

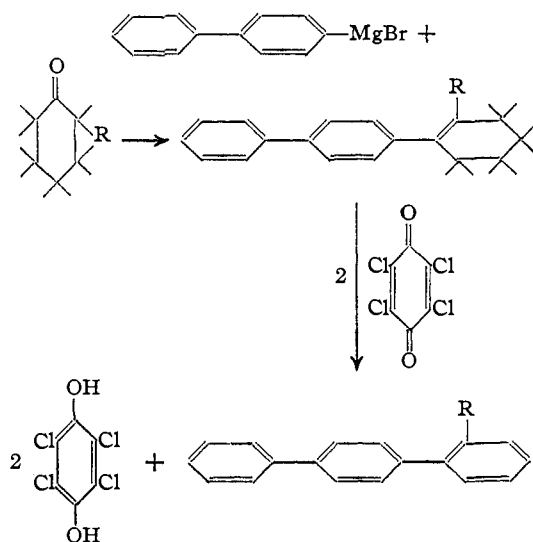
NOTES

Low Temperature Dehydrogenations. II

BY RICHARD T. ARNOLD, CLAIR COLLINS AND WM. ZENK

In an introductory report¹ it was shown that several different types of hydroaromatic compounds can be dehydrogenated at comparatively low temperatures by making use of chloranil or other quinones with high oxidation potentials.

This method has now been extended to reactions leading to the preparation of unsymmetrical biphenyl, terphenyls, etc., according to the scheme



Of course, the synthesis of substituted cyclohexenes in the first step here is limited to those molecules which do not have groupings present which will react rapidly with the Grignard reagent. However, these groups ($-\text{NO}_2$, etc.) are not affected in the dehydrogenation reaction with chloranil as they are when sulfur or selenium is used.

A convenient and cheap synthesis of chloranil has been described² and confirmed in this Laboratory. It makes use of the action of concentrated hydrochloric acid on benzoquinone in the presence of hydrogen peroxide (30%). This preparation practically eliminates the cost of these dehydrogenations, especially when it is realized that three-fourths of the hydroquinone which results can be recovered and converted quantitatively to the quinone by nitric acid.

- (1) Arnold and Collins, *THIS JOURNAL*, **61**, 140 (1939).
 (2) M. Gallati, *Ann. chim. applicata*, **22**, 602 (1932).

It has been demonstrated recently³ that sulfur can be used to prepare certain unsymmetrical biphenyls in satisfactory yields, but in the terphenyl and phenylnaphthalene series the classical dehydrogenations are disappointing.^{4,5} The procedure described in this paper gives very satisfactory yields (50–70%) in all of these cases.

Thermal rearrangements have been found to be commonplace in alkyl and aryl naphthalenes in the region of 300.⁶ The use of low temperature dehydrogenation here is obvious.

Recently, the classical synthesis of terphenyls by the reaction between nitrosoamines and hydrocarbons has been extended to new cases and the conditions of the synthesis greatly improved.⁷ While this method is very general, the yields reported are not comparable with those obtained in our investigations. The results obtained are summarized in Table I.

TABLE I

Compound	Product	Yield, %
1- <i>p</i> -Biphenylcyclohexene	Terphenyl	47
1- <i>p</i> -Biphenyl-2-methylcyclohexene	2-Methylterphenyl	72
1- α -Naphthylcyclohexene	α -Phenylnaphthalene	67
1- β -Naphthylcyclohexene	β -Phenylnaphthalene	72
1- <i>o</i> -Tolylcyclohexene	2-Methylbiphenyl	72

At present we are investigating the efficacy of chloranil as a dehydrogenating agent for straight chain hydrocarbons.

Experimental

1-*p*-Biphenyl-2-methylcyclohexene.—Ninety-five cubic centimeters of a Grignard solution (prepared from 100 g. of 4-bromobiphenyl, in 500 cc. of ether) was treated with 12 cc. of 2-methylcyclohexanone in an equal volume of benzene. The reaction mixture was decomposed with dilute sulfuric acid. Dehydration was accomplished by heating for one hour with 20% oxalic acid. The benzene layer was fractionated and the residue distilled in a sausage flask; yield 6.75 g.

2-Methylterphenyl.—A solution containing 3.58 g. of the above cyclohexene derivative, 7.3 g. of chloranil and 25 cc. of commercial xylene was refluxed for ten hours, cooled, and filtered, giving 4.55 g. of chloranilhydroquinone. The filtrate was diluted with an equal quantity of ether,

- (3) Sherwood, Short and Stansfield, *J. Chem. Soc.*, 1832 (1932).
 (4) Von Braun, Irmisch and Nelles, *Ber.*, **66**, 1472 (1933).
 (5) Fieser and Hershberg, *THIS JOURNAL*, **60**, 940 (1938).
 (6) Mayer and Schiffner, *Ber.*, **67**, 67 (1934).
 (7) France, Heilbron and Hey, *J. Chem. Soc.*, 1283 (1939).

washed with dilute alkali, dried, and fractionated. The residue was distilled in a small sausage flask and yielded 2.53 g. of the methylterphenyl which melted at 91–92° after recrystallization from methanol.⁷

Anal. Calcd. for C₁₈H₁₆: C, 93.34; H, 6.60. Found: C, 92.97; H, 6.58.

Terphenyl.—A sample (1.46 g.) of *p*-biphenylcyclohexene, 3.3 g. of chloranil and 18 cc. of dry xylene were refluxed and the reaction worked up as described in the preceding section; yield of terphenyl 0.63 g. The product melted at 210–211.5°. The identity of the substance was checked by preparing the nitro derivative; melting point 275°.⁷

α -Phenylnaphthalene.—Five grams of α -naphthylcyclohexene prepared as described in the literature⁸ was refluxed with 11.8 g. of chloranil in 20 cc. of xylene for five hours. The reaction mixture was cooled, diluted with an equal volume of petroleum ether (30–60°) and filtered, yielding 8.4 g. of chloranil hydroquinone. The remainder was removed by basic extraction. The resulting fractionation yielded 3.33 g. of α -phenylnaphthalene. The structure was checked by the formation of its nitro derivative which melted at 129–130°. The literature reports 132°.⁸

β -Phenylnaphthalene.⁹—Following the same procedure as given above, β -naphthylcyclohexene was dehydrogenated to give β -phenylnaphthalene in a yield of 72%. The constitution of this molecule was proved by direct oxidation to β -phenyl 1,4-naphthoquinone; melting point 108–109°.⁹

2-Methylbiphenyl.—This substance was obtained by refluxing a solution containing 12 g. of *o*-tolylcyclohexene, 36 g. of chloranil, and 115 cc. of xylene. The yield of pure product obtained by fractionation was 8.5 g. (72.6%).³

(8) Weiss and Waidich, *Monatsh.*, **46**, 456 (1925).

(9) Chattaway and Lewis, *J. Chem. Soc.*, **65**, 873 (1894).

SCHOOL OF CHEMISTRY
UNIVERSITY OF MINNESOTA
MINNEAPOLIS, MINNESOTA RECEIVED FEBRUARY 5, 1940

Catalytic Action of 8-Hydroxyquinoline on the Oxidation of *p*-Phenylenediamine

BY FREDERICK BERNHEIM AND PHILIP HANDLER¹

8-Hydroxyquinoline can, under certain conditions, catalyze the oxidation of cysteine to cystine.² It has now been shown that it has a catalytic effect on the oxidation of *p*-phenylenediamine and certain related substances. Figure 1 shows this effect on *p*-phenylenediamine recrystallized from water and from alcohol. The oxygen uptake was measured at 37° in the Warburg apparatus. Successive recrystallizations of the diamine have no effect on the catalysis, showing that the 8-hydroxyquinoline is not simply removing an antioxidant. Addition of metal ions such as the cupric, ferric and vanadate does not

(1) One of us (P. H.) is indebted to the Markle Foundation for its support during this work.

(2) F. Bernheim and M. L. C. Bernheim, "Symposia on Quantitative Biology," Vol. VII, 1939, in press.

enhance the catalytic effect which is, therefore, probably not due to a metal-8-hydroxyquinoline complex. The catalysis is not affected by 0.02 *M* cyanide or pyrophosphate. It has an optimum *pH* at about 6.5 and the rate falls off rapidly in alkaline solutions. The oxidation product is deeply colored, which is characteristic of the polymer of the quinone diamine and which can be reduced by hydrosulfite. On isolation and hydrolysis with acid it gives free ammonia. From the oxygen uptake figures a small percentage of further oxidation products must be formed which have not been isolated.

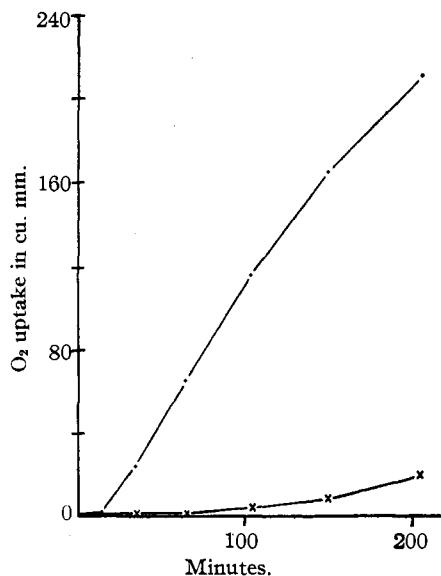


Fig. 1.—The oxygen uptake of 3.0 mg. of *p*-phenylenediamine in 2.0 cc. of water at *pH* 6.7: ×—×, control; ·—·, with 0.05 mg. of 8-hydroxyquinoline. The short latent period is characteristic.

8-Hydroxyquinoline has no effect on the oxidation of *o*-phenylenediamine, catechol or hydroquinone in acid or alkaline solutions. It has a comparatively small effect on the oxidation of *p*- and *o*-aminophenols in alkaline solutions (*pH* 7.8). 2-Hydroxyquinoline and certain other quinoline derivatives are without catalytic action.

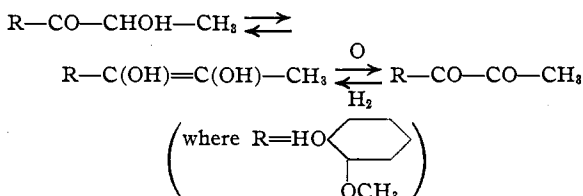
DEPARTMENT OF PHYSIOLOGY AND PHARMACOLOGY
DUKE MEDICAL SCHOOL
DURHAM, NORTH CAROLINA RECEIVED JANUARY 26, 1940

The Mechanism of Plant Respiration

BY HAROLD HIBBERT

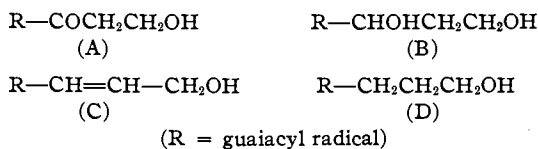
The discovery (see following note) in the ethanolysis products from spruce wood of methyl guaiacyl diketone alongside the previously re-

ported α -hydroxypropiovanillone¹ raises a question of considerable biochemical significance. The latter product, in its ene-diol form, is evidently the "donator" in a new oxidation-reduction system, the newly discovered diketone being the "acceptor."



Such a system with its presumptive accompanying dioxypropylene guaiacolase is thus closely related to the ene-diol catechol, -ascorbic acid and -dioxymaleic acid systems shown recently by Szent-Györgyi and co-workers² to form an integral part of the cycle of changes involved in plant (and presumably animal) respiration. The wide occurrence of this new oxidation-reduction system in various forms of higher plant life^{1,3} and the fact that both methyl guaiacyl diketone and α -hydroxypropiovanillone apparently are derived from methyl glyoxal provide additional support for the author's theory of plant synthesis⁴ in which this intermediate of carbohydrate metabolism appears to play such an extraordinarily important role.

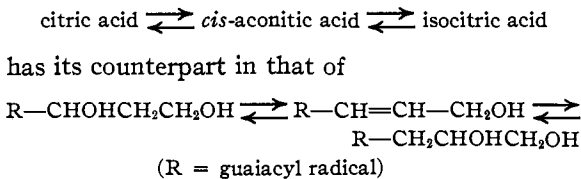
In the suggested new system of plant respiration the roles of oxalacetic, malic, fumaric, and succinic acids are taken by (A), (B), (C) and (D), respectively



Of these, coniferyl alcohol (C) is known to be a very widely distributed plant product.

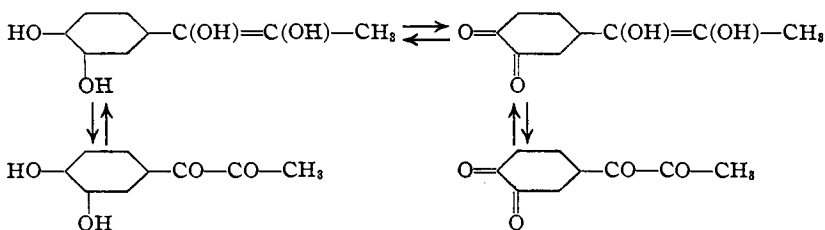
It may also be pointed out that in this new conception the important biological system⁵ known to function in intermediary metabolism

(1) Cramer, Hunter and Hibbert, *THIS JOURNAL*, **61**, 509 (1939).
 (2) For review see *Ber.*, **72**, 53 (1939).
 (3) (a) Hunter, Cramer and Hibbert, *THIS JOURNAL*, **61**, 516 (1939); (b) Brickman, Pyle and Hibbert, *ibid.*, **61**, 523 (1939).
 (4) Hibbert, *ibid.*, **61**, 725 (1939).
 (5) Martius and Knoop, *Z. physiol. Chem.*, **242**, 1 (1936); Martius, *ibid.*, **247**, 104 (1937); **257**, 29 (1938); Krebs and Johnson, *Enzymologia*, **4**, 148 (1937); Johnson, *Biochem. J.*, **83**, 1046 (1939).

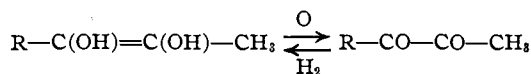


these last three products having a close biochemical relationship to the above ene-diol form. Obviously the same considerations apply to the case of the corresponding syringyl compounds obtained in the ethanolysis of hard woods.³

Since in the early stages of plant growth the phenolic substances present are unmethoxylated, presumably the above new oxidation-reduction mechanism is represented there by a *di*-ene-diol system



in which not only the catechol \rightleftharpoons orthoquinone portion can function, but also the side chain grouping, as indicated by the changes



Such a combination is quite unique in cell oxidation systems and presumably is intimately related to the very much slower rate of reduction-oxidation changes involved in plant, as contrasted with animal, cell respiration.

It seems very probable that the above oxidation-reduction phenomena are intimately associated with (a) the very marked change in color taking place when chlorine and other oxidizing agents are brought into contact with unbleached pulps, and (b) the discoloration of newsprint and other papers in the presence of light and air.

Experiments with this new system on plant and animal tissues are to be undertaken and a full discussion of the subject is to appear in a forthcoming publication wherein the role of the ene-diol oxidation-reduction system as the almost certain forerunner of lignin synthesis is to be discussed comprehensively.

Structure of the Ethanolysis Products from Spruce and Maple Wood

BY LEO BRICKMAN, J. J. PYLE, W. L. HAWKINS AND HAROLD HIBBERT

A re-investigation of the "aldehyde fraction" obtained in the ethanolysis of maple and spruce wood¹ has shown that two of the constituents previously identified (incorrectly) as syringoyl- and vanilloyl-acetaldehydes are, in reality, 1,2-diketones, namely, the benzil derivatives, methyl-4-hydroxy-3,5-dimethoxyphenyl diketone (C₆H₃(OH)(OCH₃)₂-CO-CO-CH₃) (A) and methyl guaiacyl diketone (C₆H₂(OH)(OCH₃)-CO-CO-CH₃) (B), respectively. Proof of this has been found in the synthesis of the benzils by oxidation of the corresponding benzoin, namely, α -hydroxypropiovanillone and α -hydroxypropiosyringone, by means of copper sulfate and pyridine. The monosemicarbazone of (A) melts at 213° and its disemicarbazone at 240°, while the mono-2,4-dinitrophenylhydrazone of (B) melts at 226–227° and its monosemicarbazone at 214–215°. No depression in melting point was found on admixture with the corresponding products isolated from the ethanolysis products.

The mistake in identity arose as a result of the aldehyde-like properties possessed by these 1,2-diketones.

A full account of the supporting chemical evidence is to be given in a forthcoming publication.

(1) Pyle, Brickman and Hibbert, *THIS JOURNAL*, **61**, 2198 (1939).

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MONTREAL, CANADA

RECEIVED JANUARY 11, 1940

Purification of High Molecular Weight Fatty Esters

BY LORAN O. BUXTON AND ROLAND KAPP

In the course of our research it became necessary to prepare relatively large quantities of substantially acid-free high molecular weight fatty esters. We have found that the following process is more satisfactory for removing substantially all of the unreacted fatty acids than the usual methods.

The procedure most suitable is as follows. The unreacted alcohol is distilled from the esterification mass, and the residual mixture of free fatty acids, crude ester, and catalyst is dissolved in 2 to 5 parts by weight of a solvent such as ethylene dichloride to 1 part of ester. A con-

venient sample (10 to 20 g.) of the solvent solution of the crude ester is dissolved in an alcohol-ether mixture, and titrated with standard 0.5 *N* alcoholic potassium hydroxide. On the basis of this titration value an equivalent weight of concentrated aqueous potassium hydroxide, preferably of 38% strength, is added slowly with constant stirring to the solvent solution of the ester mixture. In a relatively short time the potassium soap of the unreacted fatty acids will rise to the surface as a flocculent aggregate, and any mineral acid present as catalyst will also precipitate out as the potassium salt. The solvent solution is filtered without suction, and the soap mass is washed with a small amount of fresh ethylene dichloride to remove traces of neutral ester, and the filtrate distilled. It is not necessary to dry the filtrate.

By this process we have been able to obtain quantitatively the yields of methyl and ethyl esters of lauric, oleic, linoleic, stearic and ricinoleic acids, from the original esterified mass prepared with the respective crude acids. The process also has been applied successfully to the preparation of relatively pure mono- and di-naphthenates of diethylene glycol. The esters obtained in this manner have acid values from 0.5 to 1.0 and can be purified further by vacuum distillation. Relatively large amounts of ester can be purified in this manner without the formation of troublesome emulsions and without the hazards hitherto inherent in the use of ether.

NOPCO LABORATORIES
NATIONAL OIL PRODUCTS COMPANY
HARRISON, NEW JERSEY

RECEIVED FEBRUARY 20, 1940

Lupine Studies. XVI.¹ The Isolation of Nonalupine from *Lupinus andersonii* Wats

BY JAMES FITTON COUCH

The isolation of nonalupine from *Lupinus sericeus* has been reported recently.¹ In that species this alkaloid is associated with spathulatine first isolated from *L. marianus*.² Nonalupine has now been isolated from *L. andersonii*, a perennial, Pacific States lupine, which has not previously been examined chemically. Spathulatine was not found in the last named species.

Experimental

Material.—The plant used in this investigation was collected by the writer on the south road, Crater Lake Mt.,

(1) Previous paper, No. XV, *THIS JOURNAL*, **62**, 554 (1940).

(2) J. F. Couch, *ibid.*, **46**, 2507 (1924).

Oregon, on August 24, 1930. At that time the plant was just beginning to bloom. The plants were dried and shipped to Washington, D. C. The whole plant with the exception of the roots was used.

Isolation of the Alkaloid.—The finely ground plant (7.415 kg.) was moistened with alcohol containing 75 g. of acetic acid and then extracted with alcohol. The alkaloid was recovered by the process previously described.³

The crude alkaloid weighed 130.4 g. or 1.76% of the plant material. It was negative to the modified Grant test for sparteine, practically insoluble in petroleum ether, slightly soluble in ethyl ether, and completely soluble in cold acetone. On standing the sirupy alkaloid solidified to a mass of crystals embedded in a thick sirup.

The mass was washed with cold ethyl acetate, which removed most of the sirup. The crystals were then recrystallized several times from hot ethyl acetate with the addition of a little norit and finally from methyl isobutyl ketone. The melting point was constant at 91–92° (cor.). Mixed with nonalupine from *L. sericeus* there was no alteration in the melting point. The substance was dried to constant weight for analysis.

Anal. Calcd. for C₁₅H₂₁ON₂: C, 72.50; H, 9.74; N, 11.28. Found: C, 72.37, 72.39; H, 9.55, 9.57; N, 11.28, 11.20.

The alkaloid was similar in all chemical and physical respects with nonalupine.

(3) J. F. Couch, *THIS JOURNAL*, **56**, 2434 (1934).

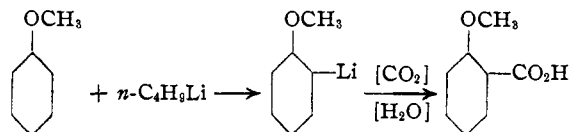
PATHOLOGICAL DIVISION
BUREAU OF ANIMAL INDUSTRY
WASHINGTON, D. C.

RECEIVED JANUARY 26, 1940

Lateral Metalation of Methyl Phenyl Sulfide

BY HENRY GILMAN AND F. J. WEBB

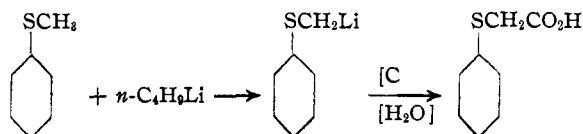
Metalation by organometallic compounds of a great variety of ethers invariably involves hydrogen situated *ortho* to the hetero element. Some of the types examined are: aryl alkyl ethers, diaryl ethers, and cyclic ethers like furan, benzofuran and dibenzofuran. The following reaction with anisole is typical.



The same general reaction takes place with the sulfur analogs of the diaryl ethers and the cyclic ethers mentioned, with but one exception. Metalation of dibenzofuran by a variety of organometallic compounds involves the 4-position (*ortho* to the hetero element); however, the exceptional case has been noted with the related heterocycle, dibenzothiophene. Although metalation of dibenzothiophene by organolithium and organopotassium compounds also involves the 4-posi-

tion, metalation by phenylcalcium iodide introduces the metal in the 3-position, or *meta* to the hetero element.¹

We now find that metalation of methyl phenyl sulfide proceeds quite unlike the related anisole, and instead of giving an *ortho* nuclear metalation product² yields exclusively a lateral metalation product.



There is a possibility that nuclear metalation may have occurred initially, and that the lithium then migrated to the methyl group. This remains to be established. In this connection, it is interesting to note that *o*-, *m*- and *p*-tolylsodiums rearrange laterally to benzylium.³ The metalation of other sulfur and related types is being examined, together with some syntheses of these new reactive compounds such as the bridging of the 1- and 9-positions in dibenzofuran types by hetero elements and groups.

Experimental

A solution containing approximately 0.2 mole of *n*-butyllithium was divided into two equal parts. To one portion was added 12.4 g. (0.1 mole) of methyl phenyl sulfide in 30 cc. of ether; and to the other portion was added 10.8 g. (0.1 mole) of anisole in 30 cc. of ether. Each of the mixtures was stirred and refluxed for fifteen hours, and then carbonated by solid carbon dioxide. By means of the usual procedures, there was isolated from the reaction with methyl phenyl sulfide, 7.32 g. (43.5%) of phenylmercaptoacetic acid (m. p., 61–63°). This compound was identified by comparison with an authentic specimen prepared from thiophenol and chloroacetic acid in accordance with the directions of Gabriel.⁴ In addition, there was recovered 3.7 g. or 29.8% of methyl phenyl sulfide, which raises the yield of phenylmercaptoacetic acid to 62% on the basis of methyl phenyl sulfide not recovered.

The reaction with anisole gave 4.92 g. or 32.4% of *o*-methoxybenzoic acid; 0.65 g. or 5.37% of 2,2'-dimethoxybenzophenone; and 1.9 g. or 17.6% of recovered anisole. All solids were identified by the method of mixed melting points.

From a check experiment with methyl phenyl sulfide there was obtained 5.9 g. or 35.2% of phenylmercaptoacetic acid (m. p. 61–63°) and 4.5 g. or 36.3% of recovered methyl phenyl sulfide.

(1) Gilman and Jacoby, *J. Org. Chem.*, **3**, 108 (1938); Gilman, Jacoby and Pacevitz, *ibid.*, **3**, 120 (1938).

(2) Phenoxathiin and *N*-ethylbenzothiazole are known to metalate *ortho* to a hetero element, and with the former compound *ortho* to the oxygen linkage.

(3) Gilman and Pacevitz, *THIS JOURNAL*, **62**, 672 (1940); Gilman, Pacevitz and Baine, *ibid.*, **62**, May (1940).

(4) Gabriel, *Ber.*, **10**, 1629 (1879).

We have just observed that *ethyl* phenyl sulfide with *n*-butyllithium gives *o*-ethylmercaptobenzoic acid.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

RECEIVED FEBRUARY 26, 1940

Hydrogenation of Wood

BY H. P. GODARD, JOSEPH L. MCCARTHY AND HAROLD HIBBERT

Studies on hydrogenation of lignin and other plant materials at high pressures have now shown that maple and spruce wood meals readily undergo hydrogenation. The two latter products were first freed from resin, fats, etc., by the customary preliminary extraction treatment with alcohol-benzene, alcohol, and water in the order named, then dried, suspended in anhydrous dioxane, the copper-chromium oxide catalyst added and the mixture then subjected to the action of hydrogen at around 250 to 280° at a pressure of 5000–6000 pounds per square inch (333–400 atm.) for periods of twelve to sixteen hours.

The main products isolated were (a) 4-*n*-propylcyclohexanol-1, b. p. 92–95° (7 mm.), refractive index n_D^{25} 1.4633, and (b) 4-*n*-propylcyclohexanediol-1,2, b. p. 107–110° (1 mm.), refractive index n_D^{25} 1.4808; some higher boiling oils also were obtained. These substances undoubtedly originate from the lignin present in the wood, the combined yields of (a) and (b) in the preliminary work, when calculated on the total (Klason) lignin present originally, amounting to around 60 to 70% in the case of maple and about 35 to 40% in the case of the spruce meal. Similar results were obtained using wood meal previously extracted with cold 5% alkali, although in these cases the yields were somewhat lower.

Presumably other suspending media such as tetralin, decalin, cyclohexane, as well as the above solvents (a) and (b), can be used in place of dioxane, and these are being actively investigated.

It is of considerable interest that the accompanying carbohydrate-polysaccharide components also undergo simultaneous hydrogenation and hydrogenolysis as indicated by the large absorption of hydrogen (about 3.2 moles of hydrogen per 100 g. of wood meal). The nature of these reactions and of the resulting products are also under investigation.

DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY
MCGILL UNIVERSITY
MONTREAL, CANADA

RECEIVED FEBRUARY 12, 1940

The Effect of Chlorine Substitution on the Fungistatic Properties of Acetic and Propionic Acids

BY CHARLES HOFFMAN, T. R. SCHWEITZER AND GASTON DALBY

In a recent paper the fungistatic properties of β -iodopropionic acid were reported in connection with a study of a series of normal, branched-chain, and substituted fatty acids.¹ It was shown that β -iodopropionic acid had remarkable fungistatic properties which apparently depended to some extent on the nature of the iodine atom itself. The effect of substituents is also of interest from the point of view of the relationship of molecular structure to fungistatic power. Monochloroacetic, α -chloropropionic, and β -chloropropionic acids are readily available and their fungistatic curves illustrate the effect of the introduction of a single chlorine atom in all possible positions.

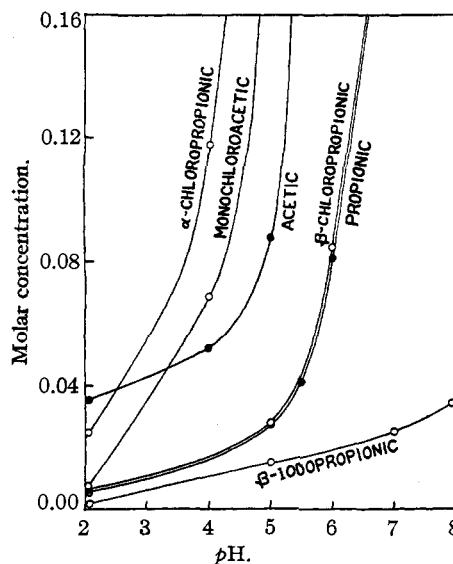


Fig. 1.—Molar concentrations of the indicated acids at various pH values necessary to inhibit mold for forty-eight hours at 37.5°.

The method used was as previously reported.¹ β -Chloropropionic acid has a curve practically identical with that of propionic acid itself and is markedly different from the β -iodopropionic acid curve which is indicated on the graph for comparison. The introduction of chlorine on the alpha carbon of propionic acid sharply decreases its fungistatic properties. Monochloroacetic acid is also much less effective than acetic acid except

(1) Hoffman, Schweitzer and Dalby, *Food Research*, 4, 539 (1939).

in the very high pH ranges. A chlorine atom on the carbon next to the carboxyl affects the fungistatic properties of the acid, whereas the same substituent on the beta carbon atom has no effect. Constitutional factors are therefore of considerable significance on the biological effect of fatty acids.

Langmuir² pointed out that halogen substitution had an appreciable effect on the dissociation constant of a fatty acid. The theory³ is rather widely held that the biological activity of an acid is dependent on the dissociation constant; that is, the less ionized the acid, the more powerful its biological effect. The relative fungistatic properties of acetic and monochloroacetic, and of propionic and α -chloropropionic acids, when compared with their respective dissociation constants are in agreement with this theory. In the case of propionic and β -chloropropionic acids, however, the fungistatic properties are not so closely related to the dissociation constants. Propionic acid has a dissociation constant of 1.33×10^{-5} , and β -chloropropionic acid 8.59×10^{-5} ,² but the two acids have essentially identical fungistatic properties.

(2) Langmuir, *Chem. Rev.*, **6**, 465 (1929).

(3) (a) Tekelenburg, *Nederland. Tijdschr. Hyg. Microbiol. Serol.*, **2**, 176 (1927); (b) Bach, *Bull. sci. pharmacol.*, **39**, 7 (1932).

WARD BAKING COMPANY
NEW YORK, N. Y.

RECEIVED JANUARY 17, 1940

The Preparation of Aurin Tricarboxylic Acid*

BY DUNCAN A. HOLADAY

Recent work in this Laboratory required the use of pure aurin tricarboxylic acid. Several methods of preparing this compound were tried, including those of Scherrer and Smith,¹ Heisig and Lauer,² and Caro.³ A product satisfactory for use in the determination of aluminum was obtained by each of these methods, but in no instance did the product contain more than 70% aurin tricarboxylic acid based on the air-dried material. The content of dye was determined by titration with titanium trichloride solution.⁴

In the course of the work it was observed that the material prepared by Caro's method would undergo a further reaction on treatment with a second portion of the oxidizing mixture (sodium

* Not copyrighted.

(1) Scherrer and Smith, Bureau of Standards Res. Paper RP1118.

(2) Heisig and Lauer, *Org. Syntheses*, **9**, 8 (1929).

(3) Caro, *Ber.*, **25**, 941 (1892).

(4) Evensen and Nagel, *J. Ind. Eng. Chem., Anal. Ed.*, **3**, 167 (1931).

nitrite-sulfuric acid solution). A study of this reaction developed the following modification of Caro's procedure which has several advantages over previously described preparations and yields a product of high purity. The methods of Heisig and Lauer, and of Scherrer and Smith, require that the temperature be kept below 5°. In the following procedure the reaction is not highly exothermic, and therefore no rigid temperature control is necessary. Caro recommends a purification with sodium bisulfite, which is difficult to perform and in the author's hands does not yield a pure product. In the modified procedure no purification of the reaction product is necessary except the removal of inorganic salts.

Experimental Part

Five grams of finely powdered sodium nitrite was added slowly and with vigorous stirring to 36 cc. of sulfuric acid, avoiding evolution of oxides of nitrogen. To this solution an intimate mixture of 10 g. of methylene-disalicylic acid⁵ and 5 g. of salicylic acid was added in small portions with vigorous stirring. After addition of all of the solid material, the mixture was allowed to stand for an hour with occasional stirring. It was then poured into a solution of 5 g. of sodium nitrite in 36 cc. of sulfuric acid, stirred, and allowed to stand overnight. The reaction mixture was added slowly to one liter of cold water, allowed to stand for an hour, and filtered on a Büchner funnel. The precipitate was suspended in one liter of warm water (50°) and filtered. This suspension and filtration was repeated, the free water removed by drawing air through the funnel, and drying was completed in a vacuum oven at 70°. The yield of dry product was 10.5 g. It titrated 97% aurin tricarboxylic acid.

(5) Vanino, "Präparative Chemie," Vol. II, 1937, p. 585.

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RECEIVED DECEMBER 15, 1939

Type III Surface Tension Curves with Minimum in Dilute Solution in Pure Hydrocarbons

BY M. E. L. MCBAIN AND L. H. PERRY

Many properties of colloid systems in water are usually explained in terms of free ions, so that it becomes interesting to examine non-ionizing solvents to see in how far similar behavior is to be found where free ions are almost or quite lacking. One very striking property of many colloidal electrolytes in water is that in very dilute solution they lower the surface tension to about one-third that of water. The surface tension is then at a minimum and thereupon rises to a flat maximum in slightly less dilution. Some non-electrolytic detergents likewise similarly lower the surface

tension of water to an almost equal extent in very dilute solution, but it then remains constant on further concentration. The existence of these type III curves has been thoroughly established¹ and they are of special interest because the positive adsorption actually observed by a number of methods does not accord with the requirements of the Gibbs theorem as ordinarily applied to surface tension measurements.

Using hydrocarbons as solvents, we have found that type III curves with minima do actually occur in non-ionizing media. This is shown in Fig. 1 for pure lauryl sulfonic acid dissolved in

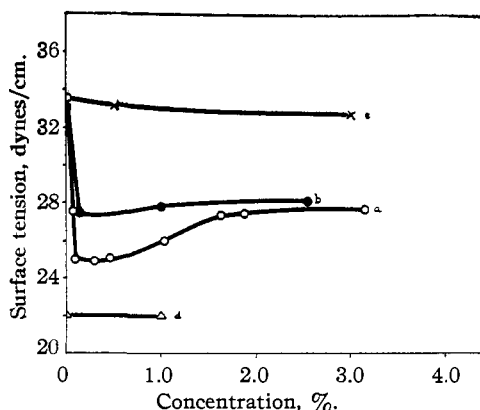


Fig. 1.—Surface tension curves in hydrocarbon solutions: Type III curves for lauryl sulfonic acid in (a) Nujol and (b) mineral oil; Type I curves for (d) lauryl sulfonic acid in *n*-heptane and (e) butyric acid in Nujol.

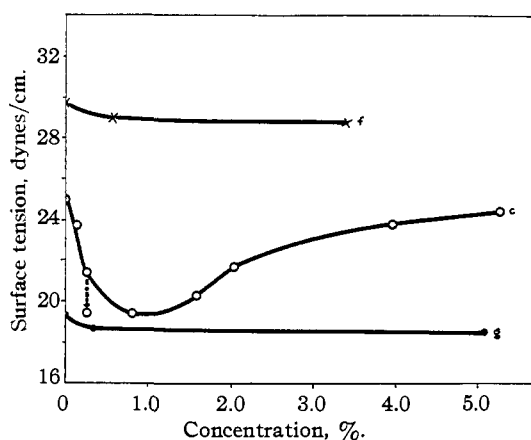


Fig. 2.—Surface tension curves in hydrocarbon solutions of lauryl sulfonic acid: Type I curves for (f) benzene and (g) iso-octane; Type III curve for (c) hydrogenated tetra-isobutylene, showing with vertical dashed line the time effect in lowering of surface tension in very dilute solutions only.

(1) McBain and Mills, Reports on Progress in Physics, **5**, 30 (1939); McBain, Vinograd and Wilson, THIS JOURNAL, **62**, 244 (1940); McBain and Wood, Proc. Roy. Soc., **174A**, in press (1940); McBain, Mills and Ford, THIS JOURNAL, **68** in press (1940).

(a) Nujol, (b) mineral oil, and, in Fig. 2, (c) hydrogenated tetra-isobutylene. The results were obtained with the DuNoüy ring tensiometer at 27°, first sweeping the surface to remove contamination. These solutions unlike most of the others to be mentioned leave a film within the ring.

On the other hand, lauryl sulfonic acid in solvents such as iso-octane, xylene, benzene and heptane scarcely lowers the surface tension. For iso-octane the value 19.3 dynes/cm. falls steadily with concentration to 18.5 in 5% solution (type I curve). For benzene the value 29.7 of the pure solvent becomes 28.7 for 3.4%, and for *n*-heptane the value of 22.2 is not changed when 1% of acid is added. These results are summarized in Table I.

TABLE I

SOLUTIONS OF $C_{12}H_{25}SO_3H$ IN HYDROCARBONS SHOWING SURFACE TENSION OF SOLVENT, σ_0 ; OF 1% SOLUTION, σ_1 ; AT MINIMUM, $\sigma_{min.}$, IF ANY; AND TYPE OF SURFACE TENSION CURVE

Solvent	σ_0	σ_1	$\sigma_{min.}$	Type
Nujol	33.5	25.9	24.8 at 0.2%	III
Mineral oil	33.0	27.8	27.4 at 0.18%	III
Benzene	29.7	29.3	none	I
Xylene	27.8	27.3	none	I
Tetra-isobutylene	25.3	22.5	22.3 at 0.15%	III
Hydrogenated tetra-isobutylene	25.0	19.5	19.4 at 0.8%	III
Decane	23.7	22.3	none (?)	I, III (?)
Heptane	22.2	22.2	none	...
Iso-octane	19.5	19.2	none	I

It is interesting to compare a surface tension curve in Nujol and in the similar mineral oil with that in water,¹ where the surface tension at the minimum is the same in all three cases, though that of water is as high as 72 dynes. The first thought, that solvents whose own surface tension is already as low as this minimum could not be lowered, is negated by the result in hydrogenated tetra-isobutylene, where it drops from 25 dynes to 19.4. However, the two intervening solvents, benzene and xylene, are not similarly affected by lauryl sulfonic acid. They are lowered but slightly and yield no minimum, showing that surface tension of the solvent is no sufficient guide.² Decane appears to be on the borderline among saturated hydrocarbons.

Polar compounds are not enough. For example, nonyl glucoside and another excellent detergent, a polyethylene oxide derivative, scarcely

(2) Interesting contrasts between spreading behavior of hexane and benzene on mica surfaces have been reported by Bangham, Mosallam and Saweris, Trans. Faraday Soc., **34**, 554 (1938); Nature, **140**, 237 (1937).

lower the surface tension of Nujol or hydrogenated tetraisobutylene. The measurements are hampered, however, by low solubility and a tendency to separate on cooling. In water, Woo's unpublished measurements show that they lower the surface tension from 72 to 31 dynes in extreme dilution, namely, 0.02 and 0.2% solutions, respectively, thereafter remaining constant up to 1% solution.

The sulfated sodium naphthenic or petroleum soaps supplied by the Sherwood Petroleum Company are oil-soluble, not water-soluble. They actually raise the surface tension of *n*-hexane from the value 20.2 to 20.4 or 20.5 for 10% solution and to 22.3 for 50% solution, thus giving a type II curve.

A number of especially interesting solutes of different types could not be tested on account of their insolubility, but a non-electrolytic detergent showed no appreciable lowering in Nujol although 14 and 24% solutions gave the small lowerings of 0.5 and 2.0 dynes. Butyric acid likewise is ineffective, the lowering being 0.5, 0.9 and 2.0 dynes for 1, 9 and 20% solutions, respectively. Lauric acid in 3% solution gave the distinctly greater lowering of 2 dynes. Triethanolamine oleate in 0.5 and 9% gave a lowering of 1 dyne and 2 dynes; thymotic acid in 1% solution 0.8 dynes; and stearic acid gave 1 dyne lowering for 0.7%. Calcium and zinc stearates have practically no effect.

It is evident that appreciable lowering and the production of a type III curve in these hydrocarbons require such a degree of polarity that the solute forms a strong electrolyte or colloidal electrolyte in water.

The only explanation to account for the minimum found in a type III curve is that put forward by McBain³ based upon the electrical double layer. Now in the present non-ionizing solvents this would have to be a condensed Helmholtz double layer of the classical type instead of the partly diffuse type existing in water. However, the Helmholtz double layer is adequate for explaining lowering of surface or interfacial tension.

These novel observations evidently should suggest many other approaches and experiments to investigators in this field and are significant as a guide to other phenomena in hydrocarbon systems.

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(3) McBain, Ford and Wilson, *Kolloid. Z.*, **78**, 1 (1937).

Alkanolamines. VIII. Reaction of Ethanolamines on *p*-Nitrobenzoic Acid

BY M. MELTSNER, DANIEL GREENFIELD AND HARRY ROSENZWEIG

In some of the previous papers of this series^{1,2,3,4} it was shown that alkanolamines, but not their salts, may reduce an aromatic nitro group and that the unreduced and reduced compounds may form addition compounds with the alkanolamines. This is now confirmed by the following experiment on the action of ethanolamines on *p*-nitrobenzoic acid.

Experiment I.—One mole of ethanolamine and one mole of *p*-nitrobenzoic acid were heated at 100° for four hours. The brown solid residue, after extraction with ether and chloroform, was crystallized from alcohol. A white compound of m. p. 168° was obtained. An ether extraction of this substance from dilute hydrochloric acid yielded *p*-nitrobenzoic acid while the hydrochloric acid layer on evaporation gave a white solid, m. p. 82°, corresponding to ethanolamine hydrochloride. The white compound was therefore an addition product, $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}\cdot\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$.

Similarly diethanolamine yielded $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}\cdot\text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2$, m. p. 138°, and triethanolamine yielded $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}\cdot\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3$, m. p. 116°.

Experiment II.—One mole of ethanolamine was refluxed with one mole of *p*-nitrobenzoic acid in an oil-bath for two hours. The reaction mixture was treated several times with cold water and filtered. The filtrate was evaporated to dryness on the water-bath and the residue extracted with alcohol. Evaporation of the alcohol gave a solid identified as *p*-aminobenzoic acid by its positive test for the amino group, its melting point (186°) and the melting point of the dinitrobenzoate (195°). The dry residue, insoluble in alcohol, was recrystallized from hot water and gave $\text{NO}_2\text{C}_6\text{H}_4\text{COOH}\cdot\text{NH}_2\text{CH}_2\text{CH}_2\text{OH}$.

The residue, insoluble in cold water, was extracted with chloroform to isolate some more *p*-aminobenzoic acid and then recrystallized from hot water. There was obtained in large amounts a pale yellow compound, m. p. 130°, which was identified as the addition product of two moles of ethanolamine and one mole of azoxybenzoic acid: N calcd., 13.72; found, 13.64. The compound can be reduced to yield *p*-aminobenzoic acid. Hydrolysis of the compound with alkali gave *p,p'*-azoxybenzoic acid which was identified by means of its ethyl ester. Hydrolysis of the compound with hydrochloric acid yielded monoethanolamine hydrochloride.

Experiment III.—Four moles of diethanolamine and one mole of *p*-nitrobenzoic acid were heated for two hours at 180°. The reaction mixture was washed with chloroform, extracted with hot water and filtered. On cooling, yellow crystals are obtained and identified as *p*-aminobenzoic acid.

(1) Meltner, *et al.*, *THIS JOURNAL*, **57**, 2554 (1935).

(2) Kremer, *ibid.*, **59**, 1681 (1937).

(3) Kremer and Kress, *ibid.*, **60**, 1081 (1938).

(4) Meltner, *et al.*, *ibid.*, **60**, 1236 (1938).

The authors wish to express their thanks to Mr. Jack Riseman for assistance in connection with Experiment II.

DEPARTMENT OF CHEMISTRY
THE CITY COLLEGE
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NEW YORK, N. Y. RECEIVED JANUARY 27, 1940

The Oxidation-Reduction Potential of Vitamin K₁

BY BYRON RIEGEL, FERRIN G. SMITH¹ AND CARL E. SCHWEITZER

Because of the increasing physiological importance of oxidation-reduction systems, the oxidation-reduction potential of pure synthetic vitamin K₁ has been determined. Such potentials are also important for elucidating the structures of quinones and for this reason, at the suggestion of Professor L. F. Fieser, we first measured the potential of the vitamin in potent alfalfa concentrates. This value, 358 mv., in conjunction with the C-H analysis and the absorption spectrum first published by Dam, Karrer, *et al.*,² provided strong evidence that vitamin K₁ was a 2,3-dialkyl-1,4-naphthoquinone. This was evident from the values of Table I.

TABLE I

	E_0 in mv.
1,4-Naphthoquinone	484 ^a
2-Methyl-1,4-naphthoquinone	408 ^a 422 ^b
2,3-Dimethyl-1,4-naphthoquinone	340 ^a

^a L. F. Fieser and M. Fieser, *THIS JOURNAL*, **57**, 491 (1935).

^b J. W. H. Lugg, A. K. Macbeth and F. L. Winzor, *J. Chem. Soc.*, 1457 (1936).

This information together with other known facts led to the prediction of the first specific structure³ for vitamin K₁ which later proved to be correct.

Karrer and colleagues⁴ have reported the oxidation-reduction potential $E_m = +5$ mv. for vitamin K₁. It is not absolutely clear, from their experimental data, how their value compares with other quinone potentials because they did not use the customary method. However, from a consideration of the pH of the solvent used it seems that their value of the oxidation-reduction potential E_0 is about 400 mv. This estimation does

(1) Abbott Research Fellow.

(2) H. Dam, A. Geiger, J. Glavind, P. Karrer, W. Karrer, E. Rothschild and H. Salomon, *Helv. Chim. Acta*, **22**, 310 (1939).

(3) L. F. Fieser, D. M. Bowen, W. P. Campbell, M. Fieser, E. M. Fry, R. N. Jones, B. Riegel, C. E. Schweitzer and P. G. Smith, *THIS JOURNAL*, **61**, 1925 (1939).

(4) P. Karrer and A. Geiger, *Helv. Chim. Acta*, **22**, 945 (1939).

not take into account a possible junction potential.

In the fractionation of alfalfa extracts it was found that a stock solution of 3% vitamin K₁ concentration had the best keeping qualities and gave the most reliable potentials over a period of time. More highly refined concentrates showed considerable variation in both bioassay and potential upon storage. Because of these variations and the occasional presence of other substances which affected the oxidation-reduction curve it seemed advisable to delay publication until the determination could be made on the pure vitamin.

The length of time required to establish equilibrium (in some instances twenty-four hours for the complete titration) in the case of the refined concentrates made it necessary to employ a stable reference electrode. The Ag-AgCl electrode was found to be very suitable for this purpose since it is stable for at least several weeks.

The oxidation-reduction potential of pure vitamin K₁ was found to be 363 mv. at 20°.

Experimental

The preparation of the vitamin K active concentrates⁵ from alfalfa has been described. The synthetic vitamin K₁ used in this work was prepared according to the method of Fieser.⁶

In the solvent used, 95% ethanol 0.2 *N* in hydrochloric acid and 0.2 *N* in lithium chloride, the positive potential of the Ag-AgCl electrode against the hydrogen electrode in the same solvent was approximately 200 mv. This value varies somewhat in different lots of the same solvent depending on the exact chloride ion concentration. However, it is necessary to determine the potential against the hydrogen electrode only once for any one lot of solvent. In the solvent used for the determination of the potential of the pure vitamin the Ag-AgCl electrode gave a value of +203 mv. against the hydrogen electrode. The solubility of the vitamin at room temperature was found to be about 5 mg. per ml. in the above solvent. This same solvent was used to prepare the very dilute solution of titanium trichloride used in the potentiometric titrations. Both platinized and bright platinum electrodes were used and gave the same results although the platinized electrodes seemed to reach equilibrium more rapidly.

Two independent determinations, checking within 1 mv., gave a potential of +160 mv. for the vitamin against the Ag-AgCl electrode. Thus the vitamin potential, E_0 , against the hydrogen electrode is 363 mv. All measurements were made at 20°.

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(5) B. Riegel, C. E. Schweitzer and P. G. Smith, *J. Biol. Chem.*, **129**, 495 (1939).

(6) L. F. Fieser, *THIS JOURNAL*, **61**, 3467 (1939).

The Preparation of *unsym*-Difluorotetrachloroethane

BY WILLIAM T. MILLER

No very convenient methods for the preparation of *unsym*-difluorotetrachloroethane have appeared in the literature, although it has been synthesized by the chlorination of difluorotrichloroethane [$\text{CHCl}_2\text{CF}_2\text{Cl}$].¹ In this work, it was found possible to obtain the desired compound satisfactorily from trifluorotrichloroethane² [$\text{CF}_2\text{Cl}-\text{CCl}_2\text{F}$] and aluminum chloride. The simplicity of the experimental procedure and cheapness of the starting materials make the product readily available for the first time.

This reaction is not entirely a simple replacement of fluorine by chlorine as some gaseous products are formed³ and too long heating leads to the formation of hexachloroethane. It was probably for this last reason that Henne and Newman⁴ obtained little of the difluoro compound after refluxing trifluorotrichloroethane with aluminum chloride for forty-eight hours.

Experimental

Two hundred cc. of trifluorotrichloroethane² and 40 g. of finely powdered aluminum chloride were refluxed on a steam-bath for five hours. The surface of the aluminum chloride turned dark during this period. Distillation of the product through a 50×1 cm. column packed with glass helices yielded 51 g. of *unsym*-difluorotetrachloroethane, b. p. 90–91°, m. p. 40–41°, and a very small residue composed principally of hexachloroethane. The lower boiling material distilled almost entirely below 48° but was shown by freezing to contain appreciable amounts of $\text{CF}_2\text{ClCCl}_3$. Longer periods of reaction yielded increased quantities of hexachloroethane.

- (1) Locke, Brode and Henne, *THIS JOURNAL*, **56**, 1726 (1934).
- (2) "Freon 113" of Kinetic Chemicals, Inc., Carney's Point, N. J.
- (3) Compare U. S. Patent 1,994,035 (*C. A.*, **29**, 2974 (1935)).
- (4) Henne and Newman, *THIS JOURNAL*, **60**, 1697 (1938).

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Some Addition Compounds of Phthaleins and Metallic Salts*

BY GEORG SACHS AND LILI RYFFEL-NEUMANN

K. H. Meyer and A. Hantzsch in 1907¹ described some compounds produced by addition of metallic salts to phenolphthalein, its lactoid dimethyl ether and its quinonoid dimethyl ether ester in non-aqueous solvents. No compound

(* Contribution from the 2nd² Chemical Institute of the University of Vienna.

- (1) K. H. Meyer and A. Hantzsch, *Ber.*, **40**, 3479 (1907).

of this kind seems to have been prepared since except a zinc chloride addition compound of the hexamethyl ether of phloroglucin-phthalein.² It is surprising that these compounds are all colored, although the organic component might be colorless or even, as, *e. g.*, in the case of dimethoxyphenolphthalein, incapable of assuming a quinonoid structure.

By extending the Meyer and Hantzsch method to other phthaleins we found a number of definite types of addition compounds. As metallic salts we used stannic chloride and antimony pentachloride. Besides phenolphthalein and its dimethyl ether, the phthaleins we dealt with were 3,6-dimethylfluoran, fluorescein and the lactoid dimethyl ether of fluorescein. All addition compounds we obtained were colored. It may be pointed out that all phthaleins mentioned above give colored addition products with acids also and that there is a certain connection between those two series of addition compounds.

The substances were prepared by mixing the component solutions in the manner adopted by Meyer and Hantzsch, a deep tint indicating the formation of an addition compound. In several cases the metal chloride was added without solvent, or cooling was necessary. If the resulting substance did not separate by itself, it was precipitated by a second liquid.

The substances formed differed widely in their stability toward water. Those derived from dimethylfluoran were the most stable. Some of them were, because of their extreme sensitivity to moisture, obtainable only in a closed apparatus. A few substances were so unstable that they could not be weighed for testing and the analysis had to be limited to the determination of the proportion of some constituents. In such cases the addition of indifferent molecules of the solvent could not be controlled.

The compounds we prepared are collected in Table I. The compounds prepared by Meyer and Hantzsch from the same components are inserted and denoted by "M. and H."

The compound (4) mentioned by Meyer and Hantzsch could not be obtained. Instead compound (5) resulted, but, whereas Meyer and Hantzsch claim that the substance was formed slowly, (5) precipitated at once.

Except substance (9) which has a more complicated formula and substance (11) which is a salt

- (2) H. Lund, *Chem. Zentr.* **102**, II, 2695 (1931).

TABLE I
 REACTANTS, PROPERTIES AND ANALYSES OF THE ADDITION COMPOUNDS

No.	Phthalein	Metal chloride and mole ratio to one of phthalein	Solvent (and precipitant)	Description—Color and crystal form	M. P., °C.	Formula P =	Metal, %		Chlorine, %		Found
							Calcd.	Found	Calcd.	Found	
1	Phenol	1 SnCl ₄	Nitrobz. (CS ₂)	Red	78-79	P-SnCl ₄ ·BzNO ₂	Sn, 17.28	17.36	OCH ₃ , 4.52	4.28	
2		1 SnCl ₄	Anisole (CCl ₄)	Pale red		P-SnCl ₄ ·BzOMe	Sn, 0.83*	0.77*	N, 0.10*	0.11*	
3		1 SnCl ₄	Benzonitrile (CCl ₄)	Pale red		P-SnCl ₄ ·BzCN					
4	Phenol dimethyl ether ^a	1 SnCl ₄	Nitrobz. (CS ₂)	Red	128	P-SnCl ₄	Sn, 12.46	11.67			
5		1 SnCl ₄	Nitrobz. (CS ₂)	Pink		2P-SnCl ₄	Sb, 0.69*	0.69*			
6	3,6-Dimethyl-fluoran ^b	2 SbCl ₅	CCl ₄	Carmine		P-SbCl ₅	Sn, 17.03	17.88	15.18	15.18	
7		1 SnCl ₄	CCl ₄	Yellow		P-SnCl ₄	Sb, 20.16	21.35	24.10	24.39	
8		1 SnCl ₄	Anisole	Red rhombic and prism		P-SnCl ₄ ·BzOMe	Sn, 17.03	17.88	17.59	20.36	
9	3,6-Dimethyl-fluoran ^b	20 SnCl ₄	Anisole	Irregular lamina	139, dec.	2P-3SnCl ₄ ·2BzOMe	Sn, 21.53	22.53	23.51	25.73	
10		1 SbCl ₅	CCl ₄	Yellow	203	P-SbCl ₅	Sb, 19.42	19.80	28.27	29.32	
11		2 SbCl ₅	CH ₃ COOH	Or.-yel. needles recryst. from Me ₂ CO or CHCl ₃	203	P-SbCl ₅ ·HCl·AcH	Sb, 16.82	17.27	17.02	29.42	
12	Fluorescein	0.5 SnCl ₄	Nitrobz. (CCl ₄)	Yel.-brown		2P-SnCl ₄	Sn, 12.84	12.27	11.96	15.34	
12a		1 SnCl ₄	Nitrobz. (CCl ₄)	Yel.-brown		2P-SnCl ₄	Sn, 12.84	11.75	15.34	16.33	
13	Fluorescein dimethyl ether ^c	0.5 SnCl ₄	CCl ₄	Yellow		P-SnCl ₄	Sn, 19.13	18.95	22.86	23.61	
13a		1 SnCl ₄	CCl ₄	Yellow		P-SnCl ₄	Sn, 19.13	19.24	22.86		

* Analyses (M. and H. = analyzed by Meyer and Hantzsch) * indicates atomic ratio rather than % analysis
^a E. Grande, *Gazz. chim. ital.*, **26**, 1, 222 (1896); R. Meyer and O. Spengler, *Ber.*, **38**, 1328 (1905).
^b F. Kehrman and J. Knop, *ibid.*, **44**, 3510 (1911).
^c H. v. Liebig, *J. prakt. Chem.*, **88**, 26 (1913).

of the acid, HSbCl₆, all the compounds listed are included in four different classes: (A) SnCl₄·2P, substances (5), (12); (B) SnCl₄·P, substances (4), (7), (13); (C) SnCl₄·P·Solvent, substances (1), (2), (3), (8); (D) SbCl₅·P, substances (6), (10).

The chemical nature of the classes A, C and D seems to be clear. They are complex compounds of coordinated hexavalent tin or antimony, one molecule of the phthalein occupying a single coordination valence. The substances of class B may be interpreted by the hypothesis that the phthalein occupies two coordinated valences or they may be considered as bimolecular compounds with two coordination centers. They are mostly less deeply colored and are mainly formed if solvents lacking secondary valences are used.

GLASGOW, SCOTLAND RECEIVED SEPTEMBER 22, 1939

The Condensation of Phenol and Ethylene Oxide

BY RICHARD A. SMITH

The monophenyl ether of ethylene glycol was first prepared by the reaction between phenol and ethylene oxide in a sealed tube.¹ In this way, by heating at 180° for eight hours, we obtained an 85% yield based on the phenol.

More frequently, however, it has been prepared by the reaction of ethylene chlorohydrin with a phenol salt.² We find that using this latter method and refluxing the mixture for eight hours gives, after distillation through a 6-foot column and collection within 0.5°, 1.10 moles of phenoxy glycol (b. p. 165° at 80 mm.), or a 55% yield, from 2 moles of phenol. This same reaction, carried on in a sealed tube for eight hours, gives a 62.5% yield of the same purity.

We now find that by heating, without rocking, molar equivalents of phenol and ethylene oxide in an autoclave charged with hydrogen at tank pressure for four hours until the temperature reaches 200°, the pressure at that time being in excess of 2500 pounds per sq. in., and then allowing it to cool and redistilling the product in a vacuum, a yield of 94% of phenoxy glycol of the same purity is obtained.

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(1) Roithner, *Monatsh.*, **75**, 614 (1894).

(2) Bentley, Haworth and Perkin, *J. Chem. Soc.*, **69**, 164 (1896); Smith and Niederl, *This Journal*, **53**, 808 (1931); Bellman, U. S. P. 1,841,481 (1932).

The Physical Constants of Pentanol-3

BY FRANK C. WHITMORE AND J. D. SURMATTIS

Pure pentanol-3 was required in large quantity for work in progress in this Laboratory. Since the physical constants for the carbinol reported in the literature¹ show wide disagreement, a study was made on the purity of material synthesized in the laboratory and that obtained from Sharples Solvents Corporation.

Propionaldehyde, b. p. 48.0° at 736 mm., n_{20}^D 1.3636, was prepared by dehydrogenation of *n*-propyl alcohol with a copper catalyst. It was treated in four 8-mole lots with ethylmagnesium chloride in anhydrous ethyl ether. The crude product obtained in 67% yield after distillation through a column of approximately 25 theoretical

(1) Brunel, *THIS JOURNAL*, **45**, 1334 (1923); Lucas and Moyses, *ibid.*, **47**, 1460 (1925); Morris and Cortese, *ibid.*, **49**, 2644 (1927); Sherrill Otto and Pickett, *ibid.*, **51**, 3027 (1929); Timmermans and Hennaut-Roland, *J. chim. phys.*, **29**, 529 (1932); Clark and Hallonquist, *Trans. Roy. Soc. Can.*, [3] **24**, 115 (1930); Lauer and Stodola, *THIS JOURNAL*, **56**, 1216 (1934); Brooks, *ibid.*, **56**, 1998 (1934); Packendorff, *Ber.*, **67**, 905 (1934).

plates, was refractionated through a column, 2 × 260 cm. of the total condensation partial take-off type, having approximately 85 theoretical plates. From this distillation a yield of 90% of constant boiling and constant index material resulted. The boiling point was determined in a laboratory Cottrell apparatus, with a thermometer calibrated against one checked by the Bureau of Standards; the refractive index was determined by a Valentin refractometer: b. p. 114.4° at 740 mm., n_{20}^D 1.4104, d_{20}^4 0.8218.

Approximately 2800 g. of Sharples pentanol-3 was distilled through a column of approximately 16 theoretical plates, and then refractionated twice through the 85-plate column described above. Of the starting material 27% was obtained with the physical constants: b. p. 114.3–114.5° at 741.5 mm., n_{20}^D 1.4102–1.4104, d_{20}^4 0.8203.

SCHOOL OF CHEMISTRY AND PHYSICS
PENNSYLVANIA STATE COLLEGE
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COMMUNICATIONS TO THE EDITOR

THE TOTAL SYNTHESIS OF A NON-BENZENOID STEROID¹

Sir:

We reported in the last paper² that a derivative of hexahydronaphthalene results from the addition of maleic anhydride to 2,5-dimethyl-1,5-hexadiene-3-yne. It has now been found that an analogous reaction occurs when the hydrocarbon I³ is heated with one mole of maleic anhydride at 130° without solvent. The crystalline product, from ethyl acetate or benzene, has m. p. 249–251° (cor.) with decomposition, and is converted in low yield to 15,16-dihydro-17-cyclopenta[a]phenanthrene (III), m. p. 132–133° (cor.), by heating with palladium-charcoal. This hydrocarbon did not depress the m. p. of an authentic specimen⁴ kindly furnished by Dr. Erich Mosettig. *Anal.*⁵

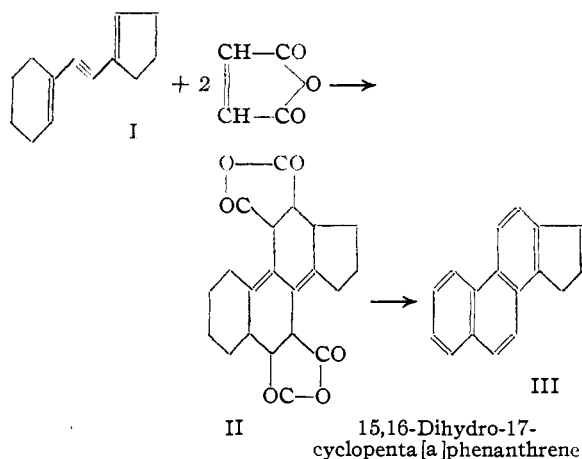
(1) This work is supported by Bankhead-Jones funds. (Not subject to copyright.)

(2) Butz, Gaddis, Butz and Davis, *J. Org. Chem.* (recently submitted for publication). The present communication is the fourth paper in the series "Synthesis of Condensed Ring Compounds."

(3) Pinkney, Nesty, Wiley and Marvel, *THIS JOURNAL*, **58**, 972 (1936).

(4) Burger and Mosettig, *ibid.*, **59**, 1307 (1937).

(5) By Arlington Laboratories, Arlington, Virginia.



Calcd. for $C_{21}H_{20}O_6$: C, 68.5; H, 5.5. Found: C, 68.7; H, 5.6. Calcd. for $C_{17}H_{14}$: C, 93.5; H, 6.5. Found: C, 93.5; H, 6.5. Structure II is tentatively assigned to the compound $C_{21}H_{20}O_6$ on the basis of analogy with the hexahydronaphthalene previously² described and the absorption curve of the solution in ethanol, λ max. 2555 Å., ϵ 19,000. It is suggested that a compound of this