Derivatives of Acetoacetic Acid. Part VIII. The Synthesis of Coumarins from Aryl Acetoacetates.†*

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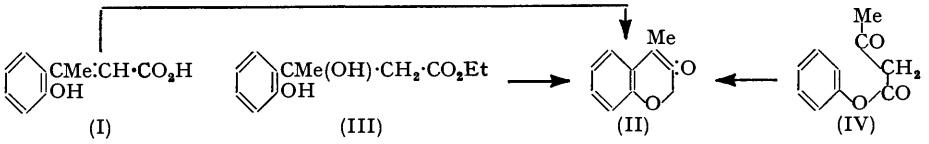
[Reprint Order No. 4551.]

Aryl acetoacetates, which are readily obtained by reaction of a phenol with diketen in the presence of a basic catalyst, *e.g.*, triethylamine, are converted into coumarins by sulphuric acid. The yields obtained from the acetoacetates of a variety of substituted phenols, in general, ran parallel to those obtained from the Pechmann reaction.

Since aryl acetoacetates did not give chromones with phosphoric oxide, the mechanism postulated by Ahmed and Desai (*Proc. Indian Acad. Sci.*, 1937, **5**, *A*, 277) for the Simonis reaction must be rejected. It was established that aryl acetoacetates under these conditions were converted, in low yield, into aryl 2 : 6-dimethyl-4-pyrone-3-carboxylates.

Two essentially similar views have been put forward regarding the mechanism of the Pechmann synthesis of coumarins from phenols and β-keto-esters (cf. Sethna and Shah, *Chem. Reviews*, 1945, **36**, 1; Wawzonek, "Heterocyclic Compounds," Edited by Elderfield, Wiley, 1951, Vol. II, p. 181). Robertson, Waters, and Jones (*J.*, 1932, 1681) suggested that a substituted cinnamic acid (I) is an intermediate, whilst Ahmed and Desai (*Proc. Indian Acad. Sci.*, 1937, **5**, *A*, 277) believed that the intermediate is a β-hydroxy-β-phenylbutyric ester (III). A third proposal, that of Dallemagne and Martinet (*Bull. Soc. chim.*, 1950, **17**, 1132), will be discussed later.



These views do not preclude the possibility that the reaction proceeds through a phenyl acetoacetate (IV) which may cyclise if an activated hydrogen atom is present in the *ortho*-position. Hofheim and Schmidt (U.S.P. 2,351,366) claimed the preparation of phenyl acetoacetate from diketen and phenol in the presence of basic catalysts, and we have found this method to be a general one. Aryl acetoacetates were generally unstable, solid esters often liquefying with formation of the parent phenol within a few weeks. Liquid esters decomposed on attempted distillation.

Aryl acetoacetates, in many cases, cyclised on treatment with sulphuric acid: the

* Part VII, preceding paper.

† B.P. 682,457 (2/2/1950), see also Nordt and Delfs, G.P. 823,140 (3/12/1949).

results are tabulated below together with the yields afforded by the Pechmann reaction as described in the literature.

The results show that the yields of coumarins obtained from aryl acetoacetates are, in most cases, similar to those obtained in the Pechmann reaction, and that the effect of electron-donating substituents is similar in both reactions (cf. Pechmann and Duisberg, *loc. cit.*; Fries and Klostermann, *loc. cit.*; Clayton, *loc. cit.*). The yields obtained from the tolyl and xylyl esters indicate that the effects of directive substituents on coumarin yield are in the order *para* > *meta* > *ortho* ~ *vic.-meta* to the point of attack in the cyclisation reaction, *ortho* and *vic.-meta* (*i.e.*, adjacent to the ester group) substituents being without significant directive influence.

Dey and Lakshminarayanan (*J. Indian Chem. Soc.*, 1932, **9**, 153) found that the Pechmann condensation of β-naphthol with acetoacetic ester gave both a benzocoumarin and a benzochromone. β-Naphthyl acetoacetate with 90% sulphuric acid gave a poor yield of a mixture from which was obtained the expected styryl derivative of 2-methyl-5 : 6-benzochromone, indicating that the product was probably similar to that obtained in the Pechmann reaction.

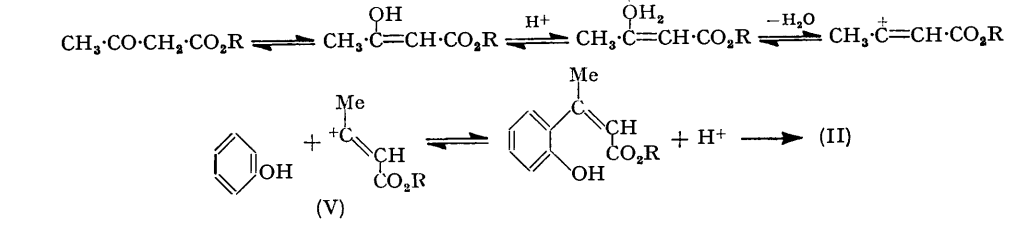
	H_2SO_4, %	Coumarin, %	Lit. yield, %
Phenol	75	11	21 [1]
Resorcinol	98	14 [2] 85 95·5 [4]	30—40 [2] 82—90 [3]
Quinol	75	36·5	20—34 [5]
Catechol	75—98	nil	nil [6]
Pyrogallol	98	69	— [7]
m-Cresol	75	75	71 [8]
p- ,, ...	,,	71	40 [8] 70 [9]
o- ,, ...	,,	19	— [10]
2 : 3-Xylenol * ...	75	63·5	—
2 : 4- ,, * ...	90	48	50 [11] 97 [12]
2 : 5- ,, * ...	75—98	nil	nil [13]
3 : 4- ,, * ...	75	87	58 [11]
3 : 5- ,, * ...	90	49·5	30—40 [11, 14]
α-Naphthol	80	100	85—100 [15]
p-Chlorophenol	75	1·75	3 [14]
4-Chloro-*m*-cresol	,,	1·1	— [16]

* OH = 1.

[1] Peters and Simonis, *Ber.*, 1908, **41**, 831. [2] Sethna, Shah, and Shah, *Current Sci.*, 1937, **6**, 93 ($AlCl_3$ was used as condensing agent). [3] *Organic Syntheses*, Wiley, 1941, Vol. 21, 23. [4] Figures refer to use of hydrochloric acid in acetic acid as condensing agent. [5] Borsche, *Ber.*, 1907, **40**, 2732; de Benneville and Connor, *J. Amer. Chem. Soc.*, 1940, **62**, 3067. [6] Pechmann and Graeger, *Ber.*, 1901, **34**, 378. [7] Pechmann and Duisberg, *Ber.*, 1883, **16**, 2119, yield not given. [8] Fries and Klostermann, *Ber.*, 1906, **39**, 871. [9] Patel and Bokil, *Chem. Abs.*, 1943, **37**, 5969 (80% sulphuric acid being used). [10] The condensation with sulphuric acid fails in this case although the use of aluminium trichloride affords the coumarin (ref. 2 above). [11] Clayton, *J.*, 1908, 2016. [12] Flynn and Robertson, *J.*, 1936, 215 (86% sulphuric acid being used). [13] Goodall and Robertson, *ibid.*, p. 426. [14] Adams and Mecorney, *J. Amer. Chem. Soc.*, 1944, **66**, 802. [15] Robertson, Sandrock, and Hendry, *J.*, 1931, 2426; Auwers and Meissner, *Annalen*, 1924, **439**, 132. [16] Chakravarti and Bannerjee, *J. Ind. Chem. Soc.*, 1936, **13**, 619; yield not given.

Adams and Mecorney (*loc. cit.*) showed 4-chloro-3 : 5-xylenol to be unique in giving only a chromone on condensation with acetoacetic ester and sulphuric acid. 4-Chloro-3 : 5-xylyl acetoacetate was readily hydrolysed by 75% sulphuric acid but 98% acid gave a 33% yield of 6-chloro-2 : 5 : 7-trimethylchromone.

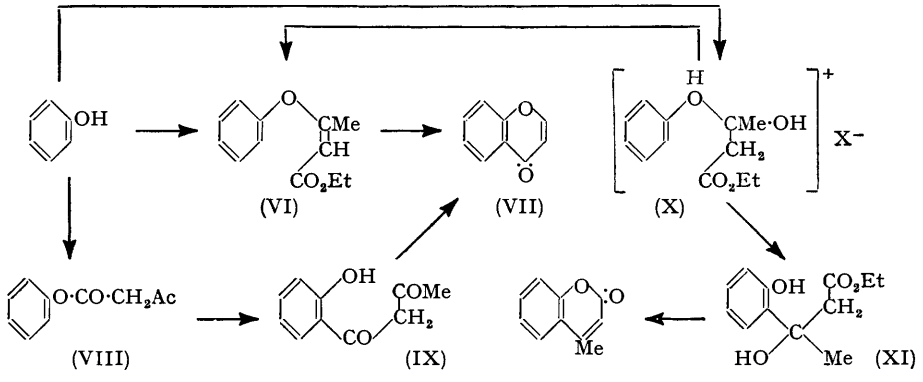
The results obtained are not contrary to the mechanism suggested by Robertson, Waters, and Jones (*loc. cit.*), although the possibility that the Pechmann condensation may



proceed *via* the aryl acetoacetate has been demonstrated. In either case, the controlling step is the condensation of the ester on the *ortho*-position of the phenol, and it is suggested that, for the Pechmann reaction, this involves first the formation of the carbonium ion (V)

which may then attack the nucleus in the manner usual in aromatic cationoid reactions. Such alkylations are reversible and the condensation would proceed only if substitution takes place in the *ortho* position so that coumarin formation follows (a π-complex between the carbonium ion and the aromatic system might afford a more accurate description of the transition state). Accepted theories concerning the orientation of cationoid substitution explain many of the results obtained by using substituted phenols, although the question is complicated by such side-reactions as sulphonation and hydrolysis.

The Simonis reaction between phenols and β-keto-esters, giving chromones (Petschek and Simonis, *Ber.*, 1913, **46**, 2014), takes place only in the presence of phosphoric oxide, phosphorus oxychloride, or, in very exceptional cases, with sulphuric acid. Three mechanisms have been proposed: the first involving the formation of a β-phenoxyacrylic acid derivative (VI) followed by ring closure to the chromone (VII) (Robertson, Waters, and Jones, *loc. cit.*), and the second proceeding *via* a phenyl acetoacetate (VIII) followed by a Fries type of rearrangement to an *o*-acetoacetylphenol (IX) and subsequent ring closure (Ahmed and Desai, *loc. cit.*). In the third mechanism (Dallemagne and Martinet, *loc. cit.*) it is supposed that both the Pechmann and the Simonis reaction proceed through the 'onium salt (X) formed by combination of the phenol, β-ketonic ester, and the acid catalyst. This hypothetical intermediate, according to the French workers, can either dehydrate to a β-phenoxyacrylic ester and thence to a chromone (favoured by α-substitution of the keto-ester and by increased acidity of the phenol, *e.g.*, with halogen or nitro-substitution), or the intermediate may rearrange to (XI), which on elimination of water and alcohol would afford the coumarin.

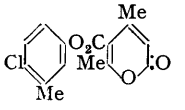
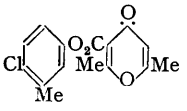


There seems little essential difference between this mechanism for chromone formation and that of Roberston *et al.* (*loc. cit.*). Since many coumarins are formed in very high yield, and in many cases even under the conditions of the Simonis reaction, which, even in favourable cases, gives chromones only in poor yields, it is necessary to assume that, in Dallemagne and Martinet's mechanism, the rearrangement to (XI) must take place much more readily than does the relatively simple dehydration to (VI). Also, the proposed mechanism does not account for recent observations by Mentzer and his co-workers (Mentzer, Molho, and Vercier, *Compt. rend.*, 1952, **232**, 1488; Mentzer and Pillon, *ibid.*, 1952, **234**, 444) that certain substituted phenols, which in the Pechmann reaction give coumarins in high yield (*e.g.*, resorcinol), afford chromones simply when heated with a β-keto-ester, *e.g.*, ethyl α-benzylacetoacetate, in the absence of catalyst.

In order to test the mechanism proposed by Ahmed and Desai (*loc. cit.*), the aceto-acetate of 4-chloro-*m*-cresol, a phenol known to give chromones in the Simonis reaction (Chakravarti and Bannerjee, *loc. cit.*), was heated with phosphoric oxide. The product, isolated in poor yield, was shown not to be a chromone, and acid hydrolysis gave carbon dioxide, 4-chloro-*m*-cresol, and 2 : 6-dimethyl-γ-pyrone, indicating the structure (XIII). The possible formulation (XII) was eliminated by an independent synthesis of this substance. The absence of chromone disproves Ahmed and Desai's mechanism.

It was also shown that the conversion of an aryl acetoacetate into an aryl 2 : 6-

dimethyl-γ-pyrone-3-carboxylate by phosphoric oxide is a general reaction, exhibited by phenols (*a*) which readily afford coumarins in the Pechmann reaction, *e.g.*, 3 : 4-xylenol, (*b*) which fail to give coumarins but give chromones in the Simonis reaction, *e.g.*, 2 : 5-xylenol, and (*c*) which give coumarins and chromones in the Pechmann and Simonis reactions, respectively, *e.g.*, 2 : 4-xylenol and 4-chloro-*m*-cresol.

(XII)   (XIII)

A most interesting parallel may be drawn between the above reaction and the Simonis reaction on the one hand, both taking place in the presence of phosphoric oxide to give derivatives of γ-pyrone, and, on the other hand, the formation of *iso*dehydroacetic acid (and ester) from the self-condensation of acetoacetic ester and the Pechmann reaction, both being effected by sulphuric acid, giving derivatives of α-pyrone. The action of phosphoric oxide in the Simonis reaction and in the formation of phenyl 2 : 6-dimethyl-γ-pyrone-3-carboxylates, is that of a dehydration catalyst causing the linkage, with elimination of water, of an enol and a phenol group and of two enol groups, respectively. The uncatalysed formation of chromones observed by Mentzer *et al.* (*loc. cit.*) can possibly be attributed to high-temperature etherification to the phenoxyacrylic ester, followed by cyclisation.

Experimental

M. p.s were carried out using a Kofler block and are corrected.

Phenyl Acetoacetate.—Diketen (84 g.) was added dropwise during 1 hr. to an agitated mixture of phenol (94 g.) and triethylamine (0·5 c.c.) at 70—80°. After a further 0·5 hr.' heating, an almost quantitative yield was obtained of *phenyl acetoacetate*; this formed prisms, m. p. 48—49°, from chloroform–light petroleum (b. p. 60—80°) (Found: C, 67·55; H, 5·65. $C_{10}H_{10}O_3$ requires C, 67·4; H, 5·6%). Phenyl acetoacetate decomposed to phenol on attempted distillation at 1 mm.; it is believed that the product, b. p. 130—142°/17 mm., obtained by Hofheim and Schmidt (*loc. cit.*) must have been a mixture.

This ester (10 g.) and sulphuric acid (75%; 30 c.c.) were heated at 50° for 6 hr., and then poured into water. An ethereal extract after treatment with sodium hydroxide solution to remove phenol, and evaporation, gave 4-methylcoumarin (1·0 g., 11%), m. p. 88° (Peters and Simonis, *loc. cit.*, give m. p. 90°).

To a solution of phenyl acetoacetate (89 g.) in nitrobenzene (100 c.c.) at 100° was added anhydrous aluminium trichloride (67 g.) in nitrobenzene (300 c.c.) with agitation during 0·5 hr. After 3 hr. at 100°, the product was cooled and shaken with hydrochloric acid (50 c.c. of concentrated acid and 50 c.c. of water); the oily layer was distilled, giving 4-methylcoumarin (11·0 g., 14%), b. p. 180°/15 mm.

m-*Hydroxyphenyl Acetoacetate.*—An agitated suspension of resorcinol (55 g.) in boiling benzene (200 c.c.) containing triethylamine (0·4 c.c.) was treated with diketen (45 g.) added during 1 hr., and heating was continued for a further 0·5 hr. The solvents were then removed under reduced pressure, giving the *ester* (96 g., 99%), which, on crystallisation from aqueous methanol, formed plates, m. p. 103° (Found: C, 61·9; H, 5·2. $C_{10}H_{10}O_4$ requires C, 61·85; H, 5·2%).

The acetoacetate (48·5 g.) was added during 15 min. to sulphuric acid (98%; 100 c.c.) with agitation and cooling, the temperature being maintained at 70°. After being heated at 70° for a further 0·5 hr. the deep red solution was poured into water, giving 7-hydroxy-4-methylcoumarin (37·4 g., 85%), which formed needles, m. p. 186°, from methanol (Pechmann and Duisberg, *loc. cit.*, give m. p. 185°). A solution of the ester (19·4 g.) in acetic acid (50 c.c.) was saturated with dry hydrogen chloride. Next morning the product was poured into water, giving the coumarin (16·8 g., 95·5%), m. p. 180—182°.

p-*Hydroxyphenyl Acetoacetate.*—This *acetoacetate* was prepared in 98% yield (crude) from quinol, as described for the *meta*-compound, and formed prisms, m. p. 98°, from ethyl acetate–light petroleum (b. p. 60—80°) (Found: C, 61·7; H, 5·3%).

The ester (10 g.) was heated with sulphuric acid (75—80%) at 50° for 24 hr. and then poured

into water. 6-Hydroxy-4-methylcoumarin had m. p. 248° after crystallisation from aqueous ethanol (Borsche, *loc. cit.*, gives m. p. 243°).

o-*Hydroxyphenyl Acetoacetate.*—This ester was obtained from catechol as an oil which failed to give any coumarin on treatment with 75—98% sulphuric acid.

Pyrogallol Monoacetoacetate.—The reaction of pyrogallol with diketen as previously described, followed by the removal of solvent, gave an oil which, although it slowly solidified, could not be purified by recrystallisation. The crude product (20 g.) and concentrated sulphuric acid (30 c.c.) were kept at 60—70° for 0·5 hr., and then poured into water. The precipitate (12·5 g., 69%), on crystallisation from aqueous methanol, gave 7 : 8-dihydroxy-4-methylcoumarin, m. p. 244° (Pechmann and Duisberg, *loc. cit.*, give m. p. 235°).

m-*Tolyl Acetoacetate.*—The ester was prepared from *m*-cresol (54 g.), triethylamine (0·5 c.c.) and diketen (42 g.) at 60—70° in the usual way. The product failed to crystallise but afforded a 2 : 4-*dinitrophenylhydrazone* as plates, m. p. 148—149°, from ethyl acetate–light petroleum (b. p. 60—80°) (Found : C, 54·6; H, 4·45; N, 14·9. $C_{17}H_{16}O_6N_4$ requires C, 54·85; H, 4·35; N, 15·05%). Cyclisation of the ester (20 g.) was best effected with 75% sulphuric acid (60 c.c.) at 50° for 24 hr. Crystallisation of the product (75%) from aqueous alcohol gave 4 : 7-dimethylcoumarin, m. p. 132° (Fries and Klostermann, *loc. cit.*, give m. p. 132°).

p-*Tolyl Acetoacetate.*—Prepared from *p*-cresol and diketen in the normal way and crystallised from chloroform–light petroleum (b. p. 40—60°), the *acetoacetate* (crude yield, 97%) formed clusters of needles, m. p. 65—66° (Found : C, 68·6; H, 6·35. $C_{11}H_{12}O_3$ requires C, 68·75; H, 6·3%). Heating of the ester (10 g.) with sulphuric acid (30 c.c.; 75—80%) at 50° for 24 hr. gave 4 : 6-dimethylcoumarin in 71% yield, m. p. 150—151°. The use of 98% acid at 20° gave only a 5% yield (Fries and Klostermann, *loc. cit.*, give m. p. 150°).

o-*Tolyl Acetatoacetate.*—This ester was obtained as an oil which gave a 2 : 4-*dinitrophenylhydrazone*, prisms, m. p. 125°, from *iso*propanol (Found : C, 55·25; H, 4·25; N, 14·7%). The ester was cyclised as for the *para*-compound, the solution poured into water, the product extracted with ether, the extracts washed with sodium hydroxide solution (10%), and the solvent evaporated. The coumarin (crude yield : 18—19%) formed needles, m. p. 112—113°, after recrystallisation from ethyl acetate–light petroleum (b. p. 60—80°) (Found : C, 75·65; H, 5·8. Calc. for $C_{11}H_{10}O_2$: C, 75·85; H, 5·8%). Since the material failed to give a precipitate with bromine in acetic acid [claimed by Desai (cf. Sethna and Shah, *loc. cit.*, p. 26) to be a diagnostic test for chromones], the product must be 4 : 8-dimethylcoumarin (Dey, *J.*, 1915, 1637, gives m. p. 118°) and not the isomeric 2 : 8-dimethylchromone (Simonis and Lehmann, *Ber.*, 1914, **47**, 697, give m. p. 115°).

2 : 3-*Xylyl Acetoacetate.*—Diketen (8·7 g.) was added dropwise during 0·5 hr. to an agitated, boiling solution of 2 : 3-xylenol (12·2 g.) in benzene (20 c.c.) containing triethylamine (0·2 c.c.). After being refluxed for 0·5 hr., the product was evaporated, giving the acetoacetate as an oil (21·4 g.). The ester (5 g.) was treated with sulphuric acid (15 c.c.; 98, 90, and 75%), and the mixtures set aside at room temperature for 24 hr. 4 : 7 : 8-*Trimethylcoumarin* (yields : 36, 60, and 63·5, respectively) formed needles, m. p. 145°, from aqueous ethanol (Found : C, 76·45; H, 6·5. $C_{12}H_{12}O_2$ requires C, 76·55; H, 6·45%).

2 : 4-*Xylyl Acetoacetate.*—The ester (an oil) was prepared from 2 : 4-xylenol and diketen as above. Cyclisation was carried out as with 2 : 3-xylyl acetoacetate, the products being isolated as described under the *o*-tolyl ester, giving the coumarin in 5, 48, and 24% yields, with sulphuric acid of 98, 90, and 75% concentration, respectively. 4 : 6 : 8-Trimethylcoumarin formed needles, m. p. 113—114°, from light petroleum (b. p. 60—80°) (Flynn and Robertson, *loc. cit.*, give m. p. 114—114·5°).

2 : 5-*Xylyl Acetoacetate.*—Prepared as previously described from 2 : 5-xylenol and diketen, the oily acetoacetate, on treatment with sulphuric acid (75, 80, or 98%) at 20° for 24 hr. and isolation as described under *o*-tolyl acetoacetate, failed to give any trace of coumarin.

3 : 4-*Xylyl Acetoacetate.*—Treatment of 3 : 4-xylenol with diketen as previously described afforded the *acetoacetate*, as needles, m. p. 45°, from light petroleum (b. p. 40—60°) (Found : C, 69·65; H, 6·65. $C_{12}H_{14}O_3$ requires C, 69·9; H, 6·85%). Treatment of the ester (5 g.) with sulphuric acid (15 c.c.; 80%) at room temperature for 24 hr., followed by isolation in the usual way, gave 4 : 6 : 7-trimethylcoumarin (86%), which recrystallised from aqueous alcohol as needles, m. p. 170—171° (Clayton, *loc. cit.*, gives m. p. 169—170°).

3 : 5-*Xylyl Acetoacetate.*—Acetoacetylation of 3 : 5-xylenol gave the *acetoacetate*, as needles, m. p. 48—49°, from light petroleum (b. p. 40—60°) (Found: C, 69·95; H, 6·9%). Cyclisation of the ester (5 g.) with sulphuric acid (90%; 15 c.c.) at 20° for 20 hr. gave a 49·5% yield of coumarin; more concentrated acid and shorter reaction times gave lower yields. 4 : 5 : 7-

Trimethylcoumarin formed plates, m. p. 183—184·5°, from ethanol (Clayton, *loc. cit.*, gives m. p. 175—176°).

α-*Naphthyl Acetoacetate.*—This *acetoacetate* was prepared by the standard method from α-naphthol and diketen in 86% yield; it crystallised as prismatic needles, m. p. 65—66·5°, from benzene–light petroleum (b. p. 40—60°) (Found: C, 73·5; H, 5·4. $C_{14}H_{12}O_3$ requires C, 73·65; H, 5·3%). Treatment of the ester (10 g.) with sulphuric acid (90%; 30 c.c.) at 20° for 24 hr. gave 4-methyl-7 : 8-benzocoumarin (6·4 g., 69·5%) which had m. p. 171°, after recrystallisation from ethanol (Appel, *J.*, 1935, 1031, gives m. p. 169·5—170·5°). Use of 80% sulphuric acid gave a quantitative yield of coumarin, m. p. 163—165°.

β-*Naphthyl Acetoacetate.*—Prepared from β-naphthol, the *acetoacetate* was obtained in 98% yield, and crystallised from ether–light petroleum ether (b. p. 60—80°) as plates, m. p. 80—81° (Found: C, 74·0; H, 5·3%). Both α- and β-naphthyl acetoacetates were more stable on storage than those derived from substituted phenols. Treatment of the ester (10 g.) with 98% or 80% sulphuric acid (30 c.c.) at room temperature afforded no significant amount of alkali-insoluble product, but with 90% acid a solid product (1·8 g.), m. p. 135—140°, was obtained. Repeated recrystallisation from ethanol did not raise this m. p. (Dey and Lakshminarayanan, *loc. cit.*, give m. p. 179° for the expected coumarin). The material (0·50 g.) with alcoholic sodium ethoxide and benzaldehyde afforded the styrylchromone (0·30 g.), m. p. 205—206° (Dey and Lakshminarayanan, *loc. cit.*, give m. p. 198°), and in acetic acid solution gave a precipitate with bromine in the same solvent indicating the presence of chromone (Desai, *loc. cit.*).

p-*Chlorophenyl Acetoacetate.*—The reaction of *p*-chlorophenol with diketen gave the *aceto-acetate* (crude yield 95%) which formed needles, m. p. 54—55°, from chloroform–light petroleum (b. p. 40—60°) (Found: C, 56·85; H, 4·25. $C_{10}H_9O_3Cl$ requires C, 56·5; H, 4·25%). Treatment of the ester (10 g.) with sulphuric acid (75%; 30 c.c.) at room temperature overnight, and recrystallisation of the crude product from ethanol gave 6-chloro-4-methylcoumarin as needles (0·16 g.), m. p. 184—185° (Clayton, *loc. cit.*, gives m. p. 184—185°).

4-*Chloro*-m-*tolyl Acetoacetate.*—This ester solidified when first obtained but was unstable and soon liquefied. Treatment of the crude ester (10 g.) with sulphuric acid (75%; 30 c.c.) at 20° overnight and isolation gave a small yield of 6-chloro-4 : 7-dimethylcoumarin (0·10 g.), m. p. 208—210° after crystallisation from acetic acid (Chakravarti and Bannerjee, *loc. cit.*, give m. p. 208°).

4-*Chloro*-3 : 5-*xylyl Acetoacetate.*—The *acetoacetate*, obtained in 97% yield, formed needles, m. p. 68—70°, from light petroleum (b. p. 60—80°) (Found: C, 60·0; H, 5·05. $C_{12}H_{13}O_3Cl$ requires C, 59·9; H, 5·45%). Treatment with 75% sulphuric acid at room temperature overnight resulted in complete hydrolysis to 4-chloro-3 : 5-xylenol. The acetoacetate (30 g.) and sulphuric acid (98%; 100 c.c.) were heated at 90° for 1 hr. and then set aside for 2 days. The product was poured into water, and the precipitate washed with sodium hydroxide solution (10%), giving 6-chloro-2 : 5 : 7-trimethylchromone (9·2 g.), which crystallised from aqueous ethanol as needles, m. p. 145° (Adams and Mecorney, *loc. cit.*, give m. p. 145—146°). The styryl derivative, prepared by the method of Heilbron, Barnes, and Morton (*J.*, 1923, 2559), had m. p. 186—187° (Adams and Mecorney, *loc. cit.*, give m. p. 186—186·5°).

Reactions with Phosphoric Oxide.—(a) 4-*Chloro*-m-*tolyl acetoacetate.* The ester (10 g.) was heated with phosphoric oxide (10 g.) at 100° for 3 hr., and the dark, tarry product was then triturated with cold water and ether. The ethereal extract was well washed with 5% sodium hydroxide solution and with water, dried, and evaporated, giving a residue (1·1 g.), crystallisation of which from chloroform–light petroleum (b. p. 60—80°) gave 4-*chloro*-m-*tolyl* 2 : 6-*dimethyl*-γ-*pyrone*-3-*carboxylate* as prismatic needles, m. p. 90—91° (Found: C, 61·85; H, 4·6; Cl, 12·15. $C_{15}H_{13}O_4Cl$ requires C, 61·55; H, 4·45; Cl, 12·1%). When the ester (0·3 g.) was refluxed with hydrochloric acid (10%; 10 c.c.) for 2 hr., carbon dioxide was evolved; extraction of the product with ether (2 × 10 c.c.) and evaporation of the extract gave 4-chloro-*m*-cresol (1·3 g.), m. p. 66°. The aqueous layer was saturated with potassium hydroxide and re-extracted with ether (10 × 10 c.c.) (cf. Feist, *Annalen*, 1890, **257**, 291), and the solvent evaporated giving 2 : 6-dimethyl-γ-pyrone (1·1 g.), m. p. 136° (Feist, *loc. cit.*, gives m. p. 132°).

4-Chloro-*m*-cresol (2·1 g.) was heated at 100° for 0·5 hr. with *iso*dehydroacetyl chloride (1·86 g.); hydrogen chloride was rapidly evolved. The product was crystallised from benzene–light petroleum (b. p. 60—80°), giving 4-*chloro*-m-*tolyl* iso*dehydroacetate* (1·95 g.) as needles, m. p. 101—102° depressed on admixture with the above ester (Found: C, 61·5; H, 4·4; Cl, 12·0. $C_{15}H_{13}O_4Cl$ requires C, 61·55; H, 4·45; Cl, 12·1%).

(b) 3 : 4-*Xylyl acetoacetate.* The ester (15 g.) was heated with phosphoric oxide (15 g.) as described above and, on isolation, a solid product (4·6 g.), m. p. 96—102°, was obtained.

Crystallisation from benzene–light petroleum (b. p. 60—80°) gave 3 : 4-*xylyl* 2 : 6-*dimethyl-γ-pyrone*-3-*carboxylate* as needles, m. p. 109° (Found: C, 70·25; H, 6·0. $C_{16}H_{16}O_4$ requires C, 70·55; H, 5·9%). Hydrolysis as above gave 2 : 6-dimethyl-γ-pyrone.

(c) 2 : 5-*Xylyl acetoacetate*. The ester (10·3 g.) was heated with phosphoric oxide (7·5 g.) at 100° for 1 hr., more phosphoric oxide (5 g.) added, and heating continued for another hour. Isolation as above gave a solid residue (2·75 g.) which crystallised from aqueous methanol, giving 2 : 5-*xylyl* 2 : 6-*dimethyl-γ-pyrone*-3-*carboxylate* as plates, m. p. 101° (Found: C, 70·6; H, 6·0%). Hydrolysis gave 2 : 5-xylenol and 2 : 6-dimethyl-γ-pyrone.

(d) 2 : 4-*Xylyl acetoacetate*. The ester (11·7 g.) when heated with phosphoric oxide (12·5 g.) for 2 hr. at 100° and isolated as above gave a solid (4·5 g.), m. p. 105—109°, which, on crystallisation from aqueous methanol, gave 2 : 4-*xylyl* 2 : 6-*dimethyl-γ-pyrone*-3-*carboxylate* as prismatic needles, m. p. 116° (Found: C, 70·3; H, 5·8%).

The author thanks Messrs. A. R. Philpotts and W. Thain for light-absorption measurements recorded in the various Parts of this series, Professor E. R. H. Jones for gifts of materials used in the work described in Part III, the Agricultural Research Council under whose auspices Dr. Fenwick's work referred to in Part IV was done, and the Management of the British Industrial Solvents Division of the Distillers Company Limited for permission to publish these eight papers.

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[*Received, August 1st*, 1953.]