

rivatives were prepared. Diphenyl- β -naphthylmethyl chloride was obtained by the action of hydrogen chloride on the carbinol. When the chloride was treated with molecular silver, the free radical, diphenyl- β -naphthylmethyl, resulted.

2. The radical was isolated in the crystalline state. A careful study was made of its reactions with oxygen, iodine and acids, and of the effect of light. The conductivity of the free radical, diphenyl- β -naphthylmethyl, was determined in sulfur dioxide. The conductivities of the chlorides and bromides of triphenylmethyl, diphenyl- α -naphthylmethyl and diphenyl- β -naphthylmethyl were determined in both sulfur dioxide and hydrogen cyanide. These compounds, especially the bromides, were found to be good conductors. The molecular weight of diphenyl- β -naphthylmethyl was determined in 8 solvents whose freezing points covered the range from -22° to $+80^{\circ}$. It was found that the hexa-arylethane was dissociated from 15% to 50%.

3. Experiments were carried out to find what effect changes in concentration of the free radical would have upon the dissociation and upon the color of the solutions. It has been found that the resulting changes in color intensity are independent of the changes in dissociation. It has also been found that the changes in color intensity which result from variations in temperature are, again, not parallel to the changes in dissociation which are thus produced. These facts point to the conclusion that color formation in solutions of free radicals is not due wholly to dissociation of the hexa-aryl ethane into the tri-aryl methyl. The most satisfactory explanation of the facts is the hypothesis that in addition to dissociation we have tautomerization of the benzenoid tri-arylmethyl into the quinonoid form. The equilibrium between the dimolecular and monomolecular forms on the one hand and the equilibrium between the two monomolecular tautomers on the other hand, are not equally influenced by changes either in concentration or in temperature.

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NOTES

Addendum to "The Electron Theory of Valence as Applied to Organic Compounds."¹ In order to avoid any misunderstanding the following considerations on the rupture of carbon valences by oxidation, as emphasized by the author in lectures on the subject, should be included in the discussion of oxidation and reduction of organic compounds in the above named article. The discussion was not intended to be exhaustive but simply emphasized certain facts bearing on the subject.

¹ THIS JOURNAL, 46, 1293 (1922).

It is worthy of note that the rupture of the union of two carbon atoms by oxidation—involving the loss of two electrons by one of the atoms or jointly by both—takes place with particular ease when we have two neighboring carbonyl groups— CO.CO —, as in oxalic acid, ortho-diketones, etc. In this case there are no “exposed” valences as in the oxidation of an olefin to a glycol, an aldehyde to an acid, etc., which were emphasized as the *easiest* form of oxidation. But it is noteworthy that the structure is undoubtedly a highly *polar* one. Thus for oxalic acid, we have² $\text{H}^+ \text{O}^- \overset{\oplus}{\text{C}} \overset{\ominus}{\text{C}} \text{O}^- \text{H}$, and the high polarity of the field surrounding the

carbon atoms evidently loosens the union between the two and exposes the electrons held by them somewhat in the same way, but not going quite so far, as in the case of actual ionization in a similar field. For cyanogen $\text{N} \equiv \overset{\oplus}{\text{C}} \overset{\ominus}{\text{C}} \equiv \text{N}$, the nitrile of oxalic acid, the effect, as is well known, goes so far that we have actual hydrolysis, exactly as for chlorine, potassium cyanide and potassium cyanate being formed by the action even of aqueous alkali through a rupture of the $\text{C}^+ \text{C}^-$ union.

For dicarbonyl derivatives in general similar relations seem to underlie the break of a carbon chain with an escape of electrons.

The effect of neighboring highly polar charges is seen also in the oxidation of alcohols to aldehydes and ketones, which is, as it should be, not as easily accomplished as the further oxidation of an aldehyde to an acid.

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A Modified Schiff's Solution.—The writer has for some time desired a test solution for aldehydes which would overcome the patent objections to Schiff's solution, and which would at the same time have a chemical basis easily comprehended by the student of elementary organic chemistry. The objections to the use of Schiff's solution are (1) it stains the hands and clothing, (2) it requires several hours for preparation, especially if carefully made, using the minimum amount of sulfur dioxide, and (3) it may not be heated, and one has constantly to warn students to prevent them from falling into this error.

Various aldehyde tests are mentioned in the literature but they are in general of a complex nature, and not so easily carried out as the Schiff test. For this reason, experiments were made to vary the “reducing” agent used in the Schiff solution. It was found that much better results could be obtained by the substitution of sodium hyposulfite for sulfur

² Stieglitz, “Qualitative Analysis,” The Century Co., 1911, vol. II, p. 823.

dioxide. The solution made as outlined in this paper is perfectly colorless, will not stain the container nor the hands, and there are no precautions necessary for keeping it. It may be put in clear glass bottles and left unstoppered in the light. A very desirable feature is its ease of preparation; to make up a large quantity requires but a few minutes.

If this solution is boiled for 1 minute (no longer) it first becomes red, and then again practically colorless. It may now be heated in testing for aldehydes, in order to hasten the test. Used in this way the solution here described will give the aldehyde test in about half the time required for the ordinary Schiff test, although without heating the test is usually a little slower than with the Schiff solution.

A small amount of acid does not interfere with the test, but if the solution is to be heated, it should first be made neutral to litmus.

Directions for Preparation of Test Solution.—Rosaniline hydrochloride (0.005 g.) is dissolved in 50 to 100 cc. of hot water, filtered if necessary, diluted to 300 cc. and the solution well cooled with running water. To the cooled solution is added 6 g. of sodium hyposulfite ($\text{Na}_2\text{S}_2\text{O}_4$). This will completely dissolve in a few minutes, after which the solution is ready for use.

In the tests with aldehydes given in the Table 2 cc. of test solution was used, and about 2 drops of the substance being tested. The figures give the time in seconds for the development of a positive test.

	Schiff's solution ¹ Sec.	Modified solution Sec.	Mod. sol. previously boiled for 1 min. Sec.
Formaldehyde (40%).....	5	20	5
Acetaldehyde (conc.).....	5	10	3-5
Benzaldehyde.....	8-10	15-17	5-7
Citral.....	30-35	35-40	10-15
Furfural.....	6	20	10
Acetone.....	no test	no test	<i>faint</i> 20
Acetophenone.....	no test	no test	10-15
Alcohol.....	no test	no test	no test
Camphor (in alcohol).....	no test	no test	no test
Eugenol.....	no test	no test	<i>faint</i> 20-30
Allyl alcohol.....	<i>faint</i> 20-25	no test	no test

¹ Prepared from directions in Mulliken, "Identification of Pure Organic Compounds," J. Wiley and Sons, London, 1911, vol. I, p. 15.