

Organic Chemistry.

Action of Magnesium on the Vapours of the Alcohols. Preparation of Allylene. By EDWARD H. KEISER and MARY B. BREED (*Chem. News*, 1895 **71**, 118—120).—Magnesium glows when heated in a current of the vapour of methylic, ethylic, or propylic alcohol; a large volume of gas is at the same time given off, and a black, coherent mass remains, which, on treatment with water and a small quantity of ammonium chloride, evolves a moderately rapid current of allylene. The gas evolved during the glowing of the magnesium had the following percentage composition.

	With methylic alcohol.	With ethylic alcohol.	With propylic alcohol.
CO ₂	0·8	0·0	0·0
CO.....	0·6	0·4	3·5
CH ₄ or saturated hydrocarbons.....	19·7	11·1	19·9
C ₂ H ₂ } or unsaturated {	—	10·0	17·8
C ₂ H ₄ } hydrocarbons.. {	—	4·0	
H.....	78·9	72·9	57·8

The decomposition of the same alcohols by passing the vapour over heated iron, yielded gases of the following percentage composition.

	Methylic alcohol.	Ethylic alcohol.	Propylic alcohol.
CO ₂	3·8	0·5	0·6
CO.....	26·8	8·0	16·4
Saturated hydrocarbons	1·6	13·0	23·6
Unsaturated hydrocarbons.....	—	4·0	16·7
Hydrogen.....	67·4	63·8	42·7

In the case of the magnesium, the carbonic oxide is reduced. Allylic, isobutylic, and amylic alcohols were found to behave in a similar manner; a small quantity of acetylide was found in the black residue in the case of propylic alcohol. The production of allylene from propylic and allylic alcohols, in the manner described, proceeds with such facility that it is recommended as a method of preparing allylene.

D. A. L.

Crystalline Copper-ferrocyanides. By J. MESSNER (*Zeit. anorg. Chem.*, **8**, 368—393).—When potassium ferrous ferrocyanide, K₂Fe(FeC₆N₆), is treated with ferric salts and water, a violet amorphous precipitate is obtained, containing from 6 to 12 per cent. of potassium, according to the temperature at which the action takes place. If a cupric salt is employed in place of the ferric salt, then a beautiful, violet compound is obtained, which, like the iron compound, is converted by oxidation into a green powder. This violet com-

pound, which probably has the composition $K_2CuFe_2(FeC_6N_6)_2$, is slowly and incompletely decomposed by boiling with alkali carbonates or hydroxides, and the solution so obtained contains copper, which can be precipitated by hydrogen sulphide. If the violet compound is decomposed by potassium carbonate, the solution, on cooling, deposits crystals of the compound obtained by boiling copper ferrocyanide with potassium ferrocyanide; this compound cannot, however, be obtained pure. When sodium carbonate is employed in place of potassium carbonate, the compound $Na_2Cu(FeC_6N_6)$ is obtained in beautiful, brown, quadratic prisms.

Sodium cuproferrocyanide, $Na_2Cu_2(FeC_6N_6)$, is obtained by adding a cold saturated solution of the double cyanide of copper and sodium to a hot solution of sodium ferrocyanide. It crystallises from the solution, on cooling, in colourless, microcrystalline, six-sided prisms, and may be dried in a vacuum over sulphuric acid. It is also obtained by boiling a solution of sodium ferrocyanide with cuprous cyanide, and, after adding a small quantity of neutral sodium sulphite, cooling the solution in a current of hydrogen. The compound contains 27.5 per cent. of water. When exposed to the air, it slowly oxidises and turns brown. When heated at 100° , it turns brown and loses part of its water of crystallisation, but the whole of the water of crystallisation can only be removed by ignition. At 200° , it glows and decomposes, and at 180° , it is converted into a brown powder which still contains water. It is insoluble in water, alcohol, and ether, dissolves in alkali cyanides with decomposition, and is decomposed by acids and alkalis.

Sodium cupriferrrocyanide, $Na_2Cu(FeC_6N_6)$, is formed when cupric salts are boiled with a solution of sodium ferrocyanide. It is most easily prepared by boiling copper ferrocyanide, prepared from copper sulphate and hydroferrocyanic acid, with sodium ferrocyanide, and, after filtering off the amorphous precipitate, allowing the filtrate to evaporate exposed to the air. Or it can be obtained by passing a current of air through the hot mother liquors of the cuprous salt and then allowing the oxidised compound to crystallise. It crystallises in lustrous, brown, four-sided prisms, is insoluble in cold water, and decomposes when boiled with water or with dilute acids or alkalis. It dissolves in potassium cyanide with evolution of cyanogen, and yields potassium cuprous cyanide and potassium ferrocyanide. When copper ferrocyanide is boiled with a solution of sodium ferrocyanide, a bright green compound is produced, which is converted into the brown compound after one to two hours' boiling; this phenomenon does not take place in the case of the potassium salts. The author was unable to determine whether the green substance is a definite compound, as it is very easily decomposed. The mother liquors of sodium cupriferrrocyanide and sodium cuproferrocyanide, when mixed with dilute acids, yield white, amorphous precipitates, which are probably the acids $H_2Cu(FeC_6N_6)$ and $H_2Cu_2(FeC_6N_6)$. When freshly prepared, they dissolve in alkali carbonates and hydroxides, and quickly decompose to yield ferrocyanic acid.

Potassium cuproferrocyanide, $K_2Cu_2(FeC_6N_6)$, is obtained in like manner to the sodium salt by boiling copper cyanide with a solution

of potassium ferrocyanide containing a small quantity of potassium sulphite, or by boiling potassium cuprous cyanide or cuprous chloride with potassium ferrocyanide. It crystallises in colourless cubes if the solution is quickly cooled. When the solution is slowly cooled, it is obtained mixed with partially oxidised crystals of a yellow to brown colour. It contains 18.7 to 20.4 per cent. of water, and closely resembles the sodium salt.

The author was unable to obtain potassium cupriferrrocyanide in a pure state, as under all conditions the cupro-salt is formed at the same time.

Ammonium cuproferrocyanide is obtained by boiling copper cyanide with a solution of ammonium ferrocyanide containing ammonium sulphite and passing hydrogen through the mixture. It crystallises in small, colourless, six-sided prisms, decomposes rapidly under water, or on exposure to air, or in a vacuum, with formation of hydroferrocyanic acid, and is at once decomposed by acids and alkalis. It can also be obtained by treating a solution of the sodium salt with ammonium nitrate.

Ammonium cupriferrrocyanide is obtained by boiling copper ferrocyanide with a solution of ammonium ferrocyanide. The solution thus obtained must be filtered as quickly and as hot as possible. It crystallises in brownish-red cubes, can be dried in a vacuum over sulphuric acid, and has properties similar to those of the sodium salt.

Magnesium cuproferrocyanide is obtained by boiling copper cyanide with a solution of magnesium ferrocyanide. It crystallises in beautiful, colourless, six-sided prisms, turns brown on exposure to air and in a vacuum over sulphuric acid, and is less stable than the analogous sodium and potassium salts.

Magnesium cupriferrrocyanide is easily obtained by boiling copper ferrocyanide with magnesium ferrocyanide. It separates in violet-brown crystals and contains 44.3 to 44.5 per cent. of water.

Calcium cupriferrrocyanide crystallises in small, brown, quadratic prisms, and can be dried in a vacuum over sulphuric acid.

Strontium cupriferrrocyanide and *barium cupriferrrocyanide* are obtained in crystals having the same form and colour as the calcium salt.

Calcium, strontium, and barium cuproferrocyanides are obtained by boiling copper cyanide with the corresponding ferrocyanides. They crystallise in colourless, six-sided prisms, which cannot be distinguished from one another, but the pure compounds cannot be obtained as the simple ferrocyanide always separates with them, and an excess of ferrocyanide is necessary in their preparation, as the cuproferrocyanides are not soluble in water except in the presence of an excess of ferrocyanide.

Copper ferrocyanide ammonia, $\text{Cu}_2(\text{FeC}_6\text{N}_6) \cdot 8\text{NH}_3$, is obtained by adding a solution of ammonium ferrocyanide in strong ammonia to a solution of cuprous chloride in the strongest ammonia, and allowing the mixture to remain for a few hours. It crystallises in beautiful, black, lustrous prisms, is very sparingly soluble in ammonia, and is not decomposed by cold absolute alcohol. The crystals, on exposure to air, quickly decompose into ammonia, copper ferrocyanide, and the compound $\text{Cu}_2(\text{FeC}_6\text{N}_6) \cdot 4\text{NH}_3$. With dilute acids, it yields copper

ferrocyanide and ammonium salts. When evaporated on the water bath in its own mother liquor, it is converted into ammonium cupri-ferrocyanide and amorphous compounds.

E. C. R.

A New Alcohol from Lanolin. By G. MARCHETTI (*Gazzetta*, 1895, **25**, i, 42—49).—After hydrolysing lanolin by heating it on the water bath with alcoholic sodium ethoxide, distilling off the solvent, acidifying with sulphuric acid, and extracting the cholesterols, alcohols, and aliphatic acids with ether, a residue of *lanolinic alcohol*, $C_{12}H_{24}O$, remains; on purification with alcohol and chloroform, it is obtained as a white, odourless powder, or as spheroidal concretions, melting at 102—104°. It is soluble in hot alcohol, chloroform, or benzene, but insoluble in potash or ether; it is precipitated unchanged by acids from its solution in sodium ethoxide, and is not acted on by iodine or acetic anhydride. The *benzoate*, $C_{12}H_{23}OBz$, forms a white, waxy mass, melting at 65—66°, which decomposes on exposure to the air, and is hydrolysed by sodium ethoxide.

Lanolinic acid, $C_{12}H_{22}O_3$, is prepared by oxidising lanolinic alcohol with chromic acid in acetic acid solution; it is a white, crystalline powder, melting at 75—77°, and is soluble in alcohol, ether, chloroform, benzene, or alkali carbonates, but is insoluble in water. Its *barium salt*, $(C_{12}H_{21}O_3)_2Ba$, crystallises with $1H_2O$ which is lost at 150°, and decomposes when heated.

W. J. P.

The Polymerides of Epichlorhydrin. By EMANUELE PATERNÒ (*Gazzetta*, 1894, **24**, ii, 541—544).—The author supplements Oliveri and Paternò's cryoscopic examination of the polymeride of epichlorhydrin (*Abstr.*, 1894, i, 486) by new determinations in benzene and acetic acid, and by boiling point determinations in benzene; the results of these experiments indicate that the substance probably has the molecular composition $(C_3H_5ClO)_6$. The behaviour in freezing benzene shows that the compound has marked alcoholic properties; on treatment with cold alcoholic potash, it yields an oil, which boils at 250—300° with slight decomposition, and yields about 53 per cent. of ethoxyl by Zeisel's method; it possibly has the composition $C_{12}H_{20}(OEt)_4O_4$.

W. J. P.

Amorphous Condition of Fused Substances. By CHARLES TANRET (*Compt. rend.*, 1895, **120**, 630—632).—The glucose pentacetins (this vol., i, 321) crystallise in needles, whilst the hexacetins of racemo-inositol and the active inositols form hard and somewhat bulky crystals. If, however, they are melted in narrow tubes and allowed to cool, they all solidify in amorphous forms, which melt at 40—50° below the normal melting points. When the amorphous forms are melted, they gradually change into the crystalline forms with normal melting points, the change being more rapid the smaller the difference between the melting points of the crystallised and amorphous forms. The change from amorphous to crystalline is accompanied by development of heat, and is strictly analogous to the conversion of plastic sulphur into the crystalline form. It would follow that there is no essential difference between the allo-

tropic modifications of the element and the crystallised and amorphous forms of the compounds in question.

Many other carbon compounds behave like the acetins and solidify in an amorphous form when melted and suddenly cooled. When heated, however, the amorphous forms become crystalline with development of heat, the change being very rapid in some cases and gradual in others.

C. H. B.

Combination of Sugars with Primary Hydrazines: Amidoguanidine, and Arabinose. By R. RADENHAUSEN (*Chem. Centr.*, 1894, ii, 776; from *Zeit. Ver. Rübenzuck.-Ind.*, 1894, 768—770; compare H. Wolff, *Abstr.*, 1894, i, 315).—Amidoguanidine reacts with arabinose in alcoholic solution, a condensation with the aldehyde group occurring with separation of water; the product crystallises in small, white needles, melts at 125° (uncorr.), and dissolves in water and in alcohol, but not in ether.

The reaction between hydrazine hydrate and arabinose gives rise to a deep-seated decomposition of the sugar, and no crystalline product has been isolated. Nitrobenzoylhydrazine and arabinose, however, form a condensation product, which crystallises in snow-white tablets, and melts at 178°; it is insoluble in cold water, and is decomposed into the parent substances when heated with water—a behaviour which is remarkable, since all compounds of hydrazines with aldehydes which have been prepared heretofore are stable in hot water.

A. G. B.

A Second Achroodextrin obtained by the Action of Diastase on Starch. By CARL J. LINTNER and GEORG DÜLL (*Chem. Centr.*, 1894, ii, 864; *Zeit. ges. Brauw.*, 1894, 17, 339—340).—The new dextrin, hitherto overlooked because it forms only a small proportion of the products of conversion, has the formula $(C_{12}H_{20}O_{10})_3 + H_2O$. The opticity is $[\alpha]_D = 183^\circ$, and the cupric reduction $R = 26.5$ — 26.8 . No evidence of a third achroodextrin, $(C_{12}H_{20}O_{10})_2 + H_2O$, has been obtained. This new achroodextrin II has the same composition as that of the substance described by Brown and Morris as typical maltodextrin, but the opticity and cupric reduction given for this substance leave no doubt that it is not pure, but contains both achroodextrin I and isomaltose.

A. G. B.

Wax Found in the Treatment of Cotton and Linen Fibre for the Manufacture of Paper. By CLAYTON BEADLE (*Chem. News*, 1895, 71, 164—165).—Occasionally when disintegrating fibre that has been treated under pressure with $3\frac{1}{2}$ per cent. caustic soda and bleached with calcium hypochlorite at 32°, a deposit forms on surfaces in the beater. This consists of aluminium, iron, and calcium salts mixed with a sweet-smelling waxy substance, soluble in ether, melting at 47.5°, having a saponification equivalent of 19.46 (KHO), and yielding 91.04 per cent. of insoluble fat acids. It is not noticed in the raw fibre.

D. A. L.

Derivatives of Active α -Hydroxybutyric acid. By PHILIPPE A. GUYE and CHARLES JORDAN (*Compt. rend.*, 1895, 120, 632—635).—

The ethereal salts of the lævogryrate α -hydroxybutyric acid (this vol., i, 333) were prepared in the usual way; their physical properties are as follows, the alkylic radicles being primary in all cases.

	Boiling point.	Sp. gr. at 15°.	Specific rotatory power $[\alpha]_D$.	Product of asymmetry $P \times 10^6$.
Ethylic salt	169°	0.978	-1.9	319
Normal butylic salt..	200	0.982	-9.7	309
Isobutylic salt.....	197	0.965	-7.7	309
Racemic amylic salt..	209	0.950	-8.5	286
Heptylic salt.....	245	0.928	-6.1	233
Octylic „	255	0.916	-5.3	209

The maximum of P corresponds with the propylic salt, the value being 330. The rotatory power also passes through a maximum, but the two maxima do not coincide.

The results obtained with the various amylic salts are as follows.

	$[\alpha]_D$.
1. Racemic hydroxybutyric acid and active alcohol	+1.5
2. Lævogyrate hydroxybutyric acid and racemic alcohol.	-8.5
3. „ „ „ and lævogryrate alcohol.....	-7.3
4. Dextrogryate „ „ and lævogryrate alcohol	+8.1

These results afford further proof of the superposition of the effects of different asymmetrical carbon atoms in the same molecule. The calculated rotatory power of ethereal salt No. 3 is -7.0, and the observed value -7.3; in the case of No. 4 the calculated and observed values are +7.8 and +8.1 respectively (compare this vol., ii, 149 and 195).
C. H. B.

Condensation of Ketones with Ethylic Salts of Dibasic Acids under the Influence of Sodium Ethoxide. By HANS STOBBE (*Ber.*, 1895, 28, 1122-1123).—In consequence of the publications of Japp and Davidson (*Trans.*, 1895, 132) and Meyenberg (this vol., i, 334), the author states that he is extending his research (*Abstr.*, 1894, i, 594), and examining the condensation of various ketones and diketones with ethylic succinate, pyrotartrate and malonate, and of the last with ethylic acetoacetate. From acetone and ethylic malonate, two acids have already been obtained melting at 74-76° and at 146-148°.
C. F. B.

Condensation of Ethylic Malonate with Acetone. By KARL AUWERS (*Ber.*, 1895, 1130-1133).—In an attempt to synthesise nor-camphoric acid, now given up on account of Meyenberg's paper (this vol., i, 334), ethylic dimethylacrylate, $\text{CMe}_2\text{CH}\cdot\text{COOEt}$, was condensed by heating it with ethylic potassiomalonate and a little alcohol at 98°, and a compound, $\text{CH}(\text{COOEt})_2\text{CMe}_2\text{CHK}\cdot\text{COOEt}$, was obtained; the ethylic salt, after the potassium is replaced by hydrogen, boils at 194° under 43 mm. pressure, and has sp. gr. = 1.064 at

13.5°. When hydrolysed with rather strong acids, it yields $\beta\beta$ -dimethylglutaric acid, $\text{CMe}_2(\text{CH}_2\cdot\text{COOH})_2$; this melts at 100–101°, and, when treated with acetic chloride or distilled under atmospheric pressure, yields an anhydride melting at 124°.

β -Bromisovaleric acid was prepared by treating dimethylacrylic acid with hydrobromic acid saturated at 0°; it melts at 73.5°.

C. F. B.

Conversion of Carbamide into Cyanamide. By CHARLES MOUREU (*Bull. Soc. Chim.*, 1894, [3], 11, 1068–1070; compare Fenton, *Trans.*, 1882, 262).—Carbamide is readily and energetically dehydrated by sulphurous chloride, abundance of sulphurous anhydride and hydrogen chloride being evolved when the two are mixed. After the excess of the reagent has been removed by means of sodium carbonate solution, the cyanamide is extracted from the product with ether.

JN. W.

Mercuric Compound of Thiophen: Estimation of Thiophen in Benzene. By GEORGES DENIGÈS (*Compt. rend.*, 1895, 120, 628–630).—The compounds of mercury with thiophen hitherto known are formed from the chloride under special conditions, but the author finds that thiophen combines readily with mercuric sulphate in acid solution, and also with mercuric acetate and chloride under similar conditions. The reagent is prepared by dissolving 50 grams of mercuric oxide in 200 c.c. of sulphuric acid diluted with 1000 c.c. of water. If 200 c.c. of this liquid is mixed with 1 c.c. of thiophen, it rapidly becomes turbid at the ordinary temperature, but the liquid should be first gently heated, and finally boiled.

A basic mercuriothiophen sulphate, $(\text{HgSO}_4, \text{HgO})_2\text{C}_4\text{SH}_4 + \text{H}_2\text{O}$, separates as a heavy, coherent, white, precipitate, formed of radiating spherulids, and is washed with boiling water and dried. It loses 1 mol. H_2O at 100–110°, and may be heated for a long time at 120–130°, or even at 150°, without undergoing any further change. Above 200°, sulphurous anhydride and thiophen are given off. It is insoluble in water and neutral solvents, but dissolves in acids, with gradual liberation of thiophen, as indicated by the isatin and alloxan or alloxantin reactions, the change being accelerated by heat. Hydrogen sulphide or alkali sulphides precipitate the mercury and liberate thiophen, but ammonia and caustic alkalis have no action even on heating.

The ease with which this compound is formed, and its insolubility, affords a valuable means of detecting and estimating thiophen in commercial benzene.

C. H. B.

Hexamethylene. By NICOLAI D. ZELINSKY (*Ber.*, 1895, 28, 1022–1025).—Hexamethylene, prepared by reducing iodo-hexamethylene (Baeyer, *Abstr.*, 1894, i, 174) in alcoholic solution with zinc and hydrochloric acid, boils at 81–82°, has the sp. gr. 0.7764 at 20°/4°, and the refractive index 1.4258. Hexahydrobenzene, prepared by the direct reduction of benzene with hydriodic acid (Kishner, *J. Russ. Chem. Soc.*, 1894, 375), on the other hand, boils at 72–73°, has the sp. gr. 0.7488, and the refractive index 1.4101, so that the two com-

pounds seem to be distinct. The hydrocarbon, prepared by the reduction of iodoexamethylene with hydriodic acid at 220° , has properties which are intermediate between those of the two substances just described, and probably contains both of them.

A. H.

The Use of Metallic Aluminium in the Synthesis of Aromatic Hydrocarbons. By CORNELIUS RADZIEWANOWSKI (*Ber.*, 1895, 28, 1135—1140).—Instead of aluminium chloride, aluminium itself, together with either hydrochloric acid or mercuric chloride, may be used to effect the Friedel-Crafts synthesis. A small quantity of aluminium shavings is placed in excess of benzene, gaseous hydrogen chloride passed in for 20 minutes, and the mixture allowed to remain until the metal turns brown and a copious evolution of hydrogen begins; the chloride or bromide of the other radicle is then added drop by drop, the mixture being cooled with water, or the chloride or bromide is added drop by drop to a mixture of aluminium shavings and mercuric chloride with excess of benzene, the mixture being cooled with ice. Diphenylmethane and ethylbenzene were prepared by both methods from benzylic chloride and ethylic bromide respectively; isopropylbenzene, from isopropyl chloride, by the first method only. This method does not bring about the condensation with chloroform to triphenylmethane, nor with benzylic chloride to anthracene. The second method will effect the first of these condensations, but not the second. The yield was usually 60—70 per cent. of the theoretical.

C. F. B.

Argon in Combination. By MARCELLIN BERTHELOT (*Compt. rend.*, 1895, 120, 581—584).—When argon is mixed with benzene vapour and subjected repeatedly to the action of the silent electrical discharge, the benzene being renewed from time to time, condensation takes place and a product is formed similar to that obtained from benzene and nitrogen under similar conditions; it is a yellow resinous odorous substance which when heated yields alkaline vapours and an abundant carbonaceous residue.

If the molecular weight of argon were 42, it would stand in this respect in the same relation to nitrogen as ozone does to oxygen.

C. H. B.

Ethylquinone. By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1894, [3], 11, 1130—1131).—*Ethylquinone*, prepared from dimethylanilethylquinonimide (this vol., i, 417), crystallises in brilliant, golden-yellow plates, or long, prismatic needles. It has a powerful odour, and its vapour irritates the eyes and nose. It melts at 38.2° , and is readily volatile at ordinary temperatures. The corresponding *quinol*,



prepared by reducing the quinone with sodium hydrogen sulphite, crystallises in colourless plates or prismatic needles, and melts at $112\text{--}113^{\circ}$; it sublimes easily. The solution in alkalis soon becomes coloured.

JN. W.

Purification of Guaiacol by strongly Cooling it. By LUDWIG WENGHÖFFER (*Chem. Centr.*, 1894, ii, 565; from *Pharm. Zeit.*, 1894, 39, 576—577).—Liquid guaiacol is kept for a day at a temperature of -100° and then separated, by a peculiar artifice, into two layers; the larger and clearer of these is "Riedel-Pictet guaiacol," the other is a brownish-yellow residue. Riedel's guaiacol has a sp. gr. at 24° of 1.1099, and dissolves to the extent of 1 part in 88 parts of water; the Riedel-Pictet guaiacol has sp. gr. = 1.1171 at 24° , and dissolves in 80 parts of water; the residue from the above treatment has sp. gr. = 1.0889 at 24° , and dissolves in 200 parts of water. The three products yield 46 grams, 49 grams, and 8 grams of acetyl-guaiacol per 50 grams, respectively, when acetylated. Guaiacol purified in this manner does not become coloured when exposed to light, and is only feebly coloured by strong sulphuric acid.

A. G. B.

Aromatic Selenium Compounds. By P. CAMILLE CHABRIÉ (*Bull. Soc. Chim.*, 1894, [3], 11, 1080—1083).—A criticism of Krafft and his collaborators (*Abstr.*, 1894, i, 88, 448). The author has prepared various aromatic selenium compounds by synthesis with aluminium chloride. Phenyllic hydroselenide is completely soluble in alcohol, and forms definite crystals melting at 60° ; the analytical results, moreover, are in good agreement with those calculated from the formula PhSeH ; it cannot, therefore, be a mixture of phenyllic selenide and diselenide with selenium, as stated by Krafft. It is true that the analytical results agree equally well with those required by diphenylic diselenide, but it is not likely to be the latter, as it forms compounds with mercury analogous to the mercaptides. Diphenylic diselenoxide is an oily liquid boiling at 230° (65 mm.), and not a crystalline solid, as stated by Krafft; neither does it decompose into phenylic selenide when distilled. The dibromide melts at 120° . *Chlorodiphenylic selenoxide*, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{SePhO}$, occurs as a bye-product in the aluminium chloride process; it crystallises well, and melts at 94° .

JN. W.

Manufacture of Orthonitraniline. By JOSEPH POKORNÝ (*Chem. Centr.*, 1894, ii, 556; from *Bull. Soc. Indust. Mulhouse*, 1894, 280—284).—Forty grams (?) of acetanilide is gradually added to 80 kilos. of sulphuric acid (66°B), while the liquid is well stirred and the temperature not allowed to rise above 50° ; a mixture of 36 kilos. of nitric acid ($36\text{--}37^{\circ}\text{B}$) with 40 kilos. of sulphuric acid (66°B) is allowed to flow into this solution of acetanilide, which is kept at a temperature of $40\text{--}50^{\circ}$, the application of cold and agitation being continued until the temperature of the liquid falls continuously. On the following day, the liquid is poured into 200 litres of hot water, whereon a yellowish precipitate, consisting of ortho- and par-nitracetanilide is thrown down. To deacetylate the mixture, it is heated by steam until all the precipitate is dissolved; the liquor is then cooled to 50° and poured into 200 kilos. of ice which is kept well stirred. Orthonitraniline is thus precipitated, whilst par-nitraniline may be thrown down from the mother liquor by mixing

it with 180 kilos. of soda-lye (36° B) and cooling with ice. The yield is 25 per cent. of ortho- and 60 per cent. of para-nitraniline.

A. G. B.

Action of Phthalic Chloride on Nitranilines. By BRONISLAW PAWLEWSKI (*Ber.*, 1895, **28**, 1118—1120).—The results differ somewhat, especially as regards the melting points, from those of Dobreff (this vol., i, 360). With excess of phthalic chloride, nitrophthalanils, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} N \cdot C_6H_4 \cdot NO_2$, are obtained; with excess of the nitraniline, nitrophthalanilides, $C_6H_4(CO \cdot NH \cdot C_6H_4 \cdot NO_2)_2$; the numbers given are melting points.

Nitrophthalanils; 1:4, white, amorphous, 262—263°; 1:3, white, amorphous or crystalline, 242—244°; 1:2, yellowish needles, 200—203°. *Nitrophthalanilides*; 1:4, yellowish powder, 232—234°; 1:2, silky yellowish needles, 180—184°; 1:3 (?), 232—234°.

C. F. B.

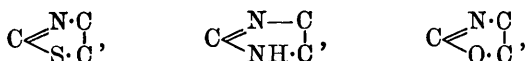
Derivatives of Benzylamine. By PAUL FRIEDLÄNDER and M. MOSCZYC (*Ber.*, 1895, **28**, 1140—1145).—1:4-Dimethylamidobenzylamine, $NMe_2 \cdot CH_2 \cdot C_6H_4 \cdot NH_2$, is obtained by heating 1:4-nitrobenzyl chloride with dimethylamine in alcoholic solution, and reducing the product with stannous chloride; it is a colourless syrupy liquid, and boils with slight decomposition at above 300°; its *sulphate*, with H_2SO_4 , crystallises in lustrous, yellowish plates. The corresponding *diethyl* compound boils at 212—214° under 40 mm. pressure. The methyl compound can be diazotised, and then yields with β -naphthol a basic azo-dye which crystallises in red needles and melts at 120°. It can also be converted by the diazo-reaction into the cyanide, the *platinochloride* of which was prepared.

If 1:4-toluenitrile is chlorinated at the boiling temperature, and the product treated with concentrated sulphuric acid, *w*-chloro-1:4-toluamide is formed, and by warming this with aqueous dimethylamine, *w*-dimethylamine-1:4-toluamide is obtained; this melts at 144°. Dilute alkalis convert it into the *acid*, $NMe_2 \cdot CH_2 \cdot C_6H_4 \cdot COOH$, melting at 235°, the *platinochloride* of which melts at 220—224°; when reduced with sodium amalgam, the acid yields dimethylamine and paratoluic acid. *w*-Chlorotoluic acid reacts with *w*-dimethylamine-paratoluic acid, yielding *dimethylamidodibenzylparadicarboxylic acid*, $COOH \cdot C_6H_4 \cdot CH_2 \cdot CH(NMe_2) \cdot C_6H_4 \cdot COOH$, which melts at 268—270°; the *hydrochloride* and *picrate* melt at 227° and 212° respectively. *w*-Chloroparatoluamide is converted by sodium ethoxide into an *ethoxy-compound* which melts at 112°, and is hydrolysed by soda to *w*-ethoxyparatoluic acid, $OEt \cdot CH_2 \cdot C_6H_4 \cdot COOH$, melting at 87°.

Paratoluic acid is converted by phosphorus pentachloride into the chloride, and when this is chlorinated at the boiling temperature, and that fraction of the product which boils at 265—270° treated with dimethylamine, *w*-dimethylamidoparatoluic acid is obtained. The aniline derivatives prepared were $NHPh \cdot CH_2 \cdot C_6H_4 \cdot CO \cdot NHPh$, m. p. 183°; $NHPh \cdot CH_2 \cdot C_6H_4 \cdot CONH_2$, m. p. 150°; $NHPh \cdot CH_2 \cdot C_6H_4 \cdot COOH$, m. p. 50°.

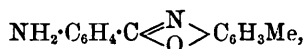
C. F. B.

Amido-derivatives of Benzenylamidophenols. By EUGEN LELLMANN and LUDWIG EBEL (*Ber.*, 1895, **28**, 1127—1129).—It has been already shown (*Abstr.*, 1894, i, 79) that substances containing the second of the groups—



like those containing the first, are substantive colouring matters; it is now shown that compounds containing the third of these groups are also substantive dyes.

1 : 4- and 1 : 3-*Amidobenzenyl*-1 : 2-*amido*-1 : 4-*cresols*,



were obtained by reducing with stannous chloride the corresponding nitrotylic salts of nitrobenzoic acids, themselves prepared by the action of 1 : 4- and 1 : 3-nitrobenzoic chlorides on nitrocresol [$\text{Me} : \text{NO}_2 : \text{OH} = 1 : 3 : 4$]. The 1 : 4-base crystallises in two different forms, which melt at 187° and 188°; the colourless 1 : 3-base melts at 143—144°. Both bases yield red substantive dyes when diazotised, and combine with β -naphthol, &c. C. F. B.

The Carbodiphenylimides. By WILHELM V. MILLER and JOSEF PLÖCHL (*Ber.*, 1895, **28**, 1004—1012).—Schall has described (*Abstr.*, 1892, 1452) three isomeric carbodiphenylimides, the α - and β -compounds being, according to him, stereoisomerides, whilst the β - and γ -compounds are physical isomerides. The authors have repeated his experiments, and find that there are only two distinct substances, the empirical formulæ of which are the same, but that the β -modification has three times the molecular weight of the α -form, its molecular weight having been determined by the cryoscopic method in benzene solution. The γ -form appears to be simply a mixture of varying amounts of the α - and β -compounds. A. H.

Phenylimidocarbonates. By ARTHUR HANTZSCH and LUDWIG MAI (*Ber.*, 1895, **28**, 977—984).—Phenylimidocarbonates, $\text{NPh} \cdot \text{C}(\text{OR})_2$, are obtained by adding isocyanophenylchloride, $\text{NPh} \cdot \text{CCl}_2$, (1 mol.) to a solution of a substituted sodium phenoxide (2 mols.) in ether and alcohol, and heating the mixture at 100°; when heated with strong hydrochloric acid, they yield aniline and carbonates, $\text{CO}(\text{OR})_2$. If only 1 mol. of sodium phenoxide is used, phenylimidochloroformates, $\text{NPh} \cdot \text{CCl} \cdot \text{OR}$, are obtained; when heated with alcohol, these yield phenylamidocarbonates (urethanes), $\text{NHPh} \cdot \text{COOR}$; and when heated with sodium derivatives of phenols, mixed phenylimidocarbonates, $\text{NPh} \cdot \text{C}(\text{OR}') \cdot \text{OR}$ are formed. These last could not be shown to exist in geometrically isomeric forms, an identical product, $\text{NPh} \cdot \text{C}(\text{OPh}) \cdot \text{OC}_6\text{H}_4\text{Br}$, being obtained either by the action of $\text{NaO} \cdot \text{C}_6\text{H}_4\text{Br}$ on $\text{NPh} \cdot \text{CCl} \cdot \text{OPh}$, or of NaOPh on $\text{NPh} \cdot \text{CCl} \cdot \text{OC}_6\text{H}_4\text{Br}$. By these reactions the following substances were prepared; the numbers are melting points.

Phenylic phenylimidocarbonate, 136°. 1 : 4-*Bromophenylic phenyl*-

imidocarbonate, 106° ; di-1 : 4-bromophenylic carbonate, 171° . Phenyllic phenylimidochloro-formate, $42-45^{\circ}$; boils at 180° under 15 mm., at $199-200^{\circ}$ under 22 mm. pressure. 1 : 4-Bromophenylic phenylimidochloro-formate, 45° ; boils at 227° under 23 mm., at 223° under 22 mm. pressure; 1 : 4-bromophenylic phenylamidocarbonate, 144° ; 1 : 4-chlorophenylic phenylamidocarbonate, 138° . Phenyllic 1 : 4-bromophenylic phenylimidocarbonate, 83° .

Isocyanophenylchloride reacts with piperidine in ethereal solution as it does with aniline, and yields phenyldipiperidylguanidine, $\text{NPh}\cdot\text{C}(\text{NC}_5\text{H}_{10})_2$, melting at 84° . The phenylimidochloro-formates (see above) also react with piperidine and with ammonia, yielding "isocarbamides," $\text{NPh}\cdot\text{C}(\text{NHR}')\cdot\text{OR}$. Of these, phenyl-1 : 4-bromophenylisocarbamide, 142° , was prepared with ammonia; diphenylpiperidylisocarbamide, 86° , and phenyl-1 : 4-bromophenylpiperidylisocarbamide, 91° , with piperidine.

C. F. B.

Preparation of Paraquinones from Indophenols. By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1894, [3], 11, 1129—1130).—Indophenol, $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, and its homologues are hydrolysed by acids into dimethylparaphenylenediamine and quinone or homologues of the compound. The substance is merely dissolved in moderately strong sulphuric acid (7 parts of 40 per cent. acid), and the cooled solution extracted with ether. The product obtained on removing that solvent is then distilled with steam and recrystallised from a mixture of alcohol and ether. With the indoparaxylols, indocarvacrol, and indothymol, the yield of the quinone is quantitative, but with indophenol and the indocresols somewhat less, the stability of the molecule appearing to decrease as the number of groups attached to the benzene nucleus increases.

JN. W.

Indophenols. By PIERRE H. BAYRAC (*Bull. Soc. Chim.*, 1894, [3], 11, 1131—1136).—The author has prepared several indophenols by the process used in the preparation of indothymol (Abstr., 1892, 1311), namely, by oxidising mixtures of dimethylparaphenylenediamine and the respective phenols with potassium dichromate in acetic acid solution, the diamine hydrochloride being prepared at the time by reducing paranitrosodimethylaniline hydrochloride with zinc dust. The yield is usually good.

The indophenols appear to crystallise in the triclinic system. They are practically insoluble in water, although the latter is coloured an intense blue by the trace dissolved, but they dissolve freely in the usual organic solvents yielding violet or blue solutions. As stated in the preceding abstract, they are hydrolysed by mineral acids into dimethylparaphenylenediamine and the respective quinones.

Dimethylanilquinonimide (indophenol), $\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\cdot\frac{1}{2}\text{H}_2\text{O}$, crystallises in steel-gray needles, and darkens at 100° , owing to the loss of its water of crystallisation; the anhydrous salt melts at $133-134^{\circ}$. Dimethylanilorthotoluquinonimide crystallises in rhombic needles, green by reflected light, and melts at 123° . The corresponding meta-compound crystallises in prisms, golden-yellow by reflected light, and melts at $117-118^{\circ}$. Dimethylanilparaxyloquinonimide,

$\text{O}:\text{C}_6\text{H}_2\text{Me}_2:\text{N}:\text{C}_6\text{H}_4:\text{NMe}_2$ ($\text{O}:\text{Me}_2:\text{N} = 1:2:5:4$), crystallises in reddish-brown plates and melts at $125-126^\circ$. *Dimethylanilethylquinonimide*, $\text{O}:\text{C}_6\text{H}_3\text{Et}:\text{N}:\text{C}_6\text{H}_4:\text{NMe}_2$ ($\text{O}:\text{Et}:\text{N} = 1:2:4$), crystallises in long, rhombic plates, golden-yellow by reflected light, and melts at $83-84^\circ$. *Dimethylanilthymoquinonimide*, $\text{O}:\text{C}_6\text{H}_2\text{MePr}:\text{N}:\text{C}_6\text{H}_4:\text{NMe}_2$ ($\text{O}:\text{Me}:\text{Pr}:\text{N} = 1:3:4:6$), crystallises in triclinic, rhomboidal plates, also golden-yellow by reflected light, and melts at $87-88^\circ$.

JN. W.

Reduction of Aromatic Nitro-derivatives in Neutral Solution: Formation of Aromatic Hydroxylamines. By AUGUSTE LUMIÈRE, LOUIS LUMIÈRE, and ALPHONSE SEYEWITZ (*Bull. Soc. Chim.*, 1894, [3], 11, 1038—1045; compare Bamberger, *Abstr.*, 1894, i, 373, 412, and Wohl, *ibid.*, 409, 450).—Wohl and Bamberger's method of reducing nitro-compounds to β -hydroxylamines by means of zinc dust and water is not applicable to the nitrophenols and nitranilines, as these substances are completely reduced to the corresponding amidophenols and diamines by that reagent. The method, however, promises to be of commercial importance for the preparation of the latter bases, as the yield is extremely good, and the products pure. Ortho- and para-amidophenol and ortho- and para-phenylenediamine can be prepared in this way, and certain dinitro-compounds, such as dinitrobenzene, dinitronaphthalene, and 1:2:4-dinitrophenol, appear to undergo a similar reduction.

The homologues of nitrobenzene, on the other hand, readily yield substituted hydroxylamines, provided a small quantity of calcium or other chloride be present. β -*Paratolylhydroxylamine*, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{OH}$, crystallises from benzene in well-developed plates and melts at $92-93^\circ$. It is easily oxidised to paramethylazoxybenzene, azoxy-paratoluene, or amidocresol, and is, of course, a powerful reducing agent. The *hydrochloride* crystallises in colourless needles. The *nitroso-derivative*, $\text{NO}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}\cdot\text{OH}$, forms colourless crystals and melts at $57-58^\circ$. *Additive compounds* with benzaldehyde and formaldehyde were also prepared; the benzaldehyde compound is crystalline and melts at 120° . Paratolylhydroxylamine may be used as a developer in photography. β -*Orthotolylhydroxylamine* is an oil having properties similar to those of the para-compound. β -*Paraxylhydroxylamine*, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NHOH}$ ($\text{Me}_2:\text{NHOH} = 1:4:5$), forms colourless crystals and melts at $88-89^\circ$. The *hydrochloride* crystallises in colourless plates. α -Nitronaphthalene yielded a liquid product having strong reducing properties, but nothing could be isolated from it but α -naphthylamine.

JN. W

Action of Hydroxylamine on Phthalic Anhydride. By GIORGIO ERRERA (*Gazzetta*, 1894, 24, ii, 469—474).—*Hydroxylamine phthalylhydroxamate*, $\text{OH}\cdot\text{NH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{COO}\cdot\text{NH}_2\cdot\text{OH}$, is prepared by mixing alcoholic solutions of hydroxylamine hydrochloride and sodium ethoxide, separating the deposited sodium chloride and adding phthalic anhydride to the solution; the salt separates as a colourless, crystalline substance soluble in water; its solutions give a red coloration with ferric chloride, and reduce Fehling's solution. It decomposes at $130-135^\circ$, yielding phthalylhydroxylamine, hydroxyl-

amine, and water; ammonium phthalylhydroxamate is also formed as a product of secondary action.

By employing a smaller proportion of hydroxylamine than that used in the above preparation, sodium phthalylhydroxamate is obtained.

W. J. P.

Isomerism in the Azo-series. By ARTHUR HANTZSCH (*Ber.*, 1895, **28**, 1124—1126).—The compounds obtained by Bamberger (this vol., i. 351) from nitrodiazobenzene salts and α -naphthol are not, as he thinks, stereochemically isomeric, but are structurally isomeric, the $\cdot\text{N}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$ group occupying, in the α - and β -compound respectively (melting at 277—279° and 235°), the 4- and 2-positions with respect to the OH of the naphthol. This is shown by the fact that the two compounds, when reduced with stannous chloride, yield respectively 4 : 1- and 2 : 1-amidonaphthol.

C. F. B.

Methylphenyldithiobiuret and Methylphenylthiuret. By EMIL FROMM and ERNST JUNIUS (*Ber.*, 1895, **28**, 1096—1101; compare *Abstr.*, 1893, i, 575).—*Methylphenyldithiobiuret* (*biuramine*) was prepared by heating methylaniline with perthiocyanic acid, $\text{C}_2\text{H}_2\text{N}_2\text{S}_3$, at 100°; it forms white crystals, melts at 156°, and dissolves in alkalis, but not in dilute acids. When it is oxidised with iodine, it reacts as if it had the constitution $\text{NMePh}\cdot\text{C}(\text{SH})\cdot\text{N}\cdot\text{C}(\text{SH})\cdot\text{NH}$, and yields *methylphenylthiuret*, $\text{NMePh}\cdot\text{C}\leq\text{N}\text{>}\text{C}\cdot\text{NH}$. This substance could not be isolated, but it acts as a monacid base, and its *hydrochloride*, *hydrobromide*, and yellow *hydriodide* melt respectively at 232°, 220°, and 193°; when boiled with aqueous potash, it yields ammonia and methylaniline.

C. F. B.

Condensation of Methylphenyldithiobiuret with Aldehydes and Ketones. By EMIL FROMM and ERNST JUNIUS (*Ber.*, 1895, **28**, 1102—1113).—When methylphenyldithiobiuret (compare preceding abstract) is mixed with an aldehyde or ketone, $\text{O}\cdot\text{CXR}$, and hydrogen chloride passed into the mixture, it reacts as if it had the constitution $\text{NMePh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$, and yields compounds $\text{NMePh}\cdot\text{CS}\cdot\text{N}\langle\text{CXR}\rangle\text{NH}$. With acetone, it yields α -methylphenyl-dithio-dimethylketuret, melting at 152°; with benzaldehyde, α -methylphenyldithiophenylalduret, melting at 168°; with acetaldehyde, the reaction is anomalous. When the above-mentioned keturet and alduret are dissolved in cold alcoholic soda, and the solutions allowed to remain with benzylic chloride, *monobenzyl derivatives* are formed, melting respectively at 85° and 127°. When these are heated on the water bath with strong hydrochloric acid, they are decomposed; the keturet yields, besides methylaniline, ammonia, carbonic anhydride, hydrogen sulphide, benzylic hydrosulphide, and bisulphide, some acetone and benzylic imidotrithiodicarboxylate,



doubtless formed by the action of benzylic hydrosulphide on the compound $\text{CSOH}\cdot\text{NH}\cdot\text{COSC}_6\text{H}_5$ first formed. In the case of the

alduret, the last compound is not formed; benzaldehyde is liberated in place of acetone, and benzylic hydrosulphide reacting more readily with it than it does with acetone, the compound $C_6H_5 \cdot CH(SC_2H_5)_2$ is obtained, and no benzylic imidotrithiodicarboxylate. This substance is however obtained, together with the compound mentioned, if excess of benzylic hydrosulphide is present from the beginning of the reaction. *Benzylic imidotrithiodicarboxylate* crystallises in yellowish needles, and melts at $144-145^\circ$; when treated with alcoholic ammonia, it yields monothiobiuret.

C. F. B.

Combination of Benzaldehyde with Hydrocyanic acid in Dilute Solution. By E. UTSCHER (*Chem. Centr.*, 1894, ii, 675—676; from *Pharm. Post*, 27, 417—421).—Contrary to Glücksmann the author maintains that the combination of benzaldehyde with hydrogen cyanide is a very rapid process even in dilute solution. Benzaldehyde was mixed with hydrocyanic acid and alcohol in the proportion of 1 part of the acid to 6 parts of the aldehyde, the solution containing 0.1 per cent. of hydrogen cyanide in one experiment and 0.2 per cent. in another. In the case of the 0.2 per cent. solution, 0.0845 per cent. of acid was left uncombined after 60 hours, 0.0245 per cent. after five days, and 0.0137 per cent. after 10 days. In water with 0.1 per cent. of hydrogen cyanide, the combination is more gradual. The author has already shown that benzaldehyde cyanhydrin is not completely decomposed by dilute potash. Hydrogen cyanide which has been mixed with excess of ammonia, then with excess of nitric acid, and with N/10 silver nitrate solution, shows when titrated by Volhard's method a lower content of hydrogen cyanide the longer the time which is allowed to elapse between the addition of the nitric acid and of the silver nitrate; thus, in a quarter of an hour the amount indicated dropped from 0.503 per cent. to 0.495 per cent. Glücksmann used a hydrocyanic acid solution of about half this strength; he also employed too small a proportion of benzaldehyde.

A. G. B.

Condensation of Mandelic acid with Phenols. By AUGUSTIN BISTRZYCKI and J. FLATAU (*Ber.*, 1895, 28, 989—991).—When mandelic acid (5 parts) is heated with phenol (7 parts) in the presence of 73 per cent. sulphuric acid (20 parts), a compound is formed which is probably *hydroxydiphenylacetic lactone*, $CHPh < \begin{smallmatrix} C_6H_5 \\ CO \end{smallmatrix} > O$; the yield is 22 per cent. of the theoretical. The lactone melts at $113-114^\circ$, and boils at 337° ; when boiled with aqueous, sodium carbonate, it yields the sodium salt of the acid, which itself melts at $85-87^\circ$. In a similar manner *phenyl-1:4-cresylacetic acid* and its lactone were obtained from mandelic acid and 1:4-cresol; they melt at 118° and 106° respectively.

C. F. B.

Coumarincarboxylates and a New Synthesis of Coumarin. By PIETRO BIGINELLI (*Gazzetta*, 1894, 24, ii, 491—503).—*Ethyllic metahydroxycoumarin- β -carboxylate*,
$$\begin{array}{c} C(OH) \cdot CH \cdot C \cdot C(COOEt) \cdot CH \\ | \qquad \qquad \qquad || \qquad \qquad \qquad | \\ CH = CH \cdot CO \text{-----} CO \end{array}$$
 is

obtained by adding concentrated sulphuric acid to a solution of quinol in ethylic oxalacetate; it exists in two modifications which are separated by crystallisation from alcohol and ether; the least soluble modification crystallises in yellow laminæ melting at 177—178°, whilst the more soluble crystallises in yellow prisms melting at 180—182°. The former isomeride may be converted into the modification of higher melting point by boiling with dilute alcohol, and the author concludes that they are stereoisomerides. The ethylic salts are accompanied by small quantities of the free *acids* which are, however, best prepared by hydrolysing these salts with potash, adding acid, and crystallising from water; the one acid crystallises in thin, yellow needles melting at 279—280°, whilst the other forms acicular laminæ melting at 283—284°. When heated at 280—290°, the acids distil with partial decomposition, and are deposited in yellow laminæ melting at 289°. The *sodium* salt crystallises from water in needles containing $1\text{H}_2\text{O}$, which is lost at 100°, but is deposited from alcohol in prisms containing $\frac{1}{2}\text{H}_2\text{O} + \frac{1}{2}\text{EtOH}$; the salt is very soluble in water, and, on treatment with acids, yields the acid melting at 280°.

Although carbonic anhydride is evolved on heating the above acid, the hydroxycoumarin cannot be isolated from the residue, and can only be prepared from the acid by the process described below.

Methylic metamethoxycoumarin-β-carboxylate, $\text{OMe}\cdot\text{C}_9\text{H}_7\text{O}_2\cdot\text{COOMe}$, is obtained by treating the above acid in methylic alcoholic potash solution with methylic iodide; it crystallises in needles, melts at 131—132°, and is readily hydrolysed by alkalis yielding the corresponding *acid*, which crystallises in yellow laminæ melting at 246—247°. On heating the acid with iron dust, or its sodium salt with caustic soda, the metamethoxycoumarin melting at 102—103° is obtained; on treatment with hydriodic acid, it yields the meta-hydroxycoumarin melting at 249°.

W. J. P.

Triacetylgallic acid. By PAUL CAZENEUVE (*Bull. Soc. Chim.*, 1894, [3], 11, 937).—A reply to Schiff (this vol., i, 368).

Triacetylgallic acid. By PAUL SISLEY (*Bull. Soc. Chim.*, 1894, [3], 11, 938—939).—Boettinger's triacetylgallic acid (*Abstr.*, 1884, 1178) is identical with the author's diacetylgallic acid (this vol., i, 283). Boettinger's pentacetyltannin (*loc. cit.*) is identical with the triacetylgallic acid of Schiff and the author (*loc. cit.*).

As diacetylgallic acid does not give a colour reaction with ferric chloride, the absence of a coloration with that reagent must not be taken as conclusive evidence of the absence of phenolic hydroxyl from the molecule.

JN. W.

Hemipinic acid and its Ethereal Salts. By RUDOLF WEGSCHEIDER (*Monatsh.*, 1895, 16, 75—152; compare *Abstr.*, 1882, 1206, and 1891, 712).—Hemipinic acid, $\text{C}_6\text{H}_2(\text{OMe})_2(\text{COOH})_2 = [1 : 2 : 3 : 4]$, is most readily obtained by treating opianic acid oxime with potash, or by oxidising opianic acid itself with potassium permanganate. This acid appears to exist in only one modification; the different melting points, varying from 160° to 178°, given by different authori-

ties, are due to the fact that it is partially converted into the anhydride even before it melts. The amount of anhydride thus formed depends on the length of time during which the acid is heated, and consequently the melting point also varies with the rate of heating.

The monalkylic salts of hemipinic acid form two isomeric series, the α and β , the normal alkylic salts only one.

	Methylic.	Ethylic.	Normal propylic.
Normal salt, m. p. =	61—62°	72°	43—45°
α -acid salt, m. p. =	121—122	144·0—145°	119·0—120·0° and 131—132·0°
β -acid salt, m. p. =	137—138	147·5—149	111·5—112·5 and 125—125·5

The α -monethylic and both α - and β -monopropylic hemipinate occur in desmotropic forms. The two α -ethylic salts have the same melting point, but differ in other physical properties. The propylic salts have the melting points given above.

All the monalkylic salts when heated yield hemipinic anhydride and the corresponding alcohol.

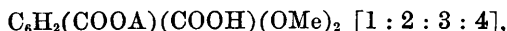
The α -ethereal salts are best obtained—(1) By the oxidation of the true ethereal salts of opianic acid. (2) By boiling hemipinic anhydride with the requisite alcohol; a small quantity of the β -salt is also formed in this reaction. (3) By heating potassium hydrogen hemipinate with alcohols and alkylic iodides; this reaction is, however, incomplete. (4) By the hydrolysis of the normal ethereal salts.

The α -ethereal salts give a yellow coloration and milky turbidity with very dilute ferric chloride solution.

The isomeric β -derivatives are best obtained by saturating a solution of the acid in alcohol with dry hydrogen chloride. The β -salts are the first products formed, but if the saturation is carried out for several hours at the boiling point of the alcoholic solution, normal salts are also obtained, and these, in the presence of the hydrogen chloride, become hydrolysed to the α -salts.

The silver salts of both α - and β -derivatives, when heated at 200—230° under a pressure of 21 mm., are decomposed, and yield ethylic veratrate, together with hemipinic acid.

The α -salts have the constitution $C_6H_2(COOH)(COOA)(OMe)_2$ [1 : 2 : 3 : 4], since they are obtained by the oxidation of the corresponding opianates; and the constitution



for the β -series follows from the law of V. Meyer and Sudborough. The author discusses the theories of Friedel and of Henry, regarding the etherification of acids, by means of alcohol and hydrogen chloride, in the light of the recent observations of Meyer and Sudborough. Henry's hypothesis, according to which the etherification is preceded by the addition of the elements of the alcohol to the carbonyl group of the acid, is considered the more probable. It may be, however, that it is the hydrogen chloride and not the alcohol which unites with the carbonyl group. The presence of substituting groups in the ortho-positions may thus prevent the formation of such additive compounds, just as according to Meyer and Sudborough's theory such

groups can prevent the direct entry of alkyl radicles. If this is true, then we must expect to meet similar phenomena in the formation of imido-ethers, amidines, and amidoximes. Similarly diortho-substituted aldehydes should be incapable of taking part in reactions which require the formation of additive compounds.* Hemipinic and camphoric acids exhibit very similar phenomena when etherified, but as the constitution of camphoric acid has not been definitely determined, the two series cannot be very closely compared. It can be shown, however, that the etherification does not depend on the strength of the carboxylic group, as in hemipinic acid the weaker carboxylic group is the first to be etherified, but in camphoric acid the reverse is true. By the action of alkalis on the normal ethereal salts of both acids, the first carboxylic group to be hydrolysed is the one which is the first to be etherified.

J. J. S.

Preparation of Ethylenediphenylsulphone. By ROBERT OTTO and K. MÜHLE (*Ber.*, 1895, **28**, 1120—1122).—*Ethylenediphenylsulphone* (Escales and Baumann, *Abstr.*, 1887, 123) can be conveniently prepared by oxidising ethylenedithiophenyl, prepared from ethylenic dichloride and sodium thiophenoxide (*J. pr. Chem.*, [2], **51**, 518), with permanganate in acetic acid solution, and removing the admixed manganese oxide with sulphurous anhydride.

C. F. B.

Derivatives of Benzylideneacetophenone. By CARL GOLDSCHMIDT (*Ber.*, 1895, **28**, 986).—Benzylideneacetophenone yields two *oximes*, melting respectively at 68° and 140°; the latter is gradually transformed into the former when kept. It also yields two *nitro-derivatives*; one melts at 159°, the other is an oily 1:2-derivative, which yields 2'-phenylquinoline when reduced with stannous chloride.

C. F. B.

Paratoluoylorthobenzoic acid and Benzophenonedicarboxylic acid. By HEINRICH LIMPRICHT (*Ber.*, 1895, **28**, 1134—1135).—Paratoluoylorthobenzoic acid could not be obtained crystallised with H₂O, as Friedel and Crafts describe it; the melting point, further, was 138—139° instead of 146°. When oxidised with permanganate, it yields *benzophenonedicarboxylic acid*, CO(C₆H₄·COOH)₂, which crystallises with H₂O and also anhydrous; the anhydrous acid melts at 239°, its *methylic salt* at 107°. With acetic anhydride, the acid yields a *diacetyl derivative*, melting at 182°. The *acid chloride* melts at 110°, and, when treated with zinc-ethyl in ethereal solution, yields the *ketone*, CO(C₆H₄·CO·C₂H₅)₂, which melts at 105°.

C. F. B.

A Colour Reaction of Carbazole. By GIACOMO CARRARA (*Gazzetta*, 1894, **24**, ii, 535—540).—On heating carbazole (1 mol.) with salicylaldehyde (2 mols.) and concentrated sulphuric acid at 100—110°, an intensely blue product is obtained; it contains, in addi-

* V. Meyer (*Ber.*, 1895, **28**, 1267) has shown that this is probably true for Perkin's reaction.—J. J. S.

tion to carbazolemono- and di-sulphonic acids, an amorphous reddish colouring matter, which forms a barium salt, contains much sulphur, and is soluble in water, alcohol, ether, and benzene. It dyes mordanted silk and cotton, and is still under investigation.

W. J. P.

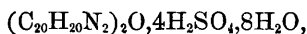
New Series of Colouring Matters. By CHARLES FRIEDEL (*Bull. Soc. Chim.*, 1894, [3], 11, 1027—1028).—*Dimethyldiazidomethyl-*

diphenylchloromethane hydrochloride,
$$\text{N} \begin{array}{c} \text{CMe} \text{---} \text{CH} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \cdot \text{CMeCl} \cdot \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \\ \text{CH} \text{---} \text{CMe} \end{array} \text{N} \cdot \text{HCl},$$

formed by the action of phosphoric oxychloride on methylacetanilide at 120°, is probably a condensation product of methylacetanilide with its acetyl derivative, as hydrogen chloride and methylaniline are eliminated in the reaction. It crystallises from alcohol, in which it dissolves to a crimson solution, in small needles, which are blue by reflected and red by transmitted light. As the *dihydrochloride* is practically colourless, the base promises to be of use as an indicator in alkalimetry, for the acid solution is coloured crimson even by aniline; the colour is discharged, however, by carbonic anhydride and acetylacetone, although it is not affected by phenol. The hydrochloride dyes wool and silk as well as cotton mordanted with tannin, but the colour, although unaffected by soap, is not very fast to light, and is of course discharged by acids.

When the hydrochloride is boiled with alkali sulphites, it is converted into the *sulphite* $\text{C}_{20}\text{H}_{20}\text{N}_2\text{SO}_3$, a substance crystallising in small, golden, rhomboidal plates having a greenish metallic lustre; this is insoluble in water, but soluble in hot alcohol, yielding a violet solution, and is decomposed by hydrochloric acid. The *benzoate* crystallises in small needles having a greenish, metallic lustre. The *nitrate* and *acetate* are also coloured.

When a stream of air is passed through the boiling hydrochloric acid solution of the sulphite, the latter is converted into *dimethyldiazidomethyl-diphenylmethylic oxide*, $(\text{C}_{20}\text{H}_{20}\text{N}_2)_2\text{O} \cdot \text{H}_2\text{O}$, which is precipitated in crimson flakes by caustic alkalis, and crystallises from alcohol in orange prisms. The *sulphate* of this oxide,



crystallises in colourless, rectangular plates, and is rose-coloured when anhydrous. The oxide is reconverted into the original chlorinated base by the action of phosphoric oxychloride in benzene solution, but by the prolonged action of this reagent is transformed into a *blue colouring matter*, which is also formed from the original hydrochloride by oxidation with air in presence of alkali.

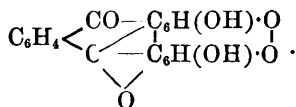
On distilling the hydrochloride with zinc dust, a *leuco-base*, $\text{C}_{20}\text{H}_{22}\text{N}_2$ or $\text{C}_{20}\text{H}_{24}\text{N}_2$, is obtained as a colourless oil, boiling at about 260°. The *platinochloride* of this base was prepared. JN. W.

Coloured Sulphonic Derivatives of Triphenylmethane. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1894, [3], 11, 1188—1190).—Solutions of "acid rosaniline," $\text{OH} \cdot \text{C}[\text{C}_6\text{H}_3(\text{SO}_3\text{Na}) \cdot \text{NH}_2]_3$, and other sulphonated colouring matters of the same type, are decolourised by

caustic alkalis, but quickly regain their colour on the addition of ammonium chloride. Rosenstiehl's view that the free substance is alcoholic and colourless does not offer any explanation of these facts, and is, in fact, in direct contradiction to them. If, however, it be granted that the free substance is acidic and coloured, whilst its sodium salt is colourless, an explanation is at once forthcoming. The ammonium salt, like the sodium salt, will be colourless, but prone to dissociation, so that, when the ammonium chloride is added, a considerable amount of the free acid will be liberated, and the colour restored. If this assumption be true, a solution of the dye, which has been decolorised by excess of ammonia, should tend to regain its colour on heating, but lose it again on cooling, unless the ammonia has been expelled by the heat, and this is actually the case. A further confirmation is found in the behaviour of an alkaline solution to which an equivalent amount of ammonium chloride has been added; on evaporating the solution to dryness, the residue, which can contain nothing but sodium chloride and the free hydroxylic substance, or its anhydride, regains the colour of the dye.

JN. W.

Cœruleïn. By MAURICE PRUD'HOMME (*Bull. Soc. Chim.*, 1894, [3], 11, 1136—1138).—When cœruleïn is fused with aniline hydrochloride, a blue colouring matter is formed, which dyes bluish-green with iron and chromium mordants, and blue with those of aluminium. The condensation can be effected with the base itself by heating with a slight excess until the product appears to be dry, 2 mols. of aniline entering into combination, and 2 mols. of water being eliminated. The condensation product, after removal of the excess of aniline at 180°, is a violet powder, brownish-red by reflected light. It is sparingly soluble in water, but easily in concentrated sulphuric acid to a solution, which is blue when diluted, and from which the base is precipitated in greenish flocks by alkalis. The acetate dyes mordanted cotton greenish-blue, and wool and silk blue without mordants, but the colours are not fast to soap, owing to the liberation of the greenish base by the alkali. The base does not combine with the mordants of the aluminium group, so that its molecule does not contain hydroxyl. Since 2 mols. of water are eliminated in the condensation, it is probable that the cœruleïn molecule contains two hydroxyl groups; and as it also contains a phenylanthranol nucleus, its constitution may possibly be represented by the formula



JN. W.

1 : 4-Dimethylnaphthol. By STANISLAO CANNIZZARO and AMERICO ANDREOCCHI (*Gazzetta*, 1895, 25, i, 53—59).—The oxidation product of the dimethylnaphthol obtained by the decomposition of santanous acid (*Abstr.*, 1894, i, 143), is probably an oxydimethylnaphthol of the constitution $\text{C}_6\text{H}_4 < \begin{array}{c} \text{CMe} \cdot \text{CH} \cdot \text{OH} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{CMe} \cdot \text{CO} \end{array}$; it yields a crystalline oxime which

melts at 175°, and a *monhydrazone*, crystallising in long, red needles melting at 83–84°, and, on reduction, yields the original dimethylnaphthol. On treatment with hydrochloric acid, the oxime yields a green crystalline *anhydride*, which is converted into a stable and volatile *isomeride* by alcoholic potash; this substance crystallises in red needles and melts at 173°.

An *acetyldimethylnaphthylamine*, $C_{10}H_5Me_2NHAc$ [= 1 : 4 : 2], is obtained by heating the dimethylnaphthol with acetamide under pressure; it crystallises in small, colourless prisms melting at 218–220°. On hydrolysis with sodium ethoxide at 150°, it yields the corresponding *dimethylnaphthylamine*, which crystallises in colourless prisms melting at 74°, boils at 333° under 745 mm. pressure, and gives the above acetyl derivative with acetic anhydride. On oxidation with permanganate, the amine yields an *azodimethylnaphthalene*, which crystallises in small, red needles melting at 253°; it is accompanied by a colourless, crystalline *acid*, still under examination.

W. J. P.

Phenolnaphthaleïn. By GEORGE F. JAUBERT (*Ber.*, 1895, **28**, 991–994).—Although phenol and naphthalic anhydride do not condense when heated together in the presence of most dehydrating agents, they do so when aluminium chloride is the agent used. The product, *phenolnaphthaleïn*, $CO < \overset{O^-}{C_{10}H_6} > C(C_6H_4 \cdot OH)_2$ [$CO : C = 1 : 1'$], is a white substance, and melts and decomposes at 120° when amorphous, and at 200° when crystalline; its solution in alkalis has a red colour, with rather more of a bluish shade than is the case with phenolphthaleïn. With phosphorus pentachloride, it yields a *chloride*, $C_{24}H_{14}O_2Cl_2$, melting at 180°; with hydroxylamine, a *yellowish oxime* melting at 220°.

C. F. B.

Action of Carbamide on Quinones. By SIRO GRIMALDI (*Gazzetta*, 1895, **25**, i, 78–79).—Phenanthraquinone and carbamide readily interact, giving two crystalline *compounds*, the one of which, $C_{15}H_{10}N_2O_2$, melts at 299°, whilst the other, $C_{16}H_{12}N_4O_2$, does not melt at 320°, and yields a crystalline *dinitro-derivative*, $C_{16}H_{10}N_4O_2(NO_2)_2$. With thiocarbamide and ammonium thiocyanate, phenanthraquinone yields a *dithioureide*, $C_{16}H_{12}N_4S_2$. β -Naphthaquinone reacts with carbamide, forming a *monoureide*, $C_{11}H_8N_2O_2$; anthraquinone similarly yields a *monoureide*, $C_{15}H_{10}N_2O_2$, whilst quinone gives a crystalline *monoureide*, $C_7H_6N_2O_3$, which does not melt at 320°.

W. J. P.

Essence of Cananga. By ALBERT REYCHLER (*Bull. Soc. Chim.*, 1894, [3], **11**, 1045–1051).—Cananga oil from Java has a sp. gr. = 0.9058 at 21°, a refractive index, $\mu = 1.49655$, and a specific rotatory power, $[\alpha]_D = -28.5^\circ$. The proximate constituents appear, on the whole, to be the same as those of essence of Ylang-ylang (this vol., i, 294), but their relative amounts are different. Thus, on hydrolysis, the cananga essence also yields acetic and benzoic acids, but only in small proportion, whilst a relatively large amount of volatile oil is obtained; this, again, contains but a small quantity of the alcoholic substance, the major portion consisting of a sesquiterpene.

The *sesquiterpene* boils at 252–257°; the sp. gr. = 0.9024 at 17°; the specific rotatory power, $[\alpha]_D = -32.2^\circ$ at 20°; the refractive index, $n = 1.50187$ at 17°. The molecular refraction = 66.8, and the iodine number = 255, so that two ethylene linkings are present in the molecule. The specific rotatory power, like that of other sesquiterpenes, is diminished, or even reversed, by heating at temperatures above 250°.

The *alcohol*, $C_{10}H_{18}O$, boils at 98–102° (20–21 mm.); the molecular refraction = 48.81, so that two ethylene linkings are present in the molecule, a conclusion confirmed by the iodine absorption.

Amongst the other substances isolated was an *oil* boiling at 166–173°, which, on oxidation with chromic acid mixture, yielded an acid, $C_9H_{10}O_3$, probably anisic acid.

Heine and Co., in a communication to the author, state that in addition to ylangol, they have isolated from essence of Ylang-ylang either geraniol, or some isomeride of that substance. J. N. W.

Action of Nitrous acid on Oximes of the Camphor (Camphane) Series. By ANGELO ANGELI and E. RIMINI (*Ber.*, 1895, 28, 1077–1078).—Camphoroxime, in glacial acetic acid solution, reacts with sodium nitrite; the product, $C_{10}H_{16}N_2O_2$, is crystalline, and melts at 43°. Camphenoxime yields a similar compound, $C_{10}H_{14}N_2O_2$, which melts at 47°. Both substances are insoluble in acids and alkalis, and neither of them gives Liebermann's reaction. Menthoneoxime appears to react with sodium nitrite in a similar manner (compare following abstract). J. B. T.

Conversion of Camphor into an Isomeric Unsaturated Compound. By ANGELO ANGELI (*Ber.*, 1895, 28, 1127).—The compound $C_{10}H_{16}N_2O_2$, obtained (preceding abstract) by the action of nitrous acid on camphoroxime, is attacked by cold strong sulphuric acid, a gas being evolved and a compound, $C_{10}H_{16}O$, isomeric with camphor, formed. This is an oily liquid, and yields an *oxime* melting at 106°. Both ketone and oxime immediately decolorise permanganate, and are therefore unsaturated compounds. C. F. B.

Camphor. By FERDINAND TIEMANN (*Ber.*, 1895, 28, 1079–1093).—*Camphorimine nitrate*, $C_{10}H_{16}NH.HNO_3$, is formed by the action of nitrous acid on camphoroxime; it is crystalline, and melts at 156°. *Camphorimine* is also crystalline, melts above 90°, evolves ammonia, and yields a number of decomposition products when exposed to air; it readily forms salts with acids, most of which are crystalline, and from them camphor may be regenerated. By the action of methylic iodide, *methylcamphorimine hydriodide*, $C_{10}H_{16}NMe.HI$, is formed.

Camphenylnitramine, $C_8H_{14} < \begin{smallmatrix} CH \\ | \\ C-NH \cdot NO_2 \end{smallmatrix}$, is formed, along with the imine; with alcoholic potash, it readily yields a crystalline *potassium* salt, which explodes violently on heating, and yields camphoric acid when oxidised with potassium permanganate. Determinations of its refractive power show that it contains a double linking (com-

pare preceding abstracts). By the action of hydriodic acid, camphor is formed; with ammonia, camphorimine is regenerated. The reaction has been studied in the case of other ketones and aldehydes; these differ both in the yield and also in the manner in which their oximes react with nitrous acid, but the method may be employed with advantage to convert isonitrosocamphor into camphorquinone.

Camphoroxime is readily converted into campholenitrile by the action of dehydrating agents (sulphuric acid, hydriodic acid), and this easily yields the amide by fusion with potash; when boiled with potash, it gives the amide and acid successively. The oxime and amide are lævogyrate, the nitrile and acid, like the original camphor, dextrogyrate. When the α -nitrile is hydrolysed with acids and the product treated with alkali, *isamidocamphor*, $C_{10}H_{15}O \cdot NH_2$, is formed; it is a saturated primary base, extremely stable towards alkalis, readily changed by acids, has an unpleasant odour, is crystalline, melts at 39° , and boils at 254 — 256° under normal pressure, and at 152° under 65 mm. pressure. The *salts* crystallise readily, and, when their solutions are heated, β -campholenamide, $C_{10}H_{17}NO$, is precipitated; this is also formed by the action of ammonia on β -campholenic acid (m. p. 52°), it melts at 86° , regenerates the acid by treatment with potash, and has been recently described by Béhal (this vol., i, 241); he appears to have prepared it from a mixture of the α - and β -nitriles; of these, the latter is more readily hydrolysed by potash than the former; his nitrile, regenerated from the hydrogen iodide derivative, yields a mixture of α - and β -amide (m. p. 92°). α -Campholenitrile is readily prepared by heating camphoroxime with sulphuric acid (20 per cent.); it boils at 225° . β -Campholenitrile is best obtained by the prolonged heating of camphoroxime with dilute hydriodic acid; it boils at 217° . No optically active β -campholene derivatives have been prepared.

Hydroxydihydrocamphenolactone, $C_{10}H_{16}O_2$, is formed when isamidocamphor hydrochloride is allowed to remain for some time in aqueous solution at the ordinary temperature; it is also obtained by heating α - or β -campholenic acid with strong acids; it boils and undergoes partial decomposition at 255° , is insoluble in water and soda at ordinary temperatures, and is not changed by boiling with water and calcium carbonate or, in ethereal solution, by treatment with ammonia. A *bromine derivative* is formed by the interaction of β -campholenic acid and bromine.

Hydroxydihydrocampholenic acid, $C_{10}H_{18}O_3$, crystallises in lustrous, colourless needles, melts at 105° , and is stable when pure, but traces of foreign substances cause its rapid conversion into the lactone. When quickly hydrolysed with alcoholic potash, the lactone is frequently converted into campholene, but the pure acid and α - and β -campholenic acids are very stable towards alkalis; statements to the contrary made by various observers are due to the use of acids containing a little lactone; the varying descriptions given of α - and β -campholenic acids is due to the same cause, since a trace of mineral acid suffices to convert α -campholenic acid into the lactone, and the latter always yields some β -campholenic acid when distilled. Attention is drawn to the considerable alterations in boiling and melting

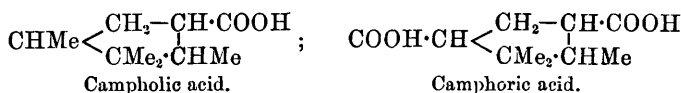
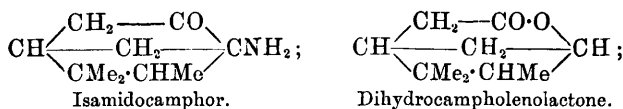
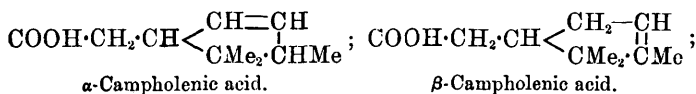
point produced in campholene derivatives caused by the presence of traces of impurity.

In discussing the constitution of camphor, exception is taken to Bredt's formula on the ground that it does not satisfactorily explain the behaviour of camphoroxime as a syn-derivative; if Bredt's formula is correct, the oxime should contain the complex $\text{CMe} \cdot \text{C} \cdot \text{CH}_2$ $\begin{smallmatrix} \text{N} \cdot \text{OH} \\ || \end{smallmatrix}$ and campholenic acid, campholic acid, and camphoric acid should have the formulæ $\text{CH}_2 \cdot \text{C}_8\text{H}_{13} \cdot \text{COOH}$, $\text{C}_8\text{H}_{14}\text{Me} \cdot \text{COOH}$, and $\text{C}_8\text{H}_{14}(\text{COOH})_2$ respectively, they ought, therefore, to yield similar decomposition products, and campholenic acid should be readily converted into the other

acids. To overcome this objection, the formula $\text{CH} \begin{smallmatrix} \text{CH}_2 - \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CMe}_2 \cdot \text{CHMe} \end{smallmatrix} \text{CH}$ is suggested for camphor; its conversion into cymene is preceded by the formation of a dihydrocarvone, $\text{CHPr}^{\beta} \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH} \end{smallmatrix} \text{CMe}$. The

corresponding formula for fenchone, $\text{CH} \begin{smallmatrix} \text{CH} \cdot \text{CHMe} \\ \diagup \quad \diagdown \\ \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CMe} - \text{CO} \end{smallmatrix} \text{CH}$, obtains support from Wallach's work (*Annalen*, 1895, 284, 341).

For camphene and pinene, the formulæ $\text{CH} \begin{smallmatrix} \text{CH} = \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CMe}_2 \cdot \text{CHMe} \end{smallmatrix} \text{CH}$ and $\text{CH} \begin{smallmatrix} \text{CH}_2 - \text{CH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{CMe}_2 \cdot \text{CHMe} \end{smallmatrix} \text{C}$ respectively are deduced; the latter is in complete accord with investigations by the author and F. W. Semmler, which will be published shortly. The formulæ of the more important compounds referred to above are as follows.



In a supplementary note, Béhal's later communication (this vol., i, 241) is summarised and discussed. Béhal regards the campholenic acids as stereoisomeric, although unable to prepare an optically active form of the β -acid; the author points out that, although according to the above formula it contains an asymmetric carbon atom, the optical activity is lost as soon as a compound of the α -series is converted into the β -series, even though haloid acids are excluded; he considers

that this supports his formula, and shows that the optical activity is dependent on the asymmetry or otherwise of the carbon atom in the CMe group.
J. B. T.

Derivatives of Quercetin. By CARL T. LIEBERMANN (*Monatsh.*, 1895, 16, 180—182).—A reply to J. Herzig's criticisms on some of the author's previous analyses (*Abstr.*, 1884, 1365). It is shown that these old analyses agree very well with the new formula, $C_{15}H_{10}O_7$, suggested for quercetin by Herzig.
J. J. S.

Action of Potassium Permanganate and of Hydriodic acid and Red Phosphorus on Rottlerin. By PIETRO BAROLOTTI (*Gazzetta*, 1894, 24, ii, 480—484; compare *Abstr.*, 1894, i, 301).—Rottlerin is readily oxidised by alkaline permanganate in the cold with formation of benzoic and oxalic acids; chromic acid attacks rottlerin very slowly, and only very little benzoic acid is formed.

Resinous products are obtained on heating rottlerin with hydriodic acid in sealed tubes at 210—220°, but, on heating at the same temperature with hydriodic acid and red phosphorus, a pleasant-smelling oil, lighter than water, is formed; it boils at 140—240°, and the fractions boiling at 140—150° and at 230—240° have the same composition, namely $C_{10}H_{16}$ or $C_{11}H_{18}$. The examination of this oil is being continued.
W. J. P.

Yeast Glucose. By CARL J. LINTNER and E. KRÖBER (*Ber.*, 1895, 28, 1050—1056).—Dried yeast, when extracted with water at ordinary temperatures, yields an enzyme which readily hydrolyses maltose; the temperature of maximum action is about 40°, and it is therefore different from invertin and from maize glucose, which act most readily at 52—53° and 57—60° respectively. The enzyme becomes inactive at 55°. Up to 35°, its action is proportional to the temperature, the quantity present, and the time of action remaining constant. Increase in the quantity of enzyme does not proportionately accelerate the inversion; the addition of chloroform considerably retards the hydrolysis, only about 70 per cent. of maltose being decomposed after 24 hours. The enzyme is without action on dextrin. Full analytical details are given, and the results are tabulated and illustrated by curves.
J. B. T.

Protochlorophyll. By NICOLAI A. MONTEVERDE (*Ann. Agron.*, 1895, 21, 90; from *Acta horti. Petropolit.*, 1894, 201—217).—Etiolated leaves contain, besides xanthophyll and carotene, a colouring matter termed "protochlorophyll," which shows a red fluorescence; its absorption spectrum has a band corresponding with the chlorophyll band III, and another band at some distance from the chlorophyll band II, whilst the band I of chlorophyll is entirely wanting. The spectrum is displaced a little towards the right by alkalis. The substance in alcoholic solution is transformed by a few drops of hydrochloric or nitric acid into "protochlorophyllane." Protochlorophyll is separated as follows. The leaves are cut up, extracted with boiling water, pressed, and put into alcohol of 95°. The alcoholic solution

is precipitated with baryta, and the precipitate treated with alcoholic potash (10 per cent.). The alkaline solution of protochlorophyll thus obtained is straw coloured, with a feeble, red fluorescence.

When the alcoholic extract from etiolated wheat was exposed to sunlight, the chlorophyll band I appeared in three seconds, and the protochlorophyll spectrum gradually disappeared.

The spectrum, which Pringsheim and Tschirch considered to be characteristic of etioline, is a mixture of the spectra of slightly modified chlorophyll, protochlorophyll, carotene, and xanthophyll.

N. H. J. M.

Action of Inorganic Chlorides on Piperidine and the Fatty Amines. By C. A. AUGUST MICHAELIS (*Ber.*, 1895, 28, 1012—1019).—*Thiopiperidine*, $(C_5NH_{10})_2S$, is obtained by the action of sulphur chloride, SCl_2 , on piperidine; it crystallises in long prisms, which melt at 74° , and have a characteristic odour. It is not attacked by dilute alkalis, but dissolves in dilute acids, forming a clear solution, which soon decomposes, sulphur being deposited and sulphurous anhydride evolved. The *platinochloride* is a chocolate-brown precipitate, and the *picrate* melts at 144 — 145° . *1-Thionylpiperidine*, $(C_5NH_{10})_2SO$, is obtained by the action of thionyl chloride on piperidine; it crystallises in white plates, and melts at 46° . It dissolves in acids, but very rapidly decomposes. When exposed to the air, thionylpiperidine is converted into a substance, $C_5H_{11}NSO_2$, which melts at 70° and deliquesces on further exposure to the air. It can also be obtained by passing a current of sulphurous anhydride into a solution of piperidine in dry ether. *Thiodiethylamine* is an almost colourless liquid, which boils at 84 — 86° (15 mm. pressure), and resembles monothiopiperidine in its other properties. *Thionyldiethylamine* is a light yellow oil, which boils at 118° (27—28 mm. pressure), and also resembles the corresponding piperidine derivative.

Tripiperidinephosphinozide, $(C_5H_{10}N)_3PO$, is obtained by the action of phosphorus oxychloride on piperidine, and forms large plates which melt at 75 — 76° . It dissolves in strong hydrochloric acid, and is not decomposed when this solution is heated. It does not form either a nitroso-derivative or an acetyl derivative. The *hydrochloride* crystallises in slender needles, and the *platinochloride* melts at 215° .

A. H.

Derivatives of 4'-Phenylquinaldine and 4'-Phenylquinoline. By WILHELM KOENIGS and FRANZ MEIMBERG (*Ber.*, 1895, 28, 1038—1046).—The *sulphate* of phenylquinoline crystallises in nacreous tablets melting at 195 — 196° ; the *hydrochloride* melts at 96 — 97° , and forms double chlorides with many metallic chlorides; the *picrate* melts at 224° . The *methiodide* crystallises in long, compact, yellow needles, which melt at 222° . The *platinochloride* of the *methochloride* melts and decomposes at 253° . The methochloride is converted, by treatment with a cold solution of potassium ferricyanide, into

1': 4'-methylphenylquinolone, $C_6H_4 < \begin{smallmatrix} CPh:CH \\ NMe \cdot CO \end{smallmatrix}$, which separates from ether in serrated crystals melting at 143 — 144° . When a solution of 4'-phenylquinoline in fuming sulphuric acid is allowed to stand, two

isomeric *monosulphonic acids* appear to be formed, both of which contain the sulphonic acid group in the 4'-phenyl residue. 4'-*Phenyltetrahydroquinoline* is produced by the action of tin and alcoholic hydrochloric acid on phenylquinoline, and crystallises in white, lustrous plates melting at 74°. The *hydrochloride* melts at 193—194°, the *sulphate* at 158°; the *platinochloride* decomposes and melts at 215°. The *acetyl* derivative crystallises in white plates and melts at 120°, and the *benzoyl compound* forms white needles melting at 147°. *Methylphenyltetrahydroquinoline* is an oil, which yields a *picrate* melting at 222—224°. The *nitrosamine* of phenyltetrahydroquinoline crystallises in flat, yellow needles, melts at 72°, and gives Liebermann's reaction. When treated with alcoholic hydrochloric acid, it is converted into the isomeric 4'-*phenylparanitrosotetrahydroquinoline*, which crystallises in small, green plates, and melts and decomposes at 199·5°. This compound is converted by reduction into 4'-phenylparamidoquinoline, which crystallises from chloroform in flat, faintly-coloured needles melting at 205°. Its ethereal solution has an intense blue fluorescence. The *picrate* melts at 233—234°, and the *platinochloride* forms orange-yellow needles.

The *hydrochloride* of 4'-phenylquinaldine crystallises in long, silky needles melting at 218—220°, and forms double chlorides with many metallic chlorides. The *picrate* crystallises in flat, yellow needles, and melts at 205—206°. The *methiodide* forms broad, yellow needles decomposing and melting at 205°; the *platinochloride* of the *methochloride* melts and decomposes at 245°. 4'-*Phenyltetrahydroquinaldine* crystallises in large, yellow-coloured tablets melting at 66—67°, whilst the *hydrochloride* melts at 221°. The *nitrosamine* forms small, yellowish needles melting at 97—98°.

With the object of obtaining 4'-phenylparahydroxyquinoline synthetically, the *paranisidide* of *benzoylacetone* was prepared by heating benzoylacetone with paranisidine. It crystallises in yellow needles, and melts at 107—108°. When heated with dilute or concentrated sulphuric acid, this compound is decomposed into its constituents, and does not yield the desired quinoline derivative. A. H.

3-Methoxy-4'-phenylquinaldine: New Synthesis of γ -Phenylquinaldinic acid. By WILHELM KOENIGS and GEORG JAEGLÉ (*Ber.*, 1895, 28, 1046—1050).—3-Methoxy-4'-phenylquinaldine is formed when the condensation product of acetophenone and paraldehyde is heated with paranisidine, nitrobenzene, and hydrochloric acid. The free base crystallises from benzene in thick tablets melting at 76°. The *hydrochloride* melts at 205·5°, the *sulphate* at 201°, the *picrate* indefinitely at 185—190°, and the nitrate at 169—170° with decomposition. The *platinochloride* melts and decomposes at 232—234°. 3-Hydroxy-4'-phenylquinaldine is formed when the base is boiled with hydrobromic acid. It melts at 248°, and is soluble in both acids and alkalis.

γ -Phenylquinaldinic acid can be obtained directly by heating benzoylacrylic acid with aniline, nitrobenzene, and hydrochloric acid; a yield of about 15—20 per cent. of the acid used being obtained.

A. H.

Constitution of Pyrazolones. By SIEGFRIED RUHEMANN and ROBERT S. MORELL (*Ber.*, 1895, **28**, 987—989).—In the light of Claisen and Haase's recent research (this vol., i, 193), the authors assign the formulæ $\begin{smallmatrix} \text{N}=\text{CH} \\ | \\ \text{NPh}\cdot\text{CO} \end{smallmatrix} > \text{CMe}\cdot\text{COOEt}$, $\begin{smallmatrix} \text{N}=\text{CH} \\ | \\ \text{NH}\cdot\text{CO} \end{smallmatrix} > \text{CH}\cdot\text{COOEt}$, and $\begin{smallmatrix} \text{N}=\text{CH} \\ | \\ \text{NH}\cdot\text{CO} \end{smallmatrix} > \text{CH}$, or $\begin{smallmatrix} \text{NH}\cdot\text{CH} \\ | \\ \text{NH}\cdot\text{CO} \end{smallmatrix} > \text{CH}$ to the ethylic methylphenylpyrazolonecarboxylate (*Trans.*, 1892, 798), ethylic isopyrazolonecarboxylate, and isopyrazolone (*Abstr.*, 1894, i, 476; this vol., i, 20) prepared by them. The first of these, when treated with hydrochloric acid, yields the corresponding acid; this is comparatively stable, and melts and decomposes at 189°. C. F. B.

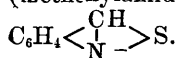
Antipyrine Patents. By R. v. ROTHENBURG (*Ber.*, 1895, **28**, 1124).—A reply to Knorr (this vol., i, 396). C. F. B.

Derivatives of Orthonitrobenzylic Thiocyanate. By SIEGMUND GABRIEL and THEODOR POSNER (*Ber.*, 1895, **28**, 1025—1029).—Orthonitrobenzylic thiocyanate is converted by ammonium sulphide into orthonitrobenzylic bisulphide, which yields *orthamidobenzylic hydrosulphide*, $\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{SH}$, on reduction with tin and hydrochloric acid; its *hydrochloride* melts at 170—172°. This substance is converted by the action of iodine into *orthamidobenzylic bisulphide*, which forms granular crystals, and melts at 90—91°. The *acetyl*-compound crystallises in needles, and melts at 202—205°.

Orthonitrobenzylic thiocyanate is converted by sulphuric acid in the cold into *orthonitrobenzylic carbaminthiolate*,



which crystallises in colourless needles, and melts at 115—117°. This substance is converted by reduction into a base, which is an oily liquid, boils at 242—242.5°, and has a characteristic odour, somewhat resembling that of quinoline. The *platinochloride* forms brownish needles. This compound is isomeric with benzothiazole (methenylamidophenyl mercaptan), and is probably *benzisothiazole*,



A. H.

Halogenised Amines. By SIEGMUND GABRIEL and THEODOR POSNER (*Ber.*, 1895, **28**, 1029—1038; compare *Abstr.*, this vol., i, 190).—Thiocarbamide reacts with *orthamidobenzylic chloride* in a similar way to the thiamides, *orthobenzylene-ψ*-thiocarbamide, $\text{C}_6\text{H}_4 < \begin{smallmatrix} \text{CH}_2\cdot\text{S} \\ | \\ \text{NH}\cdot\text{C}\cdot\text{NH} \end{smallmatrix}$, being produced. This substance crystallises from chloroform in lustrous, white, rhombic plates, and melts at 136—137°. It is readily soluble in acids; the *platinochloride* melts at 221—223° with sudden decomposition, and the *picrate* forms yellow needles and melts at 236°. This compound, which has previously been prepared by Cassirer, who gave to it the name thiocyanorthotoluidine, is formed by the reduction of orthonitrobenzylic thiocyanate (*Abstr.*, 1893, i, 16).

When heated with aniline, it yields a product which is identical with the benzophenyldihydrothiometadiazine prepared by Söderbaum and Widman (Abstr., 1890, 178), the constitution of which was proved by Paal and Vanvolxem (Abstr., 1894, i, 621) to be represented by the formula $C_6H_4 < \begin{smallmatrix} CH_2 \cdot S \\ NH \cdot C : NPh \end{smallmatrix}$. The same substance is formed by the action of orthamidobenzyl chloride on phenylthiocarbamide.

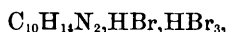
This view of the constitution of orthobenzylene- ψ -thiocarbamide is borne out by the behaviour of the substance towards oxidising agents. Barium permanganate converts it into the barium salt of an acid substance, the *silver* salt of which has the formula $C_6H_5N_2O_3SAg$, and is a colourless microcrystalline powder. This silver salt is decomposed by hydrochloric acid with evolution of sulphurous anhydride, and formation of a base, the *hydrochloride* of which crystallises in lemon-yellow, vitreous prisms. The free *base*, $C_6H_4 < \begin{smallmatrix} CH \cdot N \\ NH \cdot CO \end{smallmatrix}$, is an almost white, amorphous mass, and is identical with the quinazolone produced by the condensation of orthamidobenzaldehyde with carbamide.

When the silver salt of the oxidation product of orthobenzylene- ψ -thiocarbamide is treated with silver iodide, methylation, accompanied by elimination of sulphurous anhydride, takes place. The compound produced crystallises in well-developed prisms, melts at 180° , and forms crystalline salts with acids. It is probably a *benzaldehydomethylcarbamide*, but the position of the methyl group has not yet been determined with certainty. A. H.

Existence of Coniine in "Sambucus Nigra." By G. DE SANCTIS (*Gazzetta*, 1895, 25, i, 49—53).—The dilute sulphuric acid extract of the stems and leaves of the common elder (*Sambucus nigra*) contains coniine. The alkaloid was identified by analyses of its salts, and to its presence in the elder is doubtless to be traced the effect which a decoction of the leaves and stems of this tree has on the nervous system. W. J. P.

Constitution of Nicotine. By VINCENZO OLIVERI (*Gazzetta*, 1895, 25, i, 59—77).—On oxidising nicotine in potassium carbonate solution with potassium permanganate, on the water bath, nicotinic, carbonic, oxalic, and acetic acids are formed, together with free nitrogen, and possibly β -hydroxypropionic acid. With the exception of the acid last mentioned, the same products are obtained on oxidising nicotinedibenzylammonium chloride with alkaline permanganate. By the action of acetic chloride on nicotine, a mixture of the alkaloid and its acetyl derivative seems to be obtained.

With bromine, nicotine hydrobromide forms a *perbromide*,



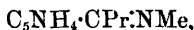
which crystallises in beautiful red needles; it is converted into nicotine by ammonia, and into monobromonicotine by warm dilute

potash. If the hydrobromide is treated with excess of bromine, a *perbromide* of dibromonicotine hydrobromide, $C_{10}H_{14}Br_2N_2 \cdot HBr \cdot HBr_3$, is formed; it is a red, viscous mass, which is converted by alcoholic potash into a resin containing a small proportion of dibromonicotine.

On adding iodine solution to nicotine hydriodide, a reddish precipitate separates, which decomposes at 200° with evolution of iodine and methylic iodide, and on distillation with potash yields methylamine. Methylamine and a small proportion of nicotinic acid are obtained on heating nicotine at 250 – 280° in a closed tube for 24 hours.

The dipiperidyl, $C_{10}H_{20}N_2$, obtained by Leibrecht by reducing nicotine with sodium ethoxide, is readily prepared by reducing the base with sodium amyloxide; it contains two imido-groups, and yields an oily *dinitroso*-derivative with potassium nitrite; an oily *dibenzoyl* derivative can also be prepared, together with a viscous *dicarbamide*, $C_{10}H_{20}(N \cdot CO \cdot NH_2)_2$, the *platinochloride* of which forms an amorphous yellow powder, melting and decomposing at 171° .

The author considers that none of the constitutional formulæ hitherto suggested for nicotine satisfactorily explain the various reactions of the alkaloid, and believes that the constitution



which he now proposes, is the most probable one.

W. J. P.

Methylxanthine, a Product of the Metabolism of Theobromine and Caffeine. By STANISLAS BONDZYNSKI and RUDOLF GOTTLIEB (*Ber.*, 1895, **28**, 1113–1118).—When rabbits, dogs, or men are dosed with theobromine or with caffeine, *monomethylxanthine*, $C_6H_6N_4O_2$, appears in the urine. This substance can be obtained crystalline; it melts and decomposes at about 310° , dissolves in 1592 parts of water at 18° and in 109 parts when boiling; in 7575 of absolute alcohol at 17° and in 2250 at the boiling temperature. It yields *silver*, *barium*, and *sodium derivatives*, the last with $4H_2O$, one atom of hydrogen in its molecule having been replaced, apparently, by metal.

C. F. B.

Quinine Hydrochloro-sulphate. By CHARLES LEPIERRE (*Bull. Soc. Chim.*, 1894, [3], **11**, 1138–1139).—The author confirms Grimaux's results (*Abstr.*, 1893, i, 115). Quinine hydrochloro-sulphate is homogeneous, and forms crystals several cm. long; it is exceedingly soluble, and the solution is stable, with the exception that, like solutions of all quinine salts, it slowly absorbs oxygen from the air. On account of its great solubility, the salt affords an excellent means of hypodermically injecting large doses of quinine.

JN. W.

Constitution of Cinchonine. By WILHELM V. MILLER and GEORG RHODE (*Ber.*, 1895, **28**, 1056–1077).—The oily compound previously obtained by the action of dilute acetic acid on cinchonine (*Abstr.*, 1894, i, 432), is termed *cinchotoxine*, $C_{19}H_{22}N_2O$; it crystallises slowly below 0° in absence of moisture, and melts at 58 – 59° . It is a strong base, and liberates ammonia from its salts. The *oxalate* is identical in appearance with cinchonine oxalate. The *hydrogen*

tartrate crystallises in colourless concentric needles. The *picrate* and the salts of mineral acids crystallise with difficulty on account of their solubility; various crystalline double salts with zinc chloride, platinum chloride, and mercuric chloride have also been prepared. The only difference between methylcinchonine and methylcinchotoxine is in crystalline habit; they are believed to have the same constitution, and both yield identical derivatives. In physiological properties cinchotoxine and methylcinchotoxine resemble digitoxine, and have no antipyretic action; this characteristic property of cinchonine appears to be caused by the presence in it of a carbon-nitrogen linking, which is resolved in the preparation of cinchotoxine.

Pasteur's cinchonicine, prepared by fusing cinchonine bisulphate, has been obtained in crystals, and is probably identical with cinchotoxine, the only difference yet observed is in crystalline form. *Cinchotoxine phenylhydrazone*, $C_{25}H_{18}N_4$, is crystalline, and melts at 148° .

By the action of nitrous acid on cinchotoxine two compounds are formed, which are separated by treatment with soda; the insoluble substance is the *nitroso-derivative*, $C_{19}H_{21}N_3O_2$, which crystallises in clear, colourless prisms melting at 98° . It is feebly basic, dissolves in mineral acids, and evolves nitrous anhydride when heated with hydrogen bromide. With phenylhydrazine, it yields two *phenylhydrazones*, melting at 149° and 163° respectively, and a third compound which has not yet been examined. The lower melting hydrazone, $C_{23}H_{27}N_5O$, crystallises in concentric prisms, and forms orange-coloured salts with acids. When heated at 100° , it loses 12.19 per cent. of weight; the product is very sparingly soluble, and forms salts which resemble those of the original hydrazone. The second compound from nitrous acid and cinchotoxine has the formula $C_{19}H_{20}N_4O_3$, and crystallises in granular aggregates of colourless prisms, melting and decomposing at $198-199^\circ$; it dissolves in alkalis with a yellow colour, and evolves nitrous anhydride when heated with hydrogen bromide.

Cinchotenine reacts like cinchonine with dilute acetic acid; the product has not been isolated, but with phenylhydrazine it yields two phenylhydrazones, the one, $C_{24}H_{25}N_4O_2$, crystallises with 3 or 3.5 H_2O in long, slender needles, melts at about 286° , according to the rapidity of heating, dissolves in acids with a reddish-yellow, in alkalis with a yellow, coloration, and is reprecipitated from the latter by carbonic anhydride. The second phenylhydrazone crystallises in rhombic plates, melts at 196° , and is soluble in dilute, but not in concentrated, soda.

As a further guide to the constitution of the cinchonic compounds, the silver salts of dehydrocinchonine and dehydrocinchine were prepared; they are colourless, amorphous, give varying analytical results, and do not resemble the salts of the higher acetylenes described by Krafft and Reuter.

The molecular refraction of cinchotine dihydrochloride = 105.5, that of cinchonine dihydrochloride = 104.81; this indicates that the latter base contains a vinyl, the former an ethyl, group; the theoretical difference in molecular refraction = 0.4 and 2.1 for a vinyl group and a diagonal linking respectively. The molecular

refraction of cinchine = 89.7, that of dihydrocinchine = 88.1, indicating the presence of an acetylene linking in the latter, and of a vinyl group in the former, the calculated difference in molecular refraction = 1.77.

The constitution of cinchonine is fully discussed, and the bearing of Skraup's and Koenigs' recent investigations considered. The conversion of merochinine into γ -methyl- β -ethylpyridine renders the author's previous formula for cinchonine improbable; they propose therefore

to substitute for it the following—
$$\text{CMe} \begin{array}{c} \text{CH}(\text{CH}:\text{CH}_2) \cdot \text{CH}_2 \\ \text{C}(\text{OH})(\text{CH}_2 \cdot \text{C}_6\text{NH}_5) \\ \text{CH}_2 \text{-----} \text{CH}_2 \end{array} \text{N}.$$

J. B. T.

Alkaloids of Calabar Beans. By ALEX. EHRENBURG (*Chem. Centr.*, 1894, ii, 439; from *Verh. Vers. deutsch. Naturf. u. Artze.*, ii, 102).—If a salt of eserine (physostigmine) is distilled with solution of caustic alkali in a current of hydrogen, no red colouring matter is produced, but amongst the products of decomposition are methylamine and carbonic anhydride. The residual liquid contains a new base, *eseroline*, which is colourless when crystallised from absolute alcohol, but turns red by the action of moisture. If eserine is heated in a sealed tube with alcoholic ammonia at 150°, eseroline and methylcarbamide are formed, proving the probable formula of eserine to be $\text{NHMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_{13}\text{H}_{16}\text{NO}$. When heated with aqueous alkalis in presence of air, it first yields rubreserine, $\text{C}_{18}\text{H}_{16}\text{N}_2\text{O}_2$, which crystallises in red needles, but which is gradually converted into *eserine-blue*, which is a true dye, colouring silk and wool without mordants.

Eseridine, which accompanies eserine, is distinguished from the latter by not yielding rubreserine under the influence of alkalis and air. A third alkaloid isolated by the author, *eseramine*, $\text{C}_{16}\text{H}_{25}\text{N}_4\text{O}_3$, crystallises from alcohol in slender, white needles. It is not identical with Harnack's calabarine, as it does not produce tetanus. The author doubts whether calabarine really exists as such in the beans.

L. DE K.

Apoquinine Derivatives. By EDUARD LIPPMANN and FRANZ FLEISSNER (*Monatsh.*, 1895, 16, 34–44).—Apoquinine, obtained by the action of dilute hydrochloric acid on quinine (compare Hesse, *Annalen*, 205), is really a mixture of apoquinine, apoquinine hydrochloride, and isomerides of quinine. Approximately, pure apoquinine may be obtained on recrystallising from ether the product formed by heating quinine with dilute hydriodic acid (sp. gr. 1.25–1.35). The base sinters at 160°, melts and decomposes at 210°, and yields the following salts:—A *platinochloride*, $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{PtCl}_6$, which is a yellow, crystalline powder; an *oxalate*, $(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2 \cdot 3\text{C}_2\text{H}_2\text{O}_4$, which crystallises in needles; and an *hydriodide*, $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2 \cdot 2\text{HI}$, which crystallises in yellow prisms. *Ethylapoquinine* is obtained on heating a mixture of apoquinine, sodium ethoxide, and alcoholic ethylic chloride in sealed tubes at 100°. It crystallises in grains and melts sharply at 182°, whereas the isomeric ethylcupreine, or “quinethylin” of Grimaux (*Compt. rend.*, 112, 114), softens at 160°. *Ethylapoquinine platinochloride*, $\text{C}_{19}\text{H}_{21}\text{EtN}_2\text{O}_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$, crystallises in pale yellow, flocculent masses.

G. T. M.