the 162-membered polyethylene glycol are shown in columns three and four, respectively. Visually estimated intensities[7] are recorded in columns five (from Sauter's paper[4]), six (for the oxide), and seven (for the glycol), respectively.

In connection with the foregoing table the following remarks may be noted. Sauter's lines 1 and 2 apparently are present in traces on the best negatives for the oxide and glycol obtained in the present study but are too weak in intensity for measurement. Lines 3 and 5 would fall within about 0.2 mm. of the inner and outer edges of line 4 so that they would practically be unresolvable for the crystal-to-plate distance employed. The remainder of the data, however, appeared to be conclusive enough not to warrant the long exposure times necessary to bring out lines 1, 2, 3 and 5 at a longer crystal-to-plate distance. Certain groups of diffraction effects in Sauter's table appear as bands in the powder diagrams. In Table I these have been bracketed and the mean position of the observed band is given in columns 3 and 4. For example, Sauter's numbers 11, 12, 13, 14, 15 have sin θ values which would result in haloes falling within the inner and outer edges of the band on the present oxide negative whose mean position is given by a sin θ value of 0.231. Finally the very weak halo at sin θ = 0.482 (Sauter's No. 32) is present in the best negative for the glycol but is not included in Table I because it is too weak in intensity for accurate measurement.

The general agreement among Sauter's data for polymerized ethylene oxides, and the present data for the polymerized ethylene oxides and polyethylene glycols prepared by Pullman and Hibbert is very satisfactory. The only anomalous features are the absence of line 23 from the present polymerized ethylene oxide negatives, and the definitely stronger relative intensity of line 22 in the oxide compared with the glycol photographs. In this connection, however, it should be noted that line 23 is of weak intensity and is, moreover, clearly present on the glycol negatives. These features may be purely fortuitous or may have something to do with the relative physical characteristics of the samples. In general the glycols are more hygroscopic than the corresponding oxides, probably because the former comprise only one polymeric species while the latter probably contain appreciable fractions of higher (less hygroscopic) polymers. In comparing the relative intensities of Sauter with those observed in the present investigation it must also be borne in mind that the former were estimated on fiber diagrams whereas the latter were obtained from powder diagrams.

A consideration of the data presented in Table I, and a comparison between Fig. 1 of this paper and Fig. 2 of that of Sauter,[4] leads to the conclusion that, in so far as the diffraction of x-rays is concerned, there is no essential difference either between the polymerized ethylene oxides and the polyethylene glycols prepared by Pullman and Hibbert or between these and the polymerized ethylene oxides prepared by Lohmann for Sauter's investigation.

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[7] m. = medium; s. = strong; v. = very; w. = weak.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

A New Reagent for Structure Determination

BY RALPH CONNOR[1] AND JOHN H. VAN CAMPEN

In the identification of organic compounds those tests are especially valuable which can be carried out quickly on small amounts of material and which show, by the production of a color or precipitate, the presence of a specific group or structure. In work with active methylene compounds it has often been desirable to have a reliable *general* test for such substances. The production of colors with ferric chloride solution is limited in usefulness because many active methylene compounds (for example, the malonic esters) do not react with this reagent. The present paper describes a test which has frequently been of value and which, under the conditions specified later, is general for substances which contain hydrogen on a carbon atom bearing at least *one* acyl group or *two* other activating groups.

The test consists of the addition of an alcoholic solution of mercuric chloride to a solution of the unknown in alcohol containing sodium ethoxide.

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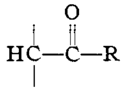
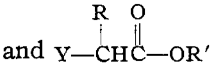
The formation of a *white* (or occasionally, cream-colored) precipitate is a *positive* test. The negative test is the formation of a deep yellow precipitate similar to that obtained when the sodium ethoxide and mercuric chloride solutions are mixed in the absence of an additional reactant.

Over two hundred organic compounds have been tested with this reagent and *it seems advisable to limit the test to neutral compounds which do not contain elements other than carbon, hydrogen and oxygen.* Considering this limitation, the classes of compounds with which the test will be concerned include ketones, aldehydes, esters, hydrocarbons, ethers, acetals, alcohols, quinones and anhydrides. Of these, the last five types fail to give a positive test. Aldehydes and ketones with hydrogen on the carbon atom bearing the carbonyl group give a positive test. The only esters which give a positive test are those which have both hydrogen and a labilizing group on the carbon bearing the carboxyl group. While acetylenes have not been investigated thoroughly, they apparently give a positive test and are certainly the only hydrocarbons to do so.

A few substances (such as anthrone) give colors with sodium ethoxide solution and others (such as ethyl formate) give white precipitates with sodium ethoxide; in such cases the results of the test are not significant. Likewise, the formation of reduction products of mercuric chloride should not be considered as either positive or negative, but merely as indicating the presence of a structure susceptible to oxidation.

The limitation of this test to neutral compounds containing no elements other than carbon, hydrogen and oxygen is imposed because the results of the test are anomalous when it is applied to other compounds. This is not a serious limitation, however, since many tests are available for acidic and basic compounds and for those containing elements in addition to carbon, hydrogen and oxygen. The test in its present form is specific for the structures  $\mathrm{H\overset{|}{\underset{|}{C}}{-}\overset{\overset{O}{\|}}{C}{-}R}$ and  $\mathrm{Y{-}\overset{\overset{R}{|}}{C}H\overset{\overset{O}{\|}}{C}{-}OR'}$ (where Y is a labilizing group and R may be hydrogen, alkyl or aryl); few tests are available for such structures. This is a quick and satisfactory method, for example, of distinguishing between mono- and di-substituted malonic esters and for detecting the presence of a monosubstituted product in a disubstituted malonic ester.

From the types of compounds which undergo the reaction and from the efficiency of sodium ethoxide as a catalyst, it seems probable that the reaction is one of the enol form. The mechanism of the mercuration may then involve addition to the double bond of the enol[2] or the formation of intramolecular chelation products similar to those proposed by Johnson[3] and by Carothers[4] for other reactions of similar systems.

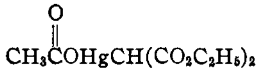
The reaction upon which this test is based is probably similar to that obtained by other workers[5] with mercuric compounds, but apparently sodium ethoxide is a more efficient catalyst and permits the omission of the periods of reflux previously used. As applied in this test, the reaction usually occurs instantly and always within a few minutes.

The compounds obtained from these reactions have been assigned various structures.[5] With malonic ester and mercuric chloride or mercuric acetate the possibilities suggested include the following

$\mathrm{Hg{=}C(CO_2C_2H_5)_2}$ $\mathrm{HOHgCH(CO_2C_2H_5)_2}$

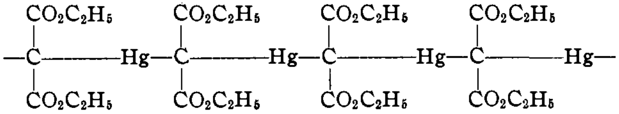
$\mathrm{(C_2H_5O_2C)_2CHHgCH(CO_2C_2H_5)_2}$

$\mathrm{(ClHg)_2C(CO_2C_2H_5)_2}$



$\mathrm{CH_3\overset{\overset{O}{\|}}{C}OHgCH(CO_2C_2H_5)_2}$

For the present purpose a discussion of the structures of the products is not pertinent. However, the possibility of the formation of structures similar to the following should be pointed out



$$\mathrm{-\overset{\overset{CO_2C_2H_5}{|}}{\underset{\underset{CO_2C_2H_5}{|}}{C}}-Hg-\overset{\overset{CO_2C_2H_5}{|}}{\underset{\underset{CO_2C_2H_5}{|}}{C}}-Hg-\overset{\overset{CO_2C_2H_5}{|}}{\underset{\underset{CO_2C_2H_5}{|}}{C}}-Hg-\overset{\overset{CO_2C_2H_5}{|}}{\underset{\underset{CO_2C_2H_5}{|}}{C}}-Hg-}$$

Although we have no definite evidence for such structures, the intractable nature of the products leads us to believe that linear polymers of this type may be formed.

Experimental Part

Procedure.—The mercuric chloride solution was prepared by dissolving 10 g. of mercuric chloride in 100 ml. of commercial absolute ethanol. The sodium ethoxide solution was prepared by dissolving 1.0 g. of sodium in 100 ml. of commercial absolute ethanol. For use by students it has been convenient to keep these solutions in indicator

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[2] Sandborn and Marvel, THIS JOURNAL, **48**, 1409 (1926); Griffith and Marvel, *ibid.*, **53**, 789 (1931); Wright, *ibid.*, **57**, 1993 (1935).

[3] Johnson, *ibid.*, **55**, 3029 (1933).

[4] Carothers and Berchet, *ibid.*, **55**, 2807 (1933).

[5] Hoffmann, *Ber.*, **31**, 2215 (1898); Biilmann, *ibid.*, **35**, 2571 (1902); Schoeller and Schrauth, *ibid.*, **42**, 777 (1909); Schrauth and Schoeller, *ibid.*, **41**, 2087 (1908); Naik and Patel, *J. Indian Chem. Soc.*, **9**, 185 (1932); *ibid.*, **9**, 533 (1932).

bottles fitted with medicine droppers. To 1 ml. of sodium ethoxide solution was added 2 drops of the unknown, followed by 5 drops of the mercuric chloride solution. The mixture was shaken vigorously and the result observed after one minute.

Influence of Conditions upon the Reaction.—The relative amounts of reactants indicated above were selected after a series of tests with acetophenone, using varying amounts of the mercuric chloride and sodium ethoxide solutions. An excess of mercuric chloride over that necessary for reaction with acetophenone gave a yellow-orange precipitate which masked the white. Mercuric acetate seemed to be fully as satisfactory as the chloride and gave the same type of products. Mercuric nitrate, however, was reduced by sodium ethoxide and was unsatisfactory. Mercuric sulfate was too insoluble for use in alcohol solution. Dilute aqueous potassium hydroxide solution could be used to replace the sodium ethoxide but the formation of the white product was very slow and it was necessary to allow the test to stand for some time before judging the results.

The results are summarized below. In the lists of compounds tested, compounds with more than one functional group are given with the last-discussed series; thus, ketonic esters are given with the esters, cyano esters with the nitriles, etc. In each series the compounds giving a white precipitate are listed under "positive," those giving a yellow or orange precipitate under "negative," and compounds which give other results are listed under "special reactions."

Neutral Compounds Containing no Elements Other than Carbon, Hydrogen and Oxygen

HYDROCARBONS

Positive—Phenylacetylene.

Negative—Benzene, 2-pentene.

ALCOHOLS

Negative—Allyl alcohol, ethyl alcohol, ethylene glycol, isoamyl alcohol, triphenylcarbinol.

ETHERS

Negative—Acetal, anisole, *n*-butyl ether, ethyl ether.

ALDEHYDES

Positive—Acetaldehyde, heptaldehyde.

Negative—Anisaldehyde, benzaldehyde, piperonal, *p*-tolualdehyde.

Special Reactions—Formaldehyde reduced the mercuric chloride and paraldehyde first gave a yellow precipitate which turned lighter on standing.

ANHYDRIDES

Negative—Acetic, benzoic, *n*-butyric, cinnamic and isobutyric anhydrides.

KETONES

Positive—Acetone, acetophenone, benzalacetophenone, benzylacetophenone, 2-butanone, *n*-butyrophenone, desoxybenzoin, dibenzoylmethane, 2-heptanone, *p*-methylacetophenone, 2-octanone, α,γ-dibenzoyl-β-phenylpropane, pinacolone, propiophenone, 2-undecanone.

Negative—Benzalpinacolone, benzophenone, xanthone.

Special Reactions—Anthrone, benzoin, furfuralacetophenone, mesityl oxide and phenanthraquinone gave such deep colors with sodium ethoxide solution that the color of the precipitate was obscured. Some of these also apparently caused reduction of the mercuric chloride. Carvone, cyclohexanone and 1,1-dibenzoylethane also gave slight colors with the sodium ethoxide solution but the precipitate formed when the mercuric chloride was added was distinctly white.

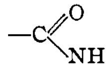
ESTERS

Positive—Ethyl acetoacetate, ethyl α-benzoylisovalerate, ethyl α-benzylacetoacetate, ethyl benzylmalonate, ethyl *n*-butylmalonate, ethyl α,γ-dibenzoyl-β-phenylbutyrate, ethyl α-ethylacetoacetate, ethyl ethylmalonate, ethyl malonate, ethyl α-methylacetoacetate, ethyl methylmalonate, ethyl phenylacetate, ethyl phenylmalonate, methyl phenylacetate.

Negative—Benzyl acetate, benzyl propionate, *n*-butyl acetate, ethyl acetate, ethyl benzoate, ethyl α-benzoylcinnamate, ethyl *n*-butyrate, ethyl cinnamate, ethyl crotonate, ethyl diethylmalonate, ethyl α-ethyl-β-hydroxybutyrate, ethyl isobutyrate, ethyl isovalerate, ethyl myristate, ethyl β-phenylpropionate, ethyl propionate, ethyl sebacate, ethyl succinate, isoamyl acetate, isoamyl benzoate, methyl benzoate, methyl cinnamate, methyl oxalate, phenyl acetate, triacetin.

Special Reactions—Ethyl α-acetyl-β-phenyl-γ-benzoylbutyrate and ethyl α-benzalacetoacetate gave colors with sodium ethoxide solution and the color of the precipitate formed when mercuric chloride was added could not be determined. Ethyl benzalmalonate and ethyl formate gave white precipitates with sodium ethoxide solution; however, the final reaction products were yellow.

Compounds Acidic or Basic or/and Containing Elements Other than Carbon, Hydrogen and Oxygen

Many *phenols* gave bright colors with sodium ethoxide solution and some reduced the mercuric chloride; only guaiacol gave a positive test. *Nitro compounds* gave negative tests in which the colors varied, depending upon the influence of sodium ethoxide on the nitro compound. Nitromethane, the only aliphatic nitro compound tested, gave a white precipitate with sodium ethoxide solution, but this became yellow when the mercuric chloride solution was added. No generalizations can be made concerning the behavior of *amines*—some gave positive tests, some negative tests and some reduced the mercuric chloride. The test may prove of some value with *amides*. It was found that the grouping  $—C\begin{matrix}{}^{\nearrow O}\\{}_{\searrow NH_2}\end{matrix}$ gave a positive test. The only exceptions were *o*-acetotoluide, which gave a positive test, and thiourea, which gave a black precipitate (mercuric sulfide). *Sulfonamides* ($—SO_2NH_2$), gave a negative test. All the *nitriles* tested (except ethyl cyanoacetate) gave a negative test. *Acids, salts of acids* and *quaternary ammonium salts* formed the yellow precipitate only. The specific compounds tested are listed below.

PHENOLS

Positive—Guaiacol.

Negative—*o*-Chlorophenol, *m*-cresol, *o*-cresol, *p*-cresol, β-

naphthol, phenol, phenyl salicylate, phloroglucinol, vanillin.

Special Reactions—Catechol, hydroquinone, orcinol and resorcinol monomethyl ether all gave colored solutions with sodium ethoxide. The first three of these also reduced the mercuric chloride. A color was also formed with sodium ethoxide and α-naphthol, but the precipitate formed with mercuric chloride was distinctly yellow. Resorcinol gave a negative test but the precipitate darkened on standing. Salicylaldehyde gave a white precipitate with sodium ethoxide; the addition of mercuric chloride solution gave a yellow solution but the white precipitate apparently remained.

Amines

Positive—*n*-Butylethylamine, diethylamine, isoamylamine, methyl anthranilate, *o*-toluidine.

Negative—1-Amino-2,4-dimethylaniline, aniline, *o*-anisidine, *m*-bromoaniline, *o*-bromoaniline, *p*-bromoaniline, di-*n*-butylamine, tri-*n*-butylamine, *p*-chloroaniline, N,N-diethylaniline, diphenylamine, N-ethylaniline, ethyl *p*-aminobenzoate, ethyl anthranilate, α-naphthylamine, nicotine, *m*-toluidine, *p*-toluidine.

Special Reactions—β-Naphthylamine and benzidine reduced the mercuric chloride. *p*-Aminoazobenzene, *p*-aminophenol and *p*-anisidine gave colors with sodium ethoxide solution and apparently reduced the mercuric chloride as well.

Nitriles

Positive—Ethyl cyanoacetate.

Negative—Acetonitrile, benzonitrile, isocapronitrile, phenylacetonitrile, *o*-tolunitrile, *p*-tolunitrile, *n*-valeronitrile.

Acids

Negative—Acetic acid, *m*-aminobenzoic acid, anthranilic acid, *p*-hydroxybenzoic acid, salicylic acid.

Special Reactions—Malonic acid formed a white precipitate when treated with the sodium ethoxide solution. Acids will give only a clear solution when the test is applied to them, unless an excess of sodium ethoxide is present. In the case of acetic acid, for example, it was necessary to add an additional portion of sodium ethoxide in order to obtain a precipitate.

Nitro Compounds

Negative—*o*-Bromonitrobenzene, *p*-bromonitrobenzene, *p*-chloronitrobenzene, *m*-dinitrobenzene, *o*-dinitrobenzene, methyl *m*-nitrobenzoate, *m*-nitroaniline, *p*-nitroaniline, *o*-nitroanisole, *p*-nitroanisole, *m*-nitrobenzaldehyde, *o*-nitrobenzaldehyde, nitrobenzene, *m*-nitrobenzoic acid, *o*-nitrobenzoic acid, *p*-nitrobenzoic acid, *p*-nitrobenzyl acetate, *p*-nitrophenol, *m*-nitrotoluene, *o*-nitrotoluene, *p*-nitrotoluene.

Special Reactions—2,4-Dinitrobenzaldehyde, *o*-nitroaniline, *o*-nitrophenol, picric acid and 1,3,5-trinitrobenzene gave colors with sodium ethoxide solution. Nitromethane gave a white precipitate with the sodium ethoxide solution but when a mercuric chloride solution was added, a yellow precipitate, characteristic of the negative test, was obtained.

Amides

Positive—Acetamide, *o*-acetotoluide, benzamide, α-bromopropionamide, urethan.

Negative—Acetanilide, β-acetonaphthalide, *p*-acetotoluide, benzanilide, N-methylacetanilide, phenacetin, phthalimide.

Special Reactions—*p*-Nitroacetanilide gave a colored solution with sodium ethoxide solution, but a typical negative test was obtained when the mercuric chloride solution was added. Succinamide was apparently quite insoluble in the sodium ethoxide solution and the addition of mercuric chloride solution gave a yellow precipitate; upon standing, however, a white precipitate was formed. Thiourea gave a negative test but the precipitate quickly became dark.

Salts

Negative—Ammonium benzoate, tetraethylammonium bromide, tetramethylammonium chloride, tetramethylammonium iodide.

Miscellaneous

Positive—Benzal-*p*-bromoacetophenone.

Negative—Benzenesulfonamide, *p*-bromobenzaldehyde, carbazole, *o*-chlorobenzaldehyde, *p*-chlorobenzyl acetate, dicresyl-*o*-sulfobenzoate.

Summary

A mercuric chloride test for structure determination has been described. It is recommended for use with neutral compounds which contain no elements other than carbon, hydrogen and oxygen; it gives a positive test with ketones and aldehydes which have hydrogen on the alpha carbon atom and with esters having at least one hydrogen and one labilizing group on the alpha carbon atom. The behaviors of over two hundred organic compounds with this reagent have been described.

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