evolution of hydrogen bromide yielded a bromide melting at 174–175°. The bromide was not the dibromide of *p*-methoxystilbene, m. p. 177°.

Preparation of α,β-Diphenylethyl Ether. (a) By the Action of Nitrogen Trioxide.—Seven grams of phenylbenzylcarbinol was dissolved in dry ether and nitrogen trioxide, obtained as before, passed into the solution overnight. The ether was evaporated and the residue extracted with methyl alcohol, which dissolved the unchanged carbinol, leaving 0.5 g. of a substance melting at 129–130°.

Several other experiments, in which dry nitrogen trioxide was used, failed to produce the compound.

(b) By the Action of Hydrochloric Acid.—Three grams of phenylbenzylcarbinol was dissolved in ether and 4 cc of concentrated hydrochloric acid and anhydrous calcium chloride were added. The mixture was allowed to stand for one hour and then refluxed for an hour. More anhydrous calcium chloride was added and the flask set aside for three and one-half days. The ether solution was filtered and evaporated. The residue was dissolved in hot methyl alcohol, and on cooling 1.95 g. of slightly impure carbinol crystallized out. This material was extracted with a small amount of methyl alcohol, which left 0.135 g. of ether melting at 123–127°.

Properties and Analyses of α,β-Diphenyl Ethyl Ether.—The ether was purified by recrystallization from boiling methyl alcohol. It crystallized in needles, m. p. 129.5–130.5° (uncorr.), was readily soluble in chloroform, slightly soluble in ether or alcohol and insoluble in petroleum ether.

Anal.[4] Subs., 0.0512: CO_2, 0.1675; H_2O, 0.0322. Calcd. for $C_{28}H_{26}O$: C, 88.88; H, 6.87. Found: C, 89.21; H, 7.04.

Mol. wt.: Calcd. for $C_{28}H_{26}O$: mol. wt., 378. Mol. wt. in camphor: subs., 0.0031; wt. of camphor, 0.0478; depression of melting point, 6.4°. Mol. wt. found: 383.8.

Summary

p-Methoxyphenylbenzylcarbinol and phenylbenzylcarbinol have been found to be dehydrated to their ethers under certain acidic conditions.

SALT LAKE CITY, UTAH

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

THE ABSORPTION SPECTRA OF THE GAMMA-PYRONES AND PYROXONIUM SALTS[1]

BY R. C. GIBBS, JOHN R. JOHNSON AND E. C. HUGHES[2]

RECEIVED JULY 15, 1930 PUBLISHED DECEMBER 18, 1930

The unusual properties of the pyrone ring have resulted in considerable speculation concerning its structure. Investigations of the physical and chemical properties of the compounds in this group have led to the formulation of several different structures for the nucleus, none of which has been firmly established or generally accepted.

[4] Analysis made by Mr. Berne Woolley of this Laboratory.

[1] The investigations upon which this article is based were supported by grants from the Heckscher Foundation for the Advancement of Research, established at Cornell University by August Heckscher.

[2] Heckscher Research Assistant in Chemistry and Physics at Cornell University, 1928–1930.

Qualitative investigations of the ultraviolet absorption spectra of γ-pyrone, γ-dimethylpyrone, some of their derivatives and their salts have been reported.[3] Xanthene and xanthone have been studied in relation to the flavones.[4] The absorption of chelidonic acid and pyrone have been examined quantitatively by Riegel and Reinhard.[5]

It has been suggested as a result of a number of investigations from different angles of attack that the products of the action of acids upon the pyrones are oxonium compounds.[6]

In order to clarify the problem we have made a quantitative study of the series: γ-pyrone, γ-benzopyrone (chromone) and xanthone, and some of their derivatives. The investigation of the ultraviolet absorption spectra has been made with the Hilger sectorphotometer method as employed by Orndorff, Gibbs and McNulty.[7] The cells used were 0.331 cm. and 1.00 cm. thick. Beer's law was found to hold for all of the solutions over the range of concentrations indicated in the legends on the graphs. The molecular absorption coefficient is represented by ϵ.

The spectra of the following compounds were examined in absolute alcohol and alcoholic hydrogen chloride: pyrone (Fig. 1, A and B), dimethylpyrone (Fig. 1, E and F), benzopyrone, (Fig. 2, D and E) and xanthone (Fig. 2, A and B). Since there is a partial dissociation of the hydrochloride of dimethylpyrone in ionizing solvents, the absorption was also measured in an ether solution of hydrogen chloride. Xanthone and dimethylpyrone were also examined in sulfuric acid. The compound of dimethylpyrone with dimethyl sulfate, which has been shown to be an oxonium compound[21] was examined in alcohol (Fig. 3, D) and, to obviate any effects due to dissociation, in pure dimethyl sulfate (Fig. 3, E). The curves for the acid solutions of each of these compounds resemble those for the neutral solutions, except that the bands are shifted slightly toward the red. It is evident, therefore, that the formation of oxonium complexes produces no profound change in the structure of the ring.

A possible objection which might be raised to the above conclusion is that Kendall[6e] has stated that the compounds of dimethylpyrone with numerous organic acids are colored. We have found that these compounds, when made from dimethylpyrone which had been sublimed and recrystal-

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[3] (a) Baly, Collie and Watson, *J. Chem. Soc.*, **95**, 144 (1909); (b) Boon, Wilson and Heilbron, *ibid.*, **105**, 2176 (1914); (c) Hantzsch, *Ber.*, **52**, 1535 (1919).

[4] Tasaki, *Acta Phytochim.*, **3**, 1 (1927); *C. A.*, **22**, 1591 (1928).

[5] Riegel and Reinhard, THIS JOURNAL, **48**, 1334 (1926).

[6] (a) Collie and Tickle, *J. Chem. Soc.*, **75**, 710 (1899); (b) Walden, *Ber.*, **34**, 4185 (1901); (c) Baeyer, *ibid.*, **43**, 2337 (1910); (d) McIntosh, THIS JOURNAL, **32**, 542 (1910); (e) Kendall, *ibid.*, **36**, 1222 (1914); (f) Rördam, *ibid.*, **37**, 557 (1915); (g) Gomberg and Cone, *Ann.*, **376**, 183 (1910). The last-named investigators are, however, opposed to the view that these salts are oxonium compounds.

[7] Orndorff, Gibbs and McNulty, THIS JOURNAL, **47**, 2767 (1925).

lized, are *colorless*. When a sample of Kahlbaum's dimethylpyrone was used without purification, as Kendall did, colored compounds were produced.

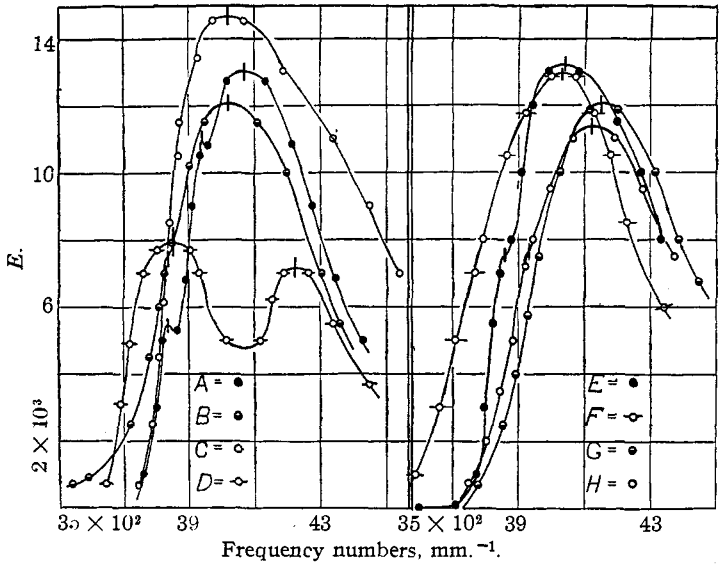

Fig. 1.—Pyrone: A, in alcohol (concn., 0.0002 to 0.00035 molar); B, same plus 5000 moles of HCl (concn., 0.0003 to 0.0005 molar). Dimethylpyrone: C, in water; D, in concd. sulfuric acid; E, in absolute alcohol, or the same plus 200 moles of sodium ethoxide; F, in absolute alcohol plus 200 moles of HCl; G, in anhydrous ether; H, same plus 2500 moles of HCl. The concentration range used in E, F, G and H was 0.0002 to 0.007 molar.

These observations lead to the conclusion that the structure of the nucleus of the pyrone ring is the same in the free pyrone as in the pyroxonium compounds. This is analogous to the similarity of the absorption spectra of the amines and the corresponding ammonium compounds.[8]

The earliest formula suggested for the pyrones is the ketone form, I, and the salts were considered to be the result of the addition of acid to either of the two oxygen atoms, II*a* and *b*. From a study of the absorption spectra Hantzsch[3c] made the suggestion that the salts were of the coördination type as shown in III. It was then suggested by other investigators[9] that an inner salt formula, IV*a*, would explain the anomalous properties of the pyrones. This formula is a modern conception of the formula IV*b* suggested by Baly[3a] in 1909. It is to be noted that the inner salt formula has a nucleus which is benzenoid and that the ketonic formula

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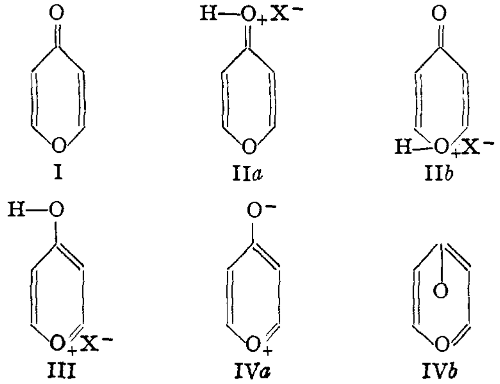
[8] Hartley, *J. Chem. Soc.*, **47**, 685 (1885); Baker and Baly, *ibid.*, **91**, 1122 (1907); Hantzsch, *Ber.*, **44**, 1783 (1911).

[9] Heilbron, Barnes and Morton, *J. Chem. Soc.*, **123**, 2559 (1923).



FORMULAS OF PYRONE AND PYROXONIUM SALTS

has a structure which is analogous to the quinoid structure in the benzene series. Heilbron, Barnes and Morton[9] suggest the possibility of an equi-

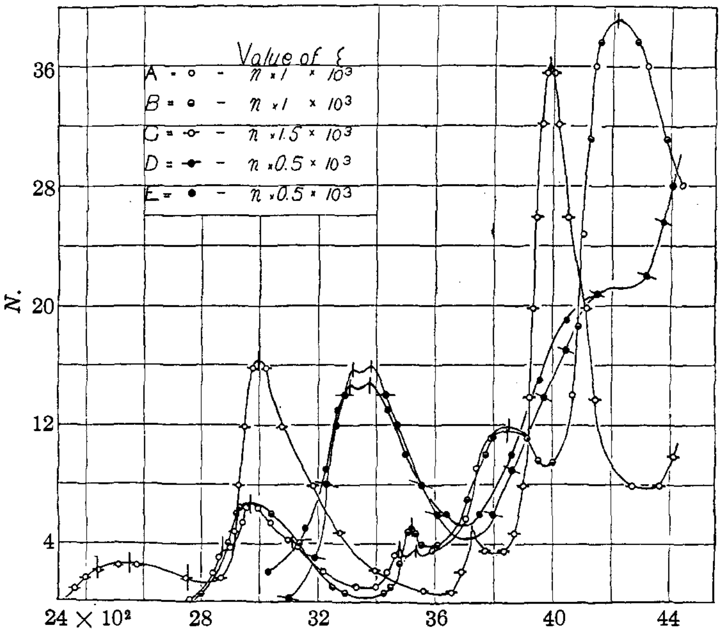


Fig. 2.—Xanthone: A, in absolute alcohol; B, same plus 5000 moles HCl; C, in concd. sulfuric acid. The concentration range used in A, B and C was 0.00003 to 0.005 molar. Benzopyrone: D, in absolute alcohol; E, the same plus 5000 moles HCl. The concentration range in D and E was 0.00005 to 0.005 molar.

librium existing between the two forms. Since the shift from the quinoid to the benzenoid type of structure always produces a marked change in the absorption spectrum, such an equilibrium could be detected by this method.

However, the absorption spectrum of dimethylpyrone in neutral alcohol is identical with that in alkaline alcohol (Fig. 1, E), and very similar to that in alcoholic hydrogen chloride (Fig. 1, F). This indicates that the pyrones do not exist in such an equilibrium in solution. Baly[3a] has reported a considerable difference between the absorption spectra in neutral and alkaline solutions. However, water was present in his solutions and it is known that the pyrone ring is unstable in the presence of aqueous alkali. In our measurements, on the other hand, absolute alcohol was used as the solvent.

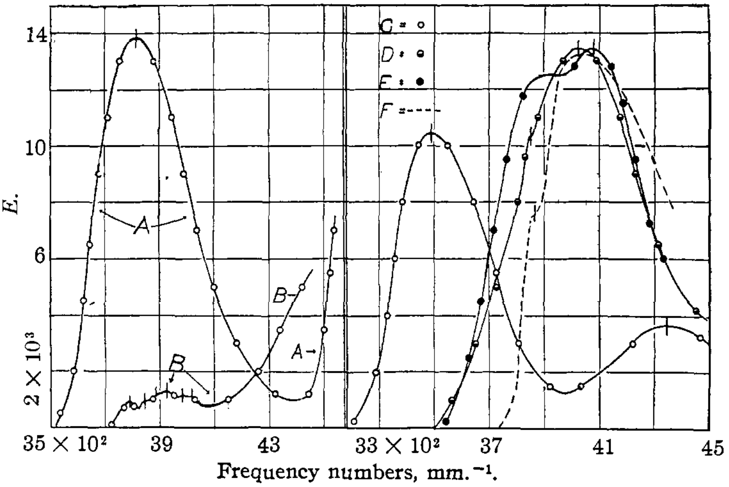
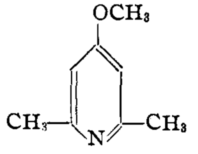
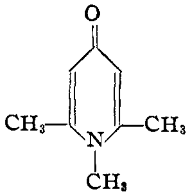


Fig. 3.—A, 1,2,6-Trimethyl-4-pyridone, in absolute alcohol (concn., 0.00035 to 0.004 molar); B, 4-methoxy-2,6-dimethylpyridine, in absolute alcohol (concn., 0.0007 to 0.004 molar); C, 2,4,6-trimethylpyroxonium perchlorate in alcohol (concn., 0.0004 to 0.0015 molar); D, dimethylpyrone + dimethyl sulfate in alcohol; E, dimethylpyrone in pure dimethyl sulfate (concn. of D and E, 0.0002 to 0.0017 molar); F, dimethylpyrone, see Fig. 1.

To obtain further information as an aid in deciding among the proposed structures, the product of the action of aqueous ammonia upon the oxonium complex of dimethylpyrone and dimethyl sulfate was studied. This reaction yields 4-methoxy-2,6-dimethylpyridine, V, a compound in which



V



VI

only the benzenoid structure is possible. The absorption spectrum of this substance is compared with that of its ketonic isomer, 1,2,6-trimethyl-4-pyridone, VI (Fig. 3, A and B). This comparison illustrates the great change in character and intensity of absorption that occurs upon transition from the benzenoid to the quinoid type of structure. The spectrum of the pyridone derivative bears a close resemblance to that of pyrone, but that of the pyridine derivative does not. This indicates that the pyrones and salts correspond to the ketonic formula. Evidently, as a result of the treatment with ammonium carbonate, the cyclic nucleus of dimethylpyrone has undergone a rearrangement. Since the product of this action is 4-methoxy-2,6-dimethylpyridine, it is assumed that the oxonium compounds are formed through the residual valences of the ketonic oxygen and not those of the ether oxygen. This assumption is supported by several investigators using different methods of study.[10] The free pyrone compounds would therefore be best represented by the ketonic structure I and the salts of the pyrones by the oxonium type of structure, II*a*.[11]

Xanthene and xanthydrol are known to have a quinoid type structure and have been examined in comparison with the absorption spectra of xanthone (Fig. 4, A and B). To illustrate the similarity between the absorption spectra of these three compounds, the frequencies of their maxima have been arranged in Table I.

TABLE I

ABSORPTION MAXIMA IN MM.$^{-1}$

Xanthone	2965	3470	3533	3850	4215
Xanthene		3425	3538		4050
Xanthydrol		3445	3533		4215

This would indicate that the pyrone group in xanthone is similar to the central portion of the molecule in xanthene and xanthydrol, that is, quinoid in structure.

In order to establish that the structure of pyrone and its derivatives is of the quinoid type, it would be desirable to show that analogous compounds, in which the structure is known to be of the benzenoid type, exhibit entirely different absorption spectra. The compounds resulting from the

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[10] Maass and McIntosh, THIS JOURNAL, **34**, 1273 (1912); Kendall and Carpenter, *ibid.*, **36**, 2498 (1914); Tschelinzeff, *Bull. soc. chim.*, [4] **35**, 741 (1924). The above statement should not be construed to mean that it is impossible for the ring oxygen to form an oxonium compound. The evidence is simply that the formation of oxonium compounds occurs with much greater ease through the ketonic oxygen, and that such oxonium compounds are much more stable than those derived from ethers.

[11] This would explain the failure of the attempts by Gibson and Simonsen [*J. Chem. Soc.*, 2307 (1928)] to resolve derivatives of pyrone in the form of salts. They conclude that their failure indicates that the salts have the coördination formula, III, but the attachment of the acid to the ketonic oxygen would also preclude the possibility of a resolution.

action of acids on xanthydrol have been formulated as oxonium compounds having a benzenoid structure[12] and should therefore show very different absorption spectra from those of xanthydrol, xanthene and xanthone in a neutral solvent. Trimethylpyroxonium perchlorate has also been formulated as being an oxonium compound of benzenoid structure.[13] A comparison of the absorption spectra of these oxonium salts with their pyrone analogs would possibly furnish information concerning the structure of the latter. However, the spectrum of xanthydrol in absolute alcoholic hydrogen chloride is identical with xanthene in neutral and acid solvents (Fig. 4, B). This indicates that the hydroxyl group has been directly replaced by chlorine without any profound change in the molecular structure. On the other hand, in concentrated sulfuric acid and in aqueous hydrochloric acid, xanthydrol exhibits an entirely different spectrum (Fig. 4, C).

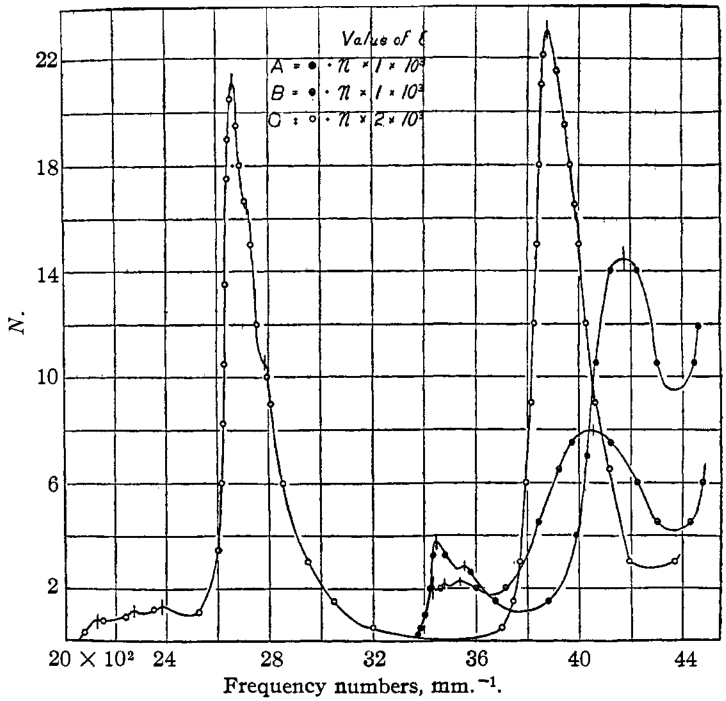

Fig. 4.—A, Xanthydrol in absolute alcohol (concn., 0.00025 to 0.001 molar); B, xanthene in alcohol, coincides with xanthene in 4 *N* alcoholic HCl and with xanthydrol in 4 *N* alcoholic HCl (concn. in all three cases, 0.00035 to 0.0017 molar); C, xanthydrol in concd. sulfuric acid (concn. 0.00008 to 0.005 molar).

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[12] Werner, *Ber.*, **34**, 3301 (1901).

[13] Baeyer and Piccard, *Ann.*, **384**, 208 (1911); **407**, 332 (1915). Hantzsch, Ref. 3c, reported the absorption spectra of this compound qualitatively.

This would indicate that the replacement or reaction of the hydroxyl group has been accompanied by a rearrangement of the cyclic nucleus.

Although the spectra of xanthydrol in the acid media differ greatly from those of xanthone, it would not be justifiable to draw conclusions as to the structure of the latter. There is considerable chemical evidence that the structure of the xanthydrol–acid complexes is not of the oxonium type.[14] The absorption spectra of fluoran[15] and of xanthene[16] in concentrated sulfuric acid are practically identical with that of xanthydrol in the same solvent. These two cannot rearrange in the way postulated for the formation of the oxonium compound of xanthydrol, without rupturing the molecule. The possibility is then indicated that the structure of these is not that of an oxonium compound. This would apply also to trimethylpyroxonium perchlorate, the spectrum of which is shown in comparison to that of dimethylpyrone (Fig. 3). If the structure is benzenoid, it should differ much more markedly from the spectrum of dimethylpyrone than it does. Hantzsch[3c] bases his deductions as to the structure of the pyrone salts upon the similarity of the spectra of these two series of salts. In the light of the above observations such a deduction is not justifiable until the structure of the perchlorate has been more firmly established.

The authors wish to acknowledge their indebtedness to Dr. C. V. Shapiro for many helpful suggestions during the course of this investigation.

Materials

The compounds used in this investigation were prepared and purified by the following methods; no particular care was given to the yield but only to the purity of the product. In the spectroscopical examination, two different samples were always used to aid in the detection of effects due to the possible presence of impurities. All melting points given are corrected.

Pyrone was prepared by the decarboxylation of chelidonic acid as described by Willstätter and Pummerer[17] and was purified by several fractionations under reduced pressure; b. p. 88.5° (7 mm.), m. p. 32.5°.

Dimethylpyrone was obtained from Kahlbaum, m. p. 132° before further purification. It was sublimed at 100° and twice recrystallized from redistilled ether; m. p. 132.1°.[18]

Benzopyrone (chromone) was prepared by the method of Ruhemann and that of Gomberg and Cone.[19] It was redistilled under reduced pressure and recrystallized from petroleum ether (boiling point, 70–80°). The melting point was 56° in accordance with Gomberg and Cone; Ruhemann gives 59°.

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[14] Gomberg and Cone, Ref. 6g and *Ann.*, **370**, 152 (1909).

[15] Orndorff, Gibbs and Shapiro, This Journal, **50**, 819 (1928).

[16] Unpublished data.

[17] Willstätter and Pummerer, *Ber.*, **37**, 3733 (1904).

[18] Collie, *J. Chem. Soc.*, **59**, 619 (1891).

[19] Ruhemann, *ibid.*, **77**, 984, 1123, 1184 (1900); Heywang and Kostanecki, *Ber.*, **35**, 2887 (1902); Gomberg and Cone, *Ann.*, **376**, 228 (1910).

Xanthone was prepared according to the directions of Holleman[20] and was recrystallized four times from 95% alcohol. A sample obtained from Kahlbaum was also purified and examined. Both samples melted at 174°.

4-Methoxy-2,6-dimethylpyridine was prepared from purified dimethylpyrone by forming trimethylpyroxonium perchlorate (m. p. 192–193°, with dec.), and treating this with a cold solution of ammonium carbonate. It was redistilled under reduced pressure; b. p. 99–100° (21 mm.); 203.5° (748 mm.); d_{16}^{24} 1.015.[21] The refractive index of the first and last drops of the fraction used was n_D^{20} 1.5082.

1,2,6-Trimethyl-4-pyridone was prepared from the above methoxylutidine by treatment of the methiodide with freshly precipitated silver oxide. It was crystallized twice from water and once from chloroform, and dried for two days at 140° under reduced pressure; m. p. 245°.[22]

Trimethylpyroxonium perchlorate was prepared by hydrolysis with perchloric acid of the product of the reaction between dimethylpyrone and methylmagnesium bromide. It was four times recrystallized from ethyl alcohol and from water; m. p. 242–245°.[23]

Xanthene was obtained by the reduction of purified xanthone with sodium in alcohol.[24] It was steam distilled and recrystallized twice from alcohol and dried at 50°; m. p. 101°. Examination of the absorption spectrum showed that it contained no xanthone.

Xanthydrol was made by the reduction of xanthone with sodium amalgam.[25] It was twice recrystallized from alcohol without heating the solution in order to prevent the formation of dixanthyl ether. It was dried under reduced pressure over sulfuric acid for three hours and used immediately; m. p. 123–124°.[26]

Absolute alcohol was obtained from the United States Industrial Alcohol Corporation and carefully redistilled before use. In special cases when particularly anhydrous conditions were required, this product was dried over calcium oxide.

Dimethyl sulfate was obtained from Kahlbaum and was dried and distilled under diminished pressure over barium oxide in an all glass apparatus. It did not give a test for free acid and was transparent to 2200 Å.

Summary

It has been observed that the ultraviolet absorption spectra of γ-pyrone, dimethylpyrone, benzopyrone and xanthone in acid solution are very similar to the spectra in neutral solution. These data lead to the conclusion that the formation of oxonium compounds in this series does not result in any profound change in the structure of the molecule.

The identity of the absorption spectra curves of dimethylpyrone in neutral and alkaline media, and their similarity to the curve in acid solution precludes the possibility of an equilibrium existing between two different types of structure of the ring.

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[20] "Organic Syntheses," John Wiley and Sons, New York, **1927**, Vol. VII, p. 84.

[21] Baeyer, *Ber.*, **43**, 2337 (1910); Baeyer and Piccard, *Ann.*, **407**, 337 (1914).

[22] Conrad and Eckhardt, *Ber.*, **22**, 81 (1889); Michaelis and Hanisch, *ibid.*, **35**, 3158 (1902).

[23] Baeyer and Piccard, *Ann.*, **384**, 215 (1911).

[24] Heller and Kostanecki, *Ber.*, **41**, 1325 (1908).

[25] "Organic Syntheses," John Wiley and Sons, Inc., New York, **1927**, Vol. VII, p. 88.

[26] Meyer and Saul, *Ber.*, **26**, 1276 (1893).

A resemblance between the absorption spectra of dimethylpyrone (and its salts) and 1,2,6-trimethylpyridone, a compound in which only the ketone structure is possible, and between those of xanthone and of xanthene and xanthydrol has been observed. On the other hand, it has been noted that the spectrum of dimethylpyrone differs greatly from that of 4-methoxy-2,6-dimethylpyridine, an analogous compound which has the benzenoid type of structure. From these observations the conclusion has been drawn that the structure of the pyrone and pyroxonium ring is best represented by a ketonic formula.

It has been pointed out that formulation of the salts of xanthydrol and of trimethylpyroxonium perchlorate as compounds of an oxonium type is open to question.

ITHACA, NEW YORK

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

ELECTROLYSIS OF GRIGNARD SOLUTIONS[1]

BY H. E. FRENCH AND MARY DRANE

RECEIVED JULY 22, 1930 PUBLISHED DECEMBER 18, 1930

In a previous article[2] there is described a series of experiments on the electrolysis of certain Grignard compounds in ether solutions, using platinum electrodes. The purpose of that investigation was to determine the quantity of a Grignard compound which is decomposed by one equivalent of electricity, and to determine the products resulting from that decomposition.

The present paper describes some experiments on the electrolysis of Grignard solutions using anodes of various metals with platinum cathodes.

Apparatus and Procedure

The electrolytic cells were made of glass tubing, and were approximately 200 × 40 mm. in size. These were closed with tight fitting cork stoppers through which the two electrodes were suspended close to the stoppers by copper wires. These electrodes were held parallel to each other and about 3 cm. apart by means of bent glass rods. Short-circuiting between the electrodes through the formation of bushy deposits of magnesium on the cathode was prevented by placing on the bottom of each cell a long glass rod with which such deposits were broken off by occasionally tilting the cell.

A glass tube of 1 cm. diameter was inserted through the center of each of the stoppers which closed the cells, and extended about 1 cm. beyond the inner faces of the stoppers. Through these tubes the cells were filled and emptied.

For anode materials the following metals were used, either in the form of the foil or as long narrow flat pieces of the metal: aluminum, tin, cadmium, zinc, bismuth, gold, silver and nickel. The areas of the anodes were approximately 20 sq. cm., while those of the platinum cathodes were about 10 sq. cm. In order to eliminate the magnesium

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[1] This paper is an abstract of the thesis submitted by Mary Drane in partial fulfilment of the requirements for the degree of Master of Arts at the University of Missouri.

[2] Gaddum and French, THIS JOURNAL, 49, 1295 (1927).