858. *Heterocyclic Syntheses with Malonyl Chloride. Part VIII.* Hydroxypyrones from 1,3-Diketones.*

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Malonyl chloride condenses with acetylacetone, to yield 3-acetyl-5-hydroxy-2-methyl-4-pyrone (I), and with benzoylacetone to yield 5-acetyl-4-hydroxy-6-phenyl-2-pyrone (IX*a*). The latter tautomerises above its melting point into the 2-hydroxy-4-pyrone (IX*b*).

The constitutions of these new products were investigated by deacetylation and conversion into pyridones, and by ultraviolet, infrared, and proton magnetic resonance spectroscopy. The fine structures of some related " pyronones " are also discussed.

1,2-Diketones, and 1,3-dicarbonyl compounds such as ethyl acetoacetate, reacted like simple ketones with malonyl chloride and yielded chloropyronodioxins. The 1,3-diketone acetylacetone, however, gave a simpler chlorine-free product, m. p. 162°.[1] We have found that this is the 4-pyrone (I), a new isomer of dehydracetic acid. Benzoylacetone and malonyl chloride gave the corresponding 6-phenyl-2-pyrone (IX*a*) which tautomerised above 168° into the 4-pyrone form (IX*b*).

The product from acetylacetone and malonyl chloride had the molecular formula $C_8H_8O_4$, indicating that it was formed by a 1 : 1 condensation. The product behaved as a strongly acidic enol and was ketonic, and its ultraviolet-light absorption and that of the derived 2,4-dinitrophenylhydrazone (Table 2) were suggestive of an aromatic chromophore.[2] The compound was not phloroacetophenone,[3] so pyrone structures were next considered. Evidence for a 5-acetyl-6-methylpyronone formulation was obtained by deacetylation with sulphuric acid, which yielded " triacetic acid lactone " (II), long known [4] as the product of deacetylation of dehydracetic acid (III). That the fine structure was 3-acetyl-6-hydroxy-2-methyl-4-pyrone (I) followed from spectroscopic results, which are discussed below.

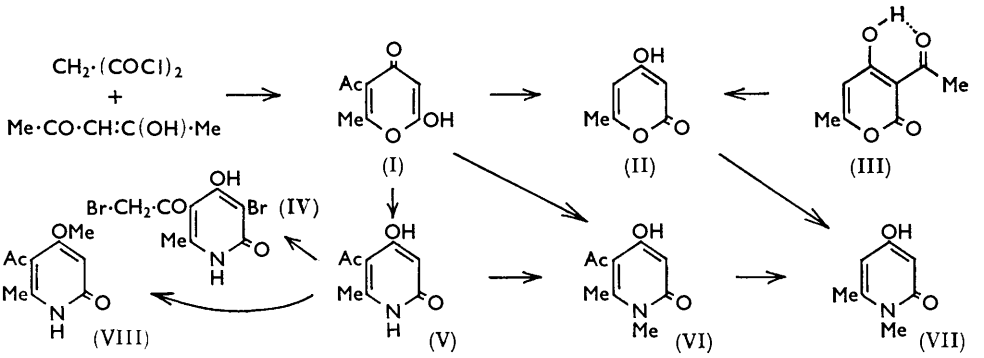
In agreement with a pyrone structure, the compound reacted with ammonia to yield a pyridone (V). This readily afforded a dibromo-derivative, for which a 3-bromo-5-bromoacetyl structure (IV) was indicated by a signal of intensity 2 in the proton magnetic resonance spectrum (Table 4). Methylation of the pyridone (V) with dimethyl sulphate and alkali gave the *N*-methyl compound (VI), as expected,[5] the same product resulting from treatment of the pyrone (I) with methylamine. Attempted deacetylation of the pyridone (V) failed, but the *N*-methyl derivative (VI) underwent the reaction smoothly and yielded 4-hydroxy-1,6-dimethyl-2-pyridone (VII), identical with the product from interaction of " triacetic acid lactone " (II) and methylamine.

With diazomethane, the pyridone (V) yielded an *O*-methyl derivative (cf. ref. 5). The

* Part VII, *J.*, 1963, 3069.

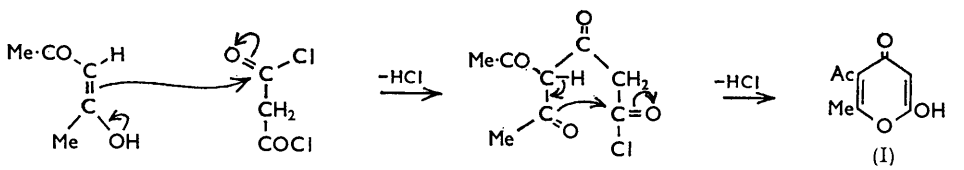
[1] Davis and Elvidge, *J.*, 1962, 3550.
[2] Braude, *Ann. Reports*, 1945, **42**, 105; Braude and Jones, *J.*, 1945, 498.
[3] Barton and Brunn, *J.*, 1953, 603.
[4] Collie, *J.*, 1891, **59**, 609; 1907, **91**, 787.
[5] Albert, " Heterocyclic Chemistry," The Athlone Press, London, 1959, p. 86.

presence of the *O*-methyl group was shown unambiguously by the proton magnetic resonance spectrum, which also showed a single ring-proton (Table 4). A resonance signal corresponding to a hydroxyl-proton could not be found, in contrast to previous experience with hydroxypyridones.[6] Hence it was concluded that the " missing " proton was present



in an amide NH group, and so was rendered undetectable by the nitrogen quadrupole relaxation. The 2-pyridone formulation (VIII) was then indicated, because of the ultraviolet absorption maximum at 271 mμ (Table 2). A maximum near 250 mμ was expected for a 2-methoxy-4-pyridone.[7] However, it must be stated that the relation between fine structure and light absorption in the dihydroxypyridine series really requires further clarification.[8] Other compounds for comparison are the 1-methylpyridone (VI) with a maximum at 292 mμ, 4-methoxy-1-methyl-2-pyridone (280 mμ),[7] and 4-ethoxy-3-ethoxycarbonyl-6-hydroxy-1-phenyl-2-pyridone (282 mμ).[6]

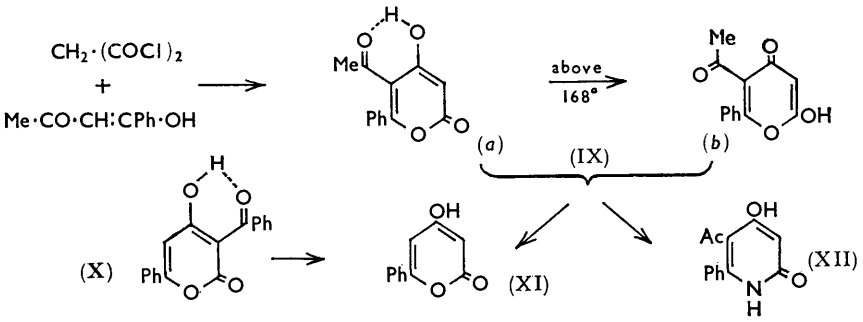
The formation of the new pyrone (I) evidently involved both *C*- and *O*-acylation of the acetylacetone by the malonyl chloride, the direction of cyclisation being immaterial:



In extension, it seemed that a markedly unsymmetrical 1,3-diketone would also give only one product, because it would be expected to react in only one sense, according to the preferred direction of enolisation. In agreement, it was found that benzoylacetone gave with malonyl chloride a 5-acetyl-6-phenylpyrone (which was characterised as a 2,4-dinitrophenylhydrazone), and no evidence was obtained for the presence of a 5-benzoyl-6-methyl isomer in the crude product.

The investigation of the reaction was at first complicated by the product's changing at its melting point (168°) into a second form (m. p. 220°). Both forms on deacetylation with sulphuric acid yielded the same product, identical with 4-hydroxy-6-phenyl-2-pyrone (XI), prepared [9] by debenzoylation of dehydrobenzoylacetic acid (X). Hence both forms were 6-phenylpyrones. That they had identical carbon skeletons was substantiated by their conversion with ammonia into a single pyridone (XII). Therefore the two compounds were hydroxypyrone tautomerides. Their orientation as (IX*a* and *b*), respectively, followed from spectroscopic observations.

[6] Butt, Elvidge, and Foster, *J.*, 1963, 3069.
[7] den Hertog and Buurman, *Rec. Trav. chim.*, 1956, **75**, 257.
[8] Davis, Elvidge, and Foster, *J.*, 1962, 3638.
[9] Arndt, Eistert, Scholz, and Aron, *Ber.*, 1936, **69**, 2373.



Fine Structure.—Previous work [10,11] had demonstrated that 4-methoxy-2-pyrones absorb in the ultraviolet region at wavelengths some 30 mμ longer than the corresponding 2-methoxy-4-pyrones, and that the carbonyl stretching frequencies are in the 1710 and 1670 cm.$^{-1}$ region, respectively. Table 1 gives the pertinent data.

TABLE 1.

Light absorptions of alkoxy-2- and -4-pyrones.[10]

Compound	$\lambda_{max.}$ (mμ) in EtOH	$10^{-3}\varepsilon$	$\nu CO_{max.}$ (cm.$^{-1}$) in $CHCl_3$	Compound	$\lambda_{max.}$ (mμ) in EtOH	$10^{-3}\varepsilon$	$\nu CO_{max.}$ (cm.$^{-1}$) in $CHCl_3$
6-Me-4-MeO-2-pyrone	280	6·3	1709	6-Me-2-MeO-4-pyrone	240	13·5	1672
6-Ph-4-MeO-2-pyrone	314	13·5	1706	6-Ph-2-MeO-4-pyrone	276	19·5	1675

Our previously described mono- and bi-cyclic 2-pyrones have shown higher-frequency absorption in the carbonyl region,[12,13] the frequency being near 1710 cm.$^{-1}$ only when hydrogen-bonding to the carbonyl group was suspected, as in 6-chloro-4-hydroxy-2-pyrone-3-carboxylic acid and its anilide.[6] The raised frequency must be caused by the electron-withdrawing substituents at the 3-position. Of the present compounds, only dehydrobenzoylacetic acid (X), with a 3-benzoyl group, has a spectrum (Table 3) which approaches in characteristics those previously found by us.

TABLE 2.

Ultraviolet absorptions in (*a*) ethanol and (*b*) dioxan.

Pyrones	$\lambda_{max.}$ (mμ)	$10^{-3}\varepsilon$	Pyridones	$_{max.}$ (mμ)	$10^{-3}\varepsilon$
(I) *a*	227	8·0	(V) *a*	237	12·2
	267	5·9		274	10·1
2,4-Dinitrophenylhydrazone from (I) *a*	270	14·6			
	358	21·6			
(II) *a*	284	7·8	(VI) *a*	292	8·5
(III) *a*	310	10·8	(VIII) *a*	271	14·6
(IX*a*) (m. p. 168°) *b*	260	11·4	(XII) *a*	252	14·5
	320	6·4		285	9·0
(IX*b*) (m. p. 220°) *b*	252	14·5			
	284	9·0			
(X) *a*	360	21·2			
(XI) *a*	221	14·0			
	232	13·5			
	260	3·6			
	322	12·0			

Before comparisons were made with the data of Table 1, it was necessary to demonstrate that our potentially tautomeric compounds existed in a monoenolic form. Not one of the compounds " triacetic acid lactone," the new 5-acetylpyrones, dehydracetic acid, and dehydrobenzoylacetic acid gave a proton magnetic resonance signal of relative

[10] Herbst, Mors, Gottlieb, and Djerassi, *J. Amer. Chem. Soc.*, 1959, **81**, 2427.
[11] Bu'Lock and Smith, *J.*, 1960, 502.
[12] Elvidge, *J.*, 1962, 2606.
[13] Davis and Elvidge, *J.*, 1962, 3553.

TABLE 3.

Infrared absorptions of pyrones (Nujol mulls).

Compound	Max. ($cm.^{-1}$)	Assignment	Compound	Max. ($cm.^{-1}$)	Assignment
(I)	1695	O=C (at 5)	(IX*b*)	1728s	O=C (at 5)
	1668	O=C (2)		1676s	O=C (4)
	1617, 1604, 1554, 1498	C=C		1622s, 1581w, 1563w, 1527	C=C
	1277s	O–C		1289sb, 1259	O–C
(II)	1719s	O=C (2)	(X)	1742s	O=C (2)
	1661w	O=C (2, H-bonded)		1628s	O=C (at 3, H-bonded)
	1630, 1594, 1543w, 1511w	C=C		1591, 1503, 1418w, 1381	C=C
	1253s	O–C		1236	O–C
(III) *	1721	O=C (2)	(XI)	1745w	O=C (2)
	1645	O=C (at 3, H-bonded)		1695	O=C (2, H-bonded)
	1613, 1548, 1353	C=C		1641, 1611s, 1579w, 1548s, 1511	C=C
	1253	O–C		1261	O–C
(IX*a*)	1713	O=C (2)			
	1685	O=C (at 5, H-bonded)			
	1622s, 1573w, 1561, 1526	C=C			
	1277sb	O–C			

* Max. (but not interpretation) from Randall, Fowler, Fuson, and Dangl, " Infrared Determination of Organic Structures," van Nostrand, Company Inc., New York, 1949, p. 231.

TABLE 4.

Proton magnetic resonance results, for 5—10% solutions in (*a*) $CDCl_3$, (*b*) $CDCl_3$ + MeOH (a minimum), (*c*) pyridine.

Compound	τ	Intensity	Multiplicity	Assignment
(I) *a*	7·37(5)	3	Doublet, *J*(6-Me/3-H) 0·5 c./sec.	Me (6)
	7·36	3	Singlet	Ac (at 5)
	4·47	1	Unresolved	H (3)
	−2·21	1	Broadened	OH (2)
(II) *b*	7·76	3	Double doublet, *J*(Me/5-H) 0·9, *J*(Me/3-H) 0·5 c./sec.	Me (6)
	4·61	1	Double quadruplet	H (3)
	4·10	1	Double quadruplet, *J*(3/5) 2·15 c./sec.	H (5)
(III) *a*	7·72	3	Doublet, *J*(6-Me/5-H) 0·6 c./sec.	Me (6)
	7·34	3	Singlet	Ac (at 3)
	4·09	1	Unresolved	H (5)
	−6·81 (concn. independent)	1	Singlet	OH (4, chelated intramolecularly)
(IV) *c* *	7·40	3	Singlet	Me (6)
	3·87	2	,,	CH_2 (in 5-substituent)
(VIII) *a*	7·58	3	Doublet, *J*(6-Me/3-H) 0·5 c./sec.	Me (6)
	7·55	3	Singlet	Ac (at 5)
	6·12	3	,,	MeO
	4·02	1	Quartet	H (3)
(IX*a*) *b*	7·77	3	Singlet	Ac(at 5)
	4·42	1	,,	H (3)
	2·45	5	,, (virtually)	Ph (6)
(IX*b*) *b*	7·83	3	Singlet	Ac (at 5)
	4·52	1	,,	H (3)
	2·49—2·0	5	Complex	Ph (6)
(X) *a*	3·35	1	Singlet	H (5)
	2·63—1·92	10	Complex	2 Ph
	−6·83 (concn. independent)	1	Singlet	OH (4, chelated intramolecularly)

* The compound appeared to quaternise pyridine, but this reaction with the solvent does not affect the structural deduction made in the text.

intensity 2 (Table 4). Hence none of these compounds existed in the dicarbonyl form [although " triacetic acid lactone " (II) and dehydracetic acid (III) are commonly represented in that way]: all are monoenols.

(*a*) *Compounds* (II) *and* (XI). These react with diazomethane to yield a mixture of 2- and 4-methoxy-derivatives,[10] so that for each pyrone both of the hydroxy-forms are evidently present in solution. The equilibria must lie very largely to the 4-hydroxy-2-pyrone side because of the ultraviolet absorption maxima (Table 2) which are very similar in position and intensity to those for the 4-methoxy-2-pyrones (Table 1) (cf. ref. 11). Structures (II) and (XI) are therefore good representations (cf. ref. 10), but both compounds must be intermolecularly hydrogen-bonded, as judged from their high melting points, sparing solubilities (even in hydroxylic solvents), and infrared absorptions (Table 3). Such hydrogen-bonding would facilitate very rapid dynamic tautomerism in solution by a mechanism not requiring mediation of the dicarbonyl form. With this postulate, the proton magnetic resonance spectrum of the " triacetic acid lactone " (II) (Table 4), which shows that effectively only one enol form is present, can be accommodated along with the other evidence.

(*b*) *Compounds* (III) *and* (X). The enol-proton resonance for these two " dehydro-acids " was found near τ −6·8, the line position in each case remaining unchanged in position with change in concentration of the solution. Strong internal chelation was therefore indicated. Dehydracetic acid (III) absorbed in the ultraviolet region at 310 mμ, like 6-chloro-3-ethoxycarbonyl-4-hydroxy-2-pyrone,[12] whilst dehydrobenzoylacetic acid, with a 6-phenyl substituent, had a maximum at a 50 mμ longer wavelength. This was to be compared with a 48 mμ shift between the maxima of the parent compounds (II) and (XI) (Table 2). These observations, the infrared absorptions (Table 3), and a comparison with the reference data (Table 1) together demonstrated that the " dehydro-acids " have the chelated 4-hydroxy-2-pyrone constitutions (III) and (X).

(*c*) *Compound* (I). The enol-proton resonance signal at τ −2·21 (Table 4) was at an appreciably higher field than for the " dehydro acids " (III) and (X), and the 3-acyl-4-hydroxy-2-pyrones previously examined,[12,13,6] and so was suggestive of a different constitution. There was a slight change in the line-position with change in concentration. The ultraviolet absorption maximum at 267 mμ (Table 2) was 27 mμ higher than for 6-methyl-2-methoxy-4-pyrone (Table 1), a bathochromic shift similar to that (30 mμ) between 6-methyl-4-methoxy-2-pyrone and dehydracetic acid (III). These facts and the absence of carbonyl absorption near 1710 cm.$^{-1}$ or at a higher frequency showed that the new product from acetylacetone and malonyl chloride was a 2-hydroxy-4-pyrone. The product therefore has the constitution (I).

That the compound did not exist in the internally chelated 5-acetyl-4-hydroxy-2-pyrone form, as expected from previous experience,[12,13] was presumably because of steric hindrance between the 6-methyl and the 5-acetyl group: scale models suggested that this was severe. Evidently in the absence of the chelate ring, the 4-hydroxy-2-pyrone system is less stable than the corresponding 2-hydroxy-4-pyrone, so that the latter form (I) is then favoured. To conclude that a 2-hydroxy-4-pyrone system would in general be more aromatic (*i.e.*, have a lower energy content, through resonance) than a 4-hydroxy-2-pyrone, would not necessarily be correct. Doubtless, the relative stabilities of these weakly aromatic systems depend in part on the nature of the other substituents, *i.e.*, those in the 3-, 5-, and 6-positions.

(*d*) *Compounds* (IX), *m. p.* 168° *and* 220°. These two enol tautomerides had absorption maxima at 320 and 284 mμ (Table 2), which indicated (from Table 1) that they were the 4-hydroxy-2-pyrone (IX*a*) and the 2-hydroxy-4-pyrone (IX*b*), respectively.

The 2-pyrone (IX*a*) showed carbonyl absorption at 1713 cm.$^{-1}$ as expected, and a second band at 1685 cm.$^{-1}$ which could be attributed to the 5-acetyl-carbonyl group if this were hydrogen-bonded. Scale models suggested that a chelate ring, as in (IX*a*), was feasible, provided that it was slightly buckled and that the phenyl group was twisted

out-of-plane of the pyrone ring. Presumably, the 6-phenyl substituent increases the acidity of the 4-hydroxyl group, so that the hydrogen bond, and thus also the chelate ring, is more stable than would be the case in the corresponding 6-methyl compound. The ring is therefore able to accommodate some deformation. The stability of the tautomeride (IX*a*), as already noted, is limited, and the compound changes, on melting, into the 2-hydroxy-4-pyrone form (IX*b*). The higher melting point of the latter may well result from intermolecular hydrogen-bonding, absent in the other form. The form (IX*b*) showed strong absorption at 1676 cm.$^{-1}$, attributable to the 4-carbonyl stretching. A second band at 1728 cm.$^{-1}$ evidently arises from the free 5-acetyl-carbonyl, which, because of the 6-phenyl substituent, is not co-planar, *i.e.*, conjugated, with the pyrone ring.

A significant difference in the proton magnetic resonance spectra of the tautomerides (IX*a* and *b*) lay in the phenyl-proton signals, the former giving a single line, and the latter a complex multiplet. This similarity to *cis*- and *trans*-stilbene [14] appeared to provide additional evidence for the respective non-coplanarity and coplanarity of the 6-phenyl group with the pyrone ring, in the tautomerides (IX*a* and *b*). It was unfortunate that the enol-proton resonance of these compounds could not be studied. They were soluble to the required extent only in solvents which associated strongly with the enol function or underwent proton-exchange with it.

Experimental

3-Acetyl-6-hydroxy-2-methyl-4-pyrone (I).—When malonyl chloride (10 c.c.) was heated on a water-bath with freshly distilled acetylacetone (10 c.c.), hydrogen chloride was evolved copiously and a product began to crystallise after 10 min. When the evolution of gas slackened, the dark product was triturated with anhydrous ether, and the solid collected. From tetrahydrofuran–ether, *3-acetyl-6-hydroxy-2-methyl-4-pyrone* (7 g., 42%) crystallised as prisms, m. p. 162° [Found: C, 57·0; H, 5·1; O, 38·3%; *M* (Rast), 144; Equiv., by titration with NaOH, 173. $C_8H_8O_4$ requires C, 57·2; H, 4·8; O, 38·0%; *M* and Equiv., 168]. The compound dissolved in aqueous sodium hydrogen carbonate with effervescence, and gave a red colour with aqueous ferric chloride.

The *2,4-dinitrophenylhydrazone* crystallised from ethanol as golden prisms, m. p. 240° (decomp.) (Found: C, 48·3; H, 3·8; N, 15·8. $C_{14}H_{12}N_4O_7$ requires C, 48·3; H, 3·5; N, 16·1%), $\nu_{max.}$(CO) (in KBr) 1674 cm.$^{-1}$.

Deacetylation of the Pyrone (I).—The pyrone (4·5 g.) in 90% sulphuric acid (15 c.c.) was heated rapidly by immersion in a bath at 136°. When a drop of the solution no longer gave a precipitate on addition to 20 c.c. of water, the reaction mixture was cooled and added to ice–water (40 c.c.). During 4 hr. at 0°, 4-hydroxy-6-methyl-2-pyrone (II) separated (2·5 g., 75%); it crystallised from boiling water and then had m. p. 192° (decomp.) (Found: C, 56·9; H, 4·6. Calc. for $C_6H_6O_2$: C, 57·1; H, 4·6%). A mixture with authentic material, m. p. 192° (decomp.), obtained in 92% yield by similar deacetylation of dehydracetic acid, had the same m. p. The pyrone gave an orange colour with ferric chloride.

5-Acetyl-4-hydroxy-6-methyl-2-pyridone (V).—(a) *Preparation.* A solution of the pyrone (I) (1 g.) in aqueous ammonia (10 c.c.; *d* 0·880) was evaporated after 3 days, and the residue triturated with ether. When crystallised from ethanol, the *5-acetyl-4-hydroxy-6-methyl-2-pyridone* (0·8 g., 70%) had m. p. 296° (Found: C, 57·5; H, 5·4; N, 8·7. $C_8H_9NO_3$ requires C, 57·7; H, 5·4; N, 8·4%). It gave a red colour with aqueous ferric chloride and was soluble in sodium hydrogen carbonate solution.

(b) *Bromination.* The pyridone (V) (0·5 g.) was warmed for 10 min. with a 10% solution of bromine in acetic acid (5 c.c.). Evaporation, and trituration of the residue with ethanol (5 c.c.), afforded *3-bromo-5-bromoacetyl-4-hydroxy-6-methyl-2-pyridone* (IV) (0·5 g., 52%), m. p. 180° (decomp.) (from ethanol) (Found: C, 29·6; H, 2·25. $C_8H_6Br_2NO_3$ requires C, 29·5; H, 2·1%).

(c) *Methylation.* (i) Sodium (1·7 g.) was interacted with methanol (20 c.c.), and the pyridone (V) (6 g.) was added, followed during 30 min. by dimethyl sulphate (9 c.c.). After 1 hr. more, the solution was boiled for 2 hr., and then cooled, made alkaline with aqueous sodium hydroxide, and extracted with chloroform. Evaporation of the extract and trituration of the residue

[14] Bhacca, Johnson, and Shoolery, " Nuclear Magnetic Resonance Spectra Catalog," Varian Associates, Palo Alto, 1962, Nos. 305, 306; Jackman, " Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p. 126.

with ether afforded *5-acetyl-4-hydroxy-1,6-dimethyl-2-pyridone* (VI) (2·6 g., 40%), m. p. 280° (decomp.) (from methanol) (Found: C, 59·0; H, 6·1; N, 7·7. $C_9H_{11}NO_3$ requires C, 59·7; H, 6·1; N, 7·7%).

A solution of the pyrone (I) (2 g.) in 25% methylamine (30 c.c.) was evaporated after 4 days, and the residue, in a little ethanol, was kept at 0° for 10 hr. Crystallisation of the solid (1·5 g., 60%) from ethanol gave the authentic pyridone (VI), m. p. 280° (decomp.), identical (infrared spectrum) with the preceding product.

(ii) The pyridone (V) (0·56 g.) in ethanol (200 c.c.) was mixed with an excess of ethereal diazomethane (100 c.c.). After 30 min., the solution was evaporated under reduced pressure, and the residue triturated with ether. When crystallised from ethanol, *5-acetyl-4-methoxy-6-methyl-2-pyridone* (VIII) (0·32 g., 52%) had m. p. 230° (Found: C, 60·1; H, 6·1; N, 7·6%).

4-Hydroxy-1,6-dimethyl-2-pyridone (VII).—The acetyl compound (VI) (0·5 g.) and concentrated sulphuric acid (1 c.c.) were heated in a bath at 180° for 7 min. Cooling, dilution with water (10 c.c.), neutralisation with barium hydroxide, filtration, and evaporation afforded 4-hydroxy-1,6-dimethyl-2-pyridone (0·11 g., 29%), m. p. 230° (from ethanol).

The same compound (mixed m. p. undepressed) was obtained by keeping 4-hydroxy-6-methyl-2-pyrone (II) (1 g.) in 25% aqueous methylamine (20 c.c.) overnight, evaporating the solution, and triturating the residue with ether. The 4-hydroxy-1,6-dimethyl-2-pyridone (0·7 g., 58%) had m. p. 230° (from ethanol) (Found: N, 10·2. Calc. for $C_7H_9NO_2$: N, 10·2%).

The Reaction of Malonyl Chloride with Benzoylacetone.—Malonyl chloride (5 c.c.) and benzoylacetone [15] (10 g.) were stirred and warmed together on the steam-bath. After *ca.* 10 min., the vigorous evolution of hydrogen chloride slackened. The product was cooled, and triturated with ether, and the solid crystallised from tetrahydrofuran–ether. *5-Acetyl-4-hydroxy-6-phenyl-2-pyrone* (IX*a*) (7 g., 50%) recrystallised from ethanol–ether and then had m. p. 168° with resolidification (Found: C, 68·2; H, 4·7%; Equiv., by titration with NaOH, 228. $C_{13}H_{10}O_4$ requires C, 67·8; H, 4·3%; Equiv., 230). No other solid product was isolated.

The *2,4-dinitrophenylhydrazone* (70%) had m. p. 285° (decomp.) (from tetrahydrofuran) (Found: C, 55·9; H, 3·8; N, 13·5. $C_{19}H_{14}N_4O_7$ requires C, 55·6; H, 3·4; N, 13·7%), $\lambda_{max.}$ (in EtOH) 280, 360 mμ.

The pyrone (IX*a*) (0·5 g.) was kept at its m. p. for 1 min. The solid was then recrystallised from ethanol. *5-Acetyl-2-hydroxy-6-phenyl-4-pyrone* (IX*b*) had m. p. 220° (decomp.) [Found: C, 67·7; H, 4·4; O, 27·5%; *M* (Rast), 253; Equiv., 229. $C_{13}H_{10}O_4$ requires C, 67·8; H, 4·3; O, 27·8%; *M* and Equiv., 230].

Deacetylation of the Pyrones (IX).—The tautomerides *a* and *b* (2·8 g.; 1 g.) were separately heated with 90% sulphuric acid (18 c.c.; 10 c.c.) in a bath at 160° for 2 min. The solutions were adedd to ice–water (150 c.c.; 100 c.c.), and the solids obtained (*ca.* 3 hr.) were separately crystallised from ethanol. The products (1·71 g., 94%; 0·3 g., 37%) each had m. p. 245—246° (decomp.) undepressed on admixture, and the infrared spectra were identical with that of 4-hydroxy-6-phenyl-2-pyrone, next described.

Debenzoylation [9] *of Dehydrobenzoylacetic Acid* (X).—The pyrone (2·5 g.) (prepared [9] from ethyl benzoylacetate [16]) was kept with 90% sulphuric acid (15 c.c.) in a bath at 160° for 2·5 min., and the product isolated as above. From ethanol, 4-hydroxy-6-phenyl-2-pyrone (1·7 g.) had m. p. 246° (decomp.) (Found: C, 70·2; H, 4·7. Calc. for $C_{11}H_8O_3$: C, 70·2; H, 4·3%).

5-Acetyl-4-hydroxy-6-phenyl-2-pyridone (XII).—Each tautomeride (IX*a* and *b*) (0·5 g.; 0·33 g.) was dissolved in aqueous ammonia (*d* 0·880) (10 c.c.; 15 c.c.) and, after 2 days, the solutions were separately evaporated, and the two residues triturated with ether. In each case the product (from ethanol) was *5-acetyl-4-hydroxy-6-phenyl-2-pyridone* (0·3 g., 60%; 0·25 g., 76%), m. p. (and mixed m. p.) 320° (decomp.) [Found, on sample from (IX*a*): C, 68·4; H, 5·2. $C_{13}H_{11}NO_3$ requires C, 68·4; H, 4·8%]. The infrared spectra were identical.

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