(0.38 mole) of 3-chloro-*N*,*N*-dimethylpropylamine in 75 ml. of anhydrous benzene as described above for the preparation of IV and V. Distillation afforded 28.0 g. (44.7%) of product, b.p. 140–142°/1.4 mm., n_D^{25} 1.547.

Anal. Calcd. for $C_{12}H_{19}ClN_2O$ (242.75): C, 59.4; H, 7.89; Cl, 14.6; N, 11.5. Found: C, 59.8; H, 7.94; Cl, 14.8; N, 11.7.

Several attempts to hydrolyze the *O*-methyl ether linkage in this molecule with 48% hydrobromic acid or concentrated hydrochloric acid under gentle reflux resulted in decomposition products which could not be purified.

Acknowledgment. We are indebted to: Mr. L. Brancone and associates for the microanalyses; Dr. H. G. Arlt, Jr., and his group for the preparation of some of the intermediates; Mr. C. Pidacks and associates for the chromatographic separations; and Mr. W. Fulmor and associates for the spectral data.

PEARL RIVER, N. Y.

[COMMUNICATION NO. 2141 FROM THE KODAK RESEARCH LABORATORIES]

The Reaction of Ketene with the 1-Phenyl-3-pyrazolidones

R. F. MOTTER AND J. W. GATES, JR.

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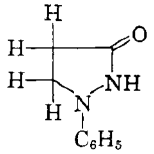
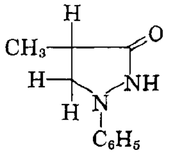
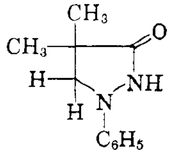
The reaction of ketene with 1-phenyl-3-pyrazolidone (I), 1-phenyl-4-methyl-3-pyrazolidone (II), and 1-phenyl-4,4-dimethyl-3-pyrazolidone (III) was studied. A mixture of the *N*-acetate (IV) and enol acetate (V) was formed in each case. The ratio of the two products formed was modified by acid and base catalysts. The structures of the products were determined by infrared and NMR spectra. Upon vacuum distillation, the enol acetates rearranged nearly quantitatively to the *N*-acetates.

Reactions involving ketene have been studied extensively and the reactions with amines, alcohols, and amides are well known. Ketene also reacts with carbonyl compounds having an enolizable hydrogen to form enol acetates. These reactions are modified by acidic and basic catalysts, as has been pointed out in two reviews.[1,2]

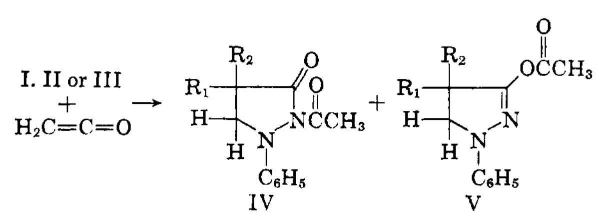
No work, however, has been published on the reaction of ketene with 3-pyrazolidones such as 1-phenyl-3-pyrazolidone (I), 1-phenyl-4-methyl-3-pyrazolidone (II) or 1-phenyl-4,4-dimethyl-3-pyrazolidone (III), which may be regarded as amides or hydrazides in which the nitrogens are contained in a heterocyclic structure. Reaction of these compounds with ketene would involve the —NH, the enol OH, or the carbonyl group.


I


II

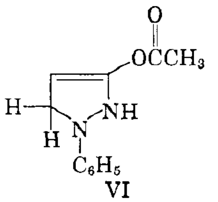

III

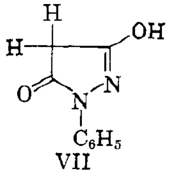
Ketene reacts with I, II, and III to yield mixtures of the *N*-acetyl derivatives, IV, and the enol acetates, V. The enol acetate (V) of III was not isolated but its presence in the reaction mixture was indicated by infrared spectra.

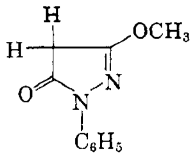


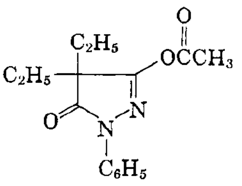
$R_1 = H$ or CH_3
$R_2 = H$
$R_1 = R_2 = CH_3$

As an enol acetate is formed by the reaction of ketene with I, II, and III, the 3-pyrazoline (VI) structure for an enol acetate must be ruled out. The infrared and NMR spectra confirm the 2-pyrazoline (V) structure as the correct one for the enol acetate. This structure is also consistent with the one reported by Conrad and Zart[3] for 1-phenyl-3-hydroxy-5-pyrazolone (VII). They proposed the enolized structure for this compound and prepared the monomethyl ether (VIII) and the monoacetate (IX) of the diethyl derivative.


VI


VII


VIII


IX

The enol acetates and *N*-acetates were distinguishable by their infrared spectra. The *N*-acetates have two carbonyl groups and, therefore, have two carbonyl absorptions in the infrared region, one at

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(1) H. J. Hagemeyer, *Ind. Eng. Chem.*, **41**, 765 (1949).

(2) G. Quadbeck, *Angew. Chem.*, **68**, 361 (1956).

(3) M. Conrad and A. Zart, *Ber.*, **39**, 2282 (1906).

5.6 μ and one at 5.8 μ. The enol acetates, however, have only one carbonyl group and one carbonyl absorption at 5.7 μ. The rest of the spectrum is also consistent with that of an ester.

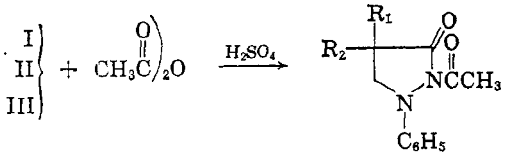
The proof of the 2-pyrazoline structure, instead of the 3-pyrazoline structure, for the enol acetates of I and II was obtained by NMR spectra. The NMR spectrum of the enol acetate of I has two symmetrical band structures for the hydrogen atoms attached to carbon atoms number 4 and number 5; each band is composed of three doublets. These are centered at 178 and 227 cps. (at 60 mc.) below the resonance position of silicon tetramethyl used as an internal standard.

This band structure, which is of the type A_2B_2, with nearly equal AB coupling constants, is impossible unless there are two hydrogen atoms each on carbon atoms 4 and 5. Moreover, if there were only a single hydrogen atom attached to carbon atom number 4, with a 3-pyrazoline structure, its resonance position would be nearly one hundred cycles lower.

The NMR spectrum of the enol acetate of II has, for the methyl at position 4, a doublet with a splitting of 6 cps. The magnitude of this splitting indicates the presence of a hydrogen atom attached also at position 4. The band structure for the hydrogens on atoms 4 and 5 is much more complicated than for the enol acetate of I because the chemical shift between these hydrogens is much smaller, and their spin-spin coupling constant is approximately equal to this chemical shift.

A proton on the N atom, which was observed for II, was not observed for the enol acetate of I or II. These results are in agreement with all of the postulated structures.

The structures of the N-acetates were confirmed by their comparison with authentic samples prepared by the reaction of the pyrazolidone with acetic anhydride.[4]


IV

$R_1 = H$ or CH_3
$R_2 = H$ or CH_3
$R_1 = R_2 = CH_3$

The enol acetates (V) were isolated in the reaction of ketene with I and II by crystallization from the reaction mixture; the enol acetate of III could not be obtained in this manner. The *N*-acetates (IV) were isolated by distillation under reduced pressure. It was found that the enol acetate (V) could be converted to the *N*-acetate (IV) by distillation. The enol acetate of II was converted in 91.5% yield by vacuum distillation to the *N*-acetate, as identified by its infrared spectrum. Slight decomposition occurred during this thermal treatment and a small amount of the parent 1-phenyl-4-methyl-3-pyrazolidone was isolated. This accounts for the fact that only the *N*-acetate of III could be isolated after distillation, the enol acetate having rearranged.

The ratio of the two products was found to vary, depending upon the source of the starting material. The yield of the enol acetate of II varied from 0 to 74.5%. This phenomenon might be attributed to the presence of catalytic impurities in the starting materials, but no difference in the free acid or base content of the various samples could be detected. The reactions were, nevertheless, repeated with the addition of an acid or a base. The results are listed in Table I. It can be seen, as stated earlier, that this reaction is modified by acidic or basic catalysts.

TABLE I

CATALYTIC EFFECTS

Reactant	Catalyst[a]	Yield of IV, %	Yield of V, %	Recovered Starting Material, %
I (Batch A)	0	24.6	58.0	—
I (Batch B)	0	69.5	25.0	—
I (Batch B)	*p*-Toluenesulfonic acid		39.6	23.9
I (Batch B)	Pyridine	84.5	0	—
II (Batch A)	0	58.2	37.3	—
II (Batch B)	0	41.4	40.0	—
II (Batch B)	*p*-Toluenesulfonic acid		27.4	65.5
III	0	81.8	0	0
III	*p*-Toluenesulfonic acid	0	0	74.0

[a] One gram of catalyst was employed when 25 g. of phenidone reacted with ketene.

EXPERIMENTAL[5]

Preparation of the N-acetate and O-acetate of 1-phenyl-3-pyrazolidone (IV and V, $R_1 = R_2 = H$) *with ketene.* A suspension of 1-phenyl-3-pyrazolidone (40 g., 0.247 mole) in benzene (300 ml.) was heated on a steam cone. Ketene[6] was passed in until all the material had dissolved and then for an additional 0.5 hr. The solvent was then removed under reduced pressure to leave an oil which solidified on cooling. The material was recrystallized from benzene-petroleum ether (b.p. 65–75°) to yield a white crystalline solid, m.p. 84–85°, 29.15 g., 58%.

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(4) C. Harries and G. Loth, *Ber.*, **29**, 513 (1896).

(5) All melting points and boiling points are uncorrected. Infrared spectra were recorded on a Baird AB-1 double-beam spectrophotometer, with rock-salt optics. NMR spectra were recorded on a 60-mc. Dual Purpose V-4302 NMR Spectrometer, made by Varian Associates.

(6) J. W. Williams and C. D. Hurd, *J. Org. Chem.*, **5**, 122 (1940).

TABLE II

REACTION OF KETENE WITH PHENIDONES I, II, AND III

Reactant	Product	M.P. or B.P.	Crystallization Solvent	Formula		Analysis			Infrared Absorption Bands, μ
						C	H	N	
I	IV[a]	b.p. 125–131°/40 μ m.p. 72–73°	Ethyl acetate–petroleum ether	$C_{11}H_{12}N_2O_2$	Calcd.	64.7	5.9		5.63,
					Found	64.7	6.2		5.80
I	V	m.p. 84–85°	Benzene–petroleum ether	$C_{11}H_{12}N_2O_2$	Calcd.	64.7	5.9	13.7	5.72
					Found	64.5	5.9	14.0	
II	IV[b]	b.p. 121–126°/30 μ	—	$C_{12}H_{14}N_2O_2$	Calcd.	66.0	6.5	12.8	5.73,
					Found	66.2	6.6	13.1	5.90
II	V	m.p. 65°	Ethyl acetate–petroleum ether	$C_{12}H_{14}N_2O_2$	Calcd.	66.0	6.5	12.8	5.68
					Found	66.1	6.4	12.9	
III[d]	IV[c]	b.p. 132–136°/100 μ m.p. 91–93°	Petroleum ether	$C_{13}H_{16}N_2O_2$	Calcd.	67.2	6.9	12.1	5.75,
					Found	67.4	6.9	11.8	5.85

[a] Prepared in 73.5% yield from I and acetic anhydride. [b] Prepared in 56% yield from II and acetic anhydride. [c] Prepared in 50% yield from III and acetic anhydride. [d] The infrared spectrum of the oil obtained from III and ketene prior to distillation had the three characteristic carbonyl absorptions at 5.65 μ, 5.75 μ, and 5.85 μ, indicating that the enol acetate was formed but rearranges to the *N*-acetate during the distillations.

Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.7; H, 5.9; N, 13.7. Found: C, 64.5; H, 5.9; N, 14.0.

The infrared absorption spectrum of the material showed a single carbonyl absorption at 5.72 μ, indicating that the material is the O-acetyl derivative.

The mother liquor was evaporated to leave an oil, b.p. 125–131°/40 μ, 12.35 g., 24.6%. This oil could then be crystallized from ethyl acetate-petroleum ether (b.p. 65–75°), m.p. 72–73°.

Anal. Calcd. for $C_{11}H_{12}N_2O_2$: C, 64.7; H, 5.9. Found: C, 64.7; H, 6.2. The infrared spectrum of this material showed two carbonyl absorptions, one at 5.63 μ and one at 5.80 μ, indicating that the material is the *N*-acetyl derivative.

The reactions of ketene with II and III were carried out as above and the products are described in Table II.

Acknowledgment. The authors are indebted to R. L. Griffith and J. K. O'Loane, of the Kodak Research Laboratories, for the preparation and interpretation of the NMR spectra.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MIAMI]

The Preparation of 3-Methyl-6- and -7-carboxy-2-quinoxalones

WILLIAM BLACKBURN, MORRIS DANZIG, HENRY HUBINGER, DONALD SOISSON, AND HARRY P. SCHULTZ

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3-Methyl-6-carboxyquinoxalone-2 and 3-methyl-7-carboxyquinoxalone-2, their esters, and dihydro derivatives have been prepared by unequivocal procedures. The ambiguous condensation of 3,4-diaminobenzoic acid with pyruvic acid was demonstrated to give only 3-methyl-7-carboxyquinoxalone-2, whereas the ambiguous condensation of ethyl 3,4-diaminobenzoate with ethyl pyruvate gave eqūal portions of 3-methyl-6-carbethoxyquinoxalone-2 and 3-methyl-7-carbethoxyquinoxalone-2.

Zehra[1] condensed 3,4-diaminobenzoic acid with pyruvic acid, obtaining a product reported as one compound—either 3-methyl-6- *or* 7-carboxyquinoxalone-2. We wish to report the syntheses by unequivocal methods of both 3-methyl-6- and 7-carboxyquinoxalone-2, as well as a study of the products obtained from the equivocal condensation reported by Zehra.

N-(2-Nitro-4-carboxyphenyl)-*dl*-α-alanine, the precursor for the preparation of 3-methyl-7-carboxyquinoxalone-2, was synthesized in virtually quantitative yield by condensing *dl*-α-alanine with 3-nitro-4-bromobenzoic acid, by modifications of the procedures of Micheel *et al.*[2] and of Holley and Holley,[3] who condensed *dl*-α-alanine with ethyl 3-nitro-4-fluorobenzoate. *N*-(2-Nitro-4-carboxyphenyl)-*dl*-α-alanine was reduced in alcohol over palladium chloride on charcoal, but better in aqueous sodium bicarbonate solution over Raney nickel catalyst. In the latter procedure the initial reduction product was probably the disodium salt

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(1) A. Zehra, *Ber.*, **23**, 3629 (1890).

(2) F. Micheel, K. Weichbrodt, and J. Plenikowski, *Ann.*, 581, 242 (1953).

(3) R. Holley and A. Holley, *J. Am. Chem. Soc.*, **74**, 1110 (1952).