275. *Comparison of the Directive Powers of Elements having Consecutive Atomic Numbers. Part III. Nitration of Halogeno-2-phenylbenzopyrylium Salts.*

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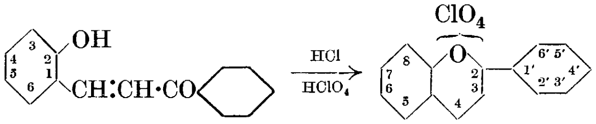
THE experiments already described (J., 1929, 2771; 1930, 2236) suggested that, on account of the high m. p.'s (often with decomposition) characteristic of the series, thermal analysis might not be easily applicable to the mixed nitration products from a phenylbenzopyrylium salt. For continuance of the programme there outlined, therefore, some other method of analysis was required.

Accordingly various halogenobenzopyrylium perchlorates were examined in which the strong $-I$ effect of the oxonium pole was opposed to the weaker $-I$ effect of the halogen in the *o*- or *p*-position, *i.e.*, cases where it appeared possible that nitration might produce a mixture of two compounds one only of which would possess a halogen labile towards alkaline reagents. Estimation would then be a matter of weighing silver halide.

The preparation of 4′- and 6-*chloro*- and -*bromo*- and 6 : 8-*dichloro*- and -*dibromo*-2-*phenylbenzopyrylium perchlorates* from the appropriate halogenated salicylideneacetophenones is herein described.



The four monohalogeno-salts on nitration give, however, 90—

100% of *m*-nitro-derivatives, identified by comparison with specimens synthesised from the appropriate *m*-nitroacetophenones and salicylaldehydes. As additional verification the isomeric *p*-nitrophenyl-salt was synthesised in one case and found to be quite distinct from the products of nitration.

When the total nitration product from 4′-chloro- or -bromo-2-phenylbenzopyrylium perchlorate was heated with piperidine for 1 hour, and the diluted solution acidified with nitric acid, a fuschia-coloured solution was formed from which perchloric acid precipitated dark red 3′-nitro-4′-piperidino-2-phenylbenzopyrylium perchlorate, m. p. 100—110°, which was also obtained from 3-nitro-4-piperidinoacetophenone and salicylaldehyde. The filtrate yielded silver halide agreeing nearly with 100% *m*-nitration.

The predominantly unidirectional course of the above nitrations renders them unsuitable for realisation of the main purpose of this work, *viz.*, comparison of the nitration of oxonium salts and the analogous quinolinium salts.

The nitration products of the two dihalogeno-salts were impure; some nitration evidently occurred in the halogen-containing nucleus, since a trace of labile chlorine could be detected by boiling with piperidine.

2-Phenylbenzopyrylium perchlorate was inert towards nitric acid and required 30—40 hours for satisfactory mononitration: the four monohalogeno-salts, however, were all mononitrated by 5—15 hours' solution in nitric acid. These results are not in harmony with the usual deactivating effect of halogens in simple aromatic molecules and constitute examples of the phenomenon mentioned by Robinson (Informal Discussion, Feb. 18th), *viz.*, that in some molecules a certain maximum of deactivation exists, beyond which the inductive action of a substituent group may become the reverse of that exhibited in less fully substituted molecules (*e.g.*, Cl in chlorobenzene : $-I, +T$; in pyrylium compounds, apparently $+I, +T$).

Labilisation of Halogens by an Oxonium Pole.—To determine whether the oxonium pole ($-I$, but no $-T$ effect) can labilise a halogen substituent, the above un-nitrated halogeno-salts were tested against the silver nitrate–acetic acid reagent (J., 1931, 810). No silver halide was detected, indicating that this type of labilisation depends much more upon a $-T$ than upon a $-I$ electronic distortion of the halogen-containing molecule.

EXPERIMENTAL.

Salicylidene-p-*chloroacetophenone.*—A warm solution of KOH (30 g.) in H_2O (25 c.c.) was added to salicylaldehyde (25 g.), 95% EtOH (80 c.c.), and *p*-chloroacetophenone (20 g.). After 1 hr., the scarlet crystals were collected and decomposed with dil. AcOH. *Salicylidene*-p-*chloroacetophenone* (12 g.) crystallised from 95% EtOH in yellow microscopic needles, m. p. 151° (decomp.) (Found : C, 69·3; H, 4·3. $C_{15}H_{11}O_2Cl$ requires C, 69·6; H, 4·3%).

4'-Chloro-2-phenylbenzopyrylium Perchlorate.—Salicylidene-*p*-chloroacetophenone (0·2 g.) in boiling AcOH (5 c.c.) was heated with HCl aq. (3 c.c.) until the solution was pale yellow; $HClO_4$ aq. (10 c.c.; *d* 1·12) was then added. *4'-Chloro-2-phenylbenzopyrylium perchlorate* separated on cooling in small yellow plates, m. p. 193°, unchanged by recrystn. from AcOH (Found : C, 52·6; H, 3·3. $C_{15}H_{10}O_5Cl_2$ requires C, 52·8; H, 3·0%).

The following compounds were prepared by methods similar to the above. *Salicylidene*-p-*bromoacetophenone* (28 g. from 28 g. of *p*-bromoacetophenone), yellow plates, m. p. 133°, from 95% EtOH (Found: C, 58·4; H, 3·7. $C_{15}H_{11}O_2Br$ requires C, 59·4; H, 3·6%). *4'-Bromo-2-phenylbenzopyrylium perchlorate*, yellow microscopic plates, m. p. 243—245° (Found : C, 44·1; H, 3·0. $C_{15}H_{10}O_5ClBr,H_2O$ requires C, 44·6; H, 3·0%). *5-Chlorosalicylideneacetophenone* (from KOH, 40 g., and H_2O, 40 c.c.; 5-chlorosalicylaldehyde, 40 g., acetophenone, 22 g., and EtOH, 120 c.c.), greenish-yellow needles, m. p. 170—171° (Found : C, 69·2; H, 4·0. $C_{15}H_{11}O_2Cl$ requires C, 69·6; H, 4·3%). *5-Bromosalicylideneacetophenone* (from KOH, 10 g., and H_2O, 10 c.c.; bromosalicylaldehyde, 13 g., acetophenone, 5·3 g., and EtOH, 30 c.c.), yellow-green plates, m. p. 162—163°, from AcOH (Found : C, 59·2; H, 3·6. $C_{15}H_{11}O_2Br$ requires C, 59·4; H, 3·6%). 3 : *5-Dichlorosalicylideneacetophenone* (from KOH, 90 g., and H_2O, 90 c.c.; dichlorosalicylaldehyde, 112·5 g., acetophenone, 60 g., and EtOH, 1000 c.c.), large yellow needles (150 g.), m. p. 183—184°, from AcOH (2 l.) (Found : C, 61·4; H, 3·5. $C_{15}H_{10}O_2Cl_2$ requires C, 61·4; H, 3·4%). 3 : *5-Dibromosalicylideneacetophenone* (from KOH, 30 g., and H_2O, 25 c.c.; dibromosalicylaldehyde, 55 g., acetophenone, 16 g., and EtOH, 150 c.c. : vigorous reaction), yellow needles, m. p. 168°, from AcOH (Found : C, 47·1; H, 2·7. $C_{15}H_{10}O_2Br_2$ requires C, 47·1; H, 2·6%).

Cyclisation of the Halogenohydroxychalkones.—In all cases the quality of the product was much better when small quantities were used. For instance, a solution of 5-chlorosalicylideneacetophenone (0·1 g.) in AcOH (10 c.c.) was boiled, after addition of 3 drops of conc. HCl, until it was orange-yellow : the process was repeated until further addition of HCl produced neither red colour nor turbidity. $HClO_4$ aq. (15 c.c.; *d* 1·12) was then added and after 1 hr. the *6-chloro-2-phenylbenzopyrylium perchlorate* was collected and air-dried; yellow powder (0·25 g.), m. p. 240°, unchanged after crystn. from AcOH–$HClO_4$ aq. (Found : C, 52·5; H, 3·0. $C_{15}H_{10}O_5Cl_2$ requires C, 52·8; H, 2·9%).

6-Bromo-2-phenylbenzopyrylium perchlorate, similarly prepared, formed yellow granular crystals, m. p. 248—250° (Found : C, 44·8; H, 2·9. $C_{15}H_{10}O_5ClBr,H_2O$ requires C, 44·6; H, 2·9%). 6 : 8-Dibromo-2-phenylbenzopyrylium perchlorate formed yellow-green plates, m. p. 257—259°.

6 : 8-Dichloro-2-phenylbenzopyrylium perchlorate (from dichlorosalicylideneacetophenone, 5 g., AcOH, 200 c.c., and conc. HCl, 75 c.c.; 5 mins.' boiling; $HClO_4$ aq., 200 c.c., *d* 1·12, then added) formed yellow-brown leaflets (5 g.), m. p. 249—250°.

Nitration of the Foregoing Halogenophenylbenzopyrylium Salts.—A solution of the substance (*x* g.) in fuming HNO_3 (20*x* c.c.) was kept at room temp.

for a definite time, H_2O (equal vol.) was then added below 0°, followed by $HClO_4$ aq. (*d* 1·12; four times the vol. of the HNO_3 used). Crystallisation was generally complete after 12 hrs. and the perchlorate was then washed with $HClO_4$ aq. and air-dried. The m. p. of the product increased and then decreased with increasing time of nitration; only the max. values are recorded.

4′-Chloro-2-phenylbenzopyrylium perchlorate gave a yellow-orange microcrystalline powder, m. p. 225—226° (9 hrs.) (Found: C, 45·8; H, 2·6. $C_{15}H_9O_7NCl_2$ requires C, 46·6; H, 2·3%), the 4′-bromo-analogue a yellow powder, m. p. 239—240° (9 hrs.) (Found: C, 42·1; H, 2·2. $C_{15}H_9O_7NClBr$ requires C, 41·8; H, 2·1%), the 6-chloro-compound yellow-brown needles, m. p. 219—222° (14 hrs.) (Found: C, 46·3; H, 2·3. $C_{15}H_9O_7NCl_2$ requires C, 46·6; H, 2·3%), the 6-bromo-compound a yellow powder, m. p. 210—214° (15 hrs.), and the 6 : 8-dichloro-compound a product, m. p. *ca.* 96° (19 hrs.), which was possibly a hydrate.

Syntheses of the m-*Nitro-2-phenylbenzopyrylium Salts corresponding to the above Perchlorates.*—A solution of the appropriate *m*-nitroacetophenone and salicylaldehyde in formic acid (99%) was saturated with dry HCl at room temp., and after 12 hrs. HCl aq. was added until no further ppt. was formed. To the filtrate was added excess of $HClO_4$ aq. The *m*-nitro-pyrylium salt which then crystallised was washed with dil. $HClO_4$ and air-dried. In some cases the products appeared to be hydrated, but the H_2O could not be removed without decomp. occurring.

4′-*Chloro*-3′-*nitro*-2-*phenylbenzopyrylium perchlorate* (from 4-chloro-3-nitroacetophenone, 0·79 g., and salicylaldehyde, 0·61 g., in 20 c.c. of formic acid; yield, 0·73 g.) had m. p. 180—190° (varying with rate of heating) (Found: C, 38·3; H, 3·4. $C_{15}H_9O_7NCl_2,4{\cdot}5H_2O$ requires C, 38·5; H, 3·8%). The m. p. *ca.* 185° is apparently that of a mixture of anhyd. salt and water. Addition of *ca.* 50% of the 9 hr. nitration product (m. p. 225—226°) raised the m. p. to 219—221°.

4′-*Bromo*-3′-*nitro*-2-*phenylbenzopyrylium perchlorate* (from 4-bromo-3-nitroacetophenone, 1·23 g., and salicylaldehyde, 0·61 g., in 25 c.c. of formic acid; yield, 1·42 g.) had m. p. 180—190° (varying with rate of heating) (Found: C, 34·9; H, 3·3. $C_{15}H_9O_7NClBr,4{\cdot}5H_2O$ requires C, 35·2; H, 3·5%). Mixed m. p. with approx. half the wt. of the 9 hr. nitration product, 232—233°.

6-*Chloro*-2-m-*nitrophenylbenzopyrylium perchlorate* (from *m*-nitroacetophenone, 1·65 g., and 5-chlorosalicylaldehyde, 1·57 g., in 40 c.c. of formic acid; yield, 1·56 g.) had m. p. 233·5° (Found: C, 46·3; H, 2·7. $C_{15}H_9O_7NCl_2$ requires C, 46·6; H, 2·3%). Mixed with the 14 hr. nitration product, it melted at 223—224°.

6-*Bromo*-2-m-*nitrophenylbenzopyrylium perchlorate* (from *m*-nitroacetophenone, 1·65 g., and 5-bromosalicylaldehyde, 2·01 g., in 45 c.c. of formic acid; yield, 0·5 g.) had m. p. 228° (Found: C, 41·4; H, 2·4. $C_{15}H_9O_7NClBr$ requires C, 41·8; H, 2·1%), lowered to 216—218° in admixture with the 15 hr. nitration product.

The 3 : 5-dihalogenosalicylaldehydes and *m*-nitroacetophenone gave low-melting solids.

Nitration of p-*Halogenoacetophenones.*—*p*-Chloroacetophenone (2·4 g.) was dropped slowly into HNO_3 (*d* 1·5; 24 c.c.) below 0° and after 5 mins. the mixture was poured on ice. Crystallisation from EtOH gave 4-*chloro*-3-

nitroacetophenone (2·8 g.), m. p. 99—101° (Found: C, 48·2; H, 2·9. $C_8H_6O_3NCl$ requires C, 48·1; H, 3·0%). 4-*Bromo*-3-*nitroacetophenone* had m. p. 117—118° (Found : C, 39·7; H, 2·4. $C_8H_6O_3NBr$ requires C, 39·3; H, 2·5%).

Synthesis of 6-*Chloro*-4′-*nitro*-2-*phenylbenzopyrylium Perchlorate.*—*p*-Nitroacetophenone (0·74 g.) and 5-chlorosalicylaldehyde (0·77 g.) in formic acid (30 c.c.) gave by the above-described method 1 g. of the *perchlorate* as orange-brown crystals, m. p. 252—253° (Found : C, 46·5; H, 2·5. $C_{15}H_9O_7NCl_2$ requires C, 46·6; H, 2·3%). Mixed with synthetic 6-chloro-3′-nitro-2-phenylbenzopyrylium perchlorate (10 parts), it melted from 222° upwards, but the 14 hr. nitration product (10 parts) lowered its m. p. to 210—212°.

Ferrichlorides.—The *compounds* tabulated below were prepared in the same way as the corresponding perchlorates, satd. $FeCl_3$ aq.–conc. HCl being substituted for $HClO_4$ aq., and were recrystallised from AcOH–$FeCl_3$ aq.

Ferrichloride.		Crystals.	M. p.	C, %.	H, %.	Calc.	
4′-Chloro-2-phenylbenzopyrylium		Yellow	179—181°	40·9	2·5	41·0	2·3
4′-Bromo-	,,	Orange-yellow	173—176	37·7	2·4	37·2	2·1
6-Chloro-	,,	Yellow	160—161	40·9	2·4	41·0	2·3
6-Bromo-	,,	Orange-yellow	158—159	37·1	2·2	37·2	2·1
6 : 8-Dichloro-	,,	Yellow-green	187—188	38·1	2·0	38·0	1·9
6 : 8-Dibromo-	,,	Green	185	32·0	1·6	32·0	1·6

3 : 4′ : 5-*Trichlorosalicylideneacetophenone.*—Prepared in the same way as the other chalkones (KOH, 4·5 g., in warm H_2O, 4 c.c.; 3 : 5-dichlorosalicylaldehyde, 8 g., 4-chloroacetophenone, 4 g., EtOH, 13 c.c.), this crystallised from much AcOH in plates, m. p. 211—212° (Found : C, 55·2; H, 2·8; Cl, 32·5. $C_{15}H_9O_2Cl_3$ requires C, 55·7; H, 2·8; Cl, 33·0%).

All the compounds described, except 4-chloro- and -bromo-3-nitroacetophenone, decompose at the m. p. All analyses are microanalyses by Dr.-Ing. A. Schœller

Correction.—In J., 1929, 2773 the text under "*Nitrations of the Perchlorate*" is misleading. Nitrations by ordinary HNO_3 (*d* 1·4) *or* by H_2SO_4–HNO_3 at 0° or 15° for times varying from 5 mins. to 24 hrs. were unsatisfactory. With fuming HNO_3 at 15°, the yields of 3′-nitro-derivative obtained after 40, 48, and 89 hrs. were 86, 70, and 68%, respectively.

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