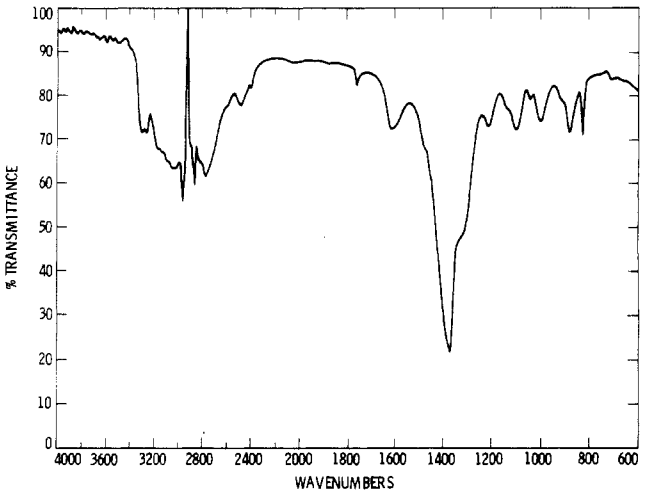

Figure 1. Infrared spectrum of methylhydrazinium nitrate.

Table I. Mass Spectrum of Methylhydrazinium Nitrate

m/z	% of base	+ ion
14	5.61	N, CH_2
15	8.80	NH, CH_3
16	6.67	NH_2, O
17	13.74	OH, NH_3
18	31.75	H_2O
26	1.54	CN
27	10.26	CNH
28	59.63	CNH_2, N_2, CO
29	20.03	$HCNH_2$, N_2H, HCO
30	45.01	NO, N_2H_2
31	36.88	HNO, N_2H_3, CH_3NH_2
36	2.51	
41	1.45	CH_2H
42	3.00	CN_2H_2
43	5.71	CN_2H_3
44	2.51	CH_3N_2H
45	47.62	CH_3NHNH
46	100.00	CH_3NHNH_2, NO_2
47	2.12	$CH_3NH_2NH_2$, HNO_2
56	0.87	
63	0.77	HNO_3

Density. The density was determined by sink-float techniques. Crystals floated in carbon tetrachloride (d^{20}_4 1.594) but sank in chloroform (d^{20}_4 1.483). In trichlorotrifluoroethane (Freon TF, FC-113; d^{25} 1.565) the crystals just barely floated, most of the crystals being submerged. The density was estimated to be approximately 1.55 g/cm^3.

The most unusual property of methylhydrazinium nitrate is its tendency to form strong solvates. Pumping at $<10^{-5}$ torr for 5 days did not remove water of solution nor did similar pumping for 4 days on a methanol solution. However, chilling to about −30 °C allowed the salt to drop out of solution and crystals did form. Methylhydrazine hydrate has also been reported to form similarly stable solvates (*8*). In air the nitrate salt rapidly attacked aluminum.

Safety. Methylhydrazinium nitrate is toxic (*9*) even when applied to the skin. The impact sensitivity is comparable to that of ammonium perchlorate (*8*).

Acknowledgment

We thank Lois Taylor and Ray F. Haack for some of the measurements.

Registry No. Methylhydrazinium nitrate, 29674-96-2; methylhydrazine, 60-34-4.

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Preparation and Molecular Structure of New Cyclic β-Diketone Schiff Bases

Ali A. H. Saeed

Department of Chemistry, College of Science, University of Basrah, Basrah, Iraq

The molecular structure of new Schiff bases derived from cyclic β-diketones was investigated by kinetic analysis and mass, IR, and UV spectroscopy. The study indicates that these Schiff bases exist as a tautomeric mixture of the enolimine–ketamine–ketimine forms.

Introduction

Previous spectral studies, IR, UV, NMR, and mass spectrometry, have clearly shown that Schiff bases derived from β-diketones are tautomerized mainly into both the ketamine and enolimine forms (*1-9*). Schiff bases derived from diamines and

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Table I. Melting Points, Boiling Points, and IR and UV Spectral Data of the Cyclic β-Diketone Schiff Bases

molecule	(bp/°C)/ (press./ torr)	IR data in Nujol mull/ cm^{-1}	UV λ_{max}/nm in ethanol	UV λ_{max}/nm in ethanol–sodium ethoxide
1	130/0.45	3240–3460[a]	335	
		1700[b]	294[d]	
		1500–1680[c]	204	
2	110/0.5	3260–3360	343 (1000)[e]	343 (1600)
		1700	248[d]	
		1500–1680	205	
3	143/0.3	3200–3380		
		1700		
		1500–1680		
4	161/0.35	3210–3460		
		1705		
		1500–1680		
5	196/0.4	3280–3390		
		1700		
		1500–1680		
6	124/0.42	3200–3460	328	
		1705	286[d]	
		1500–1680	203	
7 (mp 41 °C)		3200–3350	350 (2400)	350 (2650)
		1705	240	
		1500–1680	207	
8	138/0.48	3200–3460		
		1710		
		1500–1680		
9	157/0.35	3300–3400		
		1710		
		1500–1600		
10 (mp 125 °C)		3280–3440		
		1710		
		1500–1680		
2-acetylcyclohexanone[f]		1600, 1700, 1720		
2-acetylcyclopentanone[f]		1614, 1665, 1710, 1735		

[a] Broad band. [b] Weak, sharp peak. [c] A series of four to five medium to strong sharp peaks. [d] Shoulder. [e] Extinction coefficient in units of m^2 mol^{-1}. [f] As liquid films.

cyclic β-diketones have been assumed to exist almost entirely as ketamine and enolimine (*3*), although the condensation has been suggested to occur on the side-chain carbonyl except where steric hindrance forced condensation to occur on the ring carbonyl.

The present investigation deals with new Schiff bases prepared from monoamines and 2-acetylcyclohexanone or 2-acetylcyclopentanone; their structures were studied by kinetic analysis and IR, UV, and mass spectrometry so that straight comparison is made between them and those derived from cyclic β-diketones and diamines or straight-chain β-diketones with different amines.

Results and Discussion

The observed first-order hydrolysis rate constants (k_{obsd}) in phosphate buffer are plotted in the form – log k_{obsd}–pH for some molecules as shown in Figure 1. The straight lines are similar to those recently obtained for the hydrolysis of straight-chain β-diketone Schiff bases (*9*). Deviation from the straight line, under more acidic conditions, may indicate the presence of a species other than those which have been suggested previously, namely the enolimine and ketamine tautomers.

Mass-spectral data of all molecules (Figure 2 represents typical mass spectra) show peaks due to the ions CH_3CN^+ at *m/z* 41, CH_3CO^+ at *m/z* 43, RNH_2^+, RNH^+, cyclohexanone – H ion at *m/z* 97, cyclopentanone – H ion at *m/z* 83, $C_6H_9N^+$ and $C_5H_7N^+$ at *m/z* 95 and 81, respectively, and strong to weak peaks due to the ions $M^{+\cdot}$ – 43, $M^{+\cdot}$ – 83, $M^{+\cdot}$ – 15, $M^{+\cdot}$ – 18 ($-H_2O$ molecule), and $M^{+\cdot}$ – 17 (–OH radicals). The spectra of molecules **6–10** exhibit strong molecular ion peaks which are sometimes the base peak, whereas the base peak for most 2-acetylcyclohexanone Schiff bases depends on the kind of amine used. Accordingly, it is evident from the above results that a third tautomer, namely the ketimine, may exist in our new Schiff bases.

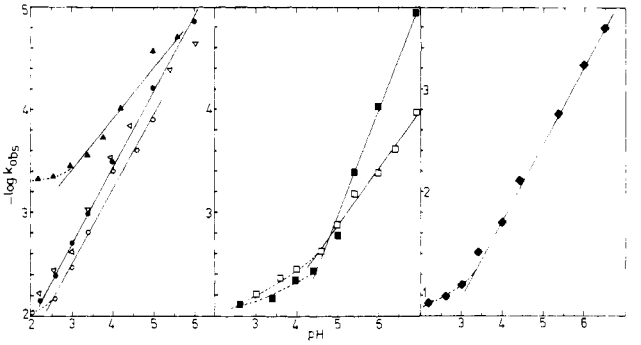


Figure 1. Plots of – log k_{obsd} vs. pH in phosphate buffer at 30 ± 1 °C: (▲) **6**, (○) **7**, (●) **8**, (△) **9**, (■) **2**, (□) **1**; (♦) **4**.

The IR spectra (Table I) show absorptions which are characteristic of the bonded OH, NH, C=O, C=N stretchings and NH bending vibrations in the hydrogen-bonded chelate enolimine and ketamine tautomers of β-diketone Schiff bases (*1–6*, *10–14*). The other absorption at 1705 ± 5 cm^{-1}, which has not been observed previously in other Schiff bases, may be attributed to the free carbonyl due to the following: (i) bonded C=O in the ketamine tautomer usually appeared below 1680 cm^{-1} (*1*, *2*, *4*, *10–14*) and (ii) lower absorptions of 2-acetylcyclohexanone and pentanone are characteristic of the hydrogen-bonded enol and keto forms, whereas the higher ones for

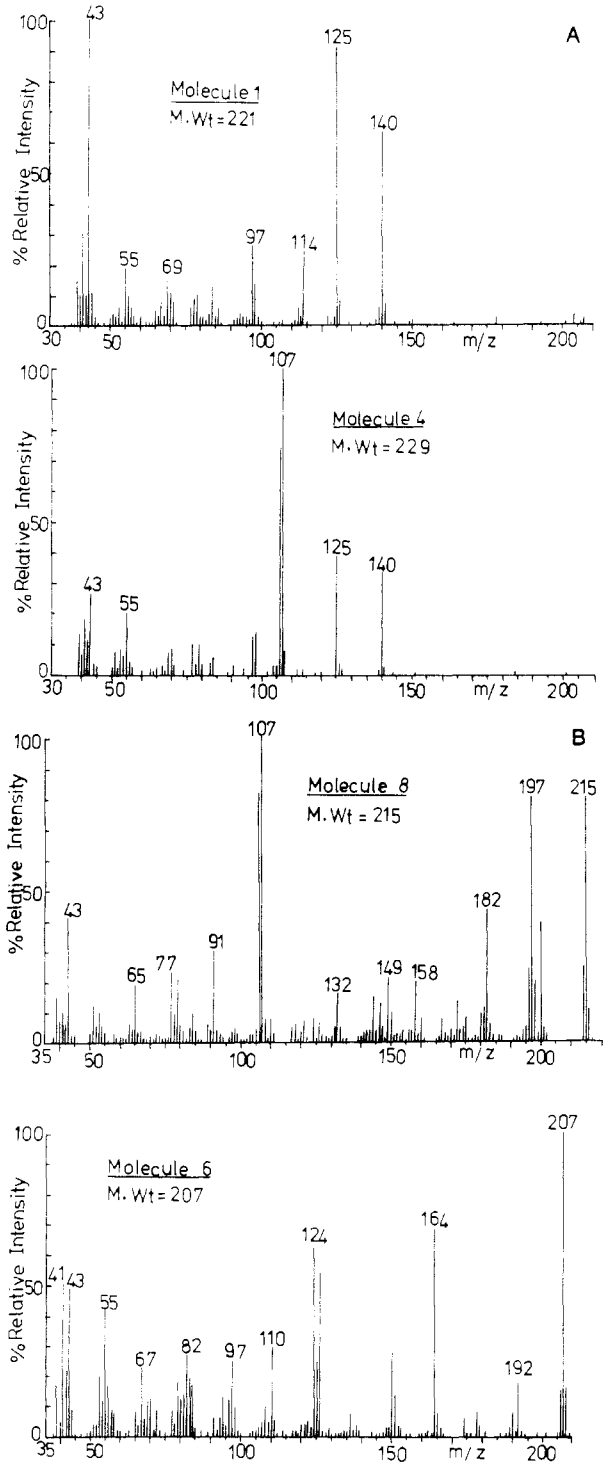


Figure 2. Mass spectra of molecules **1**, **4**, **6**, and **8**.

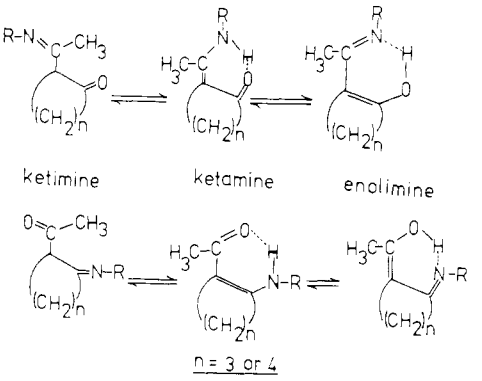
the free carbonyls (Table I). It is, therefore, the absorption at 1705 cm^{-1} which seems to be more likely for the free carbonyl of the ketimine tautomer in our Schiff bases (Scheme I).

The UV absorption bands presented in Table I are characteristic of β-diketone Schiff bases (*7*, *8*). The intensities of the longer wavelength enolimine bands of **2** and **7**, as typical examples (Table I), are increased considerably in the presence of sodium ethoxide. This indicates an increase in the enolimine over the ketamine–ketimine ratio since enolization is enhanced in such a medium.

Conclusion

On the basis of our kinetics and IR and mass-spectral observations it can be concluded that (i) the condensation reaction between the cyclic β-diketones used and monoamines, under our experimental conditions, occurs on both the side-chain and ring carbonyls, and (ii) in both cases, each Schiff base molecule may exist as a tautomeric mixture of the ketimine–enolimine–ketamine forms. It is difficult to estimate the percent content of the ketimine tautomer because of i and hence this tautomer may exist as a mixture in the same Schiff base molecule as shown in Scheme I.

Scheme I



1 ; n = 4 , R = cyclohexyl
2 ; n = 4 , R = phenyl
3 ; n = 4 , R = p-chlorophenyl
4 ; n = 4 , R = p-tolyl
5 ; n = 4 , R = p-N,N-dimethylaminophenyl
6 ; n = 3 , R = cyclohexyl
7 ; n = 3 , R = phenyl
8 ; n = 3 , R = p-tolyl
9 ; n = 3 , R = p-anisyl
10 ; n = 3 , R = p-nitrophenyl

Experimental Section

Details of the kinetic analyses, UV, IR, and mass-spectral instrumentation have already been reported (*9*, *15*).

Most of the cyclic β-diketone Schiff bases were prepared by refluxing equimolar amounts of the cyclic β-diketone, the corresponding amine, and a few drops of concentrated hydrochloric acid in an oil bath with water being collected as soon as it was formed. The mixture was then fractionally distilled under reduced pressure and the fractions which boil at the boiling points indicated in Table I were collected.

Compounds **7** and **10** were prepared by refluxing equimolar amounts of 2-acetylcyclopentanone and the appropriate amine, for 90 and 10 min, respectively. On cooling, a yellow crystalline product in every case separated which was collected and purified. Compound **7** was purified by sublimation and compound **10** by recrystallization from ethanol. All the compounds gave satisfactory elemental analyses and were submitted for review.

Registry No. **1** (ketimine), 90320-95-9; **1** (ketamine), 90321-05-4; **1** (enolimine), 90321-15-6; **2** (ketimine), 90320-96-0; **2** (ketamine), 90321-06-5; **2** (enolimine), 90321-16-7; **3** (ketimine), 90320-97-1; **3** (ketamine), 90321-07-6; **3** (enolimine), 90321-17-8; **4** (ketimine), 90320-98-2; **4** (ketamine), 90321-08-7; **4** (enolimine), 90321-18-9; **5** (ketimine), 90320-99-3; **5** (ketamine), 90321-09-8; **5** (enolimine), 90321-19-0; **6** (ketimine), 90321-00-9; **6** (ketamine), 90321-10-1; **6** (enolimine), 90321-20-3; **7** (ketimine), 90321-01-0; **7** (ketamine), 90321-11-2; **7** (enolimine), 90321-21-4; **8** (ketimine), 90321-02-1; **8** (ketamine), 90321-12-3; **8** (enolimine), 90321-22-5; **9** (ketimine), 90321-03-2; **9** (ketamine), 90321-13-4; **9** (enolimine), 90321-23-6; **10** (ketimine), 90321-04-3; **10** (ketamine), 90321-14-5; **10** (enolimine), 90321-24-7.

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Behavior of 4,5-Dihydropyridazinone Derivatives and 3-Chloropyridazine toward Alkylating Agents, Acylhydrazines, and Azides

Maher A. El-Hashash* and Sayed I. El-Nagdy

Chemistry Department, Faculty of Science, Ain Shams University, Abbassia, Cairo, Egypt

Refait M. Saleh

Chemistry Department, Faculty of Engineering, Suez Canal University, Port Said, Egypt

The pyridazinones 2 have been synthesized from the interaction of acid 1 with hydrazines. Reactions of 2 with electrophilic reagents gave O-alkylated derivatives, with $POCl_3/PCl_5$ gave chloro derivatives, and with bromine gave the oxidation product. Reaction of the chloro derivative with acylhydrazine, sodium azide, primary amines, and phenylhydrazine gave triazole derivative, tetrazole derivative, (arylamino)pyridazine, and phenylhydrazinopyridazine, respectively.

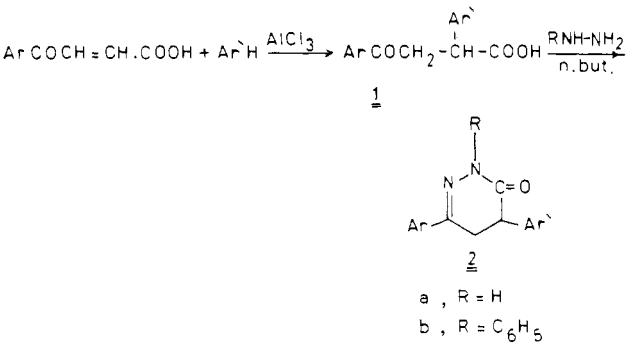
There have been reports of 4,5-dihydropyridazinones that have antihypertensive activity, although they have no classical hypotensive pharmacophor (*1*). In addition, Nannini (*2*) has recently reported that pyridazinones have analgesic and anti-inflammatory activity. We report here on the synthesis of some 4,5-dihydropyridazine derivatives via alkylation of 6-(4-chloro-3-methylphenyl)-4-(2,5-dimethylphenyl)-3-oxo-2,3,4,5-tetrahydropyridazine (**2a**), whose synthetic route was reported by El-Hashash et al. (*3*) (Scheme I). The pyridazinone **2a** could be alkylated with a variety of electrophilic reagents, namely, dialkyl sulfate and ethyl chloroacetate in dry acetone, by using anhydrous K_2CO_3 as catalyst (*4*). The products were identified as 3-O-alkylated 4,5-dihydropyridazine derivatives **3a–c**.

The compound **3c** reacts with benzylamine and/or *p*-anisidine to give the *N*-arylamide derivatives **3d** and **3e**, respectively.

Interaction of **2a** with a mixture of $POCl_3/PCl_5$ (*5*) gives 3-chloro-4,5-dihydropyridazine derivative **4**.

Recently (*6*), it was reported that 6-(substituted phenyl)-1,2,4-tetrazolo[4,3-*b*]pyridazines show activity in tests predictive of anxiolytic activity. Thus, reaction of **4** with acylhydrazines, namely, acetylhydrazine, benzoylhydrazine, and salicyloylhydrazine in refluxing butanol, gave triazolopyridazines **5a–c**. On the other hand, **4** reacts with NaN_3 in boiling DMF (*7*) to give 1,2,3,4-tetrazolopyridazine **6**.

Scheme I



Compound **4** submitted to react with *p*-toluidine, *p*-anisidine, and phenylhydrazine gave 3-(arylamino) and 3-(phenylhydrazino) derivatives **7**.

Oxidation of the dihydropyridazinone **2a** with Br_2/AcOH gave the pyridazinone derivative **8**.

Experimental Section

Melting points reported are uncorrected; the IR spectra were determined with a Pye Unicam Ltd. (Cambridge, England) part No. 641751 spectrophotometer by using the KBr wafer technique (Scheme II). (For the structural assignments cf. Table I.)

***Reaction of the Acid* 1 *with Hydrazines. Formation of Pyridazinones* (2a *and* 2b).** A solution of the acid **1** (0.01 mol) in 1-butanol (50 mL) was treated with hydrazine hydrate or phenylhydrazine (0.01 mol) and the mixture refluxed for 5 h. The solid that separated after concentration and cooling was crystallized from a proper solvent to give the desired pyridazinones **2a** and **2b**. The results are given in Table I.

***Action of Dialkyl Sulfate or Ethyl Chloroacetate on* 2a. *Formation of* 3a–c.** A mixture of **2a** (0.01 mol), anhydrous

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