

# REVIEW OF AMERICAN CHEMICAL RESEARCH.

VOL. VI. No. 3.

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.

**The Rate of Action of Water on Certain  $\alpha$ -,  $\beta$ -, and  $\gamma$ -Halogen Substituted Fatty Acids.** BY EDWIN DEBARR. *Am. Chem. J.*, 22, 333-351.—In order to determine the influence of the position of the halogen atom on the decomposition of substituted fatty acids by water, a number of acids were heated with water in sealed tubes at 150°, as it was found that the reaction could be most readily studied under these conditions. The figures given in the following table are selected from the large number obtained. In the first column are given the percentages of transformation of the respective acids at the end of one-half hour. The second column gives the time in hours when transformation ceased, and the third column the total amount changed in this time:

Acid.	I.	II.	III.
Monochloroacetic .....	4.06	30	47.11
Dichloroacetic .....	5.32	5	17.76
Trichloroacetic .....	42.38	8	100.00
$\alpha$ -Chlorpropionic.....	4.42	3	11.41
$\alpha$ -Brompropionic.....	2.93	2	7.06
$\alpha$ -Brombutyric .....	3.77	3	9.25
$\alpha$ -Chlorbutyric.....	5.80	3	7.50
$\beta$ -Chlorpropionic.....	41.50	4	50.44
$\beta$ -Chlorbutyric.....	29.97	3	37.38
$\gamma$ -Chlorbutyric.....	100.00	$\frac{1}{2}$	100.00

The order in which decomposition takes place is, excepting in the case of mono-, di-, and trichloroacetic acid, not the same as is that of the affinity constants of the acids. The order of the stability of the compounds is, however, the same as that of the

affinity. The influence of the distance of the halogen from the carboxyl group is clearly shown with the butyric acids, the rate of transformation rapidly increasing the further the halogen atom is removed from the carboxyl group. Care was taken to obtain the acids necessary for the investigation in a state of purity. As a result the physical constants determined are more trustworthy than those heretofore obtained.  $\beta$ -Chlorpropionic acid melts at  $61^\circ$  and boils at  $204^\circ$ .  $\beta$ -Chlorbutyric acid melts at  $16^\circ$ – $16.5^\circ$  and boils at  $116^\circ$  at 22 mm. pressure.  $\gamma$ -Chlorbutyric acid boils at  $196^\circ$  (22 mm.) and melts at  $12^\circ$ .

**On the Nature of the Oxyazo Compounds.** BY WILLIAM MCPHERSON. *Am. Chem. J.*, 22, 364–384.—From the work of previous investigators to determine the nature of the oxyazo compounds, it has been impossible to decide which of the following formulæ expresses the structure of these compounds: HO.R.N : N.C<sub>6</sub>H<sub>5</sub>, O.R : N—NH.C<sub>6</sub>H<sub>5</sub>. The author has obtained decisive evidence by studying the action of unsymmetrical alkylated and acylated derivatives of phenylhydrazine on ortho and para quinones. The condensation-products thus obtained, O.R : N—N.R'.C<sub>6</sub>H<sub>5</sub>, were compared with the free oxyazo compounds and the corresponding products obtained from these by direct alkylation and acylation. The results prove that all paraoxyazo compounds, as well as their salts and substitution-products, possess the general formula MO.R.N : N.C<sub>6</sub>H<sub>5</sub> (M=H, a metal, acyl, or alkyl). The work in the ortho series, while not so decisive, points to the conclusion that these compounds and their acylated derivatives are monohydrazones of orthodiketones, O.R : N—N.M.C<sub>6</sub>H<sub>5</sub> (M=H or acyl). The alkylated substitution-products, on the other hand, are azo compounds, R'O.R.N : N.C<sub>6</sub>H<sub>5</sub>. Quinonebenzoylphenylhydrazine was prepared by mixing aqueous solutions of quinone and  $\alpha$ -benzoylphenylhydrazine hydrochloride. The yellow precipitate formed melted at  $171^\circ$  after crystallization from benzene. The compound, when reduced with zinc and acetic acid, was split quantitatively into benzanilide and *p*-amidophenol. It was converted by acids and alkalis into benzoic acid and *p*-oxyazobenzene. The hydrazone which, from its method of synthesis and its properties, must have the structure represented by the formula O : C<sub>6</sub>H<sub>4</sub> : N.N.C<sub>6</sub>H<sub>5</sub>.COC<sub>6</sub>H<sub>5</sub>, is isomeric, not identical, with the compound formed by introducing the benzoyl group into *p*-oxyazobenzene. This latter substance must have, therefore, the structure C<sub>6</sub>H<sub>5</sub>CO.O.C<sub>6</sub>H<sub>4</sub>.N : NC<sub>6</sub>H<sub>5</sub>. From the following facts the conclusion is drawn that *p*-oxyazobenzene is a true azo compound : (1) In the derivatives formed by the introduction of acyl or alkyl groups these groups are joined to oxygen. (2) It has been shown by Goldschmidt and others that *o*-oxyazo derivatives

by direct acylation yield compounds which contain the acyl group joined to nitrogen. (3) Free *p*-oxyazo compounds do not react with phenylhydrazine, whereas all *p*-quinonebenzoylphenylhydrazine derivatives, like benzoquinone itself, react with this reagent with explosive violence. (4) The *p*-oxyazo compounds are soluble in dilute alkalis. The *o*-oxyazo compounds of the naphthalene series, however, are not affected by even concentrated caustic alkalis. (5) The study of the physical properties of the *p*-oxyazo compounds leads to results in accord with those obtained by chemical methods. The acetate of *p*-oxyazobenzene must have the structure  $C_6H_5.N : N.C_6H_4.O.CO.CH_3$ , since it is not identical with quinoneacetylphenylhydrazone (m. p.  $118^\circ$ ) made by the action of  $\alpha$ -acetylphenylhydrazine on quinone. The following hydrazones were prepared and compared with the corresponding derivative of the oxyazo compounds with analogous results: Toluquinonebenzoylphenylhydrazone (m. p.  $151^\circ$ ), thymoquinonebenzoylphenylhydrazone (m. p.  $132^\circ$ ),  $\alpha$ -naphthoquinonebenzoylphenylhydrazone (m. p.  $161.5^\circ$ ). When benzoquinone and  $\alpha$ -methylphenylhydrazine hydrochloride were brought together in dilute aqueous solution, an evolution of nitrogen took place and dimethyldiphenyltetrazone (m. p.  $133^\circ$ ) separated. From  $\alpha$ -benzylphenylhydrazine an analogous benzyl derivative (m. p.  $145^\circ$ ) was prepared. When  $\alpha$ -naphthoquinone was used, however, a hydrazone was formed similar in structure to the compounds prepared from the acylated hydrazines. The methyl derivative melts at  $118.5^\circ$  and the benzyl derivative at  $136^\circ$ . The benzyl ether of benzene azo- $\alpha$ -naphthol (m. p.  $102^\circ$ ), which is isomeric with the latter compound, was prepared from the azo compound and benzyl chloride. When an orthoquinone was studied the results obtained were different from those described alone. The compound formed by treating  $\beta$ -naphthoquinonehydrazone with benzoyl chloride was found to be identical with the hydrazone prepared by the action of  $\alpha$ -benzoylphenylhydrazine on  $\beta$ -naphthoquinone. The compound, which must contain the benzoyl group joined to nitrogen, crystallizes from benzene-ligroin and melts at  $191^\circ$ . When the methyl ethers were made, however, two compounds were obtained, an azo body (m. p.  $95^\circ$ ) and a quinonehydrazone (m. p.  $134.5^\circ$ ).

**The Action of Benzoyl Chloride on the Phenylhydrazones of Benzoin.** BY PAUL C. FREER. *Am. Chem. J.*, 22, 396-402.— In a previous paper (*this Rev.*, 5, 32; see also *this Rev.*, 5, 125) the author described a compound formed by the action of benzoyl chloride on  $\beta$ -benzoinphenylhydrazone. From an analysis and a molecular weight determination of the substance, it appeared that the chloride had simply effected a molecular rearrangement

and that the compound was a third phenylhydrazone of benzoin. The reaction has been investigated further and the reaction-product described found to be benzanilide. The reaction is a complex one, as the following substances were isolated in addition to benzanilide: benzil, lophine, dibenzanilide, hydrochloric acid, ammonium chloride, aniline hydrochloride, and a large amount of tar. When nitrobenzoyl chloride was used no lophine was formed. The probable course of the reaction by which the above-mentioned compounds are formed is fully explained. Nitrobenzoyl chloride reacts readily with both  $\alpha$ - and  $\beta$ -benzoinphenylhydrazone, whereas benzoyl chloride does not react with the  $\alpha$ -variety at winter temperature.

**Notes on the Space Isomerism of the Toluquinoneoxime Ethers.** BY WILLIAM CONGER MORGAN. *Am. Chem. J.*, 22, 402-407.—In a former paper (*this Rev.*, 5, 30) it was stated that certain ethers of toluquinonemetaoxime, whether formed by the action of hydroxylamine on the quinone or by nitrous acid on the corresponding cresol, showed evidence of existing in isomeric forms. By fractional crystallization of the benzoyl ester two substances have been obtained, one melting at  $193^\circ$  and one melting approximately at  $144^\circ$ . The low-melting compound, which was not obtained in a state of purity, is changed slowly into the high-melting form by repeated crystallizations from alcohol. When heated at  $120^\circ$  with alcohol the change is rapid and complete. The formation of isomers has been noted in the case of ethers prepared from acid chlorides and the sodium salt of the oxime made by the action of amyl nitrite on the sodium salt of the cresol. Under these circumstances the chance of the formation of side-products which would effect the purity of the ether is small, and, consequently, the results obtained indicate that the isomerism is due to the space relation of the atoms. The following-named substances are described: The sodium salt of toluquinone-*m*-oxime, bromtoluquinone-*o*-oxime benzoyl ether (m. p.  $184^\circ$ ), toluquinone-*o*-oxime benzoyl ether dichloride (m. p.  $149^\circ$ ), chlortoluquinone-*o*-oxime benzoyl ether (m. p.  $185$ – $193^\circ$  with decomposition).

**On the Constitution of  $\alpha$ -Dibromdinitrobenzol—Paradibromorthodinitrobenzol.** BY D. F. CALHANE AND P. M. WHEELER. *Am. Chem. J.*, 22, 449-458.—When *p*-dibrombenzene is treated with a mixture of fuming nitric acid and sulphuric acid, the resulting product consists chiefly of  $\beta$ -dibromdinitrobenzene ( $\text{Br}_1, \text{NO}_2, \text{Br}_4, \text{NO}_2, 6$ )

and a small quantity of  $\alpha$ -dibromdinitrobenzene. The authors show that the structure of the latter compound is represented by the formula  $\text{C}_6\text{H}_3\text{Br}_2\text{NO}_2(\text{Br}_1, 2\text{NO}_2, 3, \text{Br}_4)$ . This fact was estab-

lished by converting the compound into a dibromphenylenediamine (m. p.  $94^{\circ}$ - $95^{\circ}$ ) from which *o*-phenylenediamine was obtained by prolonged treatment with sodium amalgam. This result was confirmed by treating the *p*-dibromphenylenediamine with phenanthrenequinone, which gave a dibromphenanthrophenazine (m. p.  $297^{\circ}$ ), and also by treating the diamine with benzil, when dibromdiphenylchinoxaline (m. p.  $215^{\circ}$ - $216^{\circ}$ ) was formed. As such compounds are formed only from *o*-diamines the structure of  $\alpha$ -dibromdinitrobenzene was established since it was prepared from *p*-dibrombenzene.

**Phenyl Mustard Oil as a Reagent for the Detection of the Alcoholic Hydroxyl Group.** BY W. R. ORNDORFF AND F. A. RICHMOND. *Am. Chem. J.*, **22**, 458-473.—The action of phenyl mustard oil on a large number of compounds was studied, in order to discover if it exhibited the marked chemical reactivity which is characteristic of phenyl isocyanate. Its use as a reagent for the detection of the hydroxyl group is limited. It reacts to form well-crystallized compounds with primary, secondary, and tertiary alcohols, but it does not combine with unsaturated alcohols, acids, phenols, or alcohols of the benzene series. The addition-products of phenyl mustard oil and the following alcohols are carefully described: methyl, ethyl, propyl, isopropyl, isobutyl, tertiary butyl, and isoamyl alcohol. When phenyl mustard oil was heated with allyl alcohol, diphenyl urea was formed, and when glycol and glycerine were used, the chief reaction-product was thiocarbanilide. By the action of phenol on phenyl mustard oil thiocarbanilide was formed, and not the phenyl ester of thiocarbamic acid which, according to the literature, is the product of this reaction.

**The Ethers of Isonitrosoguiacol in Their Relation to the Space Isomerism of Nitrogen.** BY JOHN L. BRIDGE AND WILLIAM CONGER MORGAN. *Am. Chem. J.*, **22**, 484-489.—Since the authors have noted the existence of stereoisomerism in the case of certain quinoneoximes, it seemed advisable to repeat the work of previous investigators on isonitrosoguiacol in order to discover if isomerism exists in the derivatives of this compound. A study of the compounds already described, in addition to the benzoyl ether isonitrosoguiacol (m. p.  $188^{\circ}$  when "dipped" for ten seconds) and its dibromide (m. p.  $153^{\circ}$ - $154^{\circ}$ ) and monobromisonitrosoguiacol benzoyl ether led to the discovery of no case of stereoisomerism.

**Diazocaffeine.** BY M. GOMBERG. *Am. Chem. J.*, **23**, 51-70.—When amidocaffeine is dissolved in strong hydrochloric acid and treated with nitrous acid, a diazo compound is formed, which is stable only in solution at a low temperature. Diazo-

caffeine reacts with aromatic phenols and amines with the formation of azo compounds, which crystallize well and possess intense dyeing power. The azo dyes prepared from phenol, dimethylaniline, phenylenediamine, and  $\beta$ -naphthol are described in detail. That the caffeine molecule is not broken up by the action of nitrous acid, but that a true diazo salt of caffeine is formed was shown in two ways. First, when caffeine instead of its amido derivative was subjected to the same treatment with nitrous acid, it remained entirely unchanged; and second, the azo dyes on treatment with stannous chloride furnished almost quantitatively amidocaffeine and the corresponding aromatic body. The condensation-product of acetoacetic acid and diazocaffeine is not similar in structure to the compound found under like conditions with aromatic diazo salts. The caffeine derivative is a diazo compound,  $\text{CH}_3\text{COC} \cdot (\text{N}_2\text{C}_6\text{H}_9\text{N}_4\text{O}_2)_2 \cdot \text{COOH}$ , whereas diazo benzene chloride and acetoacetic ester give a hydrazo and a formazyl compound. Propyl and benzylacetoacetic acids give analogous compounds, the introduction of two diazo residues being made possible by the elimination of the acetyl group as acetic acid. The condensation-products,



were obtained as dark crystalline powders which could be heated to  $285^\circ$  without melting and without decomposition. Diazocaffeine and nitroethane react readily with the formation of a substance of the structure  $\text{NO}_2\text{C} \cdot \text{CH}_2 \cdot (\text{N}_2\text{C}_6\text{H}_9\text{N}_4\text{O}_2)_2$ . The compound crystallizes from a mixture of chloroform and ether in deep-blue flakes, melts at  $218^\circ$ – $219^\circ$ , and shows marked changes in color when heated with water. Nitropropane forms an analogous compound (m. p.  $237^\circ$ – $238^\circ$ ).

**The Action of Ethyl Iodide on Tartaric Ester and Sodium Ethylate.** By JOHN E. BUCHER. *Am. Chem. J.*, 23, 70–83.—Previous investigators have found it impossible to prepare symmetrical diethoxysuccinic ester by the usual synthetical methods. Neither the mono- nor disodium derivative of tartaric ester reacts with methyl or ethyl iodide, and symmetrical dibromosuccinic ester gives unsymmetrical esters when treated with alkyl halides. The author studied carefully the action of ethyl iodide on tartaric ester in the presence of sodium ethylate, and found among the products of the reaction three forms of diethoxysuccinic ester; *viz.*, the unsymmetrical and inactive and *d*-symmetrical varieties. Some of the monoethoxy derivative was also present. The proportions of the different substances varied as the proportions of the reacting substances were changed. The diethoxy derivatives were separated by saponifying the esters and adding calcium chloride when the calcium salt of unsym-

metrical diethoxysuccinic acid was precipitated. The symmetrical acid, obtained by extracting the acidified filtrate with ether, melts at  $97^{\circ}$ - $99^{\circ}$  and forms very soluble crystalline potassium and barium salts. Hydroxyethoxysuccinic acid was isolated by precipitating its lead salt. The probable course of the reaction which results in the formation of an unsymmetrical derivative from a symmetrical compound is explained by the author. Preliminary experiments indicate the formation of oxalacetic ester as an intermediate product in the reaction.

**Action of Picryl Chloride on Pyrocatechin in Presence of Alkalies.** BY H. W. HILLYER. *Am. Chem. J.*, 23, 125-128.—A compound, the constitution of which is represented by the

formula,  $C_6H_4 \begin{array}{c} \diagup O \\ \diagdown O \end{array} C_6H_2(NO_2)_2$ , is readily formed when an alco-

holic solution of picryl chloride and pyrocatechin containing sodium hydroxide is heated at  $60^{\circ}$ - $70^{\circ}$  for six hours. The author proposes to name the substance of which the above compound is a dinitro derivative, phenoxozone, on account of its analogy to phenoxazine, which is made in a similar way from picryl chloride and *o*-amidophenol, and possesses the structure

$C_6H_4 \begin{array}{c} \diagup NH \\ \diagdown O \end{array} C_6H_2(NO_2)_2$ . Dinitrophenoxozone crystallizes from

benzene, melts at  $192^{\circ}$ - $192.5^{\circ}$ , and sublimes unchanged in the form of yellow needles.

**Nitroso Derivatives of Caryophyllene and Cadinene and Their Bearing on the Characterization and Classification of the Sesquiterpenes.** BY OSWALD SCHREIMER AND EDWARD KREMERS. *Pharm. Archives*, 2, 273-301.—A number of derivatives of caryophyllene and cadinene were prepared and carefully studied.

As the substances have well-characterized physical properties they will materially assist in the study of the above compounds as well as in the investigation of other sesquiterpenes. Caryophyllene nitrosite crystallizes in deep-blue needles, melts at  $113^{\circ}$ , and has the rotation  $[\alpha]_D = +102.95$  in benzene solution. It reacts with benzylamine, forming a white crystalline compound, which melts at  $167^{\circ}$ . When exposed to the sunlight in benzene solution about 29 per cent. of the nitrogen is liberated and the  $\beta$ -compound is formed (m. p.  $146^{\circ}$ - $148^{\circ}$ ). In alcoholic solution a similar reaction takes place and a third isomer, the  $\alpha$ -compound, is formed. It melts at  $113^{\circ}$ - $114^{\circ}$ , and is either slightly dextrogyrate or inactive. By a new method of preparation a good yield of caryophyllene nitrosochloride (m. p.  $158^{\circ}$ ) was obtained. The nitrosochloride and benzylamine react

readily with the formation of two nitrobenzylamine bases (m. p.  $128^{\circ}$  and  $169^{\circ}$ ). The nitrosate of the terpene melts at  $148^{\circ}$ – $149^{\circ}$  and forms with benzylamine a nitrol base (m. p.  $128^{\circ}$ ), which is identical with the one obtained from the nitrosochloride. Contrary to the statement in the literature, the authors were able to prepare a crystalline hydrochloride of caryophyllene (m. p.  $69^{\circ}$ – $70^{\circ}$ ). Cadinene forms a nitrosate, which melts with decomposition at  $105^{\circ}$ – $110^{\circ}$ , and a nitrosochloride which melts at  $93^{\circ}$ – $94^{\circ}$ .

**A Preliminary Communication upon Ricinine.** By THOMAS EVANS. *J. Am. Chem. Soc.*, 22, 39–46.—The author shows that the substance obtained by Tuson by extracting castor beans with boiling water, to which the name ricinine was given, is identical with ricidine, which was isolated by Schulze from the same source by a different method of extraction. The compound crystallizes in small colorless prisms, melts at  $193^{\circ}$ , and gives results on analysis agreeing closely with the formulæ  $C_{16}H_{16}N_4O_4$  and  $C_{16}H_{15}N_4O_4$ . The formation of a chlorplatinate, described by Tuson, was probably due to the presence of an impurity in the ricinine investigated, since the pure compound does not form such a salt. It does not give a precipitate with silver nitrate, mercuric nitrate, or mercuric chloride, but on long standing a concentrated solution of ricinine and mercuric chloride yield a feathery crystalline product. By brominating ricinine a substitution-product (m. p.  $232^{\circ}$ ) containing two bromine atoms was obtained. On oxidation with alkaline potassium permanganate a crystalline acid, which melted at  $279^{\circ}$ – $280^{\circ}$ , was obtained.

**Benzenestearosulphonic Acid and Other Sulphonic Acids Containing the Stearic Radical.** By E. TWITCHELL. *J. Am. Chem. Soc.*, 22, 22–26.—Benzenestearosulphonic acid,  $C_6H_5SO_2H$ .  $C_{18}H_{35}O_2$ , was prepared by treating a mixture of oleic acid and benzene with concentrated sulphuric acid. The acid is a sticky, semisolid mass, soluble in water, and forms alkaline salts which are readily precipitated by acids, bases, or salts. Analogous compounds were prepared from naphthalene and phenol.

## METALLURGICAL CHEMISTRY.

H. O. HOFMAN, REVIEWER.

**The Ultimate and Rational Analysis of Clays and Their Relative Advantages.** By H. RIES. *Trans. Am. Inst. Min. Eng.*, 28, 160–166.—The rational analysis of a clay which in its simplest form gives the three mineral constituents, kaolinite, feldspar, and quartz, consists in decomposing and dissolving the