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Tautomerism in 3-Substituted-2,4-pentanediones and Their Copper Chelates

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Seventeen 3-substituted-2,4-pentanediones were synthesized. The effect of substituents in the position 3 on the tautomeric equilibria, *i. e.*, keto-, *cis*-enol- and *trans*-enol-forms, has been investigated by nuclear magnetic resonance spectroscopy. It has been found that the percentage of each tautomer depends upon the electronic and steric effects of the substituents. The relative intensity of intramolecular hydrogen bonds in these compounds was evaluated from both the NMR and IR data. It has been found from the half-wave potential data of polarographic reduction and the Cu–O stretching frequencies of 16 copper chelates of 3-substituted-2,4-pentanediones that the relative stability of the chelate decreases with an increase in the electron-withdrawing effect of the substituents.

In recent years, NMR spectroscopy has been frequently used for the study of β-dicarbonyls, especially for keto-enol tautomerism and hydrogen bonding. Burdett and Rogers examined the NMR spectra of β-diketones and β-keto esters, determined their equilibrium constants[1] and discussed the solvent effect[2] on the chemical shifts and on the tautomeric equilibrium. Lowe and Ferugson[3] studied the direction and the percentage of the enolization of several substituted benzoylacetones by infrared, ultraviolet, and NMR spectroscopy and found that the benzoylacetones were enolized toward the carbonyl close to the phenyl group. Lintvedt and Holtzclaw studied the position of the methylene proton and enolic proton resonance peaks of several substituted 1,3-diketones with respect to the electronic effects[4] of the groups substituted in the position 1 or 3 and the correlation between the position of this enolic proton resonance peak and the thermodynamic formation constants[5] of the 1,3-diketone metal chelates. They reported that, with a greater electron-releasing effect of the substituents, the hydrogen bond became stronger as the electron density on the oxygen increased. The enolic proton resonance peak was shifted toward a lower field, and the stability of the chelates was increased.

In a previous paper the tautomeric equilibria of six 3-alkylated-2,4-pentanediones[6] were reported; they had been studied using NMR spectroscopy. In this paper seventeen 3-substituted-2,4-pentanediones will be investigated in order to establish the substituent effect on the tautomerism and on the intramolecular hydrogen bond. The relative stability of these sixteen copper chelates was, further, checked by infrared spectroscopy and by polarography.

Experimental

Preparation of 3-Substituted-2,4-pentanediones and Copper Chelates. The 3-substituted-2,4-pentanediones were prepared by the established methods, references for which are listed in Table 1. The copper chelates were prepared by adding an ethanol solution of 3-substituted-2,4-pentanedione to an excess aqueous solution of cupric acetate, except in the case of bis[3-nitro-2,4-pentanediono]copper. The analytical data are shown in Table 2.

NMR Spectroscopy. The NMR spectra were obtained on a JNM-3H-60 spectrometer at 60 Mcps. All the samples were run in carbon tetrachloride. The sample concentration was 2 mol/*l*. The chemical shift values are reported in cps from internal tetramethylsilane.

Polarography. The polarograms for copper chelates were recorded using a Yanagimoto Model P-8 polarograph. Each sample solution was 10^{-3} mol/*l* with respect to the chelate, 0.1 mol/*l* with respect to potassium nitrate as the supporting electrolyte, and 1.6 g/*l* with respect to Tween-80 as the maximum suppressor. The chelate, supporting electrolyte and maximum suppressol-

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[1] J. L. Burdett and M. T. Rogers, *J. Am. Chem. Soc.*, **86**, 2105 (1964).

[2] M. T. Rogers and J. L. Burdett, *Can. J. Chem.*, **43**, 1516 (1965).

[3] J. U. Lowe, Jr., and L. N. Ferugson, *J. Org. Chem.*, **30**, 3000 (1965).

[4] R. L. Lintvedt and H. F. Holtzclaw, Jr., *J. Am. Chem. Soc.*, **88**, 2713 (1966).

[5] R. L. Lintvedt and H. F. Holtzclaw, Jr., *Inorg. Chem.*, **5**, 239 (1966).

[6] T. Shono, M. Tanaka, Y. Murotani and K. Shinra, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **88**, 1068 (1967).

TABLE 1. PREPARATION OF 3-SUBSTITUTED-2,4-PENTANEDIONES

3-Substituent	Bp (°C)	Pressure (mmHg)	Ref.
CH_3	60—62	18	6
C_2H_5	68—70	12	6
n-C_3H_7	75—77	12	6
i-C_3H_7	74—76	17	6
n-C_4H_9	114—115	35	6
i-C_4H_9	79—80	11	6
s-C_4H_9	88—89	14	6
Cl	154—156	760	b)
$COOC_2H_5$	95—98	12	7
$CH_2COOC_2H_5$	141—143	22	6
$CH_2CH_2COOC_2H_5$	151—153	14	6
$OCOCH_3$	101—102	17	8
C_6H_5	56—58[a]	—	5
CN	54—55[a]	—	7
OCH_3	57—58	15	7
COC_6H_5	30—31[a]	—	9
$CH(C_6H_5)CH_3$	49—50[a]	—	6

a) Melting point is shown.

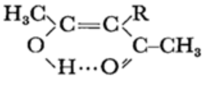
b) This compound was prepared by adding sulfuryl chloride (67.5 g) to acetylacetone (50 g) at 0—5°C over 2 hr, pouring the mixture into water (100 ml) and extracting with ether.

were dissolved in aqueous 75% dioxane. The cell temperature was maintained at 25.0±0.1°C, and oxygen-free nitrogen was bubbled through each solution for 20 min to remove dissolved oxygen before measurement.

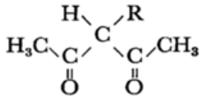
Infrared Spectroscopy. The infrared spectra in the 4000—650 cm^{-1} region were recorded on a Hitachi Model EPI-S2 spectrometer, while those in the 700—250 cm^{-1} region were recorded on a Hitachi Model EPI-L spectrometer using Nujol mulls.

Results and Discussion

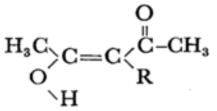
Keto-Enol Tautomeric Equilibria. In general there are three possible tautomeric isomers for 3-substituted-2,4-pentanediones; they are shown



(*cis*-enol)



(keto)



(*trans*-enol)

below. As has previously been reported, 2,4-pentanediones substituted in the position 3 with

TABLE 2. ANALYTICAL DATA FOR 3-SUBSTITUTED-2,4-PENTANEDIONE COPPER CHELATES

Code	3-Substituent	Analyses, %					
		C		H		N	
		Found	Calcd	Found	Calcd	Found	Calcd
1	CH_3	49.22	49.74	6.69	6.26		
2	C_2H_5	52.75	52.91	6.88	6.98		
3	n-C_3H_7	55.28	55.56	7.62	7.57		
4	i-C_3H_7	67.71	67.58	9.95	9.92[a]		
5	n-C_4H_9	57.54	57.82	8.02	8.09		
6	i-C_4H_9	57.74	57.82	8.28	8.09		
7	s-C_4H_9	69.31	69.20	10.29	10.32[a]		
8	Cl	36.30	36.33	3.73	3.66		
9	$COOC_2H_5$	47.28	47.35	5.43	5.46		
10	$CH_2COOC_2H_5$	49.85	49.82	5.85	6.04		
11	$CH_2CH_2COOC_2H_5$	51.54	52.00	6.18	6.55		
12	$OCOCH_3$	44.36	44.51	5.15	4.80		
13	C_6H_5	63.40	63.84	5.12	5.36		
14	CN	45.43	46.29	3.97	3.88	8.81	8.95
15	OCH_3	44.19	44.79	5.79	5.64		
16	COC_6H_5	61.59	61.34	5.02	4.72		
17	$CH(C_6H_5)CH_3$	76.92	76.44	7.91	7.90[a]		
18	NO_2[7]	34.24	34.15	3.29	3.44	7.90	7.96
19	H						

a) Analyzed as 3-substituted-2,4-pentanedione as they formed no chelates.

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7) J. P. Fackler, Jr., and F. A. Cotton, *Inorg. Chem.*, **2**, 102 (1963).

8) H. Bähm and H. Schneider, *Chem. Ber.*, **91**, 1100 (1958).

9) M. M. Coombs and R. P. Houghton, *J. Chem. Soc.*, **1961**, 5015.

TABLE 3. TAUTOMERIC EQUILIBRIA OF 3-SUBSTITUTED-2,4-PENTANEDIONES

Code	3-Substituent	Proton chemical shifts, cps			Percentage of tautomer, %		
		cis-enol OH	*trans*-enol OH	3-methine H	*cis*-enol	*trans*-enol	keto
1	CH_3	979	—	218 (Q)	36	0	64
2	C_2H_5	993	—	210 (T)	25	0	75
3	*n*-C_3H_7	998	325	219 (M)	22.2	11.1	66.7
4	*i*-C_3H_7	—	323	201 (D)	0	24	76
5	*n*-C_4H_9	989	324	212 (T)	22	5.5	72.5
6	*i*-C_4H_9	1001	324	216 (T)	40	10	50
7	*s*-C_4H_9	—	325	208 (D)	0	52.6	47.4
8	Cl	920	—	279	91	0	9
9	$COOC_2H_5$	1081	—	206	96	0	4
10	$CH_2COOC_2H_5$	1002	—	246[a]	33[d]	0	67[d]
11	$CH_2CH_2COOC_2H_5$	999	—	222 (T)	26	0	74
12	$COOCH_3$	861	—	321	20	0	80
13	C_6H_5	996	—	—	100	0	0
14	CN	1002	—	—	100	0	0
15	OCH_3	845	—	b)	c)	0	c)
16	COC_6H_5	1017	—	—	100	0	0
17	$CH(C_6H_5)CH_3$	—	—	236 (D)	0	0	100
19	H	915	—	210	93	0	7

D=doublet, T=triplet, Q=quartet and M=multiplet.

a) This signal overlaps CH_2 signal of $CH_2COO\underline{CH_2}CH_3$.

b) It is impossible to find the signal because this material cannot be purified.

c) Signal intensity at 845 cps is very low.

d) Determined using CH_2 proton signal intensity of $\underline{CH_2}COOC_2H_5$.

isopropyl and *s*-butyl groups have no *cis*-enol form. In the case of a methyl substituent, *cis*-enol and keto forms have been found. Substitution with *n*-propyl, *n*-butyl, and isobutyl groups showed *cis*- and *trans*-enol forms and the keto form. Substituents with an inductive effect different from alkyl groups as well as bulky substituents were introduced. Table 3 summarizes the chemical shift values of the enolic proton and the methine proton in the keto form, and the percentage of each tautomer obtained from the corresponding signal intensity. Table 3 shows that the substitution of carbethoxy, cyano, or benzoyl groups in the position 3 of 2,4-pentanedione results in a considerable increase in the *cis*-enol tautomer, while in the case of alkyl, acetoxy, and methoxy substituents, an increase of

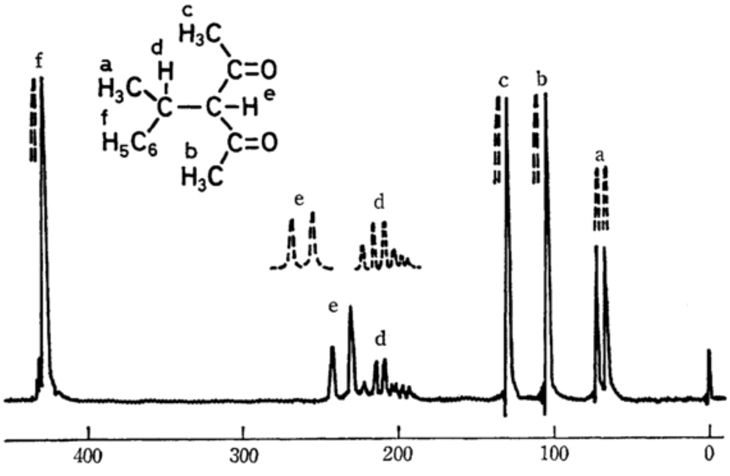

Fig. 1. NMR spectra for 3-(α-phenylethyl)-2,4-pentanedione in CCl_4 (solid line) and in *d*-DMSO (broken line).

the keto tautomer is found. Though many factors influence the keto-enol tautomeric equilibrium, the results in Table 3 can be qualitatively explained in terms of both the electronic and steric factors of the substituent. The electron density in the vicinity of the methine proton must be decreased by the substitution of electronegative groups in the position 3. The enol tautomer will, then, be more stabilized. Among keto-, *cis*-enol-, and *trans*-enol-forms, the steric hindrance between acetyl methyl groups and the 3-substituent is the largest in the *cis*-enol tautomer. The percentage of the *cis*-enol tautomer was found to decrease with an increase in the bulkiness of the substituent in the position 3. In the absence of steric hindrance, the *cis*-enol tautomer is more stabilized than the *trans*-enol tautomer by an intramolecular hydrogen bond.[1,10] The combination of the electronic and steric effects mentioned presumably influences the tautomeric equilibrium. In fact, substitution with electron-withdrawing groups, such as carbethoxy, cyano, and benzoyl groups, results in a considerable increase in the *cis*-enol tautomer. In the case of electron-releasing groups, such as alkyl, acetoxy, and methoxy, the keto tautomer increases reversely. It should be sterically impossible for 2,4-pentanediones substituted with isopropyl anb *s*-butyl groups to take the *cis*-enol form. The presence of only small amounts of the *trans*-enol form in the cases of *n*-propyl, *n*-butyl, and isobutyl substituents is presumably the result of steric hindrance, which is even larger in isopropyl and *s*-butyl groups (see Table 3). The α-phenylethyl group, which is bulkier than the isopropyl and *s*-butyl groups, was introduced in the position 3. The NMR spectrum of 3-(α-phenylethyl)-2,4-pentanedione is shown in Fig. 1. In the case of the carbon tetrachloride solution (see Fig. 1, solid line), three signals, corresponding to three protons, appear at 69 cps as a doublet, and at 104 cps and 130 cps as a singlet. Phenyl proton resonance occurs at 428 cps. The signals corresponding to the two methine protons appear in the 210—236 cps region. Using *d*-dimethyl sulfoxide as the solvent, these signals can be separated into two signals with the same intensity (*cf.* the broken line) *i.e.*, the multiplet centered at 210 cps and the doublet, at 263 cps. An examination of this spectrum leads to the conclusion that this compound has only the keto form, and no *cis*- and *trans*-enol forms, because of its great bulky substituent. The same results have been reported in the case of 3-(*t*-butyl)-2,4-pentanedione.[11]

Intramolecular Hydrogen Bond. As Table 3 shows, the *cis*-enol OH protons show considerable variations in chemical shift and all are at a very low applied magnetic field, indicating the presence of intramolecular hydrogen bonds in these compounds. With an increase in the strength of this hydrogen bond, the carbonyl stretching vibration is shifted to a lower frequency.[12,13] The *cis*-enol OH proton chemical shift values are plotted *vs.* the carbonyl stretching frequencies in Fig. 2. It is

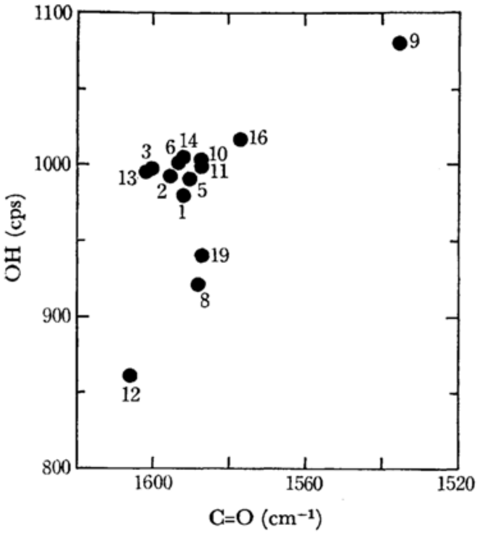

Fig. 2. Chemical shift of *cis*-enol OH proton *vs.* carbonyl stretching frequency.
(Code numbers refer to compounds of Table 3)

TABLE 4. POLAROGRAPHIC AND INFRARED SPECTRAL DATA FOR COPPER CHELATES

Code	3-Substituent	Half-wave potential (V)	Cu–O stretching frequency (cm^{-1})	C=O stretching frequency (cm^{-1})
1	CH_3	−0.87	468	1577
2	C_2H_5	−0.92	468	1570
3	*n*-C_3H_7	−0.90	467	1576
5	*n*-C_4H_9	−0.89	468	1575
6	*i*-C_4H_9	−0.94	468	1575
8	Cl	−0.65	467	1574
9	$COOC_2H_5$	−0.63	462	1582
10	$CH_2COOC_2H_5$	−0.85	465	1572
11	$CH_2CH_2COOC_2H_5$	−0.92	468	1577
12	$OCOCH_3$	−0.86	462	1587
13	C_6H_5	−0.82	471	1572
14	CN	−0.37	450	1592
15	OCH_3	−0.82	457	1579
16	COC_6H_5	−0.52	450	1583
18	NO_2	−0.29	448	1590
19	H	−0.81	455	1577

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10) G. W. Wheland, "Advanced Organic Chemistry," 3rd Ed., John Wiley & Sons, Inc., New York (1960).

11) P. Bolat and H. Militzer, *Tetrahedron Letters*, **1966**, 3599.

12) S. Forsen and M. Nilsson, *Acta Chem. Scand.*, **13**, 1383 (1959).

13) S. Forsen and M. Nilsson, *ibid.*, **14**, 1333 (1960).

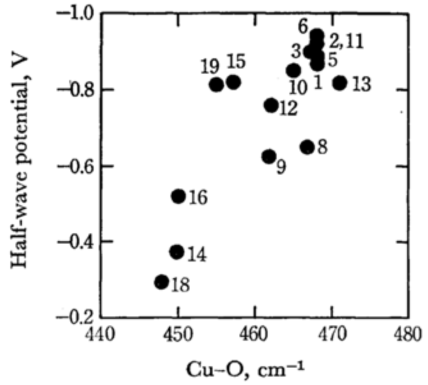

Fig. 3. Half-wave potential *vs.* copper-oxygen stretching frequency of copper chelates.
(Code numbers refer to compounds of Table 4)

found that, with an increase in the strength of the hydrogen bond, the *cis*-enol OH proton resonance signal is shifted toward a lower field.

Copper Chelates of 3-Substituted-2,4-pentanediones. The polarograms and infrared spectra of sixteen 3-substituted-2,4-pentanedione copper chelates were recorded in order to investigate their relative stability. Lintvedt *et al.*[14] reported that the reduction potential should be a function of the electronic density on and around the copper atom. The reduction potential becomes more negative as the chelate becomes more stable, because the stability of the chelate increases with an increase in the electron density near the copper ion. Much information concerning the nature of coordinate bonds and chelate rings has been obtained from the infrared spectroscopy of 2,4-pentanedione metal chelates.[15,16] Especially, the metal-oxygen stretching modes appearing in the 700—250 cm^{-1} region may directly provide information on the relative strength of coordinate bonds. Table 4 shows the half-wave potential data of the polarographic reduction, the copper-oxygen stretching frequencies, and the carbonyl stretching frequencies of copper chelates. A plot of the half-wave potentials *vs.* the copper-oxygen stretching frequencies (Fig. 3) shows that the chelate with a more negative half-wave potential tends to show a higher copper-oxygen stretching frequency. Namely, in the case of copper chelates reduced more easily when substituted with electron-withdrawing substituents, such as nitro, cyano, and benzoyl groups, coordinate bonds become weaker because the electron density near the copper atom decreases. The chelates with a higher frequency of the copper-oxygen stretching vibration also tend to show a lower carbonyl stretching frequency. The electronic effect of the substituent thus affects the electron density on the copper atom. This proves the delocalization of π-electrons in the chelate ring. Murakami *et al.*[17] have studied the delocalization of π-electrons for 2,4-pentanedione metal chelates substituted in the position 3 with phenyl and benzyl derivatives.

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