

## Justus Liebig's Annalen der Chemie.

Abstractor, GEO. A. PROCHAZKA, PH. D.

### *Constitution of Phenanthrene*, GUSTAV SCHULTZ (196, 1-32).—

Details of experiments, the outlines of which have been previously published.\* Fittig and Ostermayer † obtained phenanthrenequinone on oxidation of phenanthrene, and by further oxidation, the bibasic diphenic acid; thus establishing in the hydrocarbon the bibasic  $C_2H_2$  group. They regarded diphenic acid as a diphenylcarbon acid, though on distillation with quick-lime it did not yield diphenyl, but diphenyleneketon. ‡ Graebe § obtained diphenyl in nearly quantitative proportion, on distillation of phenanthrene with soda-lime, proving that phenanthrene, phenanthrenequinone, diphenic acid, etc., were really diphenyl derivatives. Graebe further showed that phenanthrene would form, if stilbene, dibenzyl ¶ or toluol ¶¶ were passed through incandescent tubes; the researches of Ph. Barbier,\*\* Fittig ††

and Graebe, ††† determined the constitution  $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} > CH_2$  of fluorene, the reduction product of diphenyleneketon; thus explaining the constitution of phenanthrene to the extent of  $(C_6H_4)_2(CH)_2$ .

Doebner §§ found that on oxidation, diparaditolyl will yield an acid distinct from diphenic acid; Carnelly ||| and Boernstein ¶¶ proved the same in regard to orthoparaditolyl. The author\*\*\* himself has found that diphenylbenzol yields paradiphenylcarbon acid on oxidation (see also Doebner †††), entirely different from the phenylbenzoic acid obtained in the reaction of fused caustic alkali on diphenyleneketon. These results exclude the consideration of the dipara and ortho positions of the  $C_2H_2$  group, in the question of the constitution of the phenanthrene molecule.

From the fact that diphenyleneketon is almost completely destroyed to carbon dioxide and water, on oxidation, phenylbenzoic acid completely so, A. Schmitz ††† inferred the ortho nature of phenylbenzoic acid.

\* Ber. d. d. chem. Ges., **11**, 215.

† Ibid., **5**, 936.

‡ Ann. Chem., **166**, 377.

§ Ber. d. d. chem. Ges., **6**, 63.

|| Ann. Chem., **167**, 131.

¶ Ber. d. d. chem. Ges., **7**, 48.

\*\* Compt. Rend., **79**, 1151.

†† Ann. Chem., **174**, 194.

§§ Ber. d. d. chem. Ges., **9**, 271.

|| Chem. Soc., 1877, 653.

¶¶ Inaug. diss., Bonn, 1877, 27.

\*\*\* Ber. d. d. chem. Ges., **6**, 418.

††† Ann. Chem., **172**, 115.

††† Ann. Chem., **193**, 115.

†† Ber. d. d. chem. Ges., **6**, 187; Ann. Chem., **193**, 134.

The author concludes, from the results of his experiments, that the  $C_2H_2$  group is in diortho position in the diphenyl nucleus; that the constitution assigned to phenanthrene by Fittig and Ostermayer, is the correct one. His conclusions are based upon the following experimental data:

I. Di-iododiphenic acid, obtained from the metadiamidodiphenic acid of Griess,\* by substituting iodine in place of the amido groups, yields diphenic acid on treatment with sodium amalgam.

II. The diamidodiphenic acid, obtained from dinitrodiphenic acid (m. pt.,  $253^\circ$ ), from diphenic acid, and the diamidodiphenic acid of Griess, from metaazooxybenzoic acid, are identical.

The constitution  $NH_2$    $NH_2$  is assigned to  
 $COOH$   $COOH$

the metadiamidodiphenic acid of Griess, as the barium salt on distillation with baryta (Griess), yields benzidine, the constitution of which has been determined by the author,† under the supposition that benzidine is a true derivative of the acid. On heating diamidodiphenic acid with baryta or slacked lime, a distillate is obtained, consisting largely of benzidine, but containing also another isomeric base (Struve,‡ Schultz §), which, in its pure condition, presents white needles, and melts at  $157^\circ$ . If soda-lime be taken, in place of slaked lime, the benzidine, formed, appears to be almost completely destroyed, the distillate containing only little benzidine, consisting principally of the other base. Griess found that diamidodiphenic acid undergoes a change into an isomeric acid, when heated to  $170^\circ$ . The author finds that this acid does not yield benzidine on distillation with quick-lime, but only the isomeric base. Hence, the conclusion that benzidine is the true derivative of diamidodiphenic acid. The formation of the isomeric base in the above-mentioned cases is easily explained by a molecular change of part of the acid, before the lime, etc., has had opportunity to act. Griess had obtained benzidine only, having excluded the possibility of this molecular change, by distilling the barium salt with caustic baryta.

The conversion of the acid of Griess into diphenic acid, could not be effected in direct manner by sodium amalgam.

\* Ber. d. d. chem. Ges., 7, 1609.

† Ann. Chem., 174, 227.

‡ Ber. d. d. chem. Ges., 10, 75.

§ Ibid., 9, 548.

*Di-iododiphenic acid*  $(C_6H_3)_2I_2(COOH)_2$ .—By treating the nitrate of diamidodiphenic acid (suspended in water), or the aqueous solution of the hydrochloric acid salt, with nitrous acid, the difficultly soluble, corresponding tetrazodiphenic acid salts are obtained in the form of white crystals. These, on boiling with hydriodic acid, yield di-iododiphenic acid. Di-iododiphenic acid, in its pure form, is a nearly white powder, m. pt.,  $262^\circ$ , which is readily soluble in alcohol, acetone, ether and glacial acetic acid, difficultly soluble in water. Neither the acid nor its salts could be obtained in crystals. The ammonium and sodium salts are very soluble in water; the barium salt, a light yellow powder, almost equally soluble in cold and in warm water. The mercury and silver salts are light yellow precipitates. By the action of sodium amalgam on the acid, diphenic acid was obtained.

*Diamidodiphenic acid from dinitrodiphenic acid.*—Hummel\* found that the dinitrodiphenic acid from diphenic acid directly, and the acid obtained by Struve,† by the oxidation of dinitrophenanthrenequinone, were identical. The author confirms this result. Struve believed that the diamido acid, obtained from his dinitrodiphenic acid, and the diamidodiphenic acid of Griess, were two distinct compounds. The author, by direct comparison, establishes the identity of the two acids, as they agree in their general properties, yield the same di-iododiphenic acid, and show the same behavior on ignition with lime, baryta, etc. The memoir contains also the description of a number of preliminary experiments which had been undertaken to ascertain the constitution of phenanthrene, before the above solution was found.

Sodium and orthochlorbenzoic acid ether, when acting upon each other, did not yield the hoped for corresponding diphenic ether, but salicylic acid.

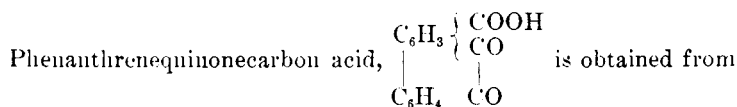
The products of the reaction of pentachloride of phosphorus upon phenanthrenequinone were not examined.

Phenanthrenecarbon acid,  $C_{15}H_{10}O_2$  or  $\begin{matrix} C_6H_3 \\ | \\ C_6H_4 \end{matrix} \begin{matrix} \{ COOH \\ CH \\ || \\ CH \end{matrix}$  is nearly insoluble in alcohol; easily soluble in alcohol ether; m. pt.,  $260^\circ$ . The alkali salts are readily soluble in water. The barium salt  $(C_{14}H_9COO)_2Ba + 6H_2O$ , crystallizes in beautiful needles. The acid is obtained from phenanthrene nitrile, on saponification with alcoholic

\* Ann. Chem., 193, 133.

† Ber. d. d. chem. Ges., 10, 75.

potash. On distillation of the acid with soda-lime, phenanthrene is obtained.



the former, on oxidation with chromic acid in glacial acetic acid solution.

**Phenanthrenequinone**, R. ANSCHUTZ and G. SCHULTZ (32, 57).

*Crude phenanthrene materials*.—1. The residues from the mother liquors obtained in considerable quantity in the course of the purification, on a large scale, of anthracene, by means of benzole (or its homologues), were subjected to fractional distillation. The fraction 310–335°, was employed. 2. The second material was purer than the former; it had been obtained as by-product in the manufacture of anthraquinone from crude anthracene, and purified by re-distillation. The fraction, 320–348°, contained about 82 per cent. of phenanthrene. Besides phenanthrene, these fractions contained anthracene (methylanthracene), fluorene, acridine, carbazol and unknown phenols.

*Phenanthrenequinone* was obtained by the action of suitable mixtures of sulphuric acid, water and potassium bichromate, upon these phenanthrene materials, either with the aid of heat, or by prolonged action (1–1½ months) at ordinary temperature. The reddish-yellow crude product obtained in this manner contained phenanthrenequinone, anthraquinone (methylanthraquinone), phenanthrene, traces of carbazol, diphenylketon, diphenic acid, a new acid, acridine and organic chromium compounds. The last four constituents were removed by treating the material, in succession, with concentrated sulphuric acid, water, very dilute cold sodium hydrate solution, and water. The solution, which is obtained by digesting the dried residue with cold ether, contains phenanthrenequinone, anthraquinone, phenanthrene, carbazol and diphenylketon; the undissolved portion consists of phenanthrenequinone and anthraquinone, which could be easily separated by a slightly warmed solution of sodium bisulphite. Phenanthrenequinone alone enters into solution, and may be precipitated by a solution of potassium bichromate in dilute sulphuric acid, and purified, by re-crystallization, from tar-oils, alcohol or dilute acetic acid.

*Behaviour of phenanthrenequinone towards lime and solutions of the alkalis*.—The author confirms the observation of Graebe in regard to the almost complete conversion of the quinone into diphenyl, on distillation with soda-lime. Soda-lime, containing considerable water, yielded fluorene, diphenylketon, fluorene alcohol, and a red sub-


stance. With 10 pts of quick-lime, the distillate contains diphenyleneketon principally, and fluorene. Partially slaked lime yields diphenyleneketon and diphenyl. The author attributes the reaction in the case of the wet soda-lime to the presence of water. According to the experiments of Baeyer and Friedlaender\* (Caro), phenanthrenequinone is converted into diphenyleneglycollic acid, on boiling with sodic hydrate solution; according to Anschuetz and Japp,† diphenyleneketon is also produced in the reaction. The authors have found, that on prolonged boiling with potash or baryta solution, fluorene alcohol is also formed. Diphenyleneglycollic acid, on prolonged boiling with baryta solution, yields fluorene alcohol principally. The formation of fluorene would be due to the action of nascent hydrogen upon diphenyleneketon or diphenylglycollic acid.

Benzoic acid and phthalic acid both, on heating with quick-lime, yield benzole and ample quantities of diphenyl; benzamide yields water, benzole and benzonitrile.

Diphenic acid yields: 1. with quick-lime, diphenyleneketon, a red substance, and traces of diphenyl; 2. with a mixture of slaked and quick-lime, diphenyleneketon, diphenyl and a red substance; 3. with slaked lime or soda-lime, diphenyl and traces of a red body. The red substance and diphenyl were also observed on heating diphenic acid with zinc-dust.

*Behavior of phenanthrenequinone towards alcoholic potash.*—30 grms of phenanthrenequinone, after boiling for eight days with alcoholic potash, gave about 15 grms pure diphenic acid (compare Huydnick ‡). The by-products which were obtained in the reaction were not examined.

*Behavior of phenanthrenequinone towards alcoholic ammonia.*—Graebe§ obtained  $C_{14}H_{11}O_2N_2$  and  $C_{28}H_{16}N_2$  by alcoholic or aqueous ammonia.

*Phenanthrenequinone oxide*  $(C_6H_4)_2$   long, yellow needles,

m. pt., 167°, is easily reconverted into the quinone by concentrated hydrochloric or sulphuric acid, and subsequent dilution. It is obtained by saturating the hot alcoholic solution of phenanthrenequinone with ammonia, or adding concentrated ammonia solution to it; brown by-products, which form in considerable quantities, were not examined.

\* Ber. d. d. chem. Ges., 10, 126, 534.

† Ibid., 11, 211.

‡ Ann. Chem., 167, 184.

§ Ber. d. d. chem. Ges., 7, 785.

By digesting the ammoniacal phenanthrenequinone solution, at  $100^{\circ}$ , in closed vessels for several days, other compounds were obtained. One of these presented small, dark brown or dark green crystals, which were insoluble in the ordinary solvents, and unaffected by  $\text{HCl}$ ,  $\text{SnCl}_2$  or sodium bisulphite. They were soluble in concentrated sulphuric acid to a beautiful blue solution, which, after digestion on the water bath, deposited on dilution a greenish-grey precipitate. This precipitate on sublimation yielded long, nearly colorless, needles; m. pt.,  $320^{\circ}$ .

Besides the dark green body, a series of other crystallizable nitrogenous substances with basic properties had formed in the reaction, which were easily soluble in alcohol.

The behavior of the quinone towards alcoholic and aqueous potash and alcoholic ammonia, especially incline the authors to give prefer-

ence to the structure  $\begin{array}{c} -\text{C}=\text{O} \\ | \\ -\text{C}=\text{O} \end{array}$  of the  $\text{C}_2\text{O}_2$  group, in phenanthrene-

quinone. They acknowledge, however, that the results obtained by them do not decide this question conclusively.

**Hydrogen Peroxide**, EM. SCHOENE, fourth paper (196, 58, 74).

*Hydrogen peroxide and the oxides of thallium.*—Schoenbein\* states that hydrogen peroxide and thallic oxide mutually reduce each other; Willm† maintains that the presence of an acid is necessary in the reaction; Weltzien‡ re-affirms the observation of Schoenbein. According to Schoenbein, thallic oxide and hydrogen peroxide do not act upon each other. From the result of a series of careful qualitative and quantitative experiments upon the action of hydrogen peroxide (aqueous solution and vapor) on thallic oxide (solution, and paper soaked in 5 per cent. thallic hydrate solution, and dried) and thallic oxide (freshly precipitated, and thallic hydrate papers which had been exposed to ozone), the author deduces as follows:

1. Thallic oxide is oxidized by hydrogen peroxide in the presence of an excess of alkali, in the same manner as the lower oxides of lead and manganese.

2. Thallic oxide is reduced in the presence of an excess of acid  
 $(2\text{H}_2\text{O}_2 + \text{T}_2\text{O}_3 \cdot \text{H}_2\text{O} + \text{H}_2\text{SO}_4 = 2\text{O}_2 + \text{T}_2\text{SO}_4 + 4\text{H}_2\text{O})$ .

3. The action of thallic oxide upon neutral hydrogen peroxide is mainly catalytic;  $\text{H}_2\text{O}_2$  is completely decomposed to  $\text{H}_2\text{O}$  and  $\text{O}$ , and

\* Journ. f. pr. Chem., 93, 38.

† Ann. Chim. Phys. [4], 5, 20.

‡ Ann. Chem., 138, 133.

only a small quantity of thallic oxide is reduced to thalious oxide, not sufficient to render the liquid alkaline.

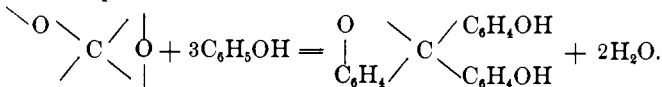
4. Thalious papers become brown in an atmosphere of hydrogen peroxide; thallic papers are not bleached, hence, the coloration of thalious papers in the atmosphere, is not conclusive for the presence of ozone in it.

Thallic oxide is slightly soluble in hydrogen peroxide solution, and is precipitated from the solution by the addition of an alkali.

*Hydrogen peroxide and the peroxides of manganese\* and lead.* †—The behavior of these oxides towards hydrogen peroxide is the same as that of thallic oxide.

*Upon Aurine,* ‡ R. S. DALE and C. SCHORLEMMER, second communication (196, 75, 91).—The body contained in commercial aurine is identical with the aurine obtained from pure phenol. The pure compound was obtained from the crude material in two ways. 1. Ammonia was conducted into the saturated spirituous solution as long as crystals continued to form. The ammonia compound was decomposed by acetic acid or hydrochloric acid, and the washed product repeatedly re-crystallized from spirits. 2. The impurities were removed by washing with cold spirits. The residue was repeatedly re-crystallized from spirits. The aurine thus obtained yields *leucaurine*,  $C_{19}H_{16}O_3$ , on reduction with zinc dust and acetic acid; it corresponds to the formula,  $C_{19}H_{14}O_3$ . The investigations of E. and O. Fisher, § and Graebe and Caro, || lead to the same formula.

The authors have sought to determine the equation explaining the formation of aurine, by eliminating the complicating elements of the reaction. Pure phenol, oxalic acid and barium phenolsulphate, were heated together. The product obtained, contained impure aurine and formic acid. The slight evolution of gas consisted of equal volumes of carbonic oxide and carbon dioxide. Hence, the equation,  $C_2H_2O_4 + 3C_6H_6O = C_{19}H_{14}O_3 + CH_2O_2 + 2H_2O$ ; oxalic acid is decomposed to formic acid, and  $O = C - O -$ , which enters into reaction with 3 molecules of phenol.



\* Thenard, *Traité de Chimie*, 7 edit., Bruxelles, 1830, 1, 209.

† Thenard, *ibid.*, 1, 217; Schoenbein, *Journ. pr. Chem.*, 75, 96; 86, 99; 93, 46; Osann *Chem. Centralbl.*, 1862, 98.

‡ *Ann. Chem.*, 166, 279; Graebe and Caro, *ibid.* 179, 184; Zulkowsky, *ibid.*, 194, 122.

§ *Ber. d. d. chem. Ges.*, 11, 195, 473, 612, 1079; *Ann. Chem.*, 194, 242.

|| *Ber. d. d. chem. Ges.*, 11, 1116, 1348.

*Ammonia aurine*,  $C_{19}H_{14}O_3(NH_3)_2$ , obtained by saturating the concentrated spirituous aurine solution with ammonia; beautiful, dark red crystals with vivid, steel blue lustre, which lose ammonia rapidly on exposure to air, yielding aurine in the form of a reddish-brown powder.

*Tetrabromaurine*,  $C_{19}H_{10}Br_4O_3$ , small brownish-green crystals with bronze lustre, soluble in alkalis with beautiful violet color. The acidulated solutions dye silk and wool dark violet. The pure compound is obtained by adding a hot saturated, glacial acetic acid, aurine solution to a mixture of glacial acetic acid with bromine. The method applied by Graebe and Caro\* in the preparation of tetrabromrosolic acid, cannot be utilized in this case.

*Acetyl chloride and acetic anhydride, and aurine*.—Graebe and Caro† obtained the compound,  $C_{19}H_{14}O_3 + (C_2H_3O)_2O$ , by the action of acetic anhydride upon aurine, at ordinary temperature or on the water bath. Small colorless plates, m. pt.,  $158^\circ$  (Graebe and Caro, 159–160°). The pure compound may be boiled with spirits, or alcohol, without change. In the presence of a slight quantity of hydrochloric acid, the solution becomes rapidly yellow, eventually yellowish-red, and on cooling, deposits brown needles. The compound of Graebe and Caro is also produced in the reaction of acetyl chloride upon aurine, in glacial acetic acid solution. It is difficult to obtain the body pure in this manner, in consequence of the partial decomposition by the hydrochloric acid which forms in the reaction.

*Compounds of aurine with acids*.— $C_{19}H_{14}O_3.HCl + C_2H_4O_2$ , light red, vividly glittering needles, obtained by saturating a hot glacial acetic aurine solution with hydrochloric acid gas. Even when perfectly dry, the compound possesses a strong acetic acid odor. At  $110^\circ$ , in a current of dry air, the acetic acid may be completely expelled; the crystals lose their lustre, and may be heated to  $200^\circ$  without further change.

The compound,  $2C_{19}H_{14}O_3.HCl + 3C_2H_5O$ , was obtained in like manner from the hot saturated, alcoholic aurine solution. At  $110^\circ$ , in a dry current of air, the alcohol escapes, leaving  $2C_{19}H_{14}O_3.HCl$ .

Similar compounds were obtained with sulphuric acid and nitric acid.

The compounds of aurine with sulphurous acid,  $(C_{19}H_{14}O_3)_2SO_3H_2 + 4H_2O$ , and the acid sulphites of the alkali metals ( $C_{19}H_{14}O_3.SO_3M$ ), are colorless.

\* Ann. Chem., 179, 201.

† Ber. d. d. chem. Ges., II, 1122.



*Contribution to the Knowledge of Pyroacemic acid*, CARL BOETTINGER (196, 92, 108).—Conclusion of the author's researches on the constitution of pyroacemic acid, the first portions of which are published in Ann. Chem., 172, 188 and 191.

*Destructive distillation of glyceric acid*.\*—Moldenhauer † states, that on distillation, glyceric acid is decomposed into carbonic acid, acetic acid, pyroacemic and pyrotartaric acids. The author has repeated the experiments of Moldenhauer, but with different results. The products obtained were gases, water, acetic acid, formic acid, an oily acid, and pyrotartaric acid. Only traces of pyroacemic acid could be detected; 1080 grms glyceric acid yielded 0.7 gm of the basic barium salt of pyroacemic acid, and 14 grms of glycuvic acid; 2 kgms of glycerine gave 2 grms of pyrotartaric acid.

*Glycuvic acid*,  $C_8H_{10}O_6$ , m. pt.,  $83^\circ$ , b. pt.,  $245-247^\circ$ , shows the properties of a keton alcohol. It is freely soluble in warm water; the solution reacts very slightly acid, and deposits the substance in large, colorless leaves. The solution in dilute alcohol yields it in long, brittle needles. It is soluble in warm sodium bisulphite solution, from which it separates on cooling. If the solution, however, is heated on the water bath for some time, it will no longer deposit anything on cooling. The ammoniacal solution is not precipitated by silver nitrate. The salts,  $C_8H_9KO_6$ ,  $C_8H_9BaO_6 + H_2O$ , and  $C_8H_9CaO_6 + H_2O$ , were obtained in translucent crystals, by concentrating the solutions of the acids neutralized with the corresponding bases. The dehydrated Ba and Ca salts, correspond to the formula  $C_8H_5BaO_4$  and  $C_8H_5CaO_4$ . The formation of glycuvic acid from glyceric acid may be expressed by the equation:  $3C_3H_5O_4 = C_8H_{10}O_6 + CO_2 + 4H_2O$ .

*Upon sulpholactic acid*.—The author demonstrates the identity of the acid obtained by Schacht, ‡ by the action of potassium sulphhydrate upon  $\alpha$ -chlorpropionic acid, and the sulpholactic acid obtained by himself from pyroacemic acid. † The acid melts at  $141-142^\circ$ ; its potassium, barium and zinc salts are very soluble in water.

In the reaction of KHS on  $\alpha$ -chlorpropionic acid, sulphodilactic acid,  $C_6H_{10}SO_4$  (Schacht), was obtained in considerable quantities. The lead salt of this acid does not dissolve in water; the barium salt dissolves with difficulty in hot water. The acid yields sulpholactic acid on prolonged treatment with hydrogen sulphide.

\* Ber. d. d. chem. Ges., 10, 266.

† Ann. Chem., 131, 188.

‡ Ann. Chem., 129, 1; ibid. 188, 322.

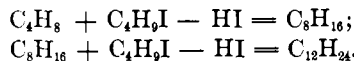
The author concludes: 1. The quantity of pyroacemic acid obtained from glyceric acid is so inconsiderable, that the formation of the acid in this manner, will offer no clue with regard to its constitutional formula. 2. The identity of the sulpholactic acid from pyroacemic acid, and from  $\alpha$ -chlorpropionic acid, proves the ketone nature of pyroacemic acid. 3. The rational formula,  $\text{CH}_3\text{CO}\cdot\text{COOH}$ , must be assigned to pyroacemic acid.

**Allyldipropylcarbinol**, PAUL and ALEX. SAYTZEFF (196, 109, 112).—Allyldipropylcarbinol,  $\text{C}_{10}\text{H}_{20}\text{O}$ , a colorless liquid, insoluble in water, b. pt.,  $192^\circ$  (769 mm), sp. gr., 0.8427, is obtained by the reaction of quantities of butyrene and allyl iodide, represented in the equation:  $(\text{C}_3\text{H}_7)_2\text{CO} + \text{C}_3\text{H}_5\text{I} + \text{Zn} = (\text{C}_3\text{H}_7)_2\text{C}_5\text{H}_9\text{CO}(\text{Zn})$ . The reaction product contains diallyl, unaltered butyrene and the carbinol. The actual yield of the carbinol was 30 per cent. of the theoretical.

The acetic acid ester boils at  $210^\circ$  (751 mm); sp. gr., 0.8733. The carbinol combines with 2Br; on oxidation with chromic acid it yields carbonic acid, butyrene, formic, butyric and propionic acids, and an inconsiderable quantity of a non-volatile acid.

**Allyldiethylcarbinol**, AL. SCHIROKOFF and AL. SAYTZEFF (196, 113, 116).— $\text{C}_8\text{H}_{16}\text{O}$ , colorless mobile liquid, b. pt.,  $156^\circ$ , is obtained by the reaction of allyl iodide, diethylketone and zinc. By the action of bichromate and sulphuric acid, there were obtained diethylketone, acetic acid, propionic acid, and a small quantity of another acid, which was not examined.

**Action of Tertiary Butyl Iodide upon Isobutylene in the Presence of Metallic Oxides**, J. LERMONTOFF (196, 116, 122).—Tertiary butyl iodide was saturated with isobutylene at  $10^\circ$ , the mixture filled into tubes containing twice the quantity of CaO requisite for the absorption of the total iodine. The tubes were sealed, and maintained at a temperature of  $100^\circ$  for twenty hours. Two products were obtained: *Isodibutylene*, identical with the compound obtained by Butlerow, by the action of sulphuric acid upon isobutylene or trimethylcarbinol, and *isotributylene*. The reaction may be expressed by the equations:



The same isotributylene was obtained by the action of tertiary butyl iodide on isodibutylene, in the presence of lime.

**Trimethylethylene and its Derivatives, and the Chemical Structure of Pinakon**, D. PAWLOW (196, 122, 128).—The author finds that tetramethylethyleneglycol, derived from tetramethylethyl-

ene, and the pinakone, obtained from acetone by the action of sodium amalgam, are identical.

Dimethylisopropylcarbinol boils at  $117^{\circ}$  (744 mm); m. pt.,  $-14^{\circ}$ ; sp. gr., 0.8232.—Tetramethylethylene is obtained from the iodide of this carbinol, by the action of alcoholic potash solution. The pure compound is a colorless liquid which is insoluble in water; b. pt.,  $73^{\circ}$  (760 mm). The bromide dissolves in ether, from which it crystallizes in long needles. The chlorhydrate is obtained by the action of fuming hydrochloric acid on the hydrocarbon, at ordinary temperature; colorless, oily liquid, which becomes solid in the cold, b. pt.,  $112^{\circ}$ . The hydroiodic compound boils at  $140^{\circ}$ , and solidifies on cooling. The chemical structure of the hydrocarbon appears from the manner of its preparation, but was further verified by its behavior on oxidation, when it yields acetone only. The hydrocarbon is easily polymerised on treatment with sulphuric acid.

The glycol was prepared from the bromide. 70 grms of the hydrocarbon gave a yield of about 7 grms of the pure glycol. The crystallized product, as obtained from the aqueous solution, melts at  $46.3^{\circ}$ , and corresponds in all its properties to pinakon hydrate,  $C_6H_{14}O_2 \cdot 6H_2O$ , from acetone.

*Nicotine and Nicotinic acid*, R. LAIBLIN (196, 129, 182).

*Preparation of nicotine*.—The aqueous tobacco extract, after concentration, was distilled with lime, the distillate slightly acidulated with a known quantity of oxalic acid, and then concentrated to the consistency of a thin syrup. This extract was decomposed by concentrated caustic potash solution, corresponding in quantity to the oxalic acid previously employed. The oily crude nicotine thus obtained, was distilled in a current of hydrogen, the distillate dissolved in ether, and precipitated by oxalic acid. The precipitate was decomposed, as before, by concentrated potash, and the base obtained, subjected to a careful fractional distillation in a slow current of hydrogen. The fraction,  $240-242^{\circ}$ , represents pure nicotine. The odor of the pure alkaloid is peculiarly narcotic, differing from that of tobacco. One hundred pounds of air-dried tobacco yielded about 600 grms of the pure product (1.2 p. c).

*Nicotinic acid*,  $C_6H_5NO_2$  (pyridinecarbon acid,  $C_5H_4NCOOH$ ), is obtained in the form of the potash salt, on oxidation of aqueous nicotine solution, by means of potassium permanganate, under precautions in regard to which reference must be had to the original. The acid is identical with the pyridinecarbon acid ( $C_5H_5NO_2$ ) obtained by Huber\*

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\* Ann. Chem., 141, 271; Ber. d. d. chem. Ges., 3, 849.

on oxidation with chromic acid mixture, and the nicotinic acid obtained by Weidel,\* on oxidation with  $\text{HNO}_3$ , to which he has assigned the formula,  $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_3$ . The acid was prepared from the silver salt by treatment with  $\text{H}_2\text{S}$ . It is also obtained on decomposing chlorohydronicotinic acid chloride by water, separation of  $\text{HCl}$  and nicotinic acid by fractional precipitation with  $\text{AgNO}_3$ ; decomposition of the silver by  $\text{H}_2\text{S}$ . Colorless needles: m. pt., 225–227°.

Silver salt,  $\text{C}_6\text{H}_4\text{AgNO}_2$ , difficultly soluble in water, voluminous, white precipitate or long, thin, colorless needles,  $(\text{C}_6\text{H}_4\text{NO}_2)_2\text{Ca} + 5\text{H}_2\text{O}$ , very difficultly soluble in water; very easily yields supersaturated aqueous solutions. The aqueous solution, on spontaneous evaporation, yields it in very large crystals.  $\text{C}_6\text{H}_4\text{KNO}_2$ , small colorless, fatty scales, extremely deliquescent. Platinum double compound,  $(\text{C}_6\text{H}_5\text{NO}_2)_2\cdot 2\text{HClPtCl}_4 + 2\text{H}_2\text{O}$ , very large, dark orange, well developed crystals (or long thin needles), obtained on the addition of concentrated  $\text{PtCl}_4$  solution to a solution of nicotinic acid in hydrochloric acid.  $(\text{C}_6\text{H}_5\text{NO}_2)_2\cdot 2\text{HClAuCl}_3$ , small, yellow scales. Hydrochloric acid compound,  $(\text{C}_6\text{H}_5\text{NO}_2)\text{HCl}$ , is obtained from the solution of nicotinic acid in dilute hydrochloric acid, on spontaneous evaporation, in small crystals or frequently in very large plates.  $\text{C}_6\text{H}_5\text{NO}_2\text{HBr}$ .

The *lime salt*, on distillation with lime, yields pyridine principally, hydrogen, (dipyridine), inconsiderable quantities of ammonia, carbonic oxide and hydrocarbons; methylamine does not form. This reaction identifies nicotinic acid as pyridinecarbon acid. The author recommends the pure lime salt as a suitable source for the preparation of pure pyridine.

*Chlorohydronicotinic acid chloride*.—A body, which appears to correspond to the formula  $\text{C}_5\text{H}_4\text{NCOC} + \text{HCl}$ , white soluble needles, was obtained by the action of pentachloride of phosphorus on potassium nicotinate. The compound is very easily decomposed. The yield was small.

*Ethyl ether of nicotinic acid*, is obtained in combination with  $\text{HCl}$  (as  $\text{C}_5\text{H}_4\text{NCO}_2\text{C}_2\text{H}_5 + \text{HCl}$ ), a crystalline compound, by the action of alcohol on chlorohydronicotinic acid chloride. On the addition of sodic hydrate to the aqueous solution, the ether separates in oily drops; it has very little permanence, and could not be obtained in a pure condition.

An attempted synthesis of nicotinic acid by the action of chloro-carbonic acid ether on pyridine, proved unsuccessful. The products

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\* Ann. Chem., 165, 328.

obtained were ethyl chloride, neutral carbonic acid ether and hydrochloride of pyridine.

*Distillation of nicotine salt with lime.*—The salt employed was  $C_{10}H_{14}N_2 + 2HCl + ZnCl_2 + 4H_2O$  (H. Vohl\*). The products obtained were: pyrrol,  $C_4H_5N$ , ammonia, methylamine, a solid base ( $C_{10}H_{11}N?$ ), large quantities of hydrogen, traces of saturated and non-saturated hydrocarbons. The chloride of the solid base ( $C_{10}H_{11}N?$ ), yields a characteristic carmine colored precipitate with  $PtCl_4$ , which is easily soluble in warm dilute alcohol, or dilute sulphuric acid to beautifully dark red solutions.

*Upon the Nature of Cohesion and its Chemical Signification*, FRIEDR. MOHR (196, 183, 213).—Not suitable for abstraction.

*Chloranilines and Chlornitranilines*, F. BEILSTEIN and A. KURBATOW (196, 214, 238).

*Dichloranilines.*—The theory admits of six different dichloranilines. Three of these were known. The other three were obtained by the author, either by reduction of corresponding nitrodichlorbenzoles, or by chlorination of monochloranilines.

1. *p-dichloraniline*,  $C_6H_3NH_2.Cl_2Cl_5$  (Jungfleisch †; Lesimple ‡), long, thick needles (from ligroin solution), which are readily soluble in alcohol, ether, and  $CS_2$ ; difficultly soluble in ligroin, very difficultly in water. *Acetyl derivative*,  $C_6H_3Cl_2NH(C_2H_3O)$ . The authors recommend in the preparation of acetyl derivatives, gradual addition of chloracetyl to the mixture of equivalent quantities of the base and glacial acetic acid, the reaction to be terminated with the aid of heat, the reaction product to be poured in water, and re-crystallized from 50 per cent. acetic acid. Dichloracetanilide, small needles, which are insoluble in  $CS_2$  and ligroin, very difficultly in cold benzole, difficultly in 50 per cent. acetic acid, and easily in alcohol; m. pt.,  $132^\circ$ . *p*-dichloraniline yields on chlorination *trichloraniline*,  $C_6H_2NH_2ClClCl$  (1. 2. 4. 5); on nitration,  $C_6H_2NH_2ClNO_2Cl$  (1. 2. 4. 5) and  $C_6H_2NH_2ClClNO_2$  (1. 2. 5. 6) (?).

2. *Unsymmetrical or (a)-o-dichloraniline*,  $C_6H_3NH_2ClCl$  (1. 3. 4.), long, broad, glistening needles, which are difficultly soluble in ligroin; m. pt.,  $71.5^\circ$ ; b. pt.,  $272^\circ$ . *Acetyl derivative*, small needles, pretty soluble in 50 per cent. acetic acid; m.pt.,  $120.5^\circ$ . On chlorination, it yields the two trichloranilines,  $C_6H_2NH_2Cl_3$  (1.3.4.6 and 1.2.3.4); on nitration,  $C_6H_2NH_2Cl_2NO_2$  (1.3.4.6) and  $C_6H_4NH_2NO_2Cl_2$  (1.2.[?]3.4).

\* Journ. pr. Chem. [2], 2, 331.

† Ann. Chim. Phys. [4]. 15, 252.

‡ Zeitschr. f. Chem., 1868, 226.

3. *Adjacent* or (*v*)-*o*-dichloraniline (1.2.3), needles which are easily soluble in alcohol, difficultly in ligroin; m. pt., 23–24°; b. pt., 252°. *Acetyl derivative* needles (from benzole solution), pretty difficultly soluble in benzole, or 50 per cent. acetic acid, very difficultly in ether or ligroin, more easily in alcohol.

4. (*a*)-*m*-dichloraniline (1.2.4.) (Authors,\* Witt †); m. pt., 63°; b. pt., 245°. *Acetyl derivative*; m. pt., 143°.

5. *Symmetrical* or (*s*)-*m*-dichloraniline (1.3.5) (Witt ‡); m. pt., 50.5°; b. pt., 259–260° (740.6 mm). *Acetyl derivative*, m. pt., 186–187°.

6. (*v*)-*m*-dichloraniline (1.2.6), is obtained in needles, from dilute alcohol; easily soluble in ligroin, or strong alcohol; m. pt., 39°. *Acetyl derivative*, needles, easily soluble in alcohol, or 50 per cent. acetic acid; m. pt., 175°.

Dichloranilines are obtained on chlorination of chloranilines, as follows: 1. *p*-chloraniline yields exclusively (*a*)-*m*-dichloraniline. 2. *o*-chloraniline yields exclusively (*a*)-*m*-dichloraniline. 3. *m*-chloraniline yields *p*-dichloraniline and (*a*)-*o*-dichloraniline.

*Nitrodichloranilines*: 1. (*s*)-*nitro-p*-dichloraniline,  $\text{NH}_2\text{ClCINO}_2\text{Cl}$  (1.2.4.5), yellow needles, easily soluble in alcohol and  $\text{CS}_2$ , pretty difficultly in 50 per cent. acetic acid, almost insoluble in ligroin; m. pt., 153°. *Acetyl derivative*, difficultly soluble in 50 per cent. acetic acid. It is obtained on nitration of *p*-dichloracetanilide. 2. *v-nitro-p*-dichloraniline,  $\text{NH}_2\text{ClCINO}_2$  (1.2.5.6.), is obtained besides the former on nitration of *p*-dichloraniline. It appears to be identical with the reaction product of ammonia upon  $\beta$ -dinitro-*p*-dichlorbenzole (Koerner). Light yellow needles; m. pt., 67–68°. *Acetyl derivative*; m. pt., 204–205°. 3. (*s*)-*nitro-(a)-o*-dichloraniline,  $\text{NH}_2\text{ClCINO}_2$  (1.3.4.6), is obtained on nitration of (*a*)-*o*-dichloraniline, or on heating nitrotrichlorbenzole,  $\text{Cl}_3\text{NO}_2$  (1.3.4.6) with ammonia; m. pt., 175°. *Acetyl derivative*; m. pt., 123–124°. 4. (*v*)-*nitro-(a)-o*-dichloraniline,  $\text{NH}_2\text{NO}_2\text{ClCl}$  (1.2.3.4[?]), forms on nitration of (*a*)-*o*-dichloraniline; m. pt., 95–96°. *Acetyl derivative*; m. pt., 152–153°. 5. (*v*)-*nitro-(v)-o*-dichloraniline,  $\text{NH}_2\text{ClCINO}_2$  (1.2.3.6), is obtained on heating (*v*)-*nitro-v*-trichlorbenzole with ammonia; m. pt., 162–163°. 6. *p-nitro-(s)-m*-dichloraniline,  $\text{NH}_2\text{ClNO}_2\text{Cl}$  (1.3.4.5), forms on nitration of (*s*)-*m*-dichloraniline; m. pt., 170–171°. *Acetyl derivative*, 222°. 7. *o-nitro-(s)-m*-dichloraniline,  $\text{NH}_2\text{NO}_2\text{Cl}_2$  (1.2.3.5); is also obtained on nitration of (*s*)-*m*-dichloraniline; m. pt., 79°. *Acetyl derivative*; m.

\* Ann. Chem., 182, 95.

† Ber. d. d. chem. Ges., 7, 160.

‡ Ber. d. d. chem. Ges., 8, 145.

pt., 138–139°. 8. *o*-nitro-(*a*)-*m*-dichloraniline,  $\text{NH}_2\text{Cl}_2\text{NO}_2$  (1.2.4.6), is obtained on nitration of dichloroacetanilide; m. pt., 100°. Acetyl derivative; m. pt., 188°. 9. *p*-nitro-(*v*)-*m*-dichloraniline,  $\text{NH}_2\text{ClNO}_2\text{Cl}$  (1.2.4.6), forms on chlorination of *p*-nitroaniline; m. pt., 188°. Acetyl derivative; m. pt., 210°.

*Trichloranilines*: 1. (*s*)-trichloraniline,  $\text{C}_6\text{H}_2\text{NH}_2\text{Cl}_3$  (1.2.4.6) (Hoffmann,\* Millst†), was obtained by chlorination of acetanilide. Long, soft needles, soluble in ether, alcohol,  $\text{CS}_2$ , etc.; m. pt., 77.5; b. pt., 262°. *Acetyl derivative*, needles obtained by the action of chloroacetyl on trichloraniline at 100° in sealed tubes. Very little soluble in ether, ligroin,  $\text{CS}_2$ , more easily in 50 per cent. acetic acid or alcohol; m. pt., 204°. 2. (*s*)-*a*-trichloraniline,  $\text{NH}_2\text{Cl}_3$  (1.2.4.5) (Lesimple‡), was obtained by chlorination of *p*-, (*a*)-*o* dichloraniline and (*v*)-*m*-monochloraniline. Thick needles; m. pt., 95–96°. Acetyl derivative; m. pt., 184–185°. 3. *v*-trichloraniline,  $\text{NH}_2\text{Cl}_3$  (1.2.3.4), is obtained besides the former on chlorination of (*a*)-*o*-dichloraniline, and *m*-chloraniline, and on reduction of nitro-*v*-trichlorobenzole; m. pt., 67.5°; b. pt., 292°. Acetyl derivative; m. pt., 120–122°.

*Nitrotrichloraniline*:  $\text{C}_6\text{HNO}_2\text{NH}_2\text{Cl}_3$  (1.2.3.4.6[?]). Nitrotrichloroacetanilide was obtained by nitrification of *a*-trichloraniline. Colorless needles; m. pt., 193°. By digestion of the anilide in sealed tubes at 100°, precipitation by water and re-crystallization from alcohol, the pure *nitrotrichloraniline* was obtained in yellow needles; m. pt., 124°. 2. A nitro derivative could not be obtained from (*s*)-trichloroacetanilide.

*Tetrachloranilines*: 1. *a*-tetrachloraniline,  $\text{NH}_2\text{Cl}_4$  (1.2.3.4.6), was obtained by chlorination of a mixture of isomeric dichloranilines; m. pt., 88°. *Acetyl derivative*, needles, m. pt., 173–174°. It is not decomposed on distillation with caustic soda solution. 2. *v*-tetrachloraniline (1.2.3.4.5) was obtained by reduction of nitro-(*v*)-tetrachlorobenzole by means of tin and hydrochloric acid; m. pt., 118°. 3. *s*-tetrachloraniline (1.2.3.5.6) (Lesimple §).

*Hydrogen Peroxide*, fifth paper, EM. SCHOENE (196, 239–258). —1. *Behavior towards ozone* (Schoenbein||; Meissner¶; C. Hoffman\*\* Engler and Nasse ††; Brodie ‡‡). The result reached by the author

\* Ann. Chem., 53, 35.

† Ann. Chem., 176, 355.

‡ Ann. Chem., 137, 125.

§ Zeitschr. f. Phys., 1868.

|| Journ. pr. Chem., 77, 130, 143, 264.

¶ Untersuchungen ueber den Sauerstoff, Hanover, 1863, 256.

\*\* Pogg. Ann., 132, 617.

†† Ann. Chem., 154, 222.

‡‡ Philos. Transact., 162, 2, 435.

with regard to neutral hydrogen peroxide solution, coincides with what Brodie has shown of the alkaline solution. 1. In the neutral decomposition of ozone and hydrogen, both lose equal volumes of oxygen. 2. The gas containing the ozone expands by a volume equalling the sum of the oxygen volumes lost by the two bodies.

With regard to the behavior of ozone towards water, the author remarks: 1. The quantity of ozone in a dry gas is very considerably decreased when it comes in contact with water. 2. After the gas has come with water, and if it remains in contact with water, the quantity of ozone decreases only slowly (in the course of 3 days the quantity of ozone had decreased one-half; after 15 days, only traces of ozone remained). 3. In the conversion of moist ozone to ordinary oxygen (at ordinary temperature), its volume expands in the ratio of 2 : 3.

*Behavior towards chlorine* (Brodie,\* Asehoff†). The quantity of oxygen evolved is equal to the quantity contained in the hydrogen peroxide. The reaction may be explained by the equations  $\text{H}_2\text{O}_2 + \text{Cl}_2 = 2\text{HCl} + \text{O}_2$  (Brodie, Weltzien‡), or  $\text{H}_2\text{O}[\text{O} + \text{O}]\text{H}_2 + \text{Cl}_2 = \text{H}_2\text{O} + \text{O}_2 + 2\text{HCl}$ .

*Upon Camphor Chlorides*, F. V. SPITZER, part first (196, 259, 264). Gerhardt,§ in a brief notice, states that on the reaction of  $\text{PCl}_5$  upon camphor,  $\text{POCl}_3$  and  $\text{C}_{10}\text{H}_{16}\text{Cl}_2$ , are formed, which latter compound yields, on distillation, an oil, presumably  $\text{C}_{10}\text{H}_{15}\text{Cl}$ . According to Pfandner,|| the product varies according to the quantity of  $\text{PCl}_5$  employed, being either  $\text{C}_{10}\text{H}_{16}\text{Cl}_2$ , or  $\text{C}_{10}\text{H}_{15}\text{Cl}$ . The author has instituted a series of experiments with varied proportions of camphor, and  $\text{PCl}_5$ , without as yet having been able to obtain  $\text{C}_{10}\text{H}_{15}\text{Cl}$ , the existence of which compound seems to him questionable (see also Montgolfier ¶). Only dichlorides seem to form in the reaction. Two isomeric dichlorides were identified; one of these melts at  $87.5-90^\circ$ , the other crystallizes in feathery needles, dissolves easily in ether, and melts at  $155-155.5^\circ$ .

*Upon some Sulphur Oxychlorides*, F. CLAUSNIZER (196, 265, 298).

\* Philos. Transact., 2, 800; Proc. Roy. Soc., 11, 442; Ann. Chim. Phys. [3], 65, 506; Journ. Chem. Soc. [2], 1, 326.

† Journ. pr. Chem., 81, 487.

‡ Ann. Chem., 115, 127, 138, 141.

§ Lehrbuch, 3, 775.

|| Ann. Chem., 115, 29.

¶ Compt. Rend., 85, 286.



*Sulphur selenium oxychloride.*—H. Rose assigned the formula  $2(\text{SeCl}_6, 5\text{SO}_3), 5(\text{SeCl}_4, \text{SeO}_2)$  to the product obtained by him in the reaction of sulphuric anhydride upon selenium tetrachloride. Berzelius has already conjectured that it was  $\text{SO}_3\text{SeCl}_4$ , contaminated with sulphuric acid. The sulphur selenium oxychloride was obtained by the author in a variety of different ways. 1. The reaction upon each other of  $\text{SeCl}_4$  (1 mol.) and  $\text{SO}_2\text{Cl}(\text{OH})$  (2 mol.) begins in the cold, but must be terminated with the aid of heat. The mass, on cooling, solidifies to a crystalline cake, which, after drying on porous clay plates over sulphuric acid, yields the pure  $\text{ClSO}_2\text{—O—SeCl}_3$ . 2. Sulphuryl chloride (1 mol.) and selenium oxychloride (1 mol.), at ordinary temperature, yield  $\text{SeCl}_4$ , apparently according to the equation  $\text{SO}_2\text{Cl}_2 + \text{SeOCl}_2 = \text{SO}_3 + \text{SeCl}_4$ . If the mixture, however, is heated to  $170\text{--}180^\circ$ , in sealed tubes for several hours,  $\text{SO}_3\text{SeCl}_4$ , is obtained. 3. Pyrosulphuric acid (1 mol.) and  $\text{SeCl}_4$  (1 mol.), when heated together, yield  $\text{SO}_3\text{SeCl}_4$  ( $\text{S}_2\text{O}_7\text{H}_2 + \text{SeCl}_4 = \text{SO}_3\text{SeCl}_4 + \text{SO}_4\text{H}_2$ ). Towards the end of the reaction a slight evolution of  $\text{HCl}$  becomes noticeable. This method of preparation is recommended as being the least expensive and troublesome. 4. Sulphuric acid,  $\text{SO}_4\text{H}_2$ , when acting upon  $\text{SeCl}_4$ , also yields sulphur selenium oxytetrachloride. The equation,  $3\text{SeCl}_4 + 2\text{SO}_4\text{H}_2 = \text{SO}_2 + 2\text{SO}_3\text{SeCl}_4 + 4\text{HCl}$ , represents the principal reaction. The reactions,  $\text{SeCl}_4 + 2\text{SO}_4\text{H}_2 = \text{SOCl}_2 + \text{S}_2\text{O}_7\text{H}_2 + 2\text{HCl}$ , and  $\text{SeOCl}_2 + 2\text{SO}_4\text{H}_2 = \text{SeO}_2 + \text{S}_2\text{O}_7\text{H}_2 + 2\text{HCl}$ , take place in a minor degree. 5. Pyrosulphuryl chloride and selenium tetrachloride react upon each other according to the equation,  $\text{Se}_2\text{O}_5\text{Cl}_2 + \text{SeCl}_4 = \text{SO}_3\text{SeCl}_4 + \text{SO}_3 + \text{Cl}_2$ . 6. Sulphurylhydroxylchloride and selenious oxychloride, when acting upon each other, lead to  $\text{SO}_3\text{SeCl}_4$ . The reaction takes place in the two stages,  $2\text{SO}_2\text{Cl}(\text{OH}) + \text{SeOCl}_2 = \text{SeCl}_4 + \text{S}_2\text{O}_7\text{H}_2$ ;  $\text{SeCl}_4 + \text{S}_2\text{O}_7\text{H}_2 = \text{SO}_3\text{SeCl}_4 + \text{SO}_4\text{H}_2$ . 7. Sulphurylhydroxylchloride and selenious anhydride react upon each other, when heated:  $2\text{SO}_2\text{Cl}(\text{OH}) + \text{SO}_2 = \text{S}_2\text{O}_7\text{H}_2 + \text{SeOCl}_2$ ;  $2\text{SO}_2\text{Cl}(\text{OH}) + \text{SeOCl}_2 = \text{S}_2\text{O}_7\text{H}_2 + \text{SeCl}_4$ ;  $\text{S}_2\text{O}_7\text{H}_2 + \text{SeCl}_4 = \text{SO}_3\text{SeCl}_4 + \text{SO}_4\text{H}_2$ . Sulphur selenium oxytetrachloride crystallizes in white needles; m. pt.,  $165^\circ$ ; b. pt.,  $183^\circ$  (Rose  $187^\circ$ ); the dry substance is decomposed at once, on exposure to air; it is violently decomposed when brought in contact with water. The vapor density determination at  $209^\circ$ , gave  $d=3.362$  (calculated 10.426). Dissociation evidently takes place:  $2\text{SO}_3\text{SeCl}_4 = 2\text{SO}_3 + \text{S}_2\text{Cl}_2 + 3\text{Cl}_2$ ; the products of dissociation combine again, on cooling, to the original substance. The author contrasts the properties of  $\text{SeSO}_3\text{Cl}_4$  and  $\text{S}_2\text{O}_3\text{Cl}_4$ .  $\text{S}_2\text{O}_3\text{Cl}_4$  forms only in the cold, and is slowly decomposed at ordinary temperatures, rapidly at the m. pt. ( $57^\circ$ ),

the products being  $S_2O_3Cl_2$ ,  $SO_2Cl_2$ ,  $Cl_2$  or  $SO_2Cl_2$  and  $SOCl_2$ .  $S_2SeO_3Cl_2$  requires the aid of heat in its formation, and is not decomposed at ordinary temperatures, in sunlight, or on heating.  $S_2O_3Cl_4$ , with little water, yields  $SO_2$ ,  $HCl$ ,  $SOCl_2$  and  $S_2O_3Cl_2$ , or  $SO_2(OH)Cl$ .  $SeSO_3Cl_4$ , with water, undergoes the same decomposition as a mixture of  $SO_3$  and  $SeCl_4$ , yielding  $H_2SO_4$ ,  $SeOCl_2$  and  $SeO_2$ , and finally  $H_2SeO_3$ . Concentrated sulphuric acid ( $H_2SO_4$ ) acts violently upon  $S_2O_3Cl_4$ :  $S_2O_3Cl_4 + 2SO_4H_2 = 3SO_2Cl(OH) + SO_2 + HCl$  (Michaelis); while it does not act at all upon  $SeSO_3Cl_4$  in the cold, and very slightly on heating:  $S_2SeO_3Cl_4 + 3H_2SO_4 = 2S_2O_7H + SeOCl_2 + 2HCl$  and  $SeOCl_2 + 2SO_4H_2 = S_2O_7 + SeO_2 + 2HCl$ . These differences would be further proofs for the theorem of Michaelis, which states: "that the affinity of selenium to chlorine is considerably greater than to oxygen, the affinities of N and O to Se are smaller, the affinities of Cl greater than the affinities of these bodies to sulphur." The author adduces a further proof in the behavior of  $SeO_2$  towards  $Se_2Cl_2$ ,  $2SeO_2 + 2Se_2Cl_2 = 2SeOCl_2 + SO_2 + S_2$ ;  $2SeOCl_2 + Se_2Cl_2 = Se_2Cl_2 + 2SOCl_2$ ;  $SOCl_2 + SeOCl_2 = SO_2 + SeCl_4$  (Michaelis).

*Sulphurylhydroxychloride*.—The author finds the b. pt., at 150–151° (726 mm). *Selenium tetrachloride*, vapor density found, 3.922 (calc. 7.63); dissociation evidently according to the equation  $2SeCl_4 = Se_2Cl_2 + 5Cl_2$ . *Selenious anhydride*, sp. gr. = 3.9538. *Selenious acid*, sp. gr. = 3.9066. *Selenium oxychloride* was obtained by heating  $SeCl_4$  (1 mol.) and  $SeO_2$  (1 mol.), in sealed tubes to 200° for several hours; b. pt., 175–176° (753 mm). *Sulphuryl chloride* is decomposed on prolonged boiling, yielding  $SO_4H_2SO_3$  and  $Cl_2$ . The pure compound boils at 72–73°, and is decomposed only slowly in contact with water at ordinary temperature.

*Sulphur-titanium oxytetrachloride*.— $ClSO_2 - O - TiCl_3$ , was obtained in the form of a white powder, in the reaction of  $SO_2(OH)Cl$  upon  $TiCl_4$ .

The corresponding *antimony* compounds could not be obtained by the action of  $SO_2(OH)Cl$ , either upon  $SbCl_3$  or  $SbCl_5$ ; neither was it possible to obtain the corresponding *tin* or *silicium* compounds in like manner from  $SnCl_4$  or  $SiCl_4$ .

The author attempted in various ways to reach the bromides corresponding to  $SO_2(OH)Cl$  or  $S_2O_3Cl_4$ , but unsuccessfully.

*The Coloring Matters and Glycoside Sugar of Persian Berries*, C. LIEBERMANN and O. HOERMANN (196, 299, 338).—

The statements of different authors (Henry,\* Kane,† Binswanger and Winkler,‡ Gellatly,§ Persoz,|| Orthel,¶ Hlasiwetz,\*\* Bolley,††Schuetzenberger,‡‡ Schuetzenberger and Bestèche,§§ Lefort,||| Stein¶¶) in regard to the coloring matters and glycoside sugar, vary considerably.

The authors sum up their own results as follows:

1. The berries, positively those of *Rhamnus infectorius* and *tinctoria*, contain, even after many years, about 12 per cent. coloring matter glycosides, besides little free coloring matter.
2. The glycoside, dissolving more difficultly in spirits, is identical with Kane's xanthorhamnin, and corresponds to the formula  $C_{48}H_{66}O_{29}$ . The more soluble glycoside, Schuetzenberger's  $\beta$ -rhamnegin, does not appear sufficiently established.
3. Xanthorhamnin does not undergo a molecular change by acids, as stated by Lefort, but is decomposed into rhamnatin and isodulcitol, the latter being the same sugar as results from quercitrin. Isodulcitol is also contained in the more soluble glycoside.
4. Rhamnatin corresponds to the formula  $C_{12}H_{18}O_5(OH)_2$ , first assigned to it by Schuetzenberger, and appears in a large number of its derivatives.
5. Xanthorhamnin and rhamnatin are not identical with quercitrin and quercetin.
6. Aqueous berry decoctions deposit a coloring matter, not originally pre-formed in the berries, Lefort's rhamnatin, a glycoside which is formed by the action of a ferment on one of the glycosides. It is not, as stated by Lefort, identical with xanthorhamnin, but probably has not yet been obtained in pure condition.

*Xanthorhamnin* was obtained in solution, by digesting the coarsely powdered berries for ten hours with boiling 85 per cent. alcohol. The pure compound presents microscopic needles of beautiful gold color; dissolves very easily in water, easily in alcohol, but is insoluble in ether, benzole, or chloroform. The air-dried substance crystallized from alcohol, contains crystal-alcohol ( $C_{48}H_{66}O_{29} + 2C_2H_6O$ ). Xanthorhamnin dissolves in alkalies without decomposition. Sugar of lead solution colors the solution orange; a beautiful orange-colored precipitate is produced on addition of ammonia. Silver nitrate yields

\* Journ. pr. Chem., 26, 226. | Traité sur l'Impression des Tissus, 1, 547.

† Phil. Mag., 23, 3.

¶ Bull. Soc. Ind. Mulh., 30, 16.

‡ Jahresber., 1849, 488.

\*\* Ann. Chem., 112, 107.

§ Edinb. New Phil. Journ., 7, 252. †† Ibid, 115, 54.

‡‡ Ann. Chem. Phys. [4], 15, 118.

§§ Bull. Soc. Ind. Mulh., 35, 456.

|| Compt. Rend., 63, 840, 1081; 67, 843.

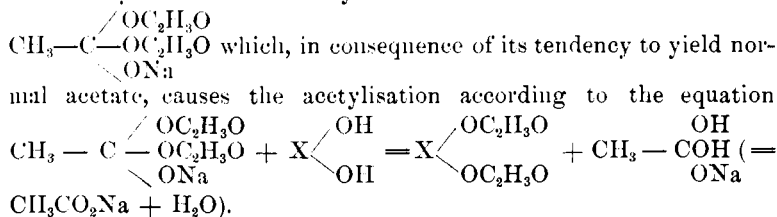
¶¶ Journ. pr. Chem., 105, 97; 106, 1.

a silver mirror.  $\text{Fe}_2\text{Cl}_6$  colors xanthorhamnin solution dark brown. Fehling's solution colors green, and is reduced on application of heat. The potassium salt,  $\text{C}_{48}\text{H}_{62}\text{O}_{29}\text{K}_4$ , is very easily soluble in water, difficultly in alcohol, and very little permanent when moist.

Xanthorhamnin, by prolonged drying at  $130^\circ$ , is partially decomposed into sugar and rhamnetin. Yeast does not produce fermentation in xanthorhamnin solutions.

*Rhamnetin*.—Dilute sulphuric acid does not act upon aqueous xanthorhamnin solution in the cold; on heating, the liquid becomes turbid and suddenly deposits a clean, intensely lemon-colored, precipitate of rhamnetin. If the application of heat is interrupted before the separation of the precipitate is perfected, the complete separation takes place slowly in microscopic crystals. Rhamnetin dissolves very little in boiling water and the ordinary solvents. Warm phenol dissolves it in considerable quantity, and yields it in crystals on cooling. The color and dyeing capacity of rhamnetin is more intense than of xanthorhamnin. Rhamnetin dissolves readily in ammonia, alkalies and alkaline carbonates. The alcohol solution yields precipitates with alum water, copper acetate, lead acetate. Fehling's solution is reduced on heating; silver nitrate, at ordinary temperature. Alumina mordant is dyed canary color; iron mordant, black.

*Dimethylrhamnetin*,  $\text{C}_{12}\text{H}_8\text{O}_5(\text{CH}_3)_2$ , is obtained on digestion of xanthorhamnin potassium, dehydrated potassa, methyl sulphate and absolute methyl alcohol, at  $120^\circ$ . Light yellowish needles; m. pt.,  $156-157^\circ$ , insoluble in water and dilute alkalies, soluble in alcohol. *Acetyl-rhamnetin*,  $\text{C}_{12}\text{H}_8\text{O}_5(\text{OC}_2\text{H}_3\text{O})_2$ , was obtained by boiling equal weights of rhamnetin and anhydrous sodium acetate with 3 to 4 parts of acetic anhydride. Acetic anhydride and sodium acetate combine to



Beautiful, white silken needles, which are easily soluble in glacial acetic acid, less so in alcohol; m. pt.,  $183-185^\circ$ .

*Propionylrhamnetin*,  $\text{C}_{12}\text{H}_8\text{O}_5(\text{C}_3\text{H}_5\text{O})_2$ , colorless needles; m. pt.,  $158-162^\circ$ . *Benzoylrhamnetin*,  $\text{C}_{12}\text{H}_8\text{O}_5(\text{OC}_7\text{H}_5\text{O})_2$ , obtained in the reaction of benzoic anhydride and rhamnetin, colorless silken needles; m. pt.,  $210-212^\circ$ . *Dibromrhamnetin*,  $\text{C}_{12}\text{H}_8\text{Br}_2\text{O}_5$ , yellow needles, easily

soluble in warm alcohol and glacial acetic acid. *Dibromacetylthamnetin*, colorless needles; m. pt., 211–212°.

*Isodulcit*.—A re-examination of the isodulcit from quercitrin proves that it does not crystallize in the forms of cane sugar (Reuss), but clinorhombic crystals (Hirschwald). The decomposition of xanthorhamnin is represented by the equation:  $C_{48}H_{66}O_{29} + 5H_2O = 2C_{12}H_{10}O_5 + 4C_6H_{14}O_6$ .

*Azophenols*, P. WESELSKY and R. BENEDIKT (196, 339, 349).—The azophenols were obtained by the action of melting potassium hydrate on mononitrophenol. *Paraazophenol* prepared from paranitrophenol (m. pt., 114°), forms beautiful, light-brown crystals, without metallic lustre; m. pt., about 204°; partial decomposition at this temperature. Formula of the air-dried substance,  $C_{12}H_{10}N_2O_2 + H_2O$ ; the crystal water escapes at 100°. The compound dissolves easily in alcohol, ether, or benzole, very difficultly in water. *Salts*: The salts of the alkalis yield beautifully orange-colored solutions.  $C_{12}H_8BaN_2O_2 + 4H_2O$ , yellow crystals, was obtained by the addition of aqueous baryta solution to the alcoholic azophenol solution. *Tetrabromoparaazophenol*,  $C_{12}H_6Br_4N_2O_2$ , gold-colored needles. Paraazophenol was also obtained by the action of paradiazophenol nitrate upon phenol potassium ( $HOC_6H_4 - N_2NO_3 + KOC_6H_5 = HOC_6H_4N = NC_6H_4OH + KNO_3$ ).

*Orthoazophenol* crystallizes without water of crystallization, in gold colored scales; m. pt., 171°. The sublimed azophenol forms beautiful reddish-yellow needles. It is insoluble in water, difficultly soluble in cold alcohol; ether dissolves it easily. The *barium* salt crystallizes in beautiful red needles. *Tetrabromorthoazophenol*, dark yellow needles, with metallic lustre.

*Metaazophenol* could not be obtained by fuming metanitrophenol with potash.

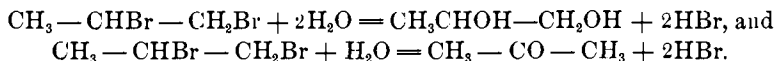
*Action of Water upon the Haloid Compounds of the Alcohol Radicals*, second paper, GUSTAV NIEDERIST (196, 349, 360).—The results of the author confirm the supposition expressed by him,\* that the haloid compounds of mono-valent and bi-valent alcohol radicals may be nearly always converted into alcohol, on treatment with an excess of water. *Methyl iodide* could be easily converted into *methyl alcohol*, *iodide of allyl* into *allyl alcohol*. The author recommends the latter reaction for the preparation of pure allyl alcohol. *Hexylene* and *hexylic alcohol* were obtained by heating *hexyl iodide* (from mannite) with water (100°). *Benzyl chloride*, at 100–110°,

\* Ann. Chem., 180, 388.

gave about 76 per cent. of the theoretical quantity of *benzyl alcohol*, and other products which were not examined.

*Haloid compounds of the olefines.* *Preparation of ethyleneglycol.* 60.5 per cent. of the theoretical quantity of ethyleneglycol was obtained by heating ethylenebromide for 130 hours, with 26 parts of water in champagne bottles, in the water bath.

*Propyleneglycol.* By boiling propylenebromide with an excess of water, *propyleneglycol* (b. pt., 186°) and *acetone* were obtained. The reactions are represented in the equations :



*Amylene bromide* (from commercial amylic alcohol), after 30 hours boiling with an excess of water, had been completely decomposed. The only product obtained (b. pt., 94-96°), appears to be amylylene oxide.

## Reports on American and Foreign Patents Relating to Chemistry.

### American Patents.

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

*January 6, 1880.*

223,212.—*Galvanic battery.* ROBERT C. ANDERSON.

223,265.—*Electro-plating with nickel.* JOSEPH WHARTON.

Brief : This improvement consists in the substitution for the nickel anodes now in use, which are usually of the cast metal, rarely pure and often alloyed, of an anode of wrought or rolled malleable nickel.

223,363.—*Manufacture of printing ink.* JULIUS KIRCHER.

Suitable for cancelling ink and postal stamps. For method of using and composition, the specification must be seen.

*January 13, 1880.*

223,442.—*Preparing a sizing material used by paper-makers.* ROBT A. FISHER.

A solution of sulphate of alumina is treated with oxide of zinc.

223,443.—*Manufacture of a white compound for paper-makers' use.* ROBT A. FISHER.

The ferric sulphate contained in impure sulphate of alumina is first reduced to ferrous sulphate, and then the solution treated with oxide of zinc, as in the preceding patent.