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.

COLUMBUS, OHIO RECEIVED MARCH 1, 1935

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 solution, 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.

Init. compn.	Cpd.		Dimethylmethylglucoside	Trimethylmethylglucoside
	Grams		1.330	1.058
	%		55.7	44.3
Extracted H_2O soln.	Yield	Calcd., g.	1.120	0.0005
		Found, g.	1.100	.022
	Purity	Calcd., %	99.9	....
		Found, %	98.2	....
Washed $CHCl_3$ 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		Dimethylmethylglucose	Trimethylmethylglucose
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.

UNITED COLLEGE OF ST. SALVATOR AND ST. LEONARD
UNIVERSITY OF ST. ANDREWS
SCOTLAND
RECEIVED OCTOBER 6, 1934

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

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[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).

The Preparation of Certain Nitrogen-Substituted Sulfon-*m*-toluidides and Sulfon-*p*-toluidides

By George H. Young

This paper is a continuation of an investigation of N-alkyl-*p*-toluene sulfonanilides.[1] Yields of 80–98% of *m*-sulfontoluidides and 60–91% of *p*-isomers were obtained. Recrystallized from methanol (the ethyl *m*-toluidide from 5:1 ethanol–ether), these compounds deposit as blunt needles or thick prisms. They are insoluble in water, difficultly soluble in ether and soluble in most other common solvents, with the meta derivatives usually having the greater solubility.

Table I

The Sulfon-*m*-toluidides

p-Toluene sulfon-*m*-toluidide	Formula	M. p., °C.	Sulfur analyses, % Calcd.	Found
N-Methyl	$C_{15}H_{17}O_2NS$	63	11.64	11.61
Ethyl	$C_{16}H_{19}O_2NS$	60.5–61	11.07	11.08
n-Propyl	$C_{17}H_{21}O_2NS$	51	10.56	10.71
Isoamyl	$C_{19}H_{25}O_2NS$	76.5	9.55	9.61

Table II

The Sulfon-*p*-toluidides

p-Toluene sulfon-*p*-toluidide	Formula	M. p., °C.	Sulfur analyses, % Calcd.	Found
N-Isopropyl	$C_{17}H_{21}O_2NS$	107	10.56	10.76
Isobutyl	$C_{18}H_{23}O_2NS$	73	10.09	10.04
n-Amyl	$C_{19}H_{25}O_2NS$	59.5–60	9.55	9.70
Isoamyl	$C_{19}H_{25}O_2NS$	89.5–90	9.55	9.43

The writer gratefully acknowledges the advice and assistance of the late Dr. W. J. Keith, who suggested this research.

[1] Young, This Journal, **56**, 2167, 2783 (1934).

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Received January 28, 1935

Preparation of 5-Keto-gluconic Acid by Bromine Oxidation

By Elmer W. Cook and Randolph T. Major

In the oxidation of glucose with bromine generated electrolytically according to the Isbell[1] method it was noticed that a reducing substance remained even after electrolysis had been continued longer than was necessary theoretically to convert the glucose to gluconic acid.

Sheppard and others[2] have observed likewise the presence of a reducing substance during the oxidation of glucose or gluconic acid with bromine.

This reducing substance has been isolated and proved to be the 5-keto-gluconic acid first described by Boutroux.[3]

Experimental

The oxidation of glucose was carried out as described by Isbell. The electrolyte consisted of 7 g. of glucose, 5 g. of calcium carbonate, and 5 g. of calcium bromide in 140 cc. of water. Electrodes of platinum were used. The electrolysis was continued for four ampere hours at a current density of 2.5 amperes per sq. dm.

At the end of the electrolysis the calcium carbonate was filtered and the resulting solution concentrated to 30 cc. Alcohol was added to a slight permanent turbidity and the solution allowed to stand for two to three weeks. The precipitate which had formed slowly during this time was filtered and dissolved in boiling water. After standing for forty-eight hours a calcium salt had settled out in the form of a fine crystalline crust consisting of small rhombohedra; yield 0.8 g. The properties[4] of this salt agreed in every respect with those of the well-known calcium 5-keto-gluconate. It reduced Fehling's solution, dissolved in about 50 parts of boiling water, and lost practically no weight when dried *in vacuo* at 85–90° (distinction from calcium saccharate). A 2% solution obtained by dissolving the calcium salt in the calculated amount of hydrochloric acid gave α^{20}_D −14°, based on the free acid.

Anal. Calcd. for $Ca(C_6H_9O_7)_2 \cdot 3H_2O$: Ca, 8.34; C, 29.98; H, 5.04. Found: Ca, 8.46; C, 30.18; H, 5.18.

[1] Isbell and Frush, *Bur. Standards J. Research* **6**, 1145 (1931).

[2] Everett, Edwards and Sheppard, *J. Biol. Chem.*, **104**, 11 (1934); Sheppard and Everett, *ibid.*, Proc. Am. Soc. Biol. Chemists, XXVIII, Annual Meeting, p. LXXX, 1934.

[3] Boutroux, *Compt. rend.*, **102**, 924 (1886); **127**, 1224 (1898).

[4] Ruff, *Ber.*, **32**, 2270 (1899); Kiliani, *ibid.*, **55**, 2820 (1922); Barch, This Journal, **55**, 3653 (1933).

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The Indium Salts of Some Organic Acids

By John B. Ekeley and Wayne W. Johnson

Indium hydroxide forms basic salts when treated with propionic, *n*-butyric, trichloroacetic, benzoic or with ortho, meta or para-toluic acids.

The propionate and the *n*-butyrate were prepared by dissolving weighed quantities of the hydroxide in a slight excess of the pure acids and the excess acid evaporated off on the water-bath until the salts were precipitated. The precipitates were boiled with alcohol, filtered, washed with ether and dried over sulfuric acid. These salts are white powders insoluble in water, alcohol, and ether; yield quantitative.

The trichloroacetate was prepared in the same manner as the two preceding salts, except that, since the salt is soluble in water, alcohol and ether, the excess of acid was removed by drying the product to constant weight at 110°; yield quantitative.

The benzoate was prepared by precipitating

ANALYSES

Salt	In, %			C, %			H. %			Cl. %		
	Calcd.	Found		Calcd.	Found		Calcd.	Found		Calcd.	Found	
$(C_2H_5COO)_2InOH$	41.31	41.40	41.48	25.91	25.72	25.80	3.99	3.93	4.02			
n-$(C_3H_7COO)_2InOH$	37.54	37.67	37.62	31.38	31.32	31.20	4.94	4.76	4.84			
$(CCl_3COO)_2InOH$	25.12	24.96	25.03	10.51	10.61	10.56	0.22	0.25	0.29	46.60	46.63	46.38
$(C_6H_5COO)_2InOH$	30.71	30.71	30.48	44.94	44.82	44.75	2.94	2.91	3.01			
o-$(C_8H_8COO)_2InOH$	28.56	28.62	28.42	47.77	47.62	47.71	3.76	3.72	3.67			
m-$(C_8H_8COO)_2InOH$	28.56	28.63	28.52	47.77	47.70	47.83	3.76	3.65	3.60			
p-$(C_8H_8COO)_2InOH$	28.56	28.41	28.39	47.77	47.70	47.86	3.76	3.71	3.80			

the salt from an acid indium sulfate solution by means of a solution of sodium benzoate and washing the precipitate with alcohol and ether; yield quantitative.

The ortho, meta and para toluates were each prepared by adding indium hydroxide to a slight excess over the theoretical quantity of the melted acid and the mixture kept in the melted state until all the hydroxide was dissolved. After being cooled, the excess acid was removed by boiling the melt in water, filtering off the salt and washing it with alcohol and ether; yield quantitative.

UNIVERSITY OF COLORADO
BOULDER, COLORADO
RECEIVED FEBRUARY 2, 1935

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d-Ribose from the Croton Bean

BY JOSEPH R. SPIES WITH NATHAN L. DRAKE

Cherbuliez and Bernhard[1] have recently isolated from the croton bean, *Croton tiglium* (L), a new glycoside, which they identified as 2-hydroxy-6-amino-purine-*d*-riboside, and which they proposed to call a "crotonoside." They did not, however, succeed in crystallizing the sugar residue obtained by hydrolysis.

The accumulation of a quantity of this material has afforded us an opportunity to examine it. We have succeeded in crystallizing the sugar residue and have conclusively established its identity as *d*-ribose, thus confirming the findings of these workers.

Experimental

Isolation of the Crotonoside.—The glycoside was extracted from the ground unshelled beans with methanol and isolated as described by Cherbuliez and Bernhard.[1] From 125 kg. of beans was obtained 345.0 g. of crude product which contained about 25% of pure crotonoside (0.07%). When recrystallized to constant melting point and dried in the Abderhalden at 110°, it decomposed at 245–247°. (All melting points were taken with standardized Anschütz thermometers.)

Anal. Calcd. for $C_{10}H_{13}O_5N_5$: C, 42.37; H, 4.59; N, 24.73. Found: C, 42.01; H, 4.47; N, 24.56.[2]

Crystallization of *d*-Ribose.—The crotonoside was hydrolyzed and the ribose isolated as described by Cherbuliez and Bernhard.[1] The sirup obtained was dried in a vacuum over phosphorus pentoxide, and when nucleated with an authentic specimen of *d*-ribose it slowly crystallized.[3] Recrystallization three times from absolute ethanol and once from dry isopropanol gave a product that melted constantly at 83–87° with previous softening at 80°. The melt, however, was cloudy; $[\alpha]^{20-25}\text{D}$ $-17.5°$ (c = 5.00 g./100 ml.); (Levene and Jacobs, 85°, $[\alpha]^{20}\text{D}$ $-19.2°$)[4] (Phelps, Isbell and Pigman, 87°, $[\alpha]^{1}\text{D}$ $-23.7°$.)[5]

Tetraacetate.—The tetraacetate (tetraacetylribose) was prepared as described by Levene and Tipson,[6] who give 110° as the melting point and $[\alpha]^{24}\text{D}$ $-52.0°$ and $[\alpha]^{25}\text{D}$ $-54.3°$ in chloroform. The present writers' product was recrystallized to constant melting point from ethanol; m. p. 108–109°; in chloroform $[\alpha]^{24}\text{D}$ $-54.1°$ (c. 6.52 g./100 ml.).

Anal. Calcd. for $C_{13}H_{18}O_9$: C, 49.06; H, 5.66. Found: C, 49.33; H, 5.88.

Phenylosazone.—The phenylosazone was recrystallized to constant melting point from 40% ethanol; m. p. 165–165.5° (Levene and LaForge, 166°).[7]

***p*-Bromophenylhydrazone.**—The *p*-bromophenylhydrazone was prepared as described by Cherbuliez and Bernhard.[1] It was recrystallized to constant melting point from an absolute ethanol–ether solution; m. p. 164° (Ekenstein and Blanksma,[8] 164°) (Levene and Jacobs,[9] 170°).

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[1] Cherbuliez and Bernhard, *Helv. Chim. Acta*, **15**, 464 (1932).

[2] The authors are indebted to Mr. H. M. Duvall of the University of Maryland for the micro Kjeldahl determination.

[3] The writers are indebted to Mr. F. P. Phelps, of the Bureau of Standards of the U. S. Dept. of Commerce, for this material.

[4] Levene and Jacobs, *Ber.*, **42**, 2469, 2474 (1909).

[5] Phelps, Isbell and Pigman, THIS JOURNAL, **56**, 747 (1934).

[6] Levene and Tipson, *J. Biol. Chem.*, **92**, 109 (1931).

[7] Levene and LaForge, *ibid.*, **20**, 429 (1915).

[8] Ekenstein and Blanksma, *Chem. Weekblad*, **10**, 664 (1913).

[9] Levene and Jacobs, *Ber.*, **42**, 2703 (1909).

BUREAU OF ENTOMOLOGY
AND PLANT QUARANTINE
U. S. DEPARTMENT OF AGRICULTURE
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The Decomposition of Acetylphthalimide

BY CHARLES D. HURD, MALCOLM F. DULL AND
J. W. WILLIAMS

It was reported earlier[1] that acetylphthalimide decomposed at 240–325° into phthalimide, acetic

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[1] Hurd and Dull, THIS JOURNAL, **54**, 2437 (1932).

acid, ketene dimer and traces of ketene. The statement regarding ketene dimer should be withdrawn for it has not been possible to obtain this substance from acetylphthalimide in subsequent experimentation. The volatile products found were acetic acid, acetic anhydride, acetone and a small quantity of ketene.

This aligns acetylphthalimide with propionyl-, *n*-butyryl- and caproylphthalimides (all $C_6H_4(CO)_2N—COCH_2R$), all of which give rise on pyrolysis to phthalimide, the acid RCH_2COOH or its anhydride, and the ketone $(RCH_2)_2CO$. In contrast, isobutyryl- and diphenylacetylphthalimides (both $C_6H_4(CO)_2N—COCHR_2$) pyrolyze satisfactorily to ketenes, $R_2C{=}C{=}O$.

For a time it was considered that the non-production of ketene dimer from acetylphthalimide (dried as before by the toluene distillation method) was due to moisture. The same results were produced, however, on acetylphthalimide which was dried in a desiccator over phosphorus pentoxide for ten months.

Ethyl acetate was found to be an excellent solvent from which to crystallize acetylphthalimide. After such a purification it was dried thoroughly as mentioned above and 50 g. of it subjected to pyrolysis. In the 6 g. of distillate which was collected during two hours there was found 1.0 g. of acetone (b. p. 56–60°, soluble in water and identified by converting to dibenzylideneacetone of m. p. 111–112°), 1.1 g. of acetic anhydride (analyzed by the method of Whitford[2] with oxalic acid and pyridine), and 3.4 g. of acetic acid. The total acidity (acetic acid + anhydride) was 4.5 g. The distillate reacted with aniline to produce acetanilide, m. p. 112–113°. If acetoacetanilide was present also its quantity was too small for identification. Evidence for ketene was found by condensing the liquid products at 0° and passing the vapors into aniline. The yield of acetanilide was 0.4–0.5 g.

The above experiment was representative of several which were performed. Variations included the manner of drying, the size of the run (up to 108 g.) and the manner of heating (free flame or salt-bath so that the temperature within the flask ascended gradually from 220 to 325°). The results were essentially the same in all.

Summary.—The volatile products from the pyrolysis of acetylphthalimide are acetic acid, acetic anhydride, acetone and a small quantity of ketene. No significant amount of ketene dimer was produced.

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[2] Whitford, This Journal, **47**, 2939 (1925).

CHEMICAL LABORATORY
NORTHWESTERN UNIVERSITY
EVANSTON, ILLINOIS

RECEIVED FEBRUARY 28, 1935

COMMUNICATIONS TO THE EDITOR

COPPER SULFIDE-WATER CONTACT ANGLES

Sir:

Evidence has been obtained in this Laboratory which indicates that the presence of an adsorbed air film is the most probable cause of the contact angle of water with copper sulfide. Wark [Wark and Cox, *Am. Inst. Min. Met. Eng.*, Tech. Pub., No. 461 (1932)] has shown that a copper sulfide surface that has been ground under water exhibits no contact angle with water. If such a polished surface is exposed to air the contact angle with water assumes a definite value.

If a copper sulfide, covellite, surface is ground under water, such a surface has a zero contact angle with water; exposed to air this surface gives a definite contact angle with water. However, when such a specimen is put into a vessel in contact with water and the water is completely removed by evaporation at reduced pressure, the specimen being finally subjected to gentle warming while the container is evacuated, it is found that the surface again exhibits a zero contact angle with water. Further, when the water is again removed from the copper sulfide and air let into the vessel, the contact angle with water is again developed. Preliminary experiments with copper xanthate indicate a similar characteristic behavior.