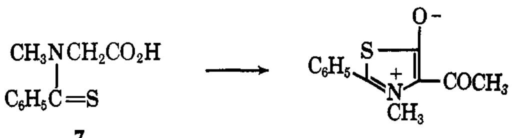
The 3,4-dimethoxybenzyl derivative (**4**) was also prepared.

The remarkable facility with which the intermediate oxazolone (**5**) undergoes electrophilic substitution probably reflects the ready polarizability of the lactone enolate grouping. This reaction is reminiscent of the uncatalyzed formation of 3-indoleglyoxyloyl chloride from oxalyl chloride and indole,[3] as well as a similar reaction of thienopyrrole.[4] Closely analogous to our reaction and that of Huisgen's group is the production of the acetylated mesoionic thiazolone **6** from thiobenzoylsarcosine (**7**) and acetic anhydride, earlier reported by Lawson and Searle.[5]



7 **6**

From the relative positions of the ring and side-chain carbonyl groups one might anticipate some potential for **3** as a chelating agent, and in fact a solution of **3** in tetrahydrofuran readily extracted the cobalt from indicating Drierite, thereby changing in color from yellow to emerald green.[6]

Experimental Section

Instrumentation.—Nuclear magnetic resonance spectra were obtained using the Varian Model A-60 spectrometer with tetramethylsilane as internal standard. For infrared spectra the Beckman IR-12 was used. The mass spectrometer employed was the Hitachi Perkin-Elmer Model RMU-6D. The Mechrolab vapor pressure osmometer was used for molecular weight determination. Combustion analyses were performed by Mr. Carmine Di Pietro of Natick Labs.

N-Acetyl-N-benzylglycine (**1**).—N-Benzylglycine sodium salt was prepared by hydrogenation (1 atm) of a solution of 0.10 mole each of glycine, benzaldehyde, and sodium hydroxide in 250 ml of methanol over 0.5 g of prereduced platinum oxide. After the theoretical uptake of hydrogen had been noted, the mixture was filtered and most of the methanol was removed by rotary evaporation. The sodium salt was obtained essentially quantitatively by precipitation with isopropyl alcohol. N-Benzylglycine sodium salt (10 g) was suspended in 20 ml of pyridine, and 10 g of acetic anhydride was added with cooling. The mixture was allowed to stand for 12 hr after becoming homogeneous, then was poured onto ice and dilute hydrochloric acid. Extraction with chloroform provided 10–11 g of acetyl derivative, mp 126–128° (lit.[7] mp 126.5) after recrystallization from acetone.

N-Acetyl-N-(3,4-dimethoxybenzyl)glycine.—Glycine was reductively alkylated with 3,4-dimethoxybenzaldehyde and acetylated as described above for **1**. Recrystallized from acetone, the product had mp 118–120°.

Anal. Calcd for $C_{13}H_{17}NO_5$: C, 58.41; H, 6.41; N, 5.24. Found: C, 58.25; H, 6.25; N, 5.24.

Anhydro-3-benzyl-4-chloroglyoxyloyl-5-hydroxy-2-methyl-1,3-oxazolium Hydroxide (**3**).—To 2.0 g of N-acetyl-N-benzylglycine was added 5 g of oxalyl chloride. The reaction that ensued was vigorous but not noticeably exothermic. After about 1 hr a solid precipitated which was collected by filtration and washed with benzene. The yield was 2.2 g (82%), and the product melted with vigorous decomposition at 123–126° after recrystallization from tetrahydrofuran. This material decomposed in the preheater of the mass spectrometer to give carbon dioxide as the volatile product of greatest mass and abundance.

Anal. Calcd for $C_{13}H_{10}ClNO_4$: C, 55.82; H, 3.60; N, 5.01; mol wt, 280. Found: C, 56.05; H, 3.66; N, 5.10; mol wt, 285 ± 9, 0.7% in benzene.

Anhydro-3-(3,4-dimethoxybenzyl)-4-chloroglyoxyloyl-5-hydroxy-2-methyl-1,3-oxazolium Hydroxide (**4**).—From 1.0 g of N-acetyl-N-(3,4-dimethoxybenzyl)glycine and 2–3 g of oxalyl chloride was prepared as above 1.2 g (95%) of a pale yellow solid, mp 112–114° dec, after recrystallization from tetrahydrofuran.

Anal. Calcd for $C_{15}H_{14}ClNO_6$: C, 53.03; H, 4.15; N, 4.12. Found: C, 53.2; H, 4.08; N, 4.23.

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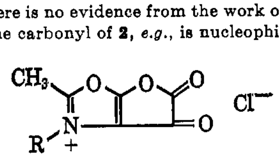
[6] A referee has suggested **8** as a plausible alternative to the oxazolone structure. However, these compounds are more reasonably acid chlorides than enol lactones because (1) an analytically pure sample of **3** reacted instantaneously with water to give hydrochloric acid, (2) the experimental molecular weight corresponds to that of **3** rather than that of **8**, which should be only half as great, (3) it is difficult to rationalize chelation in terms of structure **8**, and (4) there is no evidence from the work of Huisgen's group to suggest that the lactone carbonyl of **2**, *e.g.*, is nucleophilic.



8

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A Study of Hindered Internal Rotation in Some N-Vinyl-Substituted Amides by Nuclear Magnetic Resonance Spectroscopy[1]

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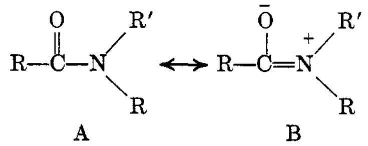
Received March 18, 1966

Pauling[3] has suggested that the C–N amide bond should possess considerable double-bond character arising from resonance between the following structures.



A B

The height of the potential energy barrier to free rotation is then dependent upon the amount of this double-bond character. Numerous workers[4–9] have utilized nmr to study various N,N-disubstituted amides and have determined energy barriers based upon the

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[1] Abstracted in part from the M.S. thesis of D. G. Gehring, University of Delaware, 1965.

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TABLE I

VALUES OF E_a AND LOG A FOR RESTRICTED ROTATION IN SOME N,N-DISUBSTITUTED AMIDES AT 60 MC

Compd	Amide	E_a,[a] kcal/mole	Log A	$\delta\nu$[b]	T_c[c]
I	N,N-Dimethylformamide	28.2 ± 2	17.2	8.1	386
II	N-Methyl-N-(β-chloroethyl)formamide	30.0 ± 2	17.4	9.1	405
III	N-Methyl-N-vinylformamide	15.7 ± 2	11.4	5.7	372
IV	N-Vinyl-N-(β-chloroethyl)formamide	21.0 ± 2	14.7	10.7	367
V	N,N-Dimethylacetamide	20.2 ± 2	16.1	10.1	343
VI	N-Methyl-N-(β-chloroethyl)acetamide	22.7 ± 2	16.2	11.9	346
VII	N-Methyl-N-vinylacetamide	14.0 ± 2	13.2	5.2	309

[a] The estimated error is based upon reproducibility only. [b] Separation in cycles per second of doublet peaks at coalescence temperature as was determined by methods in ref 9. [c] Coalescence temperature, ±1°K.

classical Arrhenius-type rate equation.[10] It was our purpose to examine some N-vinyl-substituted amides, and, by comparison with N-alkylamides, to determine the effect of the vinyl group upon the energy barrier to free rotation about the central C–N bond. One possibility is that the vinyl group will enhance the double-bond character through conjugation and the energy barrier will be raised. Alternatively, the α-carbon π orbitals may tend to overlap with the nitrogen lone-pair electrons thereby competing with the carbonyl group. This will tend to decrease the double-bond character in the C–N bond and thereby lower the energy barrier.

Gutowsky and co-workers[4,11] have established the theoretical basis for calculating rates of interconversion from the line shapes and peak maxima where nuclei exchange between two magnetically nonequivalent environments. The exchange-rate calculations were based upon measurements of the distances between maxima of the coalescing N-methyl and formyl proton doublets since the mole fractions of the rotational isomeric components were unequal in the unsymmetrically N,N-disubstituted amides. The limitations and systematic errors inherent with this technique were recently described,[9] and variation in peak doublet separation with temperature, in the absence of exchange, was shown to be the major systematic error. In order to minimize this error, $\delta\nu$ was determined at the peak coalescence temperature (T_c) using the methods described in ref 9 except for the peak ratio parameter. Because of the limitations associated with the peak separation technique, the E_a and log A values in Table I cannot be considered as absolutely correct but are considered to be sufficiently accurate for purposes of comparison. Nevertheless, we plan to reevaluate these results based upon data obtained by fitting the experimental and theoretical line shapes by means of an appropriate iterative computer program. In this way, the best possible accuracy utilizing the nmr method should be realized.[12]

Comparison of the results in Table I clearly indicate that the energy barriers are considerably lowered by N-vinyl substitution. This is good evidence for, and clearly suggests that, overlapping of the nitrogen lone pair and α-carbon π electrons also takes place. Thus, the vinyl group successfully competes with the electronegative oxygen for the unshared nitrogen electrons and the double-bond character of the C–N bond is reduced. To obtain additional evidence, we hoped to measure the potential barrier for N,N-divinylformamide. However, all attempts to synthesize this unreported amide have, thus far, been unsuccessful.

The effect of the N-β electronegative chlorine, which is present in three of the amides, should have very little influence on the amount of C–N double-bond character because of being three bonds removed. This conclusion is supported by the similarities in the E_a and log A values for amide pairs I, II and V, VI.

Attempts to measure the effects of protonating the N-vinyl amides were unsuccessful because of rapid degradation which occurred even when very small amounts of acid were added to dilute D_2O solutions of the amides.

Four other amides, N,N-bis(β-acetoxyethyl)formamide, N,N-bis(β-chloroethyl)formamide, N,N-bis(β-chloroethyl)acetamide, and N-acetylpyrrole were examined but each gave just one isomeric structure even at relatively low temperatures (−40°).

Experimental Section

A Varian Associates A-60 spectrometer with Model V-6040 variable-temperature controller was used to obtain the spectra. Radio frequency saturation was minimized, by using the lowest possible radio frequency field and a relatively fast (2 cps/sec) sweep rate. The spectral line shape parameters were average values of three separate sweeps and integrations recorded at each temperature and the errors which appear in Table I are largely representative of the inaccuracies in reproducing these spectral measurements.

Amides I and V are commercially available and were distilled prior to measurement. Amide VII was prepared by treating N-methylacetamide with acetylene at high temperature and pressure.[13] Amide II was prepared by treating N-methylethanolamine with thionyl chloride forming N-methyl-β-chloroethylamine and treating this amine with chloral to form II.[14] This structure was confirmed by nmr, mass, and infrared spectra and by elemental analysis. Amide III was prepared by dehydrochlorinating II and the product was identified from information in the literature. Amide IV was prepared by treating diethanolamine with thionyl chloride and treating this product with chloral to form N,N-bis(β-chloroethyl)formamide. Dehydrochlorination of this formamide gave IV whose structure was confirmed by nmr, mass, and infrared spectra and by elemental analysis. Amide VI was prepared by acetylating N-methyl-β-chloroethylamine and identified from literature information.

All of the amides were liquids and were further purified by vacuum distillation through an 18-in. Vigreux column prior to nmr study.

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