[Contribution from the Chemistry Laboratory of the State University of Iowa]

ISOBENZOPYRYLIUM SALTS. II. 1,3-DIPHENYL-2-BENZOPYRYLIUM SALTS

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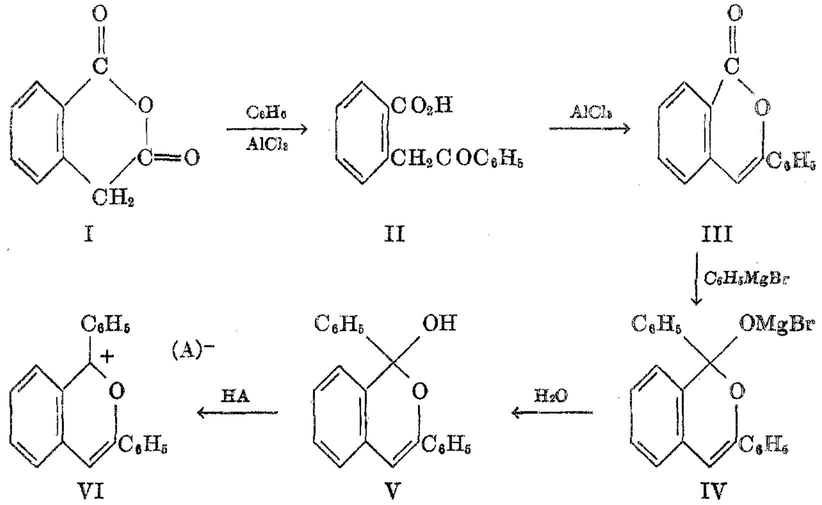
Only two examples of isobenzopyrylium salts have been described in the literature (1, 2). A third example of this type of cationic salt has now been synthesized by the reactions shown in Chart I.

CHART I



A^- is ClO_4^- ; Cl^-; $FeCl_4^-$; $FeBr_4^-$.

The intermediate, 3-phenylisocoumarin (III) had been previously made by Graebe and Trumpy (3) by the action of phosphorus pentachloride on *o*-carboxydesoxybenzoin (II) obtained by the Friedel-Crafts reaction between homophthalic anhydride (I) and benzene. In the present work it was found that both II and III were formed in this Friedel-Crafts reaction. Extraction of the crude product with cold sodium carbonate solution removed the acid (II) and left the 3-phenylisocoumarin as the insoluble fraction. Hot sodium carbonate solution hydrolyzes the isocoumarin (III) and, upon acidification, the *o*-carboxydesoxybenzoin (II) is obtained. The latter is converted to 3-phenylisocoumarin by refluxing a benzene solution with anhydrous aluminum chloride.

Addition of an excess of a solution of phenylmagnesium bromide to an ether solution of 3-phenylisocoumarin gave an addition compound (IV) which was hydrolyzed to the carbinol (V). This carbinol undergoes a double decomposition reaction splitting out water upon treatment with strong acids; *viz.*, perchloric

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acid, anhydrous hydrogen chloride, hydrochloric acid and ferric chloride, and hydrobromic acid and ferric bromide. The four orange to red-brown colored salts (Formula VI) were purified and analyzed.

The perchlorate salt (VI) was selectively ozonized. Decomposition of the ozonide by dilute alkali and hydrogen peroxide produced *o*-benzoylbenzoic acid (VII) and benzoic acid. This degradation and numerous prior studies (4) showing that Grignard reagents react with coumarins and isocoumarins by initial attack on the carbonyl function lend support to the reactions and structures in Chart I.

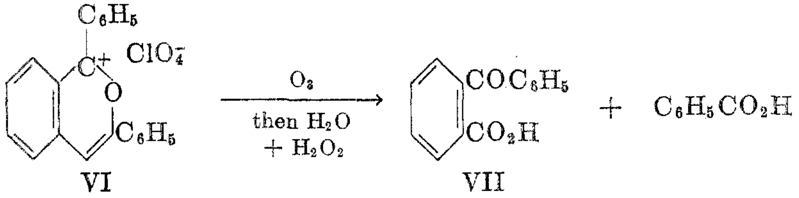
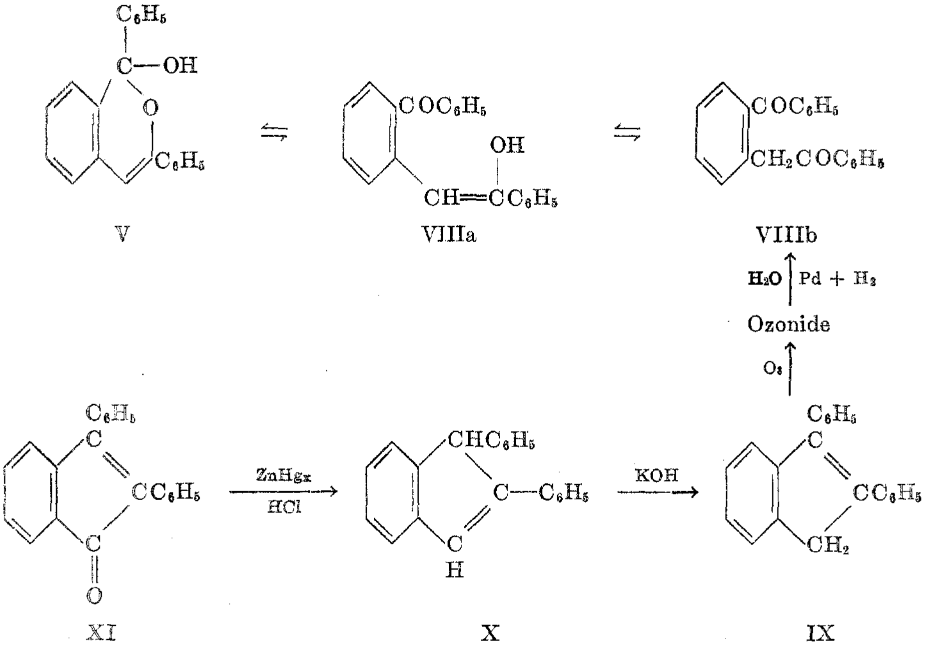


CHART II



However, the carbinol (V) could not be isolated as a pure crystalline solid. It separated as an oil which formed a glass on chilling. Structure V is that of a hemiketal which may be considered as derived from the enol form (VIIIa) of the diketone (VIIIb) (See Chart II). To test this idea a sample of the diketone (VIIIb) was synthesized starting with 2,3-diphenyl-1-indenone (XI) prepared by the procedures of Allen, Gates, and Van Allan (5). Clemmensen reduction of

XI did not produce IX, but gave a mixture of *trans*-1,2-diphenylindan and 1,2-diphenylindene (X). The latter was isomerized to 2,3-diphenylindene (IX) by the action of alcoholic potassium hydroxide. The structures X and IX and this isomerization have been established by Ruggli (6). The ozonide obtained from 2,3-diphenylindene (IX) was reductively cleaved by hydrogen and a palladium-on-charcoal catalyst to give a 35% yield of the diketone (VIII). Treatment of an absolute ether solution of this diketone with perchloric acid and acetic acid gave a low yield of 1,3-diphenyl-2-benzopyrylium perchlorate (VI) which was identical with that prepared by the sequence of reactions in Chart I.

The absorption spectra of 1,3-diphenyl-2-benzopyrylium perchlorate and ferrichloride were determined in ethylene chloride solution and are given by curves A and B of Figure 1. Curve C is that of *trans*-stilbene (compare with structure VI). Discussion and interpretation of these curves in terms of the possible resonance structures of VI is best deferred until more data is available.

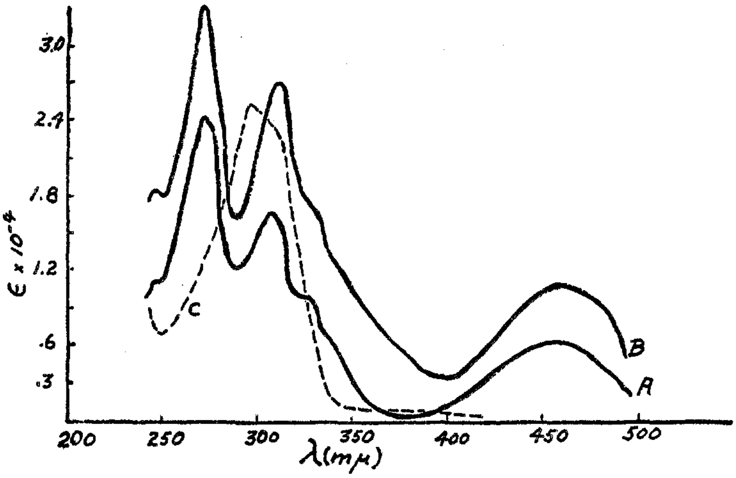


FIGURE 1. CURVE A, 1,3-Diphenyl-2-benzopyrylium perchlorate; B, 1,3-Diphenyl-2-ebnzopyrylium ferrichloride; C, *trans*-Stilbene.

EXPERIMENTAL PART

3-Phenylisocoumarin (III). To a mixture of 30 g. of homophthalic anhydride (7) in 300 ml. of thiophene-free dry benzene was added 36 g. of aluminum chloride with good stirring. The mixture was brought slowly to the boiling point and refluxed for 3 hours. After cooling the mixture, 200 ml. of water was added and the mixture acidified with concentrated hydrochloric acid. Benzene was removed by steam-distillation and the residue chilled and filtered. The solid mass was treated with 10% cold sodium carbonate solution which dissolved the *o*-carboxydesoxybenzoin present. The insoluble residue of impure 3-phenylisocoumarin was recrystallized from alcohol to give 5.7 g. of white crystals which melted at 88–89°, checking the value found in the literature (3).

The solution of *o*-carboxydesoxybenzoin (II) was acidified and 7.5 g. of free acid (m.p.

163°) collected. A mixture of 7.5 g. of *o*-carboxydesoxybenzoin and 400 ml. of benzene was distilled until the distillate was clear and free of water. Aluminum chloride (13.3 g.) was added to the remaining solution and this was refluxed with rapid stirring for 3 hours. Stirring was then slowed and 150 ml. of water cautiously added to the mixture; the solution was then acidified using 10 ml. of hydrochloric acid in excess and filtered while hot. The precipitate which separated was washed with warm dilute (3 *N*) hydrochloric acid and the washings added to the filtrate. The yield of 3-phenylisocoumarin (m.p. 88–89°) was 5.3 g. (70%). The filtrate was chilled and filtered yielding 2.7 g. of unchanged acid.

1,3-Diphenyl-2-benzopyrylium perchlorate (VI). A solution of 7.4 g. (0.03 mole) 3-phenylisocoumarin in 75 ml. of absolute ether was cooled to 0.5° and 0.09 mole of phenylmagnesium bromide in 75 ml. of ether was added with mechanical stirring. Stirring was continued for five hours at which time the complex formed was hydrolyzed with 42 g. of ammonium chloride in 245 ml. of water. The ether was separated and washed with distilled water and dried over magnesium sulfate. A cold solution of 6.35 ml. of perchloric acid in 25 ml. of acetic anhydride and 20 ml. of absolute ether was added to the dried ether solution at 0°. The orange red precipitate which separated was filtered. A small portion (0.5 ml.) of perchloric acid in 3 ml. of acetic anhydride was added to the filtrate and more crystals were collected. The salt was recrystallized from glacial acetic acid containing a drop of perchloric acid. Bright orange crystals (5.7 g., 45.3% yield) were obtained melting at 245–246°. Since these salts decompose explosively upon attempted combustion they were analyzed by determination of the perchlorate anion using tetraphenylarsonium chloride as the precipitant (2).

Anal. Calc'd for $C_{21}H_{15}ClO_5$: ClO_4, 26.01. Found: ClO_4, 26.36.

1,3-Diphenyl-2-benzopyrylium ferrichloride. The ferrichloride was prepared by the addition of 1.0 g. of ferric chloride dissolved in the minimum of hydrochloric acid, to an absolute ether solution containing 1 g. of the carbinol and 10 ml. of acetic anhydride at 0°. The ferrichloride was removed, yielding 0.65 g. (43%) of light orange crystals, m.p. 192–193°, after repeated recrystallization from glacial acetic acid, followed by washing with two 10-ml. portions of cold absolute ether.

The salt was analyzed for iron (8) and chlorine.

Anal. Calc'd for $C_{21}H_{15}Cl_4FeO$: Cl, 29.51; Fe, 11.62.
Found: Cl, 29.47; Fe, 11.38.

1,3-Diphenyl-2-benzopyrylium ferribromide. The ferribromide was prepared by the addition of 1.8 g. of ferric bromide dissolved in the minimum of hydrobromic acid, to an absolute ether solution containing 1.0 g. of the carbinol and 10 ml. of acetic anhydride at 0°. The ferribromide was removed and recrystallized from glacial acetic acid, followed by washing with two 10-ml. portions of cold absolute ether. Reddish-brown crystals (m.p. 190–191°) were obtained in 36% yield. They were analyzed for bromine and iron (8). The bromine was determined as either ionic bromine, or by the Leibig lime method (8) since a Parr bomb containing a sample of the ferribromide and sodium peroxide exploded violently.

Anal. Calc'd for $C_{21}H_{15}Br_4FeO$: Br, 48.52; Fe, 8.49.
Found: Br, 48.93; Fe, 8.79.

1,3-Diphenyl-2-benzopyrylium chloride. The chloride salt was prepared by bubbling an excess of anhydrous hydrogen chloride through an absolute ether solution of 1 g. of the carbinol. The salt was separated as light orange hygroscopic crystals (0.24 g., 28.3% yield) which melted at 165°.

Anal. Calc'd for $C_{21}H_{15}ClO$: Cl, 11.17; Found: Cl, 11.31.

Ozonolysis of 1,3-diphenyl-2-benzopyrylium perchlorate. A solution of 2 g. of the above salt in 2 l. of ethylene chloride was treated with 3% ozone for 2.3 hours. The solvent was removed under reduced pressure, 20 ml. of water was added, and the solution was warmed and made slightly basic with sodium hydroxide. Then 3 ml. of 30% hydrogen peroxide was added and the mixture boiled gently for three minutes. After cooling, the solution was extracted with ether which removed a small amount of dark red oil. The basic solution was acidified and extracted with ether. The ether layer was extracted with 10% sodium carbonate solution and this extract acidified and chilled in the ice box. White crystals of *o*-benzoylbenzoic acid which sintered at 92–93° and melted at 126–127° were obtained. When mixed with a known sample no depression of the melting point occurred. Kunckell and Knigge (9) report m.p. 93–94° for the hydrate and 127° for the anhydrous acid.

Upon concentration of the remaining solution and chilling, benzoic acid, m.p. 119–120°, was obtained..

2,3-Diphenylindene (IX). A solution of 75 ml. of alcohol and 5.8 g. of 2,3-diphenylindenone (5) was refluxed for 6 hours with 20 g. of zinc amalgam and 30 ml. of hydrochloric acid. The mixture was filtered and cooled. A white substance separated (1.4 g.) which upon recrystallization from Skellysolve "B" melted at 124–127°, in agreement with the melting point of *trans*-1,2-diphenylindan (10). The solution was concentrated and a second crop of crystals removed. Upon recrystallization from a mixture of Skellysolve "A" and "B", 2.5 g. of white crystals melting at 175–177° were obtained. This compound was identified as 1,2-diphenylindene (X) by its conversion to 2,3-diphenylindene (IX) upon heating with 1 g. of potassium hydroxide in 10 ml. of alcohol. White crystals of 2,3-diphenylindene (2.4 g.), m.p. 108° in accord with the literature value (6), separated on cooling the alcoholic solution.

α-(2-Benzoylphenyl)acetophenone (VIIIb). One gram of 2,3-diphenylindene in 25 ml. of ethyl acetate was treated with 3% ozone for one hour at −70 to −80°. The ozonide was reduced in a low-pressure hydrogenator for 19 hours at 30 lb. pressure in the presence of 0.1 g. of palladium-on-calcium carbonate catalyst. The solution was filtered and the solvent removed at reduced pressure. Approximately 0.4 g. (35% yield) of the ketone was isolated as a thick sticky liquid at room temperature which solidified upon cooling. No good method for purification could be found and the analyses showed that it was not pure.

Anal. Calc'd for $C_{21}H_{16}O_2$; C, 84.0; H, 5.33.

Found: C, 83.8; H, 4.83.

However, when an absolute ether solution of this oily diketone was treated with perchloric acid and acetic anhydride, orange crystals melting at 244–245° were obtained which were identical with those of 1,3-diphenyl-2-benzopyrylium perchlorate prepared by the action of phenylmagnesium bromide on 3-phenylisocoumarin.

SUMMARY

1,3-Diphenyl-2-benzopyrylium salts have been prepared and their structure established by ozonolysis.

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