Ring Closures from Enecarbamoyl Azides. Syntheses of Tetrahydro-3-indazolinones and 4-Imidazolin-2-ones (1)

John P. Chupp

Research Department, Agricultural Division, Monsanto Co.,
St. Louis, Missouri 63166

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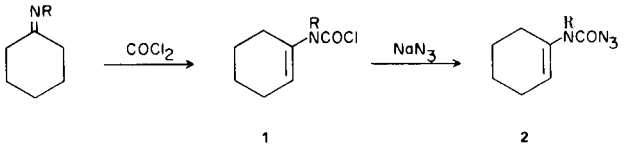
Reaction of phosgene with cyclohexylidene amines gives good yields of (1-cyclohexen-1-yl)-carbamoyl chlorides (**1**). Compound **1** can be converted to the corresponding enecarbamoyl azide (**2**), which on pyrolysis gives an improved synthesis of 1-substituted-4,5,6,7-tetrahydro-3-indazolinones (**7**). When **1** is substituted by an allylic rather than alkyl or aryl group, the major products are 4-imidazolin-2-ones (**8**) accompanied by only minor amounts of **7**. The thermolysis reaction has been extended to *N*-allylcarbamoyl azides in general, thus providing a new and facile synthesis for 1,4-disubstituted 4-imidazolin-2-ones (9). A tentative mechanism is advanced, involving intermediate azide addition to the allylic double bond.

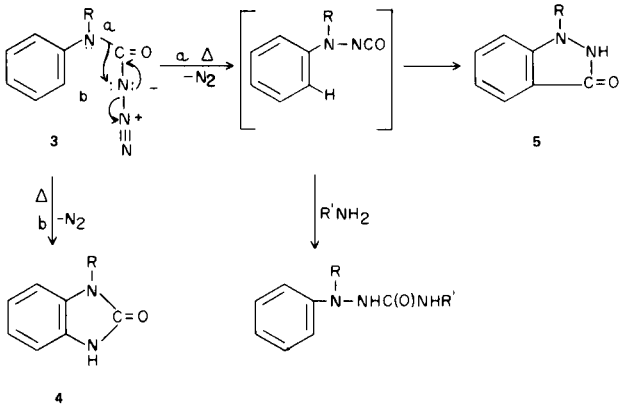
Phosgene has been found to undergo reaction with cyclohexylidene amines to form enecarbamoyl chlorides (**1**), (2) (Table I). Formation of **1** is thus analogous to the preparation of enamides from acyl chlorides and aldimines (3) and ketimines (4).

By reaction of **1** with suitable nucleophiles, convenient methods of preparing new heterocyclic materials can be devised, which utilize ring closure between the carbamoyl substituent and the activated olefin. This report concerns the ring closure behavior of some new enecarbamoyl azides (**2**) (5).



1 2

Investigating the thermolysis of a number of arylcarbamoyl azides, Stolle found a convenient synthesis of 1-substituted-3-indazolinones (**5**) (6,7). Although an intermediate nitrene has been suggested for this reaction (8), the facile decomposition under relatively mild conditions would more realistically indicate a similarity to the concerted mechanism known to occur during the Curtius rearrangement of acyl azides (9). Thus the nucleophilic carbamoyl nitrogen could attack the azido nitrogen with simultaneous loss of nitrogen, and cleavage of the carbon-carbamoyl nitrogen bond (path a).



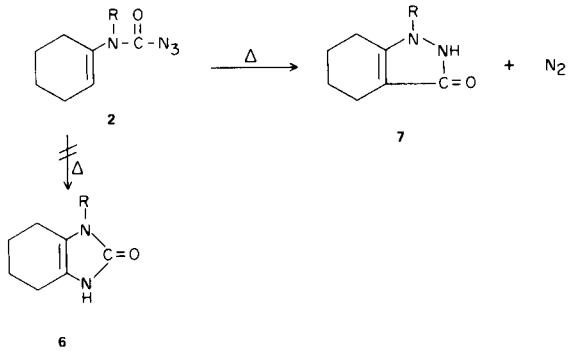
The formation of the transient anilino isocyanate intermediate has been demonstrated by isolation of semicarbazides from thermolysis of diphenylcarbamoyl azide in the presence of amines (10). In the absence of added nucleophiles, the intermediate anilino isocyanate attacks the most convenient source of high electron density, namely the *o*-carbon, to form 1-substituted-3-indazolinones (**5**). More recently (11,12), thermolysis of certain benzylcarbaniloyl azides have been shown to produce small amounts of **4** along with the main component **5**. Indeed, ratios of **5**:**4** less than unity have been obtained upon pyrolysis of azides bearing strong electron releasing groups in the *N*-aryl ring (12). The higher amount of **4** presumably arises from the greater competitiveness of the electron enriched *ortho* position (path b).

It was therefore of interest to ascertain which scheme

would apply to the pyrolysis of enecarbamoyl azides (**2**), particularly since preparative methods are limited for either product, namely 1-substituted-4,5,6,7-tetrahydro-3-indazolinones (**7**) or 1-substituted-4,5,6,7-tetrahydro-2-benzimidazolinones (**6**).

Although enecarbamoyl azides (**2**) were prepared from the corresponding chlorides (**1**) (Table I), they were isolated only as the undistilled oils; strong azide absorption at *ca.* 2200 cm^{-1} and a reasonably clean nmr spectra was deemed sufficient indication of purity for the pyrolysis experiments.

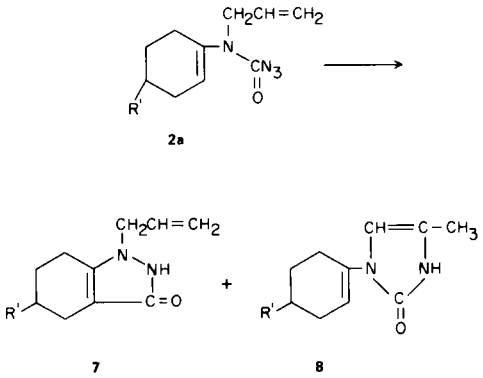
Upon refluxing **2** in chlorobenzene, nitrogen is smoothly expelled and **7** rather than **6** is formed in good yields (Table II). The enhanced nucleophilicity of the beta-carbon in **2** is apparently responsible for the fact that ring closure of **2** (R = aryl) takes place entirely in the cyclohexene ring to give **7**, with no evidence of alternative formation of 1-cyclohexen-1-yl-3-indazolinone (**5**, R = cyclohexenyl).



The pyrolysis of **2** has distinct advantages over the recently reported synthesis of **7** from 2-chloro-1-cyclohexencarboxhydrazides (13), having fewer steps from cyclohexanone, and utilizing the more available amines rather than hydrazines. Moreover, it is doubtful whether the hydrazide method is genuinely applicable for preparing a wide range of **7** (R = alkyl), as reaction of aliphatic aldehydes with hydrazine gives the azines in preference to the required hydrazone (14).

The structure of **7** is confirmed by independent synthesis *via* the hydrazide method (13) or the newly developed alkylation procedure (1). The spectral features of **7** are also consistent with the assigned tetrahydroindazolinone structure; in particular, the enolic and associative properties generally characteristic of 1-substituted-3-pyrazolinones (15,16) are also displayed by **7** (1).

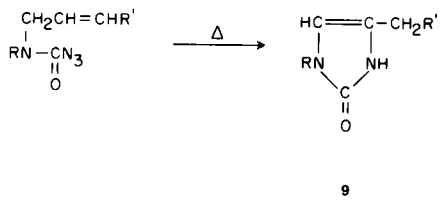
The alkylation procedure developed for the preparation of **7** (1) has been extended to allylic halides. In attempts to prepare **7h** by the azide method however, only minor amounts of it were isolated, while the major product was an isomeric material 1-(1-cyclohexen-1-yl)-4-methyl-1-imidazolin-2-one (**8a**).



Although Stolle examined pyrolysis products from a number of *N*-substituted carbaniloyl azides, curiously, he did not investigate *N*-allylic materials. The only unsaturated material apparently studied was azidoformic acid benzylidenephenylhydrazide which on heating produced a product derived from substitution of the azido nitrogen on the formyl carbon, namely 1,3-diphenyl-Δ^2-1,2,4-triazolin-5-one (8).

Since ring closure to form a 3-indazolinone derivative occurs more readily on a cyclohexenyl- rather than an *ortho* phenyl-carbon, and yet allyl(1-cyclohexen-1-yl)-carbamoyl azide preferentially closes on the allyl group, it would not be unexpected for allylcarbaniloyl azides to similarly close on the allyl moiety to form 1-aryl-4-imidazolin-2-ones (**9**, R = aryl, R′ = H). In fact **3** (R = allyl) smoothly decomposes in chlorobenzene to give **9** exclusively; there is no evidence of indazolinone formation.

Nor is pyrolysis to form imidazolinones restricted to azides **2** and **3** (R = allyl). It appears that any carbamoyl azide bearing an *N*-allyl or terminally substituted propenyl grouping will undergo similar reaction (Table III). On the other hand, 2-substituted "allylic" groupings such as methallyl pyrolyze only at high temperatures to give **5** (R = methallyl).

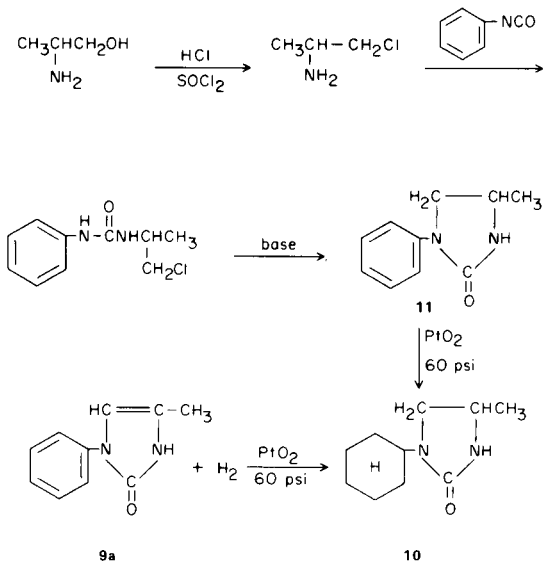


Imidazolinones **8** and **9** are easily distinguishable from the isomeric indazolinones because of the latter's aforementioned enolic properties (ir) (1). In contrast, **8** and **9** have normal strong carbonyl absorption in the 1660-1700 cm^{-1} region, and only relatively low intensity N-H

stretching frequencies at *ca.* 3400 cm^{-1}, with no OH absorption in the 2700-2200 cm^{-1} region.

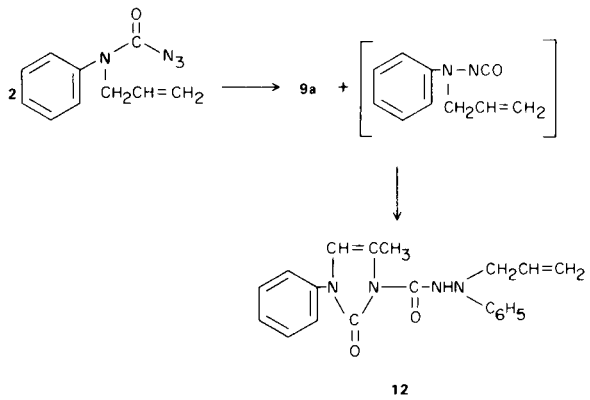
Nmr spectroscopy is also useful. Isomeric imidazolinones **8a,b** and indazolinones **7a,b** both formed from **2** are easily distinguished by the different number and kind of olefinic protons present. The -N-C*H*=C-C*H*$_3$ grouping can easily be characterized by the downfield multiplet and closely spaced upfield doublet for the olefinic proton and methyl groups respectively.

Alternative structures to the assigned imidazolinone **9** possessing this grouping can be eliminated. Thus, the melting point of **9a** differs from that reported for the isomeric 4-methyl-1-phenylpyrazolin-3-one (17) or 5-methyl-1-phenyl-4-imidazolin-2-one (18). Hydrogenation of **9a** gives the imidazolidinone **10**, with the characteristic (nmr) -N-C*H*$_2$-C*H*-C*H*$_3$ group. Finally, **10** was prepared alternatively by a method previously used for some related imidazolidinones (19).



Although yields of imidazolinones **8** and **9** are generally fair to good (see Table III), **9a** was produced in lower amounts. Responsible for the low yield was the side-reaction giving dimer **12**, presumably similar in structure to those obtained *via* thermolysis of benzylcarbaniloyl azides (12). The mechanism of formation is similar, except the imidazolinone, acylated by the unstable amino isocyanate, arises from ring closure on the *N*-allyl, rather than *N*-phenyl moiety.

The facile ring closure of allyl carbamoyl azides upon mild thermolysis, thus provides a convenient route to 1,4-di-substituted-4-imidazolin-2-ones. In the absence of activation parameters and environmental influences, it would be hazardous to definitely assign a mechanism



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from the myraid experienced from azide decompositions.

Thus, the pyrolysis and photolysis of azides have been shown to proceed through either singlet and triplet nitrenes, *via* both insertion and substitution reactions. Moreover, as mentioned before, azides can decompose from rearward displacements of nitrogen on the azido group.

It seems reasonable however, as a first approximation, to postulate addition of azide to the unactivated double bond of the allyl group. As emphasized by L'Abbe (9), mechanisms involving nitrenes represent high energy pathways, while addition of the parent azides to double bonds can proceed under exceedingly mild conditions. Thus olefinic azides containing unsaturation at least three carbon atoms removed from the azide group add intramolecularly to give stable triazolines; at 80° nitrogen is lost and cyclic imines and 1-azabicyclo (3.1.0) hexane result (20).

Although allylcarbamoyl azides are stable at room temperature, their preferential decomposition to imidazolinones **8** or **9**, rather than **4** or **6** or indazolinones **5** and **7**, would reveal the thermolysis to proceed with greater ease. This observation is reinforced by the behavior of **3c** which required refluxing orthene to effect formation of indazolinone **5a**, when ring closure on the methallyl group failed in chlorobenzene.

The lowered energy requirements thus characteristic of imidazolinone formation from allylcarbamoyl azides would therefore at least, qualify the reaction to proceed *via* an addition mechanism.

EXPERIMENTAL

All elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained on a Perkin-Elmer Infracord; nmr spectra were recorded by a Varian A-60; mass spectroscopy was measured (direct solids inlet) by a Perkin-Elmer 270 mass spectrometer. Melting points are corrected.

The specific preparation of **2a** is sufficient to provide a general procedure for the preparation of the carbamoyl chlorides (21) found in Table I.

TABLE I

Carbamoyl Chlorides ($\begin{matrix}R\\R'\end{matrix}$>NCOCl)

Material	R	R′	Yield	B.p. (m.p.)	n_D^{25}	Empirical	Analysis Calcd. C	H	N	Cl	Found C	H	N	Cl
1a	1-cyclohexen-1-yl	CH_3	62	93/0.5 mm	1.4994	$C_8H_{12}ClNO$			8.05	20.40			8.00	20.43
1b	1-cyclohexen-1-yl	$(CH_3)_2CH$	44	102-110/2 mm		$C_{10}H_{16}ClNO$	59.55	8.00	6.94		59.46	7.79	6.85	
1c	1-cyclohexen-1-yl	C_4H_9	76	100-105/0.5 mm	1.4910	$C_{11}H_{18}ClNO$	61.24	8.41	6.49		61.23	8.11	6.46	
1d	1-cyclohexen-1-yl	$(CH_3)_2CHCH_2$	70	91-95/0.7 mm		$C_{11}H_{18}ClNO$	61.24	8.41	6.49		61.43	8.18	6.58	
1e	1-cyclohexen-1-yl	C_6H_5	86	(51.5-53)		$C_{13}H_{14}ClNO$			5.94	15.04			6.03	15.19
1f	1-cyclohexen-1-yl	$3,4(Cl_2)C_6H_3$	90	(undistilled)		$C_{13}H_{12}Cl_3NO$	51.26	3.97	4.60		51.34	3.89	4.32	
1g	1-cyclohexen-1-yl	CH_2=$CHCH_2$	60	105/5 mm	1.5041	$C_{10}H_{14}ClNO$	60.15	7.07	7.01		60.10	7.06	7.25	
3a	C_6H_5	CH_2=$CHCH_2$	74	115-118/2 mm	1.5426	$C_{10}H_{10}ClNO$	61.39	5.15		18.12	61.54	5.24		18.08
3b	$3,4(Cl)_2C_6H_3$	CH_2=$CHCH_2$	55	(86-87)		$C_{10}H_8Cl_3NO$	45.40	3.05			45.41	3.09		
3c	C_6H_5	CH_2=$C(CH_3)CH_2$	82	120-122/1 mm	1.5392	$C_{11}H_{12}ClNO$	63.01	5.77	6.68		63.63	6.15	6.28	
3d	$C_6H_5CH_2$	CH_2=$CHCH_2$	90	90-92/0.1 mm	1.5393	$C_{11}H_{12}ClNO$	63.01	5.77	6.68		62.99	5.80	6.72	
3e	$C_6H_5CH_2$	CH_3	76	97-98/0.2 mm	1.5422	$C_9H_{10}ClNO$	58.86	5.49		19.31	59.01	5.56		19.12
3f	C_6H_5CH=$CHCH_2$	CH_3	88		1.5732	$C_{11}H_{12}ClNO$	63.01	5.77		16.91	63.07	5.93		16.73
3g	CH_2=$CHCH_2$	CH_2=$CHCH_2$	86	108-110/28 mm	1.4776	$C_7H_{10}ClNO$	52.67	6.31		22.21	52.64	6.50		22.13

TABLE II

1-Substituted 4,5,6,7-Tetrahydro-3-indazolinones (**7**) from Carbamoyl Azide Pyrolysis

Material	R	Yield (a)	M.p.	Empirical	Analysis Calcd. C	H	N	Found C	H	N
7a	CH_3	76	178-181	$C_8H_{12}N_2O$	63.13	7.91	18.41	63.12	7.99	18.21
7b	$(CH_3)_2CH$	32 (b)	225-227	$C_{10}H_{16}N_2O$	66.63	8.95	15.54	67.10	9.24	15.51
7c	n-C_4H_9	34	139-140	$C_{11}H_{18}N_2O$	68.01	9.34	14.42	68.22	9.45	14.50
7d	$(CH_3)_2CHCH_2$	73	165-166	$C_{11}H_{18}N_2O$	68.01	9.34	14.42	67.84	9.30	14.60
7e	C_6H_5	45 (b)	213-214 (c)	$C_{13}H_{14}N_2O$			13.08			12.97
7f	$C_6H_5CH_2$	57 (b)	188-188.5	$C_{14}H_{16}N_2O$	73.70	7.07	12.27	73.58	7.09	12.30
7g	$3,4(Cl)_2C_6H_3$	62	208-210	$C_{13}H_{12}Cl_2N_2O$	25.04 (Cl)		9.89	25.17 (Cl)		9.90
7h	CH_2=$CHCH_2$	20	107-108	$C_{10}H_{14}N_2O$	67.39	7.92	15.72	66.44	8.05	15.56
7i(d)	CH_2=$CHCH_2$	22	141-143	$C_{11}H_{16}N_2O$	68.72	8.39	14.57	68.39	8.45	14.57

(a) Yield based on carbamoyl azide. (b) Yield based on carbamoyl chloride. (c) Mixture m.p. with material prepared *via* hydrazide method (ref. 13), showed no depression. (d) From cyclization of allyl-(4-methyl-1-cyclohexen-1-yl)carbamoyl azide.

TABLE III

1,4-Substituted 4-Imidazolin-2-ones (**8,9**) from Enecarbamoyl Azide Pyrolysis

Material	R	R'	Yield	M.p.	Empirical	Calcd. C	Calcd. H	Analysis N	Found C	Found H	Found N
8a		H	50	156-161	$C_{10}H_{14}N_2O$	67.39	7.92	15.72	67.49	7.86	15.77
8b		CH_3	55	128-135	$C_{11}H_{16}N_2O$	68.72	8.39	14.57	68.56	7.86	14.66
9a	C_6H_5	H	65	170	$C_{10}H_{10}N_2O$	68.95	5.79	16.08	68.99	5.84	16.27
9b	$3,4(Cl)_2C_6H_3$	H	–	176-178	$C_{10}H_8Cl_2N_2O$	49.41	3.32	11.52	49.76	3.33	11.30
9c	$C_6H_5CH_2$	H	70	162-165	$C_{11}H_{12}N_2O$	70.19	6.43	14.88	70.70	6.49	14.65
9d	$CH_2=CHCH_2$	H	75	100-105	$C_7H_{10}N_2O$	60.85	7.30		60.75	7.23	
9e	CH_3	C_6H_5	35	159-162	$C_{11}H_{12}N_2O$	70.19	6.43	14.88	70.57	6.53	14.54

(1-Cyclohexen-1-yl)methylcarbamoyl Chloride (**1a**).

N-Cyclohexylidenemethyl amine (22) (0.22 mole) in benzene was added dropwise to a benzene solution (12.5%) containing 25 g. of phosgene. After the imine had been added the solution was refluxed for 1 1/2 hours, cooled, and the reaction mixture filtered. The filtrate was vacuum treated to remove solvent, and the residue distilled at 93° (0.5 mm) to give 23.6 g. of colorless oil (62% yield); ir (film) cm^{-1} 1740 (C=O), 1660 (C=C); nmr (carbon tetrachloride) δ 1.7 and 2.1 [2 m's, 4 protons each, cyclohexyl group (23)], 3.12 (s, 3 protons, NCH_3), 5.8 (m, 1 proton, =C*H*).

Azides were prepared from the carbamoyl chlorides but were not purified by distillation. Aqueous acetone was used, as methyl carbamate formation was appreciable when Stolle's method (6) employing aqueous methanol was employed. The procedures below for **2a** and **3a** are representative of the general preparation.

(1-Cyclohexen-1-yl)methylcarbamoyl Azide (**2a**).

Sodium azide (33 g.) was mixed with 275 ml. of 80% aqueous acetone (20% water by volume) and 30 g. (1-cyclohexen-1-yl)-methylcarbamoyl chloride added, keeping the temperature below 30°. The material was permitted to stir 18 hours, the solution filtered and the material vacuum treated at room temperature. The residue was taken up in ether, washed with water and dried over magnesium sulfate. On vacuum treatment, 25.3 g. of residue remained as product; ir (film) cm^{-1} 2110 ($-N_3$), 1670 (C=O), 1650 (C=C); nmr (carbon tetrachloride) δ 1.7, 2.1 [2 m's, 4 protons each, cyclohexyl group (23)], 2.99 (s, 3 protons, NCH_3), 5.58 (m, 1 proton, =C*H*).

Preparation of carbamoyl azides not possessing a cyclohexenyl moiety was carried out with sodium azide in refluxing aqueous acetone.

Allylphenylcarbamoyl Azide (**3a**).

Allylphenylcarbamoyl chloride (25 g., 0.128 mole) was placed in 250 ml. of 80% aqueous acetone with 32 g. (0.25 mole) of sodium azide. The mixture was refluxed for two hours, cooled, filtered and the filtrate vacuum treated to remove most of the solvent. Ether was added to the residue and the ether solution washed twice with water, then dried over magnesium sulfate. The ether solution was vacuum treated at room temperature to remove ether, giving 20 g. of residual oil; ir cm^{-1} 2120 ($-N_3$), 1670 (C=O); nmr (carbon tetrachloride) δ 4.21 (d, 2 protons, J = 6 Hz, $=CHCH_2N$), 5.0, 5.18 (m's 2 protons, $=CH_2$), 5.8 (m's, 1 proton, $C=CHCH_2$), 7.2 (m's, 5 protons, Ar*H*).

General procedures for the preparation of tetrahydro-3-indazolinones (**7**) (Table II) and 4-imidazolin-2-ones (**8,9**) (Table III) by pyrolysis of carbamoyl azides are illustrated by the following examples. The characteristic ir spectra of **7** showing the presence of a strong OH stretching but absence of carbonyl was found in all materials in Table II. Likewise the characteristic nmr spectra for $-N-CH=CCH_3$ was present in compounds from Table III with the exception of **9e** where this moiety is not present.

4,5,6,7-Tetrahydro-1-methyl-3-indazolinone (**7a**).

(1-Cyclohexen-1-yl)methylcarbamoyl azide (22.4 g., 0.124 mole) was added over *ca.* 15 minutes to 150 ml. of refluxing chlorobenzene. Lesser quantities of azide may be mixed at room temperature, prior to reflux. With larger amounts, the facile azide decomposition produces considerable frothing if pyrolysis is not carried out portionwise as above. The chlorobenzene solution is refluxed three hours after addition of azide,

then solvent is removed and the product recrystallized from methylcyclohexane to give 14.4 g. white crystals; ir cm^{-1} 2700-2200 (OH), 1680 (weak C=O); nmr (deuteriochloroform) δ 1.7, 2.4 (2 m's, 4 protons each, cyclohexenyl group) 3.5 (s, 3 protons, NCH_3), 10.2 (broad, 1 proton, OH-bonded).

1-Benzyl-4,5,6,7-tetrahydro-3-indazolinone (**7f**).

Freshly distilled benzyl(1-cyclohexen-1-yl)carbamoyl chloride (3.0 g.) was placed in 50 ml. of 85% aqueous acetone with 3 g. of sodium azide, and the mixture permitted to stir at room temperature for 24 hours. After this time the material was filtered, and the filtrate vacuum treated to remove most of the acetone. The residue was extracted with ether and washed twice with water. The dried (magnesium sulfate) ether solution was vacuum treated to remove solvent and all but 0.3 g. of residue heated three hours in refluxing chlorobenzene. After solvent removal, the material was recrystallized from absolute ethanol to give 1.4 g. of white crystals; ir cm^{-1} 2700-2200 (OH), no C=O at *ca.* 6.0 μ; nmr (deuteriochloroform) δ 1.7, 2.4 (s, m's, 4 protons each, cyclohexenyl group), 5.04 (s, 2 protons, $ArCH_2N$), 7.2 (m, 5 protons, Ar*H*), 12.6 (broad, 1 proton, OH-bonded).

N-Allyl-4,5,6,7-tetrahydro-3-indazolinone (**7h**).

Allyl(1-cyclohexen-1-yl)carbamoyl azide (9.0 g., 0.0445 mole) was refluxed in chlorobenzene for five hours. After solvent removal the residue was shown by nmr to consist to *ca.* 20% of **7h** and 80% of 1-(1-cyclohexen-1-yl)-4-methyl-4-imidazolin-2-one (**8a**). The residue was treated with *ca.* 500 ml. of boiling ether. The ether solution was decanted, and evaporated to give a solid that was recrystallized from ethyl acetate yielding 0.6 g. of crystals, m.p. 107-108°. A mixture of **7h** with the product derived from alkylation of 4,5,6,7-tetrahydro-3-indazolinone with allyl bromide (24) showed no depression; ir cm^{-1} (chloroform) 2700-2300 (OH), no C=O at 6.0 μ; nmr (deuteriochloroform) δ 1.72, 2.4 (2 m's, 4 protons each, cyclohexenyl group), 4.4 (d, 2 protons, J = 6 Hz, NCH_2), 4.95, 5.15 (m's, 2 protons, H_2C=C), 5.9 (m's, 1 proton =C*H*-CH_2), 10.8 (broad, 1 proton, N*H*).

1-(1-Cyclohexen-1-yl)-4-methyl-4-imidazolin-2-one (**8a**).

The ether insoluble material from preparation of **7h** was recrystallized from acetonitrile to give 3.8 g. of crystals; ir cm^{-1} (chloroform) 3500 (N-H), 1670 (C=O); nmr (deuteriochloroform) δ 1.7, 2.25 (2 m's, 4 protons each, cyclohexenyl group), 2.02 (d, 3 protons, J = 2 Hz, $NHC=CCH_3$), 5.9 (2 m's, 2 protons, NC=C*H*- and -N-C*H*=CCH_3), 10.3 (broad, 1 proton, N*H*).

1-Phenyl-4-methyl-4-imidazolin-2-one (**9a**).

Allylphenylcarbamoyl azide (5 g., 0.025 mole) prepared in the usual fashion (see above) was heated in chlorobenzene at reflux for two hours. The chlorobenzene was evaporated and the residue, a mushy solid was triturated with ether, to give 2.4 g. solid. This material was recrystallized from acetonitrile to give crystals; ir cm^{-1} (chloroform) 3500 (NH), 1660 (C=O); nmr (deuteriochloroform) δ 2.11 (d, 3 protons, J = 2 Hz, NCH=C-CH_3), 6.3 (m, 1 proton, NC*H*=CCH_3), 7.3-7.8 (m's, 5 protons, Ar*H*); mass spectrum (70 eV) m/e (rel intensity) 174 (100), 173 (5), 145 (20), 105 (12), 104 (36), 78 (9), 77 (25), 51 (12), 42 (14).

1-Allyl-4-methyl-4-imidazolin-2-one (**9d**).

Diallylcarbamoyl chloride (16 g., 0.10 mole) was placed in 100 ml. of 80% aqueous acetone with 13 g. of sodium azide. After refluxing for three hours, the material was cooled, filtered and the filtrate vacuum treated to remove most of the acetone. The residue was taken up in ether, washed twice with water, and the ether solution dried over magnesium sulfate. After evaporation of the ether under vacuum at room temperature, 12.4 g. of residue remained as *N,N*-diallylcarbamoyl azide. The azide (11.8 g.) was decomposed over three hours in refluxing chlorobenzene. After solvent removal, the residual oil solidified on scratching. Trituration with ether gave 7.5 g. of **9d**; ir cm^{-1} (chloroform) 3450 (NH), 1665 (C=O); nmr (deuteriochloroform) δ 2.0 (d, 3 protons, J = 1.5 Hz, CH=C-CH_3), 4.1 (d, 2 protons, J = 6 Hz, CH_2=CHCH_2N), 5.0, 5.2 (m's, 2 protons, H_2C=CH-), 5.78 (m's, 1 proton, H_2C=C*H*CH_2), 5.8 (m, 1 proton, -NC*H*=C-CH_3), 11.1 (broad, 1 proton, N*H*).

4-Benzyl-1-methyl-4-imidazolin-2-one (**9e**).

Cinnamylmethylcarbamoyl azide (4.6 g., 0.0213 mole) was heated for three hours in refluxing chlorobenzene. After solvent removal the residue was recrystallized from ethyl acetate to give 1.4 g. of crystals; ir cm^{-1} (chloroform) 3550 (NH), 1670 (C=O); nmr (deuteriochloroform) δ 3.10 (s, 3 protons, NCH_3), 3.63 (d, 2 protons, J = 1.5 Hz, $C_6H_5CH_2C$=CH), 5.62 (m, 1 proton, CH_2C=C*H*), 7.31 (s, 5 protons, Ar*H*), 10.6 (broad, 1 proton, N*H*).

1-(2-Methylallyl)-3-indazolinone (**5a**).

(2-Methylallyl)phenylcarbamoyl azide (7.8 g.) was heated five hours in refluxing chlorobenzene. There was no apparent reaction after this time, as determined by the strong absorption peak for azide at 2120 cm^{-1}, and unchanged nmr. The solvent was removed from the azide and *o*-dichlorobenzene added. After three hours reflux in this higher boiling solvent, the solution was vacuum treated to remove solvent and the residue recrystallized from ethanol, m.p. 111-113°. A mixture melting point with material derived from alkylation of 3-indazolinone and 3-chloro-2-methyl-1-propene (24) gave no depression; ir cm^{-1} (chloroform) 2800-2300 (OH), no C=O in 1660 region; nmr (deuteriochloroform) δ 1.66 [s, 3 protons, CH_2-C(CH_3)=CH_2], 4.67 [s, 2 protons, $CH_2C(CH_3)$=CH_2], 4.87 [m, 2 protons, CH_2-C(CH_3)=CH_2], 7.8 (m's, 4 protons, Ar*H*), 12.1 (s 1 proton, OH).

Anal. Calcd. for $C_{11}H_{12}N_2O$: N, 14.88. Found: N, 14.95.

1-Cyclohexyl-4-methyl-2-imidazolidin-2-one (**10**).

a. *Via* Reduction of **9a**.

Material **9a** (1.8 g., 0.01 mole) was placed in 15 ml. of glacial acetic acid with 1.5 g. of Adams catalyst (platinum oxide). The material was hydrogenated in a rocking autoclave overnight at 60 psi of hydrogen. The contents of the autoclave were filtered, the filtrate poured into water, and the white solid collected by filtration and air dried. Purification by recrystallization from methylcyclohexane gave crystals, m.p. 120-126°; nmr δ (deuteriochloroform) 1.10 (d, 3 protons, J = 6 Hz, NCHCH_3), 1-2 (m's, 10 protons, cyclohexyl protons), 2.75-4 (m's, 4 protons, all N-C*H*), 4.88 (broad, 1 proton, N*H*).

b. *Via* 2-Aminopropanol.

2-Amino-1-propanol (14 g., 0.187 mole) available either from reduction of 2-nitro-1-propanol (25) or neutralization of its hydrochloride salt, b.p. 60-63° (4 mm) was placed in 150 ml. of chloroform and excess anhydrous hydrogen chloride sparged into the stirred mixture. Then thionyl chloride (24 g., 0.2 mole) was added dropwise at 50-55° and the mixture refluxed 1.5 hours, during which time the mixture turned dark. The mixture was vacuum treated to remove solvent, then vacuum treated three separate times with 100 ml. portions of benzene to remove traces of thionyl chloride and hydrogen chloride. The residue was a brown, partly mushy solid. A portion could by purified to a light brown solid by trituration with ether. The entire residue was dissolved in water, the small amount of solid remaining, filtered off, and the acid

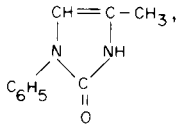
solution neutralized at 5° with 20% NaOH, extracted with ether, then dried over magnesium sulfate. To the ether solution was added 0.15 mole phenyl isocyanate. The solution was permitted to stand overnight, then vacuum treated to remove solvent. The nmr of the solid residue was consistent with the adduct structure, *N*-(2-chloroisopropyl)-*N'*-phenyl urea, although the latter was not further purified. Instead, the crude material was refluxed in 20 ml. of acetone with 50 ml. of 10% sodium hydroxide for one hour. On removal of water and acetone, the residue was eluted through a silicic acid column. Evaporation of the bulk of the eluted fractions (2-6) contained nearly pure **11**. Several of these fractions were recrystallized twice from methylcyclohexane, once from methanol and the filtrate collected from a cold chloroform solution, in efforts to remove traces of *N,N'*-diphenyl urea as an impurity. In this manner, a white solid was obtained, m.p. 101-105°; ir cm^{-1} (chloroform) 3420 (NH), 1680 (C=O); nmr (deuteriochloroform) δ 1.27 (d, 3 protons, J = 7 Hz, CH_3), 3.3-4.0 (m's, 3 protons, NC*H* and NCH_2), 5.7 (broad, 1 proton, NH), 7.7 (m's, 5 protons, Ar*H*).

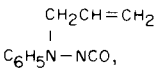
Anal. Calcd. for $C_{10}H_{12}N_2O$: C, 68.18; H, 6.86. Found: C, 68.74; H, 6.73.

Hydrogenation of 4-methyl-1-phenylimidazolidin-2-one (**11**) in acetic acid with Adams catalyst (platinum oxide) gave 1-cyclohexyl-4-methyl-2-imidazolidin-2-one (**10**), m.p. 130-133°. A mixture melting point with the material *via* reduction of **9a** was not depressed (125-133°), while the nmr of the two materials were identical.

5-Methyl-2-oxo-3-phenyl-4-imidazoline-1-carboxylic Acid, 2-Allyl-2-phenylhydrazide (**12**).

The ethyl acetate mother liquor from a recrystallization of **9a**, was vacuum treated to remove solvent. The residue (*ca.* 9 g. from several combined experiments) was dissolved in 85% chloroform-15% ethanol (v/v) and eluted through silicic acid. The first fraction eluted contained the subject compound, which after solvent evaporation and recrystallization from cold ether, melted at 89-90°; ir cm^{-1} 1730 (C=O), 1689 (C=O); nmr δ 2.38 (d, 3 protons, J = 1 Hz, =C-CH_3), 4.1 (d, 2 protons, J = 6 Hz, =CHCH_2N), 5-5.5 (m's, 3 protons, C*H*=CH_2), 6.25 (m, 1 proton, =C*H*N), 6.7-7.7 (m's, 10 protons, Ar*H*), 10.6 (broad, 1 proton, N-*H*). Mass m/e (rel intensity) (possible fragmentation mode): 348 (10) (parent ion), 174 (100),





145 (22) (174-CO,H), 105 (20) ($C_6H_5N_2$), 132 (8) (174-NCO), 91 (+) (C_6H_5N), 77 (41) (C_6H_5), 41 (11) (allyl).

Anal. Calcd. for $C_{20}H_{20}N_4O_2$: C, 68.95; H, 5.97; N, 16.08. Found: C, 69.09; H, 5.84; N, 16.03.

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