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NMR SPECTRA OF INTRAMOLECULARLY HYDROGEN-BONDED COMPOUNDS—II[1]

SCHIFF BASES OF β-DIKETONES AND *o*-HYDROXYCARBONYL COMPOUNDS

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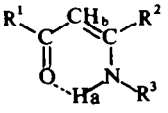
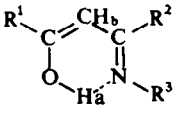
Abstract—Schiff bases of aromatic amines and β-diketones including those containing Ph end-groups have been shown to exist as the keto–amine tautomer using NMR spectroscopy. The Schiff bases derived from aromatic amines and 2-hydroxy-1-naphthaldehyde were concluded to be an equilibrium mixture of the ketoenamine and enolimine forms. The influence of electronic effects in the aromatic amines on the hydrogen-bond strength was also examined.

SCHIFF bases derived from β-diketones and aliphatic amines have been shown by Dudek[2–4] using NMR spectroscopy to exist as the keto–amine (**1a**) rather than as the enolimine (**1b**) or the ketoimine (**1c**). If either R^1 and/or R^3 were aromatic



1a



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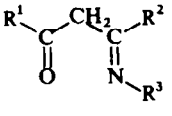
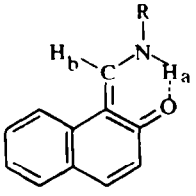


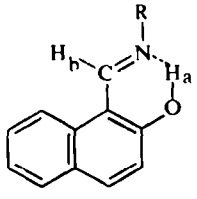
1c

residues it might be expected that the enolimine (**1b**) would be the favoured tautomeric form in view of the more delocalized system. Edwards and Petrov[5] from an IR study of chloranils of acetylacetone favour the enolimine structure as do Martin *et al.*[6] from a study of the acid dissociation constants of these compounds. Accordingly the present work was undertaken to deduce the structure of the tautomer of Schiff bases of β-diketones containing aromatic residues.

The NMR spectra of Schiff bases derived from 2-hydroxy-1-naphthaldehyde with aromatic amines were also examined because Dudek[4,7] had shown that Schiff bases of 2-hydroxy-1-naphthaldehyde with aliphatic amines exist as the keto–amine (**2a**)



2a



2b

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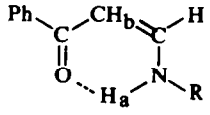
rather than as the enolimine (**2b**) even though this involves the loss of resonance energy of one aromatic ring. Again the compounds derived from aromatic amines might be expected to prefer the more conjugated enolimine tautomer (**2b**).

Dudek and Holm[2] showed that Schiff bases derived from β-diketones and aliphatic amines existed in the ketoenamine form by observing coupling between the intramolecularly hydrogen-bonded proton and the α-proton of the amine fragment. This is not possible for derivatives of aromatic amines in which there is no α-proton. It is, however, possible to distinguish between the tautomers by studying derivatives of benzoylacetaldehyde (I, R^1 = Ph, R^2 = H_b) in which there is a proton on the C atom in the chelate ring α to the nitrogen. Condensation of the amine takes place at the CO group adjacent to the Ph group as with Schiff bases of benzoylacetone.

This was demonstrated in the case of the benzylamine derivative (3, R = $PhCH_2$). Thus the methylene signal of the benzyl group in its NMR spectrum appears as a



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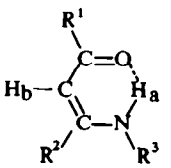
doublet at τ 5·65 (J = 6·4 c/s), the proton H_c as a pair of doublets at τ 3·08 (J = 7·2 and 12·5 c/s), and the proton H_b appears as a doublet at τ 4·28 (J = 7·2 c/s). On treatment with deuterium oxide the methylene and H_c proton signals collapse to a singlet and a doublet (J = 7·2 c/s) respectively. This data is only consistent with the compound having the proposed structure (3, R = $PhCH_2$). The low-field proton signal appears as a very broad multiplet in this spectrum. In the NMR spectra of derivatives of benzoylacetaldehyde with aromatic amines, the low-field proton signal appears as a broad doublet (see Table 1) (J = 12 c/s). The signal of the proton H_b is a doublet due to coupling with the proton H_c while that of the proton H_c is a multiplet superimposed on the aromatic signal making analysis impossible. On treatment with deuterium oxide, the low-field signal collapsed and the complex signal due to the aromatic and H_c protons was simplified.

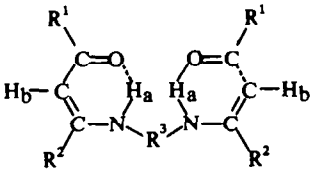
Garbisch[8] has elegantly demonstrated in the case of β-ketoaldehydes that the percentage of the hydroxymethylene component in the equilibrium mixture of the two possible enol tautomers is proportional to the coupling constant between the O—H and C—H protons of the hydroxymethylene group. It is significant that in the derivatives of benzoylacetaldehyde with both aromatic amines and with benzylamine that the coupling constant between the N—H proton and the proton H_c is 12–12·5 c/s. Forsen and Nilsson[9] similarly showed that the coupling constant of the N—H proton for 3-anilinomethylenepentan-2,4-dione was 12·5 c/s. That the value of the coupling constant is essentially the same in these compounds suggests that they all exist in the ketoenamine form to the same extent.

The NMR spectra of Schiff bases derived from acetylacetone (**1**; R^1 = R^2 = Me) and benzoylacetone (**1**; R^1 = Ph, R^2 = Me) (Table 1) similarly had broad low-field signals. As with Schiff bases of benzoylacetaldehyde, the low-field signal was shifted further downfield with electron-attracting groups in the amine fragment indicative

TABLE 1. NMR SPECTRA OF β-KETOAMINES



(1)



(2)

Structure	R^1	R^2	R^3	Solvent	H_a (τ)	H_b (τ)	Methylene signals (τ)	Methyl signals (τ)	$W_{\frac{1}{2}}$ (c/s)
1	Me	Me	H	CCl_4	0·4	5·10		8·10, 8·15	20
1	Me	Me	H	$CDCl_3$	0·22	4·94		8·02, 8·12	20
1	Me	Me	$PhCH_2$	CCl_4	−1·1	5·13	5·78 (6·5)[b]	8·10, 8·20	16
1	Me	Me	$PhCH_2$	Neat	−1·3	5·00	5·69 (6·5)[b]	8·08, 8·28	
1	Me	Me	p-$MeOC_6H_4$	$CDCl_3$	−2·3	4·80		7·95, 8·10	16
1	Me	Me	Ph	CCl_4	−2·55	4·95		8·05	16
1	Me	Me	p-$EtO_2CC_6H_4$	CCl_4	−2·75	4·85		7·95, 8·02	
1	Me	Me	p-$NO_2C_6H_4$	$CDCl_3$	−2·85	4·60		7·75, 7·80	8
2	Me	Me	CH_2CH_2	$CDCl_3$	−0·9	5·01	6·55 (7·5)[b,c]	8·00, 8·09	20
2	Me	Me	p-C_6H_4	$CDCl_3$	−2·55	4·80		7·92, 8·02	8
2	Me	Me	p,p'-$C_6H_4.C_6H_4$	$CDCl_3$	−2·6	4·78		7·90, 7·95	4
1	Ph	Me	H	$CDCl_3$	−0·2	4·30		8·05	24
1	Ph	Me	$PhCH_2$	$CDCl_3$	−1·8	4·25	5·80 (6·4)[b]	7·95	16
1	Ph	Me	p-$MeOC_6H_4$	$CDCl_3$	−2·9	4·16		7·98	
1	Ph	Me	Ph	$CDCl_3$	−3·15	4·10		7·85	12
1	Ph	Me	p-$NO_2CC_6H_4$	$CDCl_3$	−3·45	3·92		7·65	8
1	Ph	H	p-MeC_6H_4	$CDCl_3$	−2·25 (12)[b]	4·02 (8)[b]		7·68	
1	Ph	H	Ph	$CDCl_3$	−2·25 (12)[b]	4·02 (8)[b]			
1	Ph	H	p-$EtO_2CC_6H_4$	$CDCl_3$	−2·3 (12)[b]	3·92 (8)[b]			
1	Ph	H	$PhCH_2$	$CDCl_3$	−0·5 (12·5)[b]	4·28 (7·2)[b]	5·65 (6·4)[b]		

[a] $W_{\frac{1}{2}}$, width of signal at half-height.

[b] J (c/s) in parentheses.

[c] Triplet, cf. G. O. Dudek and R. H. Holm, *J. Am. Chem. Soc.* **83**, 2099 (1961); **84**, 2691 (1962).

TABLE 2. NMR SPECTRA OF SCHIFF BASES DERIVED FROM *o*-HYDROXYCARBONYL COMPOUNDS AND AMINES

Compound number	*o*-Hydroxycarbonyl compound	Amine	Solvent	OH or NH (τ)	C—H (τ)
1	Salicyladehyde	*p*-$MeOC_6H_4NH_2$	$CDCl_3$	−3·45	1·40
2	Salicylaldehyde	*p*-$MeC_6H_4NH_2$	$CDCl_3$	−3·45	
3	Salicyladehyde	$PhNH_2$	$CDCl_3$	−3·25	1·46
4	Salicyladehyde	*p*-$BrC_6H_4NH_2$	$CDCl_3$	−3·0	1·40
5	Salicyladehyde	*p*-$ClC_6H_4NH_2$	$CDCl_3$	−3·05	1·40
6	Salicylaldehyde	*p*-$EtO_2CC_6H_4NH_2$	$CDCl_3$	−2·95	1·40
7	Salicylaldehyde	*p*-$NO_2C_6H_4NH_2$	$CDCl_3$	−2·58	1·35
8	Salicylaldehyde	2,4,6-$Cl_3C_6H_2NH_2$	$CDCl_3$	−2·30	1·42
9	Salicylaldehyde	α-$C_{10}H_7NH_2$	$CDCl_3$	−2·95	1·50
10	Salicylaldehyde	$PhCH_2NH_2$	CCl_4	−2·8	1·64
11	3-Methylsalicylaldehyde	*p*-$ClC_6H_4NH_2$	CCl_4	−2·85	1·50
12	4-Methylsalicylaldehyde	*p*-$MeOC_6H_4NH_2$	$CDCl_3$	−3·45	1·45
13	4-Methylsalicylaldehyde	*p*-$MeC_6H_4NH_2$	$CDCl_3$	−3·45	1·40
14	4-Methylsalicylaldehyde	$PhNH_2$	$CDCl_3$	−3·25	1·45
15	4-Methylsalicylaldehyde	*p*-$ClC_6H_4NH_2$	$CDCl_3$	−3·05	1·42
16	4-Methylsalicylaldehyde	*p*-$EtO_2CC_6H_4NH_2$	$CDCl_3$	−2·90	1·42
17	5-Methylsalicylaldehyde	*p*-$MeOC_6H_4NH_2$	$CDCl_3$	−3·13	1·50
18	5-Methylsalicylaldehyde	*p*-$MeC_6H_4NH_2$	$CDCl_3$	−3·20	1·40
19	5-Methylsalicylaldehyde	$PhNH_2$	$CDCl_3$	−2·96	1·50
20	5-Methylsalicylaldehyde	*p*-$ClC_6H_4NH_2$	$CDCl_3$	−2·8	1·45
21	5-Methylsalicylaldehyde	*p*-$EtO_2CC_6H_4NH_2$	$CDCl_3$	−2·62	1·45
22	6-Methylsalicylaldehyde	*p*-$ClC_6H_4NH_2$	$CDCl_3$	−3·8	1·05
23	3-Methoxysalicylaldehyde	*p*-$MeOC_6H_4NH_2$	CCl_4	−3·95	1·38
24	3-Methoxysalicyaldehyde	*p*-$MeC_6H_4NH_2$	CCl_4	−3·15	1·40
25	3-Methoxysalicylaldehyde	$PhNH_2$	CCl_4	−3·05	1·40
26	3-Methoxysalicylaldehyde	*p*-$BrC_6H_4NH_2$	$CDCl_3$	−3·45	1·38
27	3-Methoxysalicylaldehyde	*p*-$ClC_6H_4NH_2$	CCl_4	−2·62	1·53
28	3-Methoxysalicylaldehyde	*p*-$EtO_2CC_6H_4NH_2$	CCl_4	−2·75	1·38
29	5-Methoxysalicylaldehyde	*p*-$MeOC_6H_4NH_2$	$CDCl_3$	−2·88	1·54
30	5-Methoxysalicylaldehyde	*p*-$MeC_6H_4NH_2$	$CDCl_3$	−2·85	1·50
31	5-Methoxysalicylaldehyde	$PhNH_2$	$CDCl_3$	−2·75	1·50
32	5-Methoxysalicylaldehyde	*p*-$ClC_6H_4NH_2$	$CDCl_3$	−2·55	1·50
33	5-Methoxysalicylaldehyde	*p*-$EtO_2CC_6H_4NH_2$	$CDCl_3$	−2·50	1·42
34	5-Bromosalicylaldehyde	*p*-$MeOC_6H_4NH_2$	$CDCl_3$	−3·50	1·45
35	5-Bromosalicylaldehyde	*p*-$MeC_6H_4NH_2$	$CDCl_3$	−3·45	1·45
36	5-Bromosalicylaldehyde	$PhNH_2$	$CDCl_3$	−3·35	1·45
37	5-Bromosalicylaldehyde	*p*-$ClC_6H_4NH_2$	$CDCl_3$	−2·95	1·61
38	5-Bromosalicylaldehyde	*p*-$EtO_2CC_6H_4NH_2$	$CDCl_3$	−3·0	1·40
39	5-Nitrosalicylaldehyde	*p*-$MeOC_6H_4NH_2$	$CDCl_3$	−4·65	1·33
40	5-Nitrosalicylaldehyde	*p*-$MeC_6H_4NH_2$	$CDCl_3$	−4·6	1·30
41	5-Nitrosalicylaldehyde[a]	$PhNH_2$	$CDCl_3$	−4·0	
42	5-Nitrosalicylaldehyde	*p*-$EtO_2CC_6H_4NH_2$	$CDCl_3$	−4·05	1·20
43	2-Hydroxy-1-naphthaldehyde	*p*-$MeOC_6H_4NH_2$	$CDCl_3$	−5·7	0·75 (broad)[b,c]
44	2-Hydroxy-1-naphthaldehyde	*m*-$MeOC_6H_4NH_2$	$CDCl_3$	−5·4	0·78 (5)
45	2-Hydroxy-1-naphthaldehyde	*o*-$MeOC_6H_4NH_2$	$CDCl_3$	−5·7	0·87 (9)
46	2-Hydroxy-1-naphthaldehyde	*p*-$MeC_6H_4NH_2$	$CDCl_3$	−5·65	0·76 (5)
47	2-Hydroxy-1-naphthaldehyde	*m*-$MeC_6H_4NH_2$	$CDCl_3$	−5·5	0·75 (broad)
48	2-Hydroxy-1-naphthaldehyde	2,6-$Me_2C_6H_3NH_2$	$CDCl_3$	−4·95	0·92 (broad)
49	2-Hydroxy-1-naphthaldehyde	$PhNH_2$	$CDCl_3$	−5·45	0·78 (broad)
50	2-Hydroxy-1-naphthaldehyde	*p*-$ClC_6H_4NH_2$	$CDCl_3$	−5·25	0·70 (broad)

TABLE 2—*continued*

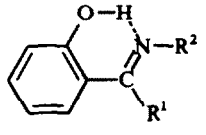
Compound number	*o*-Hydroxycarbonyl compound	Amine	Solvent	OH or NH (τ)	C—H (τ)
51	2-Hydroxy-1-naphthaldehyde	*m*-$ClC_6H_4NH_2$	$CDCl_3$	−5·1	0·75 (3)
52	2-Hydroxy-1-naphthaldehyde	*o*-$ClC_6H_4NH_2$	$CDCl_3$	−5·35	0·70 (4)
53	2-Hydroxy-1-naphthaldehyde	*p*-$EtO_2CC_6H_4NH_2$	$CDCl_3$	−5·25	0·68 (4)
54	2-Hydroxy-1-naphthaldehyde	*o*-$NO_2C_6H_4NH_2$	$CDCl_3$	−4·55	0·80 (4)
55	2-Hydroxy-1-naphthaldehyde[d]	$PhCH_2NH_2$	$CDCl_3$	−4·8	1·26 (6·4)
56	2-Hydroxy-1-naphthaldehyde	Bu^tNH_2	$CDCl_3$	−4·7	1·31 (10·5)
57	*o*-Hydroxyacetophenone	$PhCH_2NH_2$	$CDCl_3$	−6·3	7·60[e]
58	*o*-Hydroxyacetophenone	*p*-$MeOC_6H_4NH_2$	$CDCl_3$	−5·05	7·70[e]

[a] L. W. Reeves, E. A. Allan and K. O. Stromme, *Canad. J. Chem.* **38**, 1249 (1960).
[b] Broad indicates that the signal was broad and unresolved.
[c] *J* (c/s) in parentheses.
[d] Methylene signal 5·35 (3).
[e] Methyl signal.

of the strengthening of the hydrogen-bond. A good linear correlation between the position of the low-field signal and Hammett substituent constants σ was obtained. Such groups would result in a weakening of the N—H bond with the formation of a more symmetrical and thus stronger hydrogen-bond. Factors which increase the symmetry of the hydrogen-bond in β-diketones have also been shown to result in the enolic signal being displaced to lower field.[1] Consistent with these results the low-field signal in derivatives of β-diketones and aliphatic amines was less downfield than for analogous derivatives of aromatic amines because the nitrogen in the former compounds is more basic thereby resulting in a stronger N—H bond and a corresponding less symmetrical and weaker hydrogen-bond.

The width of the low-field signal is related to the rate of intermolecular exchange of the hydrogen-bonded proton and thus is sharper for compounds with stronger hydrogen-bonds.[1] Thus it can be seen from an examination of the derivatives of benzoylacetone that the signal width is related to the position of the signal, being sharpest for compounds with the strongest hydrogen-bonds.

The NMR spectra of a range of substituted salicylaldehyde-anils were also measured (Table 2). Electron-withdrawing substituents in the aromatic amine



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residue displaced the low-field signal upfield in contrast to the electronic effects found with Schiff bases of β-diketones. There was again a good linear correlation between the position of this signal and Hammett substituent constants. Schiff bases of salicylaldehydes exist as the enolimine (**4**): thus the methylene group in the NMR

TABLE 3. NEW SCHIFF BASES OF SALICYLALDEHYDES, *o*-HYDROXYACETOPHENONE, AND 2-HYDROXY-1-NAPHTHALDEHYDE

Compound[a]	M.p.	Crystals	Recryst. from	Found (%) C	H	N	Hal.	Formulae	Calc. (%) C	H	N	Hal.
8	107–109°	Yellow needles	Pet. (60–80°)	52·3	3·0	4·4	35·4	$C_{13}H_8Cl_3NO$	51·9	2·7	4·7	35·4
11	43	Yellow prisms	Pet. (40–60°)	68·3	5·2	5·1	14·7	$C_{14}H_{12}ClNO$	68·4	4·9	5·7	14·5
12	128–130	Yellow plates	Pet. (60–80°)	74·4	6·4	5·4		$C_{15}H_{15}NO_2$	74·7	6·3	5·8	
13	143–144	Orange needles	Pet. (60–80°)	79·5	6·8	5·9		$C_{15}H_{15}NO$	80·0	6·7	6·2	
14	95	Yellow needles	Pet. (60–80°)	79·5	6·3	6·3		$C_{14}H_{13}NO$	79·6	6·2	6·6	
15	165	Yellow prisms	Pet. (60–80°)	68·1	5·1	5·3	14·2	$C_{14}H_{12}ClNO$	68·4	4·9	5·7	14·5
16	121–122	Yellow needles	Pet. (60–80°)	72·2	6·1	4·95		$C_{17}H_{17}NO_3$	72·1	6·05	4·9	
17	123–124	Yellow needles	Pet. (40–60°)	74·7	5·9			$C_{15}H_{15}NO_2$	74·7	6·3		
21	97–99	Orange needles	Pet. (60–80°)	71·8	6·4			$C_{17}H_{17}NO_3$	72·1	6·05		
22	106–108	Yellow needles	Pet. (40–60°)	68·7	5·15	5·6	14·5	$C_{14}H_{12}ClNO$	68·4	4·9	5·7	14·5
23	95	Orange needles	Pet. (60–80°)	69·9	6·0	5·5		$C_{15}H_{15}NO_3$	70·0	5·9	5·4	
24	101–102	Orange needles	Pet. (60–80°)	74·8	6·3	5·8		$C_{15}H_{15}NO_2$	74·7	6·3	5·8	
25	86–87	Red-orange needles	Pet. (60–80°)	73·8	5·7	5·9		$C_{14}H_{13}NO_2$	74·0	5·8	6·2	
26	119–120	Orange needles	Pet. (60–80°) $-CH_2Cl_2$	55·0	3·9	4·6		$C_{14}H_{12}BrNO_2$	54·9	3·95	4·6	

27	111	Orange needles	Pet. (60–80°)	64·7	4·9			$C_{14}H_{12}ClNO_2$	64·3	4·6		
28	103·5–104·5	Red needles	Pet. (60–80°)	67·9	5·5	4·4		$C_{17}H_{17}NO_4$	68·2	5·7	4·7	
29	88	Orange needles	Pet. (60–80°)	70·3	5·9			$C_{15}H_{15}NO_3$	70·0	5·9		
30	112	Red needles	Pet. (40–60°)	74·9	6·5	5·6		$C_{15}H_{15}NO_2$	74·7	6·3	5·8	
31	59	Red plates	Pet. (40–60°)	74·1	5·95	6·2		$C_{14}H_{13}NO_2$	74·0	5·8	6·2	
32	106–109	Red needles	Pet. (60–80°)	64·2	5·1	4·7	13·4	$C_{14}H_{12}ClNO_2$	64·3	4·6	5·35	13·6
33	102–103	Red plates	Pet. (60–80°)	68·3	5·85	4·6		$C_{17}H_{17}NO_4$	68·2	5·7	4·7	
34	158–159	Yellow needles	Pet. (60–80°) —CH_2Cl_2	54·8	3·9	4·5	26·3	$C_{14}H_{11}BrNO_2$	54·9	3·95	4·6	25·2
37	159–160	Yellow plates	Pet. (60–80°) —CH_2Cl_2	50·6	3·3	4·4	37·2[b]	$C_{13}H_9BrClNO$	50·3	2·9	4·5	37·7[b]
39	174	Orange needles	Pet. (60–80°) —CH_2Cl_2	61·3	4·05			$C_{14}H_{12}N_2O_4$	61·75	4·45		
40	158	Yellow plates	Pet. (60–80°) —CH_2Cl_2	65·7	4·7			$C_{14}H_{12}N_2O_3$	65·6	4·7		
42	194	Yellow needles	Pet. (60–80°) —CH_2Cl_2	60·6	4·5			$C_{16}H_{14}N_2O_5$	61·15	4·5		
48	119	Orange prisms	Pet. (60–80°)	82·7	6·5	5·2		$C_{19}H_{17}NO$	82·9	6·2	5·1	
56	104	Yellow needles	Pet. (60–80°)	78·8	7·45	6·4		$C_{15}H_{17}NO$	79·3	7·5	6·1	
58	106	Lemon-yellow plates	Pet. (40–60°) —CH_2Cl_2	74·35	6·25	5·6		$C_{15}H_{15}NO_2$	74·7	6·3	5·8	

[a] See Table 1. [b] % (Cl + Br).

spectrum of N-benzyl salicylaldehydimine (**4**; R^1 = H, R^2 = $PhCH_2$) appears as a sharp singlet showing that the hydrogen-bonded proton is not bonded to nitrogen. Electron-withdrawing groups in the aromatic amine residue decrease the basicity of the nitrogen and hence reduce the tendency to form a hydrogen-bond.

The effect of substituents in anils of 2-hydroxy-1-naphthaldehyde (**2**; R = Ar) was the same as with salicylaldehyde-anils (Table 2) suggesting that they too existed in the enolimine form (**2a**). There was, however, coupling between the H_b and hydrogen-bonded protons suggesting that these compounds can be better represented as the ketoenamine. The value of the coupling constant varied between 1 and 9 c/s but was generally about 4 c/s for different substituted 2-hydroxy-1-naphthaldehyde anils. Electronic and steric effects had no systematic influence on the value of the coupling constant. A coupling constant of about 4 c/s can be taken to indicate that these compounds exist as an equilibrium mixture of the two tautomers with the enolimine tautomer present to the extent of about 65% in the mixture. A value of 12–13 c/s was taken to be the coupling constant between the proton H_b and the NH proton from the results for derivatives of benzoylacetaldehyde which are considered to exist wholly in the ketoenamine form. The coupling constant between these protons in N-benzyl-2-hydroxy-1-naphthaldehydimine (**2**; R = $PhCH_2$) was 6 c/s indicating an approximately 50% mixture of the two tautomers. Consistent with this the coupling constant between the methylene protons of the benzyl group and the NH proton is 3 c/s. The coupling constant in the benzylamine derivatives of acetylacetone, benzoylacetone, and benzoylacetaldehyde was 6·4 c/s which exist in the ketoenamine form exclusively. The coupling constant between the proton H_b and the NH proton in N-t-butyl-2-hydroxy-1-naphthaldehydimine (**2**; R = Bu^t) was 10·5 c/s indicating an even greater degree of ketoenaminic character. Dudek found for the corresponding methyl compound that the coupling constant was 8 c/s.[7a] In all cases treatment with deuterium oxide resulted in the disappearance of the low-field signal and collapse of the H_b proton signal to a sharp singlet.

The effect of substituents in the salicylaldehyde moiety of the Schiff base on the position of the hydrogen-bonded proton signal was similar to that in the parent salicylaldehydes. However, the hydrogen-bonded proton signal of derivatives of *o*-hydroxyacetophenone was much further downfield compared to the signal in *o*-hydroxyacetophenone than for the corresponding salicylaldehyde derivatives. This was particularly marked in the case of N-benzyl-2-hydroxyacetophenone-imine (**4**; R^1 = Me, R^2 = $PhCH_2$) and can be attributed to a shortening and therefore consequent strengthening of the hydrogen-bond as a result of steric interaction between the Me and benzyl groups. That this effect is much less marked in N-*p*-anisyl-7-hydroxyacetophenone imine (**4**; R^1 = Me, R^2 = *p*-$MeOC_6H_6$) is due to the chelate ring in this compound being forced slightly out of planarity by the even greater steric interaction of the Me and anisyl groups.

The rates of exchange of both the hydrogen-bonded and vinylic protons of Schiff bases of acetylacetone were examined by determining their NMR spectra after treatment with deuterium oxide. In all cases the hydrogen-bonded proton exchanged instantaneously as did the non-hydrogen-bonded amine proton in 4-aminopent-3-en-2-one (**1**; R^1 = R^2 = Me, R^3 = H). The proton H_b of this compound also underwent complete exchange within 4 hr. This is in contrast to the rate of exchange of the vinylic proton of acetylacetone which is only partially complete in this time.

That the proton H_b undergoes exchange shows that the ketoenamine (**1a**) and ketoimine (**1c**) forms are in equilibrium as protons attached to carbon do not undergo exchange at measurable rates under those conditions. Exchange must occur *via* conversion to the ketoimine tautomer followed by reversion to the ketoenamine form with the deuterium attached to carbon. The rate of interconversion of the ketoenamine and ketoimine forms of 4-aminopent-3-en-2-one must be considerably greater than that between the keto and enol forms of acetylacetone particularly when one considers that the former exists almost completely in the keto–amine form whereas acetylacetone is only 80% enolic. It was also shown that the proton H_b of 4-(*p*-methoxyanilino)pent-3-en-2-one (**1**; $R^1 = R^2 = Me$, $R^3 = p\text{-}MeOC_6H_4$) undergoes complete exchange in 24 hr whereas the proton H_b of 4-(*p*-nitroanilino)pent-3-en-2-one (**1**; $R^1 = R^2 = CH_3$, $R^3 = p\text{-}NO_2C_6H_4$) had not undergone exchange to a significant extent in this time. This probably arises because an even smaller amount of ketoimine is present at equilibrium in the latter case. Campbell and Harmer[6] have shown that electron-withdrawing groups in *p*-substituted benzoylcyclopentanones increase the degree of enolization.

It can be concluded that the N—H...O hydrogen-bond is appreciably stronger than the O—H....N hydrogen-bond since Schiff bases of β-diketones exist as the keto–amine tautomer even when the alternative enolimine form would have a significant degree of extra resonance stabilization. The results with anils of 2-hydroxy-1-naphthaldehyde confirm this. The increased degree of "enolization" of Schiff bases of β-diketones compared to the parent β-diketone can be attributed at least in part to steric effects. The amine residue would interfere with the adjacent alkyl group forcing the oxygen and nitrogen closer. Relief of the resultant electrostatic interaction in the ketoimine tautomer is brought about by "enolization". The same explanation is used to explain the high degree of enolization of sterically hindered β-diketones.[12]

EXPERIMENTAL

NMR spectra were determined for $CDCl_3$ or CCl_4 solns on a Perkin–Elmer 40 Mc/s spectrometer. Chemical shifts were reported on the τ-scale using TMS as an internal reference. The spectra of the deuterated forms were obtained by shaking the soln of the compound with 2–3 drops of D_2O and then redetermining the spectrum.

3-p-*Nitroanilino*-1-*phenylbut*-2-*en*-1-*one*. A mixture of benzoylacetone (8·0 g) and *p*-nitroaniline (6·9 g) was heated on a boiling water-bath for 6 hr in presence of 2 drops of conc HCl. The resultant oil was poured into 50% aqueous alcohol (100 ml) and the mixture allowed to stand overnight. The yellow ppt which formed was filtered off and crystallized from EtOH as yellow needles of 3-p-*nitroanilino*-1-*phenylbut*-2-*en*-1-*one* (7·0 g, 50%), m.p. 145°. (Found: N, 10·5. $C_{16}H_{14}N_2O_3$ requires: N, 10·3%).

3-p-*Toluidino*-1-*phenylprop*-2-*en*-1-*one*. Equimolar quantities of methanolic solns of *p*-toluidine hydrochloride and the sodium salt of benzoylacetaldehyde were mixed. The resulting yellow ppt was filtered off and crystallized from light petroleum (b.p. 60–80°)–CH_2Cl_2 as yellow *needles*, m.p. 121° (lit,[13] m.p. 160–163°). (Found: C, 80·7; H, 6·55; N, 5·6. $C_{16}H_{25}NO$ requires: C, 81·0; H, 6·35; N, 5·9%).

3-p-*Ethoxycarbonylanilino*-1-*phenylprop*-2-*en*-1-*one* was similarly obtained and crystallized from light petroleum (b.p. 60–80°)–CH_2Cl_2 as yellow *needles*, m.p. 146–148°. (Found: C, 72·8; H, 6·0; N, 4·95. $C_{18}H_{17}NO_3$ requires: C, 73·2; H, 5·8; N, 4·75%).

3-p-*Benzylamino*-1-*phenylprop*-2-*en*-1-*one* was prepared by adding to a soln of the sodium salt of benzoylacetaldehyde (1 mole), benzylamine (1 mole) in MeOH containing an equivalent quantity of conc HCl. The ppt was filtered off and crystallized from light petroleum as *cream plates*, m.p. 82°. (Found: C, 80·7; H, 6·2; N, 5·9. $C_{16}H_{15}NO$ requires: C, 81·0; H, 6·4; N, 5·9%).

Schiff bases of salicylaldehydes, o-hydroxyacetophenone and of 2-hydroxy-1-naphthaldehyde. An EtOH soln containing equimolar quantities of the amine and *o*-hydroxy carbonyl compound and 2-drops conc. HCl was heated on a steam-bath for 15 min. The mixture was allowed to cool and the resultant ppt filtered off and crystallized from the appropriate solvent (Tables 5 and 6).

Other Schiff bases. These were prepared and purified by using literature procedures.

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