Reaction of Cyanogen Azide with Norbornadiene

A. G. Anastassiou

Contribution No. 1153 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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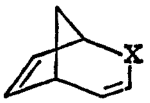
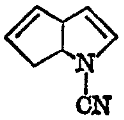
The reaction of cyanogen azide with norbornadiene leads to two major products, N-cyano-2-azabicyclo[3.2.1]-octa-3,6-diene (**1a**) and N-cyano-3-azatricyclo$[3.2.1.0^{2,4\text{-}exo}]$oct-6-ene (**14a**). Mechanisms are discussed.

Reaction and Elucidation of Products.—Cyanogen azide reacts with olefins to afford N-cyanoaziridines and/or alkylidine cyanamides.[1] It has now been found that norbornadiene behaves anomalously in this context. Thus, treatment of a dilute solution of norbornadiene in ethyl acetate with cyanogen azide at *ca.* 0° readily evolved 1 mole equiv of nitrogen. Passage of the crude product through moist alumina[2] followed by distillation afforded a colorless, stable liquid in 69% yield. Vapor phase chromatography (vpc) of this material established the presence of two components, of which the higher boiling constituted 92.8% of the mixture. The lower boiling material of the mixture was isolated by preparative vpc and was identified as the known[3] norbornenone (2). The major component, purified by distillation, has the constitution $C_8H_8N_2$. In the infrared it exhibits strong absorption at 2230 ($C{\equiv}N$) and 1640 cm^{-1} ($C{=}C{-}N$) and in the ultraviolet at 223 mμ (ϵ 4900) and 251 (2800), the latter probably being due to the $-C{=}C{-}N{-}CN$ chromophore. The nmr spectrum, Figure 1A, exhibits signals at τ 3.8 (1 H), 4.2-4.6 (2 H), 4.8 (1 H), 5.7 (1 H), 7.3 (1 H), and 8.3 (2 H), all of which are multiplets. These spectral data are clearly consistent with structures **1a**, **3**, or **4**, the last two being less likely on account of the observed high-field nmr signal.[4]



1a, X = NCN
b, X = NSO$_2$Ph
c, X = CH$_2$



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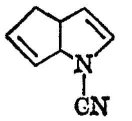

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Definitive evidence that **1a** is indeed the correct structure was obtained as follows. 2-Azabicyclo-[3.2.1]octane (**5**) was prepared by a known procedure, involving the Beckmann rearrangement of norcamphor oxime tosylate (**6**), followed by lithium aluminum hydride reduction of the resulting lactam **7**.[5] The nmr spectrum of the amine is entirely consistent with the proposed structure **5**, exhibiting signals centered at τ 6.6 (1 H), 7.1 (2 H), 7.7 (1 H), 8.2 (8 H), and 8.5 (1 H), the last being due to the N-H proton. Catalytic hydrogenation of **1a** (10% Pd-C, 1500 psi, 65°) afforded a mixture of two compounds. Of these, the component with the lower vpc retention time constituted 72.3% of the mixture and that with the higher retention time (identical with that of **5**) 19.4% of the mixture. Treatment of amine **5** with cyanogen chloride afforded the cyanamide **9**: nmr, τ 6.1 (1 H), 6.7 (2 H), 7.5 (1 H), and 8.2 (8 H). This material, when subjected to conditions employed for the reduction of **1a**, gave a two-component mixture possessing retention times identical with those of the mixture obtained from reduction of **1a**. Furthermore, the two mixtures had essentially identical nmr spectra. These data strongly suggest structures **5** and **8** for the components with the higher and lower vpc retention times, respectively. Finally, treatment of synthetic **5** with benzenesulfonyl chloride gave sulfonamide **10**. The nmr spectrum of this material exhibits multiplets centered at τ 2.2 (5 H), 5.6 (1 H), 6.3 (1 H), 7.2 (1 H), 7.6 (1 H), and 8.5 (8 H). The same benzenesulfonamide (identical nmr, no mixture melting point depression) was obtained from the hydrogenation mixture of **1a** (see Scheme I).

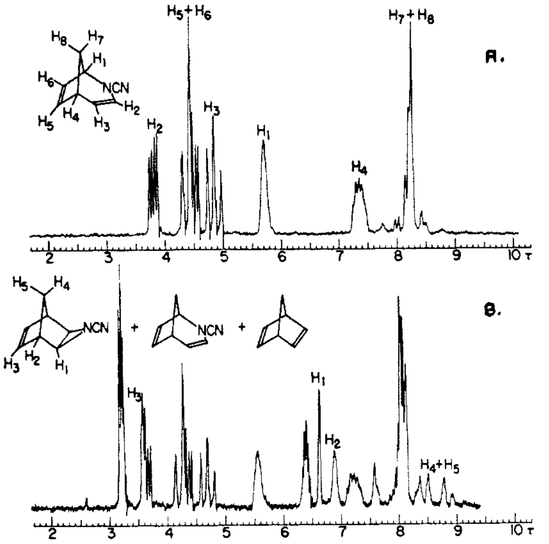

Figure 1.—Nmr spectra of (A) N-cyano-2-azabicyclo[3.2.1]-octa-3,6-diene (neat); and (B) mixture of N-cyano-2-azabicyclo-[3.2.1]octa-3,6-diene (**1a**), N-cyano-3-azatricyclo$[3.2.1.0^{2,4\text{-}exo}]$-oct-6-ene (**14a**), and norbornadiene in CD_3CN (part of the signal at τ 8.1 is due to CH_3CN, and the signal at τ 7.6 is due to solvent impurity).

After this work had been completed, Franz and Osuch[6] reported that reaction of norbornadiene with benzenesulfonyl azide affords what was tentatively formulated as **1b**. The identity (nmr, melting point) of sulfonamide **10**, obtained from synthetic **5**, to the hydrogenation product of **1b**[6] constitutes conclusive evidence for the correctness of structure **1b**. Evidence for structure **1b** has also been obtained recently from the results of a degradative study.[7]

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[1] F. D. Marsh and M. E. Hermes, *J. Am. Chem. Soc.*, **86**, 4506 (1964).

[2] To bring about the hydrolysis of any $-C{=}N{-}CN$ functions. This process did not lead to any rearrangement as indicated by the virtual identity (infrared) of the mixture before and after hydrolysis.

[3] P. D. Bartlett and B. E. Tate, *J. Am. Chem. Soc.*, **78**, 2473 (1956).

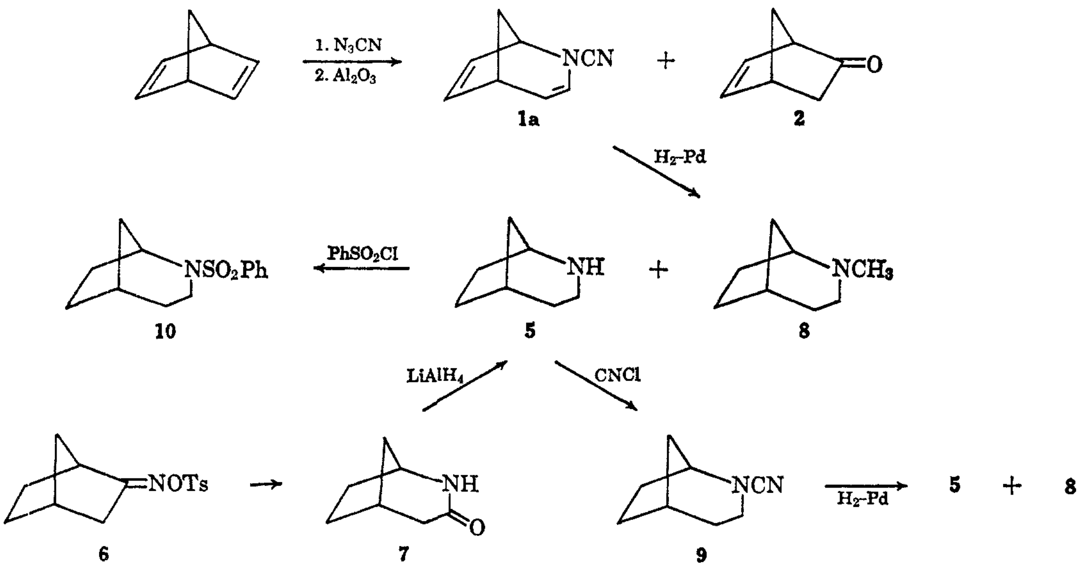
[4] The allylic methylene protons of cyclopentene appear at τ 7.72: K. B. Wiberg and B. J. Nist, *ibid.*, **83**, 1226 (1961).

[5] R. C. Elderfield and E. T. Losin, *J. Org. Chem.*, **26**, 1703 (1961).

[6] J. E. Franz and C. Osuch, *Chem. Ind.* (London), **50**, 2058 (1964).

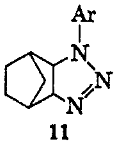
[7] A. C. Oehschlager and L. H. Zalkow, *Chem. Commun.* (London), **4**, 70 (1965).

SCHEME I



Discussion

Aryl azides react with norbornene to yield stable triazolines[8,9] (**11**). Pyrolysis of the triazolines gives, in general, mixtures of aziridines (**12a**) and anils (**13**), whereas photolysis affords predominantly aziridines.[10] On the other hand, no isolable triazolines are formed with azides bearing strongly electron-withdrawing substituents such as cyanogen azide[1,11,12] and benzenesulfonyl azide.[13-16] The aziridines *exo*-**12b** and -**12c** isolated in these cases are presumably formed either by way of an unstable triazoline intermediate[1,11] or directly from the azide.[15]



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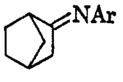
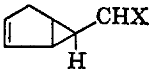
12a, X = NAr
b, X = NSO$_2$Ph
c, X = NCN



13

14a, X = NCN
b, X = NSO$_2$Ph
c, X = O



15a, X = O
b, X = NCN
c, X = CH$_2$

Unlike aziridine **12b**, the unsaturated counterpart *exo*-**14b** is unstable. Thus, when the reaction of benzenesulfonyl azide and norbornadiene was followed by nmr, it was observed[7] that although the initially formed product was *exo*-**14b**, this gradually isomerized to **1b**. At room temperature the conversion to **1b** was complete after 3 days. Similarly per acid epoxidation of norbornadiene gives[17,18] the rearranged aldehyde, *endo*-**15a**, which has recently been shown[19] to arise primarily (>93%) from isomerization of the originally formed labile epoxide, *exo*-**14c**.

In the present study the reaction of cyanogen azide with norbornadiene in CD$_3$CN and in CDCl$_3$ was monitored by nmr at −10°. As norbornadiene was rapidly consumed a complex spectrum developed, Figure 1B. This remained quantitatively the same throughout the consumption of the diene and could be accounted for completely by the presence of two products, **1a** and *exo*-**14a** in a ratio of 64:36 in CD$_3$CN and 47:53 in CDCl$_3$. The portion of the spectrum arising from *exo*-**14a** (multiplet at τ 3.7 (2 H), sharp singlet at τ 6.8 (2 H), multiplet at τ 7.1 (2 H), and an AB quartet ($J \sim 9$ cps) at τ 8.6 (1 H) and τ 9.0 (1 H)) is essentially identical with the spectra reported for the structurally related compounds *exo*-**14b**[16] and *exo*-**14c**.[19] In either acetonitrile or chloroform *exo*-**14a** slowly isomerized to **1a**. In CD$_3$CN, *e.g.*, at −10 to 0°, the ratio of **1a** to *exo*-**14a** in 3 hr changed from 64:36 (at the completion of the reaction) to 75:25 which in turn changed to 83:17 when the mixture was maintained at +10° for 0.5 hr. At room temperature the isomerization was complete in a few minutes. *The appearance of* **1a** *and exo*-**14a** *in a constant ratio throughout the consumption of reactants, coupled with the eventual conversion of exo*-**14a** *to* **1a** *requires that both compounds be primary products.* Furthermore the effect of solvent on the product ratio indicates that the transition state which generates **1a** is more polar than the transition state leading to *exo*-**14a**.

A mechanism accounting for the formation of **1a** directly from norbornadiene as well as from isomerization of *exo*-**14a**, consistent with the observed solvent effect, is as follows (Scheme II): addition of N$_3$CN to the diene gives initially the labile triazoline **16**, which

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(8) P. Scheiner, J. H. Schomaker, S. Deming, W. J. Libbey, and G. P. Nowack, *J. Am. Chem. Soc.*, **87**, 306 (1965).

(9) Thermally labile triazolines have also been obtained from ethyl azidoformate and norbornene,[10] and from phosphoryl azides and norbornene [K. D. Berlin and L. A. Wilson, *Chem. Commun.* (London), **13**, 280 (1965)].

(10) P. Scheiner, *J. Org. Chem.*, **30**, 7 (1965).

(11) F. D. Marsh, M. E. Hermes, and H. E. Simmons, to be published.

(12) A. G. Anastassiou, H. E. Simmons, and F. D. Marsh, *J. Am. Chem. Soc.*, **87**, 2296 (1965).

(13) J. E. Franz and C. Osuch, *Tetrahedron Letters*, **No. 13**, 837 (1963).

(14) L. H. Zalkow and A. C. Oehlschlager, *J. Org. Chem.*, **28**, 3303 (1963).

(15) J. E. Franz, C. Osuch, and M. W. Dietrich, *ibid.*, **29**, 2922 (1964).

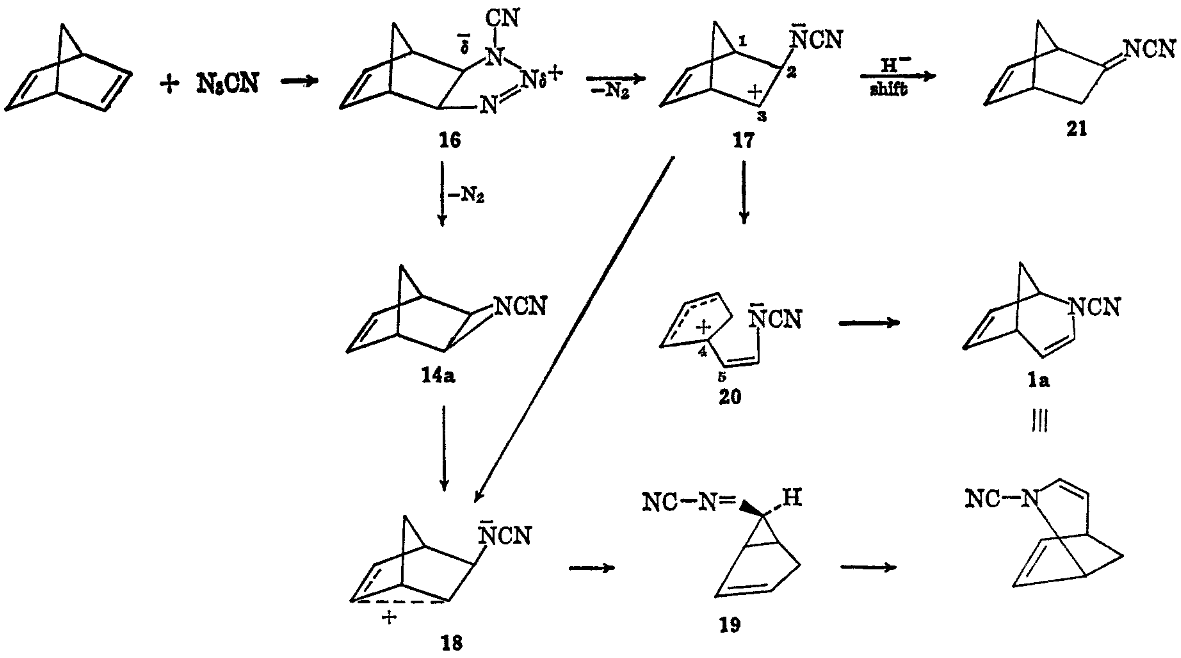
(16) L. H. Zalkow, A. C. Oehlschlager, G. A. Cabat, and R. L. Hale, *Chem. Ind.* (London), **36**, 1556 (1964).

(17) J. Meinwald, S. S. Labana, and M. S. Chadha, *J. Am. Chem. Soc.*, **85**, 582 (1963).

(18) J. T. Lumb and G. H. Whitham, *J. Chem. Soc.*, 1189 (1964).

(19) J. Meinwald, S. S. Labana, L. L. Labana, and G. H. Wahl, Jr., *Tetrahedron Letters*, **No. 23**, 1789 (1965).

Scheme II



fragments to nitrogen, *exo*-**14a**, the "hot" carbonium[20] ion **17**, and the mesomeric carbonium ion **18**. Aziridine *exo*-**14a** is then converted, possibly *via* **18**, to **19**, which possesses the correct stereochemistry for ready isomerization to **1a**. The formation of **19** from *exo*-**14a** is in keeping with the known conversion[19] of epoxide *exo*-**14c** to aldehyde *endo*-**15a**, and the skeletal arrangement of **19** to **1a** derives analogy from the recently reported thermal isomerization[21] (*ca.* 25°) of **15c** to **1c**. The direct formation of **1a** is envisioned to occur from the nonmesomeric ion **17** by way of **20**. Here the rupture of the 1,2 bond in **17** is aided by the incipient formation of a stable cyclopentenyl cation in **20** akin to that involved in the solvolysis of *syn*-7-norbornenyl tosylate.[22] Within the frame of the present mechanisms the absence of **4** in the products implies that rotation about the 4,5 bond in **20** is inhibited, possibly because of partial bonding between the -N̄CN function and the positive site nearest to it. The alkylidene cyanamide **21** is shown to form from the "hot" ion **17** *via* an *endo* C-2 to *endo* C-3 hydride shift. This process ought to occur fairly rapidly in **17** which, unlike the mesomeric ion **18**, does not impose any stringent steric requirements to the migration. However, it should be noted that structure **21** has not been established unequivocally since the assignment is based solely on the presence of norbornenone (**2**) in the hydrolyzed mixture. This could conceivably be a rearranged hydrolysis product of an isomer of **21**.[23]

Experimental Section[24]

Reaction of Cyanogen Azide with Norbornadiene.—To a rapidly stirred solution of norbornadiene (35 ml) in ethyl acetate (1200 ml) was added a solution of cyanogen azide[1] (*ca.* 4.2 g) in ethyl acetate (100 ml) over a 4-hr period. The temperature of the mixture was maintained at 0–5° with the aid of an ice–salt bath throughout the addition. After stirring at the same temperature overnight, the suspension was filtered, and the filtrate was concentrated at water-aspirator pressure and *ca.* 50° to an orange oil. This was dissolved in ether, and the resulting solution was passed through a 1 m × 2 cm chromatography column packed with 100 g of activity IV Woelm neutral alumina. Concentration of the ether eluates (*ca.* 500 ml) through a 50-cm Vigreux column at a bath temperature of *ca.* 50° and atmospheric pressure afforded 8.7 g of a residual, yellow, mobile oil. Vpc analysis of this material under conditions A[24] indicated the presence of two components which constituted 6.1 (1.5 min) and 92.8% (9.3 min) of the mixture. Distillation gave 5.39 g (69%) of a colorless mobile liquid, bp 62–72° (0.27–0.34 mm), which aside from the forerun (0.57 g) containing *ca.* 30% of ketone **2**, was essentially pure **1a**. An analytically pure sample of **1a** was obtained from a heart fraction: bp 67° (0.29 mm); $\nu_{\max}^{\text{neat}}$ strong absorption at 2230 and 1640 cm^{-1}; $\lambda_{\max}^{\text{isooctane}}$ 251 mμ (ϵ 2800) and 223 mμ (ϵ 4900); nmr (neat), multiplets centered at τ 3.8 (1 H), 4.2–4.6 (2 H), 4.8 (1 H), 5.7 (1 H), 7.3 (1 H), and 8.3 (2 H); mass spectrum, parent ion at *m/e* 132.

Anal. Calcd for $C_8H_8N_2$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.34; H, 6.29; N, 21.20.

The component with the lowest retention time (**2**) was isolated pure, from the forerun, by preparative vpc under conditions A:[24] $\nu_{\max}^{\text{neat}}$ 1745 cm^{-1}; nmr ($CDCl_3$), multiplets centered at τ 3.6 (1 H), 4.1 (1 H), 7.1 (1 H), 7.4 (1 H), 8.3 (2 H), and 8.5 (2 H); mass spectrum, parent ion at *m/e* 108.

Anal. Calcd for C_7H_8O: C, 77.75; H, 7.46. Found: C, 77.81; H, 7.52.

Catalytic Hydrogenation of N-Cyano-2-azabicyclo[3.2.1]octa-3,6-diene (1a).—A mixture of **1a** (6.0 g) and 10% palladium on charcoal (3.0 g) in 50 ml of tetrahydrofuran was shaken under a hydrogen pressure of 1500 psi at 65° for 20 hr. The catalyst was removed by filtration, and the colorless filtrate was treated with excess concentrated hydrochloric acid and concentrated under reduced pressure to a hygroscopic, white solid (6.5 g,

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(20) The formation of both "hot" and mesomeric carbonium ions is in keeping with current views concerning nitrous acid deaminations of bicyclic aliphatic amines: see, *e.g.*, J. A. Berson, "Molecular Rearrangements," Part 1, P. DeMayo, Ed., Interscience Publishers, Inc., New York, N. Y., 1963, Chapter 3.

(21) J. M. Brown, *Chem. Commun.* (London), **11**, 226 (1965).

(22) S. Winstein and E. T. Stafford, *J. Am. Chem. Soc.*, **79**, 505 (1957).

(23) If such an isomer is in fact formed, it is probably not *exo*-**14a**, which should have ample time to isomerize to **1a** prior to hydrolysis. **1a** is stable to the conditions of hydrolysis.

(24) Boiling points and melting points are uncorrected. The vpc results were obtained under the following conditions: A, a Burrall K-D temperature-programmed (75–250° in 20 min.) instrument equipped with a 2 ft × 0.25 in. stainless steel column packed with 20% Versamide 900 on Gas Chromosorb Z. The vaporizer was at 230°, and the carrier gas was helium at a flow rate of 115 cc/min; B, a Perkin-Elmer 154-B instrument equipped with a 2 m × 0.25 in. stainless steel column packed with 20% tetrakis(hydroxyethyl)ethylenediamine (THEED) on 60–80 mesh Chromosorb W (*not* acid-washed) at 119° with the vaporizer at 180°. Helium was used as the carrier gas at a flow rate of 110 cc/min.

TABLE I

RELATIVE AMOUNTS OF NORBORNADIENE, **1a**, AND *exo*-**14a** IN CD_3CN AS A FUNCTION OF TIME AND TEMPERATURE

		Compn^a			
Time, min	Temp °C	[A]	[B]	[C]	[C]/[B]
0^b	−10	56	17	27	1.6
5	−10	50	18	32	1.8
11	−10	44	20	36	1.8
16	−10	42	22	40	1.6
26	−10	38	22	40	1.8
46	−10	35	23	42	1.8
67	−10	30	24	46	1.9
92	−10	30	23	47	2.0
156	−10	29	21	50	2.4
193	−10	30	19	51	2.6
214	−10	29	20	51	2.5
0^b	0	29	19	52	2.7
4	0	29	18	53	2.9
20	0	28	18	54	3.0
0^b	10	30	16	54	3.4
5	10	29	15	56	3.7
9	10	29	13	58	4.5
25	10	29	12	59	4.9
0^b	30	28	6	66	11.0
5	30	30	4	66	16.5
10	30	30	~0	~70	

[a] A = norbornadiene, B = *exo*-**14a**, and C = **1a**. [b] Arbitrary starting point.

88%).[25] This was dissolved in water (30 ml), the aqueous solution made strongly basic with potassium hydroxide and extracted with two 30-ml portions of ether, and the ether extract dried over potassium hydroxide pellets. Concentration of the dry extracts under reduced pressure (*ca.* 10 mm) afforded a mobile liquid (3.95 g, 69%).[25] Vpc analysis of this material, under conditions B,[24] indicated the presence of two components which amounted to 72.3 (4.1 min) and 19.4% (11.2 min) of the mixture. The nmr spectrum ($CDCl_3$) of the mixture exhibits a complex array of peaks between τ 6.8 and 8.9 with a sharp methyl signal at τ 7.8.

The benzenesulfonamide **10** was prepared in the usual way[26] and was recrystallized from slightly wet ethanol to give colorless plates: mp 74–76°; nmr ($CDCl_3$), signals centered at τ 2.3 (5 H), 5.6 (1 H), 6.2 (1 H, double doublet, J = 6.0 cps), 7.2 (1 H, double triplet, J = 11.5 cps), 7.6 (1 H), and 8.4 (8 H).

Preparation of 2-Azabicyclo[3.2.1]octane (5).—The hydrochloride of **5** was prepared by a known procedure.[5] A 3.8-g sample of this material was dissolved in 20 ml of water, the resulting solution was made strongly basic with potassium hydroxide pellets and extracted with ether (25 ml), and the extracts were dried over potassium hydroxide pellets. Evaporation of the ether at *ca.* 20 mm gave 2.33 g of a semisolid which under vpc conditions B[24] had a retention time of 10.9 min. Sublimation of this material with a bath temperature of *ca.* 150° and 125 mm pressure afforded a white sublimate (1.8 g): nmr ($CDCl_3$), τ 6.6 (1 H), 7.1 (2 H), 7.7 (1 H), 8.2 (8 H), and 8.5 (1 H). Upon addition of D_2O the sharp signal at τ 8.5 disappeared: mass spectrum, parent ion at *m/e* 111.

TABLE II

RELATIVE AMOUNTS OF NONBORNADIENE, **1a**, AND *exo*-**14a** IN $CDCl_3$ AS A FUNCTION OF TIME AND TEMPERATURE

		Compn^a			
Time, min	Temp, °C	[A]	[B]	[C]	[C]/[B]
0^b	−10	68	17	15	0.9
60	−10	68	17	15	0.9
105	−10	67	17	16	0.9
0^b	0	65	16	19	1.2
16	0	65	16	19	1.2
0^b	10	66	15	19	1.3
5	10	65	14	21	1.5
22	10	65	13	22	1.7
32	10	66	12	22	1.8
0^b	20	66	10	24	2.4
6	20	65	8	27	3.5
22	20	65	5	30	6.0
0	30	65	3	32	10.6
7	30	65	2	33	16.5
21	30	65	~0	~35	

[a] A = norbornadiene, B = *exo*-**14a**, and C = **1a**. [b] Arbitrary starting point.

Anal. Calcd for $C_7H_{13}N$: C, 75.61; H, 11.79; N, 12.60. Found: C, 74.96; H, 11.68; N, 12.01.

The benzensulfonamide of **5** (mp 75–77°) had an nmr spectrum identical with that of the sulfonamide obtained from the hydrogenation mixture of **1a**. Admixture of the two samples did not depress the melting point.

Anal. Calcd for $C_{13}H_{17}NO_2S$: C, 62.12; H, 6.82; N, 5.58. Found: C, 62.09; H, 6.92; N, 5.45.

Reaction of 5 with Cyanogen Chloride. Hydrogenation of the Product.—Cyanogen chloride (10 ml) was passed through a stirred mixture of amine **5** (1.4 g), ether (10 ml), and 50% aqueous sodium hydroxide solution (3 ml) cooled in an ice bath. The temperature of the mixture was not allowed to rise above 20° throughout the addition which lasted *ca.* 0.5 hr. After stirring for an additional 3 hr at room temperature, ether (20 ml) was added, and the organic layer separated and dried over Drierite. Removal of the ether under reduced pressure afforded **9** as a low-melting solid (1.24 g, 74%): nmr ($CDCl_3$), signals centered at τ 6.1 (1 H), 6.7 (2 H), 7.5 (1 H), and 8.2 (8 H).

A mixture of **9** (1.0 g) and 10% palladium on charcoal (1.0 g) in tetrahydrofuran (40 ml) was shaken under a hydrogen pressure of 1500 psi at 65° for 15 hr. The mixtures of hydrochlorides (1.4 g) and free amines (0.5 g, 67%)[25] were obtained by a procedure similar to that described for the hydrogenation of **1a**. Vpc analysis of the amine mixture (conditions B[24]) indicated two products which amounted to 79.8 (4.1 min) and 5.5% (11.1 min) of the mixture. The nmr spectrum of this mixture was qualitatively the same as that displayed by the amine mixture from reduction of **1a**.

Nmr Study of the Reaction of N_3CN with Norbornadiene.—Solutions of cyanogen azide in CD_3CN (*ca.* 20%) and in $CDCl_3$ (*ca.* 20%) were mixed with a slight excess of norbornadiene in separate nmr tubes at *ca.* −30°. The nmr spectra of these mixtures at −10° are characterized by signals due to norbornadiene, **1a**, and *exo*-**14a** [multiplet at τ 3.7 (2 H), singlet at τ 6.8 (2 H), multiplet at τ 7.1 (2 H), and an AB quartet ($J \sim$ 9 cps) at τ 8.6 (1 H) and τ 9.0 (1 H)]. The progress of the reaction as determined from the nmr spectra of the mixtures at various time intervals is shown in Tables I and II.

Acknowledgment.—The author is indebted to Mrs. Adah Richmond for the vpc determinations.

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(25) This value was calculated on the assumption that the sole product is the methylamine **8**.

(26) See, for example, R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p 227.