with the large errors involved, this method unmistakenly indicates complete exchange in water and slightly acid solutions. It is possible, of course, that the sintered glass membrane, with its large amount of surface, might have catalyzed the exchange. However, the mobility experiments and the results of the ion-exchange separations also show complete exchange. It is interesting to note that the ferricyanide ions diffuse faster and also have the higher mobility.

Electron exchange between like-charged ions frequently has been found to be a slow process.[12] This can in part be attributed to the fact that the exchange path involves direct collision between highly charged species. The activation energy for such a process can be estimated to be at least 15 kcal./mole.[13]

It is interesting to note that all of the known examples of slow exchange involve positive ions so that the apparent inconsistency of our results with the ferrocyanide–ferricyanide system with the general pattern of behavior may be in some manner due to the fact that negative charges are involved. Thus the positive ion presumably would be present as aquo-complexes or at least as highly hydrated species and would present an external sheath mainly of hydrogen atoms, since the oxygen atoms in the water molecules should be oriented toward the metal ions. These peripheral hydrogens would be expected to bear a positive formal charge and this electron deficiency would reduce the chance of electron exchange on collision between two such ions.

On the other hand, the external nitrogen atoms in the cyanide complexes bear a negative formal charge and the central ion is thus surrounded by a sheath of electron rich atoms and this higher electron density may be responsible for the "anomalous" rapid exchange.

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(12) For a listing of many such reactions, see J. W. Gryder, *Trans. N. Y. Acad. Sci.*, II **12**, 18 (1949).

(13) M. H. Gorin, This Journal, **58**, 1794 (1936).

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The Reaction of Acrolein with Ethanol and Ethyl Orthosilicate[1]

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The reaction of acrolein with ethyl orthoformate and ethanol leads to the formation of acrolein diethyl acetal in 73% yield when ammonium nitrate is used as catalyst[2] or β-ethoxypropionaldehyde diethyl acetal (45% yield) if hydrogen chloride is the catalyst used.[3]

We have investigated the analogous reaction of acrolein with ethyl orthosilicate and ethanol, using the procedure reported for the preparation of β-ethoxybutyraldehyde diethyl acetal from crotonaldehyde.[4] Catalysis by either ammonium nitrate or hydrogen chloride gave β-ethoxypropionaldehyde diethyl acetal as the only identifiable acetal. The hydrogen chloride-catalyzed reaction was clean cut, resulting in a 76% yield. The use of ammonium nitrate as catalyst led to considerable tar formation, with a reduction in yield to 40%. The hydrogen chloride-catalyzed reaction of acrolein with ethanol alone gives a mixture of β-ethoxypropionaldehyde diethyl acetal (26% yield) and acrolein diethyl acetal (30% yield).[5]

Experimental

The ethyl orthosilicate (Carbide and Carbon technical grade) was distilled before use (b. p. 155–157° at 760 mm.). Eastman Kodak Co. acrolein was used.

Acetal Formation (Hydrogen Chloride Catalysis).—A mixture of 208 g. (1 mole) of ethyl orthosilicate, 56 g. (1 mole) of acrolein, 150 ml. (2.5 moles) of absolute ethanol and 5 ml. of a 4% solution of anhydrous hydrogen chloride in absolute ethanol was allowed to stand at room temperature for two weeks.

The mixture was then added with stirring to a solution of 100 g. (2.5 moles) of sodium hydroxide in 500 ml. of water at room temperature, and the resulting emulsion stirred for one hour. Then the organic material was extracted with ether and water salted out of the extract with anhydrous potassium carbonate. After drying over anhydrous potassium carbonate, the mixture was distilled through a short Vigreux column. Following the distillation of the ether and alcohol at atmospheric pressure, a yield of 133 g. (76%) of β-ethoxypropionaldehyde diethyl acetal, b. p. 71–73° at 13 mm., was obtained. No evidence of the presence of the lower boiling acrolein diethyl acetal was obtained. After redistillation at reduced pressure through a 60-cm. Fenske column, the acetal had the following physical properties: n^{25}_{D} 1.4035, d^{25}_{4} 0.880.

Acetal Formation (Ammonium Nitrate Catalysis).—The above proportions of reactants were used, except that the catalyst was 3 g. of U. S. P. ammonium nitrate. One month at room temperature was required for the odor of acrolein to disappear from the reaction mixture; workup of the mixture yielded 70 g. (40%) of β-ethoxypropionaldehyde diethyl acetal, together with a large amount of tar which precipitated when the alcohol was distilled from the mixture. When conducted at reflux temperature for ten to fifteen minutes, the reaction yielded a very small amount of acetal, and correspondingly more tar.

β-Ethoxypropionaldehyde 2,4-Dinitrophenylhydrazone (Not Previously Reported).—The acetal was hydrolyzed by warming with an equal volume of water containing a few drops of concentrated hydrochloric acid. One gram of the resulting aldehyde in this solution was added to a solution of 1 g. of 2,4-dinitrophenylhydrazine in 1 l. of 2 *N* hydrochloric acid. A precipitate was formed immediately. It was recrystallized twice from alcohol–water, giving shining yellow plates, m. p. 84.5–85.0° (cor.).

Anal. Calcd. for $C_{11}H_{14}N_4O_5$: C, 46.81; H, 5.00; N, 19.85. Found[6]: C, 46.61, 46.93; H, 4.86, 4.96; N, 20.64, 20.94.

Attempts to form the dinitrophenylhydrazone in the

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(1) This investigation was supported by the U. S. Navy Bureau of Ordnance under Contract NOrd 7386.

(2) Fischer and Baer, *Helv. Chim. Acta*, **18**, 514 (1935).

(3) Claisen, *Ber.*, **31**, 1014 (1898).

(4) Helferich and Hausen, *ibid.*, **57**, 759 (1924).

(5) Pingert, "Org. Syntheses," Vol. 25, p. 1 (1945).

(6) Analyses by Oakwold Laboratories, Alexandria, Va.

usual manner in boiling alcohol gave the corresponding acrolein derivative.

The semicarbazone could not be isolated.

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Di-(*p*-halophenyl)-methylcarbinols

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The miticidal activity of di-(*p*-chlorophenyl)-methylcarbinol[1,2] led to the synthesis of the analogous fluoro-, bromo- and iodocompounds. In each case the carbinol was made in good yield by the action of methylmagnesium bromide on the *p,p'*-dihalobenzophenone.[2]

The ultraviolet absorption spectra of these four carbinols, along with the unsubstituted diphenylmethylcarbinol, shown in Fig. 1, are of particular interest because of differences due to the halogen atoms. The chlorine, bromine and iodine compounds show pronounced maxima in the range of 225–240 mμ with a shift to the longer wave length for the iodine derivative. The iodine substituted carbinol is most strongly absorbent and its maximum is at the longest wave length, 240 mμ. The bromine and chlorine derivatives are both less absorbent, the former is slightly stronger, but the location of the peaks at 225–227 mμ is virtually identical. On the other hand, the fluoro- and the unsubstituted carbinols show no absorption peaks throughout the range observed (215–270 mμ).

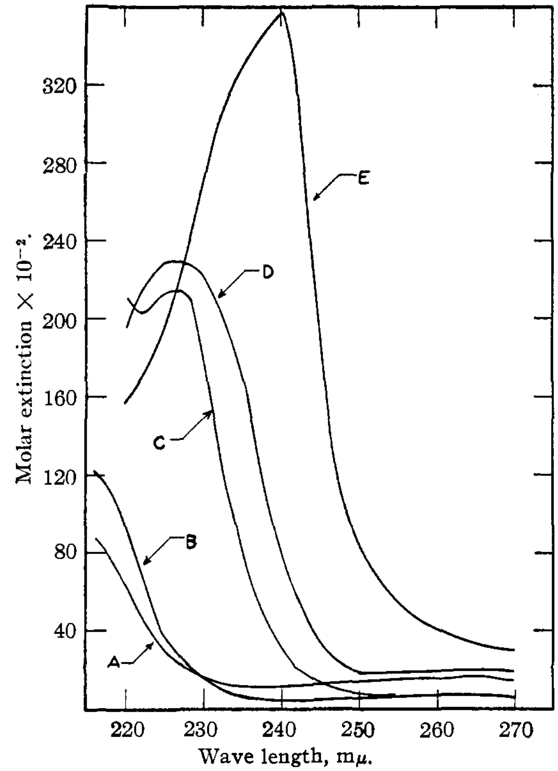

Fig. 1.—The ultraviolet absorption spectra of (A) di-(*p*-fluorophenyl)-methylcarbinol, (B) diphenylmethylcarbinol, (C) di-(*p*-chlorophenyl)-methylcarbinol, (D) di-(*p*-bromophenyl)-methylcarbinol, and (E) di-(*p*-iodophenyl)-methylcarbinol.

Experimental

Diphenylmethylcarbinol.—A sample melting 78–80° was made from phenylmagnesium bromide and ethyl acetate.[3]

Di-(*p*-chlorophenyl)-methylcarbinol.—A sample melting 69–69.5° was made from *p,p'*-dichlorobenzophenone and methylmagnesium bromide.[2]

Di-(*p*-fluorophenyl)-methylcarbinol.—The general procedure for this preparation and for the bromo- and iodocarbinols paralleled the preparation of the chlorocarbinol.[2] From 5 g. (0.023 mole) of *p,p'*-difluorobenzophenone (m. p. 105.5–107°) and 11.5 ml. of 2.2 *N* methylmagnesium bromide (0.025 mole) there was obtained 4.3 g., 80%, of carbinol as a light yellow oil which did not crystallize at 0°; $n^{25}\text{D}$ 1.5502.

Anal.[4] Calcd. for $C_{14}H_{12}OF_2$: C, 71.8; H, 5.17; F, 16.2. Found: C, 73.2; H, 5.20; F, 16.5.

p,p'-Difluorobenzophenone was obtained by the Friedel–Crafts reaction of fluorobenzene and carbon tetrachloride in 43% yield, m. p. 102–105°.[5]

Di-(*p*-bromophenyl)-methylcarbinol.—From 40.0 g. (0.089 mole) of *p,p'*-dibromobenzophenone (m. p. 173.5–175°) and 43 ml. of 2.2 *N* methylmagnesium bromide (0.095 mole) there was obtained 36.1 g. (88.7%) of crude carbinol melting 81.5–84°. Crystallization of 5 g. from petroleum ether (b. p. 60–70°) gave 3.2 g. melting 83.5–85.5°.

Anal. Calcd. for $C_{14}H_{12}OBr_2$: Br, 44.9. Found: Br, 45.2.

The *p,p'*-dibromobenzophenone was made in 23.4% yield by the Friedel–Crafts reaction of bromobenzene and carbon tetrachloride.[6]

The melting point of the carbinol, 83.5–85.5°, was almost identical with that of the 1,1-di-(*p*-bromophenyl)-ethylene, 84°, made by vacuum distillation of the carbinol.[7] To make certain that these were two different compounds a 5-g. portion of the carbinol was dehydrated by heating at 210° for twenty minutes, then refluxed with 5 ml. of 20% sulfuric acid for one-half hour. Crystallization of the crude ethylene from methanol gave 2.4 g. melting 84–85°. A mixed melting point of this ethylene with the carbinol was 57–69°.

Di-(*p*-iodophenyl)-methylcarbinol.—From 0.7 g. (0.0016 mole) of *p,p'*-diiodobenzophenone (m. p. 234–237°) and 5 ml. of 2 *N* methylmagnesium bromide (0.05 mole) there was obtained 0.5 g., 69.0%, of carbinol melting 108–109°. Two more crystallizations raised the melting point to 110–111°.

Anal. Calcd. for $C_{14}H_{12}OI_2$: I, 56.4. Found: I, 55.8.

This compound is not stable at room temperature. After a few weeks in a closed tube it turns yellow, there is an odor of iodine or possibly hydrogen iodide, and the iodine content found by analysis is lower than the calculated value.

p,p'-Diiodobenzophenone is a difficult ketone to obtain by the usual Friedel–Crafts routes. Iodobenzene with

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[1] U. S. Patent 2,430,586, November 11, 1947, R. F. Ruthruff, Oliver Grummitt and B. C. Dickinson.

[2] Grummitt, Buck and Becker, THIS JOURNAL, **67**, 2265 (1945).

[3] "Org. Syntheses," Coll. Vol. I, p. 226 (1941).

[4] By the Clark Microanalytical Laboratory, Urbana, Illinois.

[5] Bergmann, Hoffman and Meyer, *J. prakt. Chem.*, **135**, 245 (1932).

[6] Norris and Green, *Am. Chem. J.*, **26**, 497 (1901).

[7] Ashley, Grove and Henshall, *J. Chem. Soc.*, 261 (1948).