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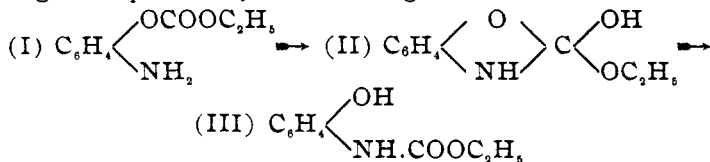
ARTHUR A. NOYES, Editor.

REVIEWERS: Analytical Chemistry, H. P. Talbot and W. H. Walker; Biological Chemistry, A. G. Woodman; Carbohydrates, G. W. Rolfe; General Chemistry, A. A. Noyes; Geological and Mineralogical Chemistry, W. O. Crosby and M. L. Fuller; Inorganic Chemistry, Henry Fay; Metallurgical Chemistry and Assaying, H. O. Hofman; Organic Chemistry, J. F. Norris; Physical Chemistry, H. M. Goodwin; Sanitary Chemistry, E. H. Richards; Industrial Chemistry, A. H. Gill and F. H. Thorp.

ORGANIC CHEMISTRY.

J. F. NORRIS, REVIEWER.

On the Molecular Rearrangement of *o*-Aminophenylethyl Carbonate to *o*-Oxyphenylurethane. BY JAMES H. RANSOM. *Am. Chem. J.*, 23, 1-50.—When *o*-nitrophenylethyl carbonate is reduced in alcoholic solution with tin and hydrochloric acid, a white crystalline compound is obtained, which melts at 86° and not at 95° as given by Bender (*Ber.*, 19, 2268). As the compound is insoluble in acids, it seemed probable that the constitution which had been assigned to it, aminophenylethyl carbonate, was incorrect. The author, accordingly, undertook a thorough investigation of the reaction, and has shown that Bender's compound is identical with *o*-oxyphenylurethane prepared from *o*-aminophenol and ethyl chlorformate. By effecting the reduction of the nitro compound at a low temperature, an oil, soluble in acids, was obtained, which proved to be *o*-aminophenylethyl carbonate. This compound readily suffered rearrangement into *o*-oxyphenylurethane. This change was studied carefully, as it seemed probable that an intermediate product was formed in the reaction. This compound would be of interest on account of the fact that it could be an addition-product of an amine and an ester, and would, therefore, throw light on the reaction between compounds of these classes. The change is expressed by the following formulae:



Formula (II) represents the constitution of the hydroxide base corresponding to the hydrochloride of ethoxymethenylaminophenol (an imido ester), if the salts of the imido esters are formed by the addition of the acid to the double bond between the carbon and nitrogen atoms. The isolation of such a compound would be of value in deciding the structure of such salts. The compound was not obtained, but the author is of the opinion that it was formed during the transformation for the following reasons: *p*-aminophenyl carbonate was found to be a perfectly stable compound, the rearrangement being peculiar to the ortho series, and, further, the rearrangement occurs only as long as the nitrogen atom holds at least one hydrogen atom. In order to determine whether the structure of the compound formed by the reduction of *o*-nitrophenylethyl carbonate is represented by formula (II) or formula (III), the action of acyl chlorides on it was studied. By the action of benzoyl chloride, a compound was readily obtained, which was identical with the substance formed by the action of ethyl chlorformate on benzoyl-*o*-aminophenol. This fact indicates that the benzoyl ester is a derivative of a substance of formula (II), but since a molecular rearrangement of aminoethylphenyl carbonate was proved, the structure was investigated from another point of view. The benzoyl ester of oxyphenylurethane is insoluble in alkalis, and has the ring structure. If the methyl ester has an analogous structure, it should exhibit the same reactions. The methyl ether was prepared from methylaminophenol and ethyl chlorformate, and also from oxyphenylurethane by direct methylation by means of diazomethane. The ester was soluble in alkalis, and was, accordingly, a derivative of a compound of formula (III). Since it has been shown that diazomethane can be used to determine delicate questions of constitution, the methyl group being introduced with such ease, it follows that formula (III) represents the structure of the compound formed from *o*-nitrophenylethyl carbonate by reduction. A careful study of the relation between the ring compound (formula II) and the hydrochloride of ethoxymethenylaminophenol was not made, but it was shown that the salt gives by hydrolysis oxyphenylurethane under the same conditions that aminophenylethyl carbonate does. This reaction is further evidence in favor of the view of the structure of the salts of imido ethers put forward by Stieglitz (*Am. Chem. J.*, 21, 108). Benzoyloxyphenylurethane (m. p. 75°.5) was prepared from benzoylchloride and oxyphenylurethane, and also from benzoyl-*o*-aminophenol and ethylchlorformate. It is insoluble in acids and alkalis, can be saponified, and yields, on dry distillation, alcohol, benzoylaminophenol, ethylbenzoate, and benzoyl carbonyl-*o*-aminophenol. The latter compound (m. p. 174°) was also prepared from carbonylaminophenol. Analogous compounds

containing the nitrobenzoyl group were prepared. Carboethoxyaminophenol phenyl carbamate, prepared from the phenol, phenyl isocyanate, and aluminum chloride melts at 116° – 118° . Carboylmethyl-*o*-aminophenol, $\text{CH}_3\text{N}(\text{C}_6\text{H}_4\text{OCO})$, was prepared

from the phenol and methyl iodide. It melts at 86° , and when heated with concentrated hydrochloric acid at 180° , yields *o*-methylaminophenol (m. p. 88° – 90°) which with benzoyl chloride forms an ester (m. p. 160° – 162°), and with ethyl chlorformate gives benzoylmethyl-*o*-aminophenylethyl carbonate (m. p. 68°). *o*-Oxyphenylmethylurethane, prepared from methyl-*o*-aminophenol and ethyl chlorformate, melts at 53° and yields a benzoyl derivative which melts at 88° – 90° . From anisidine and ethyl chlorformate, *o*-methoxyphenylurethane (b. p. 180 – 182° at 26 mm.) was prepared. By bromination a monobrom derivative (m. p. 102° .5) and a compound melting at 252° were formed. By the action of phosphorus pentachloride, a chloride was obtained, which was converted into *o*-anisidine urea (m. p. 143° – 145) by ammonia, and into the corresponding phenyl derivative (m. p. 144°) by aniline. *o*-Aminophenylethyl carbonate is an oil, and forms a hydrochloride (m. p. 150° – 152°), which forms a double salt with platinum chloride. *p*-Nitrophenylethyl carbonate melts at 68° and is converted into an amido compound (m. p. 36°) on reduction, which gives a hydrochloride (m. p. 197°) and a double chloride containing platinum (m. p. 237°). *p*-Aminophenylethyl carbonate was converted into the corresponding urea (m. p. 147° – 150°), but a transformation similar to that which took place with the ortho compound could not be brought about.

Products of the Explosion of Acetylene. BY W. G. MIXTER. *Am. J. Sci.*, 159, 1–9.—The explosion of acetylene was studied in order to test the hypothesis advanced by the author, that a sufficient frequency of molecular impacts is requisite to secure spread of explosive change throughout a gas. The gas was introduced into glass tubes 20 cm. long and 11–15 mm. internal diameter at ordinary temperature and pressure. The tubes were then sealed and heated in a furnace. When the desired temperature was reached, the gas was exploded by an electric spark produced between platinum wires sealed in the tubes. In no case was the explosion violent. The hydrogen remaining after absorbing acetylene was the measure of the decomposition; the difference between the volume of acetylene taken and the volume of gas after explosion was considered a measure of the condensation-products formed. As the result of fifteen experiments it was shown that at 325° , decomposition did not extend throughout the gas, although the energy of the system was greater than

that containing twice as many molecules at 0° in the same space—a condition in which decomposition will propagate itself. At temperatures above 325° the decomposition was self-propagating, as the impacts were of sufficient frequency to cause explosion. The results at high temperatures present the striking fact that the amount of acetylene decomposed, as measured by the residual hydrogen, is fairly constant from 350° to 450° . At 447° 50 per cent. of the acetylene was decomposed and 20 per cent. was condensed. When acetylene was exploded under conditions allowing expansion, in a tube 10 mm. in diameter, at the temperature of the room, and under a pressure of 3 atmospheres, the explosion was violent and 79 per cent. of the gas was decomposed and 5 per cent. was condensed. When the explosion took place in a bomb where no change in volume was possible, the residual acetylene amounted to almost 4 per cent. The decomposition into carbon and hydrogen in this case was probably complete. The acetylene present after the explosion was, no doubt formed from its elements at the high temperature reached in the decomposition. In the experiments in which the acetylene contained a trace of air, the presence of hydrocyanic acid was noted.

Camphoric Acid. BY WILLIAM A. NOYES. *Am. Chem. J.*, 23, 128-135.—The author suspected that the ketone prepared from dihydrociscampholytic acid (*this Rev.*, 5, 127) was 2,3,3-trimethylcyclopentanone, and, accordingly, undertook the preparation of the latter compound by a synthesis which would leave no doubt as to its structure. This synthesis has been completed with the result that the two compounds are proved to be identical. It follows from this fact that ciscampholytic acid is Δ^1 -2,3,3-trimethylcyclopentenoic acid, and that the older formula of Perkins for camphoric acid and Bouveault's formula for camphor are correct. γ -Bromisocaproic acid was condensed with the sodium derivative of methylmalonic ester. From the resulting ester of 2,3,3-tetramethylhexoic 1,2',6-acid (b. p. 180° - 187° at 20 mm. pressure) the free acid $(\text{HOOC})_2\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{COOH}$ was prepared, which crystallizes from ether in needles, which begin to decompose at 175° and give a quantitative yield of $\alpha\beta\beta$ -trimethyladipic acid when heated at 190° - 200° . The trimethyladipic acid, when distilled from lime, was converted into a ketone which yielded an oxime (m. p. 104°) identical with the one from the ketone prepared from α -hydroxydihydrociscampholytic acid. The author gives his reasons for his opinion that camphoric acid is a normal γ -lactone.

On the Rearrangement of Imido-esters. BY HENRY L. WHEELER, TREAT B. JOHNSON, MUNSON D. ATWATER, AND

BAYARD BARNES. *Am. Chem. J.*, **23**, 135-150.—A distinct part of the work described in this article was done by each of the four authors. In this review a separate paragraph, preceded by the author's initials, is devoted to the work of each.

H. L. W.—Imidoesters react slowly at ordinary temperatures with methyl and ethyl iodides, giving alkylamides. This reaction is accompanied by the formation of hydrogen iodide, which with unaltered ester gives a primary amide, and by a decomposition of part of the ester into nitril and alcohol. The products identified as the result of the action of methyl iodide on benzimidioethyl ester were methylbenzamide, benzamide, benzonitril, and a trace of cyanphenin. The result was the same at room temperature or at 100°, and in the presence of a small or large amount of methyl iodide. Ethyl iodide gave a similar result. A search was made for diethylbenzamide in the reaction-product, but without success. Benzimidioisobutyl ester and methyl iodide gave isobutyl iodide and methylbenzamide. Benzimidioisobutyl ester and isobutyl iodide gave benzonitril, benzamide, and isobutylene. In order to determine the properties of isobutylbenzamide, which was expected as a product of the above reaction, it was prepared by the Baumann-Schotten reaction, and found to be an oil which boiled at 173°-178° at 13 mm. pressure and formed crystals which melted at 57°-58°.

T. B. J.—A quantitative study of the reaction between phenylacetimidomethyl ester and methyl iodide showed that the amount of transformation taking place was independent of the quantity of methyl iodide used. The weights of phenylacetamide, phenylacetoneitril, and methylphenylacetamide from 20 grams of the imidoester were approximately 2, 4, and 6 grams, respectively. Ethylphenylacetamide crystallizes from water in colorless plates, which melt at 73°-74°.

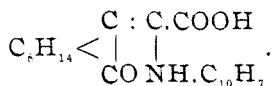
M. D. A.—Furimidomethylester was prepared from furyl cyanide; it boils at 52°-57° at 8 mm. and at 169°-172° at 762 mm. pressure. The behavior of this ester with methyl iodide is analogous to that of the other imidoesters. Methylpyromucamide, prepared by this reaction, melts at 64°. *p*-Tolenylimidomethylester (b. p. 105°.5 at 10.5 mm. pressure) suffered a transformation with methyl iodide similar to those described above. *β*-Naphthylimidoethylester was also prepared, and showed a similar reaction with ethyl iodide.

B. B.—Experiments with silver succinimide and methyl and ethyl iodides showed that the oxygen esters, which are first formed as products of the reaction, are converted by the alkylhalide into nitrogen esters. The results are therefore in accord with the facts described above. As an example of an acylimido ester benzoylbenzimidioester was studied. This compound suf-

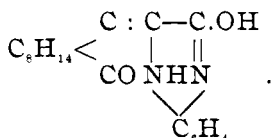
ferred no transformation with ethyl iodide, but when heated to 200° was decomposed into benzonitril and ethylbenzoate.

Anethol and Its Isomers. BY W. R. ORNDORFF AND D. A. MORTON. *Am. Chem. J.*, 23, 181-202.—The authors have subjected the work on anethol and fluid metanethol to a careful revision and find that the two substances are identical. In odor, taste, boiling-point (233°.5), melting-point (22°.5), specific gravity, and crystal form, the pure products exhibit no differences. Both substances show exactly the same chemical conduct. They yield the same dibromide (m. p. 63°-64°), monobrom dibromide (m. p. 102°), hydrochloride, picrate (m. p. about 70°), nitrosite (m. p. 130°), nitrosite anhydride (m. p. 98°), and nitrosochloride (m. p. 123°). A compound of the formula $C_{10}H_{12}O.C_6H_5.OH$ is formed by the action of alcoholic potash on anethol hydrochloride. The compound is a liquid, which distils with steam with slight decomposition. When distilled alone it breaks down completely yielding alcohol, anethol, and higher-boiling products. Anethol gives a hydrobromide analogous to the hydrochloride. When decomposed by alcoholic potash and distilled, it yields, as chief products, anethol and isoanethol. When an alcoholic solution of anethol was treated with sodium, *p*-propylanisol was formed. Anethol is rapidly and completely converted into anisoin when it is heated in acetone solution with iodine. *p*-Cresol was isolated as one of the products of the destructive distillation of anisoin.

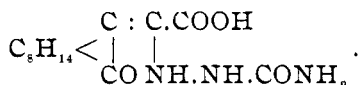
Condensation Compounds of Amines and Camphoroxalic Acid. BY J. BISHOP TINGLE AND ALFRED TINGLE. *Am. Chem. J.*, 23, 214-230.—In a previous paper (*this Rev.*, 5, 67) the authors described the action of aniline on camphoroxalic acid. The work has been extended to the study of the action of other amines on the acid, and the results show that the products of the reaction when fatty amines are used are not analogous in structure to those obtained from aromatic amines. This difference in behavior is probably due to the great difference in basicity of the two classes of amines. In the present paper the action of α - and β -naphthylamine, *o*-phenylenediamine, and semicarbazide on camphoroxalic acid is described. By the action of α -naphthylamine on the acid, in alcoholic solution at 100°, a compound was obtained which crystallizes from benzene in amber-colored crystals, and melts at 170° with decomposition. The compound resembles the aniline derivative prepared in an analogous way and probably has the following structure:



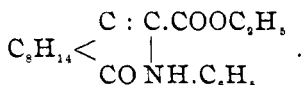
β -Naphthylamine gives a similar compound (m. p. 173°). *o*-Phenylenediamine readily condenses with the sodium salt or ethyl ester of camphoroxalic acid giving a compound (m. p. 246°) to which the following structure is assigned:



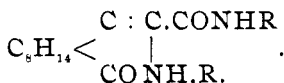
Two substances are formed by the interaction of semicarbazide and potassium camphoroxalate in presence of alcohol at 100° . They are separated by their different solubilities in ether. The soluble compound melts at 218° , the insoluble at 209° - 210° . Both have the composition represented by formula



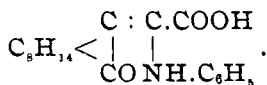
At 100° , in alcoholic solution, ethyl camphoroxalate and aniline yield the compound (m. p. 158° - 160°)



Compounds of an analogous composition were obtained from β -naphthylamine (m. p. with decomposition at 174°) and from semicarbazide (m. p. 202°). Ethylcamphoroxalate condenses with ammonia, methylamine, and ethylamine under similar conditions, but the compounds formed have the following structure:



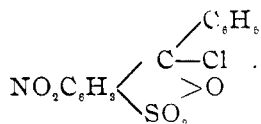
These substances will be described in a later paper. Condensation-products could not be obtained from the ester or salt of camphoroxalic acid and ethylaniline, dimethylaniline, *m*- and *p*-phenylenediamine, or urea. Ethylcamphoroxalate did not react with α -naphthylamine or dimethylaniline. Phenylcamphorformeneamine,



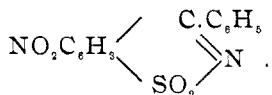
readily reacts with acid chlorides. The benzoyl derivative melts at 160° - 161° , the benzenesulphonyl compound at 133° , and the acetyl derivative, which was not obtained in pure condition, at 134° . The formation of acyl derivatives is evidence in favor of the

view of the structure of the compound represented by the above formula.

The Symmetrical Chloride of Paranitroorthosulphobenzoic Acid. BY F. S. HOLLIS. *Am. Chem. J.*, 23, 233-255.—The author gives much improved directions for the preparation of the chlorides of *p*-nitro-*o*-sulphobenzoic acid. By regulating the conditions under which the acid potassium salt of the acid is treated with phosphorus pentachloride, the resulting product consists of the unsymmetrical chloride only, or of a mixture of the chlorides, which contains 30-40 per cent. of the symmetrical chloride. The two chlorides were separated by crystallization from chloroform. The action of benzene and aluminum chloride on the two chlorides was studied under a variety of conditions. Both compounds yielded the same product, *p*-nitro-*o*-benzoylbenzenesulphone chloride, but one chlorine atom entering into the reaction. The compound crystallizes in monoclinic crystals, and melts at 177°. The author is of the opinion that the chloride has the structure represented by the following formula on account of its high melting-point and the fact that it is not acted upon by alcoholic potash:



By heating with hydrochloric acid, sulphuric acid, water, or absolute alcohol, the chloride is converted into *p*-nitro-*o*-benzoylbenzenesulphonic acid. The barium salt of this acid is of interest, as it crystallizes with three, three and one-half, six, and seven molecules of water of crystallization. The sodium, potassium, magnesium, calcium, and lead salts were also prepared. *p*-Nitro-*o*-benzoylbenzenesulphone chloride, when heated with concentrated ammonia at 100°, gave a lactim of the formula,



The compound is a granular powder (m. p. 234°), which is converted into the ammonium salt of nitrobenzoylbenzenesulphonic acid when heated with hydrochloric acid at 200°.

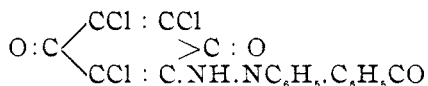
Stereoisomers and Racemic Compounds. BY HERMAN C. COOPER. *Am. Chem. J.*, 23, 255-261.—Kipping and Pope (*Proc. Chem. Soc.*, 1898, 113) have shown that on allowing a racemic mixture to crystallize from an optically active solvent, the first fractions show a preponderance of crystals of one of the

isomers. This fact would indicate that the optical isomers had different solubilities in the solvent, but since the author with Goldschmidt (*Ztschr. phys. Chem.*, 26, 711) had found that the two active carboximes have the same solubility in *d*-limonene, it seemed of interest to investigate the subject further. The sodium ammonium tartrates, the compounds investigated by Kipping and Pope, have the same solubilities in dextrose solutions of varying strength, notwithstanding the fact that they can be separated by crystallization from such solutions. The sodium hydrogen tartrates were investigated with the same result. Sodium hydrogen tartrate decomposes at 234°, the racemate at 219°, and a mixture of equal parts of the optical isomers at 222°. A mixture of approximately equal parts of the active carboximes melts at 93°, the melting-point of inactive carboximes. A slight shrinking was observed at 72°, the melting-point of the active body. On mixing equal amounts of the active sodium hydrogen tartrates in water, a cloudy precipitate of racemate appears and does not disappear until the temperature of solution of the racemate is reached. A mixture of the active carboximes has the same solubility in aqueous alcohol as the inactive variety.

A New Synthesis in the Quinazoline Group. BY MARSTON TAYLOR BOGERT AND AUGUST HENRY GOTTHELF. *J. Am. Chem. Soc.*, 22, 129-132.—When anthranilic acid was heated in a sealed tube with acetonitrile, 2-methyl-4-ketodihydroquinazoline was obtained. In this preliminary paper the authors show that this is a general reaction by preparing analogous derivatives from the nitriles of propionic, benzoic, phenylacetic, and *p*-toluic acids. The yields are good, and as the reaction proceeds as readily with aromatic as with fatty nitriles, the synthesis will be of particular value in preparing quinazoline derivatives containing aromatic groups.

A Comparison of Some Formaldehyde Tests. BY B. M. PILHASHY. *J. Am. Chem. Soc.*, 22, 132-136.—The author reports the results of a study of the various tests for formaldehyde. It is shown that the test of Trillat with dimethylaniline and sulphuric acid is untrustworthy, since the amine itself gives the color reaction which is said to be due to the aldehyde. The author concludes that phenylhydrazine hydrochloride is the best reagent for detecting formaldehyde.

The Action of α -Acylated Phenylhydrazines on the Chlorine Derivatives of Quinones. BY WILLIAM MCPHERSON AND ROBERT FISCHER. *J. Am. Chem. Soc.*, 22, 141-144.—Trichloroquinone reacts readily with unsymmetrical benzoylphenylhydrazine and forms a compound of the structure,



The two atoms of hydrogen which are removed in the condensation, reduce a part of the quinone to the corresponding hydroquinone. This reaction is of interest since hydrazones are formed from quinone and acylated phenylhydrazines. The new compound is a bright red crystalline body which melts at 158°.5.

On the Action of Certain Acid Reagents on the Substituted Ureas. BY F. B. DAINS. *J. Am. Chem. Soc.*, 22, 181-198.—The action of a number of acids, acid chlorides, and acid anhydrides on substituted ureas was studied, and in no case was the direct introduction of an acyl group observed. In all cases the temperature required to produce reaction was so high that acyl ureas were never isolated, but only their decomposition-products. The experiments presented show that the reaction between thioureas and organic monobasic acids gives fairly constant results, the products being carbon dioxide, hydrogen sulphide, water, aniline, the anilide, mustard oil, and carbanilide. With dibasic acids and acid chlorides the reaction is more complicated and varied. Reference must be made to the original paper for the large number of details given.

The History of the Constitution of the Alkaloids. BY A. R. L. DOHME. *Am. J. Pharm.*, 72, 9-25.

Racemism. BY ROBERT HART BRADBURY. *J. Franklin Inst.*, 149, 299-314.—A historical lecture.

BIOLOGICAL CHEMISTRY.

A. G. WOODMAN, REVIEWER.

Preliminary Communication on the Chemistry of Mucin. BY P. A. LEVENE. *J. Am. Chem. Soc.*, 22, 80-85.—The author has obtained a substance with acid properties from tendomucin, submaxillary mucin, and a mucoid carcinoma. Its chemical properties, as well as the analysis of its copper salt, point to its identity with chondroitinsulphuric acid. The results of this preliminary investigation seem to show that the mucins in general are not simple compounds of proteids and carbohydrates, but are proteid derivatives of an ethereal sulphuric acid.

On the Maximum Production of Hippuric Acid in Rabbits. BY W. H. PARKER AND GRAHAM LUSK. *Am. J. Physiol.*, 3, 472-484.—The authors conclude that in metabolism the proteid molecule, the same being likewise true of gelatine, may yield