

from the higher nitrates, by treatment with a fixed alkali or ammonia. A cellulose mononitrate could not, however, be obtained. If the dinitrate be acted upon by alkalis, resinous substances and various organic acids are produced. Gun-cotton is, therefore, the hexanitrate, while for the production of collodion, the tetranitrate is employed.

*On the Synthesis of Methylketole, an Isomere of Skatole*, A. BAEYER and O. R. JACKSON (13, 187).

*Contributions to the Knowledge of the Products formed by the Putrefaction of Albumen*, E. SALKOWSKI and H. SALKOWSKI (13, 187).

## Justus Liebig's Annalen der Chemie.

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

*The boiling points of the Esters and Ether esters of the Oxi-acids*, LUDWIG SCHREINER (197, 1-26).—The article refers to the preparation and regularities with regard to the boiling points (see also this JOURNAL, I, 290), of a series of esters and ether esters of glycolic, lactic,  $\alpha$ -oxibutyric and salicylic acids.

The simple esters (oxi-acid compounds, with alkyl substituted in place of the hydrogen of the acid, OH) of glycolic, lactic and oxibutyric acid, are neutral colorless liquids, which are immediately decomposed by water. An increase of the alkyl by  $\text{CH}_2$  is attended by a rise of the boiling point, by about  $10^\circ$ .

The esters of glycolic acid were obtained by the reaction of dry sodium glycolate, monochloroacetic ester and the absolute alcohol in sealed tubes at  $160^\circ$ .  $\text{C}_2\text{H}_4\text{OH.COONa} + \text{CH}_2\text{Cl.COOC}_2\text{H}_5 + \text{C}_2\text{H}_5\text{OH} = 2(\text{C}_2\text{H}_4\text{OH.COOC}_2\text{H}_5) + \text{NaCl}$ .

Oxibutyric ethyl ester was obtained in like manner, in the reaction of sodium  $\alpha$ -oxibutyrate, from butyric ethyl ester and alcohol, at  $180^\circ$ .

Lactic esters were obtained by heating pure lactic acid and absolute alcohol to  $160^\circ$ .

The glycolic ether esters are colorless neutral liquids, heavier than water, readily volatile with water vapor. They are very difficultly saponified. The compound lactic esters are partly insoluble in water. The  $\alpha$ -oxibutyric ether esters are neutral liquids, of disagreeable odor, which are very sparingly soluble in water. The boiling points of the methyl esters are lower by about  $19^\circ$  than those of the corresponding oxi-acid ethers. An increase by  $\text{CH}_2$  of the acid

alkyl in the ether esters, is attended by an increase of the boiling point, by about  $6^{\circ}$ ; if the alcoholic alkyl is increased by  $\text{CH}_2$ , the boiling point rises by about  $19^{\circ}$ .

The glycolic ether esters were obtained by the gradual addition of monochloroacetic esters to the diluted solutions of the sodium alcoholates, the lactic ether esters analogously in the reaction of sodium alcoholates and  $\alpha$ -bromopropionic esters, the  $\alpha$ -oxibutyric ether esters in the reaction of sodium alcoholates and  $\alpha$ -bromobutyric esters (Duvillier).

The specific gravities of the esters and ether esters are decreased by the addition of the  $\text{CH}_2$  group. The diminution is largest if the  $\text{CH}_2$  group enters into the acid radical; smaller, if it enters into the alcoholic OH; still smaller when entering into the acid OH.

Salicylic esters were obtained by saturating alcoholic salicylic acid solution with HCl gas. Colorless liquids, which are insoluble in water and yield a violet coloration with ferric chloride. The compound ethers were obtained in the reaction of the esters, alcoholic potash and alkyl iodide. The yield was small, and the products could be obtained only in a state of approximate purity. Considerable difficulty was experienced in the preparation of ether esters containing two different alkyls, in consequence of a partial interchange of the alkyls in the course of the operation. An increase of the alkyl of the simple salicylic esters by  $\text{CH}_2$ , is attended by a rise of the boiling point by  $6^{\circ}$ . The boiling points of the compound esters rise by  $2^{\circ}$ , if the acid alkyl is increased by  $\text{CH}_2$ ; by  $21^{\circ}$ , if the increase takes place in the alcoholic alkyl. The boiling point of the methylether of a salicylic ester is higher by  $27^{\circ}$ , than that of the corresponding simple ester.

*Methyl- and Dimethyl-diacetonamine*, TH. GOETSCHMANN (197, 27-47).—These bases correspond to the diacetonamine of Heintz, obtained in the reaction of ammonia upon acetone. Dimethyl-diacetonamine results in the reaction of dimethylamine upon acetone, most favorably at  $100-105^{\circ}$ . Platinum chloride produces in the mixture thus obtained a precipitate of a double salt of dimethylamine and dimethyl-diacetonamine,  $(\text{C}_2\text{H}_5\text{NO} \cdot \text{C}_2\text{H}_5\text{N})_2\text{PtCl}_6$ , which is difficultly soluble in water, sparingly soluble in dilute alcohol, altogether insoluble in absolute alcohol and ether, and crystallizes in yellowish-red prisms. There is no method for the separation of the dimethyl-diacetonamine platinum salt in this salt. A separation of the bases was effected by converting the platinum salts into the gold salts. Dimethylamine gold chloride dissolves readily in water.

Dimethyl-diacetonamine gold chloride,  $C_8H_{18}NOAuCl_4$ , crystallizes in long, feathery needles, readily soluble in hot water, very difficultly in cold water and alcohol, insoluble in ether. *Dimethyl-diacetonamine hydrochloride* was prepared from the gold salt. It was obtained from the alcoholic solution in crystals, which are extremely deliquescent, and also extremely soluble in alcohol. The solutions of the salt undergo partial decomposition when heated on the water-bath; the decomposition is complete if the evaporation is carried to dryness.

The base could not be liberated by alkali, in consequence of decomposition; the products are dimethylamine and mesityloxyde. *The platinum double salt*,  $C_{16}H_{36}N_2O_2PtCl_6$ , crystallizes in light red scales, which are insoluble in strong alcohol and ether. *The nitrate and sulphate*, obtained by double decomposition of the hydrochloride with the corresponding silver salts, crystallize with difficulty in small, extremely deliquescent needles. The acid oxalate crystallizes in deliquescent needles.

*Methyl-diacetonamine* was obtained by allowing the solution of methylamine in acetone to stand for several months. Alcoholic platinum chloride precipitates from the mixture the platinum and the platinum salts of the bases, which can be separated by the difference of their solubilities in water.  $C_{14}H_{32}N_2O_2PtCl_4$  crystallizes in large, light red, rhombic prisms, which are tolerably soluble in water.  $[(C_7H_{15}ON)HCl]_2PtCl_2$  crystallizes in dark red prisms. *Methyl-diacetonamine hydrochloride* is extremely deliquescent; the sulphate and nitrate were obtained in the form of colorless syrups. *The gold salt*,  $C_7H_{15}NO.HCl.AuCl_3$ , crystallizes in thin needles or short prisms, which are difficultly soluble in cold water, easily in hot water. The neutral oxalate is very deliquescent, but very difficultly soluble in absolute alcohol. The acid oxalate, which crystallizes in small, short prisms, is not deliquescent. The picrate crystallizes in yellow needles, which are only sparingly soluble in cold water, alcohol or ether, easily in hot water. Acetone bases, other than methyl-diacetonamine, also appear to form in the reaction of methylamine upon acetone.

**Contribution to the Knowledge of Quinamine**, A. C. OUDEMANS, JR. (197, 48-69).—The alkaloid \*, discovered by Hesse as a constituent of the bark of *Cinchona succirubra*, was obtained from the crude mixture of bases, on removal of quinine and cinchonidine in the form of the neutral tartrates, by digesting the portion of the alkaloids soluble in ether, with boiling 50 per cent. alcohol. The

\* Hesse, Ber. d. d. chem. Gesell., 5, 265; 10, 2157; Ann. Chem., 166, 266; de Vrij, Pharm. J. and Trans. [3], 4, 609; Howard, Pharm. J. and Trans. [3], 5, 1.

boiling alcohol dissolves these alkaloids completely; on cooling, almost the entire quantity of quinamine separates. The same method was employed for the approximate quantitative determination of the base in the crude mixture of bases, which, in this manner, was found to contain about 4.5 per cent. of quinamine. The author's analyses of the alkaloid lead to the formula,  $C_{20}H_{26}N_2O_2$ , first assigned to it by Hesse; his iodine determinations, in the well crystallized iodohydrate, to Hesse's later formula,  $C_{19}H_{24}N_2O_2$ . 100 pts. of pure ether dissolve 2.06 pts. of the alkaloid (Hesse states that it is readily soluble). The following reactions are described as being very delicate for minute quantities of the alkaloid.

1. If a drop of quinamine salt solution is cautiously allowed to flow on concentrated sulphuric acid, containing a small quantity of nitric acid, the place of contact assumes a chestnut coloration in the case of more concentrated quinamine salt solutions, a beautiful orange coloration if the solution be less concentrated. The liquid, on subsequent gradual dilution with water, becomes at first purple, finally of a light rose color.

2. Characters written on paper, with a moderately concentrated solution of the alkaloid in a *slight* excess of sulphuric acid, become brown or olive colored, if placed over a mixture of a small quantity of potassium chlorate and concentrated sulphuric acid. If the paper is then removed, the characters gradually assume a rose color.

*Quinamine salts.* The author reaffirms the statements of Hesse, with regard to iodohydrate, chlorohydrate, neutral and acid tartrate, neutral sulphate and acetate. Neither did he succeed in obtaining a crystallized bromohydrate, oxalate or acid sulphate. The *formate* was obtained in feathery crystals. The *nitrate*,  $C_{19}H_{24}N_2O_2HNO_3$ , crystallizes in monoclinic prisms; the *chlorate*, water-free, in forms of the rhombic system; the *perchlorate*, monoclinic; the *chloroplatinate*,  $2(Ch.HCl),PtCl_4$ , is difficultly soluble in pure water, easily in water that contains hydrochloric acid.

Quinamine is a monoacid base. With regard to the influence of quinamine upon the plane of polarization, reference must be had to the numerous details of the original.

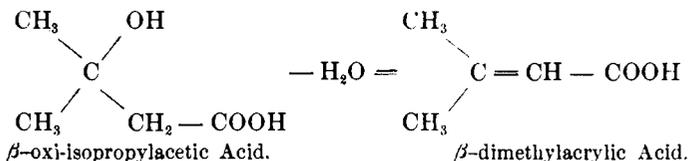
*Diallylisopropylcarbinol*, C. RJABININ and ALEX. SAYTZEFF (197, 70-72).—Diallylisopropylcarbinol,  $C_{10}H_{18}O$ , which was obtained in the same manner as diallylpropylcarbinol,\* is a colorless liquid, boiling point 182 to 185°, sp. gr. = 0.8647 (0°).

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\* Ann. Chem., 193, 362.

On oxidation with chromic acid mixture, it yields carbonic and acetic acids.

**Contributions to the History of the Oxivalerianic Acid, which forms on Oxidation of Allyldimethylcarbinol**, ALEX. SEM-LJANITZIN and ALEX. SAYTZEFF (197, 72-74).—By the reaction of  $\text{PCl}_3$  upon the ethyl ether of oxivalerianic acid,\* an acid was obtained in long glistening needles, m. pt.,  $68.5-69^\circ$ , which the authors consider to be identical with the angelic acid of Neubauer,† obtained on the oxidation of valerianic acid (from fermentation of amylic alcohol), and recently again examined by W. v. Miller.‡ The formation of the acid would be represented in



**Behavior of some Nitro-compounds towards Hydrogen Sulphide**, F. BEILSTEIN and A. KURBATORO (197, 75-85).

The authors find, as a general result of their investigation, that tri-substituted chloronitrobenzoles of unsymmetrical arrangement, are not reduced by  $\text{H}_2\text{S}$ . The Cl atom adjacent to a  $\text{NO}_2$  group is exchanged for S or HS. If two  $\text{NO}_2$  groups are next to each other, the nitro group nearest to the Cl enters into reaction with  $\text{H}_2\text{S}$ . Only in the case of not adjacent, or symmetrical, position, as in nitro-*m*-dichlorobenzole,  $\text{H}_2\text{S}$  effects a reduction of the  $\text{NO}_2$  group.

1. *Chlor-m-dinitrobenzole*,  $\text{C}_6\text{H}_3\text{Cl}(\text{NO}_2)_2$  (1,2,4), according to Jungfleisch,§ on reduction with Sn and HCl in aqueous solution, yields chloronitroaniline. The authors find this statement to be erroneous. The product obtained was chlor-*m*-phenylenediamine; m. pt.,  $86^\circ$ ; difficultly soluble in water, very easily in alcohol. Alcoholic ammonium sulphide,  $\text{K}_2\text{S}$  or  $\text{KHS}$ , convert the chlorodinitrobenzole into *m*-dinitrophenylsulphide,  $[\text{C}_6\text{H}_3(\text{NO}_2)_2]_2\text{S}$ . Yellow needles, difficultly soluble, or almost insoluble in the ordinary solvents, easily in concentrated nitric acid; m. pt.,  $193^\circ$ . On treatment with the nitric acid (sp. gr. = 1.5) at  $120^\circ$ , the sulphide is converted into dinitrophenylsulphone,  $[\text{C}_6\text{H}_3(\text{NO}_2)_2]_2\text{SO}_2$ , yellowish needles; m. pt.,  $240-241^\circ$ .

\* Ann. Chem., 185, 163.

† Ann. Chem., 106, 65.

‡ Ber d. d. chem. Gesell., 11, 1516.

§ Ann. Chim. Phys. [4], 15, 231.

2. *Nitro-p-dichlorobenzole*,  $C_6H_3ClNO_2Cl$  (1.2.4), on treatment with alcoholic  $K_2S$ , yields chloronitrophenylsulphide; with  $KHS$  (or  $NH_4HS$ ) the mercaptan,  $C_6H_3Cl(NO_2)HS$ . *Chloronitrophenylsulphide* crystallizes in dark yellow needles, which are readily soluble in benzole, nearly insoluble in alcohol; m. pt., 149–150°. *Chloronitrophenylmercaptan*, yellow plates; m. pt., 212–213°. Alcoholic ammonium sulphide converts the mercaptan into a body,  $C_{12}H_8Cl_2N_2S_3$  [or  $C_6H_3ClSH.N \left. \begin{array}{l} \diagup \\ \diagdown \end{array} \right\} S(?)$ ], of basic properties, crystallizing in yellow needles, m. pt., 147°, which is readily oxidized when heated with nitric acid (1.34), yielding a substance,  $C_6H_3ClN_2S$  (or  $C_6H_3Cl \left\langle \begin{array}{c} N \\ \parallel \\ S \end{array} \right\rangle$ ), crystallizing in large colorless needles, m. pt., 103.5°, volatile with water vapor, which are readily soluble in the ordinary solvents.

3. *Chloro-o-dinitrobenzole* (1.3.4) yields *chlornitrophenylmercaptan* with alcoholic  $KHS$ . Yellow needles; m. pt. 171°.

4. *Symmetrical nitro-m-dichlorobenzole*,  $C_6H_3Cl_2NO_2$  (1. 3. 5.), with alcoholic  $KHS$ , yields a precipitate of *tetrachlorazoxibenzide*,  $(C_6H_3Cl_2)N_2O_2$ , m. pt., 171–172°; the solution contains symmetrical *m-dichloraniline*.

**Compounds of the Camphor Group**, J. KACHLER, sixth paper, (197, 86–104).—*Borneo camphor*. The pure sublimed borneols obtained from two varieties of crude material were identical. Formula:  $C_{10}H_{18}O$ ; m. pt., 197.5–198°; point of solidification, 195°; b. pt., 212°; rotation in acetic ether solution,  $\alpha_D = +32.7^\circ$ . Nitric acid converts it into ordinary camphor.  $P_2Cl_5$  at ordinary temperature, or fuming  $HCl$ , in sealed tubes at 100°, and borneol, yield borneol chloride,  $C_{10}H_{17}Cl$ , a white, camphory, optically active, substance, which is insoluble in water, easily soluble in alcohol or ether. M. pt., 157°. It undergoes decomposition easily. When heated with water to 90–95°, it yields borneo camphene,  $C_{10}H_{16}$ ; m. pt., 51°; b. pt., 160–165°. On distillation alone, or with strong bases, borneol chloride yields liquid hydrocarbons principally.  $HBr$  and borneol appear to yield the bromide,  $C_{10}H_{17}Br$ ; m. pt., 74–75°.

The artificial borneol obtained by the method of Baubigny,\* appears from its general properties and behavior towards nitric acid and  $P_2Cl_5$ , to be identical with the natural. There is a difference in the

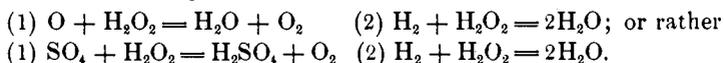
\* Compt. Rend., 63, 221.

optical behavior ; the artificial product could, however, be separated into constituents of different optical behavior.

**Glycyrrhizine**, J. HABERMANN, first paper (197, 105-125).—The author finds that liquorice-root contains a peculiar nitrogenous tri-basic acid, which forms neutral and acid salts. The acid potassium and acid ammonium salts crystallize, and are intensely sweet. The sweetness peculiar to liquorice-wood, is probably due to the presence of ammonium salts of glycyrrhizinic acid. The crystallization resulting from the solution obtained by digesting commercial *glycyrrhizine ammoniacale* with boiling glacial acetic acid, yields pure acid ammonium glycyrrhizinate on repeated recrystallizations, first from boiling glacial acetic acid, and then strong boiling alcohol. Acid ammonium glycyrrhizinate crystallizes in slightly yellowish, vividly glistening needles, which seem to correspond to the formula,  $C_{44}H_{62}NO_{18}(NH_4)$ . They are insoluble in ether, difficultly soluble even in boiling absolute alcohol, very soluble in boiling water. They become gelatinous in water of ordinary temperature. The solubility in water is very considerably increased by the addition of alkali. Neither the solution in water nor in dilute alcohol will yield the salt in crystals, but in the form of an amorphous brittle mass, having the appearance of albumen. The acid potassium glycyrrhizinate is a perfectly white, crystalline body, which exceeds in sweetness, levulose, cane sugar, or even the acid ammonium salt.

The neutral ammonium salt,  $C_{44}H_{60}NO_{18}(NH_4)_3$ , was obtained in the form of an amorphous, brittle, light brownish-yellow mass, which is extremely soluble in water and spirits, almost insoluble in absolute alcohol. The neutral potassium salt presented a yellowish-white loose friable mass, which is readily soluble in water. The barium salt was obtained by the addition of baryta water to the hot solution of the acid ammonium salt in spirits, as a yellowish flocculent precipitate, which is sparingly soluble in water. The lead salt is amorphous, brittle, soluble in glacial acetic acid, sparingly soluble in water, insoluble in alcohol or ether. Glycyrrhizinic acid,  $C_{44}H_{60}NO_{18}$ , obtained by decomposition of the lead salt by  $H_2S$ , has the appearance of dried egg albumen. It becomes gelatinous in cold water, yields a clear sticky solution in boiling water, is pretty soluble in spirits and boiling glacial acetic acid, sparingly in absolute alcohol or ether. It becomes brown at  $100^\circ$  ; the taste is sweet ; the acid decomposes the carbonates of the alkaline earths gradually on boiling. It reduces Fehling's solution on heating, nearly as rapidly as grape sugar.

**Hydrogen Peroxide**, sixth paper, EM. SCHOENE (197, 137-168).  
*Behavior of hydrogen peroxide towards the galvanic current.*—The very elaborate and careful experiments lead to the conclusion that hydrogen peroxide is not an electrolyte. In the course of the action of the galvanic current upon aqueous (acidulated) solutions of hydrogen peroxide, the solvent water (acid) alone is subjected to electrolysis, the decomposition of the hydrogen peroxide in the electrolytical liquid is a secondary reaction, consequent upon the reducing action of the electrolytical decomposition products of water, in nascent condition, upon the  $\text{H}_2\text{O}_2$  around the electrodes:



From this, it follows that hydrogen peroxide cannot form in the electrolysis of water.

**The two Isomeric Bromides**,  $\text{C}_3\text{H}_5\text{Br}_2$ , E. ERLÉNMEYER (197, 169-185).—A critical examination of the methods for the preparation of trimethylene bromide, from allyl bromide and HBr, of Kaysser,\* Lermontoff,† Reboulf‡ and Bogomolev,§ leads to the following results:

1. The most favorable conditions for the formation of trimethylene bromide are, (a) the maintenance of the largest possible excess of dry HBr to dry allyl bromide, to the conclusion or interruption of the reaction; (b) a temperature of 30-40°.

2. The more dilute (either by water or trimethylene bromide already formed) the HBr acts upon allyl bromide, the more considerable the formation of propylene bromide, in the course of the reaction, will be. After a certain degree of dilution has been attained by the formation of trimethylene bromide, the total residual HBr combines with allyl bromide very slowly at low temperature, pretty rapidly at high temperature, yielding only propylene bromide.

3. In sufficiently concentrated HBr solutions, even at temp. 0-30° or above 100°, the reaction always begins with the formation of trimethylene bromide; the formation of propylene bromide seems to begin in less dilute HBr solutions at low temperatures than at high temperatures.

The author has modified the original method of Kaysser in conformity with these results.

\* Inaug. Diss. Muenchen, 1875.

† Ann. Chem. 182, 358.

‡ Ann. Chem. Phys. [5], 14, 470.

§ Ber. d. d. chem. Gesell. 11, 1257.

**Oxichloride and Chlorides of Tungsten**, HUGO SCHIFF (197, 185, 193).—The author has repeated his experiments with regard to the action of  $P_2Cl_5$  upon  $WO_3$  (Ann. Chem., 102, 111). He reaffirms his previous results. Oxichlorides, tungsten oxitetrachloride ( $WOCl_4$ ) principally, are formed at first, these, by the further action of  $P_2Cl_5$  at higher temperature and pressure, yield hexachloride, which latter compound is partially decomposed to pentachloride and chlorine. (Compare Techn, Ann. Chem., 187, 255).

**Influence of the Isomerism of the Alcohols and Acids in the Formation of Compound Ethers**, N. MENSCHUTKIN, second paper (197, 193, 225).—*Formation of the acetic ethers of the secondary alcohols.* Results similar to those in the case of primary alcohols\* were obtained.

		INITIAL VELOCITY.		LIMITS.
		ABSOLUTE.	RELATIVE.	
a.	1. Dimethylcarbinol,	26.53	43.85	60.52
	2. Ethylmethylcarbinol,	22.59	38.10	59.28
	3. Hexylmethylcarbinol,	21.19	34.16	62.03
	4. Isopropylmethylcarbinol,	18.95	31.95	59.31
	5. Diethylcarbinol,	16.93	28.86	58.66
b.	6. Ethylvinylcarbinol,	14.85	28.42	52.25
	7. Diallylcarbinol,	10.60	21.14	50.12

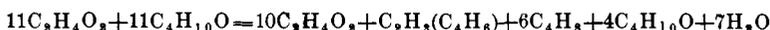
a. Saturated secondary alcohols.    b. Secondary non-saturated alcohols.    Experiments performed at  $154^\circ$  (see this JOURNAL, I, 256).

The absolute initial velocity of the first member of the series is greatest; the initial velocities of the saturated secondary alcohols of equal structure (2 and 3) appear to be constant; of the saturated secondary alcohols of different structure (4 and 5), they are lowest. The absolute initial velocity of non-saturated secondary alcohols decreases with their distance from the saturated series. In the further course of etherification the velocities of the secondary alcohols are greater than those of the primary alcohols. The relative initial velocities decrease with the increase of the molecular weight. The absolute and relative velocities, and limits of etherification, of the secondary alcohols, are considerably lower than of the primary alcohols, a characteristic distinction between the two series of alcohols.

*Formation of the acetic ethers of the tertiary alcohols. Saturated tertiary alcohols.* The process of etherification is more complicated than in the case of primary and secondary alcohols. It is normal during the first hours only. In the further stages, the reaction products are ether, water, alcohol, acid, and olefines. The process of etherification combines the following reactions: 1. Formation of

\* See this JOURNAL, I, 256.

ether and water; 2. Decomposition of ether by the water formed; 3. Dissociation of the ether to olefine and acid, and possibly; 4 and 5. Combination of the alcohol with water and acid, to alcohol and ether. The formation of olefine disturbs the ratio of equal molecules of acid to equal molecules of alcohol; the limits actually found are lower than the true limits, and hence not comparable with those of the primary and secondary alcohols. In the case of acetic etherification of trimethylcarbinol, at 154°, the relation, after the limit has been reached, may be expressed in the equation:



The formation of isobutylene is less considerable at 100°, corresponding to a higher limit, represented in  $16C_2H_4O_2 + 16C_4H_{10}O = 14C_2H_4O_2 + 2C_2H_2(C_4H_9)O_2 + 3C_4H_8 + 11C_4H_{10}O + 5H_2O$ .

The absolute initial velocities only, are comparable with those of the primary and secondary alcohols, and are very low.

	Abs. In. Vel.	Limits.	at 154°
Trimethylcarbinol.....	1.43	6.59	
Ethylidimethylcarbinol.....	0.87	2.53	
Diethylmethylcarbinol.....	1.04	3.78	
Propylidimethylcarbinol.....	2.15	0.83	
Isopropylidimethylcarbinol.....	0.86	0.85	

The limits are reached in a short time, generally after twenty-four hours.

The behavior of the *non-saturated tertiary alcohols*, is similar to that of the saturated. The relation of the limits of the tertiary alcohols appear from the following tabulation.

	$C_nH_{2n+2}O$	$C_nH_{2n}O$	$C_nH_{2n-2}O$
Dlethylmethylcarbinol,	} $C_6H_{14}O$	3.78	Allyldimethyl-
Isopropylidimethylcarbinol,		0.83	carbinol,
Propylidimethylcarbinol,		0.85	( $C_6H_{12}O$ ), 7.26
.....		Allyldiethyl-	Diallylmethyl-
.....		carbinol,	carbinol,
.....		( $C_8H_{16}O$ ), 4.72	( $C_8H_{14}O$ ), 5.36
.....		Allyldipropyl-	Diallylpropyl-
.....		carbinol,	carbinol,
.....		( $C_{10}H_{20}O$ ), 0.46	( $C_{10}H_{18}O$ ), 3.10

The introduction of more complicated groups decreases the limits. The limits of the saturated alcohols are smaller than those of the non-saturated, etc. The stability of the ethers increases with the distance from the saturated series. Allyldimethylcarbinol only is etherified in the first hour. (Initial velocity, 3.05 per cent.)

The behavior of the *phenols* on *acetic etherification* demonstrates that they are non-saturated tertiary alcohols. The course of etherification is normal.

	Initial Velocity.	Limit.
Phenol, $C_6H_5O$ .....	1.45	8.64
Paracresol, $C_7H_7O$ .....	1.40	9.56
Thymol, $C_{10}H_9O$ .....	0.55	9.46
Naphthol, $C_{10}H_7O$ .....	—	6.16

**Contributions to the Knowledge of Cinchonidine**, ZD. H. SKRAUP and G. VORTMANN (197, 226–243).—The authors have subjected the carefully purified base and a series of its salts, to renewed examination, which leads to the conclusion that the formula is not  $C_{20}H_{21}N_2O$ , as usually assumed, but  $C_{19}H_{22}N_2O$ . Platinum salt,  $C_{19}H_{22}N_2O(HCl)_2PtCl_4 + H_2O$ ; the water escapes completely at  $130^\circ$ . Chlorohydrate,  $C_{19}H_{22}N_2O.HCl + H_2O$ . The neutral sulphate of the pure base shows all those properties which Hesse describes as being distinctive for homocinchonidine. It loses its water of crystallization very easily at ordinary temperature, and takes it up again, in part, in moist air. These facts lead to the supposition that homocinchonidine is nothing else than pure cinchonidine. Cinchonidine melts at  $210.5^\circ$ , without decomposition. Point of solidification, between  $188^\circ$  and  $197^\circ$ .

On oxidation with  $KMnO_4$ , at ordinary temperature, cinchonidine yields formic acid and cinchotenicine, which is isomeric with the cinchotenicine obtained from cinchonine under like conditions.  $C_{19}H_{22}N_2O + 4O = C_{18}H_{20}N_2O_3 + CH_2O_2$ . Cinchotenicine,  $C_{18}H_{20}N_2O_3 + 3H_2O$ , crystallizes in colorless needles, which are difficultly soluble in absolute alcohol and cold water, more readily in the hot solvents, easily in dilute acids or alkalies. The aqueous solution reacts neutral.  $CO_2$  precipitates it from the alkaline solution. The behavior towards Ag, Cu and Pb salts, is perfectly analogous to that of cinchotenicine; m. pt.,  $256^\circ$ . The chemical character of the body appears to be that of a phenol. The potassium compound and chlorohydrate were obtained as syrups. The *neutral sulphate*,  $(C_{18}H_{20}N_2O_3)_2H_2SO_4 + 2\frac{1}{2}H_2O$ , crystallizes in small white prisms, which are extremely soluble in water. Platinum double salt,  $(C_{18}H_{20}N_2O_3)_2(HCl)_4PtCl_4$ , was obtained from the hot dilute hydrochloric acid solution in large colorless plates.

**Composition of Cinchonine**, ZD. H. SKRAUP (197, 352–374).—The author's analyses of the carefully purified base and a series of its salts, proved it to correspond to the formula,  $C_{19}H_{22}N_2O$ , not to  $C_{20}H_{24}N_2O$ , generally assigned it. The pure alkaloid melts at  $268.8^\circ$ ; the point of solidification was found between the limits  $209^\circ$  and  $250^\circ$

Platinum salt,  $C_{19}H_{22}N_2O(HCl)_2PtCl_4$ , light yellow precipitate, which becomes crystalline on standing. The neutral sulphate,  $(C_{19}H_{22}N_2O)_2H_2SO_4 + 2H_2O$ , of the *pure* base, crystallizes in thick prisms. Other forms were observed *only* when the base was not entirely pure. M. pt.,  $196^\circ$ . The pure dehydrated salt is very hygroscopic. Thick masses of the salt, after protracted drying, melt at  $115^\circ$  and  $130^\circ$ , being converted into cinchonidine sulphate, without loss of weight. The chlorohydrate, with 2 mols. water, crystallizes in white, long thin prisms. Neutral iodide, with 1 mol.  $H_2O$ , in very slightly yellowish, small needles; loses its water at  $100^\circ$ .

The cinchonine in commercial cinchonine, is accompanied by another alkaloid, from which it is very difficult to separate, distinguished by its great resistance towards  $KMnO_4$ . This base has been designated by the author as cinchotine, and is identical with the hydrocinchonine of Caventon and Willm. Cinchotine corresponds to the formula,  $C_{19}H_{24}N_2O$ . The sulphate,  $(C_{19}H_{24}N_2O)_2H_2SO_4 + 12H_2O$  (?) crystallizes in thin brittle prisms. The dehydrated salt is very brittle; it gradually takes up 2 mols.  $H_2O$ . The platinum double salt,  $C_{19}H_{24}N_2O(HCl)_2PtCl_4$ , was obtained from the hot dilute HCl solution, in orange colored granular crystals.

**Oxidation Products of Cinchonine**, ZD. H. SKRAUP (197, 374-384).—Potassium permanganate acts upon cinchonine sulphate at ordinary temperature, yielding cinchotenine,  $C_{18}H_{20}N_2O_3$ , and formic acid,  $C_{19}H_{22}N_2O + O_4 = C_{18}H_{20}N_2O_3 + CH_2O_2$ . Cinchotenine crystallizes in white needles, which melt at  $197-198^\circ$ , under partial decomposition. It is pretty soluble both in hot and cold water, very difficultly in absolute alcohol. It contains water of crystallization. The platinum salt,  $C_{18}H_{20}N_2O_3 \cdot 2HCl + PtCl_4$ , crystallizes in large orange prisms.

**Action of Oxidizing Agents upon the Hydrocarbons of the  $C_nH_{2n}$  Series**, O. and F. ZEIDLER (197, 243-256).—The authors have allowed potassium permanganate, in neutral, acid and alkaline solutions, chromic acid, mixtures of potassium bichromate and sulphuric acid, to act upon ethylene, propylene, isobutylene and amylene, at ordinary temperature and at  $100^\circ$ . The action of permanganate, giving the larger yield of bibasic acids, was found to be more energetic than of chromic acid. Chromic acid yields monobasic acids (formic, acetic, etc.) principally, bibasic acids (oxalic, succinic, etc.) only in small quantities. In both cases, however, the same acids are formed. In all cases under examination, it was found that the oxidizing agents attack the olefines at the double linking of the carbon atoms.

**Nitro-, Amido- and Bromsulphobenzol Acids**, L. SPIEGELBERG (197, 257-306).—The very lengthy memoir gives in detail the modes of preparation, properties and analyses, of the following bodies:

Amidobromsulphobenzol acid,  $C_6H_3.SO_3H.NH_2.Br$ , and its potassium, barium, calcium, lead and silver salts.

Dibromsulphobenzol acid,  $C_6H_3.SO_3H.Br_2$  (1.3.4), and its barium and lead salts. Dibromsulphobenzol acid (1.2.4) and its barium salts. The dibromsulphobenzol chlorides and amides, obtained from these acids.

Amidodibromsulphobenzol acid,  $C_6H_2.SO_3H.NH_2.Br.Br$  (1.3.4.6), and the potassium, barium and lead salts.

Tribromsulphobenzol acid (1.3.4.6), and the barium and potassium salt. Tribromsulphobenzol chloride, tribromsulphobenzol amide.

Amidotribromsulphobenzol acid,  $C_6H.SO_3H.Br.NH_2.Br_2$  (1.2.3.4.6), and its ammonium, potassium, barium and lead salts. Nitrodibromsulphobenzol acid; amidodibromsulphobenzol acid,  $C_6H_2.SO_3H.Br_2.NH_2$ , (1.3.4.6), and its ammonium, potassium, barium, calcium, lead and silver salts.

Nitrotribromsulphobenzol acid,  $C_6H.SO_3H.Br_2.NO_2.Br$  (1.3.4.5.6), the ammonium, potassium, barium, calcium, lead and silver salts. The corresponding amido acid and salts of the amido acid. The diazo-

compound,  $C_6H \left\{ \begin{array}{l} Br_3 \\ N = N \\ SO_3 \end{array} \right.$ , obtained from this acid.

Tetrabromsulphobenzol acid (1.3.4.5.6), the ammonium, potassium, barium, calcium, lead and silver salts. Tetrabromsulphobenzol chloride, tetrabromsulphobenzol amide.

Nitrotetrabromsulphobenzol acid,  $C.SO_3H.No_2.Br_4$  (2.3.4.5.6), and ammonium, potassium, barium, calcium and lead salts. Nitrotetrabromsulphobenzol chloride, nitrotetrabromsulphobenzol amide. Amidotetrabromsulphobenzol acid, its potassium, barium and calcium salts.

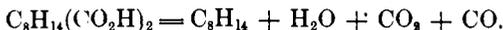
The diazo-compound,  $C_6 \left\{ \begin{array}{l} Br_4 \\ N = N \\ SO_3 \end{array} \right.$ .

**Pentabromsulphobenzol Acid**, HEINZELMAN and SPIEGELBERG, (197, 306-320).—The following results were obtained:

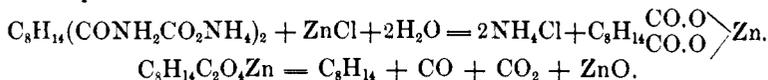
1. Pure pentabromsulphobenzol acid can be easily prepared from the amidotetrabromsulphobenzol acid,  $C.SO_3H.NH_2.Br_4$ . The acid is very readily soluble in water, the salts are extremely sparingly soluble. The chloride melts at 153-154°. 2. The amido acid,  $C.SO_3H.Br.NH_2.Br_3$ , is easily reduced to acids containing less bromine. It yields the

same pentabrom-acid, contaminated, however, with the tetrabrom-acid. 3. The pentabrom acid of Beckurts \* and Langfurth,† contained tetrabrom acid, which is indicated by the lower m. pt. of the chloride, and greater solubility of the salts prepared by them.

*Action of Dehydrating Bodies upon Camphoric Acid and its Amides*, M. BALLO (197, 321-341).—Camphoric acid, on distillation with fused zinc chloride or phosphoric acid, is decomposed, principally according to the equation:



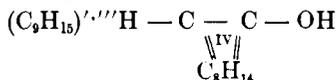
$C_8H_{14}$  = campholene, a colorless liquid, which is identical with Gille's ‡ campholene. A portion of the acid is carbonized, undergoing a more complicated decomposition, in which it yields *campho-terpene*,  $C_{20}H_{32}$  (b. pt., 160-280°). It was found that the amides could not be obtained in the presence of water. A solution of camphoric anhydride in absolute alcohol was saturated with dry ammonia. Crystals of ammonium camphoraminate were obtained, and a mother liquid which, on evaporation, leaves a syrup. This syrup appears to contain an amide or the above ammonium salt, as it yields camphoricimide,  $C_{10}H_{14}O_2NH$  (Laurent), and ammonia, on distillation. The camphoraminate, on distillation with  $ZnCl$ , yields the same products as camphoric acid.



Anhydrous phosphoric acid also saponifies the larger part of the ammonium camphoraminate, yielding the above mentioned products. A portion of the salt is, however, converted into the *nitrile*,  $C_{10}H_{14}N_2$ , a colorless, crystalline body, which is isomeric with nicotine.

The chloride,  $C_{10}H_{16}Cl_2$ , of Pfaundler,§ is oxidized to complicated chlorine compounds in the first stages of the action of nitric acid upon it, camphoric acid being the final product.

The author regards camphor as the tertiary alcohol of



which would make borneol the secondary, menthol the primary

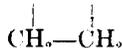
\* Ann. Chem., 181, 226.

† Ibid, 191, 205.

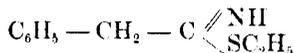
‡ Inaug. Diss., Goettingen, 1872.

§ Ann. Chem., 115, 29.

alcohol; campholene, from the fact of the formation of crymol from camphor, may be regarded as  $\text{CH}_3 - \text{C} = \text{C} - \text{C}_3\text{H}_7$ ,



*Contribution to the Knowledge of Amidines and Thiamides of Monobasic Organic Acids*, A. BERNTHSEN (197, 341-351).—*Ethers of imidothionic acids*.—Phenylacetothiamide and ethyl iodide combine below  $100^\circ$ . From the freshly prepared solution of this body NaOH precipitates *phenylacetimidothiethyl ether*,



an oily body, corresponding in its properties to those previously described by the author.\*

When carefully heated, it is decomposed according to the equation:



The same base was obtained by the method of Pinner and Klein,† by conducting HCl into a mixture of benzyleamide and mercaptan.

*Benzimidothiethyl ether*,  $\text{C}_6\text{H}_5 - \text{C} \begin{array}{l} \diagup \text{NH} \\ \diagdown \text{SC}_2\text{H}_5 \end{array}$  was obtained in the manner indicated, from benzothiamide and  $\text{C}_2\text{H}_5$ , and in the reaction of  $\text{HCl} \cdot \text{C}_6\text{H}_5\text{CN}$  and  $\text{C}_2\text{H}_5\text{SH}$ .

*Benzimidothiobenzyl ether*,  $\text{C}_6\text{H}_5 - \text{C} \begin{array}{l} \diagup \text{NH} \\ \diagdown \text{SC}_7\text{H}_7 \end{array}$  was obtained as well in the reaction of benzothiamide and benzyl chloride, as in the reaction of benzonitrile, benzylsulphhydrate and HCl. From this it would follow that the amidithio-ethers of Pinner and Klein ‡ and the compounds of Wallach, belong to the same class of substances.

\* Ann. Chem., 192, 57.

† Ber. d. d. chem. Gesell., 11, 1825.

‡ Ber. d. d. chem. Gesell., 11, 1509.