

374. *The Preparation of Pyrylium Salts from Acid Anhydrides and Acid Chlorides.*

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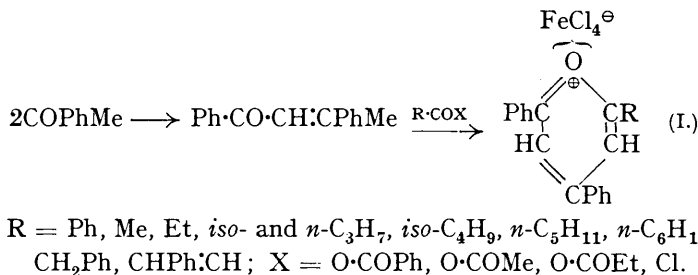
By the interaction of acetophenone (2 mols.) or dypnone with various acid anhydrides or chlorides (1 mol.) in the presence of anhydrous ferric chloride (excess), a number of 2-substituted 4 : 6-diphenylpyrylium ferrichlorides (I) have been prepared. Highest yields were obtained when acyl chlorides were used. No marked condensation occurred in the absence of ferric chloride; an earlier suggestion—that in these reactions the anhydrides are acting as ketones—therefore cannot be wholly correct. The effective intermediates may be compounds of the type $R\cdot CO\cdot Cl + FeCl_3$.

THE production of the kation of 4 : 6-diphenyl-2-methylpyrylium from acetophenone, sublimed ferric chloride, and acetic anhydride (Dilthey, *J. pr. Chem.*, 1916, **94**, 72; cf. Schneider and Ross, *Ber.*, 1922, **55**, 2775) was discussed by Le Fèvre and Pearson (J., 1933, 1197), who showed that if, in this reaction, benzoic anhydride were substituted for acetic anhydride, the ferrichloride of 2 : 4 : 6-triphenylpyrylium was obtained.

In the present work the use of other anhydrides, leading to the corresponding 2-substituted 4 : 6-diphenylpyrylium salts, has been studied; it has further been found that acid chlorides can replace anhydrides in these syntheses, with improvement of the yields

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(which are, further, in *all* the reactions tried, higher when aliphatic rather than aromatic reagents are used). Since either acetophenone or the equivalent amount of dypnone may be employed, the known facts can be summarised by the following scheme :



The suggestion of Le Fèvre and Pearson (*loc. cit.*), that acetic anhydride behaved in the original (Dilthey) condensation as a ketone, could of course be extended to cover the new reactions now recorded. However, against such a simple view must be set the observation that no salt formation can be induced by hydrogen chloride between representative acid chlorides or anhydrides and acetophenone in anhydrous ether-perchloric acid media [*i.e.*, conditions which should give the perchlorates corresponding to (I); cf. Löwenbein and Katz, *Ber.*, 1926, **59**, 1377; Le Fèvre and Le Fèvre, *J.*, 1933, 1532]. The ferric chloride cannot serve merely to generate from an anhydride the corresponding acyl chloride (since ethereal hydrogen chloride could do this), but evidently takes a more specific part in the reactions. The influence of this substance on the reactivities of acetic anhydride and benzoyl chloride has been noted previously by Knoevenagel (*Annalen*, 1913, **402**, 133) and Wedekind and Haussermann (*Ber.*, 1901, **34**, 2081), and Böeseken (*Rec. Trav. chim.*, 1903, **22**, 316) has isolated a molecular compound C₆H₅·COCl + FeCl₃ (red hygroscopic needles) which may represent the type of intermediate effective in the present experiments. The mechanism thus would have points of similarity with that proposed by Perrier (*Ber.*, 1900, **33**, 815) and Böeseken (*Rec. Trav. chim.*, 1900, **19**, 19; 1901, **20**, 102) and verified by Steele (*J.*, 1903, **83**, 1470) for the Friedel-Crafts synthesis of ketones.

Among the tabulated results on p. 1991 we have included the condensation of dypnone with acetaldehyde or benzaldehyde in the presence of ferric chloride, to the corresponding 2-methyl- or 2-phenyl-4 : 6-diphenylpyrylium ferrichlorides. These two reactions cannot be exactly analogous to those with acid anhydrides and chlorides above (although the initial action of the ferric chloride *may* be to chlorinate the aldehyde to an acyl halide), but probably involve the oxidation of an intermediate at the stage marked * :—



EXPERIMENTAL.

Interaction of Dypnone with Aldehydes and Acyl Chlorides.—Dypnone (4.4 g.) was mixed with the equivalent weight of aldehyde or chloride, and sublimed ferric chloride (4 g.) added slowly below 0°. After several hours, the mixture was heated for 1 hour on the water-bath and extracted with hot alcohol, and the separated product crystallised from acetic acid or anhydride. Acetaldehyde (1 g.) or acetyl chloride (6 g.) gave 4 : 6-diphenyl-2-methylpyrylium ferrichloride (4 g. and 4.2 g. respectively); m. p. and mixed m. p. 175°; benzaldehyde (2.3 g.) or benzoyl chloride (7 g.) gave the related 2-phenyl salt (1 g. in each case), m. p. and mixed m. p. 270—271°.

Interaction of Acetophenone with Acid Anhydrides or Chlorides.—Acetophenone (5 g.) was mixed with the equivalent weight of an acid anhydride or chloride and treated slowly, below 0°, with anhydrous ferric chloride (4 g.). Heat was evolved and an intermediate yellow compound seen. After 24 hours and 1 final hour at 100° the ferrichlorides were isolated as above.

The table shows the name of the 2-substituent of the 4 : 6-diphenylpyrylium kation, the anhydride or acyl chloride, etc., from which it was produced, the weight (g.) of the latter used, the yield (g.), and the m. p. of the product :

	Methyl	Acetic anhydride	5	2.5	175°
	Methyl	Acetyl chloride	6	3.2	175
	Methyl	Acetaldehyde	1	1.5	175
	Phenyl	Benzoic anhydride	10	0.5	271
	Phenyl	Benzoyl chloride	7	4.0	270—271
	Phenyl	Benzaldehyde	2.3	3.7	271
1	<i>Ethyl</i>	Propionyl chloride	8	5.0	166
	<i>Ethyl</i>	Propionic anhydride	9.5	4.0	166
2	<i>n-Propyl</i>	<i>n</i> -Butyryl chloride	10	5.0	198
3	<i>isoPropyl</i>	<i>iso</i> Butyryl chloride	10	4.7	258
4	<i>isoButyl</i>	<i>iso</i> Valeryl chloride	8	5.0	162
5	<i>n-Amyl</i>	<i>n</i> -Hexoyl chloride	10	4.5	144
6	<i>Hexyl</i>	Heptoyl chloride	11.2	5.0	88
7	<i>Styryl</i>	Cinnamoyl chloride	12	4.5	257
8	<i>Benzyl</i>	Phenylacetyl chloride	12	1.0	203

Analyses.

	Formula.	Found %.			Required %.		
		C.	H.	Fe.	C.	H.	Fe.
1	C ₁₉ H ₁₇ OCl ₄ Fe	—	—	12.1	—	—	12.2
2	C ₂₀ H ₁₉ OCl ₄ Fe	50.8	4.17	12.0	50.6	4.02	11.8
3	C ₂₀ H ₁₉ OCl ₄ Fe	—	—	11.8	—	—	11.8
4	C ₂₁ H ₂₁ OCl ₄ Fe	—	—	11.6	—	—	11.5
5	C ₂₂ H ₂₃ OCl ₄ Fe	52.7	4.57	11.2	52.7	4.53	11.2
6	C ₂₃ H ₂₅ OCl ₄ Fe	53.3	5.01	10.9	53.6	4.49	10.9
7	C ₂₅ H ₁₉ OCl ₄ Fe	—	—	10.1	—	—	10.4
8	C ₂₄ H ₁₉ OCl ₄ Fe	—	—	10.7	—	—	10.7

General Properties.—The ferrichlorides 1—8 form yellow to brown needles, showing a marked bluish fluorescence in ultra-violet light when dissolved in most solvents and in daylight when dissolved in water. The red-orange 2-styryl derivative is the only exception, fluorescing green in sunlight in acetic acid and in aqueous solution.

Miscellaneous Reactions.—The interaction of acetophenone with ethyl acetate or phthalic anhydride under the above conditions afforded no isolable product. Preliminary experiments with the mixed anhydrides acetic–butyric and acetic–benzoic led to normal yields of ferrichlorides, m. p. 180—230°, evidently mixtures. These were not examined further than was necessary to make certain that a unidirectional synthesis had not occurred.

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