

was obtained, a yield of 60%. It was purified by repeated crystallization from isopropyl alcohol or 70% ethanol and was obtained as colorless prisms melting at 87° (corr.). It did not give a color reaction with alcoholic ferric chloride and was insoluble in alkali.

*Anal.* Calcd. for C<sub>19</sub>H<sub>19</sub>O<sub>4</sub>: C, 73.0; H, 6.41; OCH<sub>3</sub>, 19.9. Found: C, 73.0; H, 6.0; OCH<sub>3</sub>, 19.95.

All attempts to obtain a sodium enolate through the action of sodium hydroxide or sodium methylate were unsuccessful. No evidence of appreciable enolization was obtained.

Conversion to 2,5-diphenyl-2-methoxy-4-methylfuranone-3, XVI, was brought about in two ways: (a) a solution of 0.05 g. of XV in 10 cc. of saturated methanolic hydrogen chloride, allowed to stand overnight at room temperature, and worked up in the usual way, gave 0.03 g. (67%); and (b) 0.05 g. of XV in 10 cc. of acetic anhydride and one drop of concd. sulfuric acid, after standing for thirty minutes at room temperature, and hydrolyzed in water and worked up in the usual way, gave 0.035 g. of product (70%) which was identified by mixture melting point with an authentic sample.

A sample of XV was recovered unchanged after subjecting it to the action of sodium hydrosulfite in boiling 80% ethanol for thirty minutes.

**4 - Bromo - 2,5 - dimethoxy - 2,5 - diphenyl - 4 - methyl-tetrahydrofuranone-3, XIXa** (previously described as 3-bromo - 2,2 - dimethoxy - 1,4 - diphenyl - 3 - methylbutanedione-1,4,<sup>1b</sup> XIXb) was prepared according to the directions of Lutz and Stuart.<sup>1b</sup> Attempts to reduce the compound under the following conditions were without effect: (a) 0.1 g. was dissolved in 10 cc. of methanol containing 2 drops of concd. hydrochloric acid and an excess of potassium iodide, and the mixture was then refluxed for thirty minutes; and (b) 0.05 g. was dissolved in 5 cc. of concd. acetic acid, 0.5 g. of potassium iodide was added, and the mixture was boiled for five minutes. In both cases unchanged material was recovered and identified.

**Reduction** of 0.1 g. was effected in 10 cc. of 80% ethanol with 0.5 g. of sodium hydrosulfite upon refluxing the mix-

ture for thirty minutes with stirring. On dilution with water and extraction with ether 0.06 g. (84%) of 2,5-diphenyl-2-methoxy-4-methylfuranone-3 was isolated and identified by mixture melting point.

**Catalytic hydrogenation** of 0.05 g. with 0.05 g. of palladium on calcium carbonate as catalyst in 3 cc. of ethanol, using a semi-micro hydrogenation system, showed absorption of approximately the calculated amount of hydrogen. On filtering, evaporation of the solvent, and then crystallization from 70% ethanol, 0.03 g. of 2,5-diphenyl-2-methoxy-4-methylfuranone-3 melting at 64-65° was obtained and identified by mixture melting point with an authentic sample.

### Summary

The preparation, mechanism of formation, and proof of structure of 4,4-dimethoxy-1,4-diphenyl-1,3-butanedione enol are discussed.

The benzylation of 1,4-diphenyl-1,2,4-butanetrione sodium enolate has now been shown to give the carbon-benzoyl and both of the two possible oxygen-benzoyl derivatives, but the silver salt gives largely oxygen-benzoyl derivatives.

The reactions of 4,4-dimethoxy-1,4-diphenyl-1,3-butanetrione enol are reported and include the following: benzylation of the silver salt gives largely one of the two possible oxygen-benzoates; diazomethane converts the compound into the two expected structurally isomeric methyl ethers; bromination gives the bromo diketone; and methylation of the silver salt gives the carbon-methyl derivative.

The ketal obtained from 3-bromo-1,4-diphenyl-3-methyl-1,2,4-butanetrione is shown to have a cyclic structure.

UNIVERSITY STATION  
CHARLOTTESVILLE, VA.

RECEIVED MARCH 27, 1939

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

## Halogen Substituted Benzopyrylium Salts

BY R. L. SHRINER AND ROBERT BRUCE MOFFETT

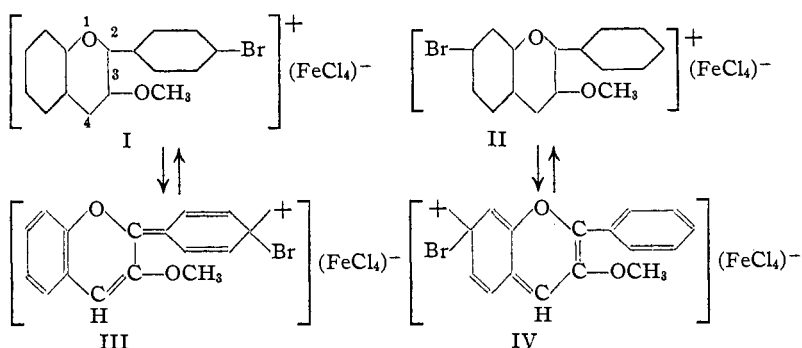
The general structure of the benzopyrylium salts has been established but the exact arrangement of the double bonds and assignment of a definite position to the positive charge have not been settled. Benzopyrylium salts differ from simple oxonium salts of ethers and  $\gamma$ -pyrones. The latter are produced by a pure addition reaction whereas the formation of benzopyrylium salts involves an actual reaction with an acid and elimination of water. In this respect they resemble the carbonium salts derived from triarylcarbinols

and hence it has been suggested that the benzopyrylium salts are carbonium or carbenium salts<sup>1</sup> in which the positive charge may be on either carbon atom 2 or 4 which has been designated as the "heteropolar atom." If this is the case it is possible that the carbonium ion may exist in several tautomeric (or resonance) forms.

(1) Dilthey, *J. prakt. Chem.*, **94**, 53 (1916); *ibid.*, **95**, 107 (1917); *Ber.*, **58**, 261 (1920); *J. prakt. Chem.*, **131**, 1 (1931); *ibid.*, **138**, 42 (1933); *Ber.*, **64**, 2082 (1931). See Hill, *Chem. Rev.*, **19**, 27 (1938); for a summary of the evidence bearing on the structure of benzopyrylium salts.

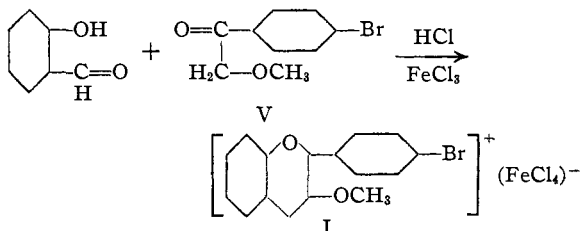
The purpose of the present work was to test this theory by preparing 3-methoxy-4'-bromoflavylium ferrichloride (I) and 3-methoxy-7-bromoflavylium ferrichloride (II) and to determine whether or not the bromine atom in each of these salts could be removed by silver nitrate, silver chloride, molecular silver or sodium ethoxide. If these molecules tautomerized to *p*-quinoid modifications (III and IV), the bromine atoms would be reactive since the structural arrangement is similar to that in allyl bromide.

Their behavior would parallel that of halogen substituted triarylmethyl derivatives in which a para-halogen atom has been shown to be reactive to molecular silver.<sup>2</sup> The bromine atom in 3-bromo-9-phenylxanthylum chloride was removed



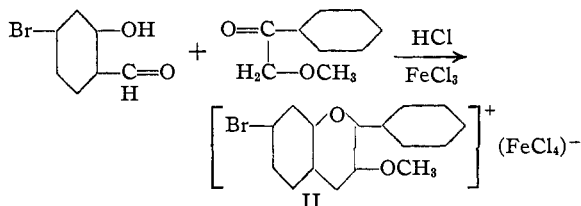
by treatment with silver chloride or hydrogen chloride.<sup>3</sup> However, chloro- and bromoflavylium perchlorates in which the halogens were in the 4'-, 6-, and 6,8-positions were found not to possess labile halogens.<sup>4</sup>

3-Methoxy-4'-bromoflavylium chloride was prepared by the direct condensation of salicyl aldehyde and *p*-bromo- $\omega$ -methoxyacetophenone (V) with dry hydrogen chloride. This method is similar to that used by Pratt and Robinson<sup>5</sup> for the preparation of 3-ethoxy-7-hydroxyflavylium chloride



The ferrichloride derivative (I) was prepared by the addition of ferric chloride to the flavylium chloride.

3-Methoxy-7-bromoflavylium ferrichloride (II) was prepared by a similar set of reactions from 4-bromo-2-hydroxybenzaldehyde and  $\omega$ -methoxyacetophenone.



Both of these benzopyrylium salts were treated with alcoholic silver nitrate, with silver chloride, and with molecular silver<sup>6</sup> and the precipitate of silver halide was examined for the presence of silver bromide. In none of the experiments could any silver bromide be detected. Concentrated hydrochloric acid and alcoholic sodium ethoxide also failed to remove bromine from these molecules.

This would seem to indicate that, at least in the case

of the simple 3-methoxy substituted flavylium salts, tautomerization to a quinoid structure does not take place.

During the study of the properties of these salts it was noted that they exhibited chemiluminescence when treated with dilute solutions of hydrogen peroxide and sodium hypochlorite.<sup>7</sup> Dilute acetone solutions of these benzopyrylium salts gave a bright flash of yellowish light when oxidized with the above reagents. The intensity of the light was not as great as that exhibited by 3-aminophthalhydrazide and the flash of light lasted only an instant. Ethanol solutions gave only a very dim flash of light due to the fact that flavylium salts react with the alcohol to produce an ethoxy<sup>8</sup> derivative.

## Experimental

*p*-Bromo- $\omega$ -methoxyacetophenone.—A modification of the method of Pratt and Robinson<sup>9</sup> for  $\omega$ -methoxyaceto-

(2) Gomberg, *Ber.*, **40**, 1847 (1907); Gomberg and Blicke, *This Journal*, **45**, 1765 (1923); Gomberg, *Chem. Rev.*, **1**, 91 (1924).

(3) Gomberg and Cone, *Ann.*, **370**, 142 (1909); Gomberg and West, *This Journal*, **34**, 1529 (1912).

(4) Le Fèvre and Le Fèvre, *J. Chem. Soc.*, 1988 (1932).

(5) Pratt and Robinson, *J. Chem. Soc.*, **121**, 1577 (1922).

(6) Gomberg and Cone, *Ber.*, **39**, 3274 (1906); Schmidlin, "Das Triphenylmethyl," Ferdinand Enke, Stuttgart, 1914, p. 52.

(7) Cottman, Moffett and Moffett, *Proc. Indiana Acad. Sci.*, **47**, 124 (1938).

(8) Hill and Melhuish, *J. Chem. Soc.*, 1161 (1935).

(9) Pratt and Robinson, *ibid.*, **123**, 745 (1923).

phenone was used. A solution of 9.4 g. of methoxyacetonitrile<sup>10</sup> in 50 cc. of dry ether was added with stirring to a solution of *p*-bromophenylmagnesium bromide which had been prepared from 4.5 g. of magnesium and 39.3 g. of *p*-dibromobenzene dissolved in 85 cc. of absolute ether and 60 cc. of dry benzene. The mixture was stirred for two hours and then decomposed by the addition of ice and dilute sulfuric acid. The ether layer was separated, the ether removed by distillation and the residue recrystallized from 40% alcohol with the aid of Norite. The yield was 15.5 g. (54%) of colorless crystals melting at 74–75.5°.

*Anal.* Calcd. for  $C_9H_9O_2Br$ : Br, 34.90; Found: Br, 34.53.

**3-Methoxy-4'-bromoflavylum Chloride and Ferrichloride.**—Dry hydrogen chloride gas was passed into a solution of 2 g. of *p*-bromo- $\omega$ -methoxyacetophenone and 1.07 g. of salicylaldehyde in 15 cc. of dry ether for two hours. The mixture was placed in the refrigerator for two days and the crystals of the salt which had separated were removed by filtration and recrystallized by solution in hot concentrated hydrochloric acid and again placing the filtered solution in the refrigerator. The crystals of the salt were removed by filtration and dried in a vacuum desiccator. About 2.5 g. of brown crystals was obtained which melted at 105.5–107° with decomposition. Analysis of this salt showed the presence of 16.41% ionic chlorine. This corresponds to the composition  $C_{16}H_{12}O_2BrCl \cdot (0.76 HCl)$ . A total halogen determination by the Parr bomb method and the above chlorine value showed 20.95% bromine. The calculated value for bromine in the above formula is 21.08%. Attempts to remove this excess hydrogen chloride without causing decomposition were unsuccessful and hence the ferrichloride derivative was prepared by adding a solution of ferric chloride in concentrated hydrochloric acid to a solution of the salt in concentrated hydrochloric acid. The ferrichloride salt separated and was removed by filtration. It was recrystallized twice from glacial acetic acid and thoroughly washed with absolute ether. Dark reddish-brown needles were obtained which melted at 148–150°.

*Anal.* Calcd. for  $C_{16}H_{12}O_2BrFeCl_4$ : C, 37.38; H, 2.34; Fe, 10.87; Cl, 27.62. Found: C, 37.65; H, 2.59; Fe, 10.99; Cl, 28.02.

**3-Methoxy-7-bromoflavylum Ferrichloride.**—Two grams of 4-bromo-2-hydroxybenzaldehyde, prepared by the Reimer-Tiemann reaction from *m*-bromophenol<sup>11</sup> according to the directions of Hodgson and Jenkinson<sup>12</sup> and 1.5 g. of  $\omega$ -methoxyacetophenone<sup>9</sup> were dissolved in 15 cc. of absolute ether, and dry hydrogen chloride was passed in. The solution turned first dark reddish-brown and then black, and at the end of two hours the mixture was jet black (greenish by transmitted light through thin layers). The mixture was allowed to stand overnight in the refrigerator but no solid separated. Evaporation of the ether left a black tarry mass. When this mass was extracted with hot concentrated hydrochloric acid, a solution was obtained which gave a small precipitate

of impure 3-methoxy-7-bromoflavylum ferrichloride upon the addition of ferric chloride dissolved in concentrated hydrochloric acid. This process of extraction was repeated about ten times until the precipitates became negligible in amount. The combined precipitates were then recrystallized from glacial acetic acid and washed with absolute ether. About 0.1 g. of fine clear yellow needles which melted at 182–185° was obtained.

*Anal.* Calcd. for  $C_{16}H_{12}O_2BrFeCl_4$ : C, 37.38; H, 2.34. Found: C, 37.52; H, 2.53.

**The Action of Molecular Silver on 3-Methoxy-4'-bromoflavylum Chloride and 3-Methoxy-7-bromoflavylum Ferrichloride.**—Both of these salts were tested as follows with molecular silver prepared according to the directions of Gomberg and Cone and Schmidlin.<sup>6</sup> About 0.01 to 0.015 g. of the flavylum salt was dissolved, or suspended, in about 2 to 5 cc. of the solvent and about 0.1 g. of molecular silver was added. The solvents used were as follows: with 3-methoxy-4'-bromoflavylum chloride, glacial acetic acid, benzene, nitrobenzene, acetophenone, pyridine, and 70% sulfuric acid; with 3-methoxy-7-bromoflavylum ferrichloride, glacial acetic acid, benzene, and acetone. The glass tubes containing these mixtures were sealed and shaken for four days. At the end of this time the tubes were broken open and the contents filtered. The precipitate was washed with acetone and water and then digested with dilute nitric acid in order to remove the excess metallic silver. The residual silver halide was tested for the presence of silver bromide by shaking the entire precipitate with 3 cc. of dilute sulfuric acid and 0.4 g. of zinc dust. After shaking this mixture for several minutes, it was filtered and the filtrate tested for bromide ion by means of the chlorine-water carbon tetrachloride test. A series of control tests were carried out using known mixtures of silver chloride and silver bromide. It was found that definite positive tests could be obtained with 0.2 mg. of silver bromide in the presence of 0.1 g. of silver chloride. The actual amount of silver chloride present made little difference as long as 0.2 mg. of silver bromide was present since this represented about the limit of the amount of bromine which readily could be detected by the chlorine water-carbon tetrachloride test.

In none of the experiments with the flavylum salts could any test for silver bromide be obtained.

**The Action of Silver Nitrate, Silver Chloride and Alcoholic Sodium Ethoxide on 3-Methoxy-4'-bromoflavylum Chloride and 3-Methoxy-7-bromoflavylum Ferrichloride.**—To about 20 mg. of the flavylum salt dissolved in acetone and water and strongly acidified with nitric acid, silver nitrate solution was added in slight excess. The solution was boiled for several minutes, filtered, and the precipitate washed with water and then with acetone, and then tested for bromide by the test described above. No trace of bromine could be found in either case.

To 10 to 30 mg. of each of the flavylum salts dissolved in 5 cc. of acetone, 150 mg. of freshly precipitated silver chloride was added and the mixture shaken for sixty-seven hours. The precipitate was found to contain no silver bromide.

A little of the flavylum salt was refluxed for ten minutes with alcoholic sodium ethoxide solution, diluted, cooled, and filtered. The filtrate was treated with silver nitrate

(10) Scarrow and Allen, *Org. Syntheses*, **13**, 56 (1933).

(11) British Dyestuffs Corp. and Hodgson, British Patent 200,714; *C. A.*, **18**, 274 (1924).

(12) Hodgson and Jenkinson, *J. Chem. Soc.*, 1740, 3041 (1927).

and the resulting precipitate tested for bromine. No trace of bromine could be found with either flavylum salt.

**Chemiluminescence of Flavylum Salts.**—The reagents<sup>7</sup> used were the following: (A) hydrogen peroxide solution 0.4%; (B) a solution of 50 cc. of 5% sodium hypochlorite was added to 350 cc. of water in which had been dissolved 20 g. of sodium hydroxide; (C) acetone solution of the flavylum salt (1, 5 and 10 mg. per 4 cc. solvent). In each test carried out in a dark room, 2 cc. of solution A, was added to 4 cc. of solution C and then 2 cc. of solution B added with shaking. A perceptible flash of light occurred with as little as 1 mg. of the salts and bright flashes were observed when 5 to 10 mg. were used. The flashes of light lasted only a second since the alkaline reagents rapidly destroy the salt structure. Alcohol solutions likewise gave only a very dim flash due to a reaction with the solvent.<sup>8</sup>

### Summary

Two flavylum salts, 3-methoxy-4'-bromoflavylum chloride and 3-methoxy-7-bromoflavylum chloride and their ferrichlorides have been prepared and the activity of the bromine atom tested. Molecular silver, silver nitrate, silver chloride or alcoholic sodium ethoxide did not remove the bromine from these salts which indicates that in these simple 3-methoxyflavylum salts no tautomerization to a quinoid structure takes place.

These flavylum salts were found to exhibit chemiluminescence when treated with dilute solutions of hydrogen peroxide and sodium hypochlorite.

URBANA, ILLINOIS

RECEIVED MARCH 9, 1939

[CONTRIBUTION FROM THE DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY, MCGILL UNIVERSITY<sup>1</sup>]

## Studies on Lignin and Related Compounds. XL. The Extraction of Birch Lignin with Formic Acid

BY MORRIS LIEFF,<sup>2</sup> GEORGE F. WRIGHT AND HAROLD HIBBERT

Conforming to the principle<sup>3</sup> that in the isolation of lignin the "extractant be considered as the first reagent in a series of reactions intended to prove structure," yellow birch wood was extracted with boiling formic acid in order to compare the properties of this birch lignin with others extracted by alternative methods.<sup>4,5</sup> The resulting extract was not so soluble as the corresponding acetic acid lignin<sup>4</sup> but it was comparatively free from hexoses and pentoses<sup>4</sup> and for this reason the conclusions to be drawn by comparison of the isolated and methylated lignins are of greater significance.

It was soon discovered that Grignard analyses *in dioxane* as a solvent were not reliable with the less soluble of these birch formic acid lignins and that *in pyridine* more satisfactory results were obtained. The lower values for active hydrogen and carbonyl obtained in dioxane are probably owing to incomplete reaction. This explains (Table I) the lower active hydrogen values obtained from the less soluble spruce formic acid lignin fraction better than the opinion previously offered,<sup>3</sup> namely, that the more insoluble fractions result

from increasing aggregation of the lignin complex because of intermolecular dehydration.

TABLE I

| Fraction                           | GRIGNARD ANALYSES OF SPRUCE FORMIC ACID LIGNINS |                         |
|------------------------------------|---|-------------------------|
|                                    | Chloroform-ether insoluble                      | Acetone-ether insoluble |
| OCH <sub>3</sub> , %               | 13.4  | 13.4                    |
| Grignard analyses {<br>in dioxane  | Act. H/kg.                                      | 4.6                     |
|                                    | RMgX added/kg.                                  | 0.7                     |
| Grignard analyses {<br>in pyridine | Act. H/kg.                                      | 6.8                     |
|                                    | RMgX added/kg.                                  | 3.1                     |
|                                    |   | 7.1                     |
|                                    |   | 3.3                     |

Comparison of the Grignard analyses in dioxane and pyridine for birch formic acid lignin (Table IV) indicates in like manner that both active hydrogen and carbonyl values are much lower in the former solvent. Just as the lower carbonyl value determined in dioxane (*ca.* 0.8 group/kg.) for spruce formic<sup>3</sup> and birch acetic<sup>5</sup> acid lignin persisted throughout the methylation process, so the higher value (*ca.* 2.7 group/kg., Table V, Column 8) likewise persists as the more nearly true carbonyl value when measured in pyridine (subtracting effects of normal ester and lactone linkages, Table IV, Column 9). Part of this higher carbonyl value (*ca.* 0.6–1.0 group per kg.) is accounted for by the carboxyl group in lignin,<sup>6,7</sup> which is not indicated

(1) With financial assistance from the National Research Council of Canada and the Canadian Pulp and Paper Association.

(2) Holder of a Bursary and Studentship under the National Research Council of Canada, 1936–1938.

(3) Wright and Hibbert, *THIS JOURNAL*, **59**, 125 (1937).

(4) Hunter, Wright and Hibbert, *Ber.*, **71**, 734 (1938).

(5) Bell, Cramer, Wright and Hibbert, *ibid.*, **71**, 746 (1938).

(6) Moore, Wright and Hibbert, *Can. J. Research*, **B15**, 532 (1937).

(7) Bell, Wright and Hibbert, unpublished results.