ORGANIC CHEMISTRY.

On some Derivatives of Hydrindonaphtheue. Adolf BAEYEB and W. H. PERKIN, JR.

By treating orthoxylene bromide with the sodium salt of malonic acid ether, both the methyl groups of xylene unite with the middle carbon atom of a malonic acid ether, forming the ether of a dicarbo-acid which contains two hydrogen atoms more than indonaphthene, and which the authors call hydrindonaphthene.

The formula of this compound may be expressed as follows :



The authors likewise produced hydrindonaphthonemono- and dicarbo-acids. (Ber. d. Ch. Ges. 1884, 122.) J. H. S. Jr.

On the Action of Hydroxylamine on Nitriles. FERD. TIEMANN.

An aqueous solution of hydroxylamine chloride on being shaken up with a concentrated ethereal solution of benzaldehydecyanhydrine, deposits after a while, crystals, the yield of which is increased by several days shaking of the mixture. The compound thus formed was found to have the formula C_8 H₁₀ N₂ O₂ and is therefore simply an addition product of benzaldehydecyanhydrine and hydroxylamine. This compound has the properties of an amidoacid, as it is dissolved readily both by acids or alkalnes.

Hydroxylamine chloride and benzonitrile unite under similar circumstance to form the addition product $C_7 H_8 N_2 O$.

This compound has properties similar to the previous one. (Ber. d. Ch. Ges. 1884, 126.) J. H. S. JR.

On p-Azo-kresol. C. LIEBERMANN and ST. V. KOSTANECKI.

The general impression that the azo-group in combining with the phenole, takes up the para-position in relation to the hydroxyl, has been found to be erroneous, as the authors were able to produce an azo-compound directly from p-cresol, in which the para-position is already occupied by the methyl group. In this case, therefore, the azo-group would have to take up another position.

Phenyl-azo-*p*-cresol

$$C_6 H_5 - N = N - C_6 H_3^{O H (1)}$$

 $C H_3 (4)$

This compound is formed by the action of diazobenzole on pcresol. It crystallizes in little leaflets with golden lustre. Melting point 108° C.

Phrenyl-azo-(o)-cresol.

$$C_{6} H_{5} - N = N - {}_{6}C H_{3}^{O H (1)}$$

 $C_{6} H_{5} - N = N - {}_{6}C H_{3}^{O H (2)}$

Prepared by the action of diazobenzol on orthocresol. Crystalizes in little leaflets or needles, with golden lustre. Melting point 128-130° C. (Ber. d. Ch. Ges. 1884, 130.) J. H. S. JR.

On a Blue Dyestuff from Pyrrol. G. L. CIMICIAN and P. SILBER.

By treating pyrrole with an aqueous solution of isatine and dilute sulphuric acid, the authors obtained a blue dyestuff. It was found, however, that glacial acetic acid was preferable to the sulphuric acid.

2 pts. isatine were dissolved in 50 pts. warm glacial acetic acid and added to the boiling solution of 1 pt. of pyrrol. The mixture turns dark blue and on being poured into cold water and neutralized with sodium carbonate it is obtained in the shape of a fine powder.

The analysis leads to the formula C_{24} H₁₈ N₄ O₃ (*Ber. d. Ch. Ges.* 1884, 142.) J. H. S. JR.

Preliminary Communication. H. KILIAN and S. KLEEMANN.

The authors state that by treating gluconic acid with strong hydrobromic acid, it is converted into normal caprolactone.

(Ber. d. Ch. Ges. 1884, 143.

J. H. S. JR.

On the Behavior of Diamines with Nitrous Acid. A. LADENBURG.

The author in a former paper had shown that orthophenylendiamine on being treated with nitrous acid forms azimidobenzole, whereas metaphenylendiamine under the same circumstances forms phenylene brown. Paraphenylendiamine, which he had not previously examined, forms the subject of this paper.

Paraphenylendiamine was converted into diacetyl paraphenylendiamine. This with nitric-acid gave nitrodiacetylparaphenylendiamine, which on being boiled 15 minutes with fuming HCl, splits up into nitrophenylendiamine. If a dilute sulphuric acid solution of this substance be treated with K N O2, a brown, amorphous precipitate is formed which has no similarity to the bodies derived from the other phenylendiamines.

Paraphenylendiamine in dilute HCl solution, on being treated with K N O₂, is changed very little at first, but after standing a long time yields a brown, amorphous precipitate with the formula C₁₂ H₁₂ N₂ O₃. (Ber. d. Ch. Ges. 1884, 147.) J. H. S. JE.

Synthesis of Piperidine. A. LADENBURG.

The author finds that piperidine is obtained from pyridine by treating its alcoholic solution with sodium. The yield is small. J. H. S. Jr.

(Ber. d. Ch. Ges. 1884, 156.)

On 1: 2: 4: Orthoxylidine. OSCAR JACOBSEN.

Nitroorthoxylol was first prepared by treating pure orthoxylol with 8 times its weight of fuming nitric acid. It crystallizes from alcohol in light yellow prisms. Melting point, 29° C. This on reduction with iron filings and acetic acid, or with tin and hydrochloric acid, gave orthoxylidine. (C₆ H₃ ¹C H₃. ⁴C H₈. ⁴N H₂.)

This compound crystallizes in tables. Melting point, 49°. Boiling point, 226° C. (Ber. d. Ch. Ges. 1884, 159.) J. H. S. JR.

On Nitroorthotoluic Acid. Oscar Jacobsen.

This compound was obtained by oxydizing 25 grms. of nitroorthoxylol with 250 c. c. nitric acid (sp. gr. 1.4) diluted with 500 c. c. water. The mixture is heated with return cooler for 48 hours. Two nitroorthotolnic acids are thus formed.

One of them melts at 179° C. The second acid melts at 152° C., and is designated by the anthor as *p*-nitroorthotolnic acid.

(Ber. d. Ch. Ges. 1884, 162.) J. H. S. JR.

Action of Methylene Chloride on Toluene and Benzene. C. FRIEDEL and J. M. CRAFTS.

With methylene chloride and toluene in presence of aluminium chloride, the principal products of the reaction were ditolylmethylene and dimethyl anthracene. No hydrogen was evolved, but small amounts of para- and metaxylene were found to have been produced. On substituting benzene for toluene, diphenylmethane and anthracene were formed, as also some toluene. The experiments are still in progress. (*Bul. Soc. Chim.*, XLI., 322.) E. W.

On two Campholurethanes, physically isomeric, analogous to the right and left Tartaric Acids of M. Pasteur. A. HALLER.

Fifty grammes of camphol of Ngai, dissolved in 150 grms. of toluene, are treated with 6 grms. of sodium. When almost all of the sodium has entered into combination, a current of dry cyanogen is passed in until the liquid begins to be colored. After agitating with water, and decanting, the mixture is distilled. The solid mass remaining is heated to 100° and the borneol which has not been acted upon passes off and sublimes. By extracting the residue with boiling water, the urethane is removed, and the residue, by extraction with alcohol, affords left-handed borneol carbonate. The left-handed urethane is deposited from the boiling water in fine needles. It fuses at 126-127° C. and the solutions rotate the polarized ray to the left, α . (D.) = -29.90°. The crystals of the right and left-handed campholurethane are compared. In the formation of these compounds borneol carbonate is always formed. Another derivative is also formed in the reaction, which is but slightly soluble in alcohol and ether. This compound appears to

have no analogous right-handed compound. Further study of this compound is proposed. (Bul. Soc. Chim., XLI., 327.) E. W.

Note on Ethyl. and Methylacetylcyanate of Ethyl. A. HELD.

After preparing ethyl- and methylacetylacetic ethers by the process of Conrad and Limpach, these products were treated with sodium ethylate, and the solution saturated with dry cyanogen chloride; the result was the formation of ethyl- and methylacetylcyanates of ethyl. The ethyl compound boils at 105° to 110° under a pressure of 15 to 20 mm. mercury; it is a colorless liquid with a pleasant, ethereal odor; Sp. Gr. 0.976 at 20°, soluble in alcohol and ether, and insoluble in water and alkaline solutions. The methyl compound is similar in solubility, etc., to the above. Sp. Gr. 0.996 at 20°. Boils at 90° to 95° under pressure of 15 to 20 mm. mercury. (*Bul. Soc. Chim.*, XLI., 330.) E. W.

On the Oxidation of Menthol by Potassium Permanganate. G. Arth.

By the action of potassium dichromate and sulphuric acid, Morija obtained a compound, C_{10} H_{18} O, which he called *menthone*. By the use of potassium permanganate and sulphuric acid, according to a method here described, the author obtained a substance which had a strong odor, recalling somewhat that of valerianic acid. It appeared to be a mixture of at least two acids, one of which was apparently C_{10} H_{18} O₃. The second acid has not yet been isolated for examination. (*Bul. Soc. Chim.*, XLI., 330.) E. W.

On the Preparation of a Propyl and an Amyl Naphthalene. L. Rowx.

A mixture of 200 gms. of naphthalene with 120 gms. propyl bromide are heated together in a flask with an inverted condenser. When distillation begins, about 10 grms. aluminium chloride are added, a little at a time, the flask being agitated during the addition. Hydrobromic acid is disengaged abundantly, and these vapors are condensed in a tared flask. The heating is continued, and when the amount of hydrobromic acid evolved is nearly the theoretical amount, the flask is allowed to cool; 3 to 400 grms. C S₂ are added to complete solution, the products are treated with water, the C S₂ is decanted, and the material is dried and distilled

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fractionally in vacuo. The main portion consists of a product $C_{10} H_{\eta} (C_3 H_{\eta})$ boiling at 262°—267° at ordinary pressures; vapor density (Meyer's method) 5.85. Probably isopropyl naphthaline. By substituting amyl chloride for propyl bromide in the above process amyl naphthalene, $C_{10} H_{\eta} (C_5 H_{11})$, was obtained, boiling at 288°—292°. The above formed compounds with picric acid, the propyl compound fusing unchanged at 89° to 90°, the amyl compound also fusing unchanged at 140° to 141°.

Small amounts of isodinaphthyl were produced, which appeared to be formed in consequence of the presence of an alcoholic chloride. (*Bul. Soc. Chim.*, XLI., 319.) E. W.

Action of Chlorinated Aldehydes on Benzene. A. Combes.

To a solution of chloral in excess of benzene, aluminium chloride was added in small portions. A perceptible reaction took place in the cold, and on heating to about 70° much HCl was evolved. By washing with water and distilling off the benzene, a compound remained, distilling *in vacuo* at 175° —185°, colorless when distilled, quite viscous, and with pleasant, aromatic odor; C₆ H₅ CCl₂, COH, HCl. Distilled in the air it loses HCl and gives, consequently, a boiling point varying between 265° and 290°. It reduces Fehling's solution and AgNO₃ and combines with difficulty with sodium bisulphite. KHO in the cold removes from it the HCl; heated, it affords benzoic aldehyd.

An attempt to obtain other aldehydes by the action of the aluminium chloride npon the chloral in benzene was unsuccessful, the product being either triphenylethane or tetraphenylethylene, the latter point remaining unsettled. (Bul. Soc. Chim., XLI., 382.) E. W.

On the Synthesis of Dimethylanthracenehydride and Diphenylethane. A. Angelbis and R. Anschütz.

On heating ethylidene chloride or bromide and benzene, with aluminium chloride, diphenylethane was formed, according to the following reaction:

$$\begin{array}{c} \mathbf{C} \mathbf{H} \mathbf{Cl}_{2} \\ | \\ \mathbf{C} \mathbf{H}_{3} \end{array} + 2 \mathbf{C}_{6} \mathbf{H}_{6} \qquad \begin{array}{c} \mathbf{C} \mathbf{H} (\mathbf{C}_{6} \mathbf{H}_{5})_{2} \\ | \\ \mathbf{C} \mathbf{H}_{3} \end{array} + 2 \mathbf{H} \mathbf{Cl} \end{array}$$

This compound boils at 150°. It is colorless, but has a blue fluorescence. The analysis of the picrate of this hydrocarbon showed that it has the formula C_{16} H_{16} , obtained according to the following reaction, 2 C H_s C H $Cl_2 + 2$ C_6 $H_6 = C_{16}$ $H_{16} + 4$ H Cl. The pure hydrocarbon melts at 178°-179° and sublimes in transparent, light yellow, flat needles. It is easy soluble in ether, benzene, carbon disulphide, hot glacial acetic acid, and alcohol.

On oxidation with an excess of chromic acid, it splits up into anthrachinone and carbon dioxide. Taking these facts into consideration, the body would have the following structural formula:



The picrate of this new hydrocarbon, is represented by the formula, $C_{16} H_{16} - C_6 H_2 (NO_2)_3 - OH$. Crystallizes in reddish blue needles, melting point 170° C. (*Ber. d. Ch. Ges.* 1884. 165.) J. H. S., JE.

On the action of Aluminium Chloride on Vinyl bromide in Benzene, and Vinyl tribromide in Benzene. A. ANGELBIS AND R. ANSCHÜTZ.

On passing a uniform current of vinyl bromide through a mixture of benzene and aluminium chloride, and then distilling the mixture, the following compounds were obtained :

1. Ethylbenzene. 2. Diphenylethane. 3. Dimethylanthracenehydride.

The authors expected that by treating vinyl tribromide in the same manner they would obtain triphenylethane, but they were unable to isolate this compound. The only product they could separate was, strange to say, diphenylethane. (*Ber. d. Ch. Ges.*, 1884. 167.) J. H. S., JR.

Remarks on the Previous Communication. R. ANSCHÜTZ. (Ber. d. Ch. Ges., 1884. 169.) J. H. S., Jr.

On the Synthesis of Anthrachinoline. C. GRAEBE.

This investigation was undertaken, with the view of determining whether the same compound would be obtained by heating anthramine, nitrobenzol and sulphuric acid together, as that derived from alizarine blue, by heating it with zine dust. This, on experiment turned out to be the case, for on heating anthramine, glycerine, nitrobenzol and sulphuric acid together, an anthrachinoline melting at 170° C. was obtained. (*Ber. d. Ch. Gcs.* 1884. 170.) J. H. S., JR.

On Sinapic Acid. I. REMSEN and R. D. COALE.

Sinapine, a base existing as sulphocyanate in the alcoholic extract of mustard seed, was made to yield the above acid by boiling with baryta water instead of with caustic potash as in the original method of von Babo and Hirschbrunn. The product crystallized from a mixture of alcohol and water in small, yellowish, transparent prisms fusing at 192°, and yielding, on analysis, results which accord best with the formula $C_{11}II_{12}O_5$, originally given by v.B. and H. Analysis of Ca and Ba salts indicate that it is a monobasic acid, with one hydroxyl. Fused with canstic potash it yields a body giving the reactions of pyrogallol. The authors believe sinapic acid to be a derivative of gallic acid, probably butylene gallic acid, and are endeavoring to effect its synthesis. (Am. Chem. Jour., 6, 50.)

Russian Chemical Society. Correspondence of O. DAVIDOFF.

M. Koutcheroff finds in regard to action of allylene on mercuric oxide and its salts, 1. That in acid solutions substances are formed which generate acetones by the action of acids. They may be considered as combinations of basic salts with $C_3 H_4 Hg O$. In alkaline solutions a substitution product of $(C_3 H_3)_2$ Hg is formed which affords allylene by the action of acids. 2. That hydration of allylene is only a special case of the above reaction. At an elevated temperature it is continuous, complex mercury compounds being formed which decompose with formation of acetone. 3. That the structure of the acetones formed depends upon that of the hydrocarbons from which they are derived. The rules for their formation are given. (*Bul. Soc. Chim.*, XLI, 388.)

E. W.