REVIEW.

SOME RECENT WORK IN ORGANIC CHEMISTRY.

By John C. Hessler.

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No review of the progress of organic chemistry can well include more than a few of the many interesting investigations that have been recorded in chemical literature. This is the case with the review of the year 1905, which is herewith presented. The writer has been forced to restrict himself to a limited number of articles that seem to have a general interest for all chemists who try to keep even slightly in touch with the organic field.

The reactions that were of chief interest in 1904 (*cf.* This Journal, Dec. 1905, p. 1553) still continue to be applied: Grignard's reaction is used more and more in the synthesis of new and of known substances; the use of powdered nickel in the presence of hydrogen as a reducing agent continues. The verifications of Baeyer and Villiger's oxonium theory have multiplied during the year, and the syntheses of polypeptides, according to the methods of Fischer and Curtius, have increased greatly in number and interest. In addition to giving brief references to some of the new work done in these fields, the writer has added a review of some articles upon the influence of light in bringing about chemical changes, and also upon a few new methods of preparing and purifying common substances used in the laboratory and in the arts.

Hydrocarbons.—Several new facts have been added to our knowledge of hydrocarbons. The first to be mentioned is that liquid fluorine, according to Moissan and Chavanne (*Compt. rend.*, **140**, 1035–36), reacts with solid methane with a violent explosion. The methane was solidified in liquid air; it became first a colorless, glassy mass, and was then transformed into white needles melting at —184°.

To the methods of preparing marsh gas hydrocarbons, Lebeau (*Compt. rend.* **140**, 1042–44), has added one more: the reaction of cold sodium-ammonia, $NaNH_3$, dissolved in liquid ammonia, with alkyl halides. Methyl chloride thus gives methane, while ethyl and propyl iodides give ethane and propane respectively. Chablay (*Compt. rend.* **140**, 1262), gives as the equation for the reaction

$$2NH_3Na + 2CH_3Cl = 2NaCl + CH_4 + CH_3NH_2 + NH_3.$$

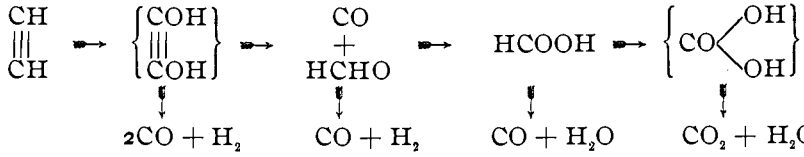
The method can also be used for preparing primary amines. In the reaction between chloroform and sodium-ammonium, acetylene and ethylene are formed, as well as sodium cyanide.

$$CHCl_3 + NaNH_3 \rightarrow CH_4 + C_2H_4 + C_2H_2 + NaCl + NaNH_2 + NaNC.$$

Acetylene and acetylene derivatives have been studied by several investigators. Nieuwland (*J. f. Gasbel.* **48**, 387–88; *Chem. Centr.* **1905**, I. 1585) gives it as his experience that when explosions result from the action of chlorinating agents upon acetylene, they are always accompanied by the formation of hexachlorethane, C_2Cl_6.

Bone and Andrew (*J. Chem. Soc.*, **87**, 1232–48), have continued the

experiments upon the combustion of hydrocarbons in ozonized air. They think that acetylene, like the other hydrocarbons studied, first takes up oxygen to form an unstable substance, which then decomposes, and that both carbon atoms in the molecule are oxidized at the same time.



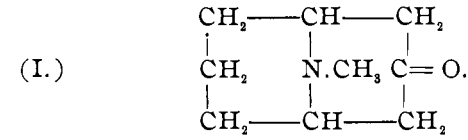
In the presence of a hot catalyzing surface acetylene unites directly with steam to form acetaldehyde. The formation of benzene was not observed in these experiments, and carbon separated as such only when there was a lack of oxygen.

The hydrocarbons allene and allylene have recently been liquefied by Lespieau and Chavanne (*Compt. rend.*, **140**, 1035–36), in the apparatus of Moissan (*Compt. rend.*, **138**, 363). Allene freezes at —146° and boils at —32°. For allylene the corresponding temperatures are —110° and —23.5° respectively. The critical temperature for allene is +120.75°; for allylene it is +129.5°.

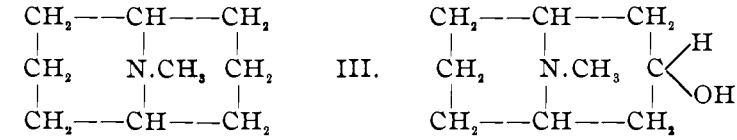
Collie (*J. Chem. Soc.*, **87**, 1540–48) has studied the action of the silent electric discharge upon ethylene and upon a mixture of ethylene and carbon dioxide. From ethylene he obtained many hydrocarbons, among which those from C_6H_{12} to $C_{15}H_{30}$ were certainly present. From ethylene and carbon dioxide he obtained aldehydes, higher hydrocarbons, and a tar.

Many researches upon the reduced benzene ring were carried out during 1905. Among them were those of Markownikow on hexahydrotoluene, (*Liebig's Ann.* **341**, 118-50), of Wallach upon methyl 1-phenyl 3-hexene (*Nachr. Ges. Wiss. Göttingen* **1905**,, 6–16). of Borsche and Lange upon hexahydrobenzenesulphonic acid (Ber. **38**, 2766–69), and of Crossley and Renouf upon 1, 1-dimethylhexahydrobenzene (*J. Chem. Soc.* **87**, 1487–1503).

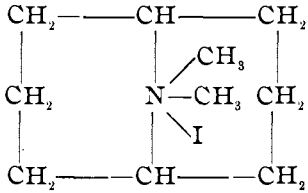
The chemistry of the cyclic compounds has been enlarged by the interesting work of Willstätter and Veraguth on the hydrocarbon cyclo-octadiene, C_8H_{12} (*Ber.* **38**, 1975–84 and 1984–91). They start with the alkaloid pseudopelletierine or methylgranatanine, to which they give the formula



This is reduced electrolytically in 50 per cent. sulphuric acid to a mixture of N-methylgranatanine (II.) and the alkamine (III.)



N-methylgranatanine (II.) is separated from the alkamine by distillation with steam. It is a base, melting at 55–58° and boiling at 196–199° at 725 mm. Its platinum double salt, $(C_9H_{17}N \cdot HCl)_2PtCl_4$, melts at 220–221°. It forms a methyl iodide compound (IV.) which is converted by silver oxide (hydroxide) into the corresponding hydroxide (V.), a solid crystallizing in large plates containing sixteen molecules of crystal water.

IV.


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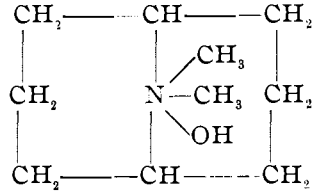
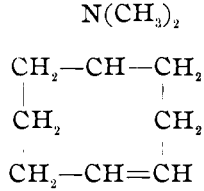
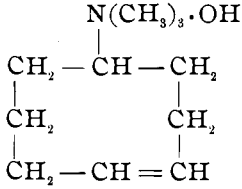
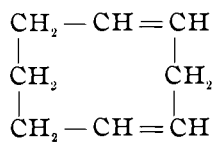


When the hydroxide is distilled, it is decomposed in part into methyl alcohol and N-methylgranatanine (II.), and in part by the breaking of the nitrogen "bridge into Δ^4-des-dimethylgranatanine (VI).

VI.


This is a basic, narcotic oil, easily volatile with steam, boiling at 89.5–92° at 14 mm. pressure. Its methyl iodide forms needles melting at 264°. The methyl iodide is converted, by means of silver oxide, into the hydroxide (VII.), and this breaks down, when distilled, into cyclooctadiene (VIII.), trimethylamine, and water.

VII.


VIII.


The position of the two double bonds in cyclooctadiene is uncertain; it may be a $\Delta^{1,4}$ (VIII.), a $\Delta^{1,5}$, or even a $\Delta^{1,3}$ derivative.

Cyclooctadiene is a volatile liquiid boiling at 39° at 16.5 mm. It decolorizes potassium permanganate solution, but does not reduce a silver solution. When allowed to stand, the hydrocarbon polymerizes to dicyclooctadiene, $C_{16}H_{24}$, a solid crystallizing from ligroin or ether in leaflets which melt at 114°. At ordinary pressure, cyclooctadiene begins to boil at 135°, but soon solidifies with explosive violence to a polymer $(C_8H_{12})_x$, which does not melt up to 300°. The hydrocarbon reacts with bromine, in part to give a dibromide, $C_8H_{12}Br_2$, and in part to give a substitution product, $C_8H_{11}Br$. When the bromides are heated with quinoline at 120–30° they lose hydrobromic acid, and a hydrocarbon, cyclooctatriene (C_8H_{10}), results. This, too, is a liquid, boiling at 36–40° at 13 mm. Attempts to remove hydrogen

from this substance, in order to get cyclooctatetrene, C_8H_8, the analogue of benzene, have not yet been successful.

The preceding reference recalls Willstätter's work upon cycloheptene, (*Liebig's Ann.*, **317**, 204). Attempts by Willstätter and von Schmaedel, (*Ber.* **38**, 1992–99), to prepare cyclobutadiene,

$$\begin{array}{c} CH - CH \\ \| \quad\quad \| \\ CH - CH \end{array},$$

have not yet succeeded, although they made its dihydride, cyclobutene,

$$\begin{array}{c} CH_2 - CH \\ | \quad\quad \| \\ CH_2 - CH \end{array}$$

This is formed by distilling cyclobutyltrimethylammonium hydroxide,

$$\begin{array}{c} CH_2 - CH \cdot N(CH_3)_3OH \\ | \quad\quad | \\ CH_2 - CH_2 \end{array}$$

Our knowledge of triphenylmethyl has been increased by Schmidlen (*Compt. rend.* **139**, 732–33), who finds that it is strongly endothermic, and by Gomberg and Cone, who find that it unites with ketones and ntriles (*Ber.* **38**, 2447–58), and with esters, with amylene, and with benzene hydrocarbons (*Ber.* **38**, 1333–44). Very recently (*Ber.* **39**, 1461–70 and 2957–70), Gomberg and Cone have published papers describing their synthesis of phenylated marsh gas hydrocarbons by means of alkyl and aryl magnesium halides and halides of triphenylmethyl. They are now attempting to get pentaphenylethyl bromide from pentaphenylethane in the hope that this will react with phenylmagnesium bromide to give the long-sought hexaphenylethane.

$$(C_6H_5)_3C - CBr(C_6H_5)_2 + C_6H_5MgBr \longrightarrow MgBr_2 + (C_6H_5)_3C - C(C_6H_5)_3.$$

They also tried the reaction of potassium triphenylmethane with triphenylchlormethane, but so far without success.

Finally, Schwalbe (*Z. f. Farben u. Textil Chemie* **3**, 461–64; *Chem. Centr.* **1905**, I., 360), gives a method of freeing benzene and its homologues from the traces of sulphur which interfere so seriously with the preparation of many dye-stuffs. The sulphur compounds usually present are thiophene and carbon disulphide; the ordinary method of removing these by shaking the hydrocarbon with concentrated sulphuric acid is accompanied by a considerable loss of hydrocarbon. Schwalbe removes the thiophene by treating the hydrocarbon with a large amount of nitrous acid; this converts the thiophene into a tar that dissolves much more readily in sulphuric acid than in the benzene hydrocarbon. The hydrocarbon is then shaken two or three times with two per cent. of its weight of concentrated sulphuric acid, and is washed with caustic soda and with water. Carbon disulphide is removed by passing into the hydrocarbon 0.25 per cent. of its weight of gaseous ammonia; this precipitates the carbon disulphide as an emulsion. The excess of ammonia is removed by dilute sulphuric acid and by water.

Halogen Derivatives.—The reactions of the alkyl halides are of such importance to organic chemistry that many investigators in the past have

studied their decomposition by heat. Recently Sabatier and Mailhe passed the vapors of alkyl chlorides over the hot (260°—320°), anhydrous chlorides of bivalent metals like nickel, iron, cobalt, cadmium, lead and barium, and over cuprous chloride, and obtained hydrochloric acid and the olefines (*Compt. rend.*, **141**, 238-41). The alkyl bromides are decomposed less, and the iodides least successfully. The authors ascribe to the metal chloride the power of first absorbing and then liberating the olefine.

$$C_nH_{2n+1}.Cl \rightarrow C_nH_{2n} + HCl.$$
$$C_nH_{2n} + ClMeCl \rightarrow Cl \cdot C_nH_{2n} \cdot MeCl.$$
$$Cl \cdot C_nH_{2n} \cdot MeCl \rightarrow C_nH_{2n} + MeCl_2.$$

The oxidation of chloroform in the sunlight has been studied quantitatively by Schoorl and Van den Berg (*Pharm. Weekbl.*, **42**, 877-88 and 897-904). They find that with an excess of oxygen the decomposition is according to the equation

$$2CHCl_3 + 5O \rightarrow 2CO_2 + H_2O + 6Cl,$$

while with little oxygen present, as is the case when chloroform is preserved in pharmacy, the equation is

$$CHCl_3 + O \rightarrow COCl_2 + HCl.$$

In the case of iodoform the decomposition in the air is also an oxidation. No hydrocarbons are formed, and the products are carbon monoxide or dioxide, water, and iodine. The reaction is one-fifth according to the equation

$$2CHI_3 + 5O \rightarrow 2CO_2 + H_2O + 6I,$$

and four-fifths according to the equation,

$$2CHI_3 + 3O \rightarrow 2CO + H_2O + 6I.$$

The authors think that the difference between the oxidation of chloroform and iodoform is due to the ready oxidation of the hydriodic acid formed; this, rather than the carbon monoxide, takes up the excess of oxygen.

$$CHI_3 + O \rightarrow COI_2 + HI$$
$$COI_2 \rightarrow CO + I_2.$$

In the case of bromoform Schoorl and Van den Berg (*Pharm. Weekbl.* **43**, 2-10; *Chem. Centr.*, **1906**, I, 441-42), conclude that the end reactions of much or little oxygen upon bromoform sealed in glass tubes and exposed to sunlight are represented by the equations

$$2CHBr_3 + 5O \rightarrow 2CO_2 + H_2O + 6Br,$$
$$CHBr_3 + O \rightarrow CO + Br_2 + HBr.$$

Jorissen and Ringer (*Chem. Weekbl.*, **2**, 799-802; *Chem. Centr.*, **1906**, I, 442), have compared the action of radium with that of ordinary diffused light and of air upon a chloroform solution of iodoform at 25°. In the presence of 5 milligrams of radium bromide the amount of iodine liberated was four times as great as when radium was absent. Other conditions were the same.

As is well known, the common method of preparing carbon tetrachloride is to pass a mixture of the vapors of carbon disulphide and chlorine through hot tubes.

$$CS_2 + 3Cl_2 = CCl_4 + S_2Cl_2.$$

Utz (*Schweiz. Wochschr. f. Pharm.*, **43**, 209-10; *Chem. Centr.*, **1905**, I, 1526), states that the chemical factory Griesheim-Electron now makes carbon tetrachloride by heating sulphur monochloride and carbon disulpide in the presence of chlorides of metals.

$$2S_2Cl_2 + CS_2 \rightarrow CCl_4 + 6S.$$

The sulphur is reconverted into the monochloride. Utz calls attention to the advantages of the use of carbon tetrachloride: it is neither inflammable nor explosive, and is an excellent solvent for oils, fats, tars, etc. Carbon tetrachloride is also used as a source of hexachlorethane, according to Hofmann and Seiler (*Ber.*, **38**, 3058–59). The tetrachloride is reduced by aluminum amalgam at 70°. The yield is 65 per cent. of the tetrachloride used.

Aromatic iodochlorides have been known since Willgerodt prepared the first one in 1886 by adding chlorine to phenyl iodide,

$$C_6H_5I + Cl_2 \rightarrow C_6H_5ICl_2,$$

but it has remained for Thiele and Peter (*Ber.*, **38**, 2842-46), to get alkyl iodochlorides. The addition of halogen is possible only at low temperatures. Thus, methyl iodide adds chlorine at —80°, forming a yellow solid, $CH_3I\begin{smallmatrix}\diagup Cl\\ \diagdown Cl\end{smallmatrix}$, but the substance decomposes at —28°. When sealed in a tube at a low temperature, however, it could be analyzed according to Carius. Water reacts with the iodochloride, producing methyl chloride and iodine chloride, which reacts further with the water.

$$CH_3ICl_2 \rightarrow CH_3Cl + ICl.$$

The dichlorides of several other alkyl iodides were prepared, also dibromides, and the attempt is being made to prepare the diiodides of the general formula $R - I\begin{smallmatrix}\diagup I\\ \diagdown I\end{smallmatrix}$.

Thiele and Peter have also succeeded in preparing derivatives of fumaric acid containing polyvalent iodine. They prepared chloriodofumaric acid,

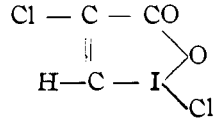
$$\begin{array}{c} Cl - C - COOH \\ \| \\ HOOC - C - I, \end{array}$$

from acetylenedicarbonic acid and iodine monochloride. This is a yellow, soluble solid that crystallizes in needles decomposing at 226–227°. Chloriodofumaric acid adds chlorine, forming the iodosochloride of chlorfumaric acid, which loses hydrochloric acid to close a ring.

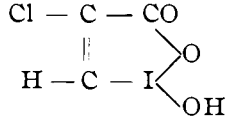
$$\begin{array}{c} Cl - C - COOH \\ \| \\ HOOC - C - I \end{array} + Cl_2 \rightarrow \begin{array}{c} Cl - C - COOH \\ \| \\ HOOC - C - I\begin{smallmatrix}\diagup Cl\\ \diagdown Cl\end{smallmatrix} \end{array} \rightarrow \begin{array}{c} Cl - C - CO \\ \| \\ HOOC - C - I\begin{smallmatrix}\diagup O\\ \diagdown Cl\end{smallmatrix} \end{array} + HCl.$$

Chlorfumaric acid iodosochloride is a yellow, crystalline powder melting at 116–120°. Alcohol reacts with it at the ordinary temperature,

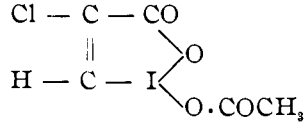
forming α-chlor-β-iodoacryllic acid, $CHI{=}CCl.COOH$, but with ice cold alcohol it gives carbon dioxide and chloracrylic acid iodosochloride,



This is a solid crystallizing in needles that melt at 146°—47°. Hot water reacts with chlorfumaric acid iodosochloride, giving iodosochloracrylic acid,



This substance, like iodosobenzoic acid (*cf.* V. Meyer and Wachter, *Ber.* **25**, 2632) forms an acetate,



The acetate crystallizes in yellow needles melting at 138°—39°.

Alcohols and Ethers.—The reactions between the monatomic alcohols and the halides of phosphorus have been studied quantitatively by Walker and Johnson (*J. Chem. Soc.* (London), **87**, 1592–97), with interesting results. They used methyl, ethyl, and *n*-propyl alcohols, and phosphorus trichloride, tribromide, and triiodide. Several equations can represent the reactions:

$$PX_3 + 3AOH \rightarrow \begin{cases} P(OH)(OA)_2 + AX + 2HX & \text{I.} \\ P(OH)_2OA + 2AX + HX & \text{II.} \\ P(OH)_3 + 3AX & \text{III.} \\ P(OA)_3 + 3HX & \text{IV.} \end{cases}$$

In only four of the nine cases studied could the reaction be represented by a simple equation: the preparation of ethyl chloride is according to equation I.; that of methyl bromide, *n*-propyl bromide and ethyl iodide were found to be represented by II. The formation of methyl chloride, ethyl bromide and *n*-propyl chloride took place *nearly* according to the equation

$$2PX_3 + 6AOH = 3AX + 3HX + P_2(OH)_3(OA)_3.$$

For methyl iodide the equation was

$$2PX_3 + 6AOH = 5AX + HX + P_2(OH)_5OA.$$

Equimolecular quantities of alcohol and phosphorus trichloride gave practically no alkyl chloride. The equation was

$$PCl_3 + AOH \rightarrow HCl + PCl_2\,OA\,;$$

but this equation does not apply to phosphorus tribromide.

Winkler (*Ber.* **38**, 3612–16), describes the preparation of pure ethyl alcohol. Commercial absolute alcohol is freed from aldehyde by standing

several days with silver oxide and potassium hydroxide ; this converts the aldehyde into acetate. Water is removed by heating the alcohol over shavings of calcium and distilling it from them. The advantage of using calcium lies in the fact that while the metal is soluble in alcohol, its oxide and hydroxide are not. The amount of calcium oxide or hydroxide formed thus gives an immediate measure of the quantity of water present. Winkler found that the hygroscopic character of absolute alcohol has been greatly overstated, since 200 cc. of absolute alcohol, left in an open beaker for fifteen minutes, had not absorbed 0.1 per cent. of water.

Chablay (*Compt. rend.* **140**, 1343–44 and 1396–98), prepares the alcoholates of sodium and potassium by mixing the solution of potassium or sodium ammonium in liquid ammonia, with the alcohol dissolved in the same solvent.

$$RCH_2OH + KNH_3 \rightarrow RCH_2OK + NH_3 + H.$$

The alcoholates of polyatomic alcohols can be prepared in the same way.

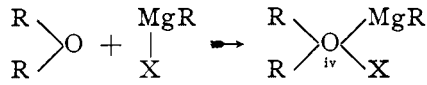
Imbert and Kraft have taken out a patent (No. 164,297; *Chem. Centr.*, **1905**, II., 1747), for a process of preparing alcoholates of the alkali metals. They dissolve the hydroxide of the metal in the alcohol and remove the water by means of calcium oxide and calcium carbide.

A study of the action of ferric chloride in sunlight upon alcohols, acids and aldehydes was carried out by Benrath (*J. pr. Chem.* [2], **72**, 220–27). In one experiment sublimed ferric chloride dissolved in anhydrous methyl alcohol was exposed to sunlight for two weeks. The solution was decolorized, and contained colorless crystals of the composition $FeCl_2 + 4CH_3OH$. The liquid contained methyl chloride, hydrochloric acid, formaldehyde and probably chlormethyl alcohol.

$$CH_3OH + 2FeCl_3 \rightarrow CH_2O + 2HCl + 2FeCl_2$$
$$CH_2O + HCl \rightarrow ClCH_2OH.$$
$$CH_3OH + HCl \rightarrow CH_3Cl + H_2O.$$

With formaldehyde solution oxidation to formic acid took place. With formic acid in the sunlight sublimed ferric chloride gave carbon dioxide, but the evolution of gas stopped in the shade. No oxalic acid was detected. Ferric chloride and ethyl alcohol gave acetaldehyde and ethyl chloride. The sublimed salt did not react with acetaldehyde in the dark, but in the light hydrochloric and acetic acids were formed.

As is well known, the method of Grignard does not give the alkyl magnesium halides themselves, but their addition products with ether. Tschelinzew has found (*Ber.* **37**, 4534) that by the catalytic action of tertiary amines the alkyl magnesium halides can be obtained as such and then converted into the double campounds of Grignard by addition of the theoretical amount of ether.



Grignard viewed these bodies as alkyl magnesium halides containing "crystal ether," but the theory of Baeyer and Villiger makes them oxonium bodies. Tschelinzew has tested the theory (*Ber.* **38**, 3664–73) by determining the heat of formation of these compounds. Because of the instability of the substances used, their preparation was carried out in the

calorimeter itself. The heat evolved was then determined. Tschelinzew's results show that the Grignard reaction goes in two phases: 1. formation of the alkyl magnesium salt; 2. union of this with the ether. The union takes place exactly like a true chemical reaction, and the compounds formed are, therefore, oxonium compounds.

Aldehydes and Ketones.—Law has found (*J. Chem. Soc.* **87,** 198–206.) that when acetaldehyde and propionaldehyde are oxidized electrolytically (he used sulphuric acid as electrolyte), there are formed, not only the acids, but also hydrocarbons and carbon dioxide.

$$R \cdot CHO + O \rightarrow RH + CO_2$$

Formaldehyde and isobutylaldehyde do not react in this way.

Lockemann and Liesche (*J. pr. Chem.* [2], **71,** 474–96), have investigated the preparation of acrolein by the heating of a mixture of boric acid and glycerol—the method of Wohl and Neuberg (*Ber.* **32,** 1352). They have found that many side-products are formed: hydrogen, oxygen, carbon monoxide, carbon dioxide, methane, ethylene, acetaldehyde and guaiacol. The presence of acetaldehyde, which was confirmed by fractional distillation and by conversion of the aldehyde into a hydrazone, caused the great stability observed in acrolein prepared by this method; the polymer, disacryl, which ordinarily forms at once, did not appear for several days. In acrolein prepared by heating glycerol with potassium hydrogen sulphate, no acetaldehyde could be detected.

Stewart (*J. Chem. Soc.* **87,** 185–88), has studied the addition of sodium hydrogen sulphite to ketones. In the series given,

$$CH_3CO \cdot H,\ CH_3CO \cdot CH_3,\ CH_3CO \cdot CH_2(CH_3),\ CH_3CO \cdot CH(CH_3)_2,\ CH_3CO \cdot C(CH_3)_3,$$

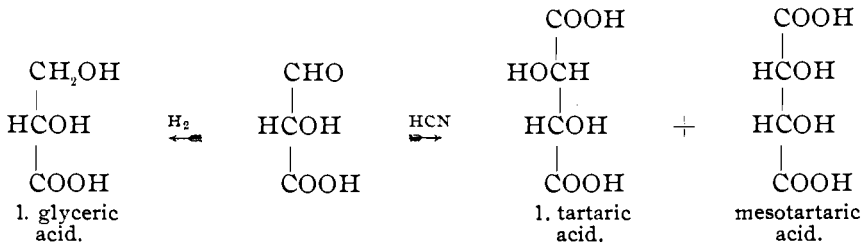
the amount of addition of bisulphite to the ketone decreased regularly as the number of methyl groups increased. Acetaldehyde gave the largest amount: 88.7 per cent. in seventy minutes, while pinacoline gave the smallest: 4.2 per cent. in ten minutes and 5.6 per cent. in seventy minutes. The method used was to titrate pure sodium bisulphite solution with iodine, and to compare the result with that given by bisulphite solution to which a ketone had been added.

Acetylacetone, acetoacetic ester and acetonedicarbonic ester added bisulphite in large amount; levulinic acid, ethyl ester and diacetylacetone much less; while maltose, lactose and glucose gave less than 10 per cent. of the theoretical addition in thirty minutes. Dimethylpyrone gave traces of the addition product.

Pastureau (*Compt. rend.* **140,** 1591–93), finds that 100 parts of acetone give, when oxidized by a 2 per cent. solution of hydrogen peroxide in presence of sulphuric acid, 21 parts of acetone peroxide, 33 parts of acetol and 75 parts of pyroracemic acid. Other ketones are oxidized in the same way.

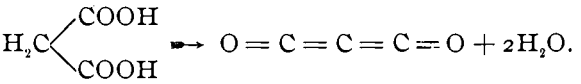
Acids.—Moissan (*Compt. rend.* **140,** 1209-11), has added carbon dioxide to potassium hydride with the formation of oxalic acid. A previous paper (*Compt. rend.* **136,** 723), states that formic acid is produced by this reaction. Moissan now finds that between —85° and + 54° the two substances do not react; above 54° formic acid is the product; but if the temperature of the potassium hydride is +80° to begin with both potassium formate and potassium oxalate are formed. Sodium hydride acts in the same way.

The configuration of the active glyceric acids has hitherto been unknown, but has now been established by Neuberg and Silbermann (*Z. physiol. Chem.* **44,** 134-46). They prepared *l*-glyceric acid by the reduction of *l*-aldehydeglyceric acid—the oxypyroracemic acid of Will (*Ber.* **24,** 406)—by means of sodium amalgam. The aldehydeglyceric acid is prepared by the hydrolysis of nitrocellulose (collodion) by means of caustic potash. By treatment of the acid with hydrocyanic acid the acid of higher carbon content (tartaric acid) is obtained; it is a mixture of levo—and mesotartaric acids.

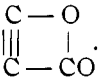


The importance of the configuration of the glyceric acids arises from their relation to alanine, serine and isoserine, cysteine, lactic acid, and diaminopropionic acid.

Diels and Wolf (*Ber.* **39,** 689-97) passed the vapor of malonic ester over phosphorus pentoxide at 300° and obtained ethylene, carbon dioxide, and a sharp smelling gas which was condensed in a cooled receiver and purified by distillation. Analysis showed that the new substance had the formula C_3O_2; the discoverers called it *carbon suboxide.* It is really the complete anhydride of malonic acid.



Carbon suboxide is a colorless, volatile liquid having an odor like acroleïn and the mustard oils. Its vapor attacks the eyes and is suffocating. The boiling point is 7° at 781 mm. The substance burns with a blue flame; with water it gives malonic acid, with ammonia and with aniline in ether solution it gives malonamide and malonanilide respectively. With anhydrous hydrochloric acid carbon suboxide gives malonyl chloride, and on standing it changes to a solid, colored substance. Michael (*Ber.* **39,** 1915) considers that the new compound is the lactone of *β*-hydroxypropinic acid,



Phenols and Phenol Acids.—Ullmann and Sponagel (*Ber.* **38,** 2211-12), have continued the work of Ullmann (*Leibig's Ann.* **332,** 3881), on the action of copper in syntheses of aromatic derivatives. They find that while sodium phenolates react only slightly with brombenzene to form phenol ethers, the introduction of a little copper causes the yield to rise to 90 per cent. of the theory. The reaction was tried with phenol, hydroquinol, pyrogallic acid, salicylic acid, and other phenol derivatives.

Tiimstra (*Ber.* **38,** 1375-85), has studied Kolbe's salicylic acid syn-

thesis anew. Chemists have generally supposed (after B. Schmitt, *J. pr. Chem.* [2], **31**, 405), that when carbon dioxide and sodium phenolate react at 110°–120° phenyl sodium carbonate is formed—

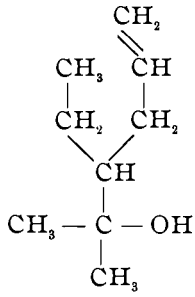
$C_6H_5ONa + CO_2 \rightarrow C_6H_5O \cdot CO \cdot ONa$.–and that this substance is transformed at 190° into sodium salicylate, $C_6H_4OH \cdot COONa$. Against this explanation are the facts established by Schmitt that phenyl sodium carbonate loses carbon dioxide readily at 120° in an open dish and is changed into sodium salicylate only in closed vessels or by very rapid heating. Tijmstra finds that phenyl sodium carbonate has a dissociation tension of more than one atmosphere at 85°, and he explains the action that takes place at 85° to 110° as the simple addition of carbon dioxide to sodium phenolate, giving phenolsodium-σ-carbonic acid, $C_6H_4(ONa) \cdot COOH$. By heating Schmitt's phenyl sodium carbonate at 110°—120° in an autoclave Tijmstra obtained a product which he decided was phenolsodium-σ-carbonic acid. This explanation accords well with the carboxylation of phenols like resorcinol and phloroglucinol, and affords an easier explanation than the ordinary one for the synthesis of oxytrimesinic acid from disodium salicylate and carbon dioxide.

Willstätter and Pfannenstiel (*Ber.* **37**, 4744-46), have obtained pure orthobenzoquinone by oxidizing pyrocatechol by means of silver oxide.

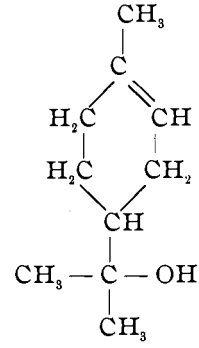
Borsche and Ockinga (*Liebig's Ann.* **340**, 85-109), have prepared new hydroxyazo bodies by condensing acylhydrazines with quinone. They used formyl-, hippuryl-, and benzoylhydrazine.

$$O = C_6H_4 = O + H_2N \cdot NH \cdot CHO \rightarrow HO - C_6H_4 - N : N \cdot CHO + H_2O.$$

Terpene Derivatives.—Perkin, Jr. and Pickles (*J. Chem. Soc.* (*London*) **87**, 655–60), have prepared certain aliphatic bodies having constitutions like terpineol and dipentene for the purpose of comparison. They find that while these bodies resemble hydroaromatic compounds in some particulars the absence of the ring still has considerable influence upon their properties. Thus dimethylethylbutenylcarbinol (see formula below), is almost like terpineol, except that the latter has a closed ring; yet the former does not give a urethane when treated with phenyl isocyanate, nor is it changed by dilute acids into a dihydroalcohol, as is the case with terpineol. Dimethylethylbutenylcarbinol is a liquid boiling at 165° and having a peppermint odor.



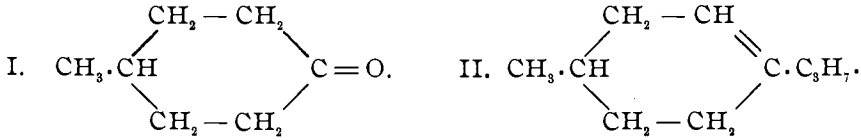
The aliphatic carbinol.



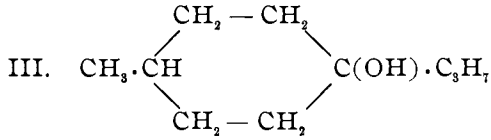
Terpineol.

Perkins Jr. has also synthesized tertiary menthol and inactive men-

thene (*Pr. Chem. Soc.* **21**, 255–56). Hexahydro-*p*-toluic acid reacts with phosphorus pentachloride and bromine, giving *a*-bromhexahydro-*p*-toluic acid. By hydrolysis with soda this is changed into the hydroxy acid, which is decomposed by sulphuric acid, giving carbon monoxide (from formic acid), and 1, 4-methylcyclohexanone; boiling point, 170°; formula I.



1,4-Methylcyclohexanone reacts readily with magnesium isopropyl iodide to form *tertiary menthol*; boiling point 95° at 25 mm.; formula III.



When this is heated with potassium hydrogen sulphate, *inactive menthene* is produced (formula II). It boils at 168°, and forms the characteristic nitrosochloride melting at 128°.

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NEW BOOKS

NOTIONS FONDAMENTALES DE CHIMIE ORGANIQUE. BY CH. MOUREU, professeur a l'École supérieure de Pharmacie de l'Université de Paris; deuxième édition, revuée et augmenteé. Paris: Gauthier-Villars. 1906. 320 pp.

In this new edition the author has revised and enlarged the previous one so as to bring it up to date. The manner of presenting the subject remains the same as before, all organic compounds being grouped to illustrate various "functions"–hydrocarbons, alcohol function, acid function, &c., the different classes of acyclic and cyclic compounds being treated under these various functions. The chapter on hydrocarbons, for example, includes all classes of hydrocarbons, acyclic and cyclic; that on alcohols, all alcohols, both fatty and aromatic, and so on. It is a very good introduction to the study of organic chemistry and fulfils well its object of pointing out to the student the broad general lines of the theory of the subject by a succinct and very general discussion of the most important classes of organic substances, considering together all those of similar function.

MARSTON TAYLOR BOGERT.

GENERAL PRINCIPLES OF ORGANIC SYNTHESES. BY P. ALEXEYEFF, Late Professor of Chemistry, University of Kieff, Russia. Authorized translation with revisions and additions by J. MERRIT MATTHEWS, PH. D., Head of Chemical Department, School of Industrial Art, Philadelphia. New York: John Wiley & Sons. 1906. 8vo., viii + 246 pages. Cloth, $3.00

In preparing a translation of Alexeyeff's book on the methods for the