over-all oxidation, probably by preempting ligand sites from the alcohol. The concurrent oxidation of acetal to ester,[10] a side reaction under our conditions, is only slightly retarded by hydroquinone but is almost eliminated by removal of the palladium salt; this side reaction is thus a true metal-catalyzed oxidation rather than a concurrent autoxidation.

Experimental Section

Oxidations were carried out in a standard, low-pressure catalytic apparatus (Parr Instrument Co., Model 3911), modified[14] to withstand the various organic media and the strongly oxidizing environment. In a typical run 50.0 ml of alcohol was charged to a 500-ml glass reactor vessel along with the desired amounts of catalyst and reoxidant, and the system was sealed, purged three times with oxygen, then pressured to 30-psig oxygen pressure and rapidly brought to the desired temperature by means of banked heat lamps. After 120 min of isothermal oxidation in this shaker-reactor, with repressuring as needed to maintain the oxygen pressure between 2.5 and 3.5 atm, the reactor was cooled and the contents were collected for analysis. Oxidations of methanol at higher temperatures and pressures (Table III) were conducted similarly, using a stainless steel, turbine-stirred autoclave.

Product identifications for commonly available aldehydes, acetals, ketones, and esters were made by matching gas chromatograph residence times with those of authentic samples on at least two stationary phases. Identifications were confirmed by one or more of the following measurements upon chromatographically isolated samples: infrared spectrum, refractive index, and density.

(14) P. T. Russotto, *Chemist-Analyst*, **53**, 85 (1964).

Pivalic aldehyde was identified by its sharp infrared spectrum, characterized by strong methyl absorption at 1485 and 2890 cm^{-1}, strong aldehyde absorption at 890, 1745 and 2710 cm^{-1}, and the absence of other functional group absorptions. Its dineopentyl acetal was characterized by its unusually simple spectrum, consisting of very strong methyl absorption along with four strong peaks in the 1000–1230-cm^{-1} range, characteristic of the acetal structure.[15] This acetal was further characterized: $n^{25}D$ 1.4092, d^{22}_4 0.8031, MR calcd 74.76, found 75.27 (error 0.68%).

2-Methylol-1,3-dioxolane, the major product from ethylene glycol oxidations, was identified by chromatographic matching with the glycolic aldehyde–ethylene glycol condensation product and its identity was confirmed by infrared spectrum, characterized by strong hydroxyl absorption near 3400 cm^{-1} and the four acetal peaks in the 1000–1230-cm^{-1} range.

Quantitative estimates of products are based upon signal strengths from thermal conductivity detectors, using integrated area measurements. For twelve different standard 10.00% solutions (*e.g.*, *n*-butyraldehyde in dioxane, *n*-butyl *n*-butyrate in 1-butanol), the average assay was 9.93%, standard deviation 0.73%.

Registry No.—Pivalic aldehyde, 630-19-3; pivalic aldehyde dineopentyl acetal, 13421-45-9; 2-methylol-1,3-dioxolane, 5694-68-8; 1-butanol, 71-36-3; ethanol, 64-17-5; methanol, 67-56-1.

Acknowledgment.—The writer gratefully acknowledges the valuable assistance of Mssrs. Paul T. Russotto and Joseph Kisutcza in obtaining much of the data.

(15) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen and Co. Ltd., London, 2nd ed., 1958, p 116.

Sterically Crowded Amines. VIII. The Synthesis and Reactions of Some Polysubstituted 2-Imidazolidinones[1]

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Received March 20, 1967

1-Alkyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinones, $(CH_3)_2\overline{CN(R)CONHC}(CH_3)CONH_2$, were obtained in good yields from 3-alkylamino-3-methyl-2-butanones, $(CH_3)_2C(NHR)COCH_3$, by reaction with potassium cyanide and ammonium carbonate (the Bucherer–Bergs procedure). Hydrolysis with dilute hydrochloric acid led, with one exception, to the corresponding 4-carboxylic acids. When R was *t*-butyl, acid hydrolysis proceeded with facile loss of the *t*-butyl group as the initial reaction and thus gave either 4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (R = H) or the corresponding 4-carboxylic acid, depending on the acid concentration. Alkaline hydrolysis appeared to follow two competitive routes, one leading to the 4-carboxylic acids as obtained also from acid hydrolysis, the other to alanine, acetone, and primary amine by ring degradation. The 3 position of the ring was found to be nitrosated and acylated readily and to undergo condensation with acetone and benzaldehyde. However, alkylation at this position proved unsuccessful.

Motivated by the possibility that alkylamino ketones,[3-5] $(CH_3)_2C(NHR)COCH_3$, might be useful for the preparation of novel α-amino-β-alkylamino acids having both amino functions on tertiary carbon atoms, the reaction of the ketones with potassium cyanide and ammonium carbonate (Bucherer–Bergs reaction) was investigated. It is well known[6,7] that ordinary ketones react in this procedure to produce hydantoins which, by hydrolysis, lead to α-amino acids. Hence the alkylamino ketones, readily prepared from the appropriate acetylenes,[3-5] might well yield structures in which steric crowding would lead ultimately, *via* hydrolysis, not only to α-amino-β-alkylamino acids, but to the corresponding β-lactams as well.

Anomalous results have occasionally been observed, however, when certain ketones possessing an α-functional group are submitted to these reaction conditions. For example, Henze[8] reported that 4-carbamyl-4-phenyl-2-oxazolidinone was obtained using benzoylcarbinol acetate as the substrate in the Bucherer–Bergs procedure. Hennion and O'Shea[9] observed that the

(1) Paper 86 on substituted acetylenes; previous paper, G. F. Hennion and G. G. King, *J. Chem. Eng. Data*, **12**, 275 (1967).

(2) P. C. Reilly Fellow, 1964–1966. Abstracted from a portion of the Ph.D. dissertation of J. E. R.

(3) G. F. Hennion and A. C. Perrino, *J. Org. Chem.*, **26**, 1073 (1961).

(4) G. F. Hennion and P. E. Butler, *ibid.*, **26**, 3341 (1961).

(5) N. R. Easton, *et al.*, *ibid.*, **26**, 3772 (1961).

(6) H. T. Bucherer and W. Steiner, *J. Prakt. Chem.*, **140**, 291 (1934).

(7) E. Ware, *Chem. Rev.*, **46**, 403 (1950).

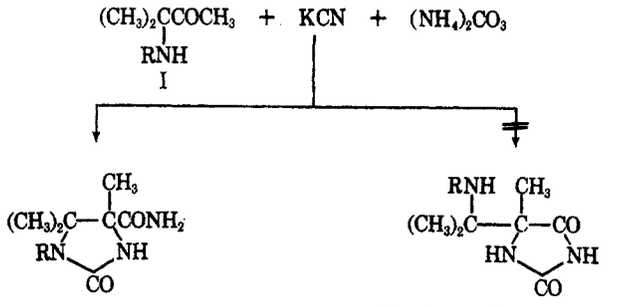
(8) H. R. Henze and W. C. Craig, *J. Org. Chem.*, **10**, 16 (1945).

(9) G. F. Hennion and F. X. O'Shea, *ibid.*, **23**, 662 (1958).

reaction of α-ketols with potassium cyanide and ammonium carbonate also did not produce the expected hydantoins but rather the isomeric 4-carbamyl-4-methyl-5,5-disubstituted 2-oxazolidinones.

In light of the previous work, it was conceivable that the Bucherer–Bergs reaction involving sterically crowded α-alkylamino ketones (I) could lead to the formation of either 5,5-disubstituted hydantoins or the isomeric 4-carbamyl-2-imidazolidinones (II) (Scheme I). This study soon revealed that the reaction followed

SCHEME I

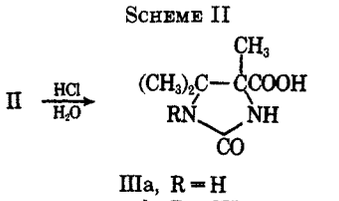


IIa, R = H (prepared indirectly)
b, R = CH_3
c, R = C_2H_5
d, R = i-C_3H_7
e, R = t-C_4H_9
f, R = CH_2=$CHCH_2$

the latter course, despite any steric encumbrance of the alkylamino group. The R group was varied in size from methyl to *t*-butyl (also allyl) and in no instance was the formation of a hydantoin observed. In addition, the parent compound (IIa, R = H) was synthesized indirectly as explained below.

Acid hydrolysis of the 1-alkyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinones (II) was found to be dependent upon the nature of the alkyl group. The carboxylic acids (III) were produced in good yields when R was hydrogen, methyl, ethyl, isopropyl, or allyl (Scheme II). The *t*-butyl compound (IIe), however,

SCHEME II



IIIa, R = H
b, R = CH_3
c, R = C_2H_5
d, R = i-C_3H_7
e, R = CH_2=$CHCH_2$

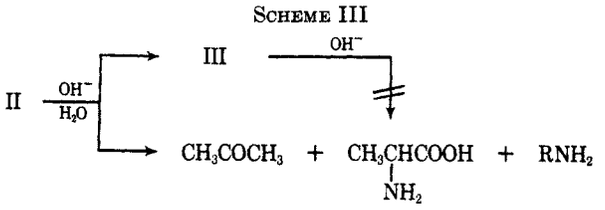
was not converted to the corresponding 4-carboxylic acid, but was hydrolyzed with loss of the *t*-butyl group to either 4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIa) or to 4,5,5-trimethyl-2-imidazolidinone-4-carboxylic acid (IIIa), depending on the reaction conditions.

The amide (IIa) was obtained by treatment of IIe with a 1:1 molar ratio of 0.4 *N* hydrochloric acid at reflux for 1 hr. Boiling for 1 hr with 5 moles of 6 *N* hydrochloric acid resulted in formation of the 4-carboxylic acid (IIIa), also obtained directly from IIa by the same reaction conditions. It can be concluded, therefore, that in the presence of aqueous acid loss of the *t*-butyl group is much more facile than hydrolysis of the amide grouping.

The atypical behavior of the *t*-butyl compound is believed to arise from steric crowding between the *t*-butyl and the *gem*-dimethyl groups located on the 5-carbon atom of the ring. As noted in Table I, the allyl group was retained when 1-allyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIf) was subjected to acid hydrolysis. This would indicate that the driving force of 1-dealkylation is not merely the stability of the resulting carbonium ion.

The products isolated when 1-ethyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIc) was heated at reflux with aqueous barium hydroxide were 1-ethyl-4,5,6-trimethyl-2-imidazolidinone-4-carboxylic acid (IIIc), acetone, and alanine. However, formation of the carboxylic acid derivative was not observed when the 1-*t*-butyl compound (IIe) was submitted to these reaction conditions. In this case, the only products isolated were alanine and acetone. The formation of the carboxylic acid (IIIc) can be explained in two different ways: (i) either there were two distinct, competitive routes for the basic hydrolysis or (ii) the amide (II) was initially converted to the acid (III) which was subsequently degraded to acetone, alanine, and primary amine (see Scheme III). The former explanation (i)

SCHEME III



appears to be correct since 1-ethyl-4,5,5-trimethyl-2-imidazolidinone-4-carboxylic acid (IIIc) was recovered unaltered after boiling for 22 hr with aqueous barium hydroxide. 4,5,5-Trimethyl-2-imidazolidinone-4-carboxylic acid (IIIa), on the other hand, was the only product isolated from the alkaline hydrolysis of the N-unsubstituted compound IIa. The upper path must therefore be the predominant route for the hydrolysis of this compound with the lower path being at most a minor side reaction.

It was found that both 1-substituted 4,5,5-trimethyl-4-carbamyl-2-imidazolidinones (II) and 1-substituted 4,5,5-trimethyl-2-imidazolidinone-4-carboxylic acids (III) undergo acylation and nitrosation at the 3 position of the ring. However, all attempts to alkylate this position were unsuccessful.

Despite the facile loss of *t*-butyl from 1-*t*-butyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone by treatment with aqueous acid, reaction with acetic anhydride and acetic acid resulted only in acetylation of the 3 position (*t*-butyl retained), yielding IVc as shown in Scheme IV. The *t*-butyl group was lost, however, when IVc was submitted to mild acid hydrolysis. The resulting compound (IVd) also was prepared by acetylating 4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIa).

The products of the nitrosation reaction were found to be independent of the concentration of nitrous acid and also of the temperature. Thus compound VIc (Table I) was obtained in each case when 1-isopropyl-

TABLE I

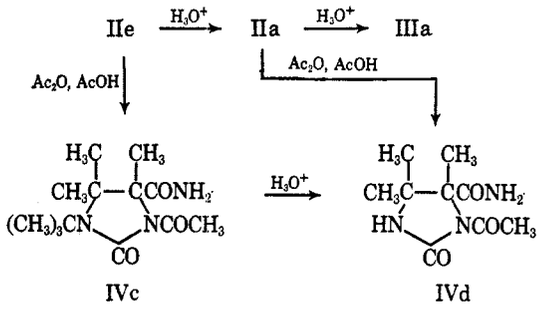
PHYSICAL PROPERTIES AND YIELDS OF 1-SUBSTITUTED 4,5,5-TRIMETHYL-2-IMIDAZOLIDINONES

$(CH_3)_2\overline{CN(R)CON(R')C}(CH_3)COX$

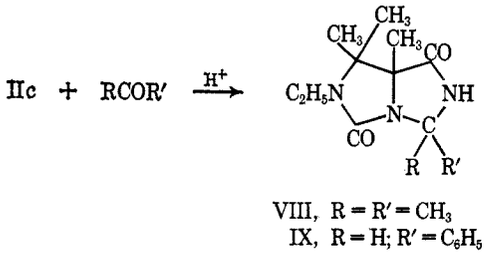
Compd	R	R'	Mp, °C	Yield, %	Molecular formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
					A. Amides (X = NH_2)						
IIa	H	H	280–281	70	$C_7H_{13}N_3O_2$	49.11	7.65	24.55	49.40	7.83	24.62
IIb	CH_3	H	205–206	69	$C_8H_{15}N_3O_2$	51.87	8.16	22.69	51.77	8.17	22.42
IIc	C_2H_5	H	153–154	85	$C_9H_{17}N_3O_2$	54.25	8.60	21.09	54.10	8.62	20.85
IId	*i*-C_3H_7	H	190–191	86	$C_{10}H_{19}N_3O_2$	56.31	8.98	19.70	56.28	9.07	19.59
IIe	*t*-C_4H_9	H	214–215	65	$C_{11}H_{21}N_3O_2$	58.12	9.31	18.49	58.14	9.19	18.62
IIf	Allyl	H	180–181	75	$C_{10}H_{17}N_3O_2$	56.85	8.11	19.89	56.79	8.47	19.61
IVa	C_2H_5	$-COCH_3$	164–165	86	$C_{11}H_{19}N_3O_3$	54.75	7.94	17.42	54.80	7.98	17.50
IVb	C_2H_5	$-COC_2H_5$	180–181	79	$C_{12}H_{21}N_3O_3$	56.45	8.29	16.46	56.59	8.56	16.58
IVc	*t*-C_4H_9	$-COCH_3$	170–172	77	$C_{13}H_{23}N_3O_3$	57.97	8.61	15.60	57.84	8.75	15.33
IVd	H	$-COCH_3$	254–255	65[a] 81[b]	$C_9H_{15}N_3O_3$	50.69	7.09	19.71	50.64	7.39	19.76
VIa	CH_3	-NO	221[c]	71	$C_8H_{14}N_4O_3$	44.85	6.59	26.16	44.92	6.88	26.04
VIb	C_2H_5	-NO	200[c]	92	$C_9H_{16}N_4O_3$	47.36	7.07	24.55	47.65	7.37	24.29
VIc	*i*-C_3H_7	-NO	233[c]	94	$C_{10}H_{18}N_4O_3$	49.57	7.49	23.13	49.43	7.58	22.94
					B. Acids (X = OH)						
IIIa	H	H	234–235	71[d] 82[e]	$C_7H_{12}N_2O_3$	48.82	7.03	16.27	49.06	7.35	15.97
IIIb	CH_3	H	203–204	81	$C_8H_{14}N_2O_3$	51.60	7.58	15.05	51.86	7.87	15.08
IIIc	C_2H_5	H	201–202	94	$C_9H_{16}N_2O_3$	53.98	8.06	13.99	53.94	8.38	13.91
IIId	*i*-C_3H_7	H	234–235	87	$C_{10}H_{18}N_2O_3$	56.05	8.47	13.08	56.20	8.58	13.16
IIIe	Allyl	H	181–183	75	$C_{10}H_{16}N_2O_3$	56.58	7.60	13.20	56.50	7.57	13.42
Va	C_2H_5	$-COCH_3$	175–178	89	$C_{11}H_{18}N_2O_4$	54.53	7.49	11.57	54.30	7.70	11.79
Vb	C_2H_5	$-COC_2H_5$	108–110	74	$C_{12}H_{20}N_2O_4$	56.24	7.87	10.93	56.21	7.91	11.23
Vc	CH_3	$-COCH_3$	164–165	80	$C_{10}H_{16}N_2O_4$	52.62	7.07	12.28	52.44	7.22	12.48
VIIa	CH_3	-NO	156[c]	50	$C_8H_{13}N_3O_4$	44.65	6.09	19.53	44.71	6.19	19.62
VIIb	C_2H_5	-NO	163[c]	89	$C_9H_{15}N_3O_4$	47.15	6.60	18.33	48.09[f]	6.56	18.35
VIIc	*i*-C_3H_7	-NO	176[c]	87	$C_{10}H_{17}N_3O_4$	49.37	7.05	17.27	49.52	6.97	17.38

[a] Prepared by the acid hydrolysis of compound IVc. [b] Prepared by acetylation of compound IIa. [c] With decomposition. [d] Prepared by the acid hydrolysis of compound IIe. [e] Prepared by the acid hydrolysis of compound IIa. [f] *Anal.* Calcd for O_2: 27.92. Found: 27.26.

SCHEME IV



SCHEME V



4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IId) was treated with 1, 2, or 3 equiv of nitrous acid in the cold or at 50°. Hence the exocyclic amide groups were relatively insensitive to reaction with nitrous acid and oxazolidinone rings were not opened. The 3-nitroso derivatives (VI and VII, Table I) were quite unstable in aqueous acid and were easily hydrolyzed to the parent amides (II) and acids (III), respectively.

It also was found that 1-ethyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIc) reacts with both acetone and benzaldehyde, yielding 3,3,7,7,8-pentamethyl-6-ethyl-1,5-diketo-2,4,6-triazabicyclo[3.3.0]-octane (VIII) and 3-phenyl-6-ethyl-7,7,8-trimethyl-1,5-diketo-2,4,6-triazabicyclo[3.3.0]octane (IX), respectively (Scheme V). All structures assigned above and those listed in Table I were supported by infrared and proton magnetic resonance spectral studies as appropriate for individual compounds. Finally, as must be clear from the discussion above, all attempts to hydrolyze or otherwise degrade the 4-carbamyl-2-imidazolidinones to α-amino-β-alkylamino acids or their lactams proved fruitless.

Experimental Section

The **3-alkylamino-3-methyl-2-butanones** used in this work were prepared by hydration of the appropriate acetylenic amines.[4] **3-Allylamino-3-methyl-2-butanone** (new) was prepared[4] from 3-allylamino-3-methyl-1-butyne in 52% yield: bp 71–74° (17–20 mm), $n^{20}D$ 1.4450, The hydrochloride had mp 167–168°.

Anal. Calcd for $C_8H_{16}ClNO$: C, 54.07; H, 9.08; N, 7.88. Found: C, 54.37; H, 9.27; N, 7.80.

1-Ethyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIc).—In a typical preparation, a stirred mixture of 48.5 g (0.375 mole) of 3-ethylamino-3-methyl-2-butanone, 32.5 g (0.5 mole) of potassium cyanide, 144 g (1.25 moles) of ammonium carbonate, and 500 ml of 50% ethyl alcohol was maintined between 55 and 65° for 5 hr and then allowed to cool to room temperature overnight. The mixture was extracted with four 100-ml portions of ether. The ethereal extracts were combined and the resulting water layer was discarded. Most of the ether was removed by slow

distillation at atmospheric pressure. The remaining ether, ethanol, and water were removed by distillation under reduced pressure (30–40 mm), yielding 54.3 g (99% yield) of a yellow-white solid, mp 147–151°. Crystallization from ethyl acetate gave 46.7 g (85% yield) of 1-ethyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIc), mp 153–154°.

1,4,5,5-Tetramethyl-4-carbamyl-2-imidazolidinone (IIb) was prepared using essentially the above procedure but with less solvent (165–175 ml).

4,5,5-Trimethyl-4-carbamyl-2-imidazolidinone (IIa).—1-*t*-Butyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIe) (4 g, 0.02 mole), 1.5 ml of 12 *N* hydrochloric acid, and 40 ml of water were boiled for 1 hr. Hydrochloric acid (6 *N*, 3 ml) was then added and the mixture allowed to cool to room temperature. The solution was then concentrated by distillation *in vacuo* to *ca.* one-half of its original volume. Cooling gave 3.6 g (88% yield) of white solid. Crystallization from a mixture of methyl acetate and methanol yielded 2.8 g (70% yield) of 4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIa), mp 280–281°.

1-Ethyl-4,5,5-trimethyl-2-imidazolidinone-4-carboxylic Acid (IIIc).—1-Ethyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIc) (6 g, 0.03 mole) in 60 ml of 6 *N* hydrochloric acid was heated at reflux for 5 hr. On cooling, 5.6 g (94% yield) of 1-ethyl-4,5,5-trimethyl-2-imidazolidinone-4-carboxylic acid (IIIc), mp 202–203°, crystallized. Recrystallization from water did not raise the melting point appreciably.

1,4,5,5-Tetramethyl-2-imidazolidinone-4-carboxylic acid (IIIb) was prepared using essentially the same procedure except that half the amount of water was used.

4,5,5-Trimethyl-2-imidazolidinone-4-carboxylic acid (IIIa) was prepared from both IIa and IIe. For example, a mixture of 1.7 g (0.01 mole) of 4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIa) and 17 ml of 6 *N* hydrochloric acid was boiled for 1 hr. The solution was concentrated to *ca.* one-third of its original volume and refrigerated overnight, yielding 1.4 g (82% yield) of 4,5,5-trimethyl-2-imidazolidinone-4-carboxylic acid (IIIa), mp 224–227°. Crystallization from a mixture of acetone and water raised the melting point to 234–235°.

Alkaline Hydrolysis of 1-Ethyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone.—In a typical procedure, 63.2 g (0.2 mole) of barium hydroxide in 640 ml of water and 20.0 g (0.1 mole) of 1-ethyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIc) was heated at reflux for 20 hr and then distilled to near dryness (distillate retained). The residue was dissolved in 250 ml of water and neutralized with 9 *M* sulfuric acid. The precipitated barium sulfate was removed by filtration. The clear solution was concentrated by vacuum distillation to a volume of *ca.* 75 ml. On cooling, 5.3 g (30% yield) of 1-ethyl-4,5,5-trimethyl-2-imidazolidinone-4-carboxylic acid (IIIc) crystallized. The filtrate was further concentrated to *ca.* 50 ml, diluted with 450 ml of absolute ethanol, and refrigerated, yielding 3.1 g (50% yield) of alanine. The benzoyl derivative had mp 162–163° (lit.[10] mp 166°).

The original distillate was acidified to a pH of 2–3 with 6 *N* hydrochloric acid. The acidic solution was distilled at atmospheric pressure and the first 25 ml collected. This distillate was diluted to a volume of 100 ml with absolute ethanol. 2,4-Dinitrophenylhydrazine was added to a 10-ml aliquot of this solution, yielding 0.9 g (56% yield) of the 2,4-dinitrophenylhydrazone derivative of acetone, mp 123–124° (lit.[11] mp 126°).

4,5,5-Trimethyl-4-carbamyl-2-imidazolidinone (IIIa).—Following a similar procedure, 1.7 g (0.01 mole) of IIa and 6.3 g (0.02 mole) of barium hydroxide in 64 ml of water yielded 1.4 g (82% yield) of 4,5,5-trimethyl-2-imidazolidinone-4-carboxylic acid. No detectable amounts of acetone or alanine were produced.

1-Ethyl-3-acetyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IVa).—A mixture of 8.0 g (0.04 mole) of 1-ethyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIc), 8 ml of acetic anhydride, 8 ml of acetic acid, and 0.4 ml of 12 *N* hydrochloric acid was heated on a steam bath for 1 hr. The excess acetic anhydride, acetic acid, and hydrochloric acid were removed by vacuum distillation leaving a yellow viscous oil. The oil was dissolved in 25 ml of ethyl alcohol and 0.4 ml of 12 *N* hydrochloric acid and then heated on a steam bath for 1 hr. The solution was concentrated by vacuum distillation leaving a white oily solid. Acetone (20 ml) was added. A white solid resulted when the acetone was removed by vacuum distillation. Crystallization from acetone gave 8.3 g (86% yield), mp 164–165°.

3-Acetyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IVd).

A. From 4,5,5-Trimethyl-4-carbamyl-2-imidazolidinone.—The method employed to prepare this compound was essentially the same as above except that the product crystallized directly from the reaction mixture.

B. From 1-*t*-Butyl-3-acetyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone.—A mixture of 5.4 g (0.02 mole) of IVc, 1.5 ml 12 *N* hydrochloric acid, and 40 ml of water was refluxed for 1 hr. The reaction mixture was concentrated by vacuum distillation to *ca.* one-third of its original volume. On cooling, 2.2 g (65% yield) crystallized from solution. The melting point was not raised appreciably by crystallization from acetonitrile.

1-Ethyl-3-nitroso-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (VIb).—In a typical preparation, 4.95 g (0.025 mole) of IIc, 8.2 ml of 6 *N* hydrochloric acid, and 50 ml of water was stirred continuously and maintained at 0° (ice bath). A solution of 3.46 g (0.05 mole) of sodium nitrite in 50 ml of water was added dropwise over a period of 30 min. The mixture was stirred at 0° for 1 additional hr. The yellow solid was collected and washed with cold water, yielding 5.2 g (92% yield) of 1-ethyl-3-nitroso-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone, mp 198–200° dec. Crystallization from a mixture of methanol and water raised the melting point to 200–201° dec.

1-Ethyl-3-nitroso-4,5,5-trimethyl-2-imidazolidinone-4-carboxylic Acid (VIIb).—Compound IIIc (10 g, 0.05 mole) was dissolved in a solution containing 6.92 g (0.1 mole) of sodium nitrite, 2.0 g (0.05 mole) of sodium hydroxide, and 100 ml of water. To this mixture, 24.8 ml of 6 *N* hydrochloric acid was added dropwise with stirring over a period of 30 min (ice bath). The mixture was stirred for 1 additional hr and the resulting yellow solid collected and washed with cold water. This yielded 10.2 g (89% yield) of product, mp 159° dec. Crystallization from ethyl acetate raised the melting point to 163° dec.

3,3,7,7,8-Pentamethyl-6-ethyl-1,5-diketo-2,4,6-triazabicyclo-[3.3.0]octane (VIII).—1-Ethyl-4,5,5-trimethyl-4-carbamyl-2-imidazolidinone (IIc) (8 g, 0.04 mole) was dissolved in 100 ml of acetone containing 0.3 ml of 12 *N* hydrochloric acid. The mixture was heated at reflux for 5 hr, cooled to room temperature, filtered, and concentrated to near dryness *in vacuo:* yield 6.6 g (70% yield), mp 162–164°. Crystallization from ethyl acetate raised the melting point to 164–165°.

Anal. Calcd for $C_{12}H_{21}N_3O_2$: C, 60.22; H, 8.85; N, 17.56 Found: C, 60.38; H, 9.08; N, 17.78.

3-Phenyl-6-ethyl-7,7,8-trimethyl-1,5-diketo-2,4,6-triazabicyclo-[3.3.0]octane (IX).—A solution of 6.0 g (0.03 mole) of IIc, 6.3 g (0.06 mole) of benzaldehyde, 0.03 ml of 12 *N* hydrochloric acid, and 40 ml of ethyl acetate was refluxed for 8 hr. The volatiles were removed by distillation *in vacuo*, leaving a white oily solid. This material was crystallized from a mixture of petroleum ether (bp 60–70°) and ethyl acetate, yielding 5.4 g (63% yield), mp 153–155°. Two crystallizations (same solvent) gave an analytical sample, mp 155–156°.

Anal. Calcd for $C_{16}H_{21}N_3O_2$: C, 66.87; H, 7.37; N, 14.62. Found: C, 67.03; H, 7.65; N, 14.78.

Registry No.—IIa, 13584-66-2; IIb, 13584-67-3; IIc, 13584-68-4; IId, 13584-69-5; IIe, 13584-70-8; IIf, 13584-71-9; IIIa, 13584-72-0; IIIb, 13584-73-1; IIIc, 13584-74-2; IIId, 13584-75-3; IIIe, 13584-76-4; IVa, 13584-77-5; IVb, 13619-28-8; IVc, 13619-29-9; IVd, 13619-30-2; Va, 13619-31-3; Vb, 13619-32-4; Vc, 13619-33-5; VIa, 13619-34-6; VIb, 13619-35-7; VIc, 13619-36-8; VIIa, 13619-37-9; VIIb, 13619-38-0; VIIc, 13619-39-1; VIII, 13619-40-4; IX, 13619-41-5; 3-allylamino-3-methyl-2-butanone, 13619-42-6; 3-allylamino-3-methyl-2-butanone hydrochloride, 13619-43-7.

Acknowledgments.—The authors express their thanks to Air Reduction Chemical Co., N. Y., for generous samples of 3-methyl-1-butyn-3-ol, to Messrs. James Gilliam, R. G. Meister, Charles Ashbrook, and H. L. Hunter of the Lilly Research Laboratories, Indianapolis, Ind., for the analytical determinations, and to Eli Lilly and Co. for partial support of this work.

(10) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1960, p 300.

(11) See ref 10, p 316.