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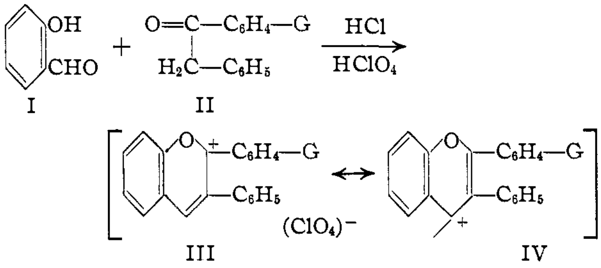
Benzopyrylium Salts. V. Preparation and Properties of Substituted 2,3-Diphenylbenzopyrylium Perchlorates

BY RICHARD R. OTTER[1] AND R. L. SHRINER[2]

Six new 2,3-diphenylbenzopyrylium perchlorates with methyl and methoxy groups in the *o*, *m*- and *p*-positions of the 2-phenyl group have been prepared by condensation of salicylaldehyde with the appropriate substituted desoxybenzoin. Conductivity studies of these salts, unsubstituted 2,3-diphenylbenzopyrylium perchlorate and tri-(*p*-anisyl)-carbonium perchlorate showed that they were all strong electrolytes in acetonitrile. The absorption spectra of these salts are also reported.

Although benzopyrylium salts have long been recognized as possessing reactive anionic groups,[3] no experimental evidence for their actual degree of ionization has been reported. Hence, a series of 2,3-diphenylbenzopyrylium perchlorates were synthesized and their conductivities studied.

Condensation of salicylaldehyde (I) with α-substituted acetophenones[4] (II) in absolute ether in the presence of hydrogen chloride and perchloric acid produced the substituted flavylium perchlorates. These may be represented by the allylic cationic resonance structures, III↔IV as far as their chemical properties indicate.[5]



G = $-CH_3$ and $-OCH_3$ in *o*-, *m*- and *p*- positions

The specific ketones used are listed in the first column of Table I and the flavylium salts derived from each in the second column.

TABLE I

(II), acetophenone	(III, IV) phenylflavylium perchlorates
α-Phenyl	3-
α-(*o*-Tolyl)-	2′-Methyl-3-
α-(*m*-Tolyl)-	3′-Methyl-3-
α-(*p*-Tolyl)-	4′-Methyl-3-
α-(*o*-Anisyl)-	2′-Methoxy-3-
α-(*m*-Anisyl)-	3′-Methoxy-3-
α-(*p*-Anisyl)-	4′-Methoxy-3-

These particular substituents (methyl and methoxy) were chosen because previous studies on the relative rates of hydrolysis of substituted benzyl bromides[6] showed that an ortho or para methoxyl group accelerated the rate by fifty times that of the unsubstituted benzyl bromide. A methyl group in the ortho or para position accelerated the rate only three to four times. This hydrolysis is usually considered a S_N1 reaction and the rate controlling step is the ionization of the halogen.[7] Since either of the resonance structures III or IV can be considered as derived from a substituted benzyl or cinnamyl derivative, the presence of methyl or methoxyl groups in the various positions in the benzene ring at position 2 might exert some influence on the dissociation as compared with the unsubstituted 3-phenylflavylium salt.

Accordingly, the conductivities of these salts

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[1] From a thesis submitted to the Graduate School of Indiana University in partial fulfillment of the requirements for the Ph.D. degree. Now at Notre Dame University, Notre Dame, Indiana.

[2] State University of Iowa, Iowa City, Iowa.

[3] Hill, *Chem. Revs.*, **19**, 27 (1936).

[4] Decker, *Chem. Zeit.*, **30**, 982 (1906); Perkin and Robinson, *Proc. Chem. Soc.*, **19**, 149 (1907); Decker and Fellenberg, *Ber.*, **40**, 3815 (1907); *Ann.*, **356**, 281 (1907); Perkin, Robinson and Turner, *J. Chem. Soc.*, **93**, 1085 (1908); see also ref. 5.

[5] Shriner and Moffett, THIS JOURNAL, **61**, 1474 (1939); **62**, 2711 (1940); **63**, 1694 (1941); **66**, 301 (1944). Shriner, Tappi Monograph No. 6, pp. 194–204 (1948).

[6] Shoesmith and Slater, *J. Chem. Soc.*, **125**, 2278 (1924); *ibid.*, 214 (1926); Shoesmith and Connor, *ibid.*, 1769 (1927). Waters and Lowry, "Physical Aspects of Organic Chemistry," D. Van Nostrand Co., New York, N. Y., 1936, p. 228.

[7] Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 113.

were determined in acetonitrile.[8] This solvent was chosen because all the salts were soluble in it without reaction and because it has a good dielectric constant of 36.7. The data obtained are given in Table III of the experimental part. For illustration, the data for four of the compounds are shown in Fig. 1, where the equivalent conductivity Λ, is plotted against the square root of the molar concentration, C. It will be noted that in dilute solution the points fall on a straight line. From

$$\Lambda = \Lambda_0 - (A + B\Lambda_0)\sqrt{C}$$

the Onsager equation the theoretical slope should be $-(A + B\Lambda_0)$ where Λ is the intercept with the conductivity axis. These theoretical slopes are shown by dashed lines in Fig. 1. A Shedlovsky[9] plot for obtaining Λ_0 was also made but gave values identical with those obtained by graphical extrapolation. The conductivity data for the other perchlorates also gave straight lines and show that all of the flavylium salts are strong electrolytes and practically completely dissociated in acetonitrile. The only differences due to the substituent methyl and methoxy groups are slight shifts in the intercept on the conductivity axis. These may be due to differences in the mobilities of the various cations.

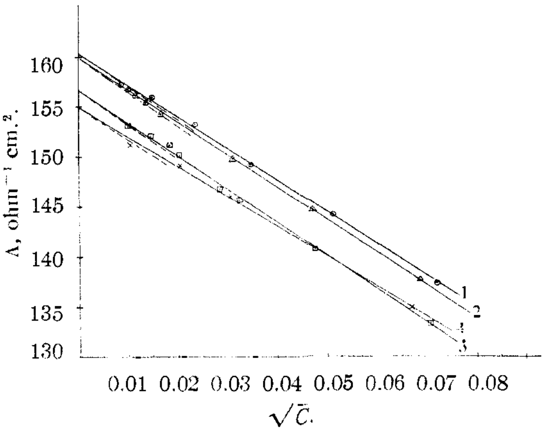

Fig. 1.—Conductivities in acetonitrile at 25°: 1, 3-phenylflavylium perchlorate, ⊙; 2, 2′-methyl-3-phenylflavylium perchlorate, ◬; 3, 4′-methoxy-3-phenylflavylium perchlorate, ⊡; 4, tri-p-anisylcarbonium perchlorate, ×.

For comparison, a sample of tri-(p-anisyl)-carbonium perchlorate[10] was prepared and its conductivity in acetonitrile determined. The data are shown by curve 4 in Fig. 1. The remarkable similarity of curve 4 with the curves for all the other benzopyrylium perchlorates, both as to slope and intercept, indicate the same general class of cationic resonance structures.

The absorption spectra of these benzopyrylium salts in ethylene chloride solution were determined and the data obtained are shown in Figs. 2 and 3. Since extensive absorption spectra data on compounds of the present type in ethylene chloride (or other similar solvents) are not available, the interpretation of the curves in Figs. 2 and 3 would depend on the contributions of the various resonance structures. There are ten cationic resonance structures (not counting Kekulé forms) which may be written for these flavylium salts. The structures III and IV (which are so useful in understanding the chemistry of their preparation and their reactions) represent only two of the possibilities.

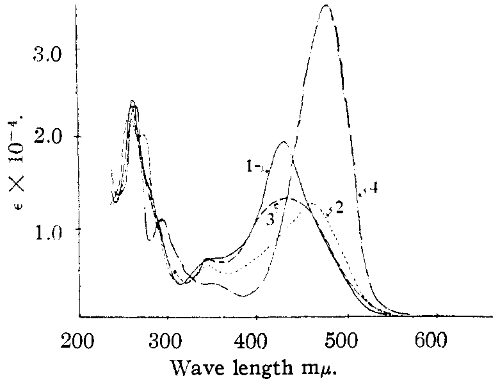

Fig. 2.—Absorption spectra in ethylene chloride: 1, 3-phenylflavylium perchlorate; 2, 2′-methoxy-3-phenylflavylium perchlorate; 3, 3′-methoxy-3-phenylflavylium perchlorate; 4, 4′-methoxy-3-phenylflavylium perchlorate.

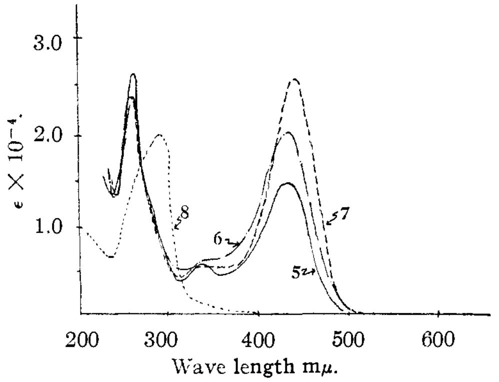

Fig. 3.—Absorption spectra in ethylene chloride: 5, 2′-methyl-3-phenylflavylium perchlorate; 6, 3′-methyl-3-phenylflavylium perchlorate; 7, 4′-methyl-3-phenylflavylium perchlorate; 8, *trans*-stilbene.

Experimental Part

α-Substituted Acetophenones.—Four of the intermediate ketones listed in Table I were made by the action of benzylmagnesium chloride on the substituted benzonitrile. The procedure for α-(o-tolyl)-acetophenone will illustrate the general method.

A solution of 29.5 g. (0.25 mole) of o-tolunitrile in 100 ml. of dry ether was added with good stirring to 500 ml. of an ether solution containing 1 mole of benzylmagnesium chloride over a period of 20 minutes. The mixture was stirred for 1.5 hours, allowed to stand for 12 hours and poured on a mixture of 1 kg. of cracked ice and 400 ml. of concentrated hydrochloric acid. The precipitate was removed by filtration, suspended in 300 ml. of water and heated to boiling. Upon cooling a yellow oil separated. The water layer of the filtrate was separated and heated under reduced pressure to remove the dissolved ether and then heated to boiling. On cooling a yellow oil separated from this solution also. Both of these oils were extracted with ether and combined. The combined extracts were dried over calcium chloride, the ether was removed by distillation and the residual oil was distilled under reduced pressure. The yield was 36.1 g. (68%) of a slightly yellow liquid which boiled at 184–189° (15–19 mm.), n^{20}_D 1.5789, d^{20}_4 1.0741.

This ketone had been prepared by Mailhe[11] but not

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[8] Walden, *Z. physik. Chem.*, **144**, 269 (1929).

[9] Shedlovsky, THIS JOURNAL, **54**, 1405 (1932).

[10] Hofmann, Kirmreuther and Thal, *Ber.*, **43**, 185 (1910).

[11] Mailhe, *Bull. soc. chim.*, **15**, 324 (1914).

characterized. Hill and Short[12] prepared the 2,4-dinitrophenylhydrazone which they describe as yellow plates from ethyl acetate and alcohol melting at 146–147°. The 2,4-dinitrophenylhydrazone of the above ketone was made. It crystallized as yellow plates from ethyl acetate and alcohol but melted at 191–191.5° (cor.).

Anal. Calcd. for $C_{21}H_{18}O_4N_4$: N, 14.35. Found: N, 14.46.

α-(*m*-Tolyl)-acetophenone.—By a similar procedure there was obtained a 69% yield of this ketone (Mailhe)[11] from *m*-tolunitrile and benzylmagnesium chloride. It was a solid which melted at 51–52°. Its semicarbazone melted at 183–184°.

Anal. Calcd. for $C_{16}H_{17}ON_3$: N, 15.80. Found: N, 15.58.

α-(*o*-Anisyl)-acetophenone.—A 74.6% yield of this ketone was obtained by treating 0.5 mole of *o*-methoxybenzonitrile with 2 moles of benzylmagnesium chloride according to the same procedure as above. It was an oil which distilled at 181–183° (6 mm.), $n^{20}{}_D$ 1.5888, $d^{20}{}_4$ 1.1235.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.50; H, 6.26.

A semicarbazone was prepared and recrystallized into monoclinic crystals from ethyl alcohol; m.p. 198–200° (cor.).

Anal. Calcd. for $C_{16}H_{27}O_2N_3$: N, 14.83. Found: N, 14.77.

α-(*m*-Anisyl)-acetophenone.—A 70% yield of this ketone was obtained by the general method. It boiled at 187–189° (7 mm.) and solidified on standing. Recrystallization from ligroin (70–90°) gave white needles; m.p. 41–42°.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24. Found: C, 79.43; H, 6.28.

A semicarbazone was prepared and recrystallized from ethyl alcohol; m.p. 152–154° (cor.).

Anal. Calcd. for $C_{16}H_{17}O_2N_3$: N, 14.83. Found: N, 14.67.

α-(*p*-Tolyl)-acetophenone.—A solution of 155 g. (1 mole) of phenylacetyl chloride in 800 ml. of dry toluene was added dropwise to 140 g. of anhydrous aluminum chloride from a dropping funnel over a period of 2 hours at a temperature of 45–50°. The mixture was warmed on a water-bath at 95° for 1.2 hours, allowed to cool and poured onto a mixture of 1 kg. of cracked ice and 400 ml. of concentrated hydrochloric acid with vigorous stirring. A yellow paste was formed which solidified to a gray solid. This solid was filtered from the toluene–water mixture and recrystallized from 450 ml. of ethyl alcohol (95%) using 4 g. of norite. The solid was filtered and washed on the Büchner funnel with three 35-ml. portions of alcohol. The yield on drying was 67.8 g. of nearly white crystals melting at 108–109°.

The toluene layer was then separated from the water layer and dried over 80 g. of calcium chloride. The toluene was removed by distillation at diminished pressure and the residue was distilled yielding 15.3 g. boiling at 135–136° (6 mm.) (m.p. 51–54°) and 65.5 g. boiling at 165–170° (4 mm.) (m.p. 86°). The latter fraction was crystallized from 250 ml. of ethyl alcohol (95%) yielding 41.1 g. of white crystals melting 107.5–108.5° (cor.). The total yield was 108.9 g. or 51.2%. A semicarbazone, prepared and recrystallized from ethyl alcohol melted at 166–167° (cor.) which checked the values reported by Isimura.[13]

α-(*o*- and *p*-Hydroxyphenyl)-acetophenone.—In a dry 1-l. round-bottomed flask was placed 155 g. (0.73 mole) of phenyl α-phenylacetate and 155 g. (1.14 moles) of aluminum chloride. The two components were intimately mixed and heated in an oil-bath at 125–135° for 5 hours. The reaction mixture was cooled to room temperature and poured onto a mixture of ice and concentrated hydrochloric acid. It was necessary to heat this mixture to achieve complete decomposition. After cooling to room temperature the mixture was extracted with one liter of ethyl ether and this ether solution was then extracted fifteen times with 150-ml. portions of 0.5% aqueous sodium hydroxide. On acidification of the combined extracts a grayish-brown precipitate of crude *p*-hydroxy-α-phenylacetophenone was formed. Two crystallizations from 50% alcohol yielded 51 g. (33%) of slightly buff colored ketone melting at 146–147.5° (cor.).

The ether solution remaining after the extractions with alkali was washed once with water and then evaporated to dryness. The residue was extracted with hot petroleum ether (b.p. 63–99°). On cooling 40 g. of orange colored *o*-hydroxy-α-phenylacetophenone was obtained. This solid was filtered and recrystallized from petroleum ether yielding 23.3 g. (15%) of yellow prisms (m.p. 57–58°).

The values of the melting points reported in the literature[14] are 151° for the *p*-hydroxy-α-phenylacetophenone and 60° for *o*-hydroxy-α-phenylacetophenone.

α-(*p*-Anisyl)-acetophenone.—A solution of 66 g. (0.31 mole) of *p*-hydroxy-α-phenylacetophenone in 125 ml. of an aqueous (10%) solution of sodium hydroxide (0.32 mole) in a 1-l. round-bottomed flask. Then with vigorous stirring 39.2 g. (0.32 mole) of dimethyl sulfate was added slowly. As the reaction proceeded the solid methyl derivative precipitated out of the solution and 500 ml. of water was added from time to time to facilitate stirring. After all the dimethyl sulfate had been added stirring was continued for one-half hour longer and the mixture was let stand at 25° overnight. The reaction mixture, which was still alkaline, was filtered and then washed several times in the Büchner funnel with water. The solid was then recrystallized from 350 ml. of methyl alcohol. Upon cooling at first a brown oil separated from which the supernatant liquid was decanted. From this liquid then separated white crystals which were filtered and washed with methyl alcohol. The yield was 31.2 g. (44.5%) of white crystals melting 74.5–75° (cor.). The oxime melted at 116–117° (cor.). Buck and Ide[15] reported a melting point of 73° for the ketone and 114° for the oxime.

General Method for Flavylium Perchlorates.—A solution of 0.05 mole of the substituted acetophenone, 5.3 ml. (0.05 mole) of salicylaldehyde (freshly distilled) and 10 ml. (0.09 mole) of perchloric acid (60%) in dry ether was prepared. The amount of the ether varied according to the solubility of the acetophenone. The solution was then chilled in an ice-water-bath and dry hydrogen chloride gas was bubbled into it. By the time the solution had become saturated with hydrogen chloride a color had developed which was usually dark red. The solution was then set in the refrigerator for 12 to 24 hours. By this time crystals of the brightly colored perchlorate had separated. The solution was then resaturated with dry hydrogen chloride and allowed to stand in the refrigerator for 6 to 18 hours longer. The product was separated by filtration and washed with dry ether on the Büchner funnel. The perchlorate was then recrystallized first from glacial acetic acid taking precautions against explosion. The recrystallized perchlorate was separated by filtration and washed on the Büchner funnel first with glacial acetic acid and then with dry ether. This procedure was not sufficient to remove the acetic acid so the perchlorate was recrystallized by dissolving in hot ethylene chloride (which had previously been dried by first shaking with phosphoric anhydride and then distilling from fresh phosphoric anhydride) and then adding to the warm (50°) solution dry ether until crystallization had just started. When crystallization was complete, the perchlorate was removed by filtration and washed on the funnel by a mixture of dry ethylene chloride and dry ether. The recovery in the last crystallization was over 90% in all cases.

It should be noted here that in the case of both 3′-methyl-3-phenylflavylium perchlorate and 3′-methoxy-3-phenylflavylium perchlorate when recrystallization from glacial acetic acid was attempted considerable decomposition took place when the solution was allowed to get hotter than 90°. Accordingly, enough solvent was used to dissolve the salt without heating the solution above 90°. No such difficulty was encountered then.

Table II gives for each perchlorate listed in column I the volume of ether used as solvent in the condensation by which it was prepared (column II), the yield of perchlorate obtained after recrystallization from glacial acetic acid (column III), the color of the crystals (column IV), the corrected melting point (column V) and the results of analysis in per cent. perchlorate (column VI).

Tri-(*p*-anisyl)-carbonium Perchlorate.—A solution of *p*-anisylmagnesium bromide was made from 7.0 g. (0.29 mole) of magnesium turnings and a solution of 35 ml. (0.27 mole)

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[12] Hill and Short, *J. Chem. Soc.*, 1123 (1935).

[13] Isimura, *Bull. Chem. Soc. Japan*, **16**, 196 (1941).

[14] Chadha, Mahal and Venkataraman, *J. Chem. Soc.*, 1459 (1933).

[15] Buck and Ide, This Journal, **53**, 1536 (1931).

TABLE II

SUBSTITUTED FLAVYLIUM PERCHLORATES

3-Phenylflavylium perchlorate	Vol. ether, ml.	Yield in %	Color	Corrected M. p., °C. (dec.)	Perchlorate, %	
					Calcd.	Found
2'-Methyl-	50	86	Bright yell.	244–245	25.08	24.82
3'-Methyl-	50	90	Bright yell.	215–216	25.08	24.97
4'-Methyl-	70 + 10 glacial acetic acid	85	Bright yell.	234–235	25.08	24.91
2'-Methoxy-	50	88	Bright yell. with sl. or. tint	225–226	24.11	24.01
3'-Methoxy-	50	95	Orange	193–194	24.11	23.95
4'-Methoxy-	50	76	Bright red	199–201	24.11	23.89

of *p*-bromoanisole in 95 ml. of ether. The reaction flask was cooled in an ice-bath and 10.6 ml. (0.085 mole) of diethyl carbonate was added slowly, after which the reaction mixture was refluxed 30 minutes, then was poured into a mixture of 100 g. of ice and 50 g. of ammonium chloride in 100 ml. of water. The ether layer was separated, dried over calcium chloride, filtered and treated with 20 ml. (0.242 mole) of 70% perchloric acid and 30 ml. of acetic anhydride. The precipitate formed was collected by filtration and washed with ether. The yield of dark green crystals was 8 g., 22%, m.p. 156–161°. By repeated solution in acetone and subsequent precipitation by the addition of an equal volume of ether, the compound was obtained as red crystals melting at 198–199°. Hofmann, Kirmreuther and Thal[10] gave the melting point as 193°.

Anal. Calcd. for $C_{22}H_{21}O_7Cl$: C, 61.0; H, 4.85. Found: C, 61.13; H, 5.03.

Conductivity Determinations.—The conductivities of solutions of these flavylium perchlorates in acetonitrile were measured by means of the usual alternating current Wheatstone bridge method. The two conductivity cells used were of the type suggested by Jones and Bollinger (see type L in Fig. 14 of their article),[16] with platinum electrodes.

The acetonitrile used as solvent was purified by distillation of Eastman Kodak Co. high grade acetonitrile from phosphoric anhydride through an all-glass apparatus including a 50-cm. fractionating column packed with glass helices. The entire distillation was conducted in an atmosphere of dry air. Before distillation all the parts of the apparatus were cleaned thoroughly with chromic acid, rinsed thoroughly with distilled water, then filled with distilled water and allowed to stand several weeks changing the water every few days. Each piece of apparatus was dried in an oven at 120–130° for 6 hours before it was assembled. While the apparatus was being assembled and until distillation a stream of nitrogen, dried by passing it through a 70-cm. tube containing "Anhydrone." The purified solvent was stored in two 6-l. reservoir flasks of the Florence type with a liquid delivery head of the type previously described. One of these was used for a receiver in the distillation and the other flask was filled from this by forcing it through a glass connecting tube. In all 12 l. of solvent was used. The

TABLE III

CONDUCTIVITY DATA

$C \times 10^4$	$\sqrt{C} \times 10^2$	Λ
3-Phenylflavylium perchlorate		
106.0	10.30	128.6
51.55	7.18	137.3
26.01	5.10	144.2
11.83	3.44	149.2
5.335	2.31	153.3
2.052	1.433	156.0
0.681	0.825	157.8
2'-Methyl-3-phenylflavylium perchlorate		
113.0	10.66	125.6
46.68	6.832	137.6
22.10	4.701	144.6
9.544	3.089	149.8
2.733	1.653	154.3
1.89	1.344	155.3
1.315	1.147	156.1
1.027	1.013	156.8
3'-Methyl-3-phenylflavylium perchlorate		
96.35	9.816	129.6
51.06	7.146	136.5
36.19	6.015	140.7
10.63	3.261	149.3
7.06	2.657	151.0
4.978	2.231	151.8
1.091	1.045	155.9
4'-Methyl-3-phenylflavylium perchlorate		
101.2	10.06	127.9
52.52	7.247	135.7
32.96	5.741	140.6
10.27	3.203	149.6
6.572	2.564	151.2
4.281	2.069	152.4
1.108	1.053	156.2
2'-Methoxy-3-phenylflavylium perchlorate		
106.0	10.30	128.9
47.28	6.876	138.0
26.03	5.102	143.6
14.89	3.858	146.7
9.830	3.135	149.9
4.828	2.197	152.2
2.697	1.642	154.9
1.132	1.064	155.7
3'-Methoxy-3-phenylflavylium perchlorate		
95.16	9.755	126.5
48.02	6.930	134.9
26.23	5.122	140.9
13.43	3.665	145.7
9.693	3.113	147.7
5.678	2.383	151.5
2.645	1.626	153.0
1.061	1.030	156.4
4'-Methoxy-3-phenylflavylium perchlorate		
96.78	9.336	125.8
49.97	7.069	132.9
22.46	4.739	140.7
10.32	3.213	145.6
8.044	2.836	146.8
4.134	2.033	150.1
3.325	1.823	151.1
2.054	1.433	152.0
0.963	0.981	153.2
Tri-*p*-anisylcarbonium perchlorate		
44.81	6.694	134.7
9.177	3.029	146.0
4.194	2.048	149.1
1.144	1.070	151.2

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(16) Jones and Bollinger, THIS JOURNAL, **53**, 411 (1931).

specific conductivity, *k*, for the acetonitrile so prepared was found to be $3.95 \cdot 10^{-7}$ ohm^{-1} cm.$^{-1}$. Walden[8] reported $k = 3.98 \times 10^{-7}$.

The solutions for measurement were in all cases prepared by weight and different concentrations obtained by weight dilution. The conductivity cells were maintained in a thermostat at 25 ± 0.05°.

Absorption Spectra.—Solutions of the perchlorates were made up in dry redistilled ethylene chloride and the absorption at various wave lengths determined by use of the Beckman spectrophotometer. The data are shown in Figs. 2 and 3.

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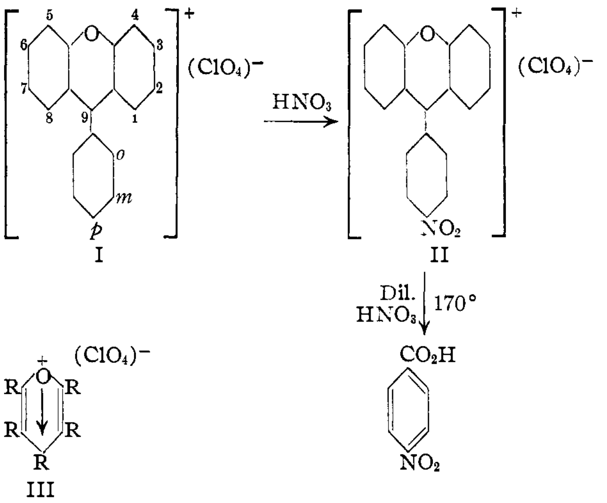
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE STATE UNIVERSITY OF IOWA]

The Structure of the Nitration Products of 9-Phenylxanthylium Salts[1]

BY R. L. SHRINER AND CALVIN N. WOLF[2a,b]

The nitration of 9-phenylxanthylium perchlorate has been shown to yield 91% of 9-(*m*-nitrophenyl)-xanthylium perchlorate as shown by hydrolysis to the carbinol and reduction to 9-(*m*-nitrophenyl)-xanthene. The structure of the latter compound was established by condensation of xanthydrol with *o*-nitraniline to 9-(*p*-amino-*m*-nitrophenyl)-xanthene from which the amino group was removed by diazotization and treatment with hypophosphorus acid. The results show that these cationic salts orient the entering nitro group predominately to the meta-position.

Le Fevre and Pearson[3] reported that 9-phenylxanthylium perchlorate (I) gave a mononitro derivative which, upon oxidation with dilute nitric acid, gave *p*-nitrobenzoic acid (yield not given). The nitration product was, therefore, considered to be 9-(*p*-nitrophenyl)-xanthylium perchlorate (II) and the authors assigned the general structure (III) for the pyrylium salt nucleus in which the arrow represented a special case of "long bond."



Nitration studies of substituted benzopyrylium salts and isobenzopyrylium salts showed that the entering nitro group was oriented to the meta-position[4,5] The para nitration reported by Le Fevre for the compound I, was a very disturbing exception to this behavior.

The question of orientation of the nitro group in the nitration of 9-phenylxanthylium salts has been reinvestigated (see Chart I). The nitration of 9-phenylxanthylium salts proceeded readily and was performed either by addition of 9-phenylxanthylium perchlorate (IV) to the nitration mixture or by addition of nitric acid to 9-phenylxanthylium sulfate obtained by dissolving 9-phenylxanthenol in sulfuric acid. Both methods gave identical results. The nitration product was isolated in nearly quantitative yield as the carbinol (VI), by pouring the reaction mixture into water and neutralizing with ammonia. This crude carbinol (VI) was a mixture and could not be fractionally crystallized but the perchlorate, ferrichloride, methoxy and ethoxy derivatives were obtained as pure crystalline compounds whose analyses and yields indicated at least a 91% yield of a pure mononitro derivative. Furthermore, reduction of VI, using the formic acid method of Kovache,[6] gave a crude nitrophenylxanthene in nearly quantitative yield. Repeated recrystallization of this crude reduction product gave pure 9-(*m*-nitrophenyl)-xanthene (VII) in 91.6% yield.

Catalytic reduction of VII gave 9-(*m*-aminophenyl)-xanthene (VIII). This compound (VIII) was different from the condensation product of xanthydrol (IX) and aniline, which was postulated by Adriani[7] to be 9-(*p*-aminophenyl)-xanthene (X) Chart II. Proof that xanthydrol actually does condense with aromatic amines at the para-position in the presence of hydrochloric acid was provided by diazotization of X and conversion of the diazonium salt to 9-(*p*-methoxyphenyl)-xanthene (XI). This compound (XI) was identical with an authentic sample of XI obtained by the addition of *p*-anisylmagnesium bromide to xanthone followed by formic acid reduction of the carbinol (XII). This was further evidence of the fact that the principal nitration product of IV was not the para derivative (II).

Conclusive evidence for the structure of V by independent synthesis of the formic acid reduction product (VII) was obtained by condensation of xanthydrol (IX) with *o*-nitroaniline in presence of hydrochloric acid to give 9-(*p*-amino-*m*-nitrophenyl)-xanthene (XIII) followed by replacement of the amino group of XIII by hydrogen (see

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[1] Presented before the Eleventh National Organic Symposium of the American Chemical Society, Madison, Wisconsin, June 20–22, 1949.

[2] (a) From a thesis submitted to the Graduate College of the State University of Iowa in partial fulfillment of the requirements of the degree, Doctor of Philosophy. (b) Ethyl Corporation, Detroit, Michigan.

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[4] Le Fevre, *ibid.*, 2771 (1929).

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