100–125 mesh column, operating at 125 °C. No *m*-acetoxytoluene (17) was detected in this analysis.

Kinetics of Peroxide Decompositions. A kinetic study of the rate of decomposition of 7 and that of benzoyl peroxide was carried out, using a modified procedure of Bartlett and Nozaki.[17] Benzoyl peroxide and 5 were weighed out and dissolved in benzene (0.028 M). These solutions were than placed in two 100-mL three-necked flasks equipped with condensers and placed in a constant temperature bath at 79.8 °C. Aliquots (2 mL) were removed at 60-min intervals and placed in a solution containing potassium iodide, water, and isopropyl alcohol. After 10 min, the liberated iodine was treated with 0.1 M thiosulfate.

(17) Bartlett, P. D.; Nozaki, K. *J. Am. Chem. Soc.* **1946**, *68*, 1686.

Acknowledgment. Financial support by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

Registry No. 6, 71549-44-5; 7, 71549-45-6; 8, 71582-23-5; 11, 134-55-4; 13, 71549-46-7; 16, 533-18-6; 17, 122-46-3; 18, 4386-39-4; benzene, 71-43-2; phenyl acetate, 122-79-2; *m*-chloro-*o*-acetoxytoluene, 6341-98-6; benzoic acid, 65-85-0; acetylsalicylic acid, 50-78-2; perbenzoic acid, 93-59-4; *o*-acetylsalicyloyl chloride, 5538-51-2; chlorobenzene, 108-90-7; *o*-acetoxybiphenyl, 3271-80-5; phenylpentachloropropanone, 71549-47-8; CO_2, 124-38-9; *o*-chlorophenyl acetate, 4525-75-1.

Biotin Model Studies. Coordination of Magnesium(II) Ion to 1-(Methoxycarbonyl)-2-imidazolidinones in Acetonitrile

Hiroki Kondo, Daikichi Horiguchi, Sadamu Ikeda, and Junzo Sunamoto*

Department of Industrial Chemistry, Faculty of Engineering, Nagasaki University, Nagasaki 852, Japan

Kaoru Tsujii

Tochigi Research Laboratories, Kao Soap Company Ltd., Ichigai-machi, Tochigi 321-34, Japan

Received June 8, 1979

Several 1-(methoxycarbonyl)-2-imidazolidinones and their analogues have been synthesized as models for 1-carboxybiotin. In their ^{13}C NMR spectra both carbonyl carbon signals shifted downfield as much as 2–5 ppm in the presence of magnesium(II) ion in acetonitrile. This has been interpreted in terms of the magnesium(II) coordination to the acylurea moiety. Formation of the magnesium(II) complex with (methoxycarbonyl)-2-imidazolidinones in solution was also revealed by IR spectroscopic studies, in which significant low-frequency shifts of carbonyl stretching vibration bands were observed.

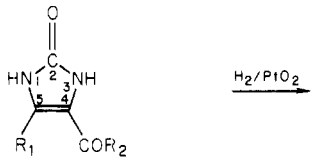
Biotin-dependent enzymes mediate a number of carboxylation, transcarboxylation, and decarboxylation reactions in biological systems.[1,2] The first step involved in these reactions is the carboxylation of biotin, usually at the expense of bicarbonate and ATP, and this reaction very likely takes place at the 1-N position of biotin.[3] A very basic question about this process is how the enzymes activate the ureido nitrogen, because it is well-known from model experiments that the nucleophilicity of the ureido nitrogen is extremely low.[4,5] In enzymic systems the reactivity of biotin seems to be enhanced by a proton transfer from a certain functional group(s) of the enzyme to the ureido carbonyl, thereby shifting the keto–enol tautomerism to afford the more nucleophilic imide nitrogen. Indeed, X-ray crystallographic studies on biotin and related compounds have proved that this carbonyl forms a hydrogen bond in crystals.[6-8] This suggests that the ureido carbonyl has a high affinity toward electrophilic reagents such as proton and metal ions even in solution.[9,10] In model studies, alterations in the reactivity of the carboxyl or methoxycarbonyl group attached to 1-N have been observed in the presence of certain divalent metal ions; these are ascribed to the metal chelation to the ureido carbonyl and carboxyl groups.[11,12] But, to the best of our knowledge, metal complex formation has never been proved in an explicit way even in model systems.[9]

We have prepared several 1-(methoxycarbonyl)-2-imidazolidinones bearing a long alkyl chain at the 4-position of the imidazolidinone ring as a model for 1-carboxybiotin in hopes of carrying out a reaction in a micellar phase, where a large rate acceleration is often achieved.[13] Although a possible involvement of the thioether moiety during the biotin catalysis via hydrogen bonding or chelation to a metal(II) ion has been suggested,[14,15] we omitted

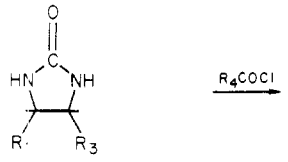
(1) J. Moss and M. D. Lane, *Adv. Enzymol. Relat. Subj. Biochem.*, **35**, 321 (1971).
(2) H. G. Wood and R. E. Bardev, *Annu. Rev. Biochem.*, **46**, 385 (1977).
(3) R. B. Guchhait, S. E. Polakis, D. Hollis, C. Feuselau, and M. D. Lane, *J. Biol. Chem.*, **249**, 6646 (1974).
(4) M. Caplow, *J. Am. Chem. Soc.*, **87**, 5774 (1965).
(5) T. C. Bruice and A. F. Hegarty, *Proc. Natl. Acad. Sci. U.S.A.*, **65**, 805 (1970).
(6) C. Bonnemere, J. A. Hamilton, L. K. Steinrauf, and J. Knappe, *Biochemistry*, **4**, 240 (1965).
(7) G. T. DeTitta, J. W. Edmonds, W. Stallings, and J. Donahue, *J. Am. Chem. Soc.*, **98**, 1920 (1976).
(8) C. Chen, R. Parthasarathy, and G. T. DeTitta, *J. Am. Chem. Soc.*, **98**, 4983 (1976).
(9) R. Griesser, H. Sigel, L. D. Wright, and D. B. McCormick, *Biochemistry*, **12**, 1917 (1973).
(10) A. S. Mildvan and M. C. Scrutton, *Biochemistry*, **6**, 2978 (1967).
(11) M. Caplow and M. Yager, *J. Am. Chem. Soc.*, **89**, 4513 (1967).
(12) N. Matsumura, H. Kawai, Y. Otsuji, and E. Imoto, *Bull. Chem. Soc. Jpn.*, **50**, 2417 (1977).
(13) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, London, 1975.
(14) J. A. Glasel, *Biochemistry*, **5**, 1851 (1966).
(15) H. Sigel, D. B. McCormick, R. Griesser, B. Prijs, and L. D. Wright, *Biochemistry*, **8**, 2687 (1969).

0022-3263/79/1944-4430$01.00/0

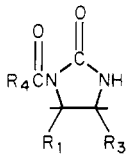
Scheme I



3a, R_1 = H; R_2 = C_5H_{11}
3b, R_1 = H; R_2 = $C_{11}H_{23}$
4a, R_1 = CH_3; R_2 = C_5H_{11}
4b, R_1 = CH_3; R_2 = $C_{11}H_{23}$



5a, R_1 = H; R_3 = C_6H_{13}
5b, R_1 = H; R_3 = $C_{12}H_{25}$
6a, R_1 = CH_3; R_3 = C_6H_{13}
6b, R_1 = CH_3; R_3 = $C_{12}H_{25}$

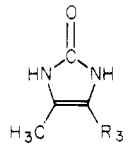


7, R_1 = H; R_3 = C_6H_{13}; R_4 = CH_3O
8a, R_1 = CH_3; R_3 = C_6H_{13}; R_4 = CH_3O
8b, R_1 = CH_3; R_3 = $C_{12}H_{25}$; R_4 = CH_3O
9, R_1 = CH_3; R_3 = $C_{12}H_{25}$; R_4 = C_2H_5
10, R_1 = CH_3; R_3 = $C_{12}H_{25}$; R_4 = p-$NO_2C_6H_4O$

this group since we regard the ureido moiety of biotin to be the most essential part for the catalysis. In addition, it will help avoid complications that might arise when we interpret experimental data. In this work we studied magnesium(II) coordination to 1-substituted carbonyl-2-imidazolidinones in acetonitrile by means of IR and ^{13}C NMR spectroscopy. The use of an aprotic solvent may be justifiable since the atmosphere of the enzyme active site(s) may be considerably different from that of the bulk aqueous phase.[16] The effect of magnesium(II) ion on the reactivity of 2-imidazolidinones and 1-substituted carbonyl-2-imidazolidinones in the same solvent will be reported elsewhere.

Results and Discussion

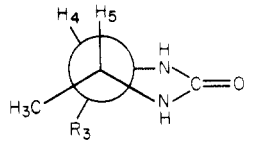
Stereochemistry of Hydrogenation and Methoxycarbonylation. 4-Dodecyl-2-imidazolidinones **5b** and **6b** were prepared in reference to the methods used for the synthesis of similar compounds (Scheme I).[17,18] Thus, 2-imidazolinones were first acylated with dodecanoyl chloride followed by catalytic hydrogenation over PtO_2 under atmospheric pressure. Both reactions gave modest to good yields as shown in Table I. One thing to note about the hydrogenation is that the introduction of a methyl group to the 5-position of the ring makes the imidazolinone somewhat resistant to hydrogenation.[18] Indeed, when 4-hexanoyl- (**4a**) or 4-dodecanoyl-5-methyl-2-imidazolidinone (**4b**) was hydrogenated under conditions that gave only fully hydrogenated products from the 5-unsubstituted counterparts (**3a** or **3b**), the partially hydrogenated compounds, 4-hexyl- or 4-dodecyl-5-methyl-2-imidazolinone (**11**), were isolated besides the fully hydrogenated products



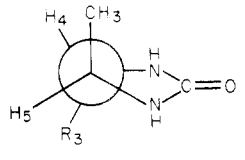
11, R_3 = C_6H_{13} or $C_{12}H_{25}$

(**6a** or **6b**). These imidazolinones could be converted to the corresponding 2-imidazolidinones by further hydrogenation over freshly prepared PtO_2. It is certain, therefore, that the reaction proceeds in a stepwise manner with the first hydrogenation occurring at the carbonyl group, unlike the case of ordinary α,β-unsaturated carbonyl compounds.[17,19]

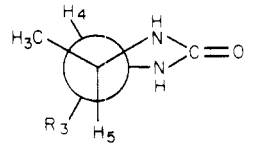
The hydrogenation of 4-acyl-5-methyl-2-imidazolinones, in principle, can afford two possible stereoisomers (cis and trans). The isolated 2-imidazolidinones, however, contained only a single isomer; structures were established by ^1H and, in particular, ^{13}C NMR. In both spectra only a single set of signals corresponding to either product, cis or trans, was observed. An attempt was made to elucidate the configuration of the actually isolated product by means of ^1H NMR. By reference to the X-ray crystallographic data on dethiobiotin,[8] the dihedral angle (ϕ) between the 4- and 5-hydrogens in the cis isomer (**12**) is assumed to be



12



13



14

23.5°. With the trans isomer there are two possible conformations (**13** and **14**), of which the former can be regarded more favorable since the bulky alkyl substituents should be more distant from each other in **13**. The estimated dihedral angles are 96.5 and 143.5° for **13** and **14**, respectively. The Karplus equation (eq 1)[20] leads to cal-

$$J_{vic} = 4.22 - 0.5 \cos \phi + 4.5 \cos^2 \phi \quad (1)$$

culated coupling constants for each configuration or conformation as follows: 7.55 Hz for **12**, 4.33 Hz for **13**, and 7.53 Hz for **14**. It is obvious that the experimentally obtained coupling constant of 7.5 Hz for **8a** is close to the calculated one for the cis isomer **12** or conformation **14** of the trans isomer. The isomer **14** has the less favored conformation, and also there is no example of selective formation of the trans isomer in similar reactions.[17,21] We, therefore, tentatively assign the configuration of the product as cis in support of the postulate made for the hydrogenation of other 2-imidazolinones.[17] Incidentally, a much higher cis/trans ratio is obtained in the hydrogenation of 1-methyl-2-phenylcyclopentene in contrast to that for 1,2-dimethylcyclopentene.[22]

(16) C. H. Fung, R. J. Feldmann, and A. S. Mildvan, *Biochemistry*, **15**, 75 (1976).
(17) R. Duschinsky and L. A. Dolan, *J. Am. Chem. Soc.*, **67**, 2079 (1945).
(18) R. Duschinsky and L. A. Dolan, *J. Am. Chem. Soc.*, **68**, 2350 (1946).
(19) D. J. Cram and G. S. Hammond, "Organic Chemistry", 2nd ed., McGraw-Hill, New York, 1964, Chapter 18.
(20) M. Karplus, *J. Am. Chem. Soc.*, **85**, 2870 (1963).
(21) J. L. Wood and V. du Vigneaud, *J. Am. Chem. Soc.*, **67**, 210 (1945).

Methoxycarbonylation or propionylation of the 2-imidazolidinones was performed by use of an excess of the corresponding acid chloride.[4,23,24] Judging from the experimental fact that several carbonyl stretching vibration bands appear in the IR spectra of methoxycarbonylated 2-imidazolidinones, the carbonyl group remains intact, and the reaction occurs on the nitrogen atom. With unsymmetrical 2-imidazolidinones (**5** or **6**) the reaction may take place at the 1- and/or 3-position of the ring. Enzymatic carboxylation of biotin occurs at the 1-position, as established by means of X-ray crystallographic analysis of 1-(methoxycarbonyl)biotin derivatives.[23] The methoxycarbonylation at 1-N of **6b** was easily ascertained by the decoupling technique in ^{1}H NMR. Before methoxycarbonylation, the 4- and 5-proton signals of **6b** appeared at almost identical chemical shifts. Upon methoxycarbonylation one of them shifted downfield about 0.5 ppm and gave a quintet with J = 6.3 Hz. When the proton signal of the 5-methyl group was saturated by resonance, the quintet changed to a doublet with the same coupling constant as before. This means that the 5-hydrogen is more deshielded than the 4-hydrogen by the methoxycarbonyl group, and the site of carbonylation is at 1-N. The fact that both enzymatic and chemical carbonylations occur at the same position suggests the possibility that the position of the enzymatic carbonylation of biotin occurring in the limited domain of an enzyme active site may also be decided by the steric factor.

^{13}C NMR Spectra. The proton-decoupled ^{13}C NMR spectrum of **6b** roughly consisted of three regions:[25,26] a low-field region for carbonyl carbon, a 50–60-ppm region for the 4- and 5-carbons, and a 10–33-ppm region for the side chain carbons. The relative chemical shifts of the 5-methyl and 4-dodecyl groups were almost invariant upon carbonylation at 1-N or magnesium(II) coordination (vide infra). Methoxycarbonylation of **6b** afforded an additional carbonyl carbon signal and a CH_3O signal at ~55 ppm. Of the two carbonyl signals, the lower field one, which was always more intense than the other, was assigned to the carbonyl carbon of the ring by the same reasoning used for the interpretation of similar spectra of 1′-*N*-(methoxycarbonyl)biotin derivatives.[3] Since the ureido carbonyl is fixed in the five-membered ring, it may have less chance of motional freedom leading to a fast relaxation of the carbonyl carbon. The ^{13}C NMR spectrum of **9** is similar to that of **8b** except for the presence of CH_2 (~30 ppm) and CH_3 (~9 ppm) signals in place of the CH_3O signal. An attempt to assign the two carbonyl signals of **9** by off-resonance decoupling failed due presumably to the fact that the coupling between the carbonyl carbon and the two hydrogens attached to the neighboring carbon or nitrogen atom was too small to detect with the spectrometer currently available to us. However, the higher field signal (157.1 ppm) lies in the same region as that for the two carbonyls of **8b**, and also it seems certain that amide carbonyls appear at lower field than urea carbonyls.[27] Hence, we tentatively assign the higher field signal to the ureido carbonyl and the lower one to 1-propionyl.

Coordination of Magnesium(II) Ion to 1-(Methoxycarbonyl)-2-imidazolidinones. The coordination of Mg(II) ion to imidazolidinone derivatives (**6b**, **8b**, and **9**) was studied by IR and ^{13}C NMR spectroscopy in acetonitrile. Addition of magnesium perchlorate up to an equimolar amount with **6b** brought about a modest downfield shift of the carbonyl carbon in the ^{13}C NMR spectrum as shown in Figure 1a, while the others remained virtually unchanged. Since **6b** serves as a monodentate ligand, unlike 1-carbonyl-2-imidazolidinones **8b** and **9**, the coordination of Mg(II) ion to **6b** is not so strong as to bring about a large shift of the carbonyl carbon signal in the ^{13}C NMR spectrum. The IR spectrum of **6b** in the presence of an equimolar amount of Mg(II) ion revealed a shift of the carbonyl stretching vibration band from 1710 to 1690 cm^{-1} (Figure

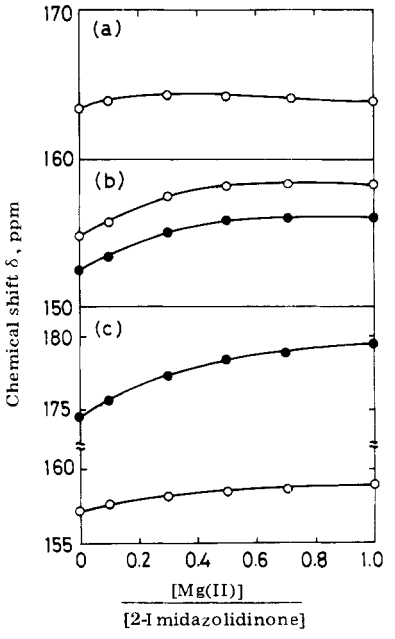


Figure 1. ^{13}C chemical shift changes of carbonyl carbons of **6b** (a), **8b** (b), and **9** (c) as a function of Mg(II) ion concentration in acetonitrile-d_3. Open and closed circles represent C-2 and C-6 signals, respectively.

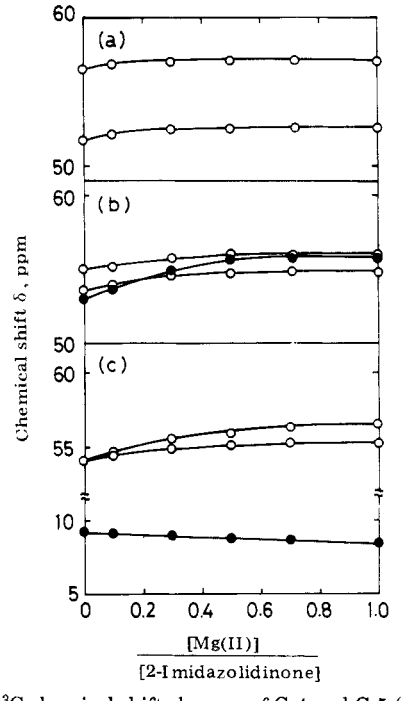


Figure 2. ^{13}C chemical shift changes of C-4 and C-5 (open circles) and C-8 (closed circles) of **6b** (a), **8b** (b), and **9** (c) as a function of Mg(II) ion concentration in acetonitrile-d_3. For numbering of carbons see structure **15**.

(22) S. Mitsui, Y. Senda, H. Suzuki, S. Sekiguchi, and Y. Kumagai, *Tetrahedron*, **29**, 3341 (1973).
(23) J. Knappe, E. Ringelmann, and F. Lynen, *Biochem. Z.*, **335**, 168 (1961).
(24) H. J. Schaeffer and P. S. Bhargava, *J. Pharm. Sci.*, **53**, 137 (1964).
(25) H. Kohn, *J. Am. Chem. Soc.*, **98**, 3690 (1976).
(26) H. Kohn, M. J. Cravey, J. H. Arceneaux, R. L. Cravey, and M. R. Willcott, III, *J. Org. Chem.*, **42**, 941 (1977).
(27) G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley, New York, 1972.

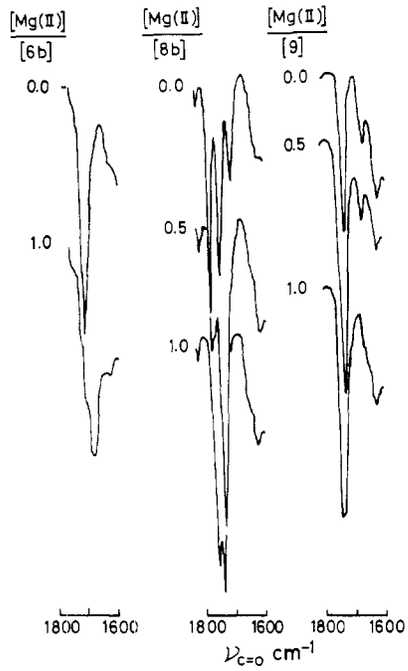
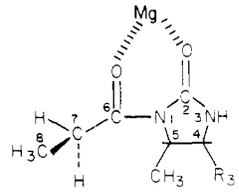


Figure 3. Infrared spectral changes in the carbonyl region of 1-carbonyl-2-imidazolidinones with different concentrations of Mg(II) ion in acetonitrile.

3), suggesting strongly the interaction of Mg(II) ion with the carbonyl group.

Upon the addition of Mg(II) ion, both carbonyl signals of **8b** gave rise to a large downfield shift (Figure 1b). Interestingly, at first the magnitude of the shift increased with the Mg(II) ion concentration, but it leveled off when the molar ratio of Mg(II) ion to **8b** reached 0.5. This was the case for other carbon signals such as C-4, C-5, and CH_3O as shown in Figure 2b. This is interpreted in terms of the formation of the 1:2 complex between the metal and the ligand. Finally, since only a single set of signals was observed for each compound, the exchange between the bound and free Mg(II) ions must be rapid under these conditions on the NMR time scale. In the absence of Mg(II) ion, the IR spectrum of **8b** had three absorption bands (1720, 1740, and 1780 cm^{-1}) in the $\nu_{C=O}$ region. As the metal ion concentration increased, the lowest and the highest frequency bands gradually disappeared (Figure 3). In the presence of an equimolar amount of Mg(II) ion, the middle band apparently split into two bands located at 1740 and 1750 cm^{-1}. Although we are unable to explain this spectral change quantitatively, it is not inconsistent with the view that it suggests a simultaneous interaction of Mg(II) ion with both carbonyl groups of **8b**.

For compound **9** the Mg(II) coordination gave rise to a downfield shift of carbonyl carbons, but the magnitude of shift was different between the two (Figure 1c). This does not necessarily mean that the interaction with Mg(II) ion is different between the two carbonyls but that it may be a reflection of the difference in the environment around each carbonyl group. That is, the ureido carbonyl of **9** is connected to two heteroatoms but 1-propionyl is not, while the two carbonyls of **8b** are put between similar heteroatoms. The main difference in the ^{13}C NMR spectra between **8b** and **9** is that a level-off phenomenon of carbonyl chemical shifts was not observed for **9** over the range of Mg(II) ion concentration adopted. This is very suggestive of the 1:1 complex formation for **9**, but the reason for it remains to be elucidated. In contrast to all other carbon signals, the C-8 signal of **9** alone showed an upfield shift upon the Mg(II) coordination (Figure 2c) though the magnitude itself was not large (0.8 ppm). As stated above, **9** as well as **8b** can act as a bidentate ligand. If we assume that the chelate ring takes a virtually planar conformation, the two hydrogens attached to C-7 (see structure **15**) will have more



15

chance to occupy the in-plane position, thereby forcing the methyl carbon way up to the shielding zone of the C-6 carbonyl.

As stated above, the coordination of magnesium(II) ion to 2-imidazolidinones and especially to 1-carbonyl-2-imidazolidinones in acetonitrile was evidenced by the present investigation. Previously, Griesser et al.[9] found that the ureido carbonyl of biotin and related compounds interacts with Mn(II) or Cu(II) ion in Me_2SO from the studies on the line broadening in ^1H NMR. Their finding is consistent with ours obtained from measurements of carbonyl shift in the ^{13}C NMR of 2-imidazolidinones upon the magnesium(II) coordination. They also observed a shift in the carbonyl vibration band of ethyleneurea from 1711 to 1690 cm^{-1} in the presence of phenol, and this was interpreted in terms of the intermolecular hydrogen bonding between the carbonyl oxygen and phenol.[9] Interestingly, the magnitude of shift is comparable to that observed for the interaction of **6b** with Mg(II) ion (from 1710 to 1690 cm^{-1}). This suggests that the ureido carbonyl bears an almost identical affinity toward a common electrophile such as a proton or the metal ions. With 1-carbonyl-2-imidazolidinones the mode of change in carbonyl vibration bands is not simple enough to allow quantitative analysis, but the results are suggestive of the stable Mg(II) chelate formation with the carbonylurea moiety. In summary, it was proved that the carbonyl groups of 1-carbonyl-2-imidazolidinones interact with certain metal ions at least in polar aprotic solvents such as Me_2SO and acetonitrile and that the polarization or electron shift in the carbonyl bond does take place to a considerable extent. A natural question will follow concerning its relevance to the reactivity change of biotin analogues. This subject is now in progress in our laboratories.

Experimental Section

IR spectra were taken with either a JASCO IRA-1 or a Hitachi 285 grating spectrophotometer. ^1H NMR spectra were run on a JEOL JMN MH-100 spectrometer at room temperature unless otherwise stated. Natural-abundance ^{13}C NMR spectra were recorded at about 50 °C on a JEOL PFT-100 spectrometer operating at 25 MHz. All chemical shift values are referred to internal Me_4Si. Melting points are uncorrected. Magnesium perchlorate and deuterated acetonitrile were obtained from Wako Pure Chemical Industries Ltd. and Merck, respectively.

2-Imidazolinone (**1**) was synthesized by the method of Hilbert:[28] ^1H NMR (Me_2SO-d_6) δ 6.24 (s, 2 H, =CH), 9.70 (br s, 2 H, NH). 4-Methyl-2-imidazolinone (**2**) was prepared according to the literature:[18] ^1H NMR (Me_2SO-d_6) δ 1.87 (s, 3 H, CH_3), 5.95 (s, 1 H, =CH), 9.50 (br s, 1 H, NH), 9.80 (br s, 1 H, NH).

4-Dodecanoyl-5-methyl-2-imidazolinone (4b). A mixture of 9.8 g (0.10 mol) of **2**, 22 g (0.10 mol) of dodecanoyl chloride, and 80 mL of nitrobenzene was cooled at 5 °C. To this was added 27 g (0.20 mol) of aluminum chloride in small portions over 45 min. Then the whole mixture was heated at 65 °C for 5 h. The

(28) G. E. Hilbert, *J. Am. Chem. Soc.*, **54**, 3413 (1932).

Table I. Elemental Analyses of Newly Prepared Compounds

compd	yield, %	mp, °C	carbon		hydrogen		nitrogen	
			calcd	found	calcd	found	calcd	found
3b	48	270–273	67.67	67.67	9.77	10.08	10.53	10.29
4b	59	212–214	68.53	68.59	10.07	10.14	9.99	9.89
5b	63	112–114	70.87	70.02	11.81	11.43	11.02	10.74
6b	95	105–108	71.59	71.58	12.02	12.32	10.44	10.16
7	97	78–83	57.87	57.70	8.83	8.95	12.27	12.37
8a	50	109–110	59.48	59.64	9.15	9.48	11.56	11.45
8b	82	98–99	66.22	65.86	10.50	10.06	8.58	8.48
9	60	96–97	70.33	70.55	11.18	11.39	8.63	8.65
10	46	129–130	63.72	63.67	8.14	8.23	9.68	9.61

Table II. ^{1}H NMR Data of Newly Prepared Compounds

(A) 4-Dodecanoyl-2-imidazolinones

compd	solvent	chemical shift							
		CH_3	CH_2[a]	β-CH_2	α-CH_2	5-H	5-CH_3	NH[b]	
3b	Me_2SO-d_6[c]	0.89 (t, J = 6 Hz, 3 H)	1.31 (m, 16 H)	1.58 (m, 2 H)	2.57 (t, J = 7 Hz, 2 H)	7.52 (s, 1 H)		10.26 (s, 1 H)	10.60 (s, 1 H)
4b	Me_2SO-d_6	0.82 (t, J = 6 Hz, 3 H)	1.20 (m, 16 H)	1.48 (m, 2 H)	2.50 (t, J = 7 Hz, 2 H)		2.21 (s, 3 H)	10.12 (s, 1 H)	10.70 (s, 1 H)

(B) 4-Dodecyl-2-imidazolidinones

compd	solvent	chemical shift					
		CH_3	CH_2[a]	5-CH_3	4-CH	5-CH	NH[b]
5b	CCl_4[d]	0.86 (t, J = 6 Hz, 3 H)	1.26 (m, 22 H)		3.04 (t, J = 6 Hz, 1 H)	3.6 (m, 2 H)	5.72 (s, 2 H)
6b	CCl_4	0.88 (t, J = 6 Hz, 3 H)	1.28 (m, 22 H)	1.12 (t, J = 6 Hz, 3 H)	3.71 (m, 2 H)		6.56 (s, 2 H)

(C) 1-Acyl-2-imidazolidinones

compd	solvent	chemical shift							
		CH_3	CH_2[a]	5-CH_3	CH_3O- or CH_3CH_2	CH_3CH_2	4-H	5-H	NH[b]
7	CCl_4	0.96 (t, J = 6 Hz, 3 H)	1.38 (m, 10 H)		3.90 (s, 3 H)		3.6–4.2 (m, 3 H)		7.64 (s, 1 H)
8a	CCl_4	0.96 (t, J = 6 Hz, 3 H)	1.36 (m, 10 H)	1.26 (d, J = 7 Hz, 3 H)	3.80 (s, 13 H)		3.8[e] (m, 1 H)	4.25 (qi, J = 7 Hz, 1 H)	7.40 (s, 1 H)
8b	CCl_4	0.90 (t, J = 6 Hz, 3 H)	1.28 (m, 22 H)	1.25 (d, J = 7 Hz, 3 H)	3.80 (s, 3 H)		3.8[e] (m, 1 H)	4.24 (qi, J = 7 Hz, 1 H)	7.40 (s, 1 H)
9	CCl_4	0.91 (t, J = 6 Hz, 3 H)	1.28 (m, 22 H)	1.20 (d, J = 6 Hz, 3 H)	1.11 (t, J = 8 Hz, 3 H)	2.79 (q, J = 8 Hz, 2 H)	3.72 (q, J = 7 Hz, 1 H)	4.38 (qi, J = 7 Hz, 1 H)	7.37 (s, 1 H)
10[f]	$CDCl_3$	0.94 (t, J = 6 Hz, 3 H)	1.33 (m, 25 H)				3.92 (q, J = 7 Hz, 1 H)	4.51 (qi, J = 7 Hz, 1 H)	6.20 (s, 1 H)

[a] Referred to the most intense peak. [b] Broad signal. [c] At 55 °C. [d] At 73 °C. [e] Overlapped by CH_3O signal. [f] Other signals: aromatic protons, δ 7.47 (d, J = 9 Hz, 2 H) and 8.32 (d, J = 9 Hz, 2 H).

cooled reaction solution was poured onto 220 g of ice, and the resulting suspension was mixed well with 100 mL of ether. The solid material was filtered off and washed with ether several times. The crude product thus obtained was recrystallized from ethanol.

4-Dodecyl-5-methyl-2-imidazolidinone (6b). Platinum oxide (1.0 g) suspended in 100 mL of acetic acid was activated by exposure to gaseous hydrogen. A solution of **4b** (5.6 g, 0.020 mol) in 300 mL of acetic acid was added to the catalyst solution in one portion. Hydrogenation was carried out at atmospheric pressure for 2 days, and then a small amount of fresh catalyst (0.1 g) was added. Hydrogenation was continued for an additional 2 days. The catalyst was filtered off and washed with hot acetic acid. The filtrate and washings were combined and evaporated in vacuo repeatedly with ethanol and finally to dryness. The crude product was recrystallized from acetone and then from acetonitrile.

When the readdition of catalyst was not done in another run, 4-dodecyl-5-methyl-2-imidazolinone (11) was obtained as a by-product in 8% yield after recrystallization from ethanol twice: mp 228–231 °C; ^{1}H NMR (CF_3CO_2H) δ 0.94 (t, J = 6 Hz, 3 H, CH_3), 1.37 (20 H, CH_2), 2.20 (s, 3 H, 5-CH_3), 2.58 (t, J = 7 Hz, 2 H, 4-α-CH_2), 9.92 (br s, 2 H, NH).

1-Propionyl-4-dodecyl-5-methyl-2-imidazolidinone (9). A 1.2-g (4.5 mmol) sample of **6b** was mixed with 2.3 g (25 mmol) of propionyl chloride in 10 mL of hexane. The reaction mixture was refluxed for 3 h. After the solvent and excess reagent were distilled off, the residue was recrystallized from hexane.

Some physical properties of newly prepared compounds in this work are summarized in Tables I and II.

Acknowledgment. The technical assistance of Messrs. T. Teshima and A. Takezako in the synthesis of some of the compounds is gratefully acknowledged.

Registry No. 1, 5918-93-4; 2, 1192-34-3; **3a**, 71647-94-4; **3b**, 71647-95-5; **4a**, 71672-50-9; **4b**, 71647-96-6; **5a**, 3656-96-0; **5b**, 71647-97-7; **6a**, 71647-98-8; **6b**, 71647-99-9; **7**, 71648-00-5; **8a**, 71648-01-6; **8b**, 71648-02-7; **9**, 71648-03-8; **10**, 71648-04-9; **11** (R_2 = $C_{12}H_{25}$), 71672-51-0; dodecanoyl chloride, 112-16-3; propionyl chloride, 79-03-8; hexanoyl chloride, 142-61-0; methoxycarbonyl chloride, 79-22-1; *p*-nitrophenoxycarbonyl chloride, 7693-46-1; acetonitrile, 75-05-8.

Notes

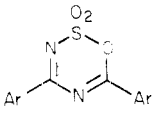
Photochemistry of 4,6-Diphenyl-2,2-dioxo-1,2,3,5-oxathiadiazine

D. F. Eaton and B. E. Smart*

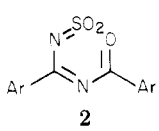
Contribution No, 2690, Central Research and Development Department, E. I. du Pont de Nemours and Company, Experimental Station, Wilmington, Delaware 19898

Received July 24, 1979

N-Sulfonylamines have been generated as reactive intermediates in solution by the base-induced dehydrochlorination of sulfamoyl chlorides.[1] 4,6-Diaryl-2,2-dioxo-1,2,3,5-oxathiadiazines (**1**), which are readily prepared from aryl nitriles and sulfur trioxide,[2] are potentially attractive precursors to the novel amidine-based *N*-sulfonylamines **2**. Some aspects of the photochemistry of **1** (Ar = Ph) and



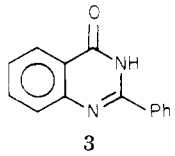
1



2

attempts to establish the intermediacy of **2** (Ar = Ph) in the photochemical transformations of **1** are reported in this paper.

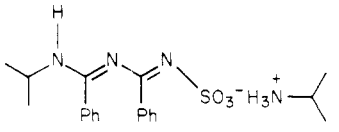
Irradiation (λ >290 nm) of **1** (Ar = Ph) in dichloromethane containing 5% by volume of ethanol or 2-methyl-2-propanol led to complete disappearance of **1**. From the crude photolysate, 2-phenyl-4(3*H*)-quinazolinone (**3**) was isolated in 40–60% yields. Under identical irradiation conditions, but in the absence of added alcohol, **3** was not detected (TLC) and only uncharacterizable materials resulted. The formation of **3** can be rationalized by the mechanism in Scheme I.



3

The ring opening of **1** to **2** and the subsequent trapping by alcohol to give aminosulfonate **4** are analogous to the chemistry observed by de Mayo and co-workers[3] in the irradiation of six-membered ring diene sulfones. de Mayo postulated sulfene intermediates that were intercepted by alcohols to give stable sulfonate esters. In the present study, however, adduct **4** is proposed to undergo further photoexcitation to give a delocalized diradical **5**, which then rearranges to **6**. The observed product **3** finally is formed upon the loss of $ROSO_2H$ from **6**.

All attempts to chemically trap **2** were unsuccessful. Dichloromethane solutions of **1** containing 2,3-dimethyl-2-butene (20× molar excess), ethyl vinyl ether (40×), or dichloroketene ethylene ketal (20×) were irradiated, but cycloadducts analogous to those reported by Burgess[1] were not detected. Potential nucleophilic trapping agents such as isopropylamine rapidly reacted with **1** in the dark to give **7**.[4]



7

In view of the failure to trap **2**, the plausibility of the photochemical conversion of the proposed intermediate **4** to **3** (Scheme I) must be established. Unfortunately, all attempts to independently synthesize **4** (R = CH_2CH_3) were unsuccessful. However, the *N*-tosyl analogue **9** was

(1) G. M. Atkins, Jr., and E. M. Burgess, *J. Am. Chem. Soc.*, **94**, 6135 (1972).

(2) P. Eitner, *Ber. Dtsch. Chem. Ges.*, **25**, 461 (1892).

(3) (a) P. de Mayo et al., *Proc. Chem. Soc., London*, 238 (1961); (b) P. de Mayo et al., *Can. J. Chem.*, **41**, 100 (1963).

(4) Alcohols do not react appreciably with **1** at room temperature in the dark. In contrast to the photochemical results, when **1** is refluxed with ethanol benzamidine-*N*-sulfonic acid,[2] $PhC(NH_2)=NSO_3H$, is isolated in 90% yield. No **3** is detected.

0022-3263/79/1944-4435$01.00/0