Steels.	Chlorate method.		Persulphate method.	
	Chromium.	Manganese.	Chromium.	Manganese.
1	1.50	0.35	1.51	0.36
2	2.88	......	2.85	0.14
Tungsten	3.50	0.12	3.49	0.13
Molybdenum	5.69	0.81	5.71	0.83

I wish to acknowledge my indebtedness to Mr. T. D. Rodgers of this laboratory for the careful manner in which he has carried out these experiments.

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REVIEW.

SOME RECENT WORK IN ORGANIC CHEMISTY.

BY LAUDER W. JONES.

Received October 30, 1905.

A review of the progress of organic chemistry must, of necessity, be a partial one. The greater part must be left untold. In preparing the following survey of the articles published by foreign investigators during the year 1904, I have chosen a few of the many interesting articles, and have been compelled, for lack of space, to exclude many which deserve mention. I hope that the ones which I have selected may be of general interest to those who are familiar with the methods and theories of organic chemistry.

During the year 1904, Grignard's reaction has been applied in a great variety of new syntheses, and seems to be at the beginning, instead of at the end, of its usefulness. Gomberg's triphenylmethyl is still an unsolved riddle. The investigations of Fischer and of Curtius which have led to the building up of so many complex polypeptides, are giving us quite substantial assurance of future success in the synthesis of natural proteins. The study of quadrivalent oxygen derivatives has been continued, and has led to the preparation of many interesting oxonium compounds. The use of powdered nickel in the presence of hydrogen at temperatures above 100° for the purpose of reduction seems to be a method of great promise which may be applied for the reduction of many classes of organic substances. On the whole, the year has given us nothing which is strikingly new, but much that is of interest and importance.

Hydrocarbons.—Some interesting results have been obtained by the slow combustion of certain hydrocarbons. Bone and Wheeler (*J. Chem. Soc.*, **83**, 1074 (1903)), in a previous article, showed that methane gave first formaldehyde and water, and, finally, carbon dioxide, carbon monoxide and water. No methyl alcohol could be detected.

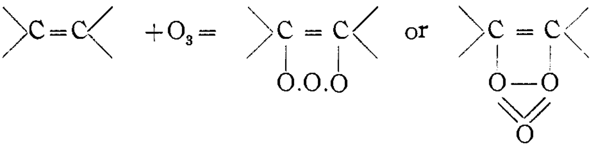
In a recent paper, Bone and Stockings (*J. Chem. Soc.*, **85**, 693–727) describe the products formed by the slow combustion of ethane at temperatures ranging from 250–500°, and at increased and diminished pressures. They observe several stages in the oxidation; first, acetaldehyde and water; second, formaldehyde, carbon monoxide and water; third, carbon monoxide, carbon dioxide and water. Methane and hydrogen are secondary products which result from the decomposition of acetaldehyde and formaldehyde.

$$CH_3O.H \rightarrow CH_4+CO$$
$$CH_2O \rightarrow H_2+CO$$

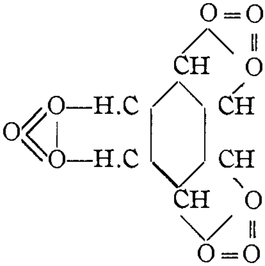
No ethyl alcohol could be detected.

Bone and Drugman (*Proc. Chem. Soc.*, **20**, 127–128), however, have observed that ozonized air (2.5 per cent.) at 100°, acts upon ethane, and yields, in addition to acetaldehyde and formaldehyde, traces of ethyl alcohol. It seems, therefore, that ethyl alcohol is the primary oxidation product of ethane. In a later article, Bone and Wheeler (*J. Chem. Soc.*, **85**, 1637–63) have presented their results with ethylene. The chief product is formaldehyde, accompanied by carbon monoxide, carbon dioxide and water.

Harries has continued his interesting experiments with ozone and organic compounds. The previous articles (*Ber.*, **36**, 1933, 2998, 3001, 3658) dealt with the action of ozone upon aldehydes, alcohols, iodobenzene, iodosobenzene and unsaturated compounds. He found that the double bond in unsaturated molecules was attacked, and the molecules were broken and oxidized by parts to aldehydes or ketones. He has recently discovered that ozone behaves in a different manner in non-dissociating solvents; ozone is absorbed by the double bond with the formation of compounds which Harries calls ozonides.

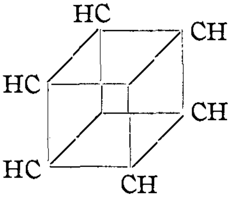


Such ozonides yield, with water, two molecules of ketone and one of hydrogen peroxide. Harries (*Ber.*, **37**, 2708) also studied the action of ozone upon caoutchouc, and succeeded in breaking the molecule into significant parts, through the intermediate formation of an ozonide. By an analysis of the ozobenzene prepared first by Renaud (*C.R.*, **120**, 1177), Harries and Weiss (*Ber.*, **37**, 3431–33) have shown that the formula $C_6H_6O_6$ is incorrect, and must be replaced by $C_6H_6O_9$. It is, therefore, benzene triozonide, and is formed by the addition of three molecules of ozone to benzene.



Pure dry benzene is treated with ozonized oxygen for one or two hours at a temperature of 5–10°. Ozobenzene is precipitated as a white, amorphous mass, which detonates when treated with warm water. By careful treatment with water, it is changed into glyoxal, CHO—CHO.

König (*Chem. Ztg.*, **29,** 30) suggests the cube as a possible space formula for benzene.



Sabatier and Mailhe (*C. R.*, **138,** 248–49) have succeeded in reducing many aromatic halogen compounds to the corresponding hydrocarbons, without, at the same time, adding hydrogen to the ring. This is accomplished by passing halogen compounds, mixed with an excess of hydrogen, over reduced nickel heated to a temperature of 270°. If several halogen atoms are present, they are replaced one after the other, not simultaneously. The presence of methyl or hydroxyl groups makes the replacement easier; amino groups facilitate it still more. Thus chlorbenzene gave benzene; chlornitrobenzene gave aniline hydrochloride. It is a singular fact that the replacement of bromine is not so easy as that of chlorine, while iodine is the hardest of all to replace.

In a second paper (*C. R.*, **138,** 407), the same authors try to extend the reaction to aliphatic halogen compounds, but without the same success, because of the dissociation of the halogen compounds at about 250°. Methyl iodide, however, gave chiefly methane, with some ethylene.

In a similar way, Darzens (*C. R.*, **139,** 868–70) reduces aromatic ketones at 190–195° to corresponding hydrocarbons.

$$C_6H_5.CO.R + 2H_2 = C_6H_5CH_2.R + H_2O$$

Thus acetophenone gave ethylbenzene; *p*-cresyl ketone gave *p*-methylethylbenzene; benzylacetone gave *n*-butylbenzene. In the last case, the reduction occurs, even though the carbonyl group is not bound directly to the benzene ring.

Godchot (*C. R.*, **139,** 604–6), by means of the method just described, reduces anthracene at 250° to tetrahydroanthracene, $C_{14}H_{14}$, and at 200° to octohydroanthracene.

Fontana and Perkin (*Elec. Chem. Ztschr.*, **11,** 99–105) oxidize anthracene to anthraquinone by passing an electric current through a solution of anthracene in acetone, to which dilute sulphuric acid and cerium sulphate have been added.

Luther and Weigert (*Sitzungsber. Kgl. Pr. Akad.*, 1904, 828–39) have found that the change of anthracene to dianthracene in the sunlight, which was observed in solution by Fritzsche, also occurs in the solid and in the vapor forms of anthracene. The reaction is a reversible one.

$$\text{Anthracene} \underset{\text{In the dark}}{\overset{\text{In the light}}{\rightleftarrows}} \text{Dianthracene}$$

The authors have studied it qualitatively and quantitatively.

Thiele and Balhom (*Ber.*, **37,** 1463–70) describe several interesting hydrocarbons called by them quinonoid hydrocarbons. In the course of experiments made with the object of preparing *p*-xylylene, $H_2C=C_6H_4=CH_2$, they obtained polymeric bodies of the same composition. By treating tetraphenyl-*p*-xylylene bromide, $C_6H_4(CBr(C_6H_5)_2)_2$, with metallic silver in the presence of benzene, they obtained tetraphenyl-*p*-xylylene, $(C_6H_5)_2C=C_6H_4=C(C_6H_5)_2$, a solid which crystallizes in red needles and melts at 239–40°. The solution is orange colored and fluorescent, and is soon decolorized by light.

Optically active benzene hydrocarbons were prepared by Klages and Sautter (*Ber.*, **37,** 649–55) by means of Grignard's reaction. They allowed benzaldehyde to act upon active amyl iodide in the presence of metallic magnesium and ether. The product obtained was treated in the usual way with dilute sulphuric acid. The chief substance formed was hexylenebenzene, $C_6H_5.CH=CH.CH(CH_3)C_2H_5$, with some of the carbinol $C_6H_5CH(OH).CH_2CH(CH_3)C_2H_5$. Hexylenebenzene is optically active, $[\alpha]_D^{15°}=+50.3°$. It may be reduced by the action of sodium upon an alcoholic solution; optically active hexylbenzene is obtained as a liquid which boils at 220° (757 mm.) and gives a value $[\alpha]_D^{14.5°}=+17.20°$. Hexylbenzene is not changed into a racemic form by six hours' heating with alcoholic potassium hydroxide at 160°.

The study of triphenylmethyl, $((C_6H_5)_3C)_2$(?), has led to no definite decision concerning the true constitution of this interesting substance. The experimental evidence (Gomberg: This Journal, **22,** 757; **25,** 317; *Ber.*, **33,** 3150; **34,** 2776; **35,** 1822, 2397, 3914;

36, 376, 3928; **37**, 1626) seems to point to the transient existence of triphenylmethyl as a univalent radical, which, in the presence of certain catalyzers, passes into a bimolecular form, distinct from the so-called hexaphenylethane. In the bimolecular state, it combines readily as an unsaturated compound with halogens to form triphenylmethyl halides. Gomberg (*Ber.*, **37**, 2033), by the action of zinc turnings upon triphenylmethyl chloride in benzene, or better still in acetone, has obtained triphenylmethyl in the form of beautiful, colorless crystals, which melt between 145° and 147°. A molecular weight determination by the freezing-point method shows that the molecule has become double. Solutions have a yellow color which Gomberg believes to be caused by the presence of the ion $(C_6H_5)_3C$. The experiments of Walden (*Ber.*, **35**, 2018) show that triphenylmethyl, triphenylcarbinol, triphenylmethyl chloride, when dissolved in liquid sulphur dioxide, are conductors and dissociated, thus bearing out the analogy of triphenylmethyl to a univalent group with base-forming properties.

Attempts to explain away the trivalent carbon have not been successful heretofore. (Norris and Sanders: *Am. Chem. J.*, **25**, 54, 117; **29**, 129; Kehrmann: *Ber.*, **34**, 3815; **35**, 622; Heintschel, *Ber.*, **36**, 320). Tschitschibabin (*Ber.*, **37**, 4709) proposed recently that triphenylmethyl is, in reality, hexaphenylethane. He points out that the so-called hexaphenylethane of Ullmann and Borsum (*Ber.*, **35**, 2877) is diphenylmethyltetraphenylmethane, $(C_6H_5)_3C.C_6H_4.CH.(C_6H_5)_2$, and not hexaphenylethane which is unknown, unless it is identical with triphenylmethyl. Gomberg, however, still maintains that his compound contains trivalent carbon, and accounts for its bimolecular condition by the assumption of associated molecules which, he says, occur in other cases, *e. g.*, the nitriles, the organic acids, etc.

Halogen Compounds.—Konowaloff (*J. Russ. Phys. Chem. Soc.*, **36**, 220–223) studied the action of dilute nitric acid upon halogen compounds, especially $(CH_3)_2CH.CH_2Cl$, $(CH_3)_2CHBr$, $(CH_3)_2CCl.C_2H_5$, and $(CH_3)_3CBr$. Thus, isobutyl chloride gave a nitro halogen compound $(CH_3)_2C(NO_2).CH_2Cl$. He found that saturated halogen compounds are more readily attacked by nitric acid than the corresponding paraffine hydrocarbons. Primary and secondary halogen derivatives yield nitro compounds with halogen in the molecule; tertiary (not aromatic) compounds yield halogen acids and unsaturated substances which may or may not be nitrated.

Halleman and Beekman (*Rec.*, **23**, 225–56; 257–64) prepare fluorbenzene, and certain substituted fluorbenzenes, by the action of concentrated hydrofluoric acid upon diazonium sulphates.

The behavior of aromatic halogen compounds towards copper, heated to temperatures ranging from 210 to 250°, has been studied quite thoroughly by Ullmann (*Ann. Chem.* (Liebig), **332**,

3881) and others associated with him. In this manner, C_6H_5I gave diphenyl to the extent of 82 per cent., while Fittig's method yields only 5 per cent. The same difference is observed in other cases. Copper could not be replaced with advantage by other metals. By this method, *o*-iodotoluene gave 2,2′-dimethyldiphenyl; β-iodonaphthalene gave 2,2′-dinaphthyl. The same method was applied with success to iodo derivatives of sulphonic acids, nitro and amino compounds, and many others.

OXYGEN COMPOUNDS.

Alcohols, Ethers, Phenols.—Grignard's reaction has been employed in a number of ways to prepare alcohols. Thus, Grignard (*C. R.*, **138,** 152–154) prepared the compounds RCO.OMgX in the usual way by acting upon the organo-magnesium halide with carbon dioxide. With a second molecule, R′MgX, these derivatives are changed into substances of the form $RR.'C(OMgX)_2$. A third molecule of the magnesium compound, R′MgX, reacts as follows:

$$RR'C(OMgX)_2 + R'MgX = RR'_2COMgX + (MgX)_2O.$$

This final product is decomposed by dilute sulphuric acid, with the formation of a tertiary alcohol. Grignard prepared in this way diethylisoamylcarbinol, isobutylisoamylcarbinol, phenyldiethylcarbinol, ethyldiphenylcarbinol.

Fallenberg (*Ber.*, **37,** 3578–81) allowed organo-metallic compounds to act upon mesityl oxide and phorone. With care, he succeeded in obtaining a tertiary alcohol by the action of methylmagnesium iodide upon mesityl oxide; it had the following structure: 2,4-dimethylpentene(3)ol(2), $(CH_3)_2C:CH.C(CH_3)_2OH$, and boiled at 46° (14 mm.). From phorone, he prepared 2,4,6-trimethylpentadiën (2.5)ol(4), $(CH_3)_2C:CH.C(CH_3)(OH)CH:C(CH_3)_2$.

The reduction of acid amides, especially in the case of the higher amides, furnishes a new and successful method of obtaining the corresponding alcohols. Bouveault and Blanc (*C. R.*, **138,** 152–54) carry out this reduction by allowing metallic sodium to act upon an alcoholic solution of the amide.

$$R.CO.NH_2 + 4Na + 4C_2H_5OH = RCH_2OH + 4NaOC_2H_5.$$

Some amine is formed, especially in the case of the lower amides. Caproic, pelargonic, and phenylacetic amides were reduced to the corresponding alcohols, with yields varying from 25 to 30 per cent. Scheuble and Loebl (*Monats. für Chem.*, **25,** 341–53, 1081–1105) substitute amyl alcohol for ethyl alcohol, and prepare many of the higher alcohols from the amides.

The method of Sabatier and Senderens was applied by Brunel (*C. R.*, **137,** 1268–69) to phenol, cresol, thymol, and carvacrol. By means of nickel and hydrogen, at temperatures between 100° and 200°, these compounds were reduced to the hexahydro alcohols. Phenol, at 170–175°, gave nearly the theoretical amount of cyclohexanol, a liquid boiling at 160–161°. Thymol gave hexahydrothymol, $C_{10}H_{19}OH$, a liquid with a mint odor; it is stereoisomeric with menthol.

The behavior of halogen ethers towards organo-magnesium derivatives is studied by Hamonet (*C. R.*, **138**, 813–14). He used ethyl-, phenyl- and benzylmagnesium bromides, and allowed these to act upon the halogen ethers,

$$CH_3.O.CH_2Br \text{ and } C_5H_{11}.O.CH_2Br.$$

$$R.O.CH_2Br + RMgBr = R.O.CH_2R + MgBr_2.$$

In this way, he prepared amylpropyl ether, benzylmethyl ether and others.

Alizarindimethyl ether was prepared by Graebe (*Ber.*, **38**, 152–53) by changing alizarin into desoxyalizarin, methylating this with dimethyl sulphate in alkaline solution, and oxidizing the resulting product with sodium chromate in acetic acid solution. The ether crystallizes in golden yellow needles.

Aldehydes and Ketones.—Investigations made by Henriet (*C. R.*, **138**, 203–5) show that the atmosphere contains a small amount of formic acid, and, in addition, some formaldehyde. He estimated the formaldehyde to be between $^1/_{100,000}$ and $^5/_{100,000}$ by passing air over mercuric oxide heated to 250°, and collecting the carbon dioxide in potash bulbs; allowance was made for the carbon dioxide previously present in the air.

Several articles by Leyewetz and Gibello (*C. R.*, **138**, 1225–27), Korber (*Pharm. Ztg.*, **49**, 608), Litterscheid and Thimme (*Ann. Chem.* (Liebig), **334**, 1) deal with the known polymeric forms of formaldehyde, and describe the preparation of many new ones.

When α-hydroxy acids are heated, they yield first lactides. Blaise (*C. R.*, **138**, 697) finds that these lactides, upon distillation, lose carbon monoxide and some carbon dioxide, and are converted into aldehydes with one less carbon atom than the α-hydroxy acid. Thus: α-hydroxycaproic acid gave *n*-pentanal; α-hydroxynonylic acid gave *n*-octanal; α-hydroxypalmitic acid gave *n*-pentadecanal. This method furnishes a means of transition from acids C_n to acids C_{n-1}.

Grignard's reaction has been used, directly or indirectly, in the preparation of aldehydes and ketones by several new methods.

Galleman and Maffezzoli, Bouveault and others use ethyl formate with organo-magnesium compounds to obtain aldehydes. The yield is poor. Tschitschibabin (*Ber.*, **37**, 186–188: Also Bodroux: *C. R.*, **138**, 92–94) found that much better results could be secured by using orthoformic esters in the usual manner.

$$HC(OR)_3 + R'MgI = R'CH(OR)_2 + ROMgI.$$

These acetals may be hydrolyzed with dilute acids, and the aldehydes obtained. Thus, C_2H_5MgI, with orthoformic ethyl ester, gave a yield of 25 per cent. of the acetal $CH_3CH.C(OC_2H_5)_2$.

Béhal and Sommelet (*C. R.*, **138,** 89–92) employ a new method to prepare aldehydes of the forms $R_2CH.CO.H$ and $RR'CH.CO.H$. They heat α-glycol ethers, $RC(OH).CH_2OX$ or $RR'C(OH).CH_2.O.X$, in which X may be an alkyl or an aryl radical, with anhydrous oxalic acid.

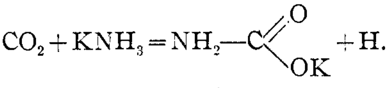
$$2RR'C(OH).CH_2.O.X + C_2H_2O_4 = 2RR'CH.CO.H + C_2O_4X_2 + 2H_2O.$$

The desired α-glycol ethers are obtained from ethyl ethoxyacetate by the action of organo-magnesium compounds. Many aldehydes were prepared in this way.

Acetylene aldehydes are synthesized by Moureu and Delange (*C. R.*, **138,** 1339–41) by treating acetylene hydrocarbons in ether solution with organo-magnesium derivatives, and an excess of ethyl orthoformate. The reaction is completed by heat, and the product is treated with dilute sulphuric acid. Acetals of acetylene aldehydes result; these may be changed into the aldehydes. Amylpropiolic acetal, $C_5H_{11}C:C.CH(OC_2H_5)_2$, hexylpropiolic acetal, $C_6H_{13}C:C.CH(OC_2H_5)_2$ and phenylpropiolic acetal, $C_6H_5C:C.CH(OC_2H_5)_2$ are some of the acetals formed by this method.

Grignard's reaction has been used in numerous instances (Acree: *Ber.*, **37,** 616, 625, 2753; Hell and Stockmayer: *Ber.*, **37,** 225; Hell and Bauer: *Ber.*, **37,** 230, 453, 1429; Klages and Heilmann: *Ber.*, **37,** 1447) to change aldehydes and ketones of the aromatic series into secondary and tertiary alcohols which may, in some cases, lose a molecule of water to give unsaturated compounds.

Acids and Acid Derivatives.—An interesting reaction is described by Rengade (*C. R.*, **138,** 629–31). Sodium ammonium, $NaNH_3$, or potassium ammonium, KNH_3, react with carbon dioxide, at temperatures below —50°, exclusively in one direction, with the formation of a carbamate,



$$CO_2 + KNH_3 = NH_2{-}C\begin{cases}{=}O\\ OK\end{cases} + H.$$

At somewhat higher temperatures (—35° to —25° for $NaNH_3$ and —10° to —5° for KNH_3), the free hydrogen reduces the carbamate partially to formate. This suggests the method employed by Moissan, in which carbon dioxide is reduced by means of sodium hydride, NaH, to formate.

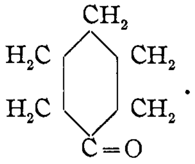
Thioformic acid is prepared according to Auger (*C. R.*, **139,** 798) by saponifying phenyl formate with sodium sulphhydrate. Sodium thioformate, $HCO.SNa$, is obtained as white hygroscopic needles. If this salt is decomposed by formic acid (not hydrochloric) in the cold, and the product is distilled under diminished pressure, thioformic acid, $H.CO.SH$, may be collected in a receiver surrounded by methyl chloride. It is found to be a liquid which soon loses hydrogen sulphide and polymerizes to a white amorphous mass.

A method of characterizing fatty acids is suggested by Locquin (*C. R.*, **138**, 1274–76). It consists in preparing the semicarbazones of acetol fatty acid esters as follows: One gram molecule of the acid to be identified is treated, in ether solution, with the calculated amount of sodium, and then with monochloracetone.

$$\mathrm{RCO.ONa + ClCH_2CO.CH_3 = RCO.O.CH_2.CO.CH_3 + NaCl.}$$

These acetol esters are then converted into semicarbazones which have definite melting-points.

Braun (*Ber.*, **37**, 3588–91) describes a new synthesis of pimelic acid. By treatment of benzoylpiperidine with phosphorus pentachloride or pentabromide, a mixture of benzonitrile and pentamethylene dihalogen is obtained. By the action of potassium cyanide, the pentamethylene compound is converted into $\mathrm{N{:}C(CH_2)_5C{:}N}$, which, upon hydrolysis, yields normal pimelic acid. If the calcium salt of pimelic acid is heated, it yields



This series of changes affords a method of changing the imide group in piperidine to the carbonyl group.

Blaise and Gault (*C. R.*, **139**, 137–39) have found that formaldehyde condenses with two molecules of ethyl oxalate in the presence of piperidine and yields a compound,

$$\mathrm{CO.OC_2H_5CO.CH.(COOC_2H_5)CH_2CH.(COOC_2H_5).CO.COOC_2H_5.}$$

By hydrolysis with dilute hydrochloric acid, this yields dioxypimelic acid, $\mathrm{COOHCO.(CH_2)_3CO.COOH}$, a crystalline solid, which, by loss of water, is changed to pyrandicarbonic acid,

$$\mathrm{COOH\overline{C{:}CH.CH_2CH{:}C—O}—COOH.}$$

Many esters of fatty acids are secured by a new method proposed by Tschitschibabin (*Ber.*, **38**, 561–66). He applies Grignard's reaction to the neutral esters of carbonic acid. The reaction may proceed in three stages as follows:

I. $\mathrm{CO(OC_2H_5)_2 + RMgX = RC(OC_2H_5)_2O.Mg.X.}$

II. $\mathrm{RC(OC_2H_5)_2OMgX + RMgX = R_2C(OC_2H_5)OMgX + C_2H_5O.MgX.}$

III. $\mathrm{R_2C(OC_2H_5)OMgX + RMgX = R_3C.O.MgX + C_2H_5OMgX.}$

If the reaction product is decomposed by dilute sulphuric acid after the first stage, an acid ester will result; if it is treated after the second stage, a ketone will be formed; after the third stage, a tertiary alcohol will be obtained. With care, it is possible to realize the first process, and obtain a yield of 80 per cent. of ester. If orthocarbonic esters are used, orthoesters of fatty acids result.

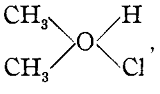
Marckwald (*Ber.*, **37**, 349–54) announces the synthesis of *l*-valeric acid, and considers that he has accomplished a true asymmetric synthesis. This he does by preparing the acid brucine salt of methylethylmalonic acid. By fractional crystallization, the less soluble form separates. When this brucine salt was heated to 170°, carbon dioxide was lost, and the brucine salt of valeric acid remained. With dilute sulphuric acid, this residue gave *l*-valeric acid, $[\alpha]_D = -1.7°$. This value corresponds to about 10 per cent. of *l*-valeric acid. Cohen and Patterson (*Ber.*, **37**, 1012–14) do not believe this synthesis is a real "asymmetric synthesis," such as Fischer, Cohen and Whiteley, Kipping and others have tried to effect, since it depends, they say, upon the separation of two enantiomorphous ions, already present in solution, by the formation of the salt of an active base. They consider the method to be identical with the one used by Pasteur.

Marckwald (*Ber.*, **37**, 1368–70), in reply, defines an asymmetric synthesis as one in which an optically active body results from a symmetrically constituted body, through the intermediate use of optically active substances, but without any analytical process. He considers the formation of *l*-valeric acid to be totally unlike the preparation of active malic acid from racemic acid, since the tartaric acid necessary must be prepared from racemic acid by an analytical process, *viz.*, by splitting according to Pasteur's method. He asserts that enantiomorphous ions are excluded, since methylethylmalonic acid reacts with brucine in chloroform or ether, non-dissociating solvents, and yields the acid brucine salt.

The structure of the lecithin molecule is determined by Willstätter and Lüdeke (*Ber.*, **37**, 3753–58). They find that free glycerolphosphoric acid, $CH_2OH.CH_2OH.CH_2O.PO_3OH$, is optically active, which determines the position of the phosphoric acid group.

Coehn and Jahn (*Ber.*, **37**, 2836–42) find that carbonic acid may be reduced to formic acid by means of the electric current, if a solution of sodium bicarbonate and potassium sulphate is chosen as the electrolyte. When a current of low density is used and carbon dioxide is conducted through the solution, formic acid is obtained. Even a pure water solution of carbonic acid gives a small amount of formic acid.

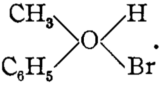
Oxonium Compounds.—The discovery of the hydrochloride of dimethyl ether,



by Friedel (*Bull. Soc. Chim.*, **24**, 160) in 1875 may be considered as the starting-point in the chemistry of quadrivalent oxygen. In 1877, van't Hoff (*Ansichten u. die Org. Chem.*, p. 62) proposed that the compounds of quadrivalent oxygen might possess basic properties. Since that time, the evidence (Dale and Schorlemmer: *Ann. Chem.* (Liebig), **196**, 84; Classen and Ponder: *Ann. Chem.* (Liebig), **223**, 142; Wallach: *Ann. Chem.* (Liebig), **246**, 181; Perkin: *J. Chem. Soc.*, **69**, 1439) in favor of basic quadrivalent oxygen compounds has gradually accumulated.

Collie and Tickle, in 1896 (*J. Chem. Soc.*, **59**, 619), rejected the old method of considering these derivatives as "molecular combinations," and decided to explain them as basic compounds of quadrivalent oxygen. They studied especially dimethylpyrone. Baeyer and Villiger (*Ber.*, **34**, 2677) have contributed very important evidence. They found that alcohols, ethers, aldehydes, ketones, acids and esters all form crystalline compounds with acids, especially with hydroferrocyanic and hydroferricyanic acids. The evidence gained by applying physico-chemical methods (Walden: *Ber.*, **34**, 4185; Lacken: *Ber.*, **35**, p. 212; Cohen: *Ber.*, **35**, 2673; Collie and Tickle: *J. Chem. Soc.*, **85**, 971; Willstätter: *Ber.*, **38**, 1461) of investigation has settled the question in favor of basic quadrivalent oxygen compounds.

Recently, Archibald and McIntosh (*Proc. Chem. Soc.*, **20**, 139) have studied the action of liquid halogen acids upon acetone, ethyl ether, ethyl alcohol and other similar compounds. They find that hydrobromic, hydrochloric and hydriodic acids all form crystalline compounds which have melting-points ranging between —120° and —9°. By the action of liquid hydrobromic acid upon anisol, they obtain an oxonium compound,



This substance must contain an asymmetric oxygen atom.

McIntosh (*Proc. Chem. Soc.*, **21**, 64–5) allowed chlorine and bromine to act upon certain alcohols and ethers, acetone, acetaldehyde and ethyl acetate at low temperatures. Crystalline compounds resulted. Thus, $CH_3OH.Br_2$, which melts at —51°, and $(CH_3)_2OBr_2$, which melts at —68°, were obtained.

Cohen and Galecliff (*Proc. Chem. Soc.*, **20**, 194–96) find that ether, when shaken with dilute nitric acid, combines with it to form a compound which may be obtained as an explosive oil by drying the ether and evaporating it. An analysis of this oil gave the composition $(C_2H_5)_2OHNO_3$. Propyl ether combines in the same way with nitric acid to yield $(C_3H_7)_2O,HNO_3$.

Carbohydrates.—Morrell and Croft (*J. Chem. Soc.*, **75**, 786; **77**, 1219; **81**, 666; **83**, 1284–92) have continued their study of the action of ferrous salts and hydrogen peroxide upon carbohydrates.

They find that frequently, in addition to the osone, other products result by the splitting of the carbohydrate. Thus, glucose and *d*-fructose, with four molecules of hydrogen peroxide, give oxalic acid, glycolic acid, glyoxalic acid, and trihydroxybutyric acid. In a more recent paper, Morrell and Bellars (*Chem News*, **90,** 158–159; British Assoc. Rept., 1904) describe crystalline substances formed by the action of guanidine upon osones, CN_3H_5, $C_6H_{10}O_6$ C_2H_6O. Glucose and maltose form addition products with guanidine.

Ofner (*Ber.*, **37,** 3362–63) has studied the action of methylphenylhydrazine upon sugars.

Leyewetz and Gibello (*C. R.*, **138,** 150–152) obtain formose and glycerose by the action of sodium sulphite upon trioxymethylene.

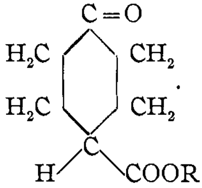
Bau (*Z. ver. Rubenzucker Ind.*, 1904, pp. 481–521) has isolated crystalline melebiose, and finds it to be a solid melting at 84–85°. The liquid which remains after the fermentation of meletriose is treated with barium hydroxide, and the barium compound which is precipitated is treated with dilute sulphuric acid. By precipitation with alcohol and ether, melebiose, $C_{12}H_{22}O_{11}+2H_2O$, was obtained.

Bertrand (*Ann. Chim. Phys.* [8], **3,** 181–288) presents a complete survey of his fascinating studies in connection with the sorbose bacterium, which, in so singular a manner, is capable of oxidizing many polyatomic alcohols and sugars. In the case of polyatomic alcohols, he finds that the group $=CH(OH)$ is changed to the carbonyl group. Thus, glycerol is changed to dihydroxyacetone, sorbitol to sorbose, mannitol to levulose. Aldoses yield by oxidation the corresponding monobasic acids which may be oxidized in turn to ketone acids, if they contain an oxidizable secondary alcohol group. Thus, gluconic acid gave, in the presence of the sorbose bacterium, oxygluconic acid. Recently, Bertrand has found that sorbose may be reduced by sodium amalgam in acid solution to a mixture of *d*-sorbitol and *d*-iditol. Dihydroxyacetone, contrary to the report of Piloty and Emmerling, is fermentable with difficulty. The reducible ketoses give no characteristic oxidation product, but are slowly destroyed by the sorbose bacterium.

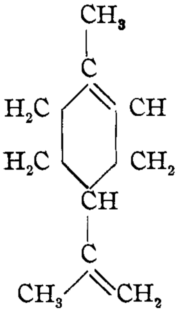
Terpenes and Camphor Derivatives.—Brühl (*Ber.*, **37,** 746, 761, 2156, 2163, 2178, 2512, 3943) has made a study of the various halogen and acyl derivatives of camphorcarboxylic acid and of camphor itself.

W. H. Perkin, Jr., (*Trans. Chem. Soc.*, **85,** 128) prepared synthetically *i*-α-campholactone, *i*-α-campholytic acid and β-campholytic acid.

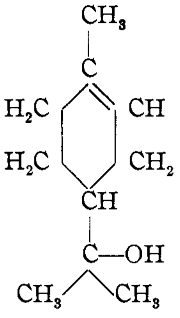
The most important discovery in connection with the terpenes was made by W. H. Perkin, Jr. (*Trans. Chem. Soc.*, **85,** 654). He has worked out a complete synthesis of terpin hydrate, terpineol, and dipentene. The starting material is the ethyl ester of δ-ketohexahydrobenzoic acid,



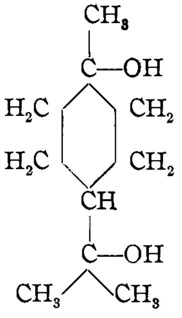
This ester is treated with magnesiummethyl iodide according to Grignard's reaction. The chief product is cis-δ-hydroxyhexahydro-*p*-toluic acid, $\overline{\mathrm{CH_2—CH_2—C(OH)(CH_3).CH_2—CH_2CH}}\mathrm{COOH}$, which, upon distillation, passes into the corresponding lactone. This lactone with concentrated hydrobromic acid is changed to δ-bromhexahydro-*p*-toluic acid, which, by digestion with pyridine or sodium carbonate, gives Δ^3-tetrahydro-*p*-toluic acid; when the ester of this acid is treated with magnesiummethyl iodide, it gives *i*-terpineol. This yields dipentene when it is treated with potassium disulphate, and terpin hydrate, when acted upon by dilute sulphuric acid. These relations are represented by the following formulae:



Dipentene.



Terpineol.



Terpin hydrate.

NITROGEN COMPOUNDS.

An interesting method of preparing normal sodium diazotate is recorded by Bamberger (*Ber.*, **37**, 629–30). It consists in treating nitrobenzene with sodium amide

$$C_6H_5NO_2 + NaNH_2 = C_6H_5N_2ONa + H_2O.$$

The yield is very small.

Sabatier and Senderens (*C. R.*, **138**, 457–60; 257–59) reduce aniline by means of nickel and hydrogen at 190° to cyclohexylamine, $C_6H_{11}NH_2$,—a colorless liquid with a strong basic odor. At the same time, dicyclohexylamine and cyclohexylaniline are formed. In a similar manner, at 160–180°, both mono- and dimethyl- and ethylaniline, are reduced to the corresponding hexahydro compounds.

Amino Acids.—Curtius and Müller (*Ber.*, **37**, 1261–79) present many new investigations connected with the diazo fatty acid esters. They have found that only α-amino acid esters can furnish diazo fatty acid esters; from β- and γ-amino acid esters, no diazo compound could be isolated; while α-β-diaminopropionic ethyl ester gave α-diazo-β-hydroxypropionic ethyl ester.

A new synthesis of *r*-leucine is described by Bouveault and Locquin (*Bull. Soc. Chim.* [3], **31**, 1180–83). By treating α-oximinoisobutylacetic ethyl ester with sodium amalgam, they obtained α-aminoisocaproic ethyl ester, and from this α-aminoisocaproic acid, which is identical with *r*-leucine. Aluminium amalgam gave better results than sodium amalgam.

Fischer (*Ber.*, **36**, 2982; **37**, 2486–2511; **37**, 2842–48; 3062–71; 3871–75) has published many very interesting articles on the synthesis of polypeptides. It is interesting to note that there is a great similarity between these artificial polypeptides and the natural peptones. This is especially true of the synthetic products which contain more than one amino acid group, that is, "mixed polypeptides." The ordinary reactions of peptones, such as the biuret test, precipitation by phosphotungstic acid, hydrolysis by trypsin, are presented by the artificial polypeptides. Fischer thinks that the building up of polypeptides is the most important step in the synthesis of peptones. It will be impossible to give a review of this extensive work. The general method of procedure by which the simple amino acids lead to dipeptides, tripeptides, tetrapeptides, etc., is as follows: A monohalogen or dihalogen acid chloride is allowed to act upon an amino acid in the presence of alkali. Thus, monochloracetyl chloride with glycine gives

$$CH_2Cl.CO.Cl + H_2N.CH_2.CO.OH = CH_2Cl.CO.NHCH_2.CO.OH + HCl.$$

If the resulting monochlor derivative is treated with aqueous ammonia, the chlorine atom is replaced by the amino group,

$$CH_2Cl.CO.NH.CH_2.COOH + NH_3 = CH_2(NH_2)CO.NH.CH_2.COOH + HCl.$$

The resulting compound is a dipeptide, glycylglycine. The same reaction may be repeated again and again. Fischer carried the reaction as far as the pentapeptide, tetraglycylglycine, $H_2N—CH_2.CO.(NH.CH_2.CO)_3NH.CH_2.COOH$. Various other di-, tri- and tetrapeptides were built up, by selecting other monohalogen or dihalogen acid chlorides, and other amino acids, such as leucine, alanine, tyrosine. Mixed polypeptides were formed by using different chlorides. Thus dileucylglycylglycine, a tetrapeptide, was prepared by Fischer.

Derivatives of α-pyrrolidinecarboxylic acid, called by Fischer "prolin," are studied by Fischer and Suzuki (*Ber.*, **37,** 2842–48), and by Fischer and Abderhalden (*Ber.*, **37,** 3871–75). This substance is of importance because it is the only imino base found in proteins.

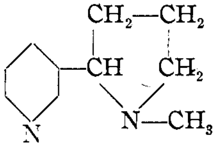
Dyes and Related Compounds.—Previous attempts to prepare quinone diimide by the reduction of quinone dichlorimide failed. Willstätter and Mayer (*Ber.*, **37,** 1494–1507) succeeded in preparing it by treating the quinone dichlorimide with hydrochloric acid in absolute ether solution. Chlorine is liberated, and the hydrochloride of quinone diimide is formed. With ammonia in ether solution this salt yields quinone diimide, a substance which crystallizes in bright yellow crystals which decompose at about 50–60°.

There is still no unanimity of opinion concerning the constitutions to be assigned to the triphenylmethane colors. Baeyer and Villiger have varied their opinion from time to time between the quinoid ammonium theory, and the theory of carbonium salts. In his last paper, Baeyer (*Ber.*, **38,** 569) considers that the quinoid structure is no longer tenable. He reverts to the carbonium theory, or a modified form of Rosenstiehl's (*C. R.*, **116,** 193) view. Many interesting suggestions concerning the structure of these compounds have been made by Hantzsch (*Ber.*, **37,** 3434), Von Braun (*Ber.*, **37,** 633, 2670), Vorländer and Siebert (*Ber.*, **37,** 3364), Straus (*Ber.*, **37,** 3277) and others.

Alkaloids.—The most important discovery of the year in connection with alkaloid chemistry, is the complete synthesis of nicotine. This was accomplished by Pictet and Rotschy (*Ber.*, **37,** 1225) in the following manner: In a previous article Pictet and Crepiéux (*Ber.*, **28,** 1904) describe the preparation of N-β-pyridylpyrrols by distilling β-aminopyridine mucate. When this substance is passed through a tube heated to redness, it is changed into the isomeric α,β-pyridylpyrrol. By the action of methyl iodide upon the potassium salt of this compound, α,β-pyridyl-N-methylpyrrol methyl iodide is formed. This is identical with the methyl iodide addition product of nicotyrine, which is obtained by the moderate oxidation of nicotine.

From this methyl iodide addition product, nicotyrine may be obtained by distilling it over heated calcium oxide. To change nicotyrine to nicotine, it requires the addition of four atoms of hydrogen. This could not be done directly, but was accomplished indirectly by preparing iodonicotyrine by the action of iodine and sodium hydroxide upon nicotyrine. The reduction of iodonicotyrine with tin and hydrochloric acid gave dihydronicotyrine. Finally, the perbromide of this dihydronicotyrine was reduced, and nicotine obtained. It appears to be identical with inactive nicotine.

Inactive nicotine was resolved into its active components by separating the crystallized tartrates into the *d*- and *l*-modifications. *l*-Nicotine, prepared synthetically, appears to be slightly different from natural *l*-nicotine. This synthesis establishes the correctness of the formula proposed by Pinner.



Through the investigations of Pauly (*Ber.*, **37**, 379), Jowett (*Trans. Chem. Soc.*, **85**, 192), and of Bertrand (*Ann. Institute Pasteur*, **18**, 672) the synthesis of adrenaline is fast approaching completion.

NEW BOOKS.

LANDOLT-BÖRNSTEIN PHYSIKALISCH-CHEMISCHE TABELLEN. Herausgegeben von DR. RICHARD BÖRNSTEIN und DR. WILHELM MEYERHOFFER. Berlin. Verlag von Julius Springer. 1905. Price, 36 marks.

The first edition of this indispensable work was published in 1883, the second in 1894, and the third has just appeared. In the first edition, 110 tables, occupying 246 pages, were prepared by six contributors. In 1894, there were 208 tables, occupying 560 pages, with seventeen contributors. The present edition contains 264 tables in 857 pages, with forty-seven contributors.

The increase in the variety of subjects tabulated is somewhat more than that suggested by the increase from 208 to 264 tables, for sometimes half a dozen or more tables in the second edition are counted as one in the present edition. So also, the 52 per cent. increase in the number of pages is much less than the actual increase in the amount of type set. The standard tables of the earlier edition have been given with type precisely equal in size to those used before, but some tables have been given in the more compact and convenient form in which six-place or seven-place logarithms are always printed, and some of the new matter is given in type which gives a fourth more lines on a page.

Like the first edition, the book gives tables for the reduction of the observations required by physical chemistry, and also a collection of the physical constants of this branch of chemistry, as well as a reference to the source of each. But the character of the book is so well known that detailed description of it is not required.