pellets for 5 hours and was then distilled. Storage was over barium oxide. Commercial triethylamine (Eastman Kodak Co.) was allowed to reflux for 2 hours over *p*-toluenesulfonyl chloride and was then distilled.

Rate Measurements.—All solvolysis rates were measured in dry acetic acid at 50.0 ± 0.1° using the sealed ampoule technique. At appropriate time intervals an ampoule was cooled to room temperature and broken; a 5-ml. aliquot was removed and quenched in 10 ml. of dioxane. Titration was against *ca.* 0.02 *M* sodium acetate in acetic acid. Modified methyl orange served as the indicator. A typical kinetic run is reproduced as Table III.

Glacial acetic acid (J. T. Baker analyzed reagent), whose water content was determined by titration against Karl Fischer reagent, was heated under reflux for 24 hours with 105% of the theoretical amount of acetic anhydride. Distillation furnished acetic acid whose water content had been reduced to less than 60 mg. per liter and which was considered dry.

Acknowledgment.—This work was supported in part by a grant from the Army Research Office (Durham) and this assistance is gratefully acknowledged. R. A. S. also wishes to acknowledge many fruitful and stimulating discussions of this and related subjects with Professor H. C. Brown of this department.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF BOSTON UNIVERSITY, BOSTON 15, MASS.]

Reactions of Active Nitrogen with Organic Substrates. I. The Monomeric Products of the Reaction with 1,3-Butadiene

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RECEIVED NOVEMBER 3, 1961

The reaction of active nitrogen with 1,3-butadiene yields important amounts of pyrrole and *cis*- and *trans*-crotononitriles which can be rationalized as resulting from addition of a nitrogen atom and loss of a hydrogen atom. Other products arise from degradative processes and include *cis*- and *trans*-1-cyano-1,3-butadiene, 3-cyano-1-butene, two nitriles tentatively identified as *cis*- and *trans*-1-cyanopentene-3, ethylene, acetylene, propylene and hydrogen cyanide, the most abundant product. A substantial quantity of polymeric material of composition approximating $(C_4H_6N)_x$ is also formed. The small dependence of the relative yields of monomeric (*i.e.*, C_4N, C_5N and C_6N) products on partial pressures of reactants suggests that they are all formed *via* the same nitrogenous intermediate. Mechanistic speculations consistent with the data are offered.

The reactions of active nitrogen with organic compounds have been studied extensively by Winkler and his co-workers.[2] With many aliphatic hydrocarbons, hydrogen cyanide is the major nitrogenous product and in some cases is the only one reported. Herron, Franklin and Bradt[3] observed the formation of nitriles, in relatively small yields, from the reaction of active nitrogen with acetylenes and propylene. The reaction with aromatic hydrocarbons has been reported to give[4] other nitrogenous products in addition to hydrogen cyanide. However, the products in the latter two cases seemed degradative in nature, *i.e.*, formed through the disruption of the organic reactants. Despite extensive study of the reaction of active nitrogen with organic compounds, little evidence of non-degradative products has been reported. It seemed, however, that, if reactions leading to such products could be found, they should provide valuable information as to the mode of interaction between active nitrogen and organic reactants. Thus, the present study has been directed toward exploring the possibility that active nitrogen reacts under suitable circumstances to yield relatively simple products without fragmentation of the carbon skeleton of the substrate and toward elucidating chemical mechanisms for such processes.

Initial experiments were concerned with an observation which Howard and Hilbert[5] recorded, without providing experimental details, that with isoprene as a substrate, "a nitrogenous low boiling liquid in good yield and generating ammonia on hydrolysis was produced." Repetition of this experiment yielded a product similar to that described by Howard and Hilbert, but gas chromatographic analysis revealed that it is a very complex mixture. Infrared analysis of the major fraction, separated gas chromatographically, indicated the formation of a nitrile and a pyrrole derivative, both non-degradative products.[1] This result encouraged exploration of the reaction of active nitrogen with substances related structurally to isoprene, *i.e.*, conjugated dienes; 1,3-butadiene was chosen as initial substrate because it was anticipated that products would be simplest and easiest to identify.

Results

The gas phase reaction of active nitrogen with 1,3-butadiene was carried out at room temperature in a conventional Pyrex flow system, the walls of which were not poisoned. The unpoisoned system was used to avoid reactions with or induced by the poisoning agents. Active nitrogen was produced by applying a microwave discharge to a highly purified nitrogen flow at pressures of 1 to 3 mm. In a few experiments a condensed discharge was employed. The results were essentially the same regardless of the means of producing active nitrogen (*cf.* Table I). The microwave discharge was employed for most of the work because it gives a cleaner and more stable system than does the condensed discharge.

The active nitrogen thus formed was allowed to react at ambient temperature with a stream of 1,3-

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[1] For a preliminary communication see A. Tsukamoto and N. N. Lichtin, *J. Am. Chem. Soc.*, **82**, 3798 (1960).

[2] For summary see H. G. V. Evans, G. Freeman and C. A. Winkler, *Can. J. Chem.*, **34**, 1271 (1956).

[3] J. T. Herron, J. L. Franklin and P. Bradt, *ibid.*, **37**, 597 (1959).

[4] P. M. Aronovich and B. M. Mikhailov, *Bull. Acad. Sci. USSR*, *Div. Chem. Sci.*, 544 (1956); P. M. Aronovich, N. Y. Belsky and B. M. Mikhailov, *ibid.*, 711 (1956).

[5] L. B. Howard and C. G. Hilbert, *J. Am. Chem. Soc.*, **60**, 1918 (1938).

butadiene about 30 cm. downstream from the discharge zone. The reaction is exothermic and warmed the reactor exterior to *ca.* 50–60°. The products were separated into two fractions by collection in two sets of traps, the first cooled at −78° and the second at −196°. The fraction collected in the second set (herein called degradative product) was mainly hydrogen cyanide and unreacted butadiene. The contents of the first trap were further separated into two fractions by trap to trap distillation. The relatively volatile products (herein called monomeric products) were distilled into a receiver and analyzed gas chromatographically. The residue which remained undistilled in the trap (herein called polymeric product) was isolated by dissolution in methylene chloride under an atmosphere of nitrogen.

Analysis by gas chromatography (*cf.* Fig. 1) revealed some 20 components in the monomeric products. However only six of these are responsible for 75% of the area under the chromatogram peaks. Eleven components are responsible for about 95% of the area. The products were separated by gas chromatography on Carbowax 20M and each was examined by infrared spectroscopy. The spectra obtained were identified by comparison with those of authentic specimens where these were available. In this manner, the following monomeric products were identified: pyrrole, *cis*- and *trans*-crotononitrile, *cis*- and *trans*-1-cyano-1,3-butadiene, 3-cyano-1-butene and two unsaturated nitriles (not conjugated) of six carbons. The distribution of the monomeric products is presented in Table I.

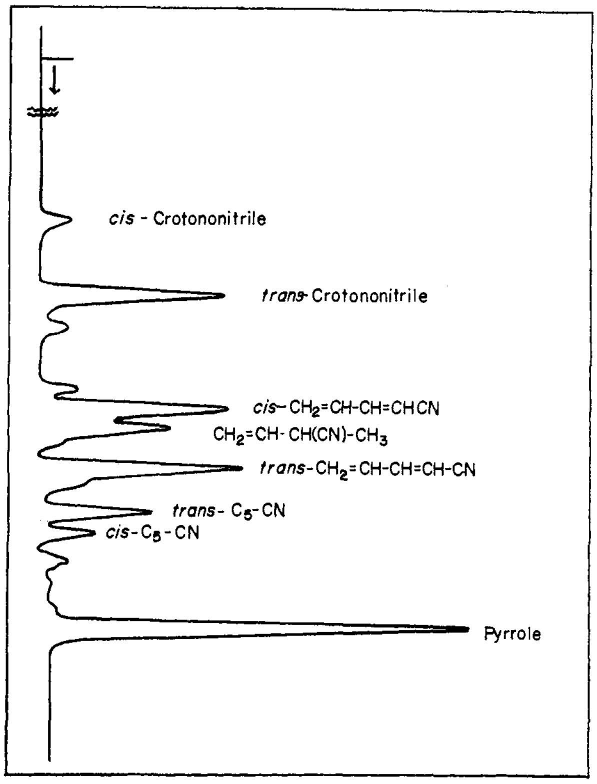

Fig. 1.—Gas chromatogram on Carbowax 20M of monomeric products from reaction of butadiene-1,3 with active nitrogen.

TABLE I

DISTRIBUTION OF CHROMATOGRAM PEAK AREAS OF MONOMERIC PRODUCTS[a]

	Reaction condition[b] 1	2	3
Pyrrole, %	28	26	24
cis-Crotononitrile, %	3	2	2
trans-Crotononitrile, %	15	10	8
cis-1-Cyanobutadiene-1,3, %	9	11	10
trans-1-Cyanobutadiene-1,3, %	10	12	13
3-Cyanobutene-1, %	7	12	10
cis-C_6–CN, %	3	4	4
trans-C_5–CN, %	6	9	8
	81	86	79

[a] The total peak areas for monomeric products are normalized to 100%. The percentage given is the average of at least 3 runs and the relative reproducibility is ±15%. [b] Condition 1, condensed discharge, total pressure 1 mm. ratio of butadiene to active nitrogen *ca.* 5, molecular nitrogen flow rate 4.0×10^{-5} mole/sec., linear flow rate 2.3 meters sec., average atomic nitrogen flow rate 1.8×10^{-6} mole/sec. Condition 2, microwave discharge, total pressure 3 mm., ratio of butadiene to active nitrogen *ca.* 5, molecular nitrogen flow rate 3.9×10^{-4} mole/sec., linear flow rate 7.5 meters/sec., atomic nitrogen flow rate 2×10^{-6} mole/sec. Condition 3, same as 2 except ratio of butadiene to active nitrogen *ca.* 0.8.

Elementary analysis of the polymeric product revealed that carbon, hydrogen and nitrogen are present in a ratio corresponding to the formula C_4H_6N. The complexity of its infrared spectrum suggests that the polymeric material is a mixture. This conclusion is supported by preliminary fractionation studies.

In addition to hydrogen cyanide and recovered butadiene the second set of traps contained other compounds, the investigation of which is in progress. Three of these products, separated by gas chromatography on silica gel and identified by comparison of their infrared spectra with those of authentic samples are ethylene, acetylene and propylene in the ratio[6] of 1:1:4.

The relative yield of each fraction was roughly determined for condition 2 of Table I and was also related to the amount of atomic nitrogen applied. The atomic nitrogen concentration was estimated by the gas phase emission titration method using nitric oxide.[7] About 40% of the active nitrogen applied was found to be converted into the nitrogenous products reported above. Of this, 30% was hydrogen cyanide and about 5% each was in the monomeric and polymeric products, respectively.

Discussion

In recent years the species present in active nitrogen have been studied by many workers.[8] It is established that ground state, ^4S, atomic nitrogen is the major species constituting active nitrogen. On the basis of chemical behavior,

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(6) Absolute total yield of the degradative products has not been established precisely as yet. The molar ratio of other components to hydrogen cyanide is in the neighborhood of $^1/_2$.

(7) P. Harteck, G. Manella and R. R. Reeves, *J. Chem. Phys.*, **29**, 608 (1958).

(8) For a summary, see K. R. Jennings and J. W. Linnett, *Quart. Revs.*, **12**, 16 (1958).

Winkler[9] and Bayes[10] have pointed out the importance of excited nitrogen molecules in the $A^3\Sigma$ state for some reactions. This species is continuously formed as a transient product of gas phase recombination of atomic nitrogen in the presence of a third body. However, the reactions of excited molecular species with hydrocarbons are considered to be negligible[9] and only atomic nitrogen is assumed to be responsible for the reaction of the system studied here. Thus the reaction with 1,3-butadiene is interpreted herein as a reaction of ground state atomic nitrogen.

The formation of products from reaction with active nitrogen without disruption of organic substrates has rarely been reported and may have been overlooked. In the present experiment a significant portion of the nitrogen was fixed in undisrupted organic molecules while about 75% of the active nitrogen reacted was fixed in hydrogen cyanide. The formation of pyrrole and of crotononitrile corresponds to introduction of one nitrogen atom and expulsion of one hydrogen atom, but the detailed mechanism of the reaction is not illuminated by the data. This type of reaction may also occur in the reaction of active nitrogen and olefins. The formation of acrylonitrile has been reported in the reaction of active nitrogen with propylene.[2] This can be interpreted in a related fashion as resulting from introduction of N and loss of H and H_2.

The formation of *cis*- and *trans*-1-cyano-1,3-butadiene and 3-cyano-1-butene corresponds to the addition of a cyano group to 1,3-butadiene and loss or gain, respectively, of a hydrogen atom. If addition of CN radical occurs, this radical must be formed from the degradative reaction of butadiene and nitrogen atoms. The formation of cyanogen radicals is suggested by the purple reaction flame observed. The formation of cyanoacetylene from active nitrogen–acetylene reaction has been explained as a cyanogen radical reaction.[3] Unfortunately little is known about the reactions of these radicals. Such knowledge would undoubtedly facilitate understanding of active nitrogen reactions.

The designation of two products as C_5CN is based on retention times, infrared spectra and the exclusion by a process of elimination of C_4CN structures. The spectral data indicate an isolated non-terminal double bond and a straight chain structure. The structures for the two C_5CN products suggested in Fig. 2, where the several postulated reactions are summarized, assume 1,4-addition of CH_2CN and H but the data are equally consistent with $\Delta^{2,3}$-isomers.

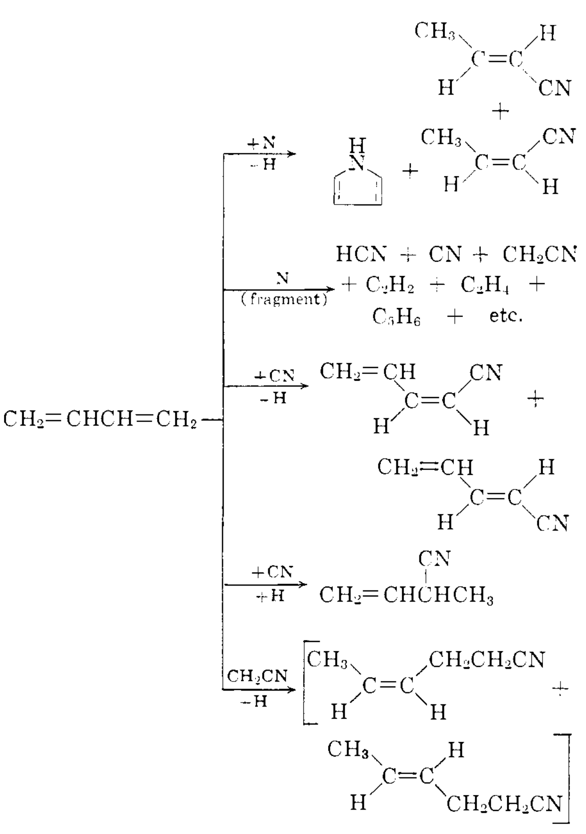

Fig 2.—Postulated reactions.

The most curious aspect of the data of Table I is the near constancy of the distribution of the products as reaction conditions vary. The substantial lack of dependence on mode of generation of atomic nitrogen is in agreement with observations of many other workers. The lack of dependence on partial pressures of reactants is surprising, however, since some of the products retain the carbon content of only one C_4H_6 molecule whereas others are derived from at least two substrate molecules. Table II summarizes the range of variation of initial concentration of the reactants.

TABLE II

PARTIAL PRESSURES IN MM. OF REACTANTS UNDER VARIOUS CONDITIONS

Condition	N_2	N	C_4H_6
1	1	0.05[a]	0.25
2	3	.015[b]	.075
3	3	.015[b]	.012

[a] Formed by condensed discharge. [b] Formed by microwave discharge.

It is, of course, only possible to speculate about the reason for this insensitivity of monomeric product ratios to initial concentrations. The data can be accommodated by the assumption that the kinetic order in all reactants is the same for formation of each product. One model meeting this condition involves product formation in competing unimolecular decompositions of an initial unstable complex of butadiene and nitrogen atom. Such a complex would have to incorporate two butadiene units in order to account for the C_4CN and C_5CN products. Equation 1 represents a view of this model which conserves spin[11] in the first step. It is possible to write specific modes of decomposition of I, not involving formation of CN and CH_2CN radicals, to account for each product. Equation 1 postulates a termolecular reaction involving molecules present at low concentrations which

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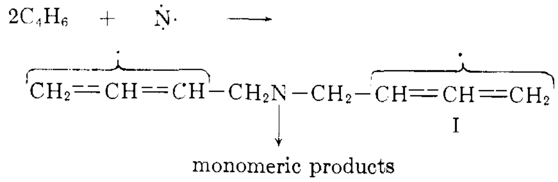
[9] G. R. Freeman and C. A. Winkler, *J. Phys. Chem.*, **59**, 371 (1955); R. Kelly and C. A. Winkler, *Can. J. Chem.*, **38**, 2514 (1960); G. J. Verbeke and C. A. Winkler, *J. Phys. Chem.*, **64**, 319 (1960).

[10] K. D. Bayes, *Can. J. Chem.*, **39**, 1074 (1961).

[11] *Cf.* K. J. Laidler and K. E. Shuler, *Chem. Revs.*, **48**, 153 (1951).



$$\mathrm{2C_4H_6 + \dot{N}\cdot \longrightarrow \overbrace{CH_2{=}CH{=}CH}^{\cdot}{-}CH_2N{-}CH_2{-}\overbrace{CH{=}CH{=}CH_2}^{\cdot}}\quad \text{I} \qquad (1)$$

$$\downarrow$$

monomeric products

perhaps could not compete with the homogeneous recombination of nitrogen atoms[3], $N + N + N_2 \rightarrow N_2^* + N_2$. The ratio of recombination of nitrogen atoms to their incorporation in monomeric product (*ca.* 12 under condition 2) is, however, not sufficiently different from the ratio of $(N_2)(N)^2/(N)(C_4H_6)^2$ (*ca.* 8 under condition 2) employed in these experiments to exclude this possibility, if it is assumed that reaction is approximately diffusion controlled in both cases.

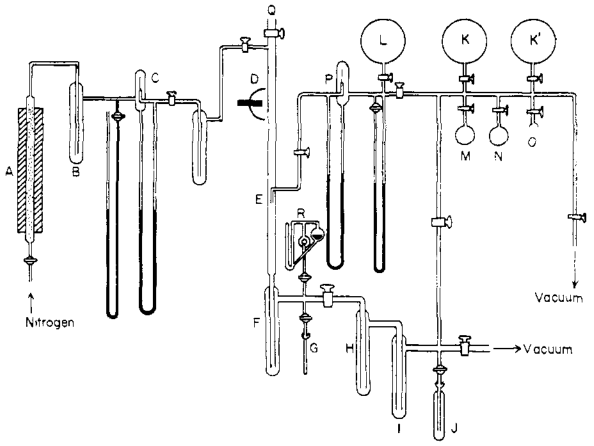


Fig. 3.—Schematic diagram of reaction apparatus.

Equations 2–5 represent one version of a reaction scheme, consistent with the data, which assumes formation of CN and CH_2CN radicals. Reaction 2 may represent formation of more than one type of radical of composition C_4H_6N and 3 represents a family of unimolecular decompositions

$$\mathrm{C_4H_6 + N \xrightarrow{k_2} C_4H_6N}\ [\text{doublet(s)}] \qquad (2)$$

$$\mathrm{C_4H_6N \xrightarrow{k_3}}\ \text{pyrrole} + \text{crotononitriles} + \mathrm{H} + \cdot\mathrm{CN} + \cdot\mathrm{CH_2CN} + \text{etc.} \qquad (3)$$

$$\mathrm{C_4H_6 + \cdot CN \xrightarrow[\pm H]{k_4} C_4CN}\ \text{products} \qquad (4)$$

$$\mathrm{C_4H_6 + \cdot CH_2CN \xrightarrow[+H]{k_5} C_5CN}\ \text{products} \qquad (5)$$

of the species C_4H_6N. If 2, a spin forbidden reaction, or a set of such reactions of identical order, is sufficiently slow compared to 3, 4 and 5, then it is the rate-determining step for formation of all the monomeric products. Their ratio is determined by the relative abundance of the various species C_4H_6N and the relative rates of the several unimolecular reactions, 3. For this to be possible, k_4 and k_5 must be much larger than k_2 so that C_4H_6 will react with $\cdot CN$ and $\cdot CH_2CN$ in preference to the more abundant nitrogen atoms. Since both 4 and 5 represent sequences of spin allowed reactions and 2, 4 and 5 are all exothermic, the requirement k_4 and $k_5 >> k_2$ is reasonable. Further detailing of mechanism of formation of monomeric products is not warranted by the data.

It is also worth noting that the ratio weight of HCN/weight of monomeric products falls in the range 1.4 ± 0.35 for conditions 1, 2 and 3 with little evidence of a systematic trend. Perhaps HCN is also formed directly in reaction 3.

The nature of the degradative products reported herein does not give much information about their mode of formation. There is little or no product derived from hydrogenation (*i.e.*, butenes) and radical coupling (*i.e.*, ethane). Formation of propylene in relatively high yield suggests the possibility of its one-step formation along with ·CN in reaction 3. Much work on degradative products remains to be done.

The efficiency of fixation of nitrogen was rather low, about 40% of the total atomic nitrogen applied (under condition 2), as estimated by nitric oxide titration, appearing in isolated products. Although the accuracy of this method is still in question,[9] the suspected error is only about 20% and is not crucial in this work. The present low efficiency indicates either reactant catalyzed recombination of atomic nitrogen[12] or that the reaction of the latter with butadiene is slow enough that normal recombination competes with it.

The composition of the polymeric material is noteworthy. It can be formulated as $(C_4H_6N)_x$,[13] which corresponds to the introduction of a nitrogen atom into the butadiene molecule followed by polymerization of this species. The reaction leading to the polymeric material is, undoubtedly, not so simple and it must be emphasized that the polymer is not a single substance. The composition of the polymer, however, remained the same when the flow rate of butadiene was changed, suggesting that it is not a mixture of a butadiene polymer and a nitrogenous polymer. Further consideration of the polymer must await its fractionation and characterization.

Acknowledgment.—This work was carried out largely under Contract AF 49(638)-2 with the Air Force of Office of Scientific Research and, in part, with support of Grant No. 702A of the Petroleum Research Fund, administered by the American Chemical Society.

Experimental

Apparatus.—The apparatus shown in Fig. 3 was used in these studies. The nitrogen (Matheson, prepurified grade, 99.996%) was conducted from the tank through copper furnace A, maintained at 450–500°, to remove traces of oxygen, and then through liquid nitrogen cooled trap B, capillary flow meter C and the discharge zone, a 20-mm. i.d. Pyrex tube. The electrical discharge was produced by a microwave generator (Raytheon, model KV-104 (NB), 2450 Mc., output 125 watts) with the tip of a Raytheon type A radiator placed 5 mm. from the tubing at D. About 30 cm. downstream the reactant was introduced through a 1-mm. i.d. jet, E. The first trap, F, was placed about 30 cm. downstream from the reaction zone. A small sampling tube, G, was attached to the system by a ball joint. The products collected in the first trap at −78° were distilled

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[12] W. Forst, H. G. V. Evans and C. A. Winkler, *J. Phys. Chem.*, **61**, 320 (1957).

[13] The analytical results showed that the polymeric material contains about 4% of oxygen and 4% of undetermined material while the rest constitutes C_4H_6N.

into this tube which was then sealed off *in vacuo*. The two -196° traps, H and I, and removable trap J were placed between trap F and a pump (Welch, model 1402). The organic reactant reservoir consisted of two 2-liter bulbs, K and K′, while the 2-liter bulb, L, served as the nitric oxide reservoir. There were also two removable traps M and N and a gas inlet, O. The reactant was led into the reaction zone through a capillary type flowmeter from the gas reservoir system.

Materials.—1,3-Butadiene was C.P. Grade (Matheson), further purified by distillation, discarding the first and the last tenth. It was degassed in the gas storage system.

Reaction Procedure.—The entire system except for the trap M containing butadiene at -196° was evacuated to below 10^{-4} mm. by using a mercury diffusion pump overnight. After closing off the reactant storage system, nitrogen was allowed to flow through the system at the desired flow rate by controlling the stopcock after flow meter C while the nitrogen purification furnace was heated to 450° and trap B was cooled at -196°. The pressure of the system and the nitrogen flow rate were interrelated; at flow rates of 3.9×10^{-4} and 4.0×10^{-5} mole/sec. the system pressure was 3.0 and 1.0 mm., respectively. After the nitrogen was allowed to flow for 30 minutes with the discharge on, traps F, H and I were cooled and 1,3-butadiene was introduced into the gas stream at the desired flow rate. Prior to the introduction of the reactant, trap M was brought to -23° by carbon tetrachloride slush and was maintained at this temperature throughout the reaction to keep the vapor pressure of liquid butadiene in the storage system constant. The reaction was carried out in most cases for 3 hours. After this reaction time the discharge was shut off and the reactant flow and then the flow of nitrogen were stopped. A few minutes after the pressure of the system reached 10^{-2} mm., or below, the stopcocks before the pump and between traps F and H were closed. The Dry Ice-bath was transferred from trap F to the evacuated sample tube G and kept there overnight with G open to trap F. Tube G was then sealed off and the collected product weighed and stored for analysis. The contents of traps H and I were expanded into a known volume and the pressure recorded. An aliquot of this gaseous product was collected and analyzed by gas chromatography. The rest of the product was collected at -196° in removable trap J, which was then removed. Cold aqueous ammonia was introduced into the trap and the contents were analyzed for hydrogen cyanide by Liebig's method.[14]

The brown material which was left in trap F was collected, after the monomeric products were removed, by dissolution in 10 ml. of methylene chloride under a nitrogen atmosphere. The resulting solution was transferred into a small flask under a nitrogen atmosphere and solvent was removed under vacuum. Failure to degas the solvent presumably resulted in incorporation of oxygen in the polymer.

Several runs were carried out with active nitrogen produced by a condensed discharge (at 1 mm.). In this case the discharge tube with two aluminum electrodes was placed between flowmeter C and trap F, and the reaction was carried out in the same manner as above.

Discharge Behavior.—A condensed discharge was used almost exclusively as the active nitrogen source by Winkler and his co-workers.[2] Although a condensed discharge was used initially in this work, difficulties were found, particularly in maintaining a constant output of active nitrogen. The system was not poisoned and it appeared that the yield of active nitrogen was strongly affected by the condition of the wall of the discharge tube and impurities in the nitrogen stream. When the system was carefully freed of impurities and the nitrogen was well purified, the yield of active nitrogen decreased with time of discharge. When a small amount of water was continuously introduced into the nitrogen stream, the yield of active nitrogen was at least doubled and the decrease in active nitrogen production with time was not observed. Molecular oxygen had the same effect but helium or xenon did not. These complications and the pulsed production of active nitrogen were considered undesirable for systematic investigation. The microwave discharge, in contrast, was found stable throughout reaction times as long as 6 hours with carefully purified nitrogen. The concentration of active nitrogen was 0.10 ± 0.01 atom/molecule of N_2 in the reaction zone at a pressure of 3 mm. If impurities were present in the nitrogen stream, the production of active nitrogen by a microwave discharge became very erratic.

Estimation of Atomic Nitrogen Concentration.—The method used is based upon the reaction of nitric oxide with atomic nitrogen. It was originally proposed by Kistiakowsky and Volpi[15] and later applied for the estimation of atomic nitrogen concentration by Harteck and his co-workers.[7] Our procedure was essentially the same as that reported by Harteck. The titration was performed before a run, after the system was conditioned well, and repeated at least twice to check the reproducibility. Generally, the results, with visual determination of the end-point, agreed within 5%.

Gas Chromatographic Analysis.—A temperature programmed F and M model 500 was used. A preliminary search for an appropriate column material to separate the monomeric products showed that Carbowax 20M is the best of a group which includes D,C-silicone oil 710, Apiezon L, didecyl phthalate, paraffin oil, silicone gum rubber and tricresyl phosphate. An 8-ft. Carbowax 20M column was mainly used for the analysis of 1–5-microliter aliquots of the monomeric products, *i.e.*, to establish relative areas of the peaks for all components. Silica gel was used as column material for analysis of the degradative products.

Fifty to one hundred microliter aliquots of the monomeric products were separated for *identification* on an analytical column (0.25 inch diameter). Each fraction, separated and purified gas chromatographically until the chromatogram showed less than 1% of contaminant, was examined by infrared spectroscopy of films between sodium chloride plates, using a Perkin–Elmer model 21 spectrophotometer. Structural assignments were made by comparison with the spectra of authentic specimens or as indicated below.

The degradative product was analyzed on an 8-ft. silica gel analytical column in essentially the same way as described for the monomeric material. Infrared spectra were determined in a 10-cm. gas cell. Products were identified by comparison of their spectra with those of commercial samples.

Preparation of Authentic Samples.—Pyrrole was a du Pont product purified by distillation. The spectra of authentic *cis*- and *trans*-crotononitrile were furnished by Dr. F. Johnson of Dow Chemical Co., Eastern Development Center.

cis- and *trans*-1-cyano-1,3-butadienes were prepared by pyrolysis of the benzoate of crotonaldehyde cyanohydrin according to the procedure reported by Snyder, Stewart and Mayers.[16] The product thus obtained as a mixture of the *cis* and *trans* isomers in the ratio of 40:60 by gas chromatographic analysis. The isomers were separated gas chromatographically with an 8-ft. Carbowax 20M column to give *cis*-1-cyano-1,3-butadiene, n^{21}_{D} 1.4848 (lit.[16] n^{20}_{D} 1.4852) and *trans*-1-cyano-1,3-butadiene, n^{21}_{D} 1.4960 (lit.[16] n^{20}_{D} 1.4960.)

Identifications by Infrared without Comparison with Authentic Samples.—The structure 3-cyano-1-butene was assigned on the basis of the following absorption frequencies (in cm.$^{-1}$) 2245, unconjugated CN (stretch); 1647, unconjugated C=C(stretch); 1463 and 1382, C—CH_3 (deformations); 1420 and 922, vinyl CH_2 (deformation); 995, vinyl CH (deformation). The compound also absorbed in the CH stretching region at 3070, 2970, 2930 and 2890. The partial assignment for the C_5CN isomers is based on the following data: for the *trans* isomer, 2245, unconjugated CN (stretch); 1680 (weak), unconjugated C=C (stretch); 1441 and 1372, C—CH_3 (deformations); 1430, —CH_2— (deformation); 967 *trans*-HC=CH (deformation); for the *cis* isomer, 2240, unconjugated CN (stretch); 1656, unconjugated C=C (stretch); 1442, 1373, C—CH_3 (deformation); 1428, —CH_2— (deformation); 702, *cis*-HC=CH (deformation). Comparison with authentic samples of *cis*- and *trans*-1-cyano-2-butene eliminated these possibilities.

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(14) M. Kolthoff and E. B. Sandell, "Textook of Quantitative Inorganic Analysis," The MacMillan Co., New York, N. Y., 1956, pp. 458–460.

(15) G. B. Kistiakowsky and G. G. Volpi, *J. Chem. Phys.*, **27**, 1141 (1957).

(16) H. R. Snyder, J. M. Stewart and R. L. Mayers, *J. Am. Chem. Soc.*, **71**, 1055 (1949). The preparation was carried out by C. Gatsonis.