Reduction of (Diazidomethylene)cyanamide (8) to Dicyandiamide.—Compound **8** was prepared according to the procedure of Hart;[16] mp 42.1–42.9° (lit.[16] mp 40.3°); $\lambda_{max}^{CHCl_3}$ 4.30 (w), 4.52 (sh), 4.63 (s), 6.25 (s), 7.56 (s), 8.90, 9.04 (m), 9.40 μ (w).

Compound **8** was reduced with hydrogen sulfide[14] to give dicyandiamide (75%), which was identified by melting point (210°), mixture melting point (210°) (lit.[26] mp 207–290°), and comparison of its infrared spectrum with that of an authentic sample.

Sodium 5-Azidotetrazole (6) from Cyanogen Azide and Sodium Azide.—*Caution: Sodium 5-azidotetrazole is exceptionally shock sensitive. See footnote 27 before attempting this synthesis.*

Cyanogen azide prepared in acetonitrile (20 ml) from sodium azide (3.25 g, 0.05 mol) and cyanogen chloride (12 g, 0.22 mol) was evacuated to 120 mm and a pot temperature of 25° to remove excess cyanogen chloride. The resulting solution was cooled at 5–10° while sodium azide (3.5 g, 0.05 mol) in water (15 ml) was added dropwise and then stirred at room temperature for 1.5 hr. The resulting solution was diluted with water (20 ml) and extracted with ether (3 × 25 ml). Sodium 5-azidotetrazole (2.65 g, 80%) was isolated from one-half of the aqueous layer as described below and identified by comparison of its infrared spectrum with that of an authentic sample.

Sodium 5-Azidotetrazole (6) from Cyanogen Bromide and Sodium Azide.—To a solution of sodium azide (3.8 g, 0.058 mol) in water (10 ml) at 0–5° was added (15 min) finely pulverized cyanogen bromide (6.8 g, 0.064 mol). The mixture was stirred at 0–5° for 30 min, and the cold solution was then extracted with ether (2 × 15 ml). The water layer was evaporated to dryness at 50° (1 mm). (*Caution:* The product may detonate if pressure is changed rapidly when the product is dry.) The resulting salt was extracted with hot acetone (3 × 25 ml). The extract was concentrated to about 35 ml and ether was added to precipitate **6** (2.56 g, 66%), λ_{max}^{KBr} 4.67, 6.84, 7.09, 8.15, 13.57 (s), 8.45, 8.86, 12.56 (m), 7.49, 8.96, 9.52, 9.82 μ (w).

Anal. Calcd for CN_7Na: C, 9.03; N, 73.70; Na, 17.28. Found: N, 73.61, 73.86; Na, 16.6.

5-Azidotetrazole.—*Caution: This compound is shock sensitive. See footnote 27 before attempting synthesis.*

An aqueous solution of **6** prepared as described above from sodium azide (7.6 g, 0.117 mol) and cyanogen bromide (6.2 g, 0.058 mol) was cooled in ice water and acidified with concentrated hydrochloric acid to pH 1. The solution was extracted with ether (3 × 50 ml), and the ether layer was dried and evaporated to dryness at room temperature under nitrogen to give 5-azidotetrazole (4.2 g, 65%) as white needles which were recrystallized once from chloroform, mp 79.6–80.2° (lit.[29] mp 72–73°), λ_{max}^{KBr} 3.25–4 (broad weak multiple bands), 4.67, 6.30, 7.08, 8.34 (s), 9.65, 12.76,13.78, 14.43 μ (m).

Anal. Calcd for CN_7H: N, 88.29. Found: N, 88.16.

Ammonium-5-azidotetrazole.—An aqueous solution of **6** prepared as described above from cyanogen bromide (6.2 g, 0.059 mol) and sodium azide (7.6 g, 0.117 mol) was acidified to pH 1 and extracted with ether (3 × 50 ml). The dried ether extract was saturated with anhydrous ammonia and filtered to separate pure ammonium-5-azidotetrazole[28] (caution[27]) as a white, crystalline solid (15.2 g, 95%), mp 185–186, λ_{max}^{KBr} 4.63, 6.77, 7.14 (s), 3.62, 3.19, 3.35, 7.03, 8.09, 8.74, 13.15 (m), 8.41, 9.52, 12.67 μ (w).

Anal. Calcd for CH_4N_8: N, 87.51. Found: N, 87.42.

Registry No.—**1**, 764-05-6; **3**, 4027-82-1; **4**, 17167-30-5; **6**, 35038-45-0; 5-azidotetrazole, 35038-46-1; ammonium-5-azidotetrazole, 35038-47-2.

Acknowledgment.—The phosphorus ylides were prepared and characterized by Dr. M. E. Hermes.

(26) E. C. Franklin, *J. Amer. Chem. Soc.*, **44**, 501 (1922).

(27) The explosive properties of sodium 5-azidotetrazole are described by E. Lieber and D. R. Levering, *J. Amer. Chem. Soc.*, **73**, 1313 (1951). The dry salt is extremely sensitive to friction, heat, electrical shock, and pressure. For example, a dry sample of **6** at 1-mm pressure will usually detonate if brought rapidly to atmospheric pressure. Great care and adequate protective equipment (shields, leather gloves, and jacket) should be used when preparing even small quanties of the *dry* compound. Samples larger than 0.1 g are best handled remotely. The salt can be prepared and handled safely in aqueous solution or as a free-flowing solid when moistened with water or mixed with an equal weight of mineral oil. We have prepared acetone solutions without event, but Lieber reports that such solutions containing traces of acetic acid may detonate and in this respect our procedure is safer.

Pure dry 5-azidotetrazole is less sensitive than its sodium salt but the same handling precautions apply. Ammonium-5-azidotetrazole is still less sensitive to shock but detonates when heated rapidly to ~190°.

(28) F. D. Marsh and D. W. Thatcher, U. S. Patent 3,374,188 (1968).

N-Cyanoaziridines and 1-Alkylalkylidenecyanamides from Cyanogen Azide and Olefins

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The reaction of molecular cyanogen azide with hydrocarbon olefins at 0–35° gives 1-alkylalkylidenecyanamides and/or 1-cyanoaziridines in high yields. Evidence is presented favoring a 1,3-dipolar concerted addition of the azide followed by opening of the resulting triazoline to a diazonium zwitterion and loss of nitrogen from this labile species to yield products. Linear and simple cyclic olefins generally produce alkylidenecyanamides as the major product, often to the exclusion of *N*-cyanoaziridines. With selected cyclic olefins this reaction is an effective means of forming either ring-enlarged or ring-contracted product. Ring-enlargement products and aziridines are also formed by reacting cyclic alkylidenecyanamides with diazomethane. The 1-alkylalkylidenecyanamides are readily hydrolyzed to ketones; the cyanogen azide reaction thus permits facile, low-temperature conversion of olefins to ketones. More highly substituted olefins often produce *N*-cyanoaziridines, and these compounds are obtained in high yield from polycyclic olefins such as norbornene and dicyclopentadiene. The *N*-cyanoaziridine produced from norbornene, 3-cyano-3-azatricyclo[4.2.1.$0^{2,4}$]octane, is cleaved with $LiAlH_4$ to the parent aziridine, which is readily converted to 7-aminonorbornane (by hydrolysis and dehalogenation) and *syn*-7-aminonorbornene (by hydrolysis and dehydrochlorination).

Since we reported the synthesis of cyanogen azide (N_3CN) in 1964,[1] two broad areas of chemical reactivity for this highly reactive compound have been defined. We disclosed at that time the facile addition of the molecular azide to olefins accompanied by nitrogen loss and formation of alkylidenecyanamides and *N*-cyanoaziridines. The reaction of cyanogen azide with acetylenes was recently reported[2] to give 1-cyanotriazoles which are in equilibrium with tautomeric α-diazo-*N*-cyanoimines. Other reported reactions of molecular

(1) F. D. Marsh and M. E. Hermes, *J. Amer. Chem. Soc.*, **86**, 4506 (1964); F. D. Marsh, U. S. Patent 3,410,658 (1968).

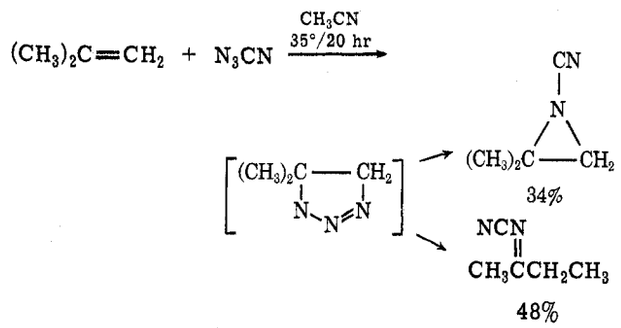
(2) M. E. Hermes and F. D. Marsh, *J. Amer. Chem. Soc.*, **89**, 4760 (1967); F. D. Marsh, U. S. Patent 3,322,782 (1967).

cyanogen azide include addition to norbornadiene[3] and polycyclic enamines.[4]

The second broad area of cyanogen azide chemistry grew from the observation that cyanogen azide decomposes to cyanonitrene[5] and nitrogen under very mild conditions. The nitrene reacts with alkanes to form cyanamides, with aromatics to form azepines, and with cyclooctatetraene, and "dimerizes" to form azodicarbonitrile. This paper will present results of addition of cyanogen azide to over 30 hydrocarbon olefins and discuss the chemistry of *N*-cyanoaziridines and 1-alkylalkyli denecyanamides, which are the products.

Results

Cyanogen azide solutions react with olefinic hydrocarbons within 24 hr at 0–35° to give high conversion to *N*-cyanoaziridines and/or 1-alkylalkylidenecyanamides with loss of nitrogen. Reaction conditions are chosen so that molecular cyanogen azide is the reacting species rather than thermally generated cyanonitrene. The reaction is illustrated for isobutylene.[6]



Cyanogen azide apparently adds exclusively in a single direction to an unsymmetrical olefin. In all cases, the nitrogen bearing the cyano group becomes attached to the more highly substituted olefinic carbon in the Markovnikov fashion.

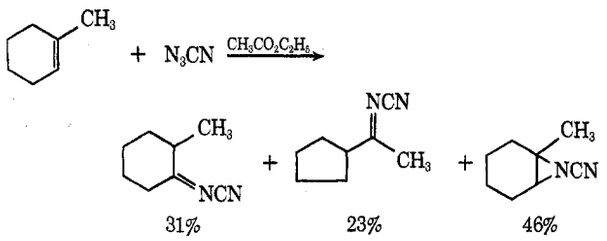
Formation of *N*-cyanoaziridines occurs by nitrogen loss and ring closure, and 1-alkylalkylidenecyanamides arise by rearrangement from the carbon bearing the –NCN group. Table I reports the products from 24 olefins, the yields, the per cent ring closure *vs.* rearrangement, and the structure and properties of alkylidenecyanamides obtained. Table II reports the properties of five *N*-cyanoaziridines obtained from olefins in Table I along with aziridines derived from norbornene, dicyclopentadiene, and tricyclopentadiene. The Experimental Section presents representative synthetic procedures.

The ratio of cyanoaziridine to alkylidenecyanamide varies greatly from olefin to olefin. In general, linear olefins, both terminal and internal, give high yields of alkylidenecyanamide by hydrogen migration, often to the exclusion of cyanoaziridines. Ethylene, propylene, 1-butene, 2-butene, 1-hexene, 1-decene, and 1-dodecene fall into this class. Simple cyclic olefins such as cyclopentene, cyclohexene, and cyclooctene are also converted exclusively to alkylidenecyanamides.

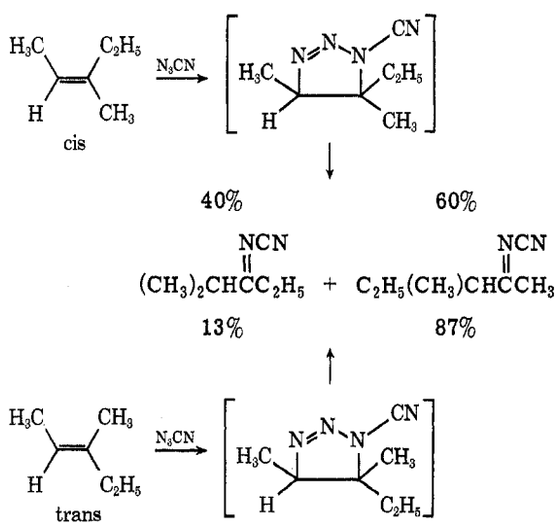
(3) A. G. Anastassiou, *J. Org. Chem.*, **31**, 1131 (1966).
(4) R. M. Scribner, *Tetrahedron Lett.*, **No. 47**, 4737 (1967).
(5) Pertinent references to the chemistry and properties of cyanonitrene are given by F. D. Marsh, *J. Org. Chem.*, **37**, 2966 (1972).
(6) In addition about 1% $(CH_3)_2C{=}NCN$ is formed from isobutylene. This C–C bond fragmentation is a major factor in only one olefin studied (1,1-dicyclopropylethylene).

More highly substituted olefins, particularly those having no hydrogen on the carbon to which the cyano-bearing nitrogen becomes attached, such as isobutylene, 2-methyl-1-butene, 3-methyl-1-butene, 3,3-dimethyl-1-butene, 1-methylcyclopentene, 1-methylcyclohexene, and methylenecyclohexane, often give significant yields of cyanoaziridine along with alkylidenecyanamides.

If two different alkyl groups are present at the carbon to which the –NCN becomes bonded, both may migrate. Thus, 1-methylcyclohexene gives in addition to the *N*-cyanoaziridine two alkylidenecyanamides, one a product of methyl migration, the other formed by methylene migration and ring contraction.



It is not possible to give a strict ordering of migratory aptitudes for the most substituted carbon, although hydrogen migrates to the exclusion of alkyl in all cases studied so far. However, steric factors play a role in determining to what extent each of two alkyl groups will migrate in a particular case. Thus, *cis*- and *trans*-3-methyl-2-pentene, in which methyl and ethyl may migrate, give different product mixtures.



We have studied the reaction of methylenecyclohexane with cyanogen azide in a variety of solvents and have noted a moderate effect on the product ratio (Table III).

Addition of cyanogen azide to the highly reactive double bond in the bicycloheptene system of norbornene, dicyclopentadiene, and tricyclopentadiene results in high yields of the corresponding *N*-cyanoaziridines.

The properties of these aziridines are given in Table II and the spectra are discussed in a later section in connection with proof of structure and chemistry of these compounds.

There are two general procedures for the olefin–cyanogen azide reaction. Cyanogen azide solutions may be combined directly with the olefin, or cyanogen

TABLE I

ALKYLIDENECYANAMIDES FROM OLEFINS AND N_3CN[h]

Olefin	Solvent	Product yield, %	Registry no.[i]	Alkylidene-cyana-mide, %[a]	NCN– on carbon no.	Rearranged group	Bp, °C (mm)	$n^{25}D$
$CH_2=CH_2$	CH_3CN	14		0				
$CH_2=CH_2$	C_6H_6	53	35092-61-6; 35092-62-7	~90[b]	1	H	Amorphous solid	
$CH_2=CHCH_3$	CH_3CN	53	3285-27-6	~90	2	H	30 (0.1)[d]	1.4480
$CH_2=CHCH_2CH_3$	CH_3CN	86[c]	35092-64-9; 35092-65-0	100	2	H	31 (0.3)	1.4532
cis-$CH_3CH=CHCH_3$	CH_3CN	88	35092-64-9; 35092-65-0	100	2	H	35 (0.2)[d]	1.4538
trans-$CH_3CH=CHCH_3$	CH_3CN	78		100	2	H		1.4540
$CH_2=C(CH_3)_2$	CH_3CN	82[c]		59	2	CH_3	30 (0.4)	1.4517[e]
$(CH_3)_2C=CHCH_3$	CH_3CN	88[c]	35095-95-5; 35095-96-6	~85	2	CH_3	30 (0.2)	1.4528
$CH_2=CHCH(CH_3)_2$	CH_3CN	86[c]		~40	2	H	41 (0.35)	
$CH_2=C(CH_3)C_2H_5$	CNCl	65		~80	2	CH_3 ~50[f,j] C_2H_5 ~50[k]	45 (0.005)[d]	1.4514–1.4561
$CH_2=CH(CH_2)_3CH_3$	CNCl	38	35096-00-5; 35147-22-9	100	2	H	46–47 (0.07)	1.4570
$CH_3CH=CH(CH_2)_2CH_3$	CNCl	65	35096-01-6; 35096-02-7	100	2 ~40 3 ~60	H[f]	45 (0.05)	1.4560
$(CH_3)_2C=C(CH_3)_2$	CH_3CN	98	35096-03-8; 35096-04-9	92	2	CH_3	40 (0.05)	1.4570
$H_2C=CHC(CH_3)_3$	CH_3CN	96		74	2	H	34 (0.03)	1.4571
cis-$CH_3CH=C(CH_3)C_2H_5$	CH_3CN	54		100	3	CH_3 40[f,l] C_2H_5 50[m]	33 (5 μ)[d]	1.4576
trans-$CH_3CH=C(CH_3)C_2H_5$	CH_3CN	61		100	3	CH_3 17[f] C_2H_5 83	32 (5 μ)[d]	1.4578
$CH_2=CH(CH_2)_7CN_3$	CH_3CN	44	35096-08-3; 35096-09-4	100	2	H	70–71 (0.4 μ)	
$CH_2(CH_2)_2CH=CH$	CNCl	96	3550-39-8	100	1	H	52–57 (0.05)	1.4944
$CH_2(CH_2)_2CH=CCH_3$[g]	CH_3CN	~100		~65	1	CH_3		
$CH_2(CH_2)_3CH=CH$	CNCl	94	3285-19-6	100	1	H	25–26 (0.2 μ)	1.5025
$CH_2=C(CH_2)_3$	CH_3CN	79		100	1	~CH_2–	62–63.5 (0.05)	1.4937
$CH_2=C(CH_2)_5$	CH_3CN	61	3281-33-2	77	1	–CH_2–	96–103 (1)	
$CH_2(CH_2)_3CH=CCH_3$	EtOAc	79		54	1	CH_3 63[f,n]	69–77 (0.05)	
					1	–CH_2[o] 37		
$CH_2(CH_2)_5CH=CH$	CH_3CN	78	35096-17-4	100	1	H	78–94 (0.4 μ)	1.5113
Bicyclo[2.2.2]octene	EtOAc	~100		94	2	H	Isolated bicyclo[2.2.2]octanone after alumina hydrolysis	

[a] (Aziridine %) = 100 − (alkylidenecyanamide %). [b] Solid material, probably trimeric. [c] Crude, before distillation. [d] Pot temperature in short-path still. [e] Contaminated with aziridine. [f] Isomer mixture. [g] Product analyzed by proton magnetic resonance only. [h] Satisfactory analytical values (±0.4% for C, H, and N) were reported for all compounds except the ethylene adduct: Ed. [i] First registry number is for syn isomer; second is for anti isomer. [j] Registry number: 35095-99-9. [k] Registry numbers: 35095-97-7; 35095-98-8 (anti). [l] Registry numbers: 35096-05-0 (syn); 35096-06-1 (anti). [m] Registry numbers: 35096-07-2 (syn); 35147-23-0 (anti). [n] Registry numbers: 35147-24-1 (syn); 35096-14-1 (anti). [o] Registry numbers: 35096-15-2 (syn); 35096-16-3 (anti).

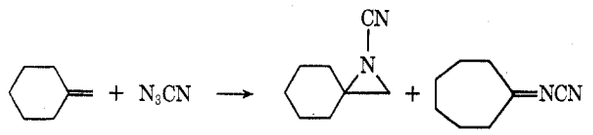
TABLE II

N-CYANOAZIRIDINES[a]

Compd	Bp °C (mm)	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
N-Cyanoaziridine (1)	30–25 (0.2)	52.9	5.9	41.2	51.8	5.9	41.3
2-Methyl-*N*-cyanoaziridine (2)		Polymerized[c]					
2,2-Dimethyl-*N*-cyanoaziridine (3)		62.5	8.4	29.1	62.4	8.3	29.3
2,2-Pentamethylene-*N*-cyanoaziridine (4)		Polymerized					
2-Methyl-2,3-tetramethylene-*N*-cyanoaziridine (5)	55 (5 μ)[b]	70.6	8.9	20.6	69.6	8.9	20.3[c]
3-Cyano-3-azatricyclo-[3.2.1.$0^{2,4}$]octane (6)	72–74 (0.1)	71.6	7.5	20.9	71.6	7.8	20.8
9-Cyano-9-azatetracyclo-[5.3.1.$0^{2,6}$.$0^{8,10}$]-undecene-3 (7)	70[d]	76.6	7.0	16.3	76.7	7.2	16.6
13-Cyano-13-azapentacyclo-[9.3.1.$1^{3,9}$.$0^{4,8}$.$0^{12,14}$]-hexadecene-5 (8)	162–164[d]	80.7	7.6	11.8	79.8	7.4	12.1

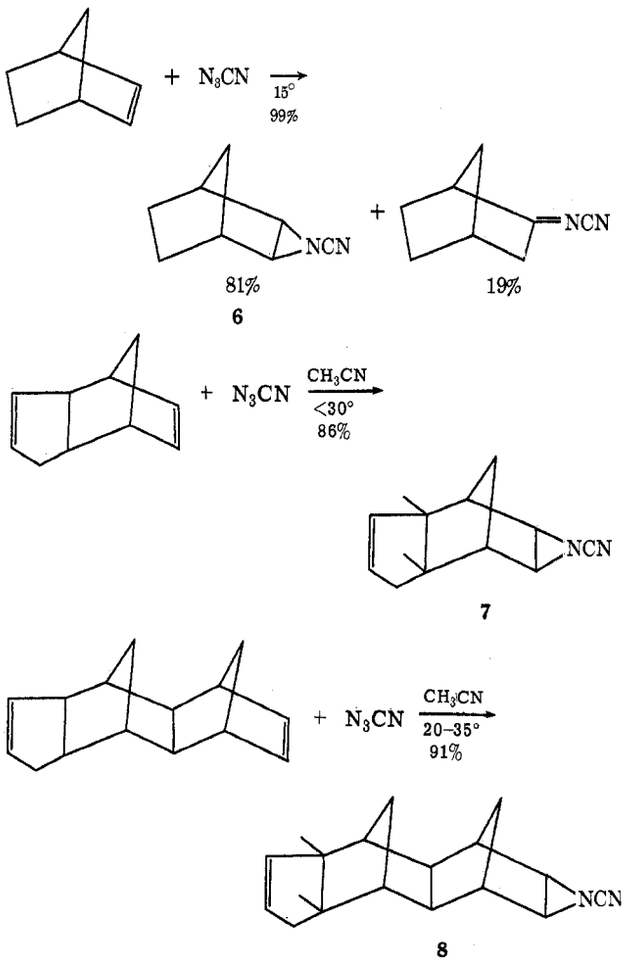
[a] Nmr data are collected in Tables V and VI. [b] Pot temperature of short-path molecular still. [c] Analyses were obtained on isomer mixtures before separation. [d] Melting point.

TABLE III



solvent	%	%
3:1 DMF–ethyl acetate	25	75
Ether	23	77
CH_3CN	30	70
Ethyl acetate	39	61
CH_3OH	48	52
3:1 acetic acid–ethyl acetate	75	25

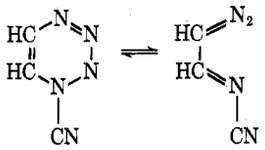
chloride may be added to a mixture of sodium azide and olefin, with or without added solvent. In this latter procedure, cyanogen azide reacts as it is formed. More volatile olefins (<5 C atoms) are best handled in barricaded steel pressure vessels.



Mechanism.—The olefin and cyanogen azide form a cyanotriazoline as the first step, but this unstable triazoline decomposes instantaneously to products with nitrogen evolution by a mechanism believed to involve zwitterionic intermediates.

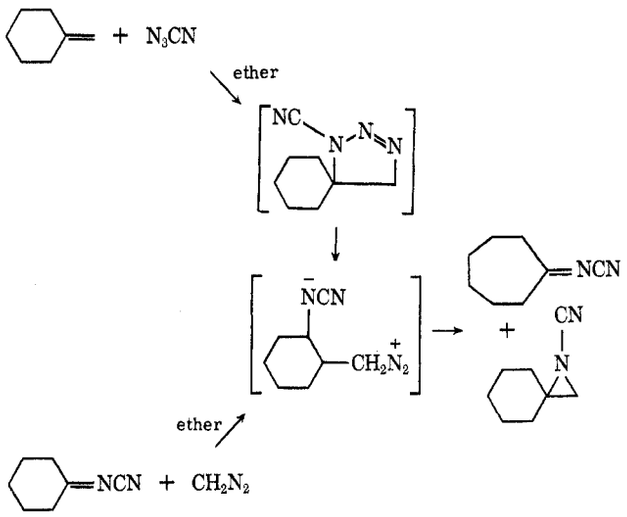
Cyanotriazolines have not been isolated as intermediates, but evidence indicates that the azide–oelfin reaction is a 1,3-dipolar, concerted addition. The evolved nitrogen is a measure of a second-order reaction, first order in each component, over essentially the whole conversion range. In addition, the rate is not greatly dependent on solvent polarity as would be expected for reactions involving highly polar intermediates in the rate-determining step. Table IV shows rate constants obtained from nitrogen evolution data.

In view of the demonstrated lability of 1-cyanotriazoles, prepared from N_3CN and acetylenes, which are in equilibrium with α-diazo-*N*-cyanoimines at room temperature involving heterolytic cleavage of the N-1–N-2 bond,[2] it is not surprising that cyanotriazolines are



unstable. Heterolytic N–N bond cleavage would lead to diazonium betaines, logical precursors of the formed products. Evidence has accumulated that such ionic intermediates are involved, and some description of this evidence is presented below.

A second method of preparing 1-cyanotriazolines was attempted. Addition of diazomethane to 1-methylethylidenecyanamide and to cyclohexylidene cyanamide did not give the expected triazoline; instead, elimination of nitrogen immediately occurred and alkylidenecyanamide and cyanoaziridine products results in ratios similar to those obtained by addition of cyanogen azide to the appropriate olefin. The following reaction path is suggested.



	Aziridine, %	Alkylidene cyanamide, %
N_3CN path	23	77
CH_2N_2 path	29	71

The inability to form stable triazolines by two atomic combinations reinforces the idea that they are unstable with respect to intermediates leading to alkylidene cyanamides and aziridines. Consideration of diazomethane addition mechanisms also indicates that the intermediate may well be the zwitterionic species shown, since such diazomethane reactions have been postulated

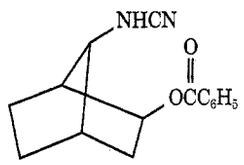
TABLE IV

REPRESENTATIVE CYANOGEN AZIDE–OLEFIN REACTION RATE CONSTANTS AT 25°

Registry no.	Olefin	Solvent	$k \times 10^5$, l. mol^{-1} sec^{-1}
563-79-1	2,3-Dimethyl-2-butene	CH_3CN	2.8
		$C_2H_5O_2CCH_3$	2.0
		$C_6H_5CH_3$	4.9
1192-37-6	Methylenecyclohexane	CH_3CN	8.0
		$CH_3CO_2C_2H_5$	5.3
		$C_6H_5CH_3$	13.7
142-29-0	Cyclopentene	CH_3CN	18.6
108-87-2	1-Methylcyclohexane	CH_3CN	0.63

to proceed by nucleophilic attack on carbon to give ionic intermediates.[7]

A possible ionic intermediate has been intercepted in the N_3CN–norbornene reaction which produces **6** and bicycloheptylidenecyanamide. Cyanogen azide, in the presence of equimolar amounts of norbornene and benzoic acid, produces a reduced yield of **6** and the related cyanamide, in approximately 4:1 ratio, along with 23% of *syn*-7-cyanamido-*exo*-1-norborneol benzoate.



This benzoate, synthesized under conditions under which the normal reaction products are stable, is probably formed by protonation of the diazonium cyanamide, loss of nitrogen, and attack of the benzoate anion at the 7 position of the resulting carbonium ion. The fact that loss of nitrogen occurs to form the *unrearranged* aziridine, rather than rearranged azetidine, indicates that the products may arise from an ion-pair structure.

That the postulated ionic intermediate is not a planar carbonium zwitterion is shown by the addition of N_3CN to *cis*- and *trans*-3-methyl-2-pentene. Generation of different product ratios from the isomeric olefins shows that the intermediates cannot be identical and retain at least some steric integrity throughout the reaction.

The preferred explanation is ring closure or rearrangement with simultaneous nitrogen loss from a diazonium zwitterion.

Properties and Chemistry of Alkylidenecyanamides.—1-Alkylalkylidenecyanamides are high-boiling, unstable oils. Separation and isolation generally involve short-path distillation at low pressure because the compounds easily resinify.

Alkylidenecyanamides absorb strongly at 2200 ± 5 and 1620 ± 10 cm^{-1} and these bands have been assigned to the carbon–nitrogen triple and double bonds. The intensity of the >C=N– band is surprisingly high; it is the strongest band in the spectrum of the crude product mixture from norbornene, even though the product contains only 19% alkylidenecyanamide.

The nmr spectra of 1-methylalkylidenecyanamides reveal syn–anti isomers that interconvert only slowly at room temperature. Table V details the absorbances

TABLE V

NMR OF METHYLALKYLIDENECYANAMIDES

NCN
‖
CH_3CR,[a]

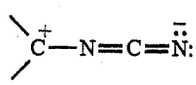
R =	Syn CH_3, τ (%)	Anti CH_3, τ (%)
CH_3	7.59 (50)	7.72 (50)
C_2H_5	7.58 (79–84)	7.71 (16–21)
$(CH_3)_2CH$	7.58 (89)	7.78 (11)
$(CH_3)_3C$	7.58 (100)	(0)

[a] Neat samples.

observed for four of these compounds. 1-Methylethylidenecyanamide (from propylene) exhibits a chemical shift of 0.13 ppm between the two methyl resonances. The deshielded methyl is assigned syn to the cyano group on the basis of its coincidence with the 1-methyl resonance of 1-methyl-2,2-dimethylpropylidenecyanamide (from 2,3-dimethyl-2-butene) in which the bulky *tert*-butyl group determines the geometry and only one methyl resonance is observed.

In intermediate cases in which the methylidenecyanamide group is flanked by a single methyl and an ethyl or isopropyl group, both syn and anti isomers are observed. It is interesting to note that the syn/anti ratios are undoubtedly equilibrium values, since similar ratios are observed in the synthesis of 1-methylpropylidenecyanamide from four different butenes (1-butene, *cis*- and *trans*-2-butene, and isobutylene), in which case four different triazoline intermediates are postulated and the cyano group is directed exclusively adjacent to the methyl in three of them and adjacent to the ethyl in the fourth (1-butene). Similar isomeric ratios were found by Karabatsos for 2,4-dinitrophenylhydrazones, phenylhydrazones, and semicarbazides of methyl ethyl ketone, methyl isopropyl ketone, and methyl *tert*-butyl ketone and substituted *N*-nitrosoamines.[8]

The nmr spectra of the alkylidenecyanamides are temperature dependent. At elevated temperatures, the resonances of 1-methylethylidenecyanamide broaden and begin to coalesce. True coalescence has not been observed, since the compound is temperature sensitive and measurements have been limited to below 90°. This indication of low-temperature isomerization may be explained by the contribution of polar resonance structures to the stabilization of linear transition states.



Shechter has recently reported temperature dependency of alkylidenesulfonamides of similar structure, in which two methyl resonances (2:1 ratio) coalesce to a single line on heating to 140°.[9]

Alkylidenecyanamides are readily converted to the corresponding ketones by dilute aqueous acid or base, or silver nitrate solution.

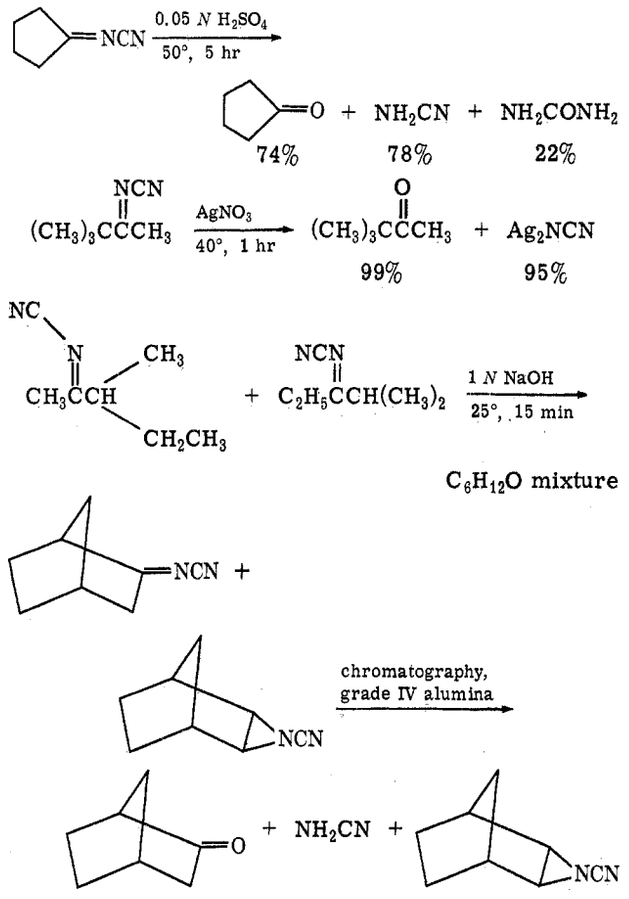
Cyanogen azide thus affords a convenient route from olefin to ketone, and high yields may be obtained using concentrated solutions and simple work-up procedures.

Semicarbazides, oximes, and phenylhydrazones may be obtained directly from alkylidenecyanamides on

(7) P. Kadaba and J. O. Edwards, *J. Org. Chem.*, **26**, 2331 (1961). H. House, E. Grubbs, and W. F. Gannon, *J. Amer. Chem. Soc.*, **82**, 4099 (1960).

(8) G. J. Karabatsos, *et al.*, *ibid.*, **84**, 753 (1962); **85**, 3624 (1963); **86**, 3351 (1964); **86**, 4373 (1964).

(9) R. F. Bleiholder and H. Shechter, *ibid.*, **90**, 2131 (1968).



treatment with standard reagents. Methylalkylidenecyanamides are oxidized with sodium hypoidite (iodoform test). A number of *tert*-alkylcyanamides have been prepared by addition of Grignard reagents to isopropylidenecyanamide.

$$(CH_3)_2C{=}NCN + RMgBr \longrightarrow R(CH_3)_2CNHCN$$

$$R = CH_3,\ C_2H_5,\ C_6H_5$$

Properties and Chemistry of *N*-Cyanoaziridines.—Several *N*-cyanoaziridines[10] have been isolated and purified during this study. Cyanoaziridines are somewhat lower boiling than alkylidenecyanamides formed from the same olefins, and separation can sometimes be achieved by careful distillation. Chromatography of olefin–N_3CN product mixtures on activated neutral alumina has afforded *N*-cyanoaziridine–ketone mixtures from which the pure *N*-cyanoaziridines **2**–**6** have been isolated (Table II). These aziridines show strong C≡N absorption near 2200 cm^{-1} with no C=N at 1640 cm^{-1}. Nmr spectra are consistent with the structures proposed (Table VI).

In all cases the nmr spectra are consistent with rapid inversion about the pyramidal nitrogen, in marked contrast to the spectra of the *N*-chloro analogs of **2** and **3** and the *N*-amino analogs of **1** and **3**, which show slow nitrogen inversion on the nmr time scale up to 120[11] and ~150°, respectively. In fact, the invertomers of the chloro analog of **2** have been isolated by Brois. The rapid nitrogen inversion in *N*-cyanoaziridines as compared to the halo compounds is not surprising in view of the ready thermal isomerization of the alkylidenecyanamides.

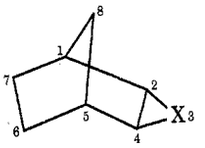
TABLE VI
PROTON MAGNETIC RESONANCE OF SIMPLE CYANOAZIRIDINES (τ)

Compd	$-CH_2N$	CHN	CH_3CN	Others
1	7.53			
2	(6.95 to 7.83; 3 H) (12 line)		8.58 (doublet) (J = 5 cps)	
3	7.66		8.57	
4	7.61			$-(CH_2)_5-$ 8.39 (10 H)
5		7.25 (triplet) (J = 3 cps)	8.44	$-CH_2CN$ 8.05 multiplet (4 H) $-CH_2CH_2-$ 8.55 multiplet (4 H)

The cyanoaziridines **1**–**5** are unstable oils which decompose readily, particularly under basic conditions.

The aziridines **6**, **7**, and **8**, which are the major products formed from norbornene, dicyclopentadiene, and tricyclopentadiene, are much more stable and are readily isolated by distillation or crystallization.

The nmr spectrum of **6** (Table VII lists nmr spectra of several polycyclic aziridines) is similar to those of the norbornene–benzenesulfonyl azide adduct **9**,[12] norbornene oxide (**10**),[13] and 3,3-dichlorotricyclo[3.2.1.$0^{2,4}$]-octane (**11**).[14] In all cases the anti 8 proton is observed



6, X = NCN
9, X = NSO_2Ph
10, X = O
11, X = CCl_2

at τ 9.1–9.4 coupled to the syn proton with $J \cong 10$ cps. The syn 8 proton is generally hidden by ethano bridge absorption. Moore has suggested that this high-field absorption is caused by bending of the methano bridge under steric pressure of the group at position 3 so that the anti H proton is crowded toward the exo protons at C_6 and C_7, thus becoming highly shielded. The syn 8 hydrogen has been identified in two ways. In the dichlorocarbene–norbornene adduct **11**,[14] proximity of the syn 8 hydrogen to the chlorine at C-3 deshields it sufficiently so that it appears at τ 7.85 (downfield from hydrogens at C-2, C-4, C-6, and C-7. In addition, Moore found for **11** and Franz, Osuch, and Dietrich[12c] for **9** and **10** that spectra run in benzene solution[15] show large shifts to higher field for all protons save syn-C-8.

(10) B. R. Balser and T. Neilson, *J. Org. Chem.*, **29**, 1057 (1964), prepared the only previously reported cyanoaziridine, methyl 4,6-*O*-benzylidene-*N*-cyano-2,3-dideoxy-2,3-imino-α-D-allopyranoside.

(11) S. J. Brois, *J. Amer. Chem. Soc.*, **90**, 506, 508 (1968); S. J. Brois, *Tetrahedron Lett.*, 997 (1968).

(12) (a) J. E. Franz and C. Osuch, *Tetrahedron Lett.*, 837 (1963); (b) L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **28**, 3303 (1963); (c) J. E. Franz, C. Osuch, and M. W. Dietrich, *ibid.*, **29**, 2922 (1964).

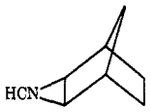
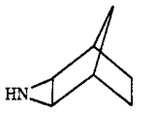
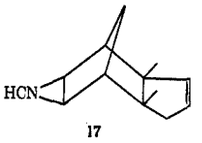
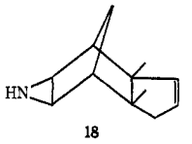
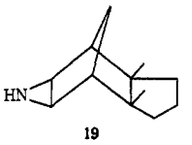
(13) K. Tori, K. Kitahonoki, Y. Takano, H. Tanida, and T. Tsuji, *Tetrahedron Lett.*, 559 (1964).

(14) W. R. Moore, W. R. Moser, and J. E. LaPrade, *J. Org. Chem.*, **28**, 2200 (1963).

(15) P. Laszlo and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **86**, 1171 (1964), have discussed the large solvent effect of benzene on substituted norbornene spectra.

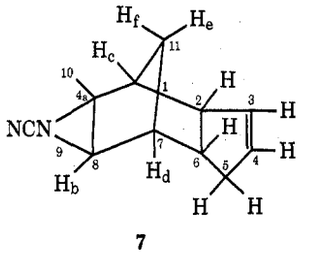
TABLE VII

NMR SPECTRA OF POLYCYCLIC AZIRIDINES (τ)

Compd	HCN	Bridgehead CH	Methano bridge CH	Others
 6	7.0 (2 H)	7.4 (2 H)	Anti, 9.2 doublet J = 10 cps (1 H)	Ethano bridge and anti methano bridge CH 8.4–8.8 (5 H)
 12	8.0 (2 H)	7.6 (2 H)	Anti, 9.3 doublet J = 10 cps (1 H)	Ethano bridge and anti methano bridge CH 8.3–8.7 (5 H)
 17	6.9 doublet J = 5 cps (1 H) 7.2 doublet J = 5 cps (1 H)	6.8 multiplet (1 H)	Anti, 9.1 doublet J = 10 cps (1 H) Syn, 8.5 doublet J = 10 cps (1 H)	Olefinic 4.3 multiplet (2 H) Remainder 6.9–7.9 (5 H)
 18	8.1 doublet J = 5 cps (1 H) 7.8 doublet J = 5 cps (1 H)	6.7 multiplet (1 H) 7.2 multiplet (1 H)	Anti, 9.0 doublet J = 10 cps (1 H) Syn, 8.4 doublet J = 10 cps (1 H)	Olefinic 4.1 singlet (2 H) NH 9.6 (1 H) Remainder 7.3–7.7 (4 H)
 19	7.9 (2 H)	7.7 (2 H)	Anti, 9.2 doublet J = 10 cps (1 H)	NH 10.0 (1 H) CH 7.6 (2 H) Trimethylene bridge } 8.0–8.7 Anti methano CH } (7 H)

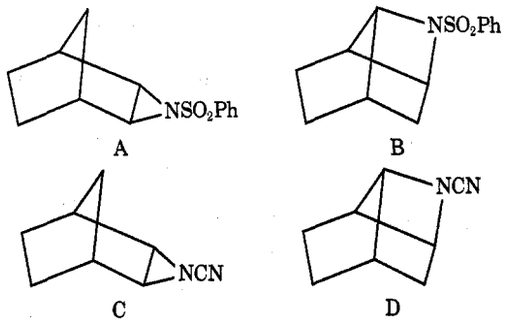
This proton appears as a doublet, $J \cong 10$ cps, split to pentuplets ($J \cong 1$ cps). We have repeated this latter experiment on **6** with similar results.

The nmr spectrum of **7**[16] is similar to that of **6**; however, protons H_a and H_b on the carbon α to nitrogen are chemically shifted because of the asymmetry introduced by the double bond. The bridgehead protons H_c and H_d also are chemically shifted, one at τ 6.8, the other under the peak at τ 6.9–7.9 which contains four other saturated CH. The anti 11 proton is at τ 9.1 (J = 10 cps) and the syn 11 stands clear of other saturated CH at τ 8.5 (J = 10 cps).

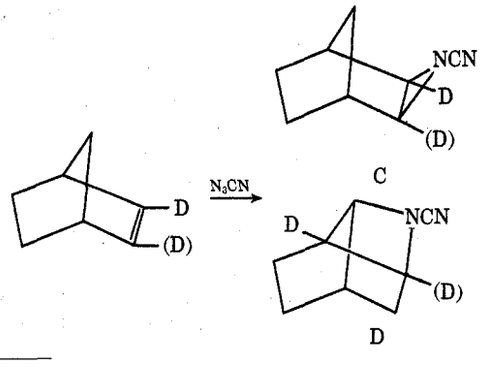


7

It became necessary to prove the structures of **6** and **9** after Zalkow[12b] alleged on the basis of ring-opening reactions that the structure of **9** could best be explained as the azetidine B rather than the aziridine A. Osuch[12c] demonstrated conclusively that **9** is A and we have used a similar method to show that **6** is C rather than D. Norbornene was treated with amylsodium and then deuterium oxide to give norbornene-*2-d*[17] containing 0.9 deuterium per molecule. Deuterated **6** obtained from this compound showed the τ 7.0 peak to be diminished to 1.1 H compared to the bridgehead absorption at τ 7.4 (2.0 H). Rearrangement to D requires one-half of the deuterium to terminate at the bridgehead



A B C D



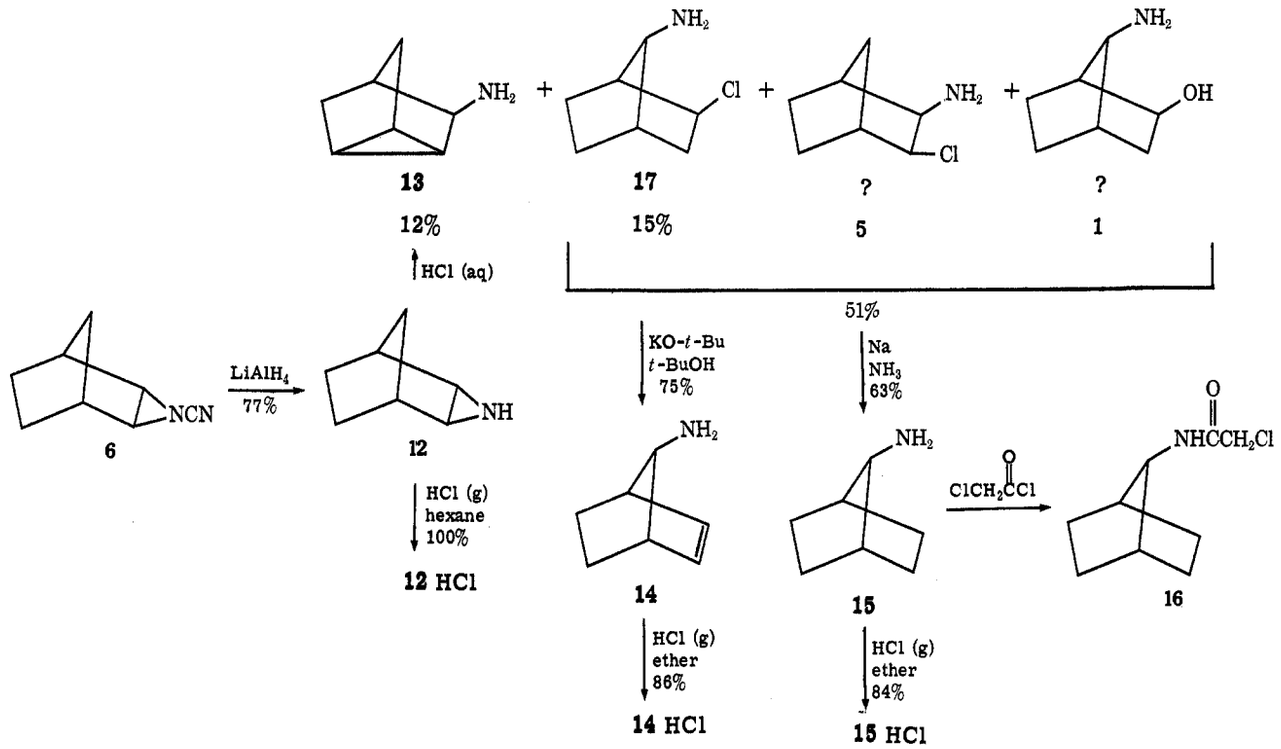
C D

(16) L. H. Zalkow, A. C. Oehlschlager, G. A. Cabat, and R. L. Hale, *Chem. Ind. (London)*, 1556 (1964), have commented briefly on the nmr of the dicyclopentadiene–benzenesulfonyl azide adduct similar to **7**.

(17) R. A. Finnegan and R. S. McNees, *ibid.*, 1450 (1961); *J. Org. Chem.*, **29**, 3234 (1964), have shown that on carbonation of the alkyl sodium–norbornene product only norbornene-2-carboxylic acid results.

CHART I

CHEMISTRY OF 3-CYANO-3-AZATRICYCLO[3.2.1.0^{2,4}]OCTANE (6) AND DERIVATIVES



with the remainder on the carbon α to nitrogen, thus decreasing each of these peaks an equal amount ($\sim$3/4 of their undeuterated intensity). Aziridine formation results in no rearrangement and explains the ratio observed.

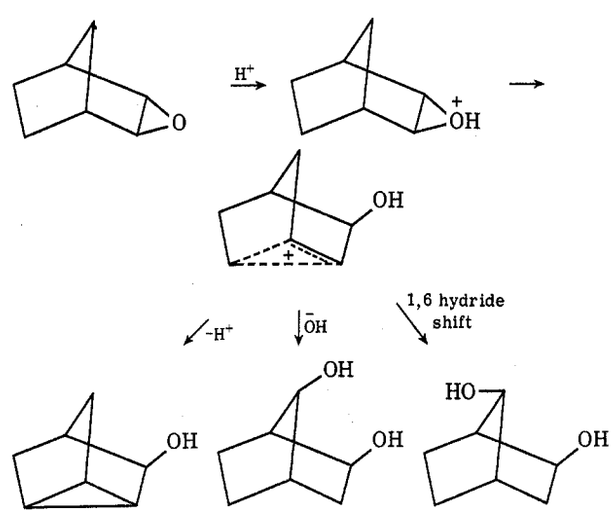
Reduction of **6** with lithium aluminum hydride (Chart I) produces the aziridine **12** in 77% yield.[18] The hydrochloride may be prepared quantitatively from hexane solution. The nmr spectrum of **12** is similar to that of **6**; however, removal of the cyano group causes an upfield shift of the HCN of 1.0 ppm.

Hydrochloric acid hydrolysis of **12** gives at least four amines. Distillation of the product yielded 3-aminonortricyclene (**13**) (containing a minor unsaturated impurity) in 12% yield. The structure of **13** was deduced from elemental analysis, spectra, and comparison with authentic material. Authentic **13** was prepared from nortricyclanone[19] and had identical infrared and nmr spectra with those of **13** obtained from **12**.

The higher boiling fraction from this hydrolysis (41–51%) was shown by gas chromatography to consist of three amines in the ratio 15:5:1. Elemental analysis indicated a chloroamine mixture containing an oxygenated material. The amine mixture was dehydrochlorinated with potassium *tert*-butoxide in 1-butanol at 80°. Only the major component reacted and a 75% yield of *syn*-7-aminonorbornene (**14**) was obtained and converted to the hydrochloride in 86% yield. The nmr and infrared spectra of **14** are identical with the spectra reported for the compound by Tanida, *et al.*[18]

The amine mixture was treated with sodium in liquid ammonia. All components reacted and a 63% yield of 7-aminonorbornane (**15**) contaminated with $\sim$10% of **14** was obtained. Pure **15** was obtained by crystallization of **15** HCl from nitromethane. The structure of **15** was established by analysis, spectra, and conversion to the chloroacetamide **16**.[20] Thus, the major hydrolysis product of the amine **12** appears to be *syn*-7-amino-*exo*-2-chloronorbornane (**17**).

Winstein and Stafford[21] studied hydrolysis of 2,3-epoxynorbornane by perchloric acid. Three products were obtained: nortricyclanol (7%), *syn*-7-*exo*-2-dihydroxynorbornane (51%), and 12% of an isomeric diol formed by 1,6 hydride shift, *anti*-7-*exo*-2-hydroxynorbornane. Hydrolysis of the epoxide with 48% hydrogen bromide led to a 15–20% (isolated) yield of *syn*-7-bromo-*exo*-2-hydroxynorbornane along with several



(18) H. Tanida, T. Tsuji, and T. Irie, *J. Org. Chem.*, **31**, 3941 (1966), prepared **12** by hydrolysis of the carbomethoxyaziridine.

(19) We thank Dr. J. R. Roland of this laboratory for the sample of **13**.

(20) W. R. Boehme, M. L. Graeme, W. G. Scharpf, E. Siegmund, E. Schipper, and M. Tobkes, *J. Med. Pharmacol. Chem.*, **4**, 183 (1961).

(21) E. T. Stafford, Dissertation, University of California at Los Angeles, 1958.

other products not further investigated, although the authors assume that nortricyclanol and *anti*-7-bromo-*exo*-2-hydroxynorbornane are present.

These results are similar to hydrolysis of **12** except for the identity of the second and third components of the high-boiling mixture. It is unlikely that either of the high-boiling materials accompanying **17** is *anti*-7-amino-*exo*-2-chloronorbornane, since simultaneous dehydrohalogenation should occur. A more likely explanation is that the minor of the two is *syn*-7-amino-*exo*-2-hydroxynorbornane (supported by elemental analysis), and the more abundant is probably 2-amino-3-chloronorbornane, which may not dehydrohalogenate under the conditions of the reaction.

Lithium aluminum hydride reduction of **7** produced the aziridine **18** in 93% yield. Reduction of **18** with hydrogen over PtO_2 gave the saturated aziridine **19** in which the hydrogens at C-2 and C-3 are magnetically equivalent, consistent with aziridine rather than azetidine structures for **7**, **18**, and **19** (Table VI).

Experimental Section

Warning.—Cyanogen azide is a hazardous material. It should be handled only in solution. Concentration to give pure material will result in volent detonation by heat or shock.

General Synthetic Methods.—Two procedures have been used for the olefin–cyanogen azide reaction. The first involves synthesis and simultaneous reaction of the azide with the olefin; excess olefin is often used as the reaction medium. Examples of this procedure given are the reactions with isobutylene and cyclopentene. This procedure is a convenient, one-step synthesis of alkylidenecyanamides and aziridines and avoids accumulation of large amounts of the azide.

In the second procedure, cyanogen azide is prepared in a solvent and the olefin is added to the preformed cyanogen azide solution with cooling or heating as dictated by the reactivity of the particular olefin. The procedures for preparation of cyanogen azide solutions are reported by Marsh.[22]

1,2,2-Trimethylpropylidenecyanamide. Reaction of an Olefin with Preformed Cyanogen Azide.—A 500-ml flask equipped with an ice-cooled condenser, magnetic stirrer, dropping funnel, thermometer, nitrogen bubbler, and gas inlet tube was flame dried and cooled to room temperature under nitrogen. The exit of the condenser was attached through a Dry Ice trap to a wet-test meter. Activated sodium azide (32.5 g, 0.5 mol) and dry acetonitrile (200 ml, 156.6 g) were added and the flask was cooled in an ice–salt bath. Cyanogen chloride (97.4 g, 1.58 mol) was distilled into the stirred reaction mixture over 1.75 hr at such a rate as to maintain a reaction temperature between 4 and 18°. When addition was complete, the reaction mixture was allowed to warm slowly to room temperature and pure 2,3-dimethyl-2-butene (88.3 g, 1.05 mol) was added. The mixture was heated at 30–38° for 16 hr, during which time approximately 0.5 mol of nitrogen was liberated. The solution was then cooled to room temperature, diluted with ether (100 ml), and filtered. Removal of the solvent and unreacted olefin from the filtrate at 0.3 mm and room temperature on a rotary evaporator gave a light straw-colored oil (60.65 g, yield 98%). Distillation of this product in a short-path still at 0.2-mm pressure and a pot temperature of 37–38° gave four colorless fractions (60.34 g, yield 97.2%, $n^{25}D$ 1.4568–1.4581).

Infrared and nmr analysis of the combined fractions indicated that the product consisted of 1,2,2-trimethylpropylidenecyanamide (92%) and *N*-cyanotetramethylaziridine (8%). Fractionation of a 31.7-g aliquot of the oil in a 17 in. × 8 mm spinning-band column separated 13 g of pure 1,2,2-trimethylpropylidenecyanamide [bp 36–38° (0.1 mm), $n^{25}D$ 1.4571] having only two unsplit resonance peaks in a 1:3 ratio at τ 7.58 and 8.79.

The lowest boiling fraction boiled very close to the main product and was not obtained in a pure form. Analysis of this fraction by nmr indicated that it contained approximately 18% of *N*-cyanotetramethylaziridine, as indicated by a single unsplit resonance at τ 8.60, and 82% of 1,2,2-trimethylpropylidenecyanamide.

Cyclopentylidenecyanamide. Simultaneous Generation and Use of Cyanogen Azide.—A 300-ml flask equipped with an ice-cooled condenser, gas inlet, nitrogen bubbler, and magnetic stirrer was flame dried and cooled to room temperature under nitrogen. Sodium azide (9.75 g, 0.15 mol) and cyclopentene (23 g) were added and the flssk was cooled in a Dry Ice–acetone bath. Cyanogen chloride (48.8 g, 0.78 mol) was added and the mixture was allowed to warm to reflux temperature (16–18°) and stirred at this temperature for 22 hr, during which time nitrogen was liberated. The reaction mixture was cooled to 10°, diluted with dry ether (50 ml), and filtered under nitrogen. The solvent was removed from the filtrate on a rotary evaporator at 1-mm pressure and 40° to give a clear yellow oil (15.85 g, 98% yield). Distillation of the oil in an acid-washed short-path still gave a colorless product (15.2 g, 94% yield), the main fractions of which had essentially constant refractive indices and melting points (determined by differential thermal analysis). A freezing-point curve showed a melting point of −20°.

Absorption bands in the infrared spectrum at 4.55 (C≡N) and 6.1 μ (>C=N–) and the mass spectrometric pattern were in agreement with the proposed cyclopentylidenecyanamide structure. A complex envelope in the nmr pattern at τ 7.17–7.63 and a second and equal weight complex pattern at τ 7.75–8.2 are in agreement with those expected for the four protons most remote from the functional group and the four protons flanking the CN=CN group.

1-Cyano-2,2-dimethylaziridine and 1-Methylpropylidenecyanamide. Pressure Tube Reaction.—Two 80-ml Hastelloy-lined pressure vessels were charged with 6.5 g (0.1 mol) of sodium azide and 20.3 g (26 ml) of acetonitrile and cooled, and to each was added 12 g (0.20 mol) of cyanogen chloride and 16 g (0.29 mol) of isobutylene. After the tubes were shaken for 20 hr at 35–36°, the contents were removed, combined, and filtered to remove the salt, and the filtrate was evaporated to remove the volatiles. Distillation through a molecular-type still gave a 50% yield of a mixture of 2,2-dimethyl-1-cyanoaziridine and 1-methylpropylidenecyanamide, boiling at a pot temperature of 40–50° (0.25 mm).

In a similar experiment at 26–27°, an 82% yield of the $C_5H_8N_2$ mixture was obtained and was shown by nmr to be 41% of 2,2-dimethyl-1-cyanoaziridine and 59% of 1-methylpropylidenecyanamide.

In a third experiment the isomer mixture was distilled through a 24 in. × 8 mm spinning-band column, and an essentially pure sample of 2,2-dimethyl-1-cyanoaziridine was obtained, bp 24–25° (0.4 mm), $n^{25}D$ 1.4422.

3-Cyano-3-azatricyclo[3.2.1.0^{2,4}]octane (6).—A solution of 50 g (0.54 mol) of norbornene in 100 ml of acetonitrile was added slowly to 0.3 mol of cyanogen azide in 100 ml of acetonitrile. The temperature of the solution was kept below 30° with ice cooling. The theoretical amount of nitrogen was evolved in 1 hr. The mixture was then warmed to 55° for about 15 min to remove excess cyanogen chloride, diluted with acetone (50 ml), and filtered under nitrogen to separate the by-product, sodium chloride. This salt gave a negative test for azide ion with 5% ferric chloride solution. Removal of the solvent and unreacted bicyclo[2.2.1]heptene on a rotary evaporator at 50° (0.3 mm) gave a light straw-colored, mobile oil (39.8 g, 99%) having an infrared spectrum essentially identical with that of the distilled product. Distillation of this product through a short-path still at 0.2 mm pressure gave four fractions (34.4 g, 96%), bp 72–74° (0.1 mm), $n^{25}D$ 1.5142–1.5150. The infrared spectrum of each fraction was essentially identical, showing strong absorptions at 4.52 (CN) and 6.07 μ (C=N).

Nmr analysis of the product shows it to be 81% aziridine **6** and 19% alkylidenecyanamide.

Pure **6** can be obtained as follows. The crude product mixed in ether solution is shaken with 1 *N* NaOH solution, which hydrolyzes the alkylidenecyanamide to norcamphor. The resulting ether solution is dried, solvents are removed, and distillation easily separates the lower boiling ketone from **6**.

Reaction of Cyanogen Azide with Norbornene in the Presence of Benzoic Acid.—A solution containing 0.076 mol of cyanogen azide in 50 ml of acetonitrile was added to a stirred suspension of 12.2 g (0.1 mol) of benzoic acid and 9.4 g (0.1 mol) of norbornene in 100 ml of acetonitrile. External cooling was employed to keep the reaction temperature below 30°. Over a 0.5-hr period 1.89 l. (100%) of nitrogen was evolved. The solvents were evaporated

(22) F. D. Marsh, *J. Org. Chem.*, **37**, 2966 (1972).

and the residual oil was dissolved in ether and extracted with sodium bicarbonate solution until there was no further evolution of carbon dioxide. From the water extracts on acidification was obtained 5.6 g (46%) of benzoic acid. The ether solution was dried over magnesium sulfate and evaporated to give 14.6 g of an oil. On cooling to −20°, a crystalline solid was formed and on treatment with 50 ml of cooled carbon tetrachloride and filtration 4.50 g (23%) of *syn*-7-cyanamido-*exo*-1-norborneol benzoate, mp 105–106°, was obtained.

Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.3; H, 6.3; N, 10.9. Found: C, 69.8; H, 6.4; N, 11.0.

The nmr spectrum of this material (20% in deuterioacetone) showed the aromatic protons (5) at τ 2.4 and 2.9 and showed NH (1) at τ 4.7. A triplet appears at τ 5.5 (1) and a quartet (1) appears at τ 7.0. A multilined band envelope appears at τ 7.85–9.4 (8).

9-Cyano-9-azatetracyclo[5.3.1.0.^{2,6}.0^{8,10}]undec-3-ene (7).—Cyanogen chloride was distilled at 1 g/min into an agitated slurry of 66 g (0.50 mol) of dicyclopentadiene, 32.5 g (0.50 mol) of sodium azide, and 300 ml of acetonitrile. The initial temperature was 25° and the reaction temperature was held below 30° with ice cooling. After 45 g (~0.75 mol) of cyanogen chloride was added, the mixture was allowed to stand for 5 hr, after which 12.4 l. of nitrogen had evolved (99%). The precipitated salt was removed by filtration, and a mixture of 150 ml of alcohol and 150 ml of ammonium chloride solution was added to hydrolyze any alkylidenecyanamides present. After 1 hr, the organic solvents were removed by evacuation and ether was added to the two-phase system (water–product) which remained. The water was removed; the ether solution was extracted with water, sodium bisulfite, and finally water, and was dried over magnesium sulfate; and the ether was removed on a rotating evaporator. Crystalline **7**, 74 g (86%), resulted which was recrystallized from 5:1 hexane–ether, mp 69.8–70.2°. The ir spectrum of this material showed it to be pure aziridine containing no ketones or alkylidenecyanamide.

Distillation of the crude reaction mixture without removing the isomeric alkylidenecyanamides by hydrolysis gave a 66% yield of $C_{10}H_{12}N_2$ isomers, bp 91–105° (1 mm). This mixture probably contains the alkylidenecyanamides formed by addition in both directions to both double bonds.

13-Cyano-13-azapentacyclo[9.3.1.1^{3,9}.0^{4,8}.0^{12,14}]hexadec-5-ene (8).—A solution of 0.15 mol of cyanogen azide in 88 ml of acetonitrile was added to a slurry of 29.7 g (0.15 mol) of tricyclopentadiene in 75 ml of acetonitrile at such a rate that the temperature remained below 35°. After 2 hr, 0.15 mol of nitrogen was evolved. Filtration yielded 29.2 g (82%) of off-white, crystalline **8**, mp 155–160°. Concentration of the acetonitrile solution gave an additional 3.3 g of **8** for a total of 32.5 g (91%). The compound was recrystallized from acetonitrile, mp 162–164°. Infrared and nmr spectra are consistent with the aziridine structure.

Hydrolysis of Cyclopentylidenecyanamide. A. Sulfuric Acid.—Cyclopentylidenecyanamide (5.4 g, 0.05 mol) was added to 25 ml of distilled water and the mixture was acidified with 6 drops of 10% sulfuric acid. The solution was stirred at 45–59° for 5 hr. After standing at room temperature for 16 hr, evaporation of the mixture to dryness under reduced pressure (0.03 mm, 40°) gave 2.35 g of a white, crystalline solid. Extraction of this solid with ether and evaporation of the extract gave crystalline cyanamide (1.65 g, 78.6% yield) which was identified by infrared analysis. An aqueous solution of an aliquot of this material when added to silver nitrate gave a yellow salt which analyzed correctly for silver cyanamide.

Anal. Calcd for CN_2Ag_2: N, 10.95. Found: N, 11.36, 11.44.

The ether-insoluble portion (0.65 g, yield 21.6%) after recrystallization from acetone gave long, white needles (0.55 g) which melted at 131–133.5°. Recrystallization from alcohol and a trace of ether gave pure urea (0.40 g, 13.3% yield) which was identified by melting point (135–136°) and mixture melting point (135–136°) with an authentic sample.

The volatile fraction was extracted with ether in a continuous extractor for 24 hr. The extract was dried over anhydrous magnesium sulfate and filtered, and the ether was removed from the filtrate on an efficient column. There remained 3.1 g (74% yield) of essentially pure cyclopentanone, which was identified by comparison of its infrared spectrum with that of an authentic sample. The 2,4-dinitrophenylhydrazone prepared from an aliquot of this product melted at 145.6–146.2°. A mixture of this product and an authentic sample of the 2,4-dinitrophenylhydrazone of cyclopentanone melted at 145.6–146.5°.

B. Silver Nitrate Solution.—To a flask equipped with a condenser, dropping funnel, magnetic stirrer, and thermometer was added silver nitrate (17.0 g, 0.1 mol) and distilled water (50 ml). When solution was complete, cyclopentylidenecyanamide (5.41 g, 0.05 mol) was added over 5 min. A mild exothermic reaction occurred and a small amount of yellow precipitate formed. Ether (5 ml) was added and the reaction mixture was heated at 40–50° for 20 min and then cooled to room temperature. Addition of ammonium hydroxide (20 ml, 14%) caused additional yellow precipitate to form. The solid product was separated by filtration, washed on a filter with distilled water, and dried over phosphorus pentoxide at 60–70° (0.1 mm) (12.70 g, yield 99.3%) The infrared spectrum of this compound was identical with that of silver cyanamide. The filtrate was extracted with ether on a continuous extractor for 20 hr and the ether layer was dried over anhydrous magnesium sulfate. Separation of the ether on an efficient column gave 4.0 g (95% yield) of cyclopentanone having an infrared spectrum identical with that of a known sample.

***tert*-Butylcyanamide from 1-Methylethylidenecyanamide and Methylmagnesium Bromide.**—A solution containing 0.10 mol of methylmagnesium bromide in 33 ml of ether was slowly added to 8.2 g (0.10 mol) of 1-methylethylidenecyanamide in 100 ml of ether so that the temperature was held below 20°.

The mixture was then added to 250 ml of 2 *N* hydrochloric acid; the ether layer was separated and dried over magnesium sulfate; and the ether was removed. Distillation gave 2.66 g (27%) of *tert*-butylcyanamide, $n^{25}D$ 1.4282, bp 54.5–57° (0.2 mm) [reported[23] bp 62–63° (0.3 mm)].

1-Cyanoaziridine.—An acetonitrile solution (55 ml) containing 13.6 g (0.20 mol) of cyanogen azide was placed in a 240-ml Hastelloy-lined pressure tube which was pressured with 18 g (0.64 mol) of ethylene. The tube was held at 21–27° for 20 hr, during which the internal pressure rose from 480 to 740 psi.

The resulting solution was poured into 500 ml of ether and about 3 g of polymeric material was filtered off. After the filtrate was evaporated to 5.5 g, the residue was distilled through a short-path still at a pot temperature of 30–35° (0.2 mm) to give about 2 g (15%) of 1-cyanoaziridine, a colorless oil.

Infrared analysis of this product showed strong absorptions at 4.50 (−C≡N) and 6.80 and 6.90 μ (−CH_2−) with no absorption at 6.0–6.2 μ characteristic of the >C=N− group and none at 7.2–7.4 μ (−CH_3).

Isolation of 1-Cyano-2-methyl-2,3-tetramethyleneaziridine (5).—A solution of 0.068 mol of cyanogen azide in 40 ml of acetonitrile was added to 9.62 g (0.10 mol) of 1-methylcyclohexene. After 5 days at room temperature 1.21 l. of nitrogen was evolved. After evaporation of the solvent and excess reactant, 7.24 g (79%) of an oil was obtained. Nmr analysis of this crude product as outlined in the discussion showed 46% of 1-cyano-2-methyl-2,3-tetramethyleneaziridine, 31% of 2-methylcyclohexylidenecyanamide, and 23% of 1-methyl-2,2′-tetramethyleneethylidenecyanamide. Analysis was performed on a distilled portion of this mixture.

Five grams of this mixture was dissolved in 25 ml of benzene and chromatographed on grade IV neutral alumina. Elution with benzene gave 3.3 g of a mixture of ketones and aziridine with no alkylidenecyanamide. Distillation gave 0.4 g of **5**, bp 55° (0.5 mm) and 1.1 g of polymeric residue. Elemental analyses and nmr spectra are given in Tables II and V.

3-Azatricyclo[3.2.1.0^{2,4}]octane (12).—A solution of 62 g (0.46 mol) of **6** in ether was added to 9.5 g (0.25 mol) of lithium aluminum hydride in 350 ml of ether over 2 hr. After an additional 0.5 hr with stirring, saturated sodium sulfate solution was added over 0.5 hr until the complexes and excess hydride were decomposed and a creamy white slurry resulted. This mixture was filtered and the solvent was evaporated from the resulting solution on a rotating evaporator.

Simple trap-to-trap distillation of the resulting solution gave 37.2 g (74%) of **12** shown by glc to contain one component.

In another run a 45% yield of **12**, bp 40° (1 mm), was obtained.

Anal. Calcd for $C_7H_{11}N$: C, 77.1; H, 10.1; N, 12.8. Found: C, 77.6, 77.2; H, 10.4, 10.4; N, 12.2, 12.4.

The aziridine **12** in hexane solution is readily converted to the hydrochloride quantitatively by the action of gaseous HCl. (In ether a discrete hydrochloride is not obtained.) The hydro-

(23) E. Schmidt and K. Wamsler, German Patent 1,018,858 (1960); *Chem. Abstr.*, **54**, 5479g (1960).

chloride, mp 148–149°, can be recrystallized from isopropyl alcohol.

Anal. Calcd for $C_7H_{12}ClN$: C, 57.7; H, 8.3; N, 9.6. Found: C, 57.4; H, 8.9; N, 9.7.

Hydrolysis of 12 with Aqueous HCl.—To 43 g (0.30 mol) of **12** was added 100 ml of concentrated hydrochloric acid. The solution was heated briefly to reflux, and then most of the hydrochloric acid was evaporated. To the solution was added ammonium hydroxide until it remained basic, and then the solution was extracted with three 100-ml portions of methylene chloride. This organic material was dried over magnesium sulfate and distilled through a 24-in. spinning-band column to give 5.2 g (12%) of impure nortricyclamine, bp 41–44.5° (10 mm), $n^{25}D$ 1.4868–1.4878.

Anal. Calcd for $C_7H_{11}N$: C, 77.1 H, 10.1, N, 12.8. Found: C, 76.9, 76.5; H, 11.6, 11.4; N, 12.3.

The nmr spectrum of this material was nearly identical with that of an authentic sample.

Continued distillation gave 23.6 g (41%) of a mixture, bp 84–85° (10 mm), $n^{25}D$ 1.5095–1.5108.

Anal. Calcd for $C_7H_{12}ClN$: C, 57.7; H, 8.3; N, 9.6. Found: C, 58.3, 58.3; H, 8.5, 8.6 N, 10.0.

Gas–liquid chromatography of this mixture showed three components present in a ratio approximating 1:5:15.

***syn*-7-Aminonorbornene (14) by Dehydrohalogenation of *exo*-2-Chloro-*syn*-7-aminonorbornane (17).**—A solution of 27 g of the above mixture and 30 g of potassium *tert*-butoxide in 250 ml of *tert*-butyl alcohol was refluxed for 44 hr. Glc indicated at this point that the major component had reacted completely, and the two lesser components were unchanged. The precipitated salt was filtered, the solution was concentrated to a volume of 70 ml, and 200 ml of 10% potassium hydroxide was added. This two-phase system was extracted three times with ether; the ether solution was dried and carefully distilled to give 11.5 g (57%, 75% based on most abundant compound) of *syn*-7-amino-2-norbornene (**14**), bp 49–51° (18 mm), along with 2.5 g of the unreacted portion of the starting materials, bp 73–75° (4 mm).

The amine **14** carbonated readily, and analytical data were determined on the hydrochloride.

Hydrogen chloride was passed into a solution of 3 g (28 mmol) of **14** in 150 ml of ether. The precipitated solid was filtered to give 3.50 g (86%) of hydrochloride.

Recrystallization of 2.5 g of the hydrochloride from 150 ml of boiling nitromethane gave 2.3 g of **14** HCl.

Anal. Calcd for $C_7H_{12}ClN$: C, 57.7; H, 8.3; Cl, 24.4; N, 9.6. Found: C, 57.3, 57.5; H, 8.2, 8.2; Cl, 24.0, 23.8; N, 9.8, 10.0.

The following nmr spectrum of **14** HCl in D_2O was obtained: τ 3.87 (2) olefinic –CH, 5.22 (3) HOD, 6.74 (1) HCN, 6.97 (2) bridgehead, 8–8.3 (2) and 8.9–9.2 (2) ethano bridge.

7-Aminonorbornane (15) and 15·HCl.—To a solution of 11.3 g (0.078 mol) of the hydrolysis mixture containing **17** in 70 ml of liquid ammonia was added sodium metal over 1 hr until a blue color persisted. A precipitate slowly formed during the addition. Ammonium chloride was added until the color faded and the ammonia was then allowed to evaporate.

The solid residue was taken up in potassium hydroxide solution (the amine separated), ether was added, and the ether layer was removed and dried. Glc showed that none of the starting materials survived this reaction.

On distillation, 5.5 g (63%) of oily solid, **15**, bp 95° (77 mm), was obtained. This material reacted readily with carbon dioxide. The nmr spectrum showed the presence of about 10% of the unsaturated amine in this sample.

To a solution of 3.0 g (27 mmol) of **15** in ether was added anhydrous hydrogen chloride. On filtration, 3.34 g (84%) of hydrochloride was obtained. Recrystallization of 2.7 g from 220 ml of 10:1 nitromethane–isopropyl alcohol gave 1.7 g. After a second crystallization, the following was obtained.

Anal. Calcd for $C_7H_{14}ClN$: C, 56.9; H, 9.6; Cl, 24.0; N, 9.5. Found: C, 56.8, 56.9; H, 9.2, 9.4; Cl, 23.9; N, 9.5, 9.7.

Aziridine 18 by $LiAlH_4$ Treatment of 7.—A solution of 83.3 g (0.48 mol) of **7** in 150 ml of ether was added to 20 g of lithium aluminum hydride in 350 ml of ether over 1 hr. The solution was allowed to stand for 1 hr; saturated sodium sulfate was added until the exothermic reaction ceased. The salts were easily filtered from the light-colored ether solution, and, on evaporation of the ether, 65 g (93%) of an oil, **18**, was obtained. (This material may be reduced to **19** without further treatment.)

Distillation at 52–54° (7 μ) through a 2-ft spinning-band column gave 27 g (39%) of impure 9-azatetracyclo[$5.3.1.0^{2,6}.0^{8,10}$]-undec-3-ene (**18**), $n^{23}D$ 1.5428, with extensive decomposition.

Anal. Calcd for $C_{10}H_{13}N$: C, 81.6; H, 8.9; N, 9.5. Found: C, 79.8, 79.8; H, 8.7, 9.1; N, 9.2, 9.3.

9-Azatetracyclo[$5.3.1.0^{2,6}.0^{8,10}$]undecane (19).—A solution of 34.6 g (0.24 mol) of crude **18** in 75 ml of ethanol was hydrogenated for 40 hr at 40 psi using 0.3 g of PtO_2 catalyst. A total of 0.22 mol of hydrogen was absorbed. Distillation of the resulting product gave 26.0 g (74%) of **19**, bp 71–74° (0.2 mm), $n^{25}D$ 1.5191.

Anal. Calcd for $C_{10}H_{15}N$: C, 80.5 H, 10.1; N, 9.4. Found: C, 80.2, 80.5; H, 10.2, 10.2; N, 9.0, 9.1.

Registry No.—**1**, 3285-26-5; **2**, 35092-47-8; **3**, 3285-28-7; **4**, 35092-49-0; **5**, 3281-02-5; **6**, 35092-51-4; **7**, 35092-52-5; **8**, 35092-53-6; **12**, 1121-38-6; **12** HCl, 35092-55-8; **14**, 14173-90-1; **14** HCl, 35092-57-0; **15**, 35092-58-1; **15** HCl, 35092-59-2; **18**, 25129-62-5; **19**, 35092-60-5; *syn*-7-cyanamido-*exo*-1-norborneol benzoate, 35096-18-5.