The further discussion of other peculiarities of the curves will be reserved for a later time, in connection with the explanation of the causes of the phenomena above described. Experiments along this line are in progress.

MISSOURI SCHOOL OF MINES,
ROLLA, MO.

REVIEW.

A Report on Some Recent Work in Organic Chemistry.

BY H. W. HILLYER.

ACCORDING to statistics obtained from the *Chemisches Centralblatt* the volume of chemical publication in its chief lines reviewed in that journal in the year 1902 is as follows:

	No. of references.	Columns of references.
General and physical	499	224
Inorganic	559	250
Organic	1775	1309
Physiological	503	209
Analytical	753	273
Technical	323	113

During the year 1903 the volume of the output has undoubtedly been at least as great. From this it may be seen how difficult it is to obtain such a view of the field as to give any just idea of the relative value of individual pieces of work. To, in any way, meet the request of the editor of this Journal for a report on organic chemistry for the period since the last general report was given in December, 1901, the reviewer must severely limit himself and in the limited field hope to please none of those who are specially interested in the pieces of work not reported. Since the work of American chemists is abstracted in this Journal, it has been decided not to mention any American work in this article. From the work of foreign chemists a few articles are chosen which contain matter of general interest, or which serve to show the kind of studies now engaging the attention of organic chemists.

A method of preparation has become prominent recently which is of such wide application that it deserves notice. It seems to have already displaced the older method of Butlerow and to be reaching out into new fields. In 1900 Grignard first published the method.[1] When metallic magnesium is brought into a solu-

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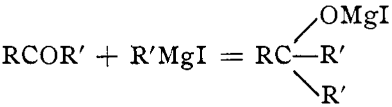
[1] *Compt. Rend.*, **130**, 1322.

tion of a halogen substitution product in anhydrous ether a vigorous reaction is set up and the magnesium is dissolved according to the general equation

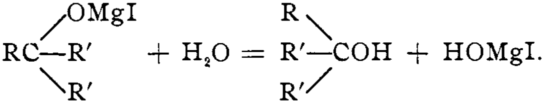
$$R.I + Mg = R.MgI.$$

Anhydrous ether seems to be the only solvent, which will answer in most cases. When the ether solution of the reaction product is evaporated, the residue contains the elements of a molecule of ether. The organic magnesium iodides will react with many classes of substances to give desirable products. For example, with acid chlorides to give compounds which by action of water yield tertiary alcohols.

$$RCOCl + R'MgI = RCOR' + MgICl.$$



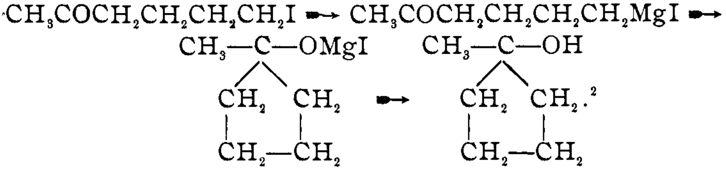
$$RCOR' + R'MgI = RC(OMgI)(R')R'$$



$$RC(OMgI)(R')R' + H_2O = (R)(R')(R')COH + HOMgI.$$

The ketones also yield tertiary alcohols.[1]

Zelinski has used the method to prepare a tertiary alcohol with formation of a closed chain by the steps indicated by the formulas



$$CH_3COCH_2CH_2CH_2CH_2I \rightarrow CH_3COCH_2CH_2CH_2CH_2MgI \rightarrow$$

[2]

Quinones yield quinoles by the same method.[3] Esters also react with the compounds HalMgR to give tertiary alcohols.[4] This process has led to a new method of making tetraphenylmethane. Ullmann and Münzhufer,[5] following the method of Grignard,[6] prepared triphenyl carbinol by action of methyl benzoate on phenyl magnesium bromide.

$$2C_6H_5MgBr + C_6H_5COOCH_3 = CH_3OMgBr + (C_6H_5)_3C—OMgBr$$

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[1] *Compt. Rend.*, **130**, 1322; *Ibid.*, **132**, 835 and 1182; *Ann. chim. phys.* (7), **24**, 457: *Ibid* (7), **27**, 548; *Ber. d. chem. Ges.*, **35**, 2138; *Ibid.*, **36**, 404, 1628 and 1632.

[2] *Ber. d. chem. Ges.*, **35**, 2684.

[3] Bamberger and Blangey: *Ibid.*, **36**, 1625.

[4] *Compt. Rend.*, **135**, 533.

[5] *Ber. d. chem. Ges.*, **36**, 404.

[6] *Compt. Rend.*, **132**, 1182.

The last product by action of water yields triphenyl carbinol. Aniline hydrochloride condenses with this to give aminotetraphenylmethane.

$$(C_6H_5)_3COH + C_6H_5NH_3Cl = (C_6H_5)_3CC_6H_4NH_3Cl + H_2O$$

By diazotizing and boiling with alcohol a good yield of tetraphenylmethane is obtained.

By action of carbon dioxide it is easy to obtain organic acids by Grignard's method. In some cases the reaction is proposed as a lecture experiment.[1]

Dihalogen compounds also react and in that way one halogen may be replaced by another halogen:

$$ClC_6H_4MgCl + I_2 = ClC_6H_4I + MgClI,$$

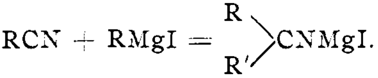
or by COOH, or made to yield carbinols.[2] By action of alkyl halides or alkyl sulphates synthetic hydrocarbons are made:

$$RMgI + R'I = RR' + MgI_2,$$[3]

and by action of chlorcarbonic ester the esters of acids may be prepared:

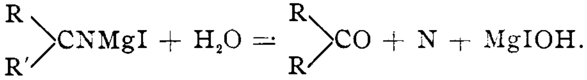
$$C_6H_5MgI + ClCOOC_2H_5 = C_6H_5COOC_2H_5 + MgICl.$$

The organo magnesium halides react also with nitriles



$$RCN + RMgI = \begin{matrix} R \\ R' \end{matrix}\!\!>CNMgI.$$

This product by action of water yields a ketone



$$\begin{matrix} R \\ R' \end{matrix}\!\!>CNMgI + H_2O = \begin{matrix} R \\ R \end{matrix}\!\!>CO + N + MgIOH.$$

Phenyl mustard oils give thioanilides.[4] Finally, dialkyl hydroxyl amines may be made, instead of the nitrogen acids which might have been expected by action of NO_2.[5]

The method of making acid chlorides,[6] proposed by Einhorn and Hollandt, in which pyridine and carbonyl chloride are the reagents, has been further applied.[7]

Another method which has till now received but little attention is that used by Auger in making malonyl chloride.[8] It is a

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[1] *Ann. chim. phys.*, **24**, 457; *Compt. Rend.*, **136**, 1138; *Ber. d. chem. Ges.*, **35**, 2519; **35**, 2687; **35**, 3672; **35**, 4415; **36**, 668; **36**, 2897.

[2] *Compt. Rend.*, **136**, 1138.

[3] *Ber. d. chem. Ges.*, **36**, 2116 and 3083.

[4] *Ibid.*, **36**, 585.

[5] *Ibid.*, **36**, 2315.

[6] *Ann. Chem.* (Liebig), **301**, 95.

[7] *Ber. d. chem. Ges.*, **35**, 3639, 3644.

[8] *Ann. chim. phys.*, (6), **22**, 347.

method of making acid chlorides by treating the acid with thionyl chloride. Since the by-products are gaseous, the advantage of the process is obvious.

$$RCOOH + SOCl_2 = RCOCl + SO_2 + HCl.$$

H. Meyer[1] has made an extended study of this reaction. It does not succeed in every case but the exceptions form an interesting study in affinity. In general those acids which ordinarily yield anhydrides with ease yield anhydrides by action of thionyl chloride. Succinic acid gives an anhydride but, curiously, monobrom and dibrom succinic acids and malic acid yield chlorides. The aromatic acids also show interesting failures to react. A great advantage of the method is that hydroxy acids yield chlorides without any replacement of the alcoholic hydroxyl. Pyridine acids yield chlorides without undesirable side reactions. Scholl has found[2] that by the action of aluminum oxychloride, Al_2OCl_4, on a mixture of benzene and mercury fulminate, a yield of 70 per cent. of the theoretical of benzaldoxime is obtained:

$$C_6H_6 + CNOH = C_6H_5CHNOH.$$

By using sublimed aluminum chloride he gets 80 per cent. of the theoretical yield of benzonitrile,

$$C_6H_6 + CNOH = C_6H_5CN + H_2O.$$

Formic aldehyde as a reagent is of increasing value. By action of formaldehyde on phenols in presence of strong hydrochloric acid, Eichengrün[3] has amplified the observation made by Störmer and Behn[4] in introducing the group $—CH_2Cl$ into the aromatic nucleus

$$HOC_6H_5 + CH_2O + HCl = HOC_6H_4CH_2Cl + H_2O.$$

Manasse has extended his previous work in making phenol alcohols by the reaction of formaldehyde on phenols in presence of weak alkalies.[5]

It has been found by Borsche and Berkhout[6] that when formaldehyde acts on paranitrophenols, using dilute sulphuric acid as the condensing agent, in many cases two molecules of the aldehyde react with one of the phenol to give methylene ethers of nitrosaliginenes. The nitrocresol,

[1] *Monatsh. Chem.*, **22**, 109. 415, 777 ; Fischer : *Ber. d. chem. Ges.*, **36**, 2094.

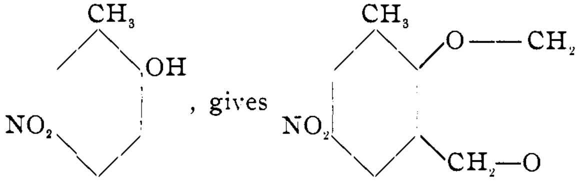
[2] *Ber. d. chem. Ges.*, **36**, 10 ; **36**, 322 ; **36**, 648.

[3] *Centrbl.*, 1902, p. 894.

[4] *Ber. d. chem. Ges.*, **34**, 2455.

[5] *Ibid.*, **35**, 3844.

[6] *Ann. Chem.* (Liebig), **330**, 82.



Other groups than the nitro group in para position do not, as far as tried, induce this style of reaction.

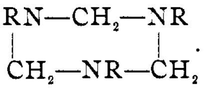
Wedekind[1] and Letterschied[2] have improved the method of Henry for making chlorinated ethers. By action of hydrochloric acid gas on a mixture of trioxymethylene and an alcohol, chlorinated methyl ethers are formed.

$$C_3H_6O_3 + 3ROH + 3HCl = 3ROCH_2Cl + 3H_2O.$$

These ethers react with salts of organic acids to give esters which, as disinfecting agents, are more powerful than formaldehyde.

Königs[1] has further developed a reaction of Ladenburg's. By action of formaldehyde on α- and γ-alkyl pyridines the group CH_2OH is substituted for hydrogen of the side-chain. The number of such groups introduced depends on the structure of the side-chain and also on the absence or presence and character of groups in the β-position.

Formaldehyde condenses with aliphatic amines as it does with ammonia to form compounds like hexamethylenetetramine, but Bischoff and Reinfeld[4] find that with aromatic amines the products are substances of the types $RHN — CH_2 — NRH$ and



$$\begin{array}{l} RN—CH_2—NR \\ |\qquad\qquad\quad | \\ CH_2—NR—CH_2 \end{array}.$$

Dimroth and Zoeppritz[5] give a new way of making oxyaldehydes. By the action of formanilide on resorcinol in presence of phosphorus oxychloride there is formed a compound which is formulated, $(HO)_2C_6H_3CH = NC_6H_5$. Alkalies change this to the aldehyde $(HO)_2C_6H_3CHO$. Pyrogallol conducts itself in the same manner.

According to Harries,[6] substances with doubly bonded carbon, when oxidized with ozone, are divided at the double bond with formation of aldehydes or ketones from the separated portions. Mesityl oxide, for example, yields acetone and pyroracemic aldehyde.

[1] *Ber. d. chem. Ges.*, **36**, 1383.

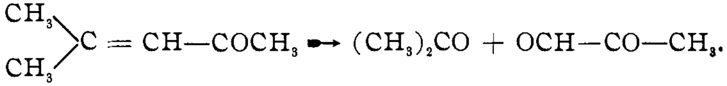
[2] *Ann. Chem.* (Liebig), **330**, 108.

[3] *Ber. d. chem. Ges.*, **34**, 4322 ; **35**, 1343.

[4] *Ibid.*, **36**, 35 and 41.

[5] *Ibid.*, **35**, 993.

[6] *Ibid.*, **36**, 1933.



$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\!C = CH{-}COCH_3 \rightarrow (CH_3)_2CO + OCH{-}CO{-}CH_3.$$

Morrell and Crofts[1] are able to obtain osones directly from the sugars by oxidizing them with hydrogen peroxide in presence of iron salts, instead of obtaining them by first making the osazones.

According to a note by Cohn and Thompson[2] benzene sulphonanilide is, like acetanilide, stable enough to endure chlorination. By action of sodium hypochlorite chlorine goes into ortho position, while, according to Wallach, phosphorus pentachloride, acting on acetanilide, yields the para compound.

Carl Neuberg[3] has found that under certain conditions unsymmetrical methylphenyl hydrazine will react with ketone sugars to give osazones, but not with aldehyde sugars. By this reagent levulose may be separated from dextrose.

Fischer and Armstrong[4] have improved their method of making aceto halogen derivatives of the sugars and have extended the study of the glucosides by further use of the aceto halogen compounds for their preparation. By causing these compounds to react on sugars they have made the new bisaccharides: glucose-galactoside, galactosoglucoside and galactogalactoside.

Fischer and Slimmer[5] have found that by the action of hydrocyanic acid on the optically active tetracetyl helicin a cyanhydrin is formed which, by hydrolysis, yields an orthohydroxy mandelic acid of small rotatory power. In this way they make use of the asymmetry of the original helicin to direct the synthesis so as to produce further asymmetry of arrangement. They effect a second similar synthesis. Zinc ethyl reacts with tetracetyl helicin to give a compound which, by action of water, is changed to tetracetyl gluco(*o*)hydroxyphenyl ethyl carbinol, $(C_2H_3O_2)_4C_6H_7O_5.OC_6H_4 - CH(OH)C_2H_5$, the aldehyde group of the helicin being changed to the secondary alcohol group. By hydrolysis the acetyl glucose is split off, having *active* (*o*)-hydroxyphenyl ethyl carbinol, $HOC_6H_5C^*H(OH)C_2H_5$.

E. Erlenmeyer, Jr., makes use of helicin to separate a racemic mixture of bases into its active components. By condensing helicin with isodiphenyl oxethyl amine, $C_6H_5{-}CH(OH){-}CH(NH_2)C_6H_5$, and crystallizing, the product is separated into two parts from which the two active bases may be obtained by action of concentrated hydrochloric acid. The author proposes to reverse the process and make use of these active bases to separate racemic mixtures of aldehydes. In connection with his work, a curious case of

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[1] *Proc. Chem. Soc.*, **18**, 55.

[2] *Ibid.*, **17**, 262.

[3] *Ber. d. chem. Ges.*, **36**, 959.

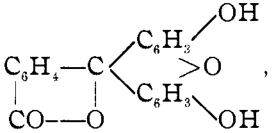
[4] *Ibid.*, **35**, 833, and **35**, 3144.

[5] *Sitzungsber.*, Berlin, 1902, p. 597.

isomerism is noted.[1] Cinnamic aldehyde with either of the above active bases gives *two* isomeric condensation products, either of which yields cinnamic aldehyde by hydrolysis, but the racemic mixture of bases gives, with cinnamic aldehyde, only *one* condensation product, different from the two mentioned.

From the fact that hydroquinone phthaleïn in alkaline solution yields a dimethyl ether, Meyer and Spengler[2] argue that it should be given the lactoid formula I.

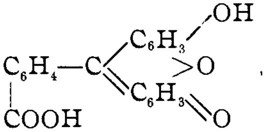
(I)



$$\begin{array}{lll} & & \diagup OH \\ & \diagup C_6H_3 & \\ C_6H_4{-}C & & >O\ , \\ |\qquad\quad | & \diagdown C_6H_3 & \\ CO{-}{-}O & & \diagdown OH \end{array}$$

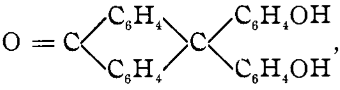
which shows it to be a double phenol rather than the quinoid formula II,

(II)



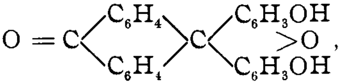
$$\begin{array}{lll} & & \diagup OH \\ & \diagup C_6H_3 & \\ C_6H_4{-}C & & >O\ , \\ | & \diagdown\!\!\diagdown C_6H_3 & \\ COOH & & \diagdown\!\!\diagdown O \end{array}$$

which shows a carboxyl that should not be methylated in alkaline solution. According to Scharwin and Kusnezof[3] anthraquinone, when fused with phenol, yields a product



$$O = C\begin{array}{l}\diagup C_6H_4\diagdown \\ \diagdown C_6H_4\diagup\end{array}C\begin{array}{l}\diagup C_6H_4OH \\ \diagdown C_6H_4OH\end{array},$$

and when fused with resorcin yields



$$O = C\begin{array}{l}\diagup C_6H_4\diagdown \\ \diagdown C_6H_4\diagup\end{array}C\begin{array}{l}\diagup C_6H_3OH \\ \qquad\quad >O\ , \\ \diagdown C_6H_3OH\end{array}$$

which dissolves in alkalies with green fluorescence and color like that of fluoresceïn. Kehrmann and Saager[4] make some oxazine compounds containing amino groups and find that when they contain two amino groups in the positions 3 and 6, like the example,

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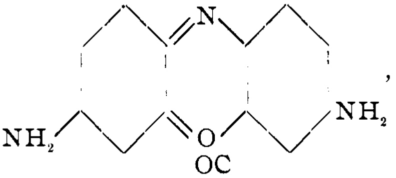
[1] *Ber. d. chem. Ges.*, **36**, 2340.

[2] *Ibid.*, **36**, 2949.

[3] *Ibid.*, **36**, 2020.

[4] *Ibid.*, **36**, 475.



they are fluorescent in solution in concentrated sulphuric acid.

Borsche and Locatelli[1] had previously found that the potassium metapurpurate, produced by the action of potassium cyanide on 2.4-dinitrophenol, is the potassium salt of nitronitrosohydroxybenzonitrile, $C_6H_2(NO_2)(NO)(OK)(CN)$. They have now found that potassium cyanide acting on dinitroorthocresol produces a similar compound with one (CN) group. Dinitroparacresol yields a compound containing two (CN) groups. They conclude that nitro phenols take on (CN) groups in places ortho to the nitro groups, provided that these nitro groups are in turn ortho to hydroxyl. The color reactions of picric acid and allied substances are in this way being cleared up.

According to Hantzsch and Dorch,[2] ferric salts give color reactions with hydroxyl compounds only, and not with the desmotropic forms of these substances. The color is due to the formation of iron salts of the compounds and not to obscure oxidation products, as has been so often supposed. The authors succeed in isolating many such iron salts.

.In his new work on mercury organic compounds, Dimroth[3] finds that some aromatic compounds, when heated to from 110° to 150° with a solution of mercuric acetate, undergo true substitution, the group $—HgOCOCH_3$ entering the nucleus in ortho or para position to the nitro and carboxyl groups, as well as to methyl and hydroxyl. Pesci has found that a cold aqueous solution of mercuric acetate acts on aniline. Dimroth interprets this result as due also to true substitution. The mercury is very firmly held in these compounds. The acetic acid radical may be replaced by a halogen by the action of a sodium halogen salt without disturbing the mercury. The phenols and anilines preserve their phenol and amine character.

Blanksma[4] finds that methyl and ethyl aniline by treatment with bromine act like aniline itself to give ortho and para compounds. Nitro groups are also introduced in the same positions, but at the same time a nitro group takes the place of the imide hydrogen with formation of nitramines. Carboxyl groups in ortho or para position to the alkylamine group are replaced. The re-

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[1] *Ber. d. chem. Ges.*, **35**, 569.

[2] *Ann. Chem.* (Liebig), **323**, 1.

[3] *Ber. d. chem. Ges.*, **35**, 2032.

[4] *Centrbl.*, 1902, II, p. 513.

action is a new instance of the ease of nucleus substitution of anilines. The author thinks this is due to the replacement of a hydrogen of the amino group and a subsequent transference of it to the nucleus. The same explanation is offered for the ease of substitution of the phenols.

New cases are constantly being brought to light in which the introduction of a substituting group has an influence not only in determining the place of introduction of new substituents, but in intensifying or diminishing the activity of the functions belonging to the original unsubstituted substance.

Klages and Storp[1] find that iodo-toluenes are reduced more easily than iodo benzene, but that iodo derivatives of hydrocarbons with other side-chains are reduced less readily. Methyl promotes, but ethyl, propyl and other radicals hinder the removal of iodine in ortho and para positions by action of hydriodic acid.

Fischer and Dilthy[2] find that while malonic ester.

$$C_2H_5—OCO—CH_2—CO—OC_2H_5,$$

easily reacts with ammonia to yield an amide, the alkyl malonic esters,

$$C_2H_5OCOCH(R)—COOC_2H_5,$$

react slowly and imperfectly and diakyl malonic esters,

$$C_2H_5OCOC(R)_2COOC_2H_5,$$

do not react at all. Fischer predicts that the study of affinity will be greatly furthered by study of the influence of substitution.

Posner brings forward another case.[3] As is well known, mercaptans and ketones condense to mercaptals under the influence of gaseous hydrochloric acid; *e. g.*,

$$CO(CH_3)_2 + 2HSR = (CH_3)_2C{=}(SR)_2.$$

The author finds that when an aromatic aldehyde or ketone contains a hydroxyl or amino group in the nucleus the formation of mercaptals is prevented. Acetylation of the hydroxyl does not counteract this effect. The position of the hydroxyl or amino group makes no difference. When a nitro group is in ortho position to the carbonyl, it also hinders the formation of mercaptal, but not so strongly as hydroxyl or the amino group. On the other hand, meta and para nitro groups greatly promote the reaction. The influence of substitution is also shown in the conduct of the mercaptals on oxidation. Those derived from ortho nitro compounds must be carefully treated to yield sulphonals or else fail entirely to yield them, while those derived from para

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[1] *J. prakt. Chem.*, **65**, 564.

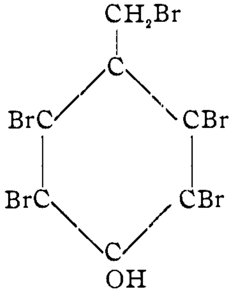
[2] *Ber. d. chem. Ges.*, **36**, 844.

[3] *Ibid.*, **35**, 2343.

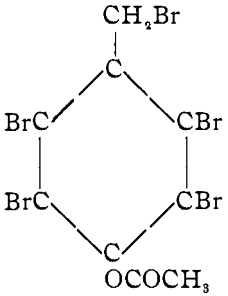
and meta nitro compounds easily yield sulphonals. The presence of the sulphone group in turn makes the nitro groups extremely difficult to reduce.

Neither Zincke[1] nor Auwers[2] have come to any final conclusion as to the formulation of the curious class of substances, being separately studied by them. By the action of halogens on those phenols having an alkyl in para position to the hydroxyl, there is at first a replacement of nucleus hydrogen. Hydrogen in the alkyl is then apparently replaced. But the compounds produced by this final step of substitution are not soluble in alkalies and seem now not to be phenols. However, they react with acetic anhydride with formation of a monoacetate as a phenol should. They are acted on easily by alcohol, aniline, aqueous acetone, or acetates with replacement of one halogen and formation of new substances, which are true phenols, easily dissolving in alkalies. The authors have proposed several formulas with the purpose of explaining their lack of power to dissolve in alkalies, but for the present purpose it will at first be best to keep the phenol formula. By bromination of paracresol the pentabrom compound

(I)



is produced. It is not soluble in alkali, but acetic anhydride gives



in which the bromine is not labile. On the other hand, alcohol and the rest of the reagents named above give with (I) compounds of the type

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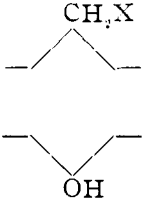
[1] *Ann. Chem.* (Liebig), **320**, [145] 45; **322**, 174 and 220; **325**, 19, 44, and 67; **329**, 1; **330**, 61.

[2] *Ber. d. chem. Ges.*, **34**, 4256; **35**, 114, 131, 425, 443, and 465.

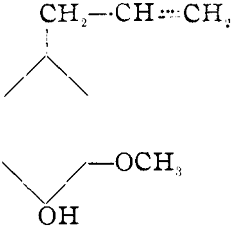


in which (X) may be

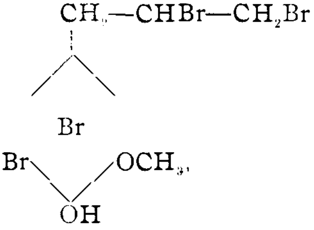
OC_2H_5, OH, NHC_6H_5 or $C_2H_3O_2$.

These compounds are true phenols, easily dissolving in dilute alkalies. With side-chains longer than methyl it is necessary, in order that the substance shall have the peculiar properties mentioned, to have one of the halogen atoms of the side-chain in connection with the carbon atom nearest the nucleus. This is shown by the fact that eugenol (I) by addition of bromine gives the tetrabromide (II),

(I)

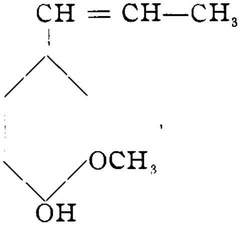


(II)

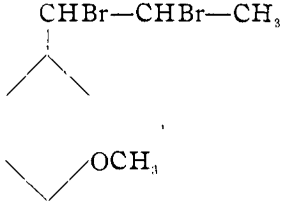


which is a true phenol and with none of its bromine labile, while isoeugenol (III) yields a dibromide (IV) and a tribromide (V),

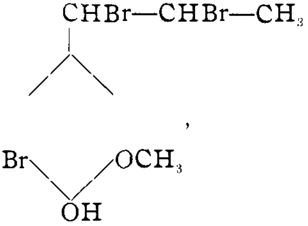
(III)



(IV)

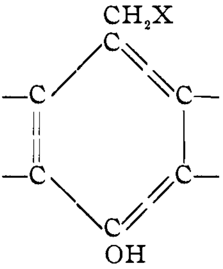


(V)

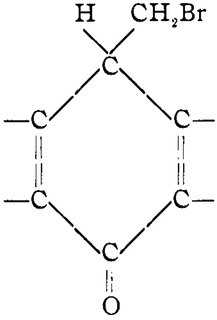


both of which are insoluble in alkalies and react with alcohol, water and acetates, with loss of bromine and formation of substances which are true phenols. There seems to be no convincing evidence to determine whether this is an extreme case of the influence of substitution by which bromine, in a distant part of the compound obscures the phenol functions of a compound of the formula (VI), or whether the substance should be represented by the quinone formula (VII).

(VI)

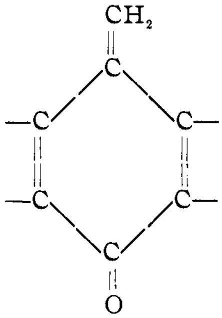


(VII)

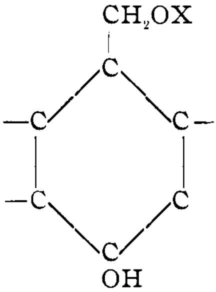


With the last thought in mind, Zincke has called substances of the class "pseudo keto bromides" or "pseudo bromides," while Auers calls them "pseudo phenols." This formula would explain the lack of phenol character. Their conduct toward alcohol and other reagents is due, according to Zincke, to the splitting off of halogen acid with formation of an intermediate methylene quinone (VIII), which then adds the reagent to give a true phenol of the type (IX)

(VIII)

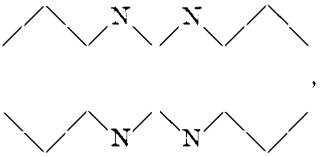


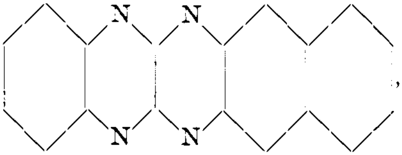
(IX)

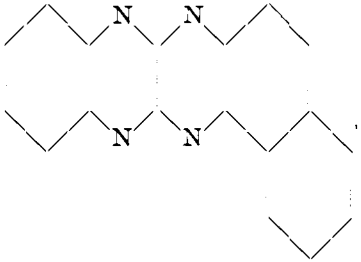


In some cases the only indication of the formation of a quinone is a temporary change of color, but with certain derivatives of diphenyl methane and of stilbene colored quinones can be isolated, which are capable of adding the reagents to yield true phenols.

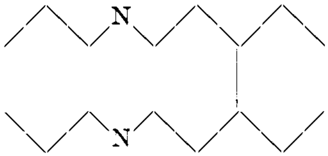
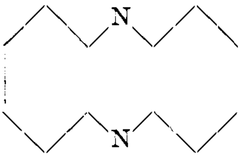
Hinsberg brings forward another case of the effect of structure on reactions. He has made a number of polycyclic compounds containing nitrogen and finds that of substances formulated,

(I)


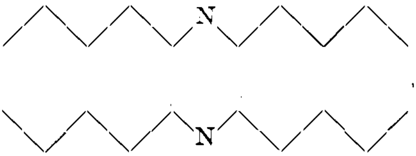
(II)


(III)


No. (II) is least stable and most like a quinone in its ease of reduction. Of the substances

(I)

and (II)


the second is more stable, while the compound formulated,



is not capable of existence, or is, at least, very unstable. He concludes that in polynuclear compounds, those containing more nuclei are less stable, especially if all of the rings are in a straight line.

Fischer having solved the problem of the sugars and of uric acid and the xanthines, has now taken up the task of synthesizing peptones. With characteristic insight and directness of attack he is obtaining results by very simple methods.[1] Glycin anhydride or glycylglycin,

$$NH_2CH_2CONHCH_2COOH, \tag{I}$$

is changed to its ester,

$$NH_2CH_2CONH.CH_2\text{—}COOC_2H_5, \tag{II}$$

and this by action of acid chlorides has a hydrogen atom of its amino group replaced by an acid radical. For example, by action of chlorcarbonic ester the ethyl ester above yields

$$C_2H_5OCONHCH_2CONHCH_2COOC_2H_5. \tag{III}$$

This, by action of ammonia, gives the amide

$$C_2H_5OCONHCH_2CONHCH_2CONH_2. \tag{IV}$$

On the other hand, the compound (III) by action of thionyl chloride gives the acid chloride (V),

$$C_2H_5OCONHCH_2CONHCH_2COCl, \tag{V}$$

which acts like other acid chlorides toward glycylglycin ester to yield still more complex amino acid amides or polypeptides.[2] By action of chloracetyl chloride on glycylglycin or ester (II) and careful saponification he is able to make the acid

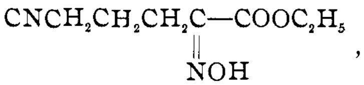
$$ClCH_2CONHCH_2CONHCH_2COOH,$$

which is changed by concentrated ammonia to the tripeptide diglycylglycin

$$NH_2CH_2CONHCH_2CONHCH_2COOH.$$

By use of other halogen chloranhydrides, polypeptides are made containing residues of acids besides that of acetic acid; for example, by use of α-brom propionyl bromide an alanyl glycylglycin is prepared.[3]

The peptone problem is also being studied by the synthesis of some of the more complex decomposition products of peptones. By reduction of isonitroso cyanvaleric ester,



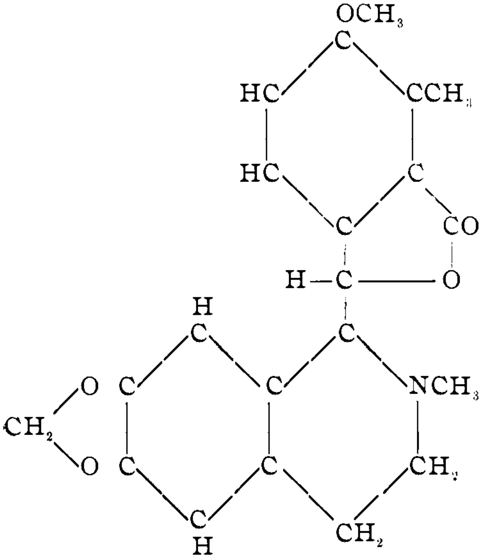
$$CNCH_2CH_2CH_2\underset{\underset{\displaystyle NOH}{\|}}{C}\text{—}COOC_2H_5 ,$$

a diamino acid[4] like lysine, except in its inactivity, was produced.

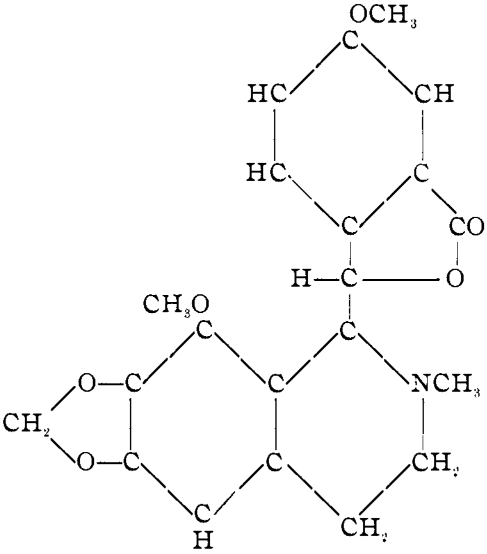
Many other workers are busy with the study of natural substances. Perkin, Herzig and Pollak, and Kostanecki and Lempi have articles on brazilin; Kostanecki and Tambor on catechin; Legler on aloin; Bertels on artemisin; Pinner contributes to the study of pilocarpin; Dobbie and Gadamer each has corydalin as a subject of research, and Gadamer has papers on berberin.

[1] *Ber. d. chem. Ges.*, **35**, 1095.
[2] *Ibid.*, **36**, 2094 and 2592.
[3] *Ibid.*, **36**, 2982.
[4] *Centrbl.*, 1902, p. 985.

Freund and Becker[1] determine that cotarnin is very closely related to hydrastin. It is hyrastin with one hydrogen replaced by the methoxy group.



Hydrastin.



Cotarnin.

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[1] *Ber. d. chem. Ges.*, **36**, 1521.

It is striking that there are now so many researches of which the unsaturated compounds form the subjects. The theory of Thiele, recently reviewed and criticized by Erlenmeyer,[1] while not complete, has apparently stimulated to work and to theoretical views besides his own. Vorländer[2] cites the work of others and brings forward new work of his own to show the mutual effect of carbonyl ($=CO$) and of ethylene groups ($=C=C=$) on one another. When they are neighboring so as to form the group ($=C=C'-C'=O$), the ethylene group becomes more active than before, it takes on other atoms more easily to give addition products. It will also take up hydrocyanic acid and other substances which are not taken up by simple ethylene compounds, but only by ($=CO$) itself. The ($=CO$), on the other hand, by its proximity to the ethylene group loses, to some extent, its own additive power. These mutual influences are still noticeable, though less strongly so when the two groups are more distant from one another in the structure. These effects of the groups are paralleled by the well-known effects the respective groups have on other near groups. Thus ($=CO$ makes chlorine or hydroxyl connected with it, in acid chloride and in acid, more active than in other relations, while its own power of making addition products is lessened by the presence of chlorine or hydroxyl. It has been suggested that it is the *negative* character of ($=CO$) which gives it this stimulant effect. To test this Vorländer ascertains the amount of sodium malonic ester which will, under given conditions, be added to the various amides of cinnamic acid,

$$C_6H_5CH=CH-C=O(NHR).$$

Some of the bases, NH_2R, from which he derives the amides are much more basic than others and should greatly modify the negativity of the ($=CO$) next to the amido groups. He finds no specific difference in the additive power of the different amides and concludes that the negativity of the carbonyl is not the effective cause of the increased activity of the ethylene group ($=C=C=$) when ($=CO$) is placed next to it. In a second article[3] Vorländer discusses the nature of radicals. The influence which certain groups have on the conductivity and other activities of compounds has been referred to the positive or negative character of those groups. Vorländer cites cases in which the same group, in different compounds, produces opposite effects and concludes that it is not best to consider the radical as positive or negative, but to take into consideration the character of the elements contained in the radical. He then cites numerous cases in which with equal positivity or negativity in two compounds

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[1] *J. prakt. Chem.* [2], **65**, 346.

[2] *Ann. Chem.* (Liebig), **320**, 66.

[3] *Ibid.*, **320**, 99.

one is reactive and the other is not. Finally, he concludes that in all the cases, whether the compounds are positive or negative, those which are reactive are *unsaturated.*

The effect of the carbonyl group in making neighboring groups reactive is seen in the ease with which methyl or methylene ketones and aldehydes react with various reagents. A new case of this is made known by the work of Delepine.[1] By the action of fuming sulphuric acid on certain aldehydes and ketones sulphonic acids are made. Barium hydroxide decomposes them with formation of sulphonic acids and carboxyl acids. The compound made from propionic aldehyde

$$CH_3C(SO_3H)_2—CHO,$$

yields, by hydrolysis, ethane disulphonic acid,

$$CH_3CH(SO_3H)_2.$$

and formic acid.

In connection with aldehydes as unsaturated compounds the new synthesis of aldehydes, discovered by Wahl,[2] is of interest. Aldehydes react with nitromethane, according to the general formula

$$R—(H)C{=}O + CH_3NO_2 = R—(H)C(OH)—CH_2NO_2.$$

Zinc chloride removes water with formation of the nitro compound

$$R—(H)C = CH—NO_2,$$

which, by reduction, is changed to the oxime

$$R—CH_2—(H)C{=}NOH,$$

and this may be hydrolyzed to the aldehyde next higher than the initial aldehyde.

Vörlander and Meyer[3] find that diazo compounds are changed by ammoniacal cuprous oxide to azo compounds when the diazo body contains either CH_3, OCH_3, or Cl in the ortho position to the diazo group but to diphenyl derivatives when the ortho group is NO_2, COOH or $COOCH_3$. For example $2CH_3OC_6H_4N_2OH$ gives

$$CH_3OC_6H_4N = NC_6H_4OCH_3$$

while $2NO_2C_6H_4N_2OH$ gives $NO_2C_6H_4C_6H_4NO_2$.

This they generalize by saying that unsaturated groups promote the production of diphenyl compounds.

An apparently new instance of trivalent carbon is the tolan trichloride of Loeb[4] which he formulates

$$C_6H_5—C^{III}(Cl)—C(Cl_2)C_6H_5,$$

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[1] *Compt. Rend.*, **133**, 876.

[2] *Ibid.*, **134**, 1145 and 1226.

[3] *Ann. Chem.* (Liebig), **320**, 122.

[4] *Ber. d. chem. Ges.*, **36**, 3059.

since it can take on chlorine to give the tolan tetrachloride

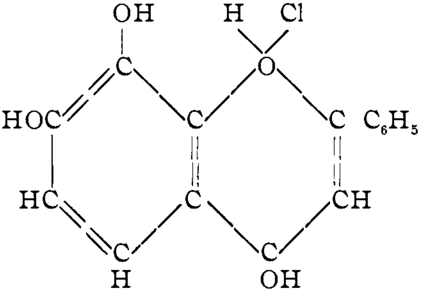
$$C_6H_5—C^{IV}(Cl)_2—C(Cl_2)C_6H_5,$$

and loses chlorine by action of zinc to give

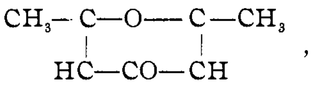
$$C_6H_5—C(Cl) = C(Cl)—C_6H_5.$$

That it does not act strongly as an unsaturated compound is by the author laid to stereochemical effect.

The idea of the tetravalence of oxygen has been a leading thought in several recent publications. Kehrmann and his associates continue to make use of this idea[1] in their study of the oxazine compounds. Buelow and von Sicherer,[2] by action of hydrochloric acid on dibenzoyl methane and phenols, make compounds of a new class called the pyranols. The direct product of the action is a hydrochloric acid salt of a non-nitrogenous base containing oxygen. From pyrogallol, for example, they make a compound to which they give the formula



From this they easily make the chlorplatinate and picrate. The free base is produced by action of sodium acetate. The authors regard this as a clear case of the tetravalence of oxygen and as confirming the idea that it is the bridge-oxygen of dimethyl pyrone



$$\begin{array}{c} CH_3—C—O—C—CH_3 \\ \quad\ |\qquad\quad\ | \\ \quad HC—CO—CH \end{array},$$

which is concerned when it unites with hydrochloric acid to form salts. An interesting fact in this connection is brought out by Coehn[3] who finds that when dimethyl pyrone is electrolyzed in 20 per cent. hydrochloric acid, the dimethyl pyrone goes with the hydrogen to the cathode and from this concludes that the pyrone with the hydrogen forms a complex "ion" like NH_4.

[1] *Ann. Chem.* (Liebig), **322**, 1.

[2] *Ber. d. chem. Ges.*, **34**, 3916.

[3] *Ibid.*, **35**, 2673.

The specific effect of certain substances as catalyzing agents has been studied by Sabatier and Senderens.[1] By passing carbon monoxide or dioxide with hydrogen over finely divided nickel heated to from 250°-280°, methane is produced. Cobalt requires a higher temperature. Other metals seem to fail. By conducting ethylene and its homologues with hydrogen over nickel heated to from 160°-200° they are reduced. Copper effects the same result. Cyclic hydrocarbons of the C_nH_{2n} series are not changed. Limonene is reduced and from this they decide that it has a double bond outside the cycle. Ipatiew finds that when organic compounds are heated to from 350°-700°, there are several types of reaction. Alcohols yield ethylene hydrocarbons and water; some ethylene hydrocarbons are rearranged to isomers; cyclic hydrocarbons are changed to ethylene hydrocarbons; ethylene oxides yield aldehydes and ketones. These reactions take place with much greater readiness in presence of aluminum oxide than with any other substance used.

In taking a rapid survey of the work of organic chemists for the past two years, the impression has been made upon the writer, that the time is soon coming when more definite conceptions of the meaning of affinity and of the process of chemical change will be held than are now current. The prominence of work on unsaturated compounds and the conception that the groups are unsaturated, which have a strong effect in modifying the activity of reaction of organic compounds, raise the question of the deeper meaning of these studies. The formation of additive compounds by substances containing the so-called tetravalent oxygen, the fact that Grignard's organo magnesium halides can be made only in ether solution and that they strongly hold the elements of ether, with many other more familiar facts seem to show that many compounds have a residual affinity. The work of Menschutkin, proving that the same substances under the same conditions of concentration and temperature will react with vastly different rapidity if the solvent is changed, shows that the solvent is not a mere space to the reacting substances. From these facts and speculations the question comes to mind whether again from the work of organic chemists much aid is not coming in the solution of the fundamental problems of chemistry. These facts and views as they have come together suggest that it may be that all compounds capable of reaction are unsaturated, that reactions are brought about by the effect of their mutual attractions, of their residual affinities, which coalesce two compounds or two compounds and a common solvent or two compounds and a "catalytic agent" into a complex, from which emerge in turn new substances which are more nearly saturated or have less affinity for each other or for the catalytic agent

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[1] *Compt. Rend.*, **134**, 574 and 659.

[2] *Ber. d. chem. Ges.*, **35**, 1047; **36**, 1990, 2014 and 2016.

or solvent. It seems probable that views along the line of those of Thiele, Werner, Flürscheim and Michael will show themselves more and more vital and productive in the near future.

NOTE.

Student's Apparatus for Determining the Hydrogen Equivalent of Metals.—The figure shows a simple apparatus for the determination of the hydrogen equivalent of metals. I have tested it with a large first-year class and found it very convenient and satisfactory. It is used in connection with a common laboratory dish, a 50 cc. graduated gas tube and a balance which weighs to centigrams or milligrams.

The gas tube, filled with water, is inverted over the dish and held in a support. The generator is supported in a little block of wood shown in outline in the figure. A strip of sheet zinc, best chemically pure, is cut to weigh 0.12 or 0.13 gram and carefully weighed. The generator is placed with the delivery tube in the dish, and water is poured in until the air is expelled. The zinc is dropped in and the exit is placed under the mouth of the gas tube. Sulphuric acid of specific gravity 1.18 is added until the water is displaced and action begins. The mouth of the generator is closed with a cork to prevent oscillation, which might carry some hydrogen out at the side tube. When action