

CCXXVII.—*Studies in the Coumarin Series. Part II.*
The Conversion of Substituted Coumarins into
Benzopyrylium Salts.

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THE action of excess of phenylmagnesium bromide on hot concentrated solutions of coumarins substituted in the 3- and 4-positions has been shown by Heilbron and Hill (J., 1927, 2005) to lead respectively to formation of 2:4-diaryl- Δ^2 -chromens (I) and 2:2-diaryl- Δ^3 -chromens (II).



A study has now been made of the reaction in dilute solution at room temperature, under conditions closely analogous to those employed by Willstätter, Zechmeister, and Kindler in the conversion of 3:5:7-trimethoxycoumarin into pelargonidin (*Ber.*, 1924, 57, 1938). With 3-methyl-, 3-phenyl-, and 3-methoxy-coumarins, reaction proceeds smoothly, giving good yields of the corresponding 2-phenylbenzopyrylium salts. On the other hand, with 4-methyl- and 4-phenyl-coumarins, only small quantities of the monoaryl salts are produced, unreacted coumarin being recovered in both cases from the reaction mixture. Attempts to increase the yield of the benzopyrylium salts by employing more concentrated solutions resulted in the formation of considerable quantities of 2:2-diphenyl-4-methyl- Δ^3 -chromen (Heilbron and Hill, *loc. cit.*) and 2:2:4-triphenyl- Δ^3 -chromen, without any corresponding increase in the amount of the monoaryl derivatives. The effect of methoxyl in position 4 is especially marked, for neither from 4-methoxy- nor from 4:7-dimethoxy-coumarin have we been able to isolate any benzopyrylium salt whatsoever. Reaction either fails to occur or under more drastic conditions leads solely to the production of the substituted Δ^3 -chromens.

In the preparation of 4-phenylcoumarin, which was carried out as described by Stoermer and Friderici (*Ber.*, 1908, **41**, 324), a hitherto undescribed modification (m. p. 92°) has been isolated which is converted into the ordinary form (m. p. 105°) when heated above its melting point.

EXPERIMENTAL.

3-Methoxycoumarin.—A mixture of sodium methoxyacetate (56 g.), salicylaldehyde (20 g.), and acetic anhydride (84 g.) was heated for 6 hours at 160°. Unchanged salicylaldehyde was removed in steam, and the tarry residue repeatedly extracted with boiling water. The crude compound, which crystallised from the cold solution, was recrystallised from alcohol in presence of animal charcoal, pure *3-methoxycoumarin* separating in colourless needles (16 g.), m. p. 162° (Found : C, 68·5; H, 4·6. $C_{10}H_8O_3$ requires C, 68·3; H, 4·5%).

3-Methoxy-2-phenylbenzopyrylium Chloride.—Phenylmagnesium bromide (prepared from magnesium, 1·5 g., and bromobenzene, 9 g., in dry ether, 300 c.c.) was slowly added to 3-methoxycoumarin (3 g.) in dry benzene (600 c.c.). After some hours the reaction mixture was shaken with concentrated hydrochloric acid (100 c.c.) and the deep orange aqueous layer was run off, washed with ether, and neutralised with dilute aqueous ammonia. The carbinol base was extracted with ether, and the dried solution saturated with dry hydrogen chloride; dark reddish-brown needles of the pyrylium chloride then separated. As the salt proved to be extremely hygroscopic, it was converted into its *ferrichloride*, which separated from glacial acetic acid in yellow needles (Found : C, 43·9; H, 3·3. $C_{16}H_{13}O_2Cl_4Fe$ requires C, 44·1; H, 3·0%).

2-Phenyl-3-methylbenzopyrylium chloride was prepared in an analogous manner. The addition of hydrogen chloride to the dry ethereal solution of the carbinol base precipitated the pyrylium salt in yellow flocks, which were collected, dissolved in glacial acetic acid, and heated with a solution of ferric chloride in the same solvent. The *ferrichloride* separated on cooling in yellow-green plates with metallic reflex, m. p. 132° (Found : C, 45·8; H, 3·3. $C_{16}H_{13}OCl_4Fe$ requires C, 45·8; H, 3·1%).

2 : 3-Diphenylbenzopyrylium Chloride.—When 3-phenylcoumarin (3 g.) in dry benzene (600 c.c.) was treated with the Grignard reagent as previously described, a copious precipitate was immediately formed. After 1 hour concentrated hydrochloric acid (120 c.c.) was added and the deep yellow acid layer was separated, washed once with ether, and neutralised with solid sodium carbonate. The carbinol base was extracted with ether, and the dried ethereal solution saturated with dry hydrogen chloride; the pyrylium chloride then separated in yellow needles, which rapidly discoloured on ex-

posure to air. The *ferrichloride* crystallised from glacial acetic acid in long yellow needles (Found: C, 52.8; H, 3.4; Fe, 12.2. $C_{21}H_{15}OCl_4Fe$ requires C, 52.4; H, 3.1; Fe, 11.6%).

2-Phenyl-4-methylbenzopyrylium chloride was prepared in the usual manner from 4-methylcoumarin (compare Peters and Simonis, *Ber.*, 1908, 41, 830) and obtained in small yield (7%) as dark green needles which rapidly liquefied on exposure to moist air. The *ferrichloride* separated from glacial acetic acid containing hydrogen chloride in greenish-brown needles (Found: C, 46.1; H, 3.5; Fe, 13.4. $C_{16}H_{13}OCl_4Fe$ requires C, 45.8; H, 3.1; Fe, 13.4%).

Unchanged 4-methylcoumarin (1 g.=33%) was recovered from the washed and dried ether-benzene solution after decomposition of the reaction mixture with concentrated hydrochloric acid.

In a second experiment more concentrated solutions were employed for the same quantities of materials (ether, 200 c.c.; benzene, 400 c.c.) without, however, effecting any increase in the yield of pyrylium chloride. From the ether-benzene solution, 2:2-diphenyl-4-methyl- Δ^3 -chromen (1 g.), m. p. 88°, was obtained in place of the 4-methylcoumarin.

4-Phenylcoumarin.—A solution of β -*o*-anisylcinnamic acid (4 g. of isomeric mixture, m. p. 122–130°) in acetyl chloride (50 g.) was kept for 17 hours at room temperature (compare Stoermer and Friderici, *loc. cit.*), the reaction mixture was then poured into water, and the solution made alkaline with sodium carbonate and extracted with ether. The dried concentrated solution gradually deposited a pale yellow solid, from which, after twice crystallising from alcohol, 4-phenylcoumarin separated in colourless needles, m. p. 92°. This new modification was also obtained in a similar manner from the pure α -modification of the acid melting at 153° (Found: C, 81.1, 81.1; H, 4.9, 4.7. $C_{15}H_{10}O_2$ requires C, 81.1; H, 4.5%).

The new low-melting form of 4-phenylcoumarin was heated just above its melting point: the solid material formed on cooling remelted at 104–105°, the melting point of ordinary 4-phenylcoumarin. The same result was obtained when the 92° modification was heated in presence of a trace of the high-melting form. In subsequent experiments demethylation of either the pure α -form of β -*o*-anisylcinnamic acid or the isomeric mixture of acids gave only the 104–105° variety of the coumarin.

2:4-Diphenylbenzopyrylium Chloride.—This salt was obtained by Löwenbein (*Ber.*, 1924, 57, 1517) by oxidation of either 2:4-diphenyl- Δ^2 -chromen or the isomeric 2:4-diphenyl- Δ^3 -chromen with ferric chloride. We have now prepared it in poor yield directly from 4-phenylcoumarin by treatment with phenylmagnesium bromide, and characterised it by the formation of its ferrichloride,

which crystallises from glacial acetic acid in golden-yellow plates [Found (micro) : C, 52.6; H, 3.4; Fe, 11.3. Calc. for $C_{21}H_{15}OCl_4Fe$: C, 52.4; H, 3.1; Fe, 11.6%].

2 : 2 : 4-Triphenyl- Δ^3 -chromen.—A solution of 4-phenylcoumarin (3 g.) in ether (80 c.c.) was treated with phenylmagnesium bromide (bromobenzene 12 g., ether 80 c.c.), and the reaction mixture gently boiled under reflux for 2 hours. After standing over-night, the product was decomposed with ice-cold ammonium chloride solution and steam-distilled. The resinous semi-solid residue crystallised on trituration with alcohol and was purified by recrystallisation from the same solvent, from which the *chromen* separated in small colourless needles, m. p. 130° (Found : C, 90.0; H, 5.8. $C_{27}H_{20}O$ requires C, 90.0; H, 5.6%). Attempts to bring about scission of the chromen by refluxing it either with 50% aqueous potassium hydroxide according to the method of Heilbron and Hill (*loc. cit.*) or with amylic-alcoholic potash were unsuccessful; the unchanged chromen was not, however, recovered as such but in what is presumably a stereoisomeric form, m. p. 162—163° (Found : C, 89.7; H, 5.7%). Neither modification was altered on prolonged boiling with glacial acetic acid, a reaction whereby, according to Löwenbein (*loc. cit.*), certain Δ^3 -chromens are converted into coumarone derivatives.

3-Methoxy-2 : 4-diphenyl- Δ^2 -chromen.—This compound was prepared by an analogous method to that described above. The non-volatile residue left after steam distillation, probably a mixture of 3-methoxy-2 : 4-diphenylchroman-2-ol and the Δ^2 -chromen, could not be induced to crystallise and was distilled under reduced pressure. The crystals which separated from the oily distillate were recrystallised from alcohol, and the *chromen* isolated in fine needles, m. p. 172° [Found (micro) : C, 84.0; H, 5.8. $C_{22}H_{18}O_2$ requires C, 84.1; H, 5.7%].

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