Organic Chemistry.

The System Water–Uranyl Oxalate–Sodium Oxalate. A. Colani (*Compt. rend.*, 1917, **165**, 111—113).—An examination of the solubility curves of the system water–uranyl oxalate–sodium oxalate at 15° and 50° shows the existence of two new compounds having the composition $Na_2(UO_2)_4(C_2O_4)_5,11H_2O$ and $Na_2(UO_2)_2(C_2O_4)_3,5H_2O$. In addition, a pentahydrate,

$$Na_2(UO_2)(C_2O_4)_2,5H_2O,$$

was obtained, the crystals of which were macroscopically identical with those of the hexahydrate described by Wyrouboff (compare *Bull. Soc. franc. Min.*, 1909, **32**, 351, 357, 364). No indication of the salt $Na_6(UO_2)_2(C_2O_4)_5,13H_2O$ described by Wyrouboff (*loc. cit.*) could be obtained. At 75°, from a solution containing 1·5 mols. of sodium oxalate to 1 mol. of uranyl oxalate, crystals were deposited having the composition $Na_{10}(UO_2)_4(C_2O_4)_9,12H_2O$.

W. G.

Isomerisation and Hydration of Citronellaldehyde by Acids. H. J. Prins (*Chem. Weekblad*, 1917, **14**, 627—630).—Formic acid (85—90%) or phosphoric acid (80%) converts citronellaldehyde into an oil which, on distillation in a vacuum, yields 10% of *iso*pulegol; 15—20% of a condensation product of 2 molecules of citronellaldehyde, b. p. 185°/13 mm.; *iso*pulegol hydrate, acicular crystals, m. p. 84—85°; and a heptacyclic glycol, $C_{10}H_{20}O_2$, m. p. 60—62°.

A. J. W.

Action of Acids on the Rotatory Power of Sucrose and Invert-sugar in the Presence of Soluble Salts. Em. Saillard (*Compt. rend.*, 1917, **165**, 116—118).—[With Wehrung.]—Sulphurous and acetic acids, at the concentrations used, have no effect on the rotatory power of sucrose in the presence of sodium chloride, but they diminish that of invert-sugar in the presence of this salt, to which they are thus antagonistic. Hydrochloric acid increases the lævorotatory power of invert-sugar in the presence of sodium chloride. Carbon dioxide is without action on the rotatory power of either sucrose or invert-sugar in the presence of sodium chloride.

W. G.

The Chemistry of Caramel. I. Caramelan. Mary Cunningham and Charles Dorée (T., 1917, **111**, 589—608).—Believing that a study of the process of the formation of caramel may have a bearing on the problem of the constitution of cellulose and the question of the production of humus, peat, and coal, the authors have begun a systematic investigation by a contribution on the nature of caramelan.

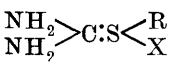
When sucrose is heated at 170—180° until the loss of weight is

12%, it loses two molecules of water, some furfuraldehyde, pungent acid vapours, and carbon dioxide being evolved as well, and leaves practically pure caramelan, $C_{12}H_{18}O_9$, or probably $C_{24}H_{36}O_{18}$, m. p. 136°. This yields a tetra-acetate, m. p. 107°, a *tetrabenzoate*, m. p. 105—108°, and an explosive *tetranitrate*. It behaves like a ketose in forming precipitates with resorcinol and phloroglucinol, and it also condenses with phenylhydrazine and semicarbazide, but the products are not simple hydrazones or semicarbazones, but derivatives of a $C_{24}H_{36}O_{18}$ molecule less several molecules of water. When shaken with 40% hydrochloric acid, caramelan is not hydrolysed as is cellulose, or hydrolysed and then converted partly into ω-chloromethylfurfuraldehyde like sucrose, but is dehydrated further to caramelin, $C_{24}H_{26}O_{13}$. Dilute sulphuric and hydrochloric acids, however, cause hydrolysis and dehydration at the same time, dextrose, methylfurfuraldehyde, furfuraldehyde, humic acid, $C_{24}H_{22}O_{11}$, and a chlorinated humic acid, $C_{24}H_{29}O_{18}Cl_3$, having been found among the products.

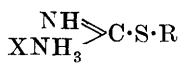
The action of various oxidising agents on caramelan has also been investigated. The products are very complex, but are mostly derivatives of a C_{23} unit. Acetaldehyde was obtained from the ozonide, indicating that a CHMe:C residue is present in caramelan, whilst dilute nitric acid yielded an insoluble, red, nitrated humic acid, $C_{23}H_{23}O_{12}\cdot NO_2$, and a soluble, ketonic nitro-acid, $C_{11}H_{15}O_{10}N$.

J. C. W.

Constitution of the Salts of *S*-Alkylthiocarbamides. John Taylor (T., 1917, **111**, 650—663).—Additive compounds of thiocarbamide with alkyl haloids have been known for a long time. Similar compounds with methyl, benzyl, and ethyl sulphates, nitrates, and thiocyanates have now been obtained, the readiness with which combination takes place falling off in the order in which the radicles are named, which is the same as in the case of the haloids. These compounds all behave like salts, in which the acidic ions respond to the usual tests. From one salt another can be made by double decomposition, so that it is possible to prepare salicylates, acetates, and phosphates, which cannot be obtained directly. Two formulæ only need therefore be considered in connexion with the constitution of these additive compounds, namely, the "sulphonium" (I) and "ammonium" (II):



(I.)



(II.)

Since the compounds with benzyl nitrite and methyl and benzyl thiocyanates are stable in boiling water, the ammonium type is improbable, but in the case of benzyl esters of strong acids, two isomerides are met with, and one of them is then of this type. The conditions for the formation of the ammonium salts are that the free mineral acids shall be present during the crystallisation of the salt, and the sulphonium salts can be obtained from them

by boiling with water alone or with a very dilute aqueous or alcoholic solution of sodium phosphate. Salts prepared by double decomposition are always of the sulphonium type, even if an "ammonium" salt is used.

Nencki (1874) described an additive compound of thiocarbamide with ethyl oxalate which has m. p. 158°, does not give a precipitate of calcium oxalate until hydrolysed, and yields a metallic sulphide when warmed with alkaline lead solutions or ammoniacal silver nitrate. An isomeride of the sulphonium type,

$$C(NH_2)_2{:}SEt{\cdot}CO_2{\cdot}CO_2{\cdot}S{\cdot}CEt(NH_2)_2,$$

is obtained if the compound of thiocarbamide with ethyl iodide is treated with silver oxalate. This has m. p. 188°, gives a precipitate of calcium oxalate at once, and produces metallic mercaptides and cyanamides with the above lead or silver solutions.

When thiocarbamide oxalate is warmed with alcohol, Nencki's compound is formed. This is explained by assuming that oxalic acid is given up by the thiocarbamide salt, that ethyl oxalate is then formed, and that this ester combines with the free thiocarbamide. Such evidence was required when a similar explanation of the action of acetaldehyde on thiocarbamide hydrochloride was advanced (Dixon and Taylor, this vol., i, 11).

For the details of the numerous salts, many of which had been described by Arndt as salts of alkyl-ψ-thiocarbamides (A., 1911, i, 918), the original should be consulted. J. C. W.

Diazomethane. F. H. Loring (*Chem. News*, 1917, **115**, 255).—An ethereal solution of diazomethane is obtained by distilling from a retort in a water-bath a mixture of 2·5 c.c. of nitrosomethylurethane, 25 c.c. of dry ether, and 1·75 c.c. of methyl-alcoholic potassium hydroxide (1 : 4), and collecting the distillate in a freezing mixture of ice and calcium chloride. G. F. M.

Preparation of Benzenesulphonic Acid. Comp. des Produits Chimiques d'Alais and de la Camargue (Brit. Pat., 101973, 1916; from *J. Soc. Chem. Ind.*, 1917, **36**, 705).—Benzenesulphonic acid is prepared by passing benzene vapour into sulphuric acid of any concentration, preferably at 120—130°. Water is eliminated as steam, and the sulphonic acid crystallises on cooling. D. F. T.

Method of Separating Benzenedisulphonic Acid from Sulphuric Acid and Converting it into a Salt. L. M. Dennis (U.S. Pat., 1227252, 1917; from *J. Soc. Chem. Ind.*, 1917, **36**, 705).—The mixture of disulphonic acid and sulphuric acid is extracted with an organic solvent, for example, benzene, and the resulting solution is treated with a suitable compound to convert the dissolved disulphonic acid into a salt. D. F. T.

The Alcohols and Bases of Vacuum Tar. Amé Pictet, O. Kaiser, and A. Labouchère (*Compt. rend.*, 1917, **165**, 113—116).—The authors have isolated from vacuum tar 4-methyl-*cyclo*hexanol, and the alcohols from C_8 to C_{11}, inclusive, of the

homologous series $C_nH_{2n-6}O$. The last four alcohols are unsaturated, and are spontaneously and fairly rapidly converted into phenols, this process being accelerated by heat. Their acetates, which are colourless, volatile liquids, instantly decolorise potassium permanganate in cold sulphuric acid solution. The bases isolated consist of a product, C_7H_9N, and the members from C_8 to C_{12}, inclusive, of the homologous series $C_nH_{2n-9}N$. The first-named base is probably a mixture of toluidines. The other bases are unsaturated, secondary amines, with odours resembling those of quinoline and its homologues. The physical properties of the alcohols and their acetates, and the bases and their picrates, are as follows:

Alcohols.			Bases.		
		Acetate.			Picrate.
Formula	B. p.	B. p.	Formula.	B. p.	M. p.
$C_7H_{14}O$ ...	170—175°		C_7H_9N	198—203°	170°
$C_8H_{16}O$ ...	185—190		C_8H_7N	225	195
$C_9H_{12}O$ ...	198—200	213—215°	C_9H_9N	247—250	184
$C_{10}H_{14}O$ ...	213—215	226—229	$C_{10}H_{11}N$	250—260	184
$C_{11}H_{16}O$ ...	226—228	240—244	$C_{11}H_{13}N$	260—265	173
			$C_{12}H_{15}N$	270—280	166

W. G.

Sozoiodol-Mercury Compounds. E. Rupp and A. Herrmann (*Arch. Pharm.*, 1916, **254**, 488—497).—Pharmaceutical preparations containing organic mercury compounds belong to two classes, namely, those containing ionisable mercury, for example, hydrargyrum benzoicum, and those, such as hydrargyrum salicylicum, containing nuclear, non-ionisable mercury. Some such preparations, which are insoluble in water, dissolve readily in a solution of sodium chloride. This solubility is due, in the case of substances of the former class, to ordinary double decomposition with formation of mercuric chloride, and in the case of substances of the latter class to the formation of the sodium salts of chloromercuri-aromatic acids by the addition of sodium chloride.

Sozoiodol-mercury $\left(C_6H_2I_2<\begin{matrix}O\text{---}\\SO_3\end{matrix}>Hg\right)$ belongs to neither of the preceding classes, and therefore the cause of its solubility in a solution of sodium chloride or potassium iodide has been investigated, and also the explanation of its orange colour. The substance has been prepared in several different ways: (1) by the reaction in hot aqueous solution between mercuric nitrate and an equivalent amount or an excess of sodium sozoiodolate (2:6-diiodophenol-*p*-sulphonate); (2) from yellow mercuric oxide and an equivalent quantity or an excess of sozoiodolic acid in aqueous solution; and (3) by adding a warm aqueous solution of sodium sozoiodolate to the equivalent amount of a mercuric acetate solution. If in the last method the order of the addition is reversed and the solutions are at the ordinary temperature, a red *substance*, $(SO_3Na\cdot C_6H_2I_2\cdot O)_2Hg$, is at first precipitated, which is converted into sozoiodol-mercury by the addition of more mercuric acetate

solution. This red substance is better obtained by digesting yellow mercuric oxide and sodium sozoiodolate (2 mols.) in lukewarm water; it dissolves in aqueous sodium chloride, forming a colourless solution.

When a solution of sozoiodol-mercury in aqueous sodium chloride is extracted with ether, the extract is found to contain mercuric chloride in nearly the theoretical amount corresponding with the equation

$$C_6H_2I_2\langle{}^{O\text{---}}_{SO_3}\rangle Hg + 2NaCl = HgCl_2 + ONa\cdot C_6H_2I_2\cdot SO_3Na.$$

The disodium sozoiodolate is difficult to isolate on account of its great solubility, but when a concentrated solution of sozoiodol-mercury in aqueous sodium chloride is acidified, sodium sozoiodolate is precipitated in slender needles containing $2H_2O$. The disodium salt forms large, rectangular crystals containing $5H_2O$, having a faintly alkaline reaction. The dipotassium salt is formed, together with potassium mercuric iodide, when sozoiodol-mercury dissolves in aqueous potassium iodide; by adding the latter very carefully, mercuric iodide is obtained in quantitative amount.

The brick-red *substance*, $C_6H_2I_2\langle{}^{O\text{—}Hg\text{---}O}_{SO_3\cdot Zn\cdot SO_3}\rangle C_6H_2I_2$, is obtained by digesting mercuric oxide and zinc sozoiodolate with warm water; it resembles the corresponding sodium salt in its behaviour. These two substances are coloured, and so also is *mercuric* 2:4:6-*tribromophenoxide*, $(C_6H_2Br_3\cdot O)_2Hg$, yellowish-red crystals, prepared from mercuric acetate and tribromophenol in aqueous-alcoholic solution; it appears, therefore, that the group ·O·Hg·O· exerts a chromophoric function, and thus the colour of sozoiodol-mercury is accounted for.

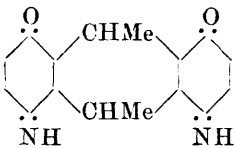
Potassium 2:6-*di-iodophenetole*-p-*sulphonate*, $OEt\cdot C_6H_2I_2\cdot SO_3K$, colourless needles, is prepared by heating potassium sozoiodolate (1 mol.) and potassium hydroxide (1·1 mols.) dissolved in a little water with an alcoholic solution of ethyl iodide (1·1 mols.) at about 130°. The corresponding *barium* salt, needles with $5H_2O$, and *mercuric* salt, colourless needles, have been prepared; 2:6-*di-iodophenetole*-p-*sulphonic acid* forms crystals with $2H_2O$, m. p. 108°.

The constitution of sozoiodolic (2:6-di-iodophenol-*p*-sulphonic) acid is proved by the facts that the acid (1) yields 2:4:6-tri-iodophenol, iodine, and phenol by heating with fuming hydrochloric acid at about 120°, and (2) is formed by treating 2:6-dihydroxymercuriphenol-*p*-sulphonic acid (Rupp and Herrmann, this vol., i, 488) with a solution of iodine.

Anogon ($OHg\cdot C_6H_2I_2\cdot SO_3Hg$) does not form a clear solution in aqueous sodium chloride, a precipitate of mercurous chloride being produced. C. S.

Action of Acetaldehyde-ammonia on Quinones. Praphulla Chandra Ghosh (T., 1917, **111**, 608—612).—*p*-Benzoquinone condenses with acetaldehyde-ammonia to form a black

compound, probably of the annexed formula, which reacts with cold nitric acid (D 1·45) to form a yellow *compound*, $C_{16}H_{12}O_6N_4$. These do not melt at 290°. Anthraquinone and acetaldehyde-ammonia react at 220° to yield a colourless, silky *compound*, m. p. 281°, to which the formula $C_6H_4<\begin{matrix}C(:CH\cdot CHO)\\C(:CH\cdot CHO)\end{matrix}>C_6H_4$ is assigned, since it forms a yellow *phenylhydrazone*, $C_{18}H_{12}(:N\cdot NHPh)_2$. J. C. W.

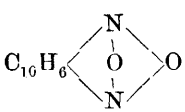


A Simple Demonstration of the Addition of Water to Terpineol under the Influence of Acids. H. J. Prins (*Chem. Weekblad*, 1917, **14**, 630—631).—When terpineol is agitated with 80% phosphoric acid at 30°, it dissolves, and crystals of terpin hydrate separate. A less complete transformation is caused by 60% sulphuric acid, but 85% formic acid does not react. A. J. W.

The Bromo-derivatives of Aloe-emodin. E. Léger (*J. Pharm. Chim.*, 1917, [vii], **16**, 5—8).—When aloe-emodin is heated in a sealed tube at 115° for eighteen hours with bromine, *pentabromoaloe-emodin*, $C_{15}H_5O_5Br_5$, slender, prismatic needles, m. p. 278·4° (corr.), is obtained. This compound is only very slowly soluble in cold dilute alkali hydroxide, but it dissolves at once on warming, and is converted into *tetrabromoaloe-emodin*, orange-red needles, m. p. 276·4° (corr.). W. G.

Equilibrium in the System: Cupric Chloride-Pyridine. J. Howard Matthews and Samuel Spero (*J. Physical Chem.*, 1917, **21**, 402—406).—Measurements of the solubility of cupric chloride in pyridine at temperatures between −17° and 95° show the existence of three compounds: $CuCl_2,6C_5H_5N$, which is the stable solid phase up to −10°; $CuCl_2,2C_5H_5N$, stable between −10° and 58°; and $2CuCl_2,3C_5H_5N$, which is the stable phase above 58°. The first of the three compounds has not been previously described. H. M. D.

Conversion of *o*-Nitroamines into *iso*Oxadiazole Oxides, and of *o*-Nitrosoamines into *iso*Oxadiazoles. Arthur G. Green and Frederick Maurice Rowe (T., 1917, **111**, 612—620).—In three earlier papers (T., 1912, **101**, 2452; 1913, **103**, 897, 2023), it was shown that many *o*-nitroamines are converted into *iso*oxadiazole oxides (furoxans, furazan oxides) when oxidised by alkaline sodium hypochlorite. 2-Nitro-1-naphthylamine and 1-nitro-2-naphthylamine are no exceptions to this generalisation, for they both yield the same naphth*iso*oxadiazole oxide or naphthafuroxan (annexed formula), m. p. 127°. This compound is the "β-naphthaquinone-dioxime peroxide" of Forster and Fierz (T., 1907, **91**, 1942) and also the "1:2-dinitroso-naphthalene" of Koreff and Ilinski. It yields β-naphthaquinonedioxime on reduction with



hydroxylamine, and this gives *naphthisooxadiazole* (*naphthafurazan*), $C_{10}H_6<\begin{matrix}N\\|\\N\end{matrix}>O$, m. p. 78°, on boiling with sodium hydroxide.

8-Nitro-1-naphthylamine does not yield a furoxan by this treatment, and 2:4-dinitronaphthylamine suffers rupture of the ring, which agrees with the authors' earlier experiences and interpretation of the mechanism of the reaction.

The oxidation of *o*-nitrosoamines by sodium hypochlorite is a similar reaction; the base passes through a quinonoid state to an *iso*oxadiazole (furazan). Thus, 1-nitroso-2-naphthylamine and 2-nitroso-1-naphthylamine both yield the above naphth*iso*oxadiazole. Similarly, *o*-nitrosoacetanilide (the free base could not be prepared) suffers hydrolysis and oxidation simultaneously, and gives benz*iso*oxadiazole (benzfurazan). Crude *m*-nitrosoaceto-*p*-toluidide likewise gives 5-methylbenz*iso*oxadiazole, $C_6H_3Me<\begin{matrix}N\\|\\N\end{matrix}>O$ (compare T., 1913, **103**, 2023). J. C. W.

The Mechanism of the Ninhydrin Reaction. A Contribution to the Theory of Colour of Salts of Alloxantin-like Compounds. J. M. Retinger (*J. Amer. Chem. Soc.*, 1917, **39**, 1059—1066. Compare Ruhemann, T., 1911, **99**, 792, 1306). —A theoretical discussion of work published elsewhere (Diss., Leipzig, 1913) in which the author suggests the following course for the whole ninhydrin reaction. The triketohydrindene hydrate hydrolyses during boiling, giving *o*-carboxyglyoxal, which reduces part of the triketohydrindene to dioxindone, which then combines with another molecule of triketohydrindene to give hydrindantine. The amino-acid or amine derived from the enzyme action gives, first, as has been shown in the alloxantin series on alkali salts (*loc. cit.*), a monobasic salt which is colourless; further boiling produces a dibasic neutralisation, and the molecule then splits into two molecules with tervalent carbon, having a free valency, this being the cause of the absorption in the visible spectrum. The difference in colour at this stage is due to the different sizes of the molecules connected with the tervalent carbon, which results in a different potential for the free affinity of the carbon, and thus a different optical effect. Exposure to air in aqueous solution decomposes the split molecules further, giving *o*-carboxymandelic acid, ammonia, carbon dioxide, water, and an aldehyde. W. G.

Acid Hæmochromogen. Ch. Dhéré (*Compt. rend. Soc. de Biol.*, 1917, **79**, 1087—1090; from *Physiol. Abstr.*, 1917, **2**, 224). —A description of simple methods for preparing acid hæmochromogen by means of sodium hyposulphite. Acid hæmochromogen is more soluble in acetone than in methyl or ethyl alcohol. It is also soluble in ether, in methylal, in amyl alcohol, in benzene, and in toluene. It is not soluble in light petroleum,

and apparently not in glycerol. The solutions are stable for some months. G. B.

The "Mechanical Denaturation" of Proteins and the Method of Drying Organs for Biological Investigation. WILHELM WIECHOWSKI (*Biochem. Zeitsch.*, 1917, **81**, 278—283).—The author confirms the observations of Herzfeld and Klinger (this vol., i, 300), according to which proteins dried on a plate become insoluble on scraping. For this reason, when organs are dried, the manipulation must be carried out in such a way that they can be dried into powder form and readily removed without such mechanical action from the material upon which they are spread. For this purpose, plates coated with solid paraffin can be used, and a preliminary account is given of a drying oven which can be employed, and which is designed to prevent the powder of the dried organs from being scattered by the current of air. S. B. S.