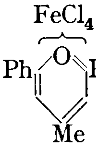
280. *Notes on* (a) *a Case of Ketonic Activity of Acetic Anhydride, and* (b) *the Condensation of Salicylaldehyde with Benzoylacetone.*

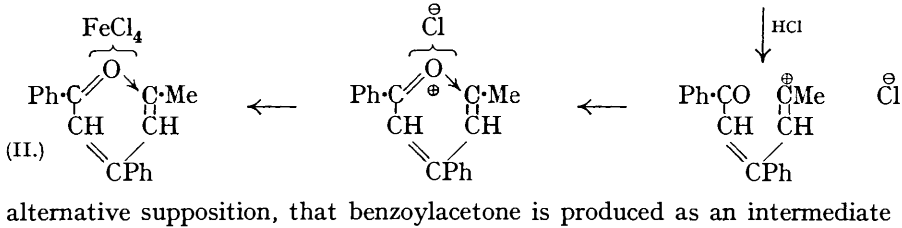
By R. J. W. Le Fèvre and J. Pearson.


(I.)

(*a*) By the action of anhydrous ferric chloride on acetophenone in acetic anhydride solution, Dilthey (*J. pr. Chem.*, 1916, **94**, 72) isolated a ferrichloride which he formulated as (I), but for which Schneider and Ross (*Ber.*, 1922, **55**, 2775) suggested the arrangement of groups shown in (II). The action of nitric acid on this compound supports the latter formula, for the *perchlorate* obtained directly from (I), prepared by Dilthey's method, gave by nitration a mixture which on oxidation afforded some *p*-nitrobenzoic acid, thereby indicating that in one of the phenyl nuclei some *p*-nitration must have been effected. Comparison with previously recorded nitrations (*e.g.*, that of 2 : 4 : 6-triphenylpyrylium perchlorate; J., 1932, 2894) shows that in (II) considerable *p*-substitution of the 4-phenyl nucleus should occur, the 2-phenyl nucleus being nitrated chiefly in the *m*-position. A salt of structure (I) would produce the 2 : 6-di-*m*-nitrophenyl derivative almost entirely (cf. J., 1929, 2771; 1930, 2236; and *loc. cit.*).

The production of (II) in the above reaction is of interest, for the acetic anhydride does not act merely as a solvent but takes part in the reaction, since in its absence only unchanged materials and dypnone can be isolated. Replacement of acetic by benzoic anhydride affords 2 : 4 : 6-triphenylpyrylium ferrichloride in low yield. In our view, therefore, the course of the reaction producing (II) may be represented thus:

$$2\text{Ph·COMe} \longrightarrow \text{Ph·CO·CH:CPhMe} \xrightarrow{\text{Me·CO·OAc}} \text{Ph·CO·CH:CPh·CH:CMe·OAc}$$



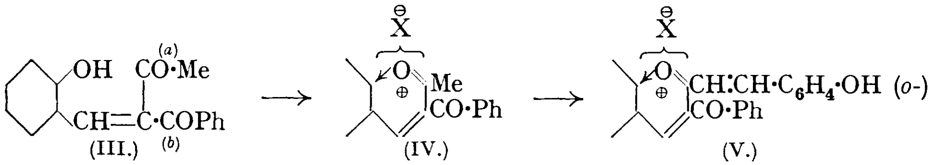
(II.)

The alternative supposition, that benzoylacetone is produced as an intermediate during the preparation of (II), is unlikely, because no interaction could be observed when acetophenone and acetic anhydride were heated together for long periods. On the other hand, it is now shown that if benzoylacetone *were* producible in this way, it could give (II) readily by further reaction with 1 mol. of acetophenone.

A previous case where acetic anhydride displays such ketonic activity is in its reaction with acetone in the presence of sulphuric acid to give 2 : 6-dimethyl-γ-pyrone (Phillippi and Seka, *Ber.*, 1921, **54**, 1089).

(*b*) Pyrylium salt formation has been considered above and in previous papers as occurring by a process of co-ordination from a carbonyl oxygen to a carbon atom with an electron sextet. It should therefore occur more readily when a group repelling electrons (+ *I*) is attached to the carbonyl group, because then the lone electrons of the oxygen can be more readily shared with another nucleus.

Thus during the ring-closure of α-benzoyl-*o*-hydroxystyryl methyl ketone (III) the dative bond can be established from either of the two carbonyl groups, (*a*) or (*b*). On the present hypothesis 3-benzoyl-2-methylpyrylium salts (IV) should be largely formed, since Me has a greater repulsive effect on electrons than has Ph. From salicylaldehyde and benzoylacetone, Chatterji and Ghosh (J., 1918, **113**, 446) prepared substances which they described as the chlorides of (IV) and of 3-acetyl-2-phenylbenzopyrylium, but as they were unable to purify these products their analyses are inconclusive; moreover, they failed to allot the two constitutions between their two compounds.



(III.) (IV.) (V.)

We doubt, however, whether they actually handled the 3-benzoyl-2-methyl salts at all, for the following reasons. A methyl group in the 2-position in a pyrylium salt is known to be reactive (Dilthey, Heilbron, *et al.*). In accordance with this, we find that salicylaldehyde and methyl ethyl ketone condense to give 2-*o*-hydroxystyryl-3-methylbenzopyrylium salts even when the ketone is in large excess, thus showing that the aldehyde has reacted more rapidly with the 2-methyl group of the presumed intermediate 2 : 3-dimethylbenzopyrylium salts than with methyl ethyl ketone. It therefore follows that any 3-benzoyl-2-methyl salt formed in Chatterji and Ghosh's experiments would have further condensed with salicylaldehyde with production of a 2-*o*-hydroxystyryl salt.

On repeating this condensation, exactly as prescribed by these authors, we obtained a brown chloride, m. p. 115—120° (contrast Chatterji and Ghosh), and thence an impure perchlorate, m. p. 135—140°, which was also produced in one stage by performing the condensation in presence of 70% perchloric acid. However, by doubling the proportion of salicylaldehyde, a 98% yield was obtained of a pure product, m. p. 221—222°, which raised the m. p. of the perchlorate obtained from Chatterji and Ghosh's product. The compounds concerned are therefore salts of *3-benzoyl-2-*o*-hydroxystyrylbenzopyrylium* (V), showing that the ring closure of (III) proceeds almost entirely in the way predicted, *i.e.*, first to (IV), and then *rapidly* to (V).

EXPERIMENTAL.

(a) *Preparation of 4 : 6-Diphenyl-2-methylpyrylium Perchlorate.*—The corresponding ferrichloride (3 g.; prepared by Dilthey's method, *loc. cit.*) was dissolved in *N*-hydrochloric acid (600 c.c.) at 60° and filtered. The clear solution so obtained was slowly treated with aqueous perchloric acid (*d* 1·12; 50 c.c.), and the resulting bright yellow precipitate was filtered off and washed with a little dilute perchloric acid. Recrystallisation from acetic acid (120 c.c.) and perchloric acid (5 c.c.) gave the *perchlorate* as a yellow microcrystalline powder, m. p. 265—266° (decomp.); yield, 1·3 g. (Found : C, 62·7; H, 4·7. $C_{18}H_{15}O_5Cl$ requires C, 62·3; H, 4·3%).

Nitration. The perchlorate (1 g.) was added, in different experiments, to (i) fuming nitric acid, (ii) a mixture (1 : 1 by vol.) of this acid with acid of *d* 1·42, and (iii) nitric acid (*d* 1·42)–sulphuric acid (5 : 1 by vol.), 30 c.c. being used in each case. The mixtures were set aside for various times, and then diluted at 0° with 30 c.c. each of glacial acetic acid and perchloric acid, followed by 60 c.c. of water. The yellow-white products were in all cases mixtures, m. p. *ca.* 90—150°.

The product from (i) after ½ hour (about 1·1 g.) was oxidised by addition of potassium permanganate (5 g.) to its suspension in 6*N*-sulphuric acid (50 c.c.) at 95°; after 10 mins. hot water was added, the solution decolorised by sulphur dioxide, filtered, and cooled. A small quantity of *p*-nitrobenzoic acid, m. p. 230—233° (raised by admixture with the pure substance), was deposited, and a small further yield was obtained by concentration of the filtrate.

Interaction between Acetophenone, Benzoic Anhydride, and Ferric Chloride.—A mixture of acetophenone (5 g.), benzoic anhydride (10 g.), and sublimed ferric chloride (5 g.) was heated at 50° for 0·5 hour. After standing at room temperature for 24 hours, the solid mass was repeatedly boiled out with alcohol, and about 1·5 g. of a yellow solid, m. p. 265—270°, remained. After crystallisation from much acetic acid, this ferrichloride had m. p. 272—274° (not depressed by admixture with 2 : 4 : 6-triphenylpyrylium ferrichloride) (Found : Fe, 10·3. Calc.: Fe, 11·0%). A mixture of this salt with Dilthey's " 4-methyl-2 : 6-diphenylpyrylium ferrichloride " of m. p. 175° had m. p. 165—168°.

Non-interaction of Acetophenone and Acetic Anhydride.—A mixture of 15 c.c. of each reagent was kept at 100° for 8 hours. Extraction with excess of cold 2*N*-sodium hydroxide, followed by acidification with hydrochloric acid and addition of aqueous ferric chloride, produced no coloration. A blank with 0·01 g. of benzoylacetone dissolved in a similar mixture showed a good enolic colour with ferric chloride.

Interaction of Acetophenone, Benzoylacetone, and Ferric Chloride.—A mixture of acetophenone (7·5 g.) with benzoylacetone (10 g.) was saturated with hydrogen chloride and left for 24 hours. The crystalline mass so formed was melted and stirred with sublimed ferric chloride (10 g.). After a further 24 hours, the dark mass was diluted with acetic acid–alcohol (1 : 1 by vol.) and filtered. The yellow crystals (5 g.; m. p. 175°) showed no m. p. depression when mixed with Dilthey's ferrichloride (*loc. cit.*), and were evidently 4 : 6-diphenyl-2-methylpyrylium ferrichloride (Found : Cl, 32·1. Calc. for $C_{18}H_{15}OCl_4Fe$: Fe, 31·9%). As additional confirmation, the perchlorate, m. p. 265°, was prepared as described above.

(b) *Attempted Preparation of* 2 : 3-*Dimethylbenzopyrylium Salts.*—Salicylaldehyde (20·5 g.), methyl ethyl ketone (12 g.), and perchloric acid (70%; 25 g.) were dissolved in dry ether (70 c.c.) and saturated with hydrogen chloride. The solution was left for 4 hours, filtered, and the residue dried. On crystallisation from acetic acid, the compound formed a microcrystalline powder, m. p. 261—262° (Dilthey, Berres, Hölterhoff, and Wubken, *J. pr. Chem.*, 1926, **114**, 179, record m. p. 257—258° for 2-*o*-hydroxystyryl-3-methylbenzopyrylium perchlorate) (Found : C, 59·6; H, 4·4. Calc. for $C_{11}H_{11}O_5Cl$; C, 51·1; H, 4·3%. Calc. for $C_{18}H_{15}O_6Cl$: C, 59·6; H, 4·2%).

In a similar preparation, but without perchloric acid and with a smaller proportion of ether (50 c.c.), the solution turned red and deposited a large quantity of crystals. When the deposition appeared to be complete, these were separated, washed with ether, and dried; in appearance they resembled bronze filings; m. p. 198—200° (De, *J. Indian Chem. Soc.*, 1927, **4**, 25, 137, describes 2-*o*-hydroxystyryl-3-methylbenzopyrylium chloride similarly, m. p. 200°). Addition of ferric chloride in acetic acid to a solution of this chloride in hot acetic acid gave on cooling red needles of a ferrichloride, m. p. 175—177° and 179—180° recrystallised (De, *loc. cit.*, records 180°).

The preparation was repeated with 20 g. of the aldehyde and 40 g. (3 mols.) of ketone; the solid which separated appeared as before, and had m. p. 180°, raised to 185—190° on admixture with the foregoing chloride.

Repetition of Chatterji and Ghosh's Condensation.—Salicylaldehyde (1·22 g.) and benzoylacetone (1·62 g.), dissolved in excess of methyl alcohol, were cooled in a freezing mixture, and hydrogen chloride was passed in for 2 hours. After standing for a few hours, the red solution was poured into dilute hydrochloric acid, and the brown solid collected and dried (1·75 g.), m. p. 115—120° (shrinking).

Perchlorate. The whole of the above solid was dissolved in boiling acetic acid, and dilute perchloric acid was added till no more precipitate was produced. The solution was then heated until all the solid was dissolved, cooled a little, separated from tar, and poured into an ice-cooled beaker (stirring); the resulting red-brown powder was collected and dried on a porous tile, m. p. 135—140°; mixed with perchlorate of m. p. 220—222° (see below), it had m. p. 155—165°.

Condensation in Presence of Perchloric Acid.—(1) The above quantities of salicylaldehyde and benzoylacetone, together with 70% perchloric acid (1·5 g.), were dissolved in dry ether (10 c.c.), saturated with hydrogen chloride, and poured into dilute perchloric acid; the tarry mass which separated solidified on standing, and was then dissolved in hot acetic acid, to which hot dilute perchloric acid was added until a precipitate was produced. After cooling, the red solid was collected and dried in a vacuum over potassium hydroxide; m. p. 103—105°.

(2) With acetic acid as solvent, similar treatment afforded the same material, m. p. 107—110°.

(3) Expt. 2 was repeated with twice the amount of salicylaldehyde. The solid was isolated by treatment with dilute perchloric acid, and crystallised as above, m. p. 220—222°; mixed with any of the above perchlorates, it caused an elevation of their m. p.'s; yield (calc. for salicylidene perchlorate) 98%. The thoroughly dried material was recrystallised from an ice-cooled beaker, and appeared as red-brown micro-prisms, m. p. 234—235° (shrinking); yield 72% (Found: C, 65·8; H, 3·8. Calc. for $C_{24}H_{17}O_7Cl$: C, 63·7; H, 3·8%. Calc. for $C_{17}H_{13}O_6Cl$: C, 58·5; H, 3·7%).

Conversion into the corresponding ψ-base or spiro*pyran.* The purified perchlorate (1 g.) was dissolved in a small quantity of hot acetic acid, and poured, with stirring, into excess 2*N*-sodium hydroxide. After 24 hours, the precipitate was collected, but as it could not be recrystallised it was purified by dissolving it in a large quantity of alcohol, filtering the solution, adding water, and boiling off the alcohol (Found: C, 80·6; H, 4·9. Calc. for $C_{24}H_{16}O_3$: C, 81·8; H, 4·6%. Calc. for $C_{17}H_{14}O_3$: C, 76·7; H, 5·3%). This yellowish-brown base could be reconverted into the initial perchlorate by treatment of its solution in concentrated hydrochloric acid with dilute perchloric acid.

UNIVERSITY OF LONDON,
UNIVERSITY COLLEGE.

[*Received, December 23rd*, 1932.
Revised, May 26th, 1933.]