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ARTHUR A. NOYES, Editor.

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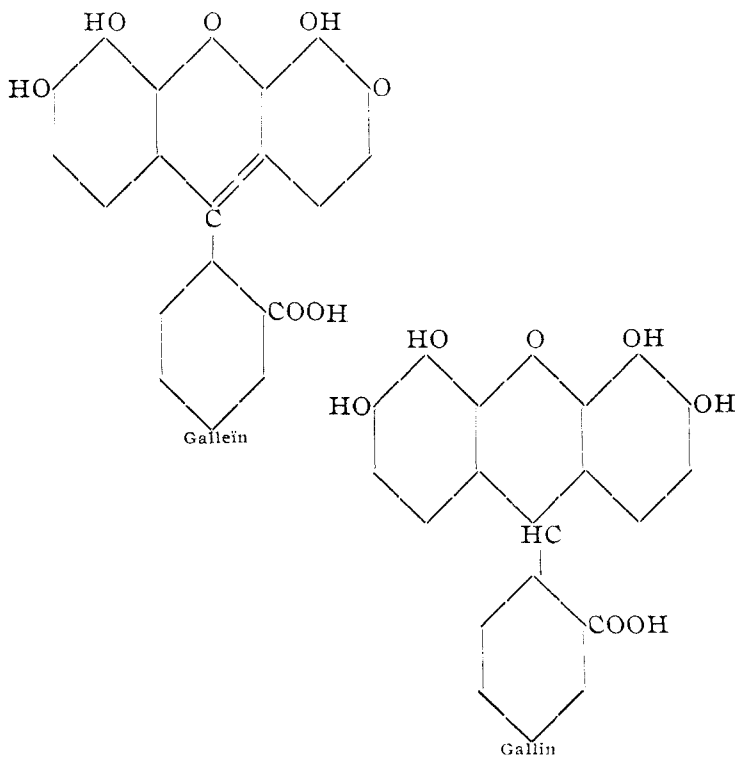
ORGANIC CHEMISTRY.

J. F. NORRIS, REVIEWER.

On Certain Colored Substances Derived from Nitro Compounds. By C. LORING JACKSON AND F. H. GAZZOLO. *Am. Chem. J.*, 23, 376-396; *Proc. Am. Acad.*, 35, 263-281.—In continuing the study of the colored substances formed by the action of sodium alcoholates on certain nitro compounds, the authors have succeeded in obtaining colored products by treating trinitroanisole or trinitrobenzene with the sodium compounds of malonic ester, acetoacetic ester, phenol, and benzyl cyanide. The compounds containing malonic ester and acetoacetic ester are stable and were found on analysis to consist of three molecules of the sodium salt of the ester combined with one of the trinitro compound. Similar experiments with sodium methylate, ethylate, or amylate and trinitrobenzene led to analogous results. The formation of compounds of this composition is noteworthy, since all the substances prepared heretofore have contained the constituents in equal molecular proportions. The compounds were obtained as highly colored precipitates by treating a solution of the nitro compound in benzene with the sodium salt of the ester made by the action of sodium on the ester in the absence of alcohol. The compounds are decomposed by dilute acids, giving the aromatic constituent unaltered, and by alcohols. When the methyl compound is allowed to stand with benzyl alcohol, the methyl groups are replaced by benzyl. The compound so formed is converted into the corresponding methyl derivative when it is boiled with methyl alcohol. Experiments with picramide, dinitroxylol, and trinitroxylol showed that an increase in the negative nature of the aromatic constituent, increases the tendency to form colored compounds. The presence of methyl groups, however, diminishes the tendency to form these com-

pounds. There was no color reaction with trinitromesitylene and sodium methylate. No colored compounds were obtained by the action of sodium alcoholates on aromatic bodies rich in negative groups, but containing no nitro groups. The authors conclude that the compounds are without doubt addition-products and not substitution-products, as suggested by Victor Meyer, and that the addition probably takes place at both the carbon and nitrogen atoms in the aromatic constituent.

The Constitution of Gallein and Coerulein. By W. R. ORNDORFF AND C. E. BREWER. *Am. Chem. J.*, 23, 425-431.—A revision of the work on the reduction-products of gallein leads to the conclusion that hydrogallein and gallol are identical with gallin. Gallein is the phthalein of pyrogallol, and gallin is the corresponding phthalin. The following formulae are assigned to the compounds from a study of their esters :



A methyl and an ethyl ester were made by boiling gallein with the corresponding alcohol and a little sulphuric acid. Gallein triphenylcarbonate was prepared by heating gallein with phenyl isocyanate. Colored tetramethyl and tetraethyl ethers were also prepared. Gallein reacts as if it had the tautomeric, lactoid formula also, for it gives a colorless tetracetate, tetrabenzoate, and tetraphenylsulphonate. It also gives colorless tetramethyl and tetraethyl ethers. Its trimethyl ether resembles closely phenolphthalein in its properties. The constitution of gallin was shown by the fact that it gives a colorless tetracetate and pentamethyl ether. The tetracetate was proved to be an acid by the preparation of a silver salt. The pentamethyl ether has no acid properties and is easily saponified. Formulae for coerulein and coerulein are proposed, which bring out the relation of these compounds to anthragallol. A description of the above-mentioned compounds will be furnished later by the authors.

Researches on the Sodium Salts of the Amides. BY HENRY L. WHEELER. *Am. Chem. J.*, 23, 453-471.—A comparative study of the rate of formation of the sodium salts of the acid amides was made, in order to obtain additional evidence for the structure of these compounds, and to determine whether stereochemical interference was noticeable in the reaction. In working out the experimental details it was found necessary to devise a new method for the preparation of the sodium salts. When a boiling solution of the amide in benzene was treated with sodium amalgam, the reaction took place readily, and a number of compounds yielded sodium derivatives, which could not be obtained by the previously existing methods. To determine whether the velocity of salt formation is dependent on the relative acidity of the molecule, the anilides of formic, acetic, oxalic, and benzoic acids were studied. The results showed that there was no relation between the two quantities; the rate of the formation of the salt of oxanilide was, for example, only a little more than half that of formanilide. That basicity does not exert the most important influence, the acyl group being the same, was shown by experiments with benzamide, benzanilide, and benzoylbenzylamine. Ammonia and benzylamine have practically the same affinity constants, yet the velocity of salt formation with benzamide was nearly 100 times as great as that with benzoylbenzylamine. Experiments with a number of compounds to determine which of the two general forms, $RNHCOH$ or $HNHCOR$, is more favorable for salt formation showed "that a disubstituted formamide gives a salt less readily than one that is monosubstituted, which would be expected from the theory of stereochem-

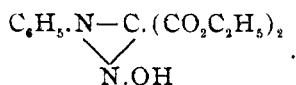
ical interference; and that when the larger or interfering radical is attached to nitrogen it has less effect in retarding the formation of sodium salts than when attached to the keto group. They, therefore, indicate that the sodium is attached to oxygen." The above statement does not always hold true, for it was found that the isomeric cycloamides, oxindol, and phthalimidine, were completely changed into their sodium salts, while, under the same conditions, benzoylbenzylamine was practically unchanged. Since stereochemical interference was found to have an influence on the reaction investigated, the amide of 2-4-6-trimethylbenzoic acid was studied. A sodium salt was readily prepared. As this acid is inactive in reactions which are supposed to involve an addition to the keto group, but does enter into reactions involving direct substitution, the fact that a sodium salt was formed from the amide points to the conclusion that, in the salt, the metal is joined to nitrogen. If this view is incorrect, then 2-4-6-trimethylbenzamide must, contrary to the theory of stereochemical interference, form an addition-product of the amide and sodium hydroxide, in the preparation of the sodium salt, in which the elements of the alkali are joined to the keto group. The elimination of water from such a compound would yield a sodium salt of the amide in which the metal is joined to oxygen. An experiment showed this to be the case. 2-4-6-Trimethyl- and 2-4-6-tribrombenzamide formed compounds with sodium hydroxide containing equal molecular quantities of the constituents. The addition-product containing bromine was prepared by pouring an excess of a solution of the amide in benzene on powdered sodium hydroxide. The fact that these addition-products have the elements of the alkali joined to the keto group and are not so-called molecular compounds, was shown by the action of benzoyl chloride on the sodium hydroxide addition-product of thioacetanilide, whereby acetanilide and thiobenzoic acid was formed.

Note on the Constitution of Diparabrombenzylcyanamide.

By C. LORING JACKSON AND R. W. FULLER. *Am. Chem. J.*, 23, 494-500; *Proc. Am. Acad.*, 35, 231-236.—In order to obtain evidence of the structure of dialkylcyanamides, di-*p*-brombenzylcyanamide was prepared and studied, as this substance crystallizes well (m. p. 133°) and yields, on decomposition, a compound which can be obtained in a pure condition. When the cyanamide was treated with dilute sulphuric acid, dibrombenzylamine, ammonia, and carbon dioxide were formed. This reaction proves that the compound has the structure represented by the formula $R_2 : N.CN$ and not the possible imide structure, $R.N : C : N.R$.

On the Action of Nitrous Acid on Ethyl Anilinomalonate.

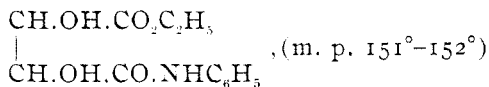
By RICHARD SYDNEY CURTISS. *Am. Chem. J.*, 23, 509-511.—When ethyl anilinomalonate was suspended in water and treated with sodium nitrite and sulphuric acid, a thick amber-colored oil was obtained, which was extremely unstable. This oil did not give Liebermann's nitroso reaction, but showed marked acid properties. It yielded well crystallized, but unstable salts when treated with sodium or potassium hydroxide. By the action of acetic anhydride two crystalline substances were obtained. From the properties of the oil the author concludes that the compound has the following structure :



On Nitromalonic Aldehyde. By HENRY B. HILL, CHARLES A. SOCH, AND GEORGE OENSLAGER. *Am. Chem. J.*, 24, 1-15.—In a former paper (*Am. Chem. J.*, 22, 89) it was shown that nitromalonic aldehyde readily reacts with acetone, and that the product formed is *p*-nitrophenol. This condensation of nitromalonic aldehyde with a number of ketones has been studied, and the conclusion is drawn that the reaction is a general one. Condensation took place most readily in dilute aqueous solution in the presence of a small amount of alkali. The reaction-mixture was allowed to stand twenty-four to forty-eight hours at ordinary temperatures, when the yield was almost quantitative. Methyl-ethyl ketone gave on condensation nitrocresol ($\text{CH}_3\text{.I.OH}_2\text{.NO}_2$). From dibenzyl ketone, 2,6-diphenyl-4-nitrophenol (m. p. 135°-136°) was prepared. This compound formed a potassium salt from which the corresponding anisol (m. p. 152°-153°) was prepared. The nitrophenol was reduced to an amido compound (m. p. 149°-150°), which was readily oxidized to diphenylbenzoquinone (m. p. 135°-136°) which in turn was reduced to a hydroquinone (m. p. 179°-180°). Nitromalonic aldehyde and acetoacetic ester gave nitrosalicylic acid ($\text{OH.I.CO}_2\text{H}_2\text{.NO}_2$). With levulinic acid, 5-nitro-2-oxyphenylacetic acid, which melts at 160°-162° when rapidly heated, was obtained. If the acid is melted by prolonged heating at 148°-149° it is converted into its lactone (m. p. 187°-188°). The ethyl ester of the acid melts at 154°-155°. 2,6-Di-carboxy-4-nitrophenol, formed from nitromalonic aldehyde crystallizes with one molecule of water of crystallization, melts when anhydrous at 213°-214°, and is converted by fuming nitric acid into picric acid.

The Preparation of Zinc Ethyl. BY ARTHUR LACHMAN. *Am. Chem. J.*, 24, 31-39.—Detailed directions for the preparation of zinc ethyl in quantity are given. The zinc-copper couple used is made by reducing a mixture of 100 parts of zinc dust and 12 parts of copper oxide powder in a stream of hydrogen. The results of a number of experiments show that the method is rapid and gives an excellent yield. The author gives some valuable information in regard to the manipulation of zinc ethyl.

The Reactions of Aniline and Hydroxylamine with Hydroxy- and Unsaturated Compounds. BY ALFRED TINGLE. *Am. Chem. J.*, 24, 45-60.—The author has undertaken an investigation of the characteristic reactions of the group $-\text{CH} : \text{C.OH}$. As the group under investigation contains two reactive elements, a double bond and a hydroxyl group, it seemed best to study in the beginning, first a compound containing no double bond but a hydroxyl group which is rendered more active by the presence of a highly negative radical, and, second, a compound containing a double bond and a negative group. As examples of these two classes of bodies, ethyl tartrate and ethyl cinnamate were used. The action of aniline and of hydroxylamine on the substances was studied, but the results do not yet warrant any definite conclusions. When ethyl tartrate was boiled with aniline, tartranilide and a body which appeared to be ethyl phenyltartrate,



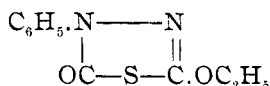
were formed. This reaction shows that the hydroxyl group, under these conditions, is inactive toward an amine. The ester did not react with hydroxylamine in a number of experiments. Aniline was found to react with neither ethyl nor sodium cinnamate. With hydroxylamine, however, there was a complicated reaction which led to the formation in aqueous solution, of an oil, which is at present under investigation, and phenylisoxazolone. When aniline was boiled with methyl salicylate the products were phenol and methylaniline. As the yield is very good the author proposes to extend the reaction to the preparation of other alkylanilines.

On the Molecular Rearrangement of the Thioncarbamic, Thioncarbanilic, and Thioncarbazine Esters: β -Alkyl- α - μ -diketotetrahydrothiazoles. BY HENRY L. WHEELER AND BAYARD BARNES. *Am. Chem. J.*, 24, 60-83.—It has already been shown by the authors that thioncarbamic esters, $\text{H}_2\text{N.CS.OR}$

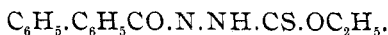
are readily converted into the isomeric thiol compounds, $H_2N.CO.SR$, by the action of alkyl halides. In the present paper are given the results of an examination of certain thion esters, $XHN.CO.OR$, under the same conditions. The experiments led to the preparation of some homologues of α - μ -diketo-tetrahydrothiazole and of sulphocyanacetic acid. When X in the above formula is C_6H_5 , the compounds, thioncarbanilic esters, react less readily with alkyl halides than the thioncarbamic esters. When X is the group C_6H_5NH , however, the compounds, thioncarbazine esters, react with great ease with both alkyl and acyl halides. To prepare phenyl thioncarbazine ester, ethyl dithiocarbonate was treated with phenylhydrazine. In addition to the compound sought, the hydrazone $C_6H_5NH.N : C.SC_2H_5.OC_2H_5$ was obtained. When this hydrazone is treated with thio-benzoic acid, the compounds unite at the double bond and subsequently break down with the formation of phenylthiolcarbazine ester and ethyl thiolbenzoate. The hydrazone can be converted into thioncarbazine ester by the action of hydrogen sulphide or hydrogen chloride. The reaction involves the formation of addition-products and the subsequent elimination of ethyl mercaptan and ethyl chloride respectively. The addition-product containing hydrogen chloride was isolated. The hydrazone reacts energetically with acetyl and benzoyl chlorides. With the latter compound an addition-product is formed, which breaks down into ethyl chloride and the compound



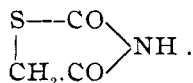
Phenylthioncarbazine ester is converted at ordinary temperatures into the corresponding thiol compound by alkyl halides. It reacts with phosgene giving ethoxyphenylthiobiazolone,



and gives a benzoyl derivative of the following structure :

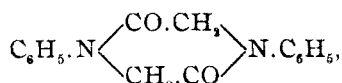


The action of chloracetic acid on ethyl thioncarbamate is analogous to that of the alkyl halides: an addition-product is first formed, which loses ethyl chloride and is thus converted into carbaminthiolglycollic acid, $H_2N.CO.SCH_2.CO_2H$. This derivative of glycollic acid loses water and passes into α - μ -diketo-tetrahydrothiazole,



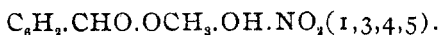
Derivatives of the above compound were prepared by replacing chloracetic acid by other halogen-substituted acids in the fatty series, and by the action of hydrochloric acid on the α -sulphocyan derivatives of the fatty acid esters. Reference must be made to the original paper for a more detailed account of the compounds mentioned and a description of a large number of esters of α -sulphocyanacetic acid and its homologues.

Formation of Indigo from Diphenyldiketopiperazine. BY M. KUHARA AND M. CHIKASHIGÉ. *Am. Chem. J.*, 24, 167-171.—When diphenyldiketopiperazine,



prepared from chloracetanilide and potassium hydroxide, was cautiously fused with potassium hydroxide, it was converted into a brown substance, which, on solution in water, was rapidly changed into indigo. It is probable that in the reaction phenylglycocoll was first formed and that this, by the action of the alkali, went over to pseudoindoxyl which in turn was converted by the oxygen of the air into indigo. This synthesis explains the formation of indigo from bromacetanilide.

The Action of Nitric Acid on Vanillin. BY WILLIAM B. BENTLEY. *Am. Chem. J.*, 24, 171-181.—Nitric acid even in a 5 per cent. solution, does not oxidize vanillin, but converts it into a mixture of nitrovanillin, dihydrodivanillin, and dinitroguaiacol. Under the proper conditions a good yield of nitrovanillin is obtained. The compound melts at 176°, and forms insoluble chromium, copper, and lead salts, and a potassium salt which crystallizes with one molecule of water of crystallization. Nitrovanillin is converted by nitric acid into dinitroguaiacol; its structure is, therefore,



By cautious treatment with potassium permanganate, nitrovanillin was oxidized to nitrovanillic acid, which was found to melt, after careful purification, at 216° and not at 202°, the melting-point assigned to it by previous investigators. The acid crystallizes with $1\frac{1}{2}$ molecules of acetic acid.