Acetylpyran-2,6-diones: Tautomeric Enolic Forms, Spectral Properties, and Reactions with Primary Amines

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The i.r., u.v., and ^{1}H- and ^{13}C-n.m.r. spectra of some acetylpyran-2,6-diones are discussed in relation to their tautomeric structures and compared with those of the acetylpyran-2,4-diones. Their reactions with primary amines to give Schiff bases, salts, pyridones or open-chain products as well as a thermal rearrangement of the Schiff bases are reported.

The enolic properties of pyran-2,6-diones (glutaconic anhydrides) have long been recognised. Early workers[1-3] assigned them 6-hydroxy-2-pyrone structures on the basis of their chemical behaviour. However, spectral studies of glutaconic anhydride[4] and its β-methyl-[5] and β-aryl-[6] derivatives have shown that they exist in the anhydride form in the solid state or in chloroform solutions.

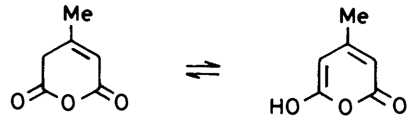
An acetyl substituent not only affects the tautomerism of the pyrandione ring but also introduces another possible site of enolization so that more than one enolic form becomes possible. The relative extents of enolization of the ring and side-chain carbonyl groups in the methyl- and/or acetyl-substituted pyran-2,6-diones (**1**)—(**4**) have been studied by examination of their u.v., i.r., and ^{1}H- and ^{13}C-n.m.r. spectra and comparison with those of diacetylpyran-2,4,6-trione (**5**) and some acetylpyran-2,4-diones (**6**)—(**8**).

The preferred tautomeric structures of compounds (**1**)—(**4**) may also be correlated with their reactions with primary amines which can occur either at the ring or at an acetyl side-chain.

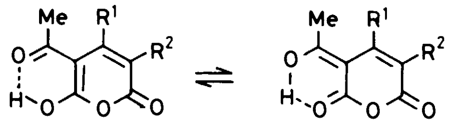
Results and Discussion

Spectral Properties and Tautomerism.—Spectral data are summarised in Tables 1 and 2. Like the unsubstituted pyran-2,6-dione, compound (**1**) exists in the anhydride form in the solid state and in chloroform solution, as shown by the presence of an anhydride carbonyl, and the absence of hydroxy, absorptions in its i.r. spectra (Nujol and CHCl$_3$) and the presence of both methylene and methine signals in its ^{1}H and ^{13}C n.m.r. spectra (CDCl$_3$). However, its u.v. spectrum changes according to solvent: in solvents of low polarity such as cyclohexane, dioxane, and chloroform, absorption occurs at 225—245 nm but in more polar solvents, such as ethanol and water, an additional band appears at 340 nm. In the non-polar solvents, the anhydride form of (**1**) has shorter conjugation and therefore absorbs at shorter wavelength than the isomeric 4-hydroxy-6-methyl-2-pyrone (284 nm in ethanol),[4] but in the polar solvents, the enolized 6-hydroxy-4-methyl-2-pyrone form with more extended conjugation is present and manifests itself in longer wavelength absorptions. In 80% DMSO–water, the absorption maximum shows a further slight red shift which intensifies with increase in pH as a result of the formation of a resonance-stabilised anion.

Introduction of an acetyl group at C-5 promotes enolization through intramolecular H-bonding as in compounds (**2**)—(**5**). This type of H-bonding is particularly favourable because it forms part of a conjugate chelate ring with extensive electron delocalisation,[7] and its strength is reflected in the very low-field hydroxy proton signals in their ^{1}H n.m.r. spectra. However, the acetyl side-chain and the C-6 carbonyl group constitute a β-dicarbonyl system so that two enolic forms such as (**a**) and (**b**) are possible. Similar equilibration has been reported for some isocoumarins[8] based on i.r. spectroscopic evidence. ^{13}C N.m.r. spectroscopy has proved particularly useful in the study of the tautomerism between possible enolic forms of a number of aliphatic β-dicarbonyl compounds.[9-11] An H-bonded carbonyl carbon generally resonates at much lower field than an olefinic carbon bearing a hydroxy group. Thus, although individual tautomers may not be separately observable on the n.m.r. time-scale, the average chemical shifts provide a means of estimating the contributions of the different enolic forms. In this way, not only the enolic tautomerism in these acetylpyran-2,6-diones may be compared with that in the acetylpyran-2,4-diones (**6**)—(**8**), but more subtle differences among the compounds (**2**)—(**5**) become detectable.

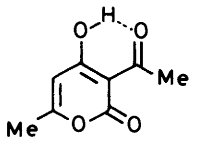


(**1**)

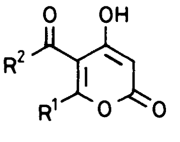


(a) (b)

(**2**) R^1 = Me, R^2 = H
(**3**) R^1 = Me, R^2 = Ac
(**4**) R^1 = H, R^2 = H
(**5**) R^1 = OH, R^2 = Ac



(**6**)



(**7**) R^1 = Me, R^2 = Me
(**8**) R^1 = Ph, R^2 = Me

The extent of enolization of the C-6 carbonyl group in compounds (**1**)—(**4**) is reflected in the C-6 resonances in their ^{13}C n.m.r. spectra. Compared with compound (**1**), which exists predominantly in the anhydride form, the C-6 signals for com-

Table 1. U.v., i.r., and ^{1}H n.m.r. spectral data for compounds (**1**)—(**15**)

	$\lambda_{max.}$/nm ($\log_{10}\varepsilon$)							
						80% (w/w) DMSO–water		
Compd.	Cyclo- hexane	Chloroform	Dioxane	Ethanol	Water	Neutral	Acidic	Basic
(**1**)	225 (3.68)	245 (3.44)	242	340 (3.19) 240 (3.03)	340 230	345 (3.78)		345
(**2**)	308[b]	312 (4.23)	312 (4.18)	345 (4.34) 275 (3.88)	342 (4.44) 275 (3.89)	345 (4.30) 275 (3.83)	320 (4.01)	348 (4.35) 278
(**3**)	320 (4.18)	322 (4.20)	322 (4.20)	360 (4.43) 280 (4.00)	355 (4.38) 283 (3.89)	361 (4.41) 280 (3.96)	330	361 282
(**4**)	306[b]	310 (4.40)	310 (4.40)	345 (4.34) 275	342 (4.42) 275 (4.02)	350 (4.40) 275	320 (3.68)	350 (4.40) 275
(**5**)	306 (4.21) 268 (w)	310 (4.22) 268 (w)	310 (4.31) 268 (w)	318 (4.46) 270 (4.15)	315 (4.42) 270 (4.07)	320 (4.49) 270 (4.10)	314 270	290
(**9a**) (^{15}N-enriched)		355 (4.50)	355 (4.50)	352 (4.39)		356 (4.45)	355	355 (w)
(**9b**)		360						
(**10a**) (^{15}N-enriched)	375 (b)[b]	375 (4.45) (b)	376 (4.45) (b)	355 (4.32) 280 (3.96)		385 368	385 368	358 280 (w)
(**10b**)		385						
(**11**)		338						
(**12**)		309 237						
(**13**)					345			
(**14**)					360			
(**15**)					321			

Table 1. (*continued*)

	v/cm^{-1}		Chemical shift,[a] δ p.p.m.		
compd.	Nujol	Chloroform	OH/NH	Me	Others
(1)	1 805 (s)	1 800 (s)		2.05 (C-4)	2.9 (–CH_2–)
	1 795 (s)	1 755 (vs)			6.05 (≥CH)
	1 745	1 665 (w)			
	1 670 (m)				
(2)	1 740 (s)	1 755 (s)		2.31 (C-4)	5.68 (C_3-H)
	1 665 (s)	1 600 (s)	16.0 (v br)	2.54 (acetyl)	
	1 595 (s)	1 605 (s)			
	1 530	1 750			
(3)	1 730 (s)	1 570 (s)	(35 °C)		
	1 690	1 700		2.35 (3 H, C-4)	
	1 650	1 650		2.56 (6 H, acetyl)	
	1 570	1 570	(0 °C)		
			16.3 (b)	2.39 (3 H, C-4)	
				2.55 (3 H, b)	
				2.68 (3 H, b)	
			(−40 °C)		
			16.3 (sh)	2.40 (3 H, C-4)	
				2.55 (3 H)	
				2.71 (3 H)	
(4)	1 765 (sh)	1 778 (s)			5.95
	1 745 (s)	1 758 (s)	14.0 (v br)	2.43 (acetyl)	(d, *J* 1.6 Hz)
	1 680 (s)	1 670 (s)			7.55
	1 605	1 615			(d, *J* 1.6 Hz)
(5)[c]	1 755 (s)	1 765 (s)	16.4 (b)	2.68	
	1 728	1 725 (m)	19.08 (sh)	2.74	
	1 540 (br,s)	1 665 (s)		2.76	
(9a)	1 730 (s)	1 732 (s)	13.52	2.39 (C-4)	5.68 (3-H)
	1 640 (s)	1 650 (m)	(d, $J_{^{15}N-H}$ 87 Hz)	2.45 (side-chain)	7.3 (Ph, m, 5 H)
	1 555 (vs)	1 605 (m)		(d, *J* 3 Hz)	
		1 570 (s)			
(9b)	1 725 (s)				
	1 650 (m)		13.50 (b)	2.39 (C-4)	5.58 (3-H)
	1 600 (s)				
	1 570 (s)			2.42 (acetyl,	7.2 (Ph, m, 4 H)
				aryl, 6 H)	
(10a)	1 712 (s)	1 725 (s)	13.52	2.43 (C-4)	7.3 (Ph, m, 5 H)
	1 680 (m)	1 660 (s)	(d, $J_{^{15}N-H}$ 87 Hz)	2.50 (m, 6 H)	
	1 660 (m)	1 605 (m)			
	1 530 (s)	1 575 (m)			
(10b)	1 712 (s)		13.5 (v br)	2.40 (C-4, aryl,	7.3 (Ph, m, 4 H)
	1 670 (s)			6 H)	
	1 620 (m)			2.52 (6 H)	
	1 520 (w)				
(11)	1 685 (m)			1.98 (C-6)	6.04 (5-H)
	1 650 (m)			2.28 (C-4)	7.35 (Ph, m, 5 H)
	1 585 (m)			2.55 (acetyl)	
	1 530				
(12)	1 670 (s)			1.92 (C-6)	5.95 (3-H)
	1 605			2.18 (C-4)	6.34 (5-H)
	1 590				7.3 (Ph, m, 5 H)
	1 540 (w)				
(13)	3 500 (br)			2.26 (C-4)	
	1 710 (s)			2.42 (acetyl)	6.0 (b, 3-H)
	1 620 (br,s)			2.70 (*N*-methyl)	
	1 550 (s)				
(14)	3 500 (br)			2.24 (C-4)	
	1 710 (s)			2.48 (acetyl, 6 H)	
	1 650 (br,s)			2.70 (*N*-methyl)	
	1 610 (s)				
(15)	3 120 (br)			2.30 (acetyl, 6 H)	
	1 755 (s)			2.52 (*N*-methyl)	
	1 670 (s)				
	1 600 (br,s)				

[a] In $CDCl_3$ for compounds **(1)**—**(12)** and in D_2O for compounds **(13)**—**(15)**. [b] Saturated solutions were used due to poor solubility. [c] ^{1}H N.m.r. data from ref. 11.

Table 2. ^{13}C N.m.r. chemical shifts in $CDCl_3$ at 35 °C (p.p.m. from Me_4Si)

Assignment	Compd.									
			(3)							
	(1)	**(2)**	35 °C	−40 °C	**(4)**	**(5)**[a]	**(9a)**	**(10a)**	**(11)**	**(12)**
C-2	(165.1)	171.0		169.2	168.8	169.1	167.6	165.0	161.9	163.9
C-3	114.4	109.3		121.2	108.4	95.8	106.7	119.3	128.5	116.9
C-4	156.3	154.2	153.6	154.5	141.6	184.0	156.1	154.8	152.1	151.0
C-5	36.3	100.0		100.5	98.5	97.7	95.8	98.3	110.3	108.6
C-6	(160.0)	157.8		156.9	159.3	157.3	160.5	159.6	147.4	144.9
C-7				200.8		203.5		200.2	202.3	
C-8		188.0		191.4	185.8	196.8	167.0	169.8		
C-4′	22.2	24.5	20.9	21.4			25.6	22.2	21.5	21.3
C-6′									20.6	21.3
C-7′			30.4 (v br)	31.7		28.0		31.5	31.6	
C-8′		25.0	27.4 (v br)	26.5	19.4	25.2	20.9	22.8		
φ-*o*							129.6	129.8	129.9	129.6
φ-*m*							126.0	125.7	127.8	128.0
φ-*p*							128.2	128.8	129.0	128.6
φ-α							136.4	136.0	138.2	138.8

[a] From ref. 11.

pounds **(2)**, **(3)**, and **(5)** are shifted upfield as the result of increase in electron-density on enolization, while that for compound **(4)** is shifted to a smaller extent indicating lower enolic character. This observation also correlates well with the differences among the carbonyl vibrations in the i.r. spectra of these compounds. While compound **(1)** clearly shows anhydride vibrations, the carbonyl vibrations of **(2)**, **(3)**, and **(5)** are close to those of 2-pyrones but those of **(4)** occur at noticeably higher frequencies, suggesting intermediate character.

It is interesting to compare the ^{13}C n.m.r. chemical shifts of the carbonyl and methyl carbons of the acetyl side-chains of compounds **(2)**—**(5)** with those in the 3-acetyl- and 5-acetylpyran-2,4-diones **(6)**—**(8)**.[11,12] H-Bonding generally shifts a carbonyl carbon signal downfield.[13] Thus, *o*-hydroxyacetophenone, where the actyl group is strongly H-bonded but has little or no enolic character, shows a carbonyl signal at δ 204.4 compared with that of acetophenone at δ 196.0.[14] The acetyl groups in the compounds **(7)** and **(8)** cannot enolize and their carbonyl and methyl signals occur in the ranges δ 202.3—204.2 and δ 32.8—31.3, respectively. Although the acetyl group in compound **(6)** can enolize, the compound exists predominantly in form **(a)** with very strong intramolecular H-bonding[11] as shown by its lowfield carbonyl (at δ 205.2) and acetyl methyl (at δ 30.3) signals. By comparison, the acetyl resonances of compounds **(2)**—**(4)** occur at remarkable high field especially when consideration is given to the presence of strongly H-bonded chelate rings. The chemical shifts of the acetyl carbonyl carbons fall in the range δ 185.8—191.4 and those of the acetyl methyl carbons in the range δ 19.4—26.5. This effect, which is specially pronounced in compound **(4)**, can only be attributed to the substantially higher degree of enolization in these side-chains than those in compounds **(6)**—**(8)**. The differences in chemical shifts reflect differences in the electron density distributions in H-bonded chelate rings in these compounds. The similar shielding effects on the acetyl carbonyl and acetyl methyl carbons of these side-chains are shown by the linear correlations between their ^{13}C n.m.r. chemical shifts (Figure). It is instructive to note that for compound **(3)**, the 3-acetyl group cannot enolize and its carbonyl and methyl signals occur at lower field than those of the 5-acetyl group. Moreover, in compound **(5)**, which is a diacetylpyran-2,4,6-trione with both acetyl groups capable of enolizing and forming H-bonded chelate rings, the 5-acetyl group gives signals at higher field than the 3-acetyl group, consistent with the more enolic character of the 5-acetyl group. This is in keeping with the lower tendency of the C-6 anhydride carbonyl than the C-4 ketonic carbonyl to enolize.

Both the ^{1}H- and ^{13}C-n.m.r. spectra of compound **(3)** show interesting temperature dependence. At 35 °C, the ^{1}H n.m.r. spectrum shows only two signals of intensity ratio 1:2 at δ 2.35 and δ 2.56 due to the C-4 methyl and to both acetyl groups, respectively. On lowering the temperature to 0 and −40 °C, not only does the hydroxy proton become observable but the acetyl resonance splits into two, indicating two non-equivalent acetyl groups. Similarly, the ^{13}C n.m.r. spectrum shows only three signals at 35 °C but at −40 °C, sharp signals are clearly observed for all the carbons, revealing an unsymmetrical structure. At 35 °C, the spectra are the 'average' of two rapidly equilibrating equivalent structures so that the hydroxy signal is too broad to be observable in the ^{1}H n.m.r. spectrum while not all of the quaternary carbons are detected in the ^{13}C n.m.r. spectrum. This facile proton exchange may be related to the exceptionally high acidity previously found for this compound.[15]

On the other hand, the n.m.r. spectra of compounds **(2)** and **(4)** do not display such temperature dependence, in spite of their acidities.[15] Analogous exchanges in these compounds would lead to structures of different stabilities so that only the more stable structures with H-bonded conjugate chelation are favoured.

The u.v. spectra of compounds **(2)**—**(4)** in cyclohexane, dioxane, and chloroform are comparable to that of 3-acetylpyran-2,4-dione **(6)** which is isomeric with **(2)**; this, therefore, lends further support for their enolic structures. However, while the spectrum of **(6)** shows little change when water or 80% DMSO–water are used, the absorptions of **(2)**—**(4)** show significant red shift by 30—40 nm together with an increase in intensity with similar solvent changes. These effects and the changes in their spectra with pH in aqueous solutions are again manifestations of the highly acidic character of **(2)**—**(4)**. Thus they exist largely as undissociated molecules in non-polar solvents but as extensively delocalised anions in polar solvents.

Reactions with Primary Amines.—Although glutaconic anhydrides are more stable than their saturated analogues towards hydrolysis,[16] ring opening can occur when they are treated with amines under appropriate conditions, to give open-chain products or pyridones.[17,18]

The low anhydride character and relative stability of the rings

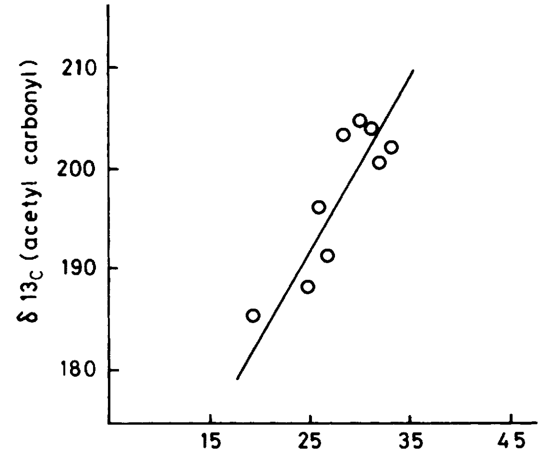
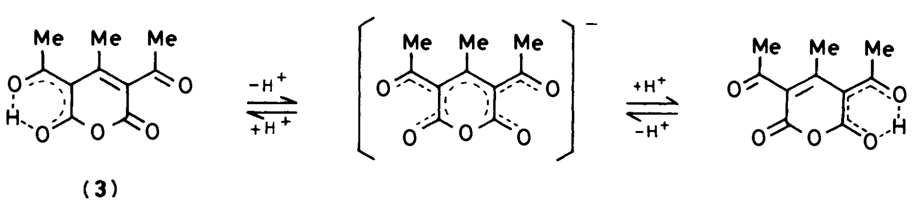
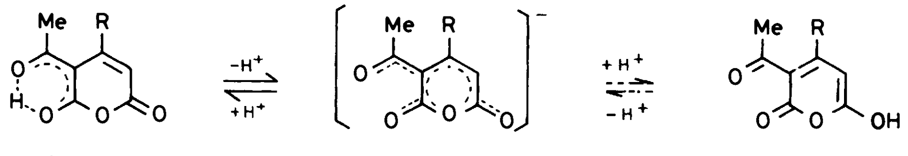


Figure. Relationship between ${}^{13}C$ n.m.r. chemical shifts of the acetyl carbonyl and acetyl methyl carbons in compounds (**2**)—(**8**) [data for compounds (**6**)—(**8**) from ref. 12]

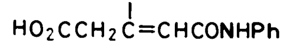


(**3**)



(**2**) R = Me
(**4**) R = H

(**9a**) Ar = Ph, R = H
(**9b**) Ar = p-MeC_6H_4, R = H
(**10a**) Ar = Ph, R = Ac
(**10b**) Ar = p-MeC_6H_4, R = Ac



$$HO_2CCH_2\overset{\overset{\textstyle Me}{|}}{C}{=}CHCONHPh$$

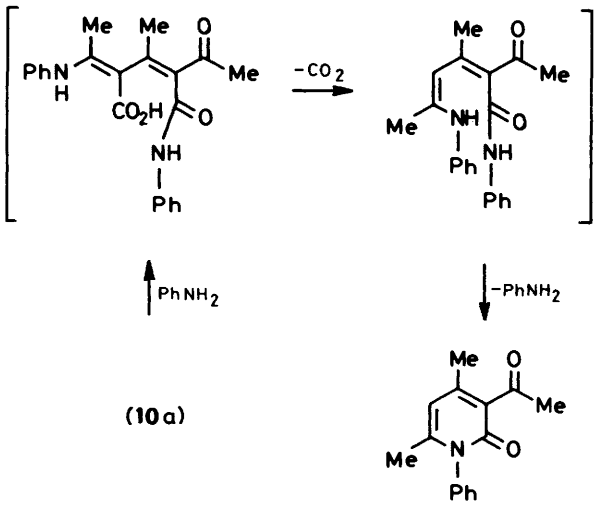
semianilide

in (**2**) and (**3**) are further demonstrated by their reactions with one equivalent of aniline or p-toluidine in ethanol, which readily yield Schiff bases (**9**) and (**10**) instead of open-chain products. The ease of formation of these Schiff bases may be attributed to the involvement of the 5-acetyl with the 6-hydroxy groups in conjugate chelation.[12] It is noteworthy that compound (**3**), having two acetyl groups, gives only a mono Schiff base since only one of the acetyl groups can form such a chelate ring. This may be compared with the previously observed reaction of aniline with compound (**5**), which forms both a mono- and a bis-Schiff base[19] as both acetyl groups of this compound are involved in conjugate chelation. Compound (**1**), without any acetyl substituent, reacts with aniline with ring opening to give the semianilide of β-methylglutaconic acid.

Both Schiff bases (**9**) and (**10**) exist predominantly in the ketoamine form, as revealed by the ${}^{1}H$ n.m.r. spectra of ${}^{15}N$-enriched samples which show large $J_{^{15}N\text{-}H}$ values in the region of 87 Hz. However, significant contributions from dipolar structures may be inferred from the absence of anhydride bands in the i.r. spectra and from their pK values, which are strikingly low for nitrogen acids.[20] The higher electron densities at C-3 and C-5 of Schiff bases (**9a**) and (**10a**) compared with their parent compounds (**2**) and (**3**) are indicated by their higher field signals in the ${}^{13}C$ n.m.r. spectra. The resonances at C-8 fall in the range δ 166—176 characteristic of similarly situated carbons in the Schiff bases previously studied.[11] The u.v. absorptions of these Schiff bases show blue or hypsochromic shifts on ionization, in contrast to those of the parent compounds which show red shifts.

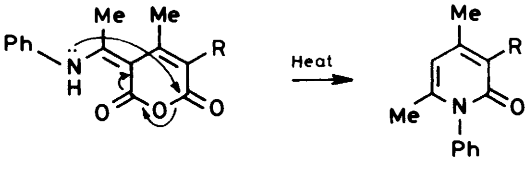
When refluxed with 2 equiv. of aniline, compound (**3**) gives a pyridone (**11**) which is also obtained by further reaction of the Schiff base (**10a**) with aniline. Compound (**11**) is probably formed *via* nucleophilic ring opening by aniline at C-2, which is activated by the electron-withdrawing effect of the 3-acetyl group, followed by decarboxylation and recyclization of the intermediate to the stable pyridone. The Schiff base (**9a**), without an acetyl group at C-3, does not react further with aniline under similar conditions.

When treated with methylamine, compounds (**2**), (**3**), and (**5**) yield equimolar salts (**13**)—(**15**) instead of Schiff bases or open-chain products, probably because of their strongly acidic character[15,19] and the higher basicity of methylamine than aniline. Reaction of the less acidic compound (**1**) with methylamine gives only a gummy mixture. The salt-like characters of (**13**)—(**15**) are evident from the extremely high solubility in water and the resemblance of their u.v. absorptions to those of their respective parent compounds in dilute NaOH solutions. The ${}^{1}H$ n.m.r. spectrum of (**13**) shows the expected three different methyl resonances, while those of (**14**) and (**15**) show three and two methyl signals, respectively, showing that, in each



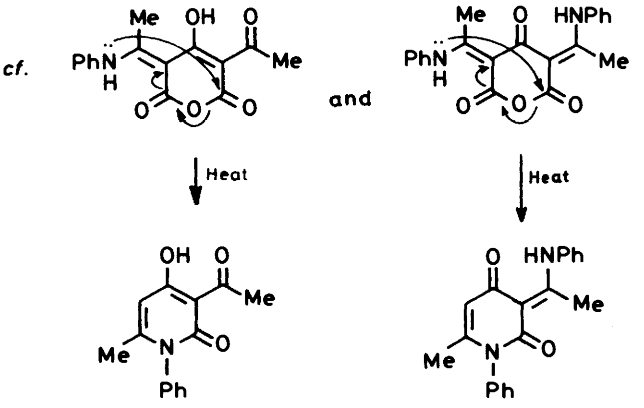
(10a)

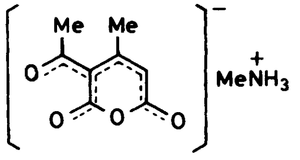
(11)

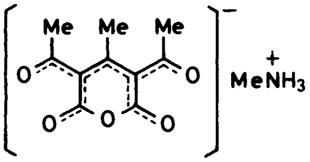


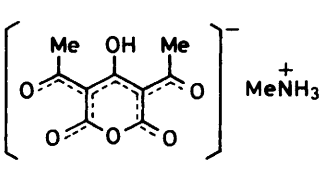
(9a) R = H
(10a) R = Ac

(12) R = H
(11) R = Ac




(13)


(14)


(15)

case, the two acetyl groups are identical in the symmetrical anion.

Thermal Rearrangements.—Pyridone (**11**) is also obtained by heating Schiff base (**10a**) at its melting point, probably as a result of intramolecular rearrangement involving the enamino side-chain as an internal nucleophile. Similar treatment of (**9a**) gives the corresponding pyridone (**12**) which could not be obtained from its reaction with excess of aniline. These thermal rearrangements are comparable to those observed previously with the mono- and bis-Schiff bases of compound (**5**).[19] The i.r. and ^{1}H- and ^{13}C-n.m.r. spectra of compounds (**11**) and (**12**) are consistent with the assigned pyridone structures. Owing to methyl substitution, ^{13}C resonances of C-4 and C-6 of (**11**) and (**12**) are shifted downfield by 9—12 p.p.m. relative to those of unsubstituted 2-pyridones.[21] The C-3 resonance in (**11**) is similarly deshielded owing to substitution by an acetyl group.

Experimental

Materials.—Compounds (**1**)—(**4**) and (**5**) were prepared according to literature procedures.[2,15,19] The Schiff bases (**9**) and (**10**) were prepared by refluxing equimolar amounts of (**2**) and (**3**), respectively, with the appropriate amine.

(**9a**), m.p. 181—183 °C (from ethanol) (Found: C, 69.5; H, 5.6; N, 5.7. $C_{14}H_{13}NO_3$ requires C, 69.13; H, 5.35; N, 5.80%).

(**9b**), m.p. 172—175 °C (from ethanol) (Found: C, 69.85; H, 6.0; N, 4.95. $C_{15}H_{15}NO_3$ requires C, 70.04; H, 5.84; N, 5.45%).

(**10a**), m.p. 153—155 °C (from ethanol) (Found: C, 67.2; H, 5.4; N, 4.7. $C_{16}H_{15}NO_4$ requires C, 67.37; H, 5.26; N, 4.90%).

(**10b**), m.p. 140—142 °C (from ethanol) (Found: C, 67.9; H, 6.0; N, 4.4. $C_{17}H_{17}NO_4$ requires C, 68.23; H, 5.68; N, 4.68%).

Reaction of Compound (**1**) *with Aniline.*—Compound (**1**) (150 mg) was refluxed with aniline (140 mg) in absolute ethanol for 2 h. The solution was evaporated almost to dryness and the residue was triturated with ether. The white solid which was the semianilide of β-methylglutaconic acid was recrystallized from ethanol (m.p. 134—136 °C); $\nu_{max.}$(Nujol) 3 300, 1 710, 1 660, 1 605, 1 550, and 1 535 cm^{-1}; δ(CDCl$_3$) 2.12 (Me), 3.65 (CH$_2$), 5.96 (⩾CH), 7.0—7.5 (aryl), and 8.9 (NH).

Reaction of Compound (**2**) *with an Excess of Aniline.*—Compound (**2**) (38 mg) was refluxed with aniline (46 mg) in ethanol for 4 h. The solution was then concentrated and cooled to yield a yellow crystalline solid whose m.p. and i.r. spectrum were identical with those of (**9a**).

Reaction of Compound (**3**) *with an Excess of Aniline.*—Compound (**3**) (42 mg) was refluxed with aniline (53 mg) in ethanol for 2 h. The yellow solution was rotary evaporated to give a gum. This was dissolved in chloroform and washed with dilute hydrochloric acid to remove excess of aniline. The chloroform layer was dried and evaporated to give a brownish solid which was recrystallized from chloroform–hexane to give pyridone (**11**) (m.p. 126—128 °C).

Reaction of Schiff Base (**10a**) *with Aniline.*—Schiff base (**10a**) (41 mg) was refluxed with aniline (13 mg) in ethanol for 3 h. The solution was worked up as above to give a solid which was identical with pyridone (**11**).

Thermal Rearrangment of Schiff Bases (**9a**) *and* (**10a**).—Each of the Schiff bases was heated at its melting point for 10—12 min in an oil-bath. The dark residue after cooling was dissolved in the minimum of chloroform and just enough ether was added to precipitate most of the colouring matter. The filtrate was evaporated and the solid recrystallized from chloroform–hexane giving cream coloured crystals of pyridone (**11**), m.p. 126—128 °C, or pyridone (**12**), m.p. 144—146 °C.

Spectral Measurements.—U.v. spectra were recorded with a Shimadzu spectrometer model UV240 using matched 1.0 cm silica cells. Concentration of the solutions ranged from 4.0×10^{-5}—9×10^{-5}M. I.r. spectra were recorded in Nujol or in chloroform on a Unicam SP 1000 spectrophotometer.

^{1}H N.m.r. spectra were recorded with a Perkin-Elmer R32 spectrometer at 90 MHz and ^{13}C n.m.r. spectra with Bruker HFX-270 and JEOL JMN FX-100 spectrometers.

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