thrice distilled to give 7.4 g. of mixed **octahydroisoquinolines (V)** having properties comparable to those of the material obtained in propylamine, boiling range 85–100° (12 mm.), $n^{25}D$ 1.4980–1.5230.

The V mixtures obtained by both procedures were separately hydrogenated in glacial acetic acid over Adams platinum oxide. In each case one equivalent of hydrogen was absorbed and there was obtained 60–70% of ***trans*-decahydroisoquinoline (VIII)**, b.p. 84–87° (12 mm.), $n^{25}D$ 1.4897. The picrate showed m.p. 173–174°; the hydrochloride melted at 222–223° (Witkop[1] reports VIII picrate, m.p. 177°; hydrochloride, m.p. 224°).

Methylation of VIII by the Eschweiler–Clarke process provided **2-methyl-*trans*-decahydroisoquinoline**, b.p. 75–80° (9 mm.), $n^{25}D$ 1.4785. The picrate melted at 233–234°; the hydrochloride melted at 221–222°; the picrolonate showed m.p. 215–216° (*cf.* ref. 2).

Reduction of Isoquinoline (I).—A mixture of 33.0 g. (0.25 mole) of I, 20.1 g. (2.9 gram atoms) of clean lithium shot and 450 ml. of *n*-propylamine was stirred at room temperature under nitrogen. Within 30 minutes the solvent began to reflux and the reaction mixture turned red and then, gradually, milky green. Refluxing continued for approximately 2 hours. The reaction mixture was stirred at room temperature for an additional 2 hours and then refluxed for 2 hours on the steam-bath. The product was worked up as before and twice distilled to give 7.4 g. of a crude **octahydroisoquinoline (V)** fraction similar to those obtained from II, boiling range 80–100° (12 mm.), $n^{25}D$ 1.5170–1.5270.

Redistillation of a higher boiling fraction afforded 2 g. of not quite pure II, b.p. 107–111° (12 mm.), identified *via* its hydrochloride salt (*cf.* ref. 12).

Hydrogenation of the V material obtained from I gave, as before, ***trans*-decahydroisoquinoline (VIII)**.

Reduction of N-Methyltetrahydroquinoline (IV).—A mixture of 24.0 g. (0.16 mole) of IV, 8.9 g. (1.3 gram atoms) of lithium shot and 400 ml. of *n*-propylamine was stirred for 6 hours without external source of heat and then refluxed for 1 hour; IV reacted much less vigorously than III. The pale green reaction mixture was worked up as before to yield 12.2 g. (50%) of what was apparently a mixture of **1-methyloctahydroquinolines (VII)**, boiling range 97–106° (13 mm.), $n^{25}D$ 1.5168–1.5240. The picrate, recrystallized from ethanol, melted at 126–127° (*cf.* Leonard, Miller and Thomas[10]).

Anal. Calcd. for $C_{10}H_{17}N$: N, 9.26. Found: N (basic), 9.42.

VII. Methiodide, prepared in ether and recrystallized from ethanol, showed m.p. 200–201°. The infrared spectrum[16] of this salt exhibited a diffuse, weak absorption band in the 1600–1700 cm.$^{-1}$ region, maximum centered at about 1640 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{20}IN$: C, 45.06; H, 6.87. Found: C, 44.92; H, 6.84.

Compound VII, hydrogenated in acetic acid solution over Adams catalyst, absorbed 1 equivalent of hydrogen to give 63% of a mixture of the *cis* and *trans* isomers of **1-methyldecahydroquinoline (X)**, b.p. 79–81° (10 mm.), $n^{25}D$ 1.4815. The picrate melted at 183–184°; the picrolonate at 196–198°; the hydrochloride melted over the range 170–210°; the methiodide showed m.p. 258°.[17]

Anal. Calcd. for $C_{10}H_{19}N$: C, 78.37; H, 12.50; N, 9.14. Found: C, 78.52; H, 12.36; N (basic), 9.16.

ADDED IN PROOF.—It already has been noted briefly (*vide supra*) that tetrahydroquinoline apparently was not reduced by the lithium–amine system, and that tetrahydroisoquinoline was more difficult to reduce and gave different products than its N-methyl derivative. These observations were taken to indicate that the N–H compounds underwent proton loss in the strongly basic reaction medium. In each case the resulting anion, the negative charge of which would be in resonance with the aromatic ring, was presumed to be the species being acted upon by the reagent. A similar interpretation recently has been advanced by R. A. Benkeser and R. F. Lambert, who studied the reduction of substituted anilines [Abstracts of Papers, 134th Meeting of the American Chemical Society, Chicago, Illinois, Sept. 7–12, 1958, p. 80-P].

Acknowledgment.—The authors wish to thank Mr. D. F. Cortright for the basic nitrogen analyses.

(16) Sadtler Laboratories, Philadelphia, Pa.

(17) *Cf.* Leonard, Miller and Thomas,[10] and references cited therein.

DECATUR, ILL.

[CONTRIBUTION NO. 19 FROM THE L. G. RYAN RESEARCH LABORATORIES OF MONSANTO CANADA LTD.]

Amino Nitriles. I. Cyclization of α-Cyanoalkylureas

BY A. F. MCKAY, G. Y. PARIS AND D. L. GARMAISE

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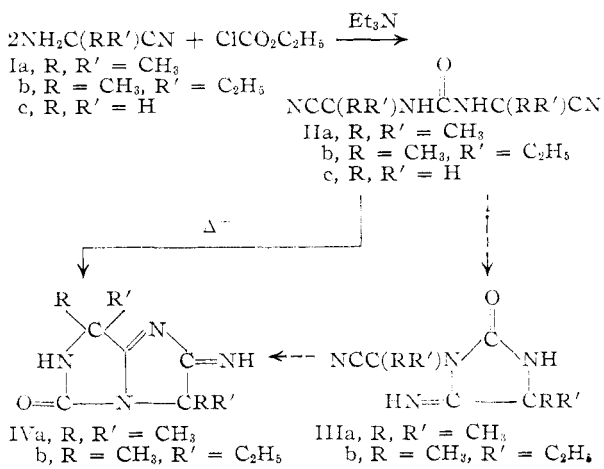
A novel cyclization reaction is described which provides a method for preparing derivatives of the new heterocyclic ring system 7(H)-imidaz[3,4-a]imidazole. The evidence for the structure of this bicyclic system is presented together with a description of the reactions of symmetrical and unsymmetrical α-cyanoalkylurea derivatives.

The cyclization of certain 1,3-bis-(α-cyanoalkyl)-urea derivatives to a bicyclic ring system was observed during a recent study of the chemistry of amino nitriles. This reaction gives substituted 2-imino-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]-imidazoles (IV). In addition, some of the 1-(β-cyanoethyl)-3-(α-cyanoalkyl)-ureas were cyclized to substituted 4-imino-2-imidazolidones. α-Cyanoalkylureas have been employed[1,2] for a long time in the synthesis of hydantoins, and Herbst and Johnson[3] demonstrated that 4-imino-2-imidazolidones (or the tautomeric 2-amino-2-imidazolones) were intermediates in their formation.

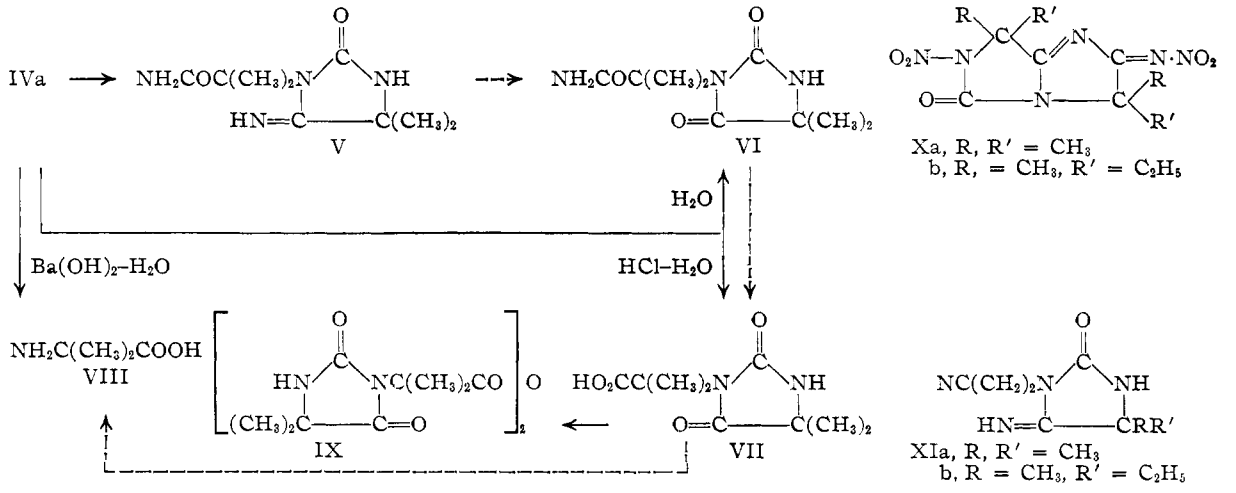
α-Aminoisobutyronitrile (Ia) combined with ethyl chloroformate in the presence of triethylamine to give a good yield (80%) of 1,3-bis-(α-cyanoiso-



(1) F. Urech, *Ann.*, **164**, 255 (1872).

(2) R. M. Herbst and T. B. Johnson, THIS JOURNAL, **54**, 2463 (1932).

(3) R. M. Herbst and T. B. Johnson, *ibid.*, **52**, 3676 (1930).



propyl)-urea (IIa). This urea derivative melted at 229° dec. with sintering at 195°. When the urea derivative IIa was placed in an oil-bath at 210°, it melted and then resolidified. The melting point of the resolidified material was 239–240° dec. 1,3-Bis-(α-cyanoisopropyl)-urea also was converted into the product melting at 239–240° dec. by refluxing with ethanol for several hours. A study of the physical and chemical properties of these two products indicated that the lower melting (229°) material was 1,3-bis-(α-cyanoisopropyl)-urea (IIa) while the product melting at 239–240° dec. was a bicyclic compound, 2-imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]imidazole (IVa). These observations suggested that the compound reported as 1,3-bis-(α-cyanoisopropyl)-urea (m.p. 238°) by Jacobson[4] was actually the cyclized compound IVa. The preparation described by Jacobson was repeated and the compound was identified by a comparison of infrared spectra and by mixed melting point determination as 2-imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]imidazole (IVa).

An examination of the infrared spectra of the compounds melting at 229° and 239–240° dec. gave the first confirmation that cyclization had occurred. The significance and assignments of the absorption bands in these spectra are described below in detail. Further evidence for the structure of the bicyclic product IVa was obtained by a study of its hydrolysis products.

Partial hydrolysis of 2-imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]imidazole (IVa) gave 3-(α-carbamylisopropyl)-4-imino-5,5-dimethyl-2-imidazolidone (V). A picrate of the latter compound was obtained by heating the bicyclic compound IVa with aqueous picric acid solution. Hydrolysis of IVa in neutral medium gave 3-(α-carbamylisopropyl)-5,5-dimethylhydantoin (VI), acid hydrolysis gave 3-(α-carboxyisopropyl)-5,5-dimethylhydantoin (VII) and complete hydrolysis with barium hydroxide solution produced the known α-aminoisobutyric acid (VIII). The anhydride IX of 3-α-(carboxyisopropyl)-5,5-dimethylhydantoin (VII) was prepared by treating the acid with benzoyl chloride.

(4) R. A. Jacobson, THIS JOURNAL, **67**, 1996 (1945).

Nitration of IVa in absolute nitric acid–acetic anhydride–ammonium chloride medium gave a good yield of 2-nitrimino-3,3,7,7-tetramethyl-5-oxo-6-nitro-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]-imidazole (Xa). 2-Nitrimino-3,7-dimethyl-3,7-diethyl-5-oxo-6-nitro-2,3,5,6-tetrahydro-7(H)-imidaz-[3,4-a]imidazole (Xb) was prepared under similar conditions. No water-insoluble nitration products were obtained when ammonium chloride was omitted from the nitration medium. This catalysis of imino group nitration by chloride ion has been observed[5] in other substituted 2-iminoimidazolidines.

1,3-Bis-(α-cyano-α-methylpropyl)-urea (IIb) like 1,3-bis-(α-cyanoisopropyl)-urea (IIa) also cyclized readily to a bicyclic compound, 2-imino-3,7-dimethyl-3,7-diethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]imidazole (IVb). One would expect the monocyclic compound III to be an intermediate in the formation of the bicyclic structure IV. However the intermediate monocyclic compounds were not isolated in the cyclization of the urea derivatives IIa and IIb. In contrast to the ease of cyclization of these urea derivatives, 1,3-bis-(α-cyanoethyl)-urea and 1,3-bis-(cyanomethyl)-urea proved quite stable to heat. They were recovered unchanged after several hours of heating under reflux in either ethanol or 1-butanol. Thus it is apparent that the alkyl substituents in the α-cyanoalkylureas facilitate ring closure. This ability of alkyl substituents to promote closures of small ring systems has been noted[6] by several authors.

Several unsymmetrically substituted ureas were prepared by treating amino nitriles with β-cyanoethyl isocyanate. 1-(β-Cyanoethyl)-3-(cyanomethyl)-urea was recovered unchanged from boiling ethanol while 1-(β-cyanoethyl)-3-(α-cyanoisopropyl)-urea and 1-(β-cyanoethyl)-3-(α-cyano-α-methylpropyl)-urea under similar conditions were converted into 3-(β-cyanoethyl)-4-imino-5,5-dimethyl-2-imidazolidone (XIa) and 3-(β-cyanoethyl)-4-imino-5-methyl-5-ethyl-2-imidazolidone (XIb), respectively.

The properties of the ureas, substituted 2-imidazolidones and substituted 2-imino-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]imidazoles, which

(5) A. F. McKay and M.-E. Kreling, *J. Org. Chem.*, **22**, 1581 (1957).

(6) M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 118–120.

Table I

α-Cyanoalkylurea Derivatives and Their Cyclized Products

Compound	Yield, %	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
1,3-Bis-(cyanomethyl)-urea	26.4	144 dec.	$C_5H_6N_4O$	43.48	43.36	4.38	4.33	40.57	40.79
1,3-Bis-(α-cyanoethyl)-urea	45	171–172 dec.	$C_7H_{10}N_4O$	50.59	50.60	6.07	6.21	33.72	33.74
1,3-Bis-(β-cyanoethyl)-urea	98.5	150–151[a]	$C_7H_{10}N_4O$	50.59	50.83	6.07	6.05	33.72	33.12
1-(β-Cyanoethyl)-3-(cyanomethyl)-urea	99	130–131	$C_6H_8N_4O$	47.36	47.49	5.30	5.67	36.82	36.91
1,3-Bis-(α-cyanoisopropyl)-urea	80	228–229 dec.	$C_9H_{14}N_4O$	55.66	55.81	7.26	7.26	28.85	28.56
1-(α-Cyanoisopropyl)-3-(β-cyanoethyl)-urea	86.5	127–128	$C_8H_{12}N_4O$	53.32	53.40	6.72	6.77	31.10	31.10
1-(α-Cyano-α-methylpropyl)-3-(β-cyanoethyl)-urea	87	110–111(164–165)	$C_9H_{14}N_4O$	55.66	55.62	7.26	7.35	28.85	28.49
1,3-Bis-(α-Cyano-α-methylpropyl)-urea	54	157–158(206–207)	$C_{11}H_{18}N_4O$	59.43	59.39	8.15	8.12	25.21	24.92
3-(β-Cyanoethyl)-4-imino-5-methyl-5-ethyl-2-imidazolidone	100	164–165	$C_9H_{14}N_4O$	55.66	55.71	7.26	7.33	28.85	28.13
3-(β-Cyanoethyl)-4-imino-5,5-dimethyl-2-imidazolidone	63	171–172	$C_8H_{12}N_4O$	53.32	53.35	6.72	6.67	31.10	30.81
2-Imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz-[3,4-a]imidazole	100	240 dec.	$C_9H_{14}N_4O$	55.66	55.49	7.26	7.52	28.85	29.10
2-Imino-3,7-dimethyl-3,7-diethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]imidazole	100	207–208 dec.	$C_{11}H_{18}N_4O$	59.43	59.39	8.15	7.91	25.21	24.88

[a] Reported m.p. 148°; W. Siefken, *Ann.*, **562**, 104 (1949).

were prepared during this investigation, are described in Table I.

Absorption Spectra.—The assignments of infrared absorption bands for the urea, 2-imidazolidone and imidaz[3,4-a]imidazole derivatives are given in Table II. The urea derivatives exhibit a C=O stretching band at approximately 1635–1645 cm.$^{-1}$. When the α-cyanoalkylurea derivatives cyclized to the corresponding substituted 3-(β-cyanoethyl)-4-imino-2-imidazolidones, the urea C=O stretching band shifted to 1666–1673 cm.$^{-1}$. The shift of the urea C=O band in going from the linear to the strained five-membered ring structure has been previously[7] noted. The new absorption band at 1741–1756 cm.$^{-1}$ is assigned to stretching vibrations of the C=N group in the 4-position of the 2-imidazolidones. The absorption band of this C=N group would be expected to be close to the band assigned to the C=O group in the 4-position in hydantoins,[8] which it is. It has been suggested[3,9] that the 4-imino-2-imidazolidones exist in equilibrium with their tautomers, the corresponding 4-amino-2-imidazolones. The infrared spectra of the 4-imino-2-imidazolidones listed in Table II indicate that they exist in the imino form in the solid state.

Both the cyanoalkylureas and the 3-(β-cyanoethyl)-4-imino-2-imidazolidones exhibit an absorption band between 2255–2270 cm.$^{-1}$ which is assigned to the C≡N group. The stretching vibration band of the C≡N group disappears in the imidaz[3,4-a]imidazole derivatives. These compounds possess a C=O stretching band at 1672–1677 cm.$^{-1}$ which corresponds to the C=O stretching band in the 2-imidazolidone derivatives. The C=N group at position 4 of the monocyclic system is now conjugated with the imino group at position 2 of the bicyclic system. This conjugation would be expected to shift the C=N band to a lower wave number. Actually the 1755 cm.$^{-1}$ band is shifted to 1733 cm.$^{-1}$. The effect of further conjugation is shown in the nitration products, 2-nitrimino-3,3,-7,7-tetramethyl-5-oxo-6-nitro-2,3,5,6-tetrahydro-7-(H)-imidaz[3,4-a]imidazole (Xa) and 2-nitrimino-3,7-dimethyl-3,7-diethyl-5-oxo-6-nitro-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]imidazole (Xb). The 1733 cm.$^{-1}$ band is shifted farther to 1671 cm.$^{-1}$ whereas the urea C=O which has a nitro group adjacent to it has shifted from 1671 to 1800 cm.$^{-1}$. This effect of an adjacent nitro group on C=O absorption band of cyclic urea derivatives has been noted previously.[7]

(7) A. F. McKay and J. R. Gilpin, This Journal, **78**, 486 (1956).

(8) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954.

(9) R. C. Elderfield, "Heterocyclic Compounds," Vol. 5, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 258.

Experimental[10]

Aminoacetonitrile (b.p. 62–63° (6 mm.)) was prepared in 72% yield by the method of Cook, *et al.*[11]

α-Aminopropionitrile Hydrochloride.—α-Aminopropionitrile hydrochloride was prepared by the procedure of Dubsky.[12] Recrystallization of the crude product from nitromethane raised the melting point from 99–105° to 130–131° dec. The reported[13] melting point is 132–138°.

β-Aminopropionitrile (b.p. 87–88° (20 mm.)) was prepared in 32% yield by the method of Buc.[14]

α-Aminoisobutyronitrile (b.p. 61–65° (23 mm.), n^{25}D 1.4175, d^{25}_4 0.885) was obtained in 64% yield by the procedure of Jacobson.[15]

Hydrogen chloride was bubbled through a solution of α-aminoisobutyronitrile (73.5 g., 0.87 mole) in ether (800 ml.) and the precipitated α-aminoisobutyronitrile hydrochloride (m.p. 146–147°) was recovered by filtration, yield

(10) Melting points are uncorrected. The microanalyses were performed by Micro Tech Laboratories, Skokie, Ill.

(11) A. H. Cook, I. Heilbron and A. L. Levy, *J. Chem. Soc.*, 201 (1948).

(12) J. V. Dubsky, *Ber.*, **49**, 1045 (1916).

(13) M. Delepine, *Bull. soc. chim.* (*France*), [3] **29**, 1183 (1903).

(14) S. A. Buc, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 93.

(15) R. A. Jacobson, This Journal, **68**, 2628 (1946).

TABLE II

INFRARED ABSORPTION BAND (CM.$^{-1}$) ASSIGNMENTS

Compound	N–H stretching modes	C≡N	C=O stretching modes	C=N	N–H bending modes
1,3-Bis-(cyanomethyl)-urea (IIc)	3360, 3190, 3130	2270	1648		1597, 1522
1,3-Bis-(β-cyanoethyl)-urea	3350, 3155, 3040	2260	1635		1580, 1540
1-(β-Cyanoethyl)-3-(cyanomethyl)-urea	3350, 3130, 3060	2265	1634		1588, 1518
1,3-Bis-(α-cyanoethyl)-urea	3355	2265	1634		1557
1-(α-Cyanoisopropyl)-3-(β-cyanoethyl)-urea	3365, 3330, 3190, 3125	2260	1647		1569, 1520
1,3-Bis-(α-cyanoisopropyl)-urea (IIa)	3370, 3135, 3125	2255	1640		1564
1-(α-Cyano-α-methylpropyl)-3-(β-cyanoethyl)-urea	3370, 3330, 3190, 3125	2270	1648		1563, 1522
1,3-Bis-(α-cyano-α-methylpropyl)-urea (IIb)	3390, 3370, 3110	2263	1646		1557
3-(β-Cyanoethyl)-4-imino-5,5-dimethyl-2-imidazolidone (XIa)	3475, 3390, 3260, 3170, 3080	2270	1673	1756	1623
3-(β-Cyanoethyl)-4-imino-5-methyl-5-ethyl-2-inidazolidone (XIb)	3275, 3190, 3090	2270	1666	1741	1570
2-Imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]imidazole (IVa)	3230, 3070		1672	1731	1588
2-Imino-3,7-dimethyl-3,7-diethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]-imidazole (IVb)	3250, 3140, 3100		1677	1733	1592
2-Nitrimino-3,3,7,7-tetramethyl-5-oxo-6-nitro-2,3,5,6-tetrahydro-7(H)-imidaz-[3,4-a]imidazole (Xa)			1800	1671[a]	
2-Nitrimino-3,7-dimethyl-3,7-diethyl-5-oxo-6-nitro-2,3,5,6-tetrahydro-7(H)-imidaz-[3,4-a]imidazole (Xb)			1793	1673[b]	
3-(α-Carbamylisopropyl)-5,5-dimethylhydantoin (VI)	3400, 3335		1698,[c] 1773 (4-C=O)		1542
3-(α-Carboxyisopropyl)-5,5-dimethylhydantoin (VII)	3260, 3100		1700(COOH),[d] 1755		
Anhydride of 3-(α-carboxyisopropyl)-5,5-dimethylhydantoin (IX)	3270, 3180		1704, 1763, 1786, 1826		

[a] N·NO$_2$ group absorption band at 1578 cm.$^{-1}$. [b] N·NO$_2$ group absorption band at 1580 cm.$^{-1}$. [c,d] These are broad strong bands which could include the absorption band at *ca.* 1672 cm.$^{-1}$ associated with the 2-keto group.

97.5 g. (91.5%). The reported[16] melting point is 144–146°.

α-Methyl-α-aminobutyronitrile (b.p. 65–68° (18 mm.)) was prepared by the general method of Aloy and Rabaut.[17] The reported[18] boiling point is 68° (14 mm.).

A solution of phenyl isocyanate (2.38 g., 0.02 mole) in absolute ether (25 ml.) was added dropwise to a solution of α-methyl-α-aminobutyronitrile (1.96 g., 0.02 mole) in absolute ether (10 ml.). The solid (m.p. 101–103°) was recovered by filtration, yield 3.45 g. (79.5%). Three crystallizations from ethanol gave a constant melting point of 102–103°.

Anal. Calcd. for $C_{12}H_{15}N_3O$: C, 66.35; H, 6.96; N, 19.35. Found: C, 66.48; H, 6.67; N, 19.19.

Reaction of Amino Nitriles with Ethyl Chloroformate.—The reaction of each amino nitrile with ethyl chloroformate was conducted under similar conditions. Thus only the reaction of α-aminoisobutyronitrile with ethyl chloroformate is described in detail. The properties of the products obtained in these experiments are described in Table I.

Ethyl chloroformate (142 g., 1.30 mole) in chloroform (250 ml.) was added dropwise over a period of 3.5 hours to a stirred solution of α-aminoisobutyronitrile (109.4 g., 1.30 moles) and triethylamine (132 g., 1.30 moles) in chloroform (600 ml.) at 0°. The cooling bath was removed and the reaction mixture was stirred at room temperature for 30 minutes. After water (600 ml.) was added, the stirring was continued for a further hour. The solid (m.p. 226–229° dec.) was removed by filtration, yield 101 g. (81%). Three rapid crystallizations from hot methanol raised the melting point to 228–229° with dec.

The amino nitrile hydrochlorides could be used in the above procedure if another mole equivalent of triethylamine were used.

Cyclization of 1,3-Bis-(α-cyanoalkyl)-ureas.—1,3-Bis-(α-cyanoalkyl)-ureas possessing two alkyl substituents on the carbon adjacent to the nitrile group were converted quantitatively into cyclic products on heating for several hours in ethanol. For example 1-(β-cyanoethyl)-3-(α-cyano-α-methylpropyl)-urea (m.p. 110–111° and 164–165°) in absolute ethanol on heating under reflux for 5 hours was cyclized to 3-(β-cyanoethyl)-4-imino-5-methyl-5-ethyl-2-imidazolidone (m.p. 164–165°). The cyclic products obtained by this procedure are described in Table I.

β-Cyanoethyl Isocyanate (b.p. 101° (9 mm.)) was prepared in 68% yield by the method of Siefken.[19]

1-Cyanomethyl-3-(β-cyanoethyl)-urea, 1,3-Bis-(β-cyanoethyl)-urea, 1-(β-Cyanoethyl)-3-(α-cyano-α-methylethyl)-urea and 1-(β-Cyanoethyl)-3-(α-cyano-α-methylpropyl)-urea.—β-Cyanoethyl isocyanate (0.96 g., 0.01 mole) in ether (10 ml.) was added dropwise to a solution of β-aminopropionitrile (0.71 g., 0.01 mole) in absolute ether (50 ml.). The precipitate (m.p. 147–149°) of crude 1,3-bis-(β-cyanoethyl)-urea was recovered by filtration and washed with ether. Two crystallizations from absolute ethanol (40 ml.) raised the melting point to 150–151°.

Aminoacetonitrile, α-aminoisobutyronitrile and α-cyano-α-methylpropylamine on treatment with β-cyanoethyl isocyanate under similar conditions gave, respectively, 1-cyanomethyl-3-(β-cyanoethyl)-urea, 1-(β-cyanoethyl)-3-(1-cyano-1-methylethyl)-urea and 1-(β-cyanoethyl)-3-(α-cyano-α-methylpropyl)-urea. These urea derivatives are described in Table I.

Hydrolysis of 2-Imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]imidazole (IVa). Method A.

(16) W. Gulewitsch and T. Wasmus, *Ber.*, **39**, 1188 (1906).

(17) J. Aloy and R. Rabaut, *Bull. soc. chim.*, (*France*), [4] **7**, 516 (1910).

(18) H. Biltz and K. Slotta, *J. prakt. Chem.*, **113**, 249 (1926).

(19) W. Siefken, *Ann.*, **562**, 104 (1949).

3-(α-Carbamylisopropyl)-5,5-dimethylhydantoin.—The compound IVa (0.7 g., 0.0036 mole) in water (50 ml.) was heated under reflux for 8 hours. The water was removed *in vacuo* and the residue was extracted with acetone (20 ml.). The acetone solution was evaporated and the residue was crystallized from ethyl acetate, yield 0.22 g. (28.6%). The melting point was raised from 208–216° with dec. to 216–217° with dec. by further crystallizations from ethyl acetate.

Anal. Calcd. for $C_9H_{15}N_3O_3$: C, 50.70; H, 7.09; N, 19.71. Found: C, 50.11; H, 7.07; N, 19.81.

Method B. 3-(α-Carbamylisopropyl)-4-imino-5,5-dimethyl-2-imidazolidone Picrate.—A saturated solution (50 ml.) of picric acid was added to a solution of IVa (0.29 g., 0.00149 mole) in water (50 ml.) and the mixture was heated at 95° for 20 minutes. The clear solution on cooling deposited a crystalline picrate (m.p. 238–240°), yield 0.57 g. (87.2%). Two crystallizations from water raised the melting point to 242–242.5°.

Anal. Calcd. for $C_{15}H_{19}N_7O_9$: C, 40.81; H, 4.34; N, 22.22. Found: C, 40.93; H, 4.78; N, 21.78.

Method C. 3-(α-Carbamylisopropyl)-4-imino-5,5-dimethyl-2-imidazolidone Hydrochloride.—2-Imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]-imidazole (2 g., 0.01 mole) was dissolved in 0.26 *N* ethanolic hydrogen chloride solution (39.6 ml.). The solution was evaporated to dryness *in vacuo* at room temperature after which the residual oil crystallized on standing, yield 2.42 g. (100%). Three crystallizations from methanol–ether solution raised the melting point from 249–250 to 253°.

Anal. Calcd. for $C_9H_{17}ClN_4O_2$: C, 43.47; H, 6.89; Cl, 14.26; N, 22.53. Found: C, 43.22; H, 6.86; Cl, 14.69; N, 22.49.

A sample of the hydrochloride on treatment with aqueous picric acid solution gave a picrate melting at 239–240°, yield 89%. A mixture melting point determination with the picrate (m.p. 242–242.5°) prepared by method B gave no depression.

Method D. 3-(α-Carboxyisopropyl)-5,5-dimethylhydantoin.—A solution of IVa (3 g., 0.0155 mole) in 3 *N* hydrochloric acid solution (100 ml.) was heated at 80° for 10 minutes. The solution was evaporated to dryness and the residue was extracted with water. The water-insoluble residue melted at 208–212°, yield 2.40 g. (72.2%). One crystallization from water raised the melting point of the 3-(α-carboxyisopropyl)-5,5-dimethylhydantoin to 215–216°.

Anal. Calcd. for $C_9H_{14}N_2O_4$: C, 50.47; H, 6.58; N, 13.08; neut. equiv., 214.22. Found: C, 50.25; H, 6.06; N, 13.19; neut. equiv., 214.5.

Method E. α-Aminoisobutyric Acid.—A solution of IVa (20 g., 0.13 mole) and barium hydroxide (19.5 g.) in water (300 ml.) was refluxed for 14 hours. The cooled solution was filtered and the precipitate washed with water. After the filtrate with washings was evaporated to dryness the residue was dissolved in water (30 ml.). This solution was acidified with glacial acetic acid and cooled. The precipitated solid (sublimes 280°) was recovered by filtration, yield 7.2 g. (68%). The infrared spectrum of this preparation was identical with the spectrum of a known commercial sample of α-aminoisobutyric acid.

Anhydride of 3-α-Carboxyisopropyl-5,5-dimethylhydantoin.—Benzoyl chloride (0.65 g., 0.0046 mole) was added dropwise to a cooled solution of 3-α-carboxyisopropyl-5,5-dimethylhydantoin and the solution was heated under reflux for 25 minutes. The reaction mixture was poured onto crushed ice and the precipitated product (m.p. 204–230°) was recovered by filtration, yield 0.51 g. (54%). Three crystallizations from absolute methanol (25 ml.) raised the melting point to 241–243°.

Anal. Calcd. for $C_{18}H_{26}N_4O_7$: C, 52.68; H, 6.39; N, 13.65. Found: C, 52.31; H, 6.48; N, 13.21.

Nitration of 2-Imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]imidazole.—2-Imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]-imidazole (3 g., 0.016 mole) was added over a period of 10 minutes to a stirred nitration mixture of ammonium chloride (1.98 g., 0.037 mole), nitric acid (10.5 g., 0.15 mole) and acetic anhydride (15.3 g., 0.15 mole) at 0°. The solution was allowed to warm up to 27° and the stirring was continued for 3 hours. This reaction mixture was poured onto ice (250 g.) and the insoluble precipitate (m.p. 202–207° dec.) was removed by filtration, yield 3.3 g. (77.3%). Four crystallizations from acetone–petroleum ether solution raised the melting point to 214–215° dec.

Anal. Calcd. for $C_9H_{12}N_6O_5$: C, 38.03; H, 4.26; N, 29.57. Found: C, 38.46; H, 4.61; N, 29.30.

2-Nitrimino-3,7-dimethyl-3,7-diethyl-5-oxo-6-nitro-2,3,5,6-tetrahydro-7(H)-imidaz[3,4-a]imidazole (m.p. 99–102°) was prepared in 69.5% yield under similar conditions. Several crystallizations from acetone–petroleum ether solution raised the melting point to 164–165° dec.

Anal. Calcd. for $C_{11}H_{16}N_6O_5$: C, 42.31; H, 5.17; N, 26.92. Found: C, 42.64; H, 5.21; N, 27.32.

Reaction of α-Aminoisobutyronitrile with Phosgene.—When phosgene was passed into a toluene solution of α-aminoisobutyronitrile following the method of Jacobson[4] a quantitative yield of crude product melting at 170–210° dec. was obtained. Repeated crystallizations from methanol raised the melting point to 240° dec. This product did not depress the melting point of a known sample of 2-imino-3,3,7,7-tetramethyl-5-oxo-2,3,5,6-tetrahydro-7(H)-imidaz-[3,4-a]imidazole (m.p. 240° dec.) which was prepared as described above by heating 1,3-di-(α-cyanoisopropyl)-urea in ethanol under reflux for several hours.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SMITH COLLEGE]

8,10-Dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene: The Dienone–Phenol Rearrangement

BY STANLEY M. BLOOM

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The synthesis of 8,10-dimethyl-2-keto-$\Delta^{1,9;3,4}$-hexahydronaphthalene (IX) is reported. The phenol, 4,8-dimethyl-5-hydroxy-1,2,3,4-tetrahydronaphthalene (XII), obtained on dienone–phenol rearrangement of (IX) demonstrates the intermediacy of the spiran intermediate (X) in the reaction studied.

Woodward and Singh[1] first demonstrated that the acid-catalyzed rearrangement of cyclohexadienones does not always follow the course of santonin (I) in its conversion to desmotroposantonin (II).[2]

(1) R. B. Woodward and T. Singh, THIS JOURNAL, **72**, 494 (1950).
(2) Huang-Minlon, C. Lo and L. J. Chu, *ibid.*, **65**, 1780 (1943).

10-Methyl-2-keto-$\Delta^{-1,9;3,4}$-hexahydronaphthalene (III) was synthesized and rearranged in acetic anhydride to 5-hydroxy-8-methyl-1,2,3,4-tetrahydronaphthalene (IV). Extending these data, Woodward and Singh suggested the structure VIa rather than VII for the phenol obtained from the acid-catalyzed rearrangement of steroid die-