–93% yields.[16] In order to keep the compound in solution it is advisable to add benzene or xylene after the reaction is well started. The addition of xylene at the first, however, may hinder the starting of the reaction. The chemiluminescence which results from the oxidation of phenanthrene Grignard reagent is readily observable if air is admitted to the reaction flask.

9-Fluorylmagnesium bromide was prepared by the reaction of fluorene hydrocarbon with ethylmagnesium bromide in boiling xylene. The ethane which formed was collected in order to measure the yield of Grignard reagent produced. Table II shows the results obtained.

These results were checked fairly closely by recovering the unreacted fluorene in the following manner. Most of the xylene was distilled from the reaction mixture and ether was added. The fluorylmagnesium bromide alone remained undissolved. The ether was removed with the aid of a pipet and a second quantity of ether added to the fluorylmagnesium bromide to wash it. The two ether solutions were combined, shaken with water and dilute acid and then evaporated. The fluorene remained in a crystalline condition and amounted to 65% of the total used. All of the yields given in Table I were calculated on the basis of a 32% yield of Grignard reagent.

9-Fluoryllithium.—This compound is readily prepared in about 80% yields by the reaction[17] of butyllithium or of methyllithium with fluorene in boiling xylene. The reaction is complete within eighteen hours. Air must be excluded rigorously from the reaction flask to prevent oxidation of the lithium hydrocarbon. The product forms a reddish-yellow colored precipitate insoluble in cold xylene.

Reactions of 9-Phenanthrylmagnesium Bromide

(a) **With Alkyl Halides.**—These reactions were carried out in a 50-50 ether-benzene solution. To the Grignard reagent from 0.1 mole of 9-bromophenanthrene was added 0.11 mole of the desired alkyl halide. The mixture was then refluxed for three hours, at the end of which time a voluminous precipitate of magnesium bromide had formed and the reaction was complete. Water and a few drops of dilute acid were added and the upper layer separated, dried and distilled.

9-Propylphenanthrene, b. p. 265–270° (22 mm.), was obtained crystalline only with difficulty. A solution in alcohol was prepared which was saturated at room temperatures. This deposited fine white plates on standing in the ice chest. Further evaporation and cooling gave more crystals. 9-Propylphenanthrene readily forms a stable picrate (yellow needles) in alcoholic solution.

9-Butylphenanthrene, b. p. 282–284° (20 mm.), may be obtained readily as fine white plates when recrystallized from hot alcohol. Its picrate resembles the picrate of 9-propylphenanthrene.

(b) **With Acetyl Chloride.**—To 0.5 mole of acetyl chloride in 50 cc. of dry benzene at 0° was added a cold

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(11) J. M. Clark, *J. Ind. Eng. Chem.*, **11**, 204 (1919).

(12) Cohen and Cormier, THIS JOURNAL, **52**, 4364 (1930).

(13) Austin, *Trans. Chem. Soc.*, 1763 (1908).

(14) Clarkson and Gomberg, THIS JOURNAL, **52**, 2886 (1930).

(15) Crompton and Walker, *Trans. Chem. Soc.*, 958 (1912).

(16) The titration method of Gilman, THIS JOURNAL, **45**, 150 (1923), was used to determine the yields.

(17) Gilman, *ibid.*, **55**, 1252 (1933).

TABLE I

DERIVATIVES OF PHENANTHRENE AND FLUORENE

Grignard reagent	Reactant	Reaction solvent	Products	M. p., °C.	Yield, %	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
9-Phenanthryl MgBr	*n*-PrBr	Et_2O-Bz	9-*n*-Propylphenanthrene	74	47.	92.62	92.51	7.38	7.49
			Picrate	134					
	n-BuBr	Et_2O-Bz	9-*n*-Butylphenanthrene	58	52	92.30	92.18	7.70	7.62
			Picrate	99.5					
	AcOCl	Et_2O-Bz	9-Acetylphenanthrene[a]	73–74	27				
			Picrate	107					
			Oxime	154–155					
	Et orthoformate	Et_2O-Bz	Phenanthrene-9-aldehyde[b]	99–100	46				
			Acetal	79–80		81.38	81.29	7.19	7.10
			Oxime	156–157					
9-Fluoryl MgBr	*n*-PrBr	Xylene	No reaction						
	n-BuBr	Xylene	No reaction						
	BzBr	Xylene	Bibenzyl	52	53				
			Bisdiphenylenethane	244–245	85				
	AcOCl	Xylene	9-Acetylfluorene[c]	107	50				
			Oxime	167		86.54	86.46	5.77	5.83
	Et orthoformate	Xylene	Amorphous polymer						
9-Fluoryl lithium	*n*-BuBr	Xylene	9-*n*-Butylfluorene	101	41	91.89	91.75	8.11	8.27
	AcOCl	Xylene	9-Acetylfluorene	107	60				
	Et orthoformate	Bz	Amorphous polymer						
Phenyl MgBr	9-Chlorofluorene	Et_2O or Bz	Bisdiphenylenethane	244–245	High				
n-Amyl MgBr		Et_2O or Bz		244–245	95				
n-Butyl MgBr	9-Chlorofluorene	Et_2O or Bz	Bisdiphenylenethane	244–245	95				
Cyclohexyl		Et_2O		244–245	93				
MgBr	9-Chlorofluorene	Bz	Bisdiphenylenethane	244–245	70				
			9-Cyclohexylfluorene	102–103	25	94.17	93.95	5.83	5.87
Ethyl MgI		Et_2O	Bisdiphenylenethane	244–245	20				
			9-Ethylfluorene[d]	106–107	65				

[a] Mosettig and van de Kamp, THIS JOURNAL, **55**, 3445 (1933), obtained this ketone by the acetoacetic ester synthesis. [b] Mosettig and van de Kamp, *ibid.*, **55**, 2995 (1933), and Shoppee, *J. Chem. Soc.*, 27 (1933), prepared this aldehyde from the corresponding acid. [c] Dziewoński and Schnayder, *Bull. intern. acad. polonaise, A*, 529–535 (1930), or *C. A.*, **25**, 5416 (1931), prepared this ketone by the Friedel–Crafts reaction. [d] Wislicenus *et al.*, *Ber.*, **26**, 2579 (1893); **35**, 759 (1902); **46**, 2772 (1913).

TABLE II

Mole of EtMgBr	0.42	0.63	0.63
Mole of fluorene	.03	.05	.05
Hours of heating	12	18	66
Gas vol., cc. S. T. P.	201	345	364
Yield, %	30	30.8	32.5

solution containing 0.11 mole of 9-phenanthrylmagnesium bromide in 75 cc. ether and 75 cc. benzene. The mixture was stirred vigorously for half an hour and allowed to warm up slowly to room temperature. It was then refluxed for two hours. The gelatinous mass was decomposed with ice and ammonium acetate solution and filtered. The benzene–ether layer was treated twice with Norite and evaporated. The solid (8.5 g.) was washed with petroleum ether and recrystallized from methanol to obtain the pure ketone. The picrate was formed readily in alcoholic solution.

(c) **With Ethyl Orthoformate.**—To a solution of 0.15 mole of the Grignard reagent in 75 cc. of ether and 75 cc. of benzene was added 0.15 mole of ethyl orthoformate. The solution was refluxed for six hours, the ether removed, and the remaining solution refluxed for another hour. On decomposing with ice and ammonium acetate solution a dark colored oil was obtained. This was slowly hydrolyzed by boiling with 25% sulfuric acid for twelve hours. The product was converted into its bisulfite compound by long shaking with a saturated aqueous solution of sodium bisulfite. It was then washed with benzene, decomposed with sodium bicarbonate and recrystallized from ethanol. In another experiment the original oil obtained from the reaction was dissolved in benzene and treated with petroleum ether. This precipitated the acetal.

Reactions of 9-Fluorylmagnesium Bromide

(a) **With Benzyl Bromide.**—A Grignard reagent was prepared from 0.19 mole of ethyl bromide in the usual manner. The ether was replaced by 80 cc. of dry xylene and 25 g. (0.15 mole) of fluorene added. After boiling for twelve hours the mixture was cooled and allowed to settle. The clear upper layer, containing considerable unreacted fluorene and ethylmagnesium bromide, was removed as completely as possible with the aid of a pipet. Cold dry xylene (80 cc.) was now added with stirring and as soon as the Grignard reagent had settled the upper layer was again removed. Thirty grams of benzyl bromide in 50 cc. of dry xylene was then added and the mixture refluxed for five hours. It was then cooled, decomposed with ice and dilute hydrochloric acid and steam distilled. The xylene, the excess benzyl bromide and probably some propylbenzene were thereby removed. The oil that remained was extracted with benzene and gave, on evaporation, a solid covered by an oil. The solid was separated mechanically and the oil washed off with cold methyl alcohol.

The solid, after recrystallization from benzene, was found to consist of bisdiphenylenethane. The oily portion was distilled and found to boil at 275–280° at 746 mm. It was thought to be bibenzyl which boils at 284° at 760 mm. Bibenzyl, however, is a solid melting at 52°. The oil, therefore, was nitrated in glacial acetic acid with fuming nitric acid to obtain a suitable derivative. A yellow solid settled out after fifteen minutes which proved to be 2,7-dinitrofluorene (0.5 g.) melting at 266–268°.

The acid solution was poured into cold water, stirred well, and the solid which precipitated filtered and dried. After recrystallizing from 80% acetic acid the material melted at 176–178°. Pure *p*,*p*′-dinitrobibenzyl melts at 179–180°. The solid weighed 3.6 g., which corresponds to a 53% yield of bibenzyl. In order to characterize the substance further, a portion was oxidized by potassium permanganate in a water–acetone mixture. The solution was filtered hot, made alkaline and heated on the water-bath to remove acetone. After cooling and acidifying, a crystalline substance melting at 233–235° was obtained. Pure *p*-nitrobenzoic acid melts at 238°.

9-Benzylfluorene has been described by Thiele and Henle[18] as a solid, m. p. 130–131°, giving a characteristic violet solution with concentrated sulfuric acid and benzaldehyde. Neither the compound nor the color reaction could be obtained from the above Grignard reaction mixture.

(b) **With *n*-Propyl and *n*-Butyl Bromide.**—With these halides no reaction whatever occurred even after boiling in xylene solution for twelve hours. The fluorene was recovered quantitatively.

(c) **With Acetyl Chloride.**—In this case the Grignard reagent was prepared as described above but the excess fluorene was not removed from the solution. The reaction was carried out in the manner described for 9-acetylphenanthrene. The product after several recrystallizations from alcohol was obtained as white needles. It readily formed an oxime.

(d) **With Ethyl Orthoformate.**—No success attended the efforts to prepare fluorene-9-aldehyde by means of the reaction between ethyl orthoformate and 9-fluorylmagnesium bromide. It has been stated that the aldehyde is unstable and changes rapidly into a polymer.[19] In our work two products were formed. The first was obtained in a yield of 40% as a white crystalline solid, m. p. 255°, soluble in benzene but insoluble in alcohol. It was not an aldehyde nor was it bidiphenylenephenanthrone (m. p. 258°) since it gave a lowered melting point when mixed with an authentic sample of that material. The second product was an amorphous solid (13% yield) which became dark brown in the air and melted at 198–200°. Supposing it to be the aldehyde acetal we treated it with acetic anhydride for the purpose of converting it into the stable aldehyde acetate. However, the product of this treatment was the same as the product m. p. 255°. Work on the identification of this substance is being continued.

Reactions of 9-Fluoryllithium

(a) **With *n*-Butyl Bromide.**—To a xylene solution of 9-fluoryllithium prepared from 0.14 mole of lithium was added 0.14 mole of *n*-butyl bromide. The mixture was refluxed for three hours, cooled and decomposed with water and dilute acid. The xylene layer was distilled under diminished pressure and yielded a white mass of crystalline 9-*n*-butylfluorene of b. p. 192–195° (33 mm.). Recrystallization from alcohol yielded shiny white plates of the pure substance.

(b) **With Acetyl Chloride.**—The reaction in this case paralleled the previously described reaction of acetyl chloride with 9-fluorylmagnesium bromide, except that a better yield was obtained.

(c) **With Ethyl Orthoformate.**—Here again no aldehyde could be isolated. The solid of m. p. 255° was not observed to appear.

Reactions of 9-Chlorofluorene.—The 9-chlorofluorene was prepared by the method of Schlenk and Bergmann[20] from 9-hydroxyfluorene. The latter substance resulted in 95% yields from the reduction of fluorenone with zinc dust in alcohol and concd. ammonium hydroxide solution. This method gives much better yields than other methods of reduction heretofore proposed.

(a) **With *n*-Butylmagnesium Bromide.**—To a Grignard reagent prepared from 0.1 mole of *n*-butyl bromide in ether solution was added 0.04 mole of 9-chlorofluorene. After refluxing for three hours the liquid had an orange-red color (probably due to traces of bisdiphenylenethylene) and a heavy white precipitate had separated. The reaction mixture was treated with water and dilute acid, but a considerable part of the solid remained undissolved. This was separated by filtration and recrystallized from benzene. It proved to be bisdiphenylenethane and gave a mixed melting point with an authentic sample of this substance of 244–245°.

The reactions of *n*-amyl, phenyl and cyclohexyl magnesium bromides in ether solution paralleled the above reaction and yielded the same product. In benzene solution all except cyclohexylmagnesium bromide gave practically quantitative yields of bisdiphenylenethane.

(b) **With Cyclohexylmagnesium Bromide in Benzene Solution.**—To a Grignard reagent prepared from 0.12 mole of cyclohexyl bromide in ether solution was added 100 cc. of dry benzene. The ether was removed by distillation and 0.06 mole of 9-chlorofluorene introduced. After refluxing for three hours and decomposing with water and acid a benzene layer was obtained which upon evaporation yielded a solid covered with an oil. The oil was dissolved from the crystals with methanol. It was obtained crystalline by distillation at reduced pressures and subsequent recrystallization. 9-Cyclohexylfluorene crystallizes in long white needles from ethanol. It shows an

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(18) Thiele and Henle, *Ann.*, **347**, 290 (1906).

(19) Wislicenus and Waldmüller, *Ber.*, **42**, 785 (1909).

(20) Schlenk and Bergmann, *Ann.*, **463**, 192 (1928).

apparent molecular weight of 239 in camphor (microdetermination); calculated 236.

The crystals remaining undissolved in methanol proved to be bisdiphenylenethane.

(c) **With Ethylmagnesium Iodide in Ether.**—Ethyl iodide (0.16 mole) was converted into the Grignard reagent in ether (100 cc.) and 9-chlorofluorene (0.08 mole) was added to the solution. Rapid reaction occurred immediately and the solution became very thick like honey. A fine white precipitate settled out. This did not increase in bulk after one hour of refluxing. Water and ice and dilute acid were added and the mixture filtered. Bisdiphenylenethane remained on the filter paper practically pure. The ether solution was dried and distilled. A light yellow oil of b. p. 160–165° (10 mm.), which soon crystallized, was obtained. It was further purified by steam distillation and recrystallization from ethanol. 9-Ethylfluorene crystallizes from solvents only with difficulty even when pure, which may account for its having been reported originally as an oil.

Summary

1. Applications of the Grignard reaction to the synthesis of anthracene, dihydroanthracene, acenaphthene, fluorene and phenanthrene derivatives have been studied. A number of new derivatives of fluorene and phenanthrene have been prepared.

2. It is believed that various solvents affect the equilibrium $2RMgX \rightleftharpoons R_2Mg + MgX_2$ and therefore influence the relative amounts of RMgX and R_2Mg present. It is proposed that R_2Mg tends to react with alkyl halides to give coupling while RMgX tends to give normal reaction. Evidence in support of these hypotheses has been presented.

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NOTES

The Partition of Tri- and Tetramethylglucoses between Chloroform and Water

By JAMES Y. MACDONALD

It has long been the practice in this Laboratory to separate tri- from tetra-substituted methylglucoses by extracting the aqueous solution of the mixture with chloroform, whereby the bulk of the tetramethylglucoses are removed while the trimethylglucoses remain in the aqueous layer. This procedure has been criticized by Haworth [Carrington, Haworth and Hirst, THIS JOURNAL, **55**, 1084 (1933)] on the ground that the trimethylglucose has a partition coefficient between the two solvents, and that a certain quantity must be carried over along with the tetramethylglucose. It is clear, however, that the possibility of a complete separation of the two types depends on the difference between their partition coefficients, and not on the value of one of them; and that wherever the difference is at all marked, a separation to any desired degree of sharpness may be obtained.

An investigation has been carried out to test the validity of this conclusion, and to find the optimum conditions for carrying out the separation.

The partition coefficients of purified specimens of the following sugars have been determined: 2,3-dimethyl-α-methylglucoside, 2,3,6-trimethylglucose, 2,3,4-trimethyl-β-methylglucoside, and 2,3,4,6-tetramethylglucose; and in addition, a mixture of the two glucosides mentioned above was separated to a purity of 97.4% with a total loss of 2.5% of the combined sugars, by a method which is recommended as a standard procedure.

The table summarizes the results of twelve experiments. The concentrations were estimated either by measuring the rotation, or by evaporating the solution and weighing the residue. Where both methods were employed, concordant results were obtained.

Substance	Orig. concn., %	Expts.	Part. coeff.	% extracted
Dimethylmethylglucoside	9.18	4	0.0366	3.5
Dimethylmethylglucoside	8.03	1	.0341	3.3
Dimethylmethylglucoside	2.75	2	.0307	3.0
Trimethylglucose	3.0	1	.012	1.3
Trimethylmethylglucoside	0.47	2	3.51	78.0
Tetramethylglucose	5.13	2	1.60	62.0

The final column gives the amount extracted by an equal volume of chloroform in one operation.

It will be noticed that the value of the coefficient for the dimethylmethylglucoside shows a definite drift, which is well outside the limits of experimental error. This is in accordance with phase-rule experience. The average value is 0.034, which is in agreement with that obtained from the data of Waine [Carrington, Haworth and Hirst, *loc. cit.*], whose two experiments give the figures 0.042 and 0.036 for a 4% solution. They also show that if Waine succeeded in extracting 85% of the sugar in eight operations, he must have used 6 liters of chloroform on 100 cc. of his solu-