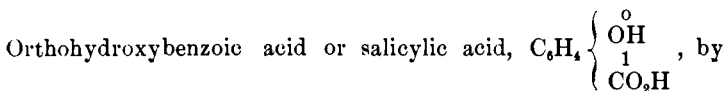


Abstracts from American and Foreign Journals.

Justus Liebig's Annalen der Chemie.

Abstractor. GEO. A. PROCHAZKA, Ph. D.

Nitrosalicylic Acids, and the Isomerisms of the benzol-derivatives, H. HUEBNER (Ann. Chem., 195, 1-55).—In the same manner in which, starting from metabrombenzoic acid, the author had formerly deduced two orthohydrogen atoms in the monosubstituted benzol, he proves the existence of two metahydrogen atoms, by a similar series of substitutions, with salicylic acid as a starting point:



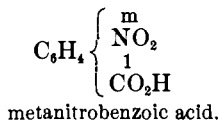
nitration, yields two metanitroortho-hydroxybenzoic acids:



α metanitroortho-hydroxybenzoic acid; β metanitroortho-hydroxybenzoic acid. The diethyl ethers of these acids on treatment with alcoholic ammonia, yield:



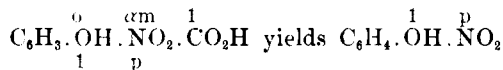
α orthoamidometanitrobenzoic acid; β orthoamidometanitrobenzoic acid, which by azotation yield:



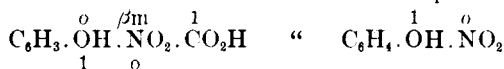
It will be seen that the two isomeric nitrosalicylic acids furnish, in substitution of their hydroxyl groups by hydrogen, the same metanitrobenzoic acid, showing that they contain two hydrogen atoms in metaposition with reference to the carboxyl group.

The different position, in the two acids, of the hydroxyl group, with reference to the nitro group, can be easily demonstrated, as the

two mononitrosalicylic acids, on heating with lime, yield two different mononitrophenols:

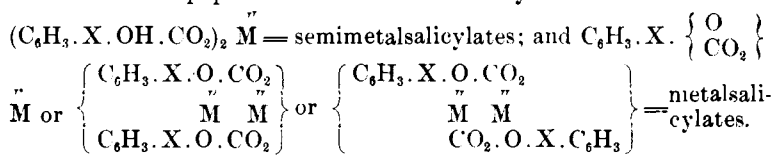


Paranitrophenol.



Orthonitrophenol.

The derivations and derivatives thus outlined are described in detail in the paper. Two series of salicylates are mentioned.



Salicylic acid, on treatment with nitric acid, yields the two isomeric mononitrosalicylic acids, one dinitrosalicylic acid, di- and trinitrophenol.

Methods for the preparation of the mononitrosalicylic acids. (1) 50 gms of nitric acid (1.5 sp. gr.) are added in small portions to a cold solution of 100 gms salicylic acid in 500 or 800 gms glacial acetic acid. The resulting liquid is diluted with 2 or 3 vol. water and cooled down very low. (2) 10 gms salicylic acid are gradually added to a mixture of 10 gms fuming nitric and 10 or 12 gms glacial acetic acid; the resulting liquid is poured in 250 cc very cold water. The precipitates obtained in both cases are mixtures, consisting substantially of the two mononitrosalicylic acids. (3) α mononitrosalicylic acid is obtained almost pure by saturating a saturated solution of salicylic acid in cold glacial acetic acid with the fumes generated in the ignition of dried plumbic nitrate. By subsequent dilution with water, a precipitate of almost pure α mononitrosalicylic acid is obtained.

The separation of the two nitrosalicylic acids is effected by appropriate utilization of the difference in solubility in water of the acids and their semibarium salts.

α *metanitroorthohydroxybenzoic*—or α *nitrosalicylic acid*, $\text{C}_6\text{H}_3 \begin{matrix} \overset{\alpha m}{\text{O}} \\ \underset{1}{\text{O}} \end{matrix} \cdot \text{OH} \cdot \text{CO}_2\text{H}$ (m. pt. 228°); long known; long colorless needles, crystallizing without water of crystallization from the aqueous solution. β *nitrosalicylic acid*, $\text{C}_6\text{H}_3 \begin{matrix} \overset{\beta m}{\text{O}} \\ \underset{1}{\text{O}} \end{matrix} \cdot \text{OH} \cdot \text{CO}_2\text{H} + \text{H}_2\text{O}$ (m. pt. 125°), seems to dissolve in water more readily than the former;

long colorless needles. The dehydrated acid (m. pt. 144°) is hygroscopic.

α monopotassium, monoammonium, magnesium, barium, semibarium, semistrontium, semicalcium, semizinc, semisilvernitosalicylate, and β monopotassium, monosodium, barium, magnesium, lead, semibarium, semistrontium, semisilver, semimercury (?) and mercury-nitosalicylate, are described.

α semibariumnitosalicylate ($C_6H_3.NO_2.OH.CO_2$)₂ Ba + 6 H₂O, small yellow needles, very soluble in water. β semibariumnitosalicylate ($C_6H_3.NO_2.OH.CO_2$)₂ Ba, gold colored scales or needles, very little soluble in water.

α monoethylnitosalicylate, m. pt. 93°, very long, colorless needles, readily soluble in alcohol; β monoethylnitosalicylate, large colorless plates, very little soluble in cold alcohol; α sodiummethylnitosalicylate, $C_6H_3.NO_2.ONa.CO_2C_2H_5$, thin yellow needles, readily soluble in alcohol; β salt, yellowish-red needle, little soluble in alcohol; α diethylnitosalicylate, m. pt. 98°, colorless needles; β diethyl-ether, oily liquid, of agreeable odor.

α nitrosalicylamide, m. pt. 225°; β nitrosalicylamide (145–146°); both long, colorless needles; α potassium, barium, calciumnitosalicylamide are readily soluble in water; α leadnitosalicylamide, soluble in a great deal of water; β barium, calcium, and basic β lead nitrosalicylamide are very little soluble in water.

The two nitrosalicylic acids were still further characterized by the preparation and examination of the following compounds: α amidosalicylic acid, α chlorohydroamidosalicylic acid, α sulphuric-amidosalicylic acid, α acetamidosalicylic acid and α magnesium, barium, calcium, zinc-acetamidosalicylate, β amidosalicylic acid; only the hydrochloric acid salt of this acid could be obtained in the same manner (evaporation of the two acids) as the corresponding α amidosalicylic acid compound.

α *metanitroorthoamidobenzoic* or α *nitramidobenzoic acid*, $C_6H_3.NO_2.NH_2.CO_2H$, m. pt. 263°; long, very thin lemon-colored crystals with silver lustre; salts described; barium, calcium, potassium, ammonium, (copper,) lead, and the hydrochloric acid salt.— β *nitramidobenzoic acid*, m. pt. 204°, long yellow needles; the salts of this acid with the just mentioned metals and acid, strontium and silver, are described.— β ethylnitramidobenzoate, m. pt. 104°, yellow scales.

Paranitrophenol, long colorless needles, soluble in water, not volatile with water vapor, m. pt. 114°. — *Ortho-nitrophenol*, m. pt. 45°, difficultly soluble in cold water, very volatile with water vapor.

The diazocompounds, obtained from the two nitramidobenzoic acids, on boiling with alcohol, yield the same *metanitrobenzoic acid* (m. pt. 141-142°), which in each case was identified by the analyses of the acid, the barium and copper salts, and of the metamidobenzoic acid (m. pt. 174°).

Nitration of the nitrosalicylic acids.—This part of the paper embraces the results of the author and H. Behaghel von Adlerskron. The two mononitrosalicylic acids, on further nitration, yield only one and the same dinitrosalicylic acid (dimetanitrosalicylic acid). $C_6H_3 \begin{matrix} \alpha m & o & 1 \\ | & | & | \\ NO_2 & .OH & .CO_2H \end{matrix}$ and $C_6H_3 \begin{matrix} \beta m & o & 1 \\ | & | & | \\ NO_2 & .OH & .CO_2H \end{matrix}$, both yield $C_6H_2 \begin{matrix} \alpha m & \beta m & o & 1 \\ | & | & | & | \\ NO_2 & .NO_2 & .OH & .CO_2H \end{matrix}$. These facts demonstrate the frequently occurring regularity, that negative constituents will enter, when acting upon substituted benzole derivates, into ortho and para-relation with reference to the most positive constituent, forming two isomeric compounds, which by further introduction of the same negative constituent, yield the same more highly substituted compound; in this case dimetanitrosalicylic acid.

The comparison of the dinitrosalicylic acids from both sources, of their mono- and dipotassium, monoammonium, monobarium, monocalcium, monolead salts and their monoethyl ethers, establishes that there is no difference between them.

β dinitrophenol $C_6H_3 \begin{matrix} o & p \\ | & | \\ NO_2 & .NO_2 & .OH \end{matrix}$, m. pt. 63-64°, is obtained as a secondary product by the further action of nitric acid on dinitrosalicylic acid. The author reserves the more thorough investigation of this latter reaction for a future period.

Researches upon the Non-saturated Acids, RUDOLPH FITTING.
Second paper (Ann. Chem., 195, 56-179).

1. Further Contributions to the knowledge of Fumaric Acid and Maleic Acid, CAMILLE PETRI (Ann. Chem., pp. 56-78).—Fumaric acid, when heated with bromine and water, is converted into dibromsuccinic acid. The reaction takes place in the cold, but only very slowly, and on long digestion. Isodibromsuccinic acid is not formed in the reaction.—Maleic acid, by digestion with bromine and water, yields isodibromsuccinic acid and fumaric acid, which latter acid by

the further action of bromine, is converted into dibromsuccinic acid. The reaction takes place readily and rapidly at ordinary temperature.

Dibromsuccinic acid, when boiled with water, is readily and completely decomposed into brommaleic and hydrobromic acids (in contradiction to the statement of Kekulé). The brommaleic acid thus obtained, m. pt. 128°, is identical with Kekulé's brommaleic and so-called metabrommaleic acid.—Isodibromsuccinic acid, in the same manner, yields isobrommaleic acid, m. pt. 177–178°, identical with Kekulé's isobrommaleic acid and so-called parabrommaleic acid.

Brommaleic and isobrommaleic acid, on treatment with nascent hydrogen, both yield fumaric and succinic acid, but not a trace of maleic acid. Maleic acid alone is not converted into fumaric acid by nascent hydrogen.

Both acids, on distillation, yield brommaleic anhydride and water, which combine again, on standing, to brommaleic acid.

Brommaleic acid, on treatment with fuming hydrobromic acid at ordinary temperature, readily yields dibromsuccinic acid; a portion of the acid, however, is converted into the isomeric isobrommaleic acid.—Isobrommaleic acid combines with hydrobromic acid only very slowly at ordinary temperature, rapidly at 100°, yielding the two dibromsuccinic acids.

On treatment with bromine and water, at ordinary temperature, brommaleic and isobrommaleic acid are both converted into tribrom-

succinic acid, $\begin{array}{c} \text{CBr}_2-\text{CO}_2\text{H} \\ | \\ \text{CBrH}-\text{CO}_2\text{H} \end{array}$, m. pt. 136–137°; small, transparent,

deliquescent crystals, extremely soluble in water, alcohol and ether, easily in benzol.

Tribromsuccinic acid is decomposed when heated in aqueous solution; carbonic acid escapes, hydrobromic acid and dibromacrylic acid are found in solution. $(\text{C}_2\text{HBr}_3) \begin{array}{l} \left\langle \begin{array}{l} \text{CO}_2\text{H} \\ \text{CO}_2\text{H} \end{array} \right. = \text{C}_2\text{HBr}_2-\text{CO}_2\text{H} + \text{CO}_2 + \text{HBr}$, the probable reaction.)

Dibromacrylic acid, m. pt. 85°, b. pt. 243–250° (under partial decomposition), beautiful, very large lamellar crystals. Barium salt, $(\text{C}_3\text{HBr}_2\text{O}_2)_2\text{Ba} + 2\frac{1}{2}\text{H}_2\text{O}$, quadrangular plates; calcium salt, $(\text{C}_3\text{HBr}_2\text{O}_2)_2\text{Ca} + 3\frac{1}{2}\text{H}_2\text{O}$, beautiful, long, colorless needles; ethyl ether, b. pt. 212–214°, colorless liquid of agreeable odor. Fuming hydrobromic and dibromacrylic acid yield, at 100–130°, another acid, m. pt. 53°, probably tribrompropionic acid, which it is very difficult to separate from unaltered dibromacrylic acid.

Bourgoin's tribromsuccinic acid differs in all its properties from the acid obtained by the author. A repetition of the experiments of Bourgoin led him to conclude that Bourgoin's acid was a mixture principally of dibromfumaric and dibromsuccinic acids.

The author concludes that brommaleic acid alone is a true derivative of maleic acid, while isobrommaleic acid is in reality bromfumaric acid, thus further confirming the constitutions assigned by Fittig (*Ann. Chem.*, **188**, 95) to fumaric acid and maleic acid.

2. Researches upon Oil of Roman Camomile. (*Ann. Chem.*, **195**, 79-130, Roman Camomile=*anthesis-nobilis*.)

1. *Organic Acids Obtained in the Saponification of Oil of Roman Camomile*, H. KOPF (*Ann. Chem.*, **195**, 81-92).—Saponification effected by alcoholic potash. Fractional distillation of the purified mixture of organic acids yielded: at 150-160°, isobutyric acid and a small quantity of an acid which was not obtained pure, seemingly methacrylic acid; at 181-187°, crystals of angelic acid; at 187-190°, a liquid mixture of about equal parts of angelic and tiglic acids; at 190-195°, crystals of tiglic acid. Valerianic acid, the ethers of which, according to Demargay, form the main constituents of the oil, or other acids, could not be found. The quantities of angelic acid and tiglic acid obtained were nearly equal, the quantity of isobutyric acid being much smaller.

Angelic acid, $C_5H_8O_2$, m. pt. 45-45.5°, b. pt. 185°. Tiglic acid, $C_5H_8O_2$, m. pt. 64.5°, b. pt. 198.5°, identical with Geuther's tiglic acid, obtained from croton oil, and Frankland's and Duppa's methylcrotonic acid. The tiglates are much less soluble in water than the angelicates. Calcium angelicate, $(C_5H_7O_2)_2Ca + 2H_2O$, much more soluble in cold than in warm water; calcium tiglate, with 3 H_2O , dissolves much more easily in hot than in cold water; barium angelicate $(C_5H_7O_2)_2Ba + 4\frac{1}{2}H_2O$, very soluble in water; tiglate $(C_5H_7O_2)_2Ba + 4H_2O$; potassium angelicate, very soluble, deliquescent; tiglate, $C_5H_7O_2K$; silver angelicate and silver tiglate, $C_5H_7O_2Ag$, white feathery crystals.

The author confirms the statement of Demargay that, by the action of heat or concentrated sulphuric acid, angelic acid is converted into tiglic acid. Pure angelic acid had been almost completely converted into tiglic acid, after 40 hours boiling.

2. *The Separate Constituents of Oil of Roman Camomile*, JULIUS KOEBIG (*Ann. Chem.*, **195**, 92-108).—By very repeated fractional distillation, the oil was divided into five principal portions. By the analysis of each of these, and by saponification with aqueous potash

in each case, it was shown that the oil consisted of a mixture of various compound ethers. It does not contain an aldehyde, or any appreciable quantity of a terpene (result in accordance with Demargay). The following ethers were found as constituents :

Isobutyric-isobutyl ether, angelic-isobutyl ether, angelic and tiglic-amyl ether ; the angelic and tiglic ethers of a new hexyl alcohol ; and the angelic and tiglic ethers of a terpene alcohol, designated as anthemol.

The oil began to boil at 140° ; the thermometer rose regularly, and with comparative rapidity to 180° . Most of the oil distilled between 180 and 200° ; the thermometer did not remain stationary, however, at any single point for any length of time. The distillation was interrupted at 220° , when partial decomposition begins. About one-third of the oil remained behind in the distillation flask.

Fraction boiling at 147 – 148° , much smaller in bulk than any of the other portions ; principally an isobutyric ether, presumably isobutyric-isobutyl ether, containing also a small quantity of what appears to be a hydrocarbon. Fraction of 177 – 177.5° , $C_6H_{10}O_2$, thin colorless liquid of agreeable camomile odor, consists of angelic-isobutyl ether, $C_6H_7O-O-C_4H_9$. Fraction of 200 – 201° , $C_{10}H_{18}O_2$, colorless, pretty viscous liquid of camomile odor, principally angelic-amyl ether, containing also a small quantity of the isomeric-tiglic ether. Fraction 204 – 205° , $C_{10}H_{18}O_2$, similar to the former, a mixture of angelic and tiglic amyl ethers, the latter preponderating. Residue at 220° , dark brown liquid, contains the angelic and tiglic ethers of the hexyl alcohol, and the angelic and tiglic ethers of anthemol.

The yield of the various alcohols from the separate fractions was small. Fractional distillation of the mixture of alcohols, obtained in the saponification of the oil with alcoholic potash, yielded them in larger quantity, admitting the verification of their properties. Isobutyl alcohol, $C_4H_{10}O$, b. pt. 107 – 108° ; further verified by the preparation of the calcium isobutyrate. Amyl alcohol, b. pt. 129 – 130° (fermentation amyl alcohol ?). Hexyl alcohol, $C_6H_{14}O$, b. pt. 152 – 153° , thin liquid of strong, not disagreeable odor ; sp. gr. = 0.8295 (15°). It is a primary alcohol, different from the normal. (The lime salt of the acid it yields on oxidation, corresponds in its formula to capronate, but is neither capronate nor isocapronate.) Anthemol, $C_{10}H_{18}O$, viscous colorless liquid of peculiar camphor odor, b. pt. 213 – 214.5° , distils under partial decomposition (polymerisation ?). The acetic ether, $C_{10}H_{18}O-C_2H_5O$, b. pt. between 232 – 238° , is a viscous oily liquid. A mixture of bichromate of potash and sulphuric acid,

acts very energetically upon anthemol. Concentrated nitric acid converts it into a brown resinous mass. On boiling with dilute nitric acid, anthemol yields paratoluic, terephthalic and perhaps terebinic (?) acid.

The author arrives at the conclusion that the tiglic ethers are real constituents of the oil.

3. *Contributions to the Knowledge of Angelic Acid and Tiglic Acid*, ALEXANDER PAGENSTECHEK (Ann. Chem., pp. 108-128).—The separation of the acids was effected by appropriate application of the difference in the behavior of their lime salts to the solvent action of water.

Tiglic acid and angelic acid, on treatment with highly saturated hydrobromic acid at ordinary temperature, both yield bromhydrotiglic acid. From tiglic acid very nearly the theoretical amount is obtained, much less from angelic acid. This latter acid besides bromhydrotiglic acid yields also other products, more soluble in carbon disulphide, the nature of which it was not possible to determine (bromhydroangelic acid?).

Bromhydrotiglic acid, $C_5H_9BrO_2$, as obtained from the carbon-disulphide solution, large clear colorless plates (crystallographic description by Bücking and Schimper); insoluble in cold water, decomposed by hot water; easily soluble in carbondisulphide; m. pt. 66-66.5°. The acid dissolves readily in aqueous sodium carbonate solution; the solution evolves carbonic acid and pseudobutylene (identified by the analysis of the bromide $C_4H_8Br_2$, b. pt. 156-158°). Most of the acid is decomposed according to the equation $C_4H_8Br-CO-ONa=C_4H_8+CO_2+NaBr$; a small quantity of the acid, however, is reconverted into tiglic acid. By prolonged boiling with water the acid is almost completely reconverted into tiglic and hydrobromic acids; a small portion of the acid is decomposed into pseudobutylene, carbonic acid and hydrobromic acid.—On proper treatment of bromhydrotiglic acid with nascent hydrogen, hydrotiglic acid in considerable quantity and very little of another solid acid, were obtained. This latter acid (m. pt. 184-194°) dissolves with difficulty in cold water, pretty easily in hot water, is not volatile with water vapor and corresponds to the formula $C_{10}H_{18}O_4$, appearing to be a bibasic acid, isomeric with sebacylic acid.

Hydrotiglic acid, $2 C_5H_{10}O_2$, b. pt. 177°, sp. gr.=0.941 (21°); thin colorless liquid, little soluble in water; odor similar to that of valerianic acid, but much weaker. The acid appears to be identical with

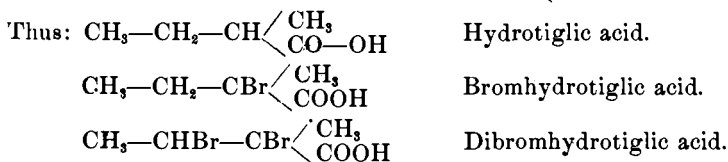
the ethylmethylacetic acid ($\text{CH}_3\text{—CH}_2\text{—CH} \begin{smallmatrix} \text{CH}_3 \\ \text{COOH} \end{smallmatrix}$), described by Saur, and the acid obtained by Schmidt and Berendes from tiglic acid by the action of hydroiodic acid. Calcium salt ($\text{C}_5\text{H}_9\text{O}_2$)₂ Ca + 5 H₂O, long, colorless, efflorescent crystals, more soluble in warm than in cold water ; silver salt, C₅H₉O₂Ag, voluminous white precipitate or colorless feathery crystals. Ethyl ether, C₄H₇—CO₂C₂H₅, colorless mobile liquid, of very pleasant fruit odor.

On treatment with bromine, tiglic and angelic acids both furnish dibromhydrotiglic acid. The former yields nearly the exact theoretical amount and no oily byproduct (Schmidt and Berendes); angelic acid yields about 70 p. c. of the theoretical amount and byproducts, the exact nature of which could not be determined.

Dibromhydrotiglic acid, large, colorless, well developed crystals (crystallographic description given in the original), insoluble in cold water, decomposed by hot water ; easily soluble in carbondisulphide ; m. pt. 86–86.5°. By heating the acid with water in sealed tubes to 100°, these were obtained as decomposition products : carbonic acid, monobrombutylene, tiglic acid and a small quantity of a syrupy, non-volatile substance, which was very soluble in water. The same products were obtained on boiling the acid with water. The acid is easily decomposed at ordinary temperature by sodium carbonate solution. Ample quantities of monobrombutylene (C₄H₇Br, b. pt. 86–88°, colorless, oily liquid of piercing odor) are formed. The products obtained by the action of nascent hydrogen on dibromtiglic acid vary, as it seems, according to the conditions under which the experiments have been performed. Tiglic acid was among the products obtained.

The authors conclude that the derivatives described are derivatives of tiglic acid, not of angelic acid.

4. *Constitution of Tiglic Acid and Angelic Acid*, R. FITTIG (Ann. Chem., 195, 128–130).—The author considers the question of the constitution of tiglic and angelic acids an open one. The results obtained confirm for tiglic acid the constitutional formula generally assigned to methylerotonic acid, $\text{CH}_3\text{—CH} = \text{C} \begin{smallmatrix} \text{CH}_3 \\ \text{COOH} \end{smallmatrix}$.



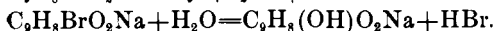
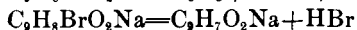
3. Upon Non-saturated Aromatic Acids (pp. 131-179).

1. *Addition Products of Cinnamic Acid*, RUD. FRIITIG and F. BINDER (Ann. Chem., **195**, 131-143).—Erlenmeyer and Swarts independently allowed hydrobromic or hydrochloric acid to act upon cinnamic acid at high temperature; the products obtained were principally carbonic acid and an oil, pronounced by the former as distyrol, $C_{16}H_{16}$, by the latter, as halogen styrol. In consequence of the high temperature applied they failed to obtain addition products.

Bromhydrocinnamic acid, $C_9H_8BrO_2$, is obtained in almost theoretical yield at ordinary temperature by the action of hydrobromic acid, saturated at 0° , on cinnamic acid. The acid is purified by recrystallization from boiling carbon disulphide. Colorless crystals, with mother-of-pearl lustre, m. pt. 137° ; very easily soluble in alcohol and ether, soluble with difficulty in cold carbon disulphide. Between $137-150^\circ$ the acid is completely decomposed into cinnamic acid and hydrobromic acid; byproducts had not formed in appreciable quantity.

Iodohydrocinnamic acid, obtained in like manner by the action of hydroiodic acid on cinnamic acid, dissolves more readily in carbon disulphide than the former. Colorless crystals, becoming slightly colored on standing; m. pt. $119-120^\circ$ under partial decomposition (separation of HI and iodine).

The two acids are identical with the compounds obtained by Glaser by the action of hydrobromic and hydroiodic acid on phenyllactic acid. The acids are completely decomposed at ordinary temperatures, or even at 0° , by sodium carbonate solution. The following reactions take place:



Styrol is the principal product; the reaction in fact furnishes the best method for its preparation. Phenyllactic acid (Glaser's) and cinnamic acid are formed only in small quantities. Styrol, C_8H_8 , b. pt. $144-144.5^\circ$, colorless oil, which on standing completely transforms into colorless glassy metastyrol. Both acids, brom and iodohydrocinnamic acids, are decomposed on boiling with water. The former yields phenyllactic and hydrobromic acid as principal products, cinnamic acid and styrol as byproducts; the latter, cinnamic acid and hydroiodic acid principally, phenyllactic acid and styrol as byproducts.

Dibromhydrocinnamic acid (prepared by Schmitt as early as 1863) is very easily obtained by very gradual addition of the calculated quantity of bromine, in carbon disulphide solution, to the carbon disulphide solution of cinnamic acid. According to the different statements of Schmitt, Erlenmeyer and Glaser, the acid furnishes, on boiling with water, β bromstyrol, carbonic acid, bromphenyllactic acid, cinnamic acid and resinous products. The authors confirm these results in general. Glaser observed the formation of cinnamic acid and resinous products, which *they* attribute to impurities of his material. Glaser's bromstyrol, which according to him distilled at 228° without decomposition, was not pure. Besides β bromstyrol, another compound, which cannot be distilled without decomposition (α bromstyrol), is evidently also formed in the reaction. Bromstyrol was obtained as a white crystalline mass (m. pt. $+7^\circ$), solidifying again completely at 0° . It distilled completely between $219-221^\circ$; the formation of hydrobromic acid was very perceptible in the distillation; the distillate did not solidify again as completely as before at 0° . Bromstyrol and bromine yield bromstyroidbromide, $C_8H_7Br_3$, m. pt. $37-38^\circ$, long colorless needles. Dibromhydrocinnamic acid is a little more stable to sodium carbonate than the monobrom acid. Upon standing, a difficultly soluble, crystalline sodium salt forms, which seems to be stable at ordinary temperature, which, however, is decomposed, if the temperature be even slightly raised.

2. *Notice on Amidohydrocinnamic Acid (phenylamidopropionic acid)*, ED. POSEN (Ann. Chem., 195, 143-145).—Bromhydrocinnamic acid yields on treatment with concentrated aqueous ammonia at 0° , styrol, amidohydrocinnamic acid, cinnamic acid and possibly phenyllactic acid. Amidohydrocinnamic acid, $C_8H_5-CH_2-CH \begin{matrix} \langle NH_2 \\ COOH \end{matrix}$ somewhat difficultly soluble in cold water, easily in hot water, easily in alcohol, almost altogether insoluble in ether and carbon disulphide. Large, colorless, well developed crystals, m. pt. $120-121^\circ$. Basic or acid properties not very pronounced.

The authors are engaged in further utilizing this reaction in the preparation of similar amido acids, more especially in the synthesis of tyrosine.

3. *Atropaic and Isatropaic Acid*, RUD. FITTIG and C. WURSTER (Ann. Chem., 195, 145-168).—*Tropaic acid*, transparent needles or plates; easily soluble in water, almost insoluble in carbon disulphide; m. pt. $117-118^\circ$; not volatile with water vapor. The acid is not altered by the action of water, even at 130° in sealed tubes. On boil-

ing with concentrated baryta hydrate solution, it yields atropaic acid and other products.

Atropaic acid was prepared by prolonged boiling of atropine with baryta hydrate solution; 100 pts atropine yield from 44–46 pts of the acid. The acid obtained by recrystallization from boiling water is impure, containing isatropaic acid. The pure acid, obtained by recrystallization from dilute alcohol (1 alcohol, 1 water), presents beautifully glistening, colorless lamellar crystals; m. pt. 106–107°. Under reduced pressure it can be distilled without decomposition. It is volatile with water vapor (in contradiction to Kraut's statement).

Isatropaic acid.—If atropaic acid is gradually heated from 100–140°, and maintained at the latter temperature for some time, it becomes solid, in consequence of its conversion into isatropaic acid. This transformation can be also effected by boiling the acid with water. Isatropaic acid is very difficultly soluble in hot water, and appears to be insoluble in cold water. It is almost insoluble in ether, carbon disulphide (characteristic difference from atropaic acid), benzol and ligroin; more readily soluble in alcohol. The warm saturated aqueous solution, on cooling and standing, deposits the acid only very slowly, in the form of a crystalline powder. Glacial acetic acid yields it in small colorless, well developed crystals; m. pt. 240–240.5°. Slight impurities lower the melting point considerably (Lossen's acid, m. pt. 200°).

If atropaic acid is treated with hydrobromic acid in the same manner as cinnamic acid, *bromhydratropaic acid* is obtained in very impure condition, although the crude product contains very nearly the theoretical percentage of bromine. The purification of the acid presents some difficulty. The concentrated solutions of the acid in carbon disulphide, benzol or chloroform, are thick syrups, which deposit crystals with difficulty. The acid is less soluble in water-free ligroin (b. pt., below 100°). By slow diffusion of ligroin into the carbon disulphide solution, the acid is obtained in large colorless, apparently triklinic crystals, which are insoluble in water; m. pt. 93–94°.

The acid is a little more stable than the isomeric bromhydrocinnamic acid. Cold sodium carbonate dissolves it without decomposition, which, however, takes place rapidly if the solution is heated. Only a trace of atropaic acid is produced, and not a trace of hydrocarbon (difference from the cinnamic acid derivative). The principal product is an acid, designated as *atrolactic acid*, altogether

different from tropaic acid. Atrolactic acid,* $C_9H_{10}O_3 + \frac{1}{2} H_2O$; water of crystallisation escapes between 80 and 85°; m. pt. of the dehydrated acid 93–94°. The acid dissolves readily in cold water; in all proportions in hot water. The lime salt $(C_9H_9O_3)_2 Ca + 8H_2O$, easily soluble in hot water, more difficultly in cold water. The barium salt, with $2H_2O$, and zinc salt, with $2H_2O$, are difficultly soluble in water. The same products were obtained by boiling bromhydratropaic acid with water; in this case atropaic acid is produced in considerable quantity. Bromhydratropaic acid dissolves in cold concentrated ammonia without decomposition. The solution is decomposed on standing, yielding amidohydratropaic acid, atrolactic acid and atropaic acid. *Amidohydratropaic acid*, $C_9H_{11}NO_2$, beautiful glistening scales; m. pt. 169.5°; difficultly soluble in cold water, very easily in hot water:

Dibromhydratropaic acid, $C_9H_8Br_2O_2$.—Atropaic acid combines with bromine as easily as cinnamic acid. The yield of dibromhydratropaic acid is very nearly theoretical. The acid dissolves readily in boiling carbon disulphide, pretty difficultly in the cold, and crystallizes in long silken needles; m. pt. 115–116°; decomposition at 140°. The acid dissolves easily in boiling chloroform, more difficultly in ligroin. The acid is decomposed on boiling with water, $C_9H_8Br_2O_2 + H_2O = C_8H_8O$ (acetophenon) $CO_2 + 2HBr$, being the principal, if not the only reaction. The same decomposition takes place in the alkaline solution in the cold. *Acetophenon*, $C_6H_5 - CO - CH_3$, m. pt. betw. 16.5–18°, b. pt. 202°, was further identified by direct comparison of its dibromide and the dibromacetophenon, $(C_6H_5 - CO - CHBr_2)$, described by Hunnius) prepared from commercial acetophenon. If dibromhydratropaic acid is heated with less water to 100° in sealed tubes, acetophenon is obtained as principal product, and *monobromatropaic acid*, $C_9H_7BrO_2$, as byproduct. This acid dissolves with difficulty in cold water, more readily in hot water. The aqueous solution yields it in needles. Chloroform and ligroin, in which it dissolves readily, especially on heating, furnish it in small well developed crystals; m. pt. 130°. The acid is not decomposed in aqueous or alkaline solution on boiling. It combines with bromine to *tribromhydratropaic acid*, $C_9H_5.C_2HBr_3.CO_2H$, m. pt. 150°; easily soluble in carbon disulphide or chloroform, less so in ligroin.

Atropaic acid combines readily with hydrogen to *hydratropaic acid*, b. pt. 264–265°, colorless heavy oil, very little soluble in water.

* Fittig calls attention to the great similarity between this acid and Glaser's phenyllactic acid, suggesting that they may be identical.

more volatile with water vapor than atropaic acid. The calcium salt crystallizes with 2 or 3 H₂O.

Dibromhydratropaic acid yields hydratropaic acid and atrolactic acid, on treatment with nascent hydrogen.

The results given lead to the formula $C_6H_5 - C \begin{matrix} \diagup CH_2 \\ \diagdown COOH \end{matrix}$ for atropaic acid, and the probable formulæ of the derivatives $C_6H_5 - CH \begin{matrix} \diagup CH_3 \\ \diagdown COOH \end{matrix}$ hydratropaic; $C_6H_5 - CH \begin{matrix} \diagup CH_2Br \\ \diagdown COOH \end{matrix}$, bromhydratropaic acid; $C_6H_5 \cdot CBr \begin{matrix} \diagup CH_2Br \\ \diagdown COOH \end{matrix}$ dibromiatropaic; $C_6H_5 \cdot CH \begin{matrix} \diagup CH_2OH^* \\ \diagdown COOH \end{matrix}$ atrolactic; $C_6H_5 \cdot C(OH) \begin{matrix} \diagup CH_3 \\ \diagdown COOH \end{matrix}$ tropaic; $C_6H_5 \cdot CH \begin{matrix} \diagup CH_2NH_2 \\ \diagdown COOH \end{matrix}$ amidohydratropaic acid.

Isatropaic acid does not yield addition products, and is probably a polymerisation product of atropaic acid.

4. *Formation of Non-saturated Hydrocarbons from the Addition Products of the Non-saturated Acids*, R. FITTIG (pp. 169-179).—The author concludes from the facts stated in the foregoing papers, that the hydrobromic addition products of the non-saturated acids, which yield hydrocarbons on neutralization with sodium carbonate, contain the Br atom and COOH group in combination with the same carbon atom. The formulæ arrived at by Perkin † for the higher homologues of cinnamic acid do not conform to this theory. The author believes that further investigation will modify these formulæ in accordance with his own theory. Perkin denies the importance of the metal atom, which the author, however, considers essential in the reaction.

$CH_3 - CH_2 - CBr \begin{matrix} \diagup CH_3 \\ \diagdown COONa \end{matrix} = CH_3 - CH_2 - C \begin{matrix} \diagup CH_3 \\ \diagdown \end{matrix} + NaBr + CO_2$, an unsaturated hydrocarbon being formed at first, which, however, does not necessarily remain so: $CH_3 - CH_2 - C \begin{matrix} \diagup CH_3 \\ \diagdown \end{matrix} = CH_3 = CH - CH = CH_3$ (pseudobutylene). In the same manner he explains the formation of acetophenon from dibromhydratropaic acid. $C_6H_5 - CBr \begin{matrix} \diagup CH_2Br \\ \diagdown COOH \end{matrix} + H_2O = C_6H_5 - C \begin{matrix} \diagup CH_2OH \\ \diagdown \end{matrix} + NaBr$ and $C_6H_5 - C \begin{matrix} \diagup CH_2OH \\ \diagdown \end{matrix} = C_6H_5 - C \begin{matrix} \diagup CH_3 \\ \diagdown O \end{matrix}$.

The Halogen Substitution Products of Ethane. First paper. WILH. STAEDEL (Ann. Chem., 195, 180-205).—1. Action of chlorine on ethylchloride. Kraemer describes ethylenechloride among the

* Under the supposition that it is not phenyllactic acid.

† Jour. Chem. Soc., 1877, ii, 660.

byproducts in the manufacture of chloral, and explains its formation by the action of chlorine on ethylchloride. Geuther mentions ethylenechloride (b. pt. 84°) among the various products of the action of chlorine on ethylchloride. These two statements induced the author to resume his own experiments, undertaken some two years ago, on very considerable quantities of material. The results obtained were the same as before,* that ethylenechloride was not formed in the reaction, that ethylidenechloride, $H_3C.CHCl_2$, was the only bichloride formed.—2. Action of chlorine on ethylidenechloride (b. pt. 59°) yielded the two possible trichlorides. Dichlorethylchloride $H_3C.CCl_3$, b. pt. $74-75^{\circ}$. Monochlorethylenechloride, $H_2ClC.CHCl_2$, b. pt. $114-115^{\circ}$, already described by Regnault and Geuther as among the products of the reaction of chlorine on ethylchloride.—3. Action of chlorine on ethylenechloride. Dichlorethylchloride does not form in the reaction. Monochlorethylenechloride, b. pt. 115° , is the only trichloride produced (Regnault).—4. Chlorine and dichlorethylchloride (b. pt. $74-75^{\circ}$) yield trichlorethylchloride, $H_2ClC.CCl_3$, b. pt. 127.5° . Geuther's dichlorethylenechloride (b. pt. $133-136^{\circ}$) was evidently a mixture of two isomers, $C_2H_2Cl_4$, having been prepared from a mixture of trichlorides.—5. Chlorine and monochlorethylenechloride. Products of constant boiling points, could not be obtained ($115-180^{\circ}$), from which the author infers that both tetrachlorides possible had formed; trichlorethylchloride, b. pt. 127.5° , and dichlorethylenechloride, b. pt. 147° .—6. Pentachlorethane and hexachlorine. The author refers to the preliminary communication by himself and E. Hahn in the Ber. d. ch.Ges.—7. Chorbrom substitution products of ethane. Julius Denzel. By prolonged action of direct sunlight on mixtures of equal molecules of bromine and ethyl chloride, colorless liquids were obtained, which distilled between 50 and 205° . By fractional distillation, four bodies were isolated.—*a.* α chlorbromethane, $H_3C.CHBrCl$, b. pt. $84-85.5^{\circ}$ (uncorr.), liquid at -20° , sp. g.= 1.667 at 16° , is attacked very slowly by alcoholic potash solution at ordinary temperature. β chlorbromethane, b. pt. $105-108^{\circ}$, which is rapidly attacked by alcoholic potash, was not among the products of the reaction.—*b.* α chlordibromethane, $H_3C.CBr_2Cl$, colorless liquid, b. pt. $123-124^{\circ}$ (uncorr.), liquid at -20° , sp. g.= 2.134 (16°), odor reminds of oil of turpentine; alcoholic potash acts upon it after 15 minutes standing.—*c.* β chlordibromethane, $BrH_2C.CHBrCl$, liquid at -20° , b. pt. $162.5-163^{\circ}$; sp. g.= 2.268 (16°); alcoholic potash acts upon it at once.—*d.* α chlortribromethane, $HBr_2C.CBr_2Cl$, liquid at -20° , b. pt. $200-201^{\circ}$ (uncorr.), sp. g.= 2.602 at

* Zschft. f. Ch., 1871, 197.

16°. The same product was obtained on treatment of α or β chloridibromomethane with bromine in direct sunlight; besides this, α chlortetra-bromomethane, $\text{HBr}_2\text{C}-\text{CBr}_2\text{Cl}$, m. pt. 32-33°, b. pt. 240°(?), sp. g.= 3.366 (16°), had also formed in the reaction.

By the action in direct sunlight of equal molecules of bromine and ethylidenechloride upon each other, three derivatives were obtained.—*a.* α dichlorbromomethane, $\text{H}_3\text{C}.\text{CBrCl}_2$, liquid at -20° , b. pt. 98-99° (unc.), sp. g.=1.552 at 16°; at ordinary temperature, alcoholic potash attacks it very slowly.—*b.* α dichloridibromomethane, $\text{H}_2\text{BrC}.\text{CBrCl}_2$, liquid at -20° , b. pt. 176-178°, sp. g.=2.27.—*c.* α dichlortribromomethane, $\text{HBr}_2\text{C}.\text{CBrCl}_2$, oily liquid, even at -20° , b. pt. 215-220°.—8. Bromine substitution products of ethane, Jul. Denzel. Action of 1 mol bromethyl and 2 mol bromine in direct sunlight, yielded ethylidenebromide (α dibromomethane), b. pt. 109-110°, and a tri bromomethane, b. pt. 187-188°. Ethylene bromide (β dibromomethane) could not be found among the products of the reaction. The author is still engaged in the examination of the products obtained by the further action of bromine.—9. Experiments with regard to the substituting action of iodine on chlorbromomethane, in sunlight, yielded negative results.

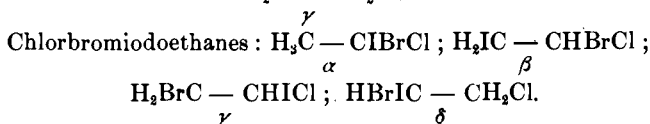
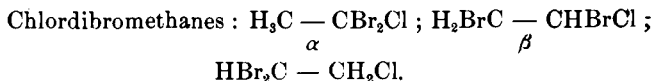
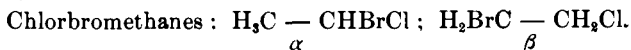
The facts thus given are considered of interest in the solution of the question of the influence of the constitution and the character of the constituents of a derivative on the course of the substitution of hydrogen in said derivative.

Chlorbrom and Bromine Substitution Products of Ethylene, JULIUS DENZEL (Ann. Chem., 195, 205-210).— α chlorbromomethylene, $\text{H}_2\text{C}=\text{CBrCl}$, obtained by the action of alcoholic potash on α or β chloridibromomethane, colorless liquid (b. pt. 62-63°), which rapidly changes into an amorphous white body by polymerisation.— α chloridibromomethylene, $\text{HBrC}=\text{CBrCl}$, obtained by action of alcoholic potash on α chlortribromomethane, liquid at -20° , sp. g.=2.275, b. pt. 141-142°.— α dichlorbromomethylene, $\text{HBrC}=\text{CCl}_2$, obtained from α dichloridibromomethane, liquid at -20° , sp. g.=1.906 (16°). Dichloridibromomethylene (b. pt. 194°?), quantity obtained too small for thorough examination. Of the bromine substitution products, which the author did not prepare, only the different statements in regard to the boiling points are given.

Nomenclature and Boiling Points of the Chlorbrom and Bromine Substitution Products of Ethane and Ethylene,* JULIUS DENZEL (Ann. Chem., 195, 210-218).—The terms of ethane, ethylene and acetylene are limited to the derivatives bearing the

* Exclusive of isomeres, which would follow from the assumption of asymmetric carbon atoms.

character of these hydrocarbons, expressed in the bond of the carbon atoms. The isomeres are distinguished by letters or numbers. The substituting elements or groups are placed one after the other in the order of their affinity, beginning with the strongest or determining affinity. Thus:



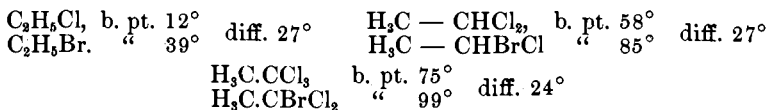
The 1 or α modifications contain the substituting atoms or groups as much as possible in combination with the same carbon atom; 2 or β , containing the second strongest affinity next to the determining affinity; 3 or γ , with the third strongest affinity next to the determining; modification 4 or δ , in which the determining affinity is isolated as much as possible from the others.

Regularities in the boiling points are perceptible as follows:

α Chloroethane, $\text{H}_3\text{C}.\text{CH}_2\text{Cl}$;	b. pt. 12°
α Chlorbromomethane, $\text{H}_3\text{C}.\text{CHBrCl}$;	" 85° diff. 73°
α Chlordibromomethane, $\text{H}_3\text{C}.\text{CBr}_2\text{Cl}$;	" 124° " 39°
α Chlortribromomethane, $\text{H}_2\text{BrC}.\text{CBr}_2\text{Cl}$;	" 201° " 77°
α Chlorotetrabromomethane, $\text{HBr}_2\text{C}.\text{CBr}_2\text{Cl}$;	" 240° " 39°

α Chlorbromomethane, b. pt. 85°	α Chlordibromomethane, b. pt. 124° diff. 39°
β " " 105° diff. 20°	

In the original this table is further extended to the comparison of the dichloroethane derivatives, the bromethanes and the ethylene derivatives. Differences of about 80, 40 and 20 occur repeatedly. In the chlorbrom substitution products each bromine atom entering raises the b. pt. by about 40° , when it attaches itself to a carbon atom already in combination with hydrogen, otherwise by 80° (the first member of the above series forms an exception to this rule). The boiling point is raised by about 25° in the exchange of a chlorine atom for a bromine atom:



etc. The derivatives of CH_4 and SiH_4 show the same regularities.

Simple Apparatus for the Regulation and Variation of Pressure in Distillations, Determinations of Boiling Points, etc., WILH. STAEDEL and E. HAHN (Ann. Chem., 195, 218-221). Not intelligible without the plates appended to the original.

Reduction of Analytical Weighings to a Vacuum, G. F. BECKER (Ann. Chem., 195, 222-227).—The author gives tables of corrections for platinum and brass weights derived from the

following equations: $w_r = w + \frac{wc}{y} - \frac{wc}{d}$, wherein w_r represents the

real weight, w the apparent weight and y the sp. gr. of the substance weighed, d the sp. gr. of the weights, c the weight of 1 cc air.

$x = w_r - w$; x represents the correction. If $w_r = 1$ gm, $x = \frac{c}{y} - \frac{c}{d}$.

The equation $\frac{dy}{dx} = -\frac{y^2}{c}$ represents the influence of the sp. gr. of the

substance of the weights on the corrections. The influence of tem-

perature is expressed in $x = c_0 (t \times 0.00366) \left(\frac{1}{y} - \frac{1}{d} \right)$. In the present

state of chemical apparatus, the influence of barometric pressure is inappreciable.

Hydrogen Peroxide. Third paper. EM. SCHOENE (Ann. Chem., 195, 228-252).—Behavior of pure *hydrogen peroxide* towards neutral *potassium iodide*. The paper begins with a review of the statements of Schoenbein, Meissner, Al. Schmidt, Weltzien, Houzeau, H. Struve and O. Loew. By a series of very careful quantitative and qualitative experiments the author arrives at the following results:

1. Pure hydrogen peroxide (vapor or in aqueous solution) separates iodine from potassium iodide.
2. Caustic potash is formed in the reaction.
3. The more dilute the solutions are, the later the reaction begins, and the more slowly it takes place.*
4. The reaction proceeds gradually, not suddenly, as in the presence of ferrous sulphate.
5. The reaction is accompanied by the evolution of oxygen.
6. More concentrated solutions (containing more than 0.2 p. c. H_2O_2) give the same intensity of iodine coloration as more dilute solutions (0.002 p. c. H_2O_2). Only when the amounts of hydrogen peroxide are smaller than 10 mgs to 1 ltr, appreciable differences in intensity of coloration are noticeable.

* Iodide of potassium and starch form a very delicate test for peroxide of hydrogen, as little as 8 one hundred-millionth part in solution being recognizable.

The action of the potassium iodide on hydrogen peroxide is catalytic. Potassium iodide causes the decomposition of the hydrogen peroxide into water and oxygen, and but a small proportion of the iodide itself is decomposed. The author explains this reaction by the following equations: (1.) $2KI + 2H_2O = 2KOH + 2HI$ (amount of dissociation depending on concentration). (2₁.) $H_2O_2 + 2KOH = K_2O_2 + 2H_2O$ and (2₂.) $H_2O_2 + 2HI = I_2 + 2H_2O$. (3.) $K_2O_2 + I_2 = 2KI + O_2$. The regenerated potassium iodide acts again in the same manner. With increasing dilution the catalytic decomposition is less energetic and complete. If the quantity of water is considerable the reactions (2₁.) and (2₂.) will take place in a minor degree and more slowly.

The author offers the same explanation for the catalytic decomposition of hydrogen peroxide by concentrated solutions of the haloid salts of the metals of alkalies and alkaline earths.

Hexylenes from the Tertiary Hexyl Alcohols and their Polymerisation Products, L. JAWEIN (Ann. Chem., 195, 253-264).—Hexylene from dimethylpropylcarbinol. The alcohol (b. pt. 122.5-123.5°) was prepared by the action of 1 mol chlorbutyryl on 2 mol zincmethyl. Yield only small, as the hexyl alcohol splits up very largely into hexylene and water. The hexylene thus obtained, and the hexylene obtained from the iodide (prepared from the alcohol), are identical. The hexylene boils at 65-67°, sp. g. 1.372 (0°). It combines with hydroiodic acid to hexyl iodide (b. pt. tolerably constant at 142°); with bromine it yields a bromide which cannot be distilled without decomposition. On oxidation with chromic acid, this hexylene yields acetone (b. pt. 57-58°), a ketone that distills at 115°, acetic and propionic acids; hence the formula $(CH_3)_2C=CHC_2H_5$. The hydrocarbon is polymerised on treatment with dilute sulphuric acid [more than 2 vol dilute acid (2 pts. H_2SO_4 to 1 pt H_2O) to 1 vol of hexylene] yielding dihexylene, b. pt. 193-197°, sp. g. 0.797 (0°), vapor density 5.88 (calc. 5.81).—Hexylene from diethylmethylcarbinol, has been already obtained by Tschalkowsky. Diethylmethylcarbinol, b. pt. 121-122.5° (758 mm), yields hexylene with b. pt. 69.5-71°, sp. g. 0.712 (0°). On oxidation with chromic acid, this hexylene yields acetic acid and a mixture of ketones, the larger portion of which distills between 80-86° (methyl ethyl ketone?), the remainder at 86-123°. Hence the formula $CH_3HC=C.CH_3.C_2H_5$. The dihexylene boils at 196-199°, sp. g. 0.809 at 0°, vapor density 5.97 (calc. 5.81).

Upon the Products of the Fusion of Potassium Mesitylene Sulphate with Potassium Hydrate, OSCAR JACOBSEN (Ann. Chem., **195**, 265-292).—The author finds that mesitol is the first product of the reaction. On fusion with potassium hydrate, pure mesitol yields oximesitylenic acid; pure oximesitylenic acid yields an oxiuvic acid, which by the further action of fused potassium hydrate, is finally, though very slowly, oxidized to trimesic acid. Hence potassium mesitylene sulphate yields all these products on fusion with potassium hydrate, if the reaction is continued for a sufficient length of time. These results would rectify the statement of Fittig and Hoogewerff,* and verify in part the results of Biedermann and Ledoux.† Fittig and Hoogewerff had assumed that oximesitylenic acid was the first product of the reaction. They considered the phenol, which they mistook for xylenol, as secondarily derived from the former by the loss of carbonic acid. Biedermann and Ledoux obtained mesitol and oximesitylenic (?) acid.

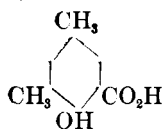
The formation of mesitol potassium from the mesitylene sulphate takes place slowly much below the fusing point of mesitol potassium, but at this lower temperature, while it forms, it is at once oxidized to oxi-acids. If, however, a considerably higher degree of heat is applied, the now rapidly forming mesitol potassium melts and rises to the surface, being altogether insoluble in the fused potassium hydrate, thus escaping further oxidation. For this reason, at lower temperature oxi-acids are principally formed, while the reaction at higher temperature produces mainly mesitol.

Mesitol, $C_8H_2(C_2H_5)_3OH$, m. pt. 68° , b. pt. 219.5° (763 mm), very volatile with water vapor, sublimes below the melting point in fine needles, little soluble in water, very easily in alcohol or ether. The solutions are not colored by ferric chloride. With concentrated sulphuric acid it yields mesitolsulphonic acid, the sodium and barium salts of which are extremely soluble in water, and in solution give an intense blue coloration with ferric chloride.—Monobrommesitol, m. pt. 80° (Biedermann and Ledoux).—Dibrommesitol, m. pt. 150° , not volatile without decomposition, slightly soluble in hot water, more readily in warm solutions of the alkaline carbonates. In its preparation water must be altogether excluded. In the presence of water, $C_8H_6O_2Br_2$ (?), dibrommetaxyloquinon is among the products formed, which is identical with the body described by Fittig and Hoogewerff as dibromxylenol. It crystallizes from alcohol in large, gold-colored plates, insoluble in water and the alkaline carbonates, m. pt. 176° .

* Ann. Chem., **150**, 333.

† Ber. d. d. ch. Ges., viii, 250.

Oximesitylenic acid, m. pt. 179° , agreed with the description given of it by Fittig and Hoogewerff.—Commercial acetomesitylene contains metaxylo; the oximesitylenic acid obtained from it contains oxitoluic acids, if the mesitylene sulphate has not been very carefully purified. To the latter impurity the author ascribes the discrepancy between the results of Ledonx and Biedermann, and Fittig and Hoogewerff, regarding this acid.—Oximesitylenic acid is also obtained at lower temperature, on fusion of mesitol sulphate with potassium hydrate; a dioximesitylenic acid does not seem to form in the reaction. Salts of oximesitylenic acid: $(C_9H_9O_3)_2, Ba + 5H_2O$, only moderately soluble in cold water, loses its water of crystallization below 100° , becomes yellow at 110° and gray at $140-150^{\circ}$, by oxidation; calcium salt with 4 H_2O , easily soluble; zinc salt with 2 H_2O , less soluble in hot than in cold water; copper salt difficultly soluble; potassium and ammonium salts without water of crystallization.—Methyl ether, colorless oily liquid, easily volatile with water vapor. When heated with concentrated hydrochloric acid to $200-205^{\circ}$, oximesitylenic acid yields metaxylenol (1.3.4.); hence the constitution



Oxiuvitic acid, $C_6H_2.CH_3.OH.(COOH)_2$, colorless needles, much more soluble in hot than in cold water. Solutions give a cherry-red coloration with ferric chloride. When slowly heated the acid melts gradually between $225-235^{\circ}$. If somewhat larger quantities are rapidly heated, fusion takes place suddenly at 275° . The barium, calcium, magnesium and sodium salts are very soluble in water. Calcium salt very difficultly soluble in cold water, pretty easily in hot water. Dimethyl ether, m. pt. 79° , long needles, very volatile with water vapor. When heated with concentrated hydrochloric acid to 200° , the acid yielded orthokresol; hence the constitution

$$C_6H_2.\overset{1}{CO_2H}.\overset{3}{CO_2H}.\overset{4}{OH}.\overset{5}{CH_3}.$$

Among the products of the reaction there was besides orthokresol, a coloring matter which dissolved in dilute sodium carbonate solution to an intensely purple liquid. This substance was obtained from the alcoholic solution in crystals with greenish reflection.

In the same manner as mesitylene, ethyldimethylbenzol yields a monobasic oxi-acid (m. pt. $147-149^{\circ}$), volatile with

water vapor, which gives a blue coloration with ferric chloride, and to which the formula $C_6H_2.C_2H_5.CO_2H.OH.CH$ will probably have to be assigned.

Analysis of Organic Compounds Containing Halogens or Nitrogen, HUGO SCHIFF (Ann. Chem., 195, 294-302).

Molecular Weight of Indigo, ERWIN v. SOMMARUGA (Ann. Chem., 195, 301-313).—Averaging the results of nine determinations, made by a modification of the method Dumas-Habermann, the author has found the vapor density of indigotin at 9.45 (air = 1). Hence the molecule of indigo, $C_{16}H_{10}N_2O_2$, calculated vapor density 9.06. The results obtained by the method of V. Meyer were lower, varying from 7.37-8.26, in consequence of the decomposition of part of the indigo. The indigotin employed in the determinations had been purified by the method of Fritsche (Journ. pr. Ch., 28, 139) and subsequent sublimation at a pressure of between 30-40 mm.

Detection of so-called Ethyldiacetic Acid in Urine, A. HILGER (Ann. Chem., 195, 314-317).—The urine in an interesting case of diabetes mellitus was found to contain ethyldiacetic acid. With ferric chloride it gave the characteristic dark cherry-red coloration. The detection of the acid was based upon the fact determined by Geuther, that, by addition of water, the acid is decomposed into acetone, alcohol and carbonic acid; 300 cc of urine were distilled with 50-60 cc concentrated HCl, to one-third. The distillate showed very decided acetone odor; after the addition of potassium hydrate and an excess of iodine solution, upon standing, it yielded the characteristic iodoform crystals. The distillate was subjected to careful fractional distillation. The portion which passed over below 56° contained acetone, which was identified by the formic acid obtained on careful oxidation with chromic acid mixture. The portion distilling above 56° does not show acetone acid, gives an ample iodoform reaction, and yields acetic and carbonic acid on oxidation with chromic acid. Attempts to prepare the acid from the urine by the method of Rupstein* proved unsuccessful. An approximate quantitative determination of the acid was effected by the quantitative determination of the iodoform obtained from the acid, assuming that 3 mol Cl_3H correspond to 1 mol acid. 60.80, or 100 cc of the urine, were strongly acidulated with hydrochloric acid and distilled to one-third. To the distillate potassium hydrate and an excess of a concentrated solution of iodine in potassium iodide

* Centrbl. f. med. Wiss., 1874, No. 55.

were at once added; the mixture was then slightly warmed and allowed to stand in a closed vessel for twenty-four hours. The iodoform obtained was weighed, after washing with cold water, and drying at ordinary temperature and over sulphuric acid. The quantities of the acid in the urine were found to vary between 0.0985–0.1909 in 100 pts. Aceton and alcohol could be also detected in the condensation products of the air exhaled by the patient.

Solanine and its Decomposition Products, A. HILGER (Ann. Chem., 195, 317–325).—The solanine (m. pt. 235°) analyzed, had been recrystallized from alcohol and dried at 100°. From the results of his analysis the author calculates the formula $C_{48}H_{87}NO_{15}$. The acetyl compound, obtained by heating 2 parts solanine with 10 parts acetic anhydride for several hours to 160°, is insoluble in water, soluble in alcohol and ether, crystallizes in long needles, and contains 23 p. c. acetyl, corresponding, according to the calculation of the author, to 6 acetyl rests, or the formula $C_{42}H_{69}(C_2H_3O)_6NO_{15}$.

On boiling with dilute hydrochloric acid, solanine yielded 36 p. c. sugar (determined as glucose by Fehling's solution) and solanidine. (Dilute sulphuric acid yielded 35.7 p. c. sugar.)

Solanidine (m. pt. 208°) had been recrystallized from ether. $C_{36}H_{41}NO_2$, the formula derived by the author from his analyses. The acetyl compound of solanidine yielded 35.4 p. c. acetyl, corresponding to 5 acetyl rests, or the formula $C_{26}H_{36}(C_2H_3O)_5NO_2$.

An equation, explaining the decomposition of solanine, cannot be derived from the quantities of sugar found and the formulæ given for solanine and solanidine.

Potassium hydrate, in solution or fused, does not act upon solanine.

Several New Uranyl Salts, R. SENDTNER (Ann. Chem., 195, 325–333). *Selenates*.— $(UO_2)SeO_4 + SeO_4H_2 + 18aq$, light yellow masses of wavellite structure, deliquescent. $2(UO_2,SeO_4)SeO_4H_2 + 12H_2O$ (?), greenish-yellow, efflorescent needles.

These salts were obtained by dissolving uranic hydrate in a dilute solution of selenic acid, and subsequent concentration. The saturated solution of uranic hydrate in selenic acid yielded, on evaporation to dryness, a varnish-like mass $UO_2SO_4 + xH_2O$.— $SeO_4(UO_2)SeO_4K_2 + 2H_2O$, granular crusts, obtained by dissolving potassium uranate in selenic acid. The salt dissolves easily in hot water, less so in cold water. $SeO_4(UO_2)SeO_4(NH_4)_2 + 2H_2O$, readily soluble in water.

Selenites.— $SeO_3(UO_2)SeO_3H_2$, yellow microscopic prisms, insoluble in water, obtained in small quantity by solution of uranic hydrate in

selenious acid, in more considerable quantity by boiling the mixed concentrated aqueous solutions of uranyl chloride and selenious acid. $\text{SeO}_3(\text{UO}_2)\text{SeO}_3\text{K}_2$, pale yellow crusts, insoluble in water. Ammonium double salt, microscopic plates, insoluble in water.

The author did not succeed in obtaining the iodide corresponding to uranyl chloride, or the uranyl iodide double compounds with potassium or ammonium iodide. Attempts to obtain uranous bromide in a manner analogous to the preparation of the chloride were likewise unsuccessful. $(\text{UO}_2)\text{Br}_2 + 7\text{H}_2\text{O}$, granular deliquescent mass. $(\text{UO}_2)\text{Br}_2 + 2\text{KBr} + 2\text{H}_2\text{O}$, yellowish-brown rhombic plates, very soluble in water. $(\text{UO}_2)\text{Br}_2 + 2(\text{NH}_4)\text{Br} + 2\text{H}_2\text{O}$, large rhombic plates. The two latter salts are decomposed by water in the same manner as the corresponding chlorides; they can be obtained in crystals from the solutions only in the presence of an excess of acid.

Upon the Influence of the Isomerism of the Alcohols and Acids in the Formation of Compound Ethers, N. MENSCHUTKIN (Ann. Chem., 195, 334-364).—The pure water-free alcohols and acids were weighed out and mixed as nearly as possible in the ratio of the molecular weights. Weighed portions of these mixtures were heated in small sealed tubes from 1 to 300 hours, at a perfectly constant temperature of 154° . The degree of etherisation was determined by dissolving the reaction products thus obtained in dilute alcohol, and titrating the unetherified acid with baryta water, using rosolic acid as an indicator. The method yields perfectly constant results.

In the manner indicated, the author determined with extreme care, the velocities and limits of the acetic acid etherification of the following alcohols: 1. Primary saturated alcohols—methyl alcohol, ethyl alcohol, propyl alcohol, normal butyl alcohol, isobutyl alcohol, normal octyl alcohol and cetyl alcohol. 2. Primary non-saturated alcohols—allyl alcohol and benzyl alcohol.

Berthelot and Péan de St. Gilles inferred from their experiments that the velocities of etherification of the primary alcohols were equal, and further, that the limit of etherification increased with the increase of the molecular weight. The author defines as absolute velocity the percentage of acid (or alcohol) etherified, with reference to the total quantity of acid or alcohol employed; as relative velocity, the percentage of etherified acid (or alcohol) with reference to the quantity of acid (or alcohol) at all capable of etherification (this latter quantity is determined in the limit of etherification); as initial velocity, the velocity of etherification in the action of molecular

quantities of alcohol and acid at 154°, at the end of the first hour. His results may be comprised as follows: 1. Methyl alcohol shows the greatest velocity; its position of all alcohols is an exceptional one. Absolute initial velocity of the methylacetic system, 55.59 p. c.; relative initial velocity, 80.8. 2a. The absolute initial velocities of the normal primary alcohols are equal, amounting to about 47 p. c.

Ethyl alcohol, 46.81; propyl alcohol, 46.50;
 Normal butyl alcohol, 46.85; octyl alcohol, 46.57.

In the further course of etherification the velocities of etherification of ethyl, propyl and normal butyl alcohol are about equal; the velocity of octyl alcohol is decidedly greater (in this case the system is, however, not homogeneous). b. Influence of isomerism:

Absolute initial velocity of isobutyl alcohol, 44.92.
 " " " " normal butyl alcohol, 46.85.

Although the initial velocity of isobutyl alcohol is smaller than that of the normal alcohol, the velocity is greater in the succeeding hours.

3a. The relative initial velocity of alcohols of the same structure decreases with an increase of the molecular weight.

Ethyl alcohol, 70.31; propyl alcohol, 69.55;
 Normal butyl alcohol, 69.61; octyl alcohol, 64.39.

b. Influence of isomerism:

Relative initial velocity of normal butyl alcohol, 69.61.
 " " " " isobutyl alcohol, 66.66.

4. Influence of the composition:

Absolute initial velocity: allyl alcohol, 36.12; benzyl alcohol, 37.98.

The absolute initial velocities of the non-saturated primary alcohols are much smaller than those of the saturated primary alcohols.

Relative initial velocity: Allyl alcohol, 60.07; benzyl alcohol, 62.52.

5. Limits of acetic systems of primary alcohols. The following limits were derived by taking the mean of experiments of 120 hours:

Methyl alcohol.....	69.59	Isobutyl alcohol.....	67.38
Ethyl alcohol.....	66.57	Octyl alcohol.....	72.34
Propyl alcohol.....	66.85	Cetyl alcohol.....	80.39
Normal butyl alcohol...	67.30	Allyl alcohol.....	59.41
		Benzyl alcohol.....	60.75

Methyl alcohol differs again from the rest of the alcohols. As to the other alcohols, the limits increase with the increase of the molecular weight. Isomerism of the alcohols does not seem to influence the limit, as will be seen by comparison of the limits of the two butyl alcohols.

The composition greatly affects the limit of etherification, as will be seen by comparison of the saturated and non-saturated alcohols.

Contributions to the Knowledge of Polyporic Acid, C. STAHLSCHMIDT (Ann. Chem., 195, 365-372).—Polyporic acid (Ann. Chem., 187, 177), the acid discovered by the author in polyporus purpurascens, is decomposed on boiling with moderately concentrated potash solution. The original purple color of the solution disappears, and the nearly colorless liquid obtained, yields, upon super-saturation with dilute sulphuric acid, a white precipitate which is a mixture of two acid compounds. Hydropolyporic acid, which constitutes the main portion of this precipitate, crystallizes in white needles, is readily soluble in hot water and alcohol, and has the composition $C_9H_9O_2$. It fuses at 162° , and sublimes, when cautiously heated. The other compound, $C_{10}H_9O$, is altogether insoluble in water, dissolves readily in boiling spirits, fuses at $156^\circ C.$, and sublimes without decomposition.

The following salts of hydropolyporic acid are described: $C_9H_9NaO_2 + 2H_2O$, colorless prisms, which are very easily soluble in water; $(C_9H_9O_2)_2Ba$, quadratic plates, difficultly soluble in water; $(C_9H_9O_2)_2Mn + 3H_2O$, very difficultly soluble in water; copper salt, a light blue crystalline precipitate; cobalt salt, white crystalline precipitate; lead salt, amorphous white precipitate; $C_9H_9O_2 Ag$, white crystalline precipitate. The methyl ether was obtained in crystals; the ethyl ether as an oily liquid.

Polyporic acid is acted upon by warm concentrated nitric acid, yielding nitropolyporic acid, $C_9H_9O_2(NO_2)$ (m. pt. 230° , little soluble in cold water, easily soluble in hot water and alcohol) and benzoic acid. A small quantity of picric acid is also formed in the reaction.

By the action of hydrochloric acid and potassium chlorate on polyporic acid, a mixture of three chlorine compounds is obtained. $C_9H_7Cl_2O_2$ (?) dissolves in boiling water, white feathery needles, m. pt. 108° ; the compound sublimes in white needles at a still higher temperature. $C_9H_6Cl_2O$, long gold colored needles, which are insoluble in water, but very easily soluble in boiling alcohol. The compound fuses at $109-110^\circ$, and sublimes at still higher temperature without decomposition.

The third chlorine compound, insoluble in water, easily soluble in boiling alcohol, forms a syrupy mass, and could not be obtained pure.

Bromine acts upon polyoric acid; crystallized compounds, however, could not be obtained.

Contributions to the Knowledge of the Ammoniacal Mercury Compounds, H. GERRESHEIM (Ann. Chem., 195, 373-386).—Millon's base, the yellow compound formed in the action of ammonia on precipitated HgO , according to the analysis of the author, corresponds to the formula $\text{Hg}_{11}\text{O}_3\text{N}_2\text{H}_4 + 2\text{H}_2\text{O}$. It is insoluble in alcohol, ether and all solvents, which do not act upon it chemically; it is slightly soluble in water. The hot concentrated aqueous solution yields it in microscopic crystals. When heated in a dry current of air it loses one-third of the total nitrogen in the form of ammonia, and $3\text{H}_2\text{O}$. Potash solution does not act upon it, even on boiling. On evaporation with potash the base is converted into a brown substance (ammonia escapes). Nitric acid converts the base into a white nitrate, insoluble in nitric acid. Hydrochloric acid yields white chloride, soluble under decomposition in an excess of the acid. Dilute sulphuric acid yields a white salt, insoluble in an excess of the acid. Concentrated acid turns it brown by dehydration; on heating, sulphurous acid is evolved. The acetic acid salt is soluble in an excess of acetic acid. From this solution nitric acid precipitates the nitrate, sulphuric acid the sulphate, etc.

The salts of the base, which are difficultly soluble in dilute acetic acid, are precipitated by addition of the corresponding salts to this solution. The salts thus obtained are white, or yellowish-white, if the acid does not possess individual color. The permanganate is red; the chromate, yellow.

The base, if employed in excess, withdraws the acid completely from all soluble salts and many insoluble salts, without being dissolved itself. On shaking a solution of potassium chloride with the base, a filtrate is obtained which contains only potassium hydrate, not a trace of chlorine. Sulphate of sodium, nitrate of potassium are decomposed in corresponding manner. Even sulphate of barium, on standing with the base and filtering, yields a filtrate containing notable quantities of caustic baryta.

The base, on treatment with iodide of ethyl, at 100° , yields a double salt, $2(\text{C}_2\text{H}_5)_4\text{NI} + 3\text{HgI}_2$, m. pt. $153-154^\circ$. Bromomethyl yields the corresponding bromine compound (m. pt. $147-150^\circ$). In the action of chloroform on the base, a gaseous compound is formed, besides the chloride and formate of the base, and mercuric cyanide and

ammonia. Carbon disulphide yields brownish-black sulphocarbonate.

The author has also utilized the insolubility of the ammoniacal mercury compound in the quantitative determination of ammonia. If sodium carbonate is added to a solution containing at least 5 eq. mercuric chloride to 1 eq. of ammonium salt, the ammonia is completely precipitated, even from very dilute solutions. The determination of the ammonia in the precipitate can be effected either by distilling the precipitate with sodic hydrate and sodium sulphide, and determining the ammonia in the distillate; or by dissolving the precipitate in hydrochloric acid and evaporating with platinic chloride and determining the weight of the ammonium platinum double salt; or by weighing the precipitate after drying it at 100°. The last method is only applicable, if the liquid contains less than 0.01 gm NH_3 in the liter. The precipitate seems to correspond to the formula $\text{Hg}_5\text{N}_2\text{O}_2\text{H}_2\text{Cl}_2$.

American Patents.

Condensed from the Official Gazette of the U. S. Patent Office, by ARNO BEHR.

June 3, 1879.

216,045.—*Restoring and preserving stone.* CH. O. LUNDBERG.

Restoring and preserving stone by first washing it with an alkaline solution to destroy the acids which have been absorbed by the stone; then applying a mixture of lime-putty, hydraulic cement and water, and then applying a solution of an alkaline silicate.

216,117.—*Process of casting steel ingots.* W. A. SWEET.

To prevent piping in ingots, the molten metal while in the mould is covered with a highly heated substance, such as charcoal or molten slag, capable of protecting the metal from the outer air and permeable by the gases evolved in casting.

216,118.—*Apparatus for the production of gas for metallurgical and other purposes.* C. TESSIÉ DU MOTAY and E. J. JERZMANOWSKY.

Oxidizing and carbonizing gases are produced in separate generators and stored in separate holders, and supplied under the desired pressure and in regulated quantities, either together or separately to metallurgic or other furnaces, for producing different temperatures, and either carbonizing or oxidizing flames.

216,207.—*Compositions for applying colors.* A. E. MERY.

A compound consisting of glue, glycerine, water, white wax, ammonia and rosin, dissolved in ether, to be mixed with the coloring matter and to be used as a paint.