apparent molecular weight of 239 in camphor (micro-determination); 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.

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-

tion, a quantity sufficient to dissolve more than half the water originally present.

Separation of 2,3-Dimethyl-α-methylglucoside and 2,3,4-Trimethyl-β-methylglucoside.

—A solution was made up containing 1.330 g. of dimethylmethylglucoside and 1.058 g. of trimethylmethylglucoside in 100 cc. of water; 50 cc. of this was extracted five times, using 50 cc. of chloroform for each extraction, and the combined chloroform extracts were washed with 50 cc. of water. The two solutions were evaporated, the residues weighed, made up to 20 cc. with water and their rotations measured. From the "apparent molecular rotation" thus found, the composition of each extract was calculated, and thus the yield of each sugar.

The table shows the results of this first extraction. The "theoretical" values are those calculated from the partition coefficients recorded above.

			Dimethyl-methyl-glucoside	Trimethyl-methyl-glucoside
Init. compn.	Cpd.			
	Grams		1.330	1.058
	%		55.7	44.3
Extracted H₂O soln.	Yield	Calcd., g.	1.120	0.0005
		Found, g.	1.100	.022
	Purity	Calcd., %	99.9	....
		Found, %	98.2	....
Washed CHCl₃ extr.	Yield	Calcd., g.	0.032	0.999
		Found, g.	.023	.928
	Purity	Calcd., %	...	97.5
		Found, %	...	97.6

The water used to wash the chloroform extract contained about 15% of the original sugars. This was extracted and the extract washed exactly as the original solution was treated. When the two aqueous solutions and the two chloroform solutions have been combined, the final result is:

Compound		Dimethyl-methylglucose	Trimethyl-methylglucose
Purity, %	Calcd.	99.9	97.4
	Found	98.3	97.4
Yield, %	Calcd.	95.5	99.6
	Found	97.4	97.6

The final wash water, which should contain only 1% of the original sugars (0.55% found), may be rejected.

It should be noted that the scheme here followed was devised partly because it approximated to that which has been usual in these Laboratories and partly because it was expected to give reasonable yields of both sugars in a fairly pure state,

without undue expenditure of time. But it is obvious that in special cases it may be modified to produce even greater purity of one component at the expense of the yield, without increasing the time spent on the process, or to obtain any desired degree of separation by the expenditure of sufficient labor. The results substantially confirm the effectiveness of the methods used here to separate mixtures of methylated sugars, and thereby to determine their relative proportions, and add weight to the arguments of Irvine and Stiller [This Journal, **54,** 1486 (1932)] in discussing the methylation of sucrose.

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Electrolytic Reduction of Imido Ethers

By Henry Wenker[1]

It has been shown that the reduction of imido ethers in acid solution with sodium amalgam yields aldehydes.[2] When, however, this class of compounds are subjected to electrolytic reduction, it was found that primary amines are formed. Since imido ethers, in form of their hydrochlorides, are available in quantitative yield from nitriles,[3] the method offers an alternative way for the reduction of nitriles to primary amines.

Experimental

The reduction is carried out at 0°, in the usual manner using lead electrodes, 2 N aqueous sulfuric acid and the hydrochlorides of the imido ethers. Six typical reductions gave the following yields: benzylamine, 76%; 3-tolubenzylamine, 70%; 4-tolubenzylamine, 94%; ethylamine, 16%; phenylethylamine, 14%; 4-ethoxybenzylamine, 66%.

4-Ethoxybenzylamine.—Since this compound has not been described hitherto, its picrate and hydrochloride were prepared and the latter analyzed. The picrate (from water) melts at 191° and the hydrochloride (from ethanol) melts at 234°.

Anal. Calcd. for $C_9H_{14}ONCl$: Cl, 18.9. Found: Cl, 18.9.

Elizabeth, N. J.   Received December 13, 1934

(1) Abstracted from Doctoral Dissertation, "Die Elektrolytische Reduction der Imidoaether. der Nitrostyrole und des β-Oxypyridins." Freiburg, Germany, 1920.

(2) Henle, *Ber.,* **35,** 3039 (1902).

(3) Pinner, *ibid.,* **16,** 353 (1883).