Radical Reactions of Tetrafluorohydrazine. Cyclic Olefins[1]

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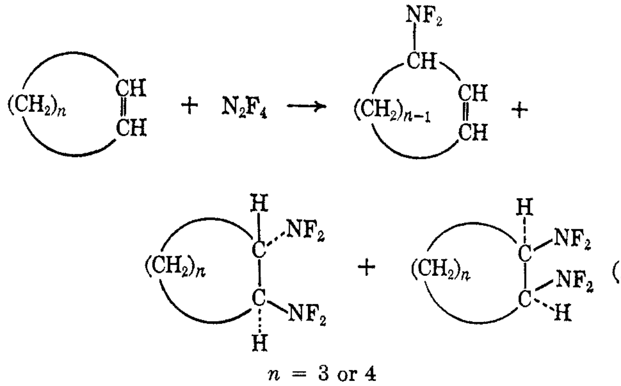
The reaction of tetrafluorohydrazine with cyclic olefins yields the normal adducts as the major products. Another reaction involving hydrogen abstraction from the α-methylenic carbon atom occurs to varying degrees with cyclopentene and cyclohexene resulting in the formation of mono(difluoramines). Reactions were conducted under various experimental conditions and the effect upon the distribution of products was noted.

Several reports[2-6] pertaining to the addition of tetrafluorohydrazine (N_2F_4) to olefins describe the formation of vicinal bis(difluoramines) *via* a radical mechanism. Hydrogen abstractions are known[7-9] in reactions of tetrafluorohydrazine with various substrates; however, it has been noted[6] that hydrogen abstraction by the difluoramino radical does not occur in the N_2F_4–olefin addition as is often observed in reactions involving radical reagents with olefinic substrates. Under more drastic conditions at elevated temperatures, hydrogen abstraction occurs readily even with saturated hydrocarbons.[10] These results prompted a further study of the reaction of N_2F_4 with cyclic olefins under various experimental conditions to determine the site of attack by the difluoramino radical, since cyclic olefins such as cyclohexene often yield both addition and substitution products when treated with radical reagents.[11-14] Formation of 3-(difluoramino)-substituted cyclic olefins would establish the allylic substitution reaction and represent the first reported example of hydrogen abstraction from olefins by NF_2 radicals. Cyclopentene, cyclohexene, and cyclooctene were employed in this study.

Reactions of the cyclic olefins with N_2F_4 were conducted in a flow reactor at 200–300° and in static reactors (neat and solution) at 30–100° to give similar product mixtures with cyclopentene and cyclohexene (eq 1). Cyclooctene gave only a mixture of *cis–trans* adducts. Absence of the mono(difluoramine) is not surprising in view of the lower reactivity of cyclooctene to hydrogen abstraction by radical reagents.[15]



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The products were the same under all conditions, varying only in their percentage of the total product mixture, with the exception that in isolated instances small quantities (<2%) of other products were detected by glpc. These minor products were never present in sufficient quantity for thorough characterization. The addition–substitution product ratios (Table I) were greater for those reactions carried out under normal conditions, *i.e.*, low reaction temperatures. Cyclohexene gave consistently slightly higher ratios than cyclopentene, particularly when the reactions were conducted neat, where only minor quantities of the substitution product were isolated. Only in reactions carried out under flow conditions at elevated temperatures did the substitution products predominate. It may be noted that in all instances the ratio of *cis/trans* adduct was greater than 1.0, indicating a slight preference for *cis* addition. A similar preference for *cis* addition was observed[2] in reaction of N_2F_4 with 2-butene and stilbene. The *cis/trans* ratio was greatest for reactions performed on the neat olefin where a qualitative rate enhancement was observed. These product ratios showed little variation in any series of reactions conducted under similar experimental conditions.

Products from the reactions were separated by fractional distillation at reduced pressure or by preparative gas chromatography. Characterization of each was accomplished by their infrared, F^{19} and H^1 nmr spectra, and elemental analysis. These data gave support to the structural assignments. Assignment of the *cis* or *trans* structure to the isomeric bis(difluoramines) was made by analogy of their physical properties with other known cyclic olefin adducts. In general, the *cis–trans* isomers may be distinguished by differences in boiling point, refractive index, density, etc.; the *trans* isomer usually displays the lower values. For instance, *trans*-1,2-dichlorocyclohexane[14] and the *trans*-1-iodo-2-per-

TABLE I

PRODUCT DISTRIBUTION IN CYCLIC OLEFIN–N_2F_4 REACTION

Reaction conditions	Product ratios			
	Cyclopentene		Cyclohexene	
	Addition–substitution	*cis/trans*	Addition–substitution	*cis/trans*
Flow	0.68	1.11	0.77	2.2
Neat (static)	10.9	3.72	53.2	3.0
Solution (90°)	5.4	1.09	7.08	1.11
Solution (30°)	9.6	1.11	11.7	1.10

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(1) This work was carried out under the sponsorship of the U. S. Army Missile Command, Redstone Arsenal, Ala., under Contract DA-01-021-ORD-11909(Z).

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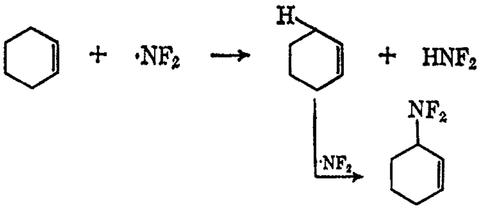
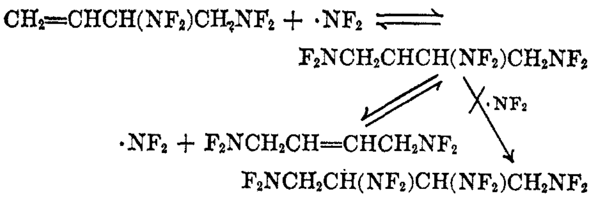
flouoroalkylcyclohexanes[16] exhibit lower values for these properties. In addition, the *trans* isomers normally show shorter retention times on glpc, and bis(difluoroamines) are known[6] to resemble the corresponding dichloro compounds in such physical properties as boiling point, solubility, and retention times on gas chromatography columns.

Addition of tetrafluorohydrazine to olefins has been described[2-4,6] as a radical reaction involving the attack of a difluoramine radical on the carbon-carbon double bond of the olefin followed by coupling of the intermediate difluoraminoalkyl radical with $\cdot NF_2$ to give the bis(difluoramine). It has been demonstrated that the reaction with cyclic olefins proceeds to a large extent in the same manner to yield the isomeric adducts. However, the reaction with the cyclic olefins, cyclopentene and cyclohexene, has been shown to occur to some extent by an alternate course involving hydrogen abstraction from the allylic position with the ultimate formation of 3-(difluoramino)-substituted cyclic olefins by coupling of the 3-cycloalkenyl radical (I) with $\cdot NF_2$ (eq 2 for cyclohexene). The presence of difluoramine as a reaction product was difficult to establish although mass spectra of many residual gas fractions were obtained. Its fate is unknown; however, its loss at the higher temperatures under which the flow reactions were conducted is not surprising, nor is the failure to detect its presence as a minor component in the other reactions. In order to substantiate to a degree hydrogen abstraction in reactions of N_2F_4 with cyclic olefins, advantage was made of the higher reactivity of 1,4-cyclohexadiene[17,18] to hydrogen abstraction when subjected to attack by radical reagents. In these reactions which occurred readily in solution at ambient temperatures (explosively when conducted neat) difluoramine was found in large quantities by mass spectral analysis. Although not isolated, it was obtained in yields of 30-40% based on olefin. Unfortunately, the difluoroamino-containing products from these reactions could not be isolated and characterized owing to slow but immediate decomposition of the liquid product mixture.



(2)

Another point of interest was the failure to obtain the tiis(difluoramines) from reactions yielding the 3-difluoramino-substituted cyclic olefins, particularly in those reactions carried to near completion with excess N_2F_4 present. In several instances the reaction of N_2F_4 with allyldifluoramines produces tris(difluoramines).[19] The difference in reactivity between the cyclic olefins and their 3-difluoramino derivatives to N_2F_4 addition is probably associated with the stability or steric conformation of the intermediate radical in the 3-difluoraminocyclohexene-N_2F_4 addition as compared with the corresponding intermediate radical for cyclohexene. This latter intermediate, although existing in equilibrium with cyclohexene and $\cdot NF_2$, is relatively more stable and readily couples with $\cdot NF_2$ to give the normal adduct. In the case of the intermediate radical for the 3-difluoramino derivative, its formation is considered probable since polar factors operating in this instance should be similar to those in the simple allyl difluoramines[19] and its final conversion into the tris-(difluoramine) is prevented by steric considerations attributed to the conformation of the intermediate and/or to a rapid equilibrium between the intermediate and the reactants. It is known[6] that the N_2F_4 addition reaction is reversible as exemplified by the isomerization of 3,4-bis(difluoramino)butene-1 to 1,4-bis(difluoramino)butene-2 when treated with N_2F_4 and the failure to saturate these olefins under the usual reaction conditions (eq 3). Furthermore, conformational effects have been shown[20] to influence reactions with substituted cyclic olefins proceeding through ionic intermediates. The influence of polar and conformation effects on the radical additions to 3-substituted cyclohexenes or cyclopentenes has not been studied. In most reactions of these cyclic olefins with radical reagents where hydrogen abstraction occurs with subsequent formation of 3-substituted derivatives, the presence of trisubstituted derivatives has not been noted. Even in the radical chlorination of cyclic olefins[14] the trichloro derivative, which would normally result from the addition of chlorine to 3-chlorocyclohexene, has not been reported. It is reasonable to assume that similar factors inhibit its formation.



$$CH_2{=}CHCH(NF_2)CH_2NF_2 + \cdot NF_2 \rightleftharpoons F_2NCH_2\dot{C}HCH(NF_2)CH_2NF_2$$
$$F_2NCH_2\dot{C}HCH(NF_2)CH_2NF_2 \rightleftharpoons \cdot NF_2 + F_2NCH_2CH{=}CHCH_2NF_2$$
$$F_2NCH_2\dot{C}HCH(NF_2)CH_2NF_2 \xrightarrow{\cancel{\cdot NF_2}} F_2NCH_2CH(NF_2)CH(NF_2)CH_2NF_2 \quad (3)$$

This study has demonstrated the ability of the difluoramino radical to abstract hydrogen atoms from the α-methylenic carbon atom of cyclic olefins and represents the first reported instance of this reaction. Surprisingly, hydrogen abstraction occurs at relatively low temperatures with limited reaction taking place at ambient temperature (30°). Major products in most instances were the normal addition products represented by the *cis-trans* isomers of the cyclic olefins.

It is of paramount importance to conduct these reactions with care since mixtures of N_2F_4 and organic materials in the presence of air constitute explosive hazards. All experimental work was carried out in remote areas employing remote control devices insofar as possible. In addition care should be exercised in the handling of the products since in many instances difluoramines are known to be thermal and impact sensitive materials.

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Experimental Section[21]

Cyclic olefins were purchased from a commercial source and employed as received. They were found to be of at least 98% purity by gas chromatography. The tetrafluorohydrazine employed was known to contain approximately 5% of volatile C–F compounds. F^{19} nmr spectra were obtained with a Varian Associates Model V-3000-B high-resolution spectrometer using a 40-Mc probe. The proton nmr spectra were obtained on a Varian Associates Model A-60 spectrometer and exhibited absorption as expected; however, owing to their complex nature they have not been discussed in this paper. Infrared spectra were obtained with Perkin-Elmer Infracord spectrophotometer. Gas chromatographic work was carried out on an Aerograph Instrument, Model 100-C, using a 5′-dinonyl phthalate on Chromosorb column at 50–100° unless otherwise noted.

Tetrafluorohydrazine–Cyclopentene Reaction.—A solution of 5.8 g (85 mmol) of cyclopentene in 30 ml of methylene chloride was introduced into a thick-walled glass Aerosol tube of 100-ml capacity. The tube was connected to a high-pressure stainless-steel manifold and the solution degassed by alternately pressurizing to 500 psi with nitrogen and evacuating to low vacuum. The system was then pressurized to an equilibrium pressure of 160 psi with tetrafluorohydrazine and heated to 90°. This temperature was held over a period of 2 hr while the tetrafluorohydrazine pressure was maintained over the range of 160–330 psi by frequently recharging as necessary. After cooling to ambient temperature the excess tetrafluorohydrazine was vented, the reactor tube removed from the manifold, and its contents were transferred to a 100-ml round-bottom flask. The methylene chloride was removed by distillation, bp 39°. The distillation was continued through an 18-in. Holtzman column to give the following fractions: (A) 1.80 g, bp 47–50° (82 mm); (B) 5.1 g, bp 60–63° (42 mm); and (C) 5.7 g, bp 63–68° (17 mm). Examination of each fraction by gas chromatography showed incomplete separation of the three components. Each fraction was separately redistilled to give (A) 1.24 g, bp 49° (81 mm); (B) 4.62 g, bp 56° (36 mm), $n^{20}D$ 1.3912, $d^{25}{}_4$ 1.316; and (C) 5.03 g, bp 67° (16 mm), $n^{20}D$ 1.3987, $d^{25}{}_4$ 1.350. This represents yields of 12.1, 31.5, and 35.5% of the three products, respectively. Fraction A was identified as 3-(difluoroamino)-cyclopentene by infrared and F^{19} nmr spectral data and elemental analysis. The F^{19} nmr spectrum displayed a doublet at ϕ −48.2 and −47.8. The infrared spectrum was characterized by strong absorption bands in the 800–1000-cm^{-1} region typical of NF_2 compounds. Vinyl proton absorption was noted in the H^1 nmr spectrum in the region of τ 3.8–4.2.

Anal. Calcd for $C_5H_7F_2N$: C, 50.42; H, 5.88; F, 31.93; N, 11.76. Found for A: C, 50.71; H, 5.66; F, 31.85; N, 12.23.

Fractions B and C were identified in a similar manner as isomeric 1,2-bis(difluoroamino)cyclopentanes. Their infrared spectra showed strong absorption in the 800–1000-cm^{-1} region. The F^{19} nmr spectra showed typical ABX patterns with the AB portion represented by a series of four doublets.[22] The secondary NF_2 groups exhibited absorption in the usual range of ϕ −30 to −55.

Anal. Calcd for $C_5H_8F_4N_2$: C, 34.88; H, 4.65; F, 44.19; N, 16.28. Found for B: C, 35.06; N, 4.81; F, 44.60; N, 16.80. Found for C: C, 34.16; H, 4.96; F, 44.20; N, 16.63.

In a similar reaction conducted at 25–30° for 24 hr yields of 8% (A), 35% (B), and 39% (C) were obtained upon distillation.

In reactions conducted under flow conditions, the system was composed of feed lines for tetrafluorohydrazine and helium connected through separate calibrated flow meters into a single line to the reactor, a copper coil 0.25 in. in diameter and 12 ft in length. The cyclopentene was introduced into the feed line from a calibrated power driven syringe at a point prior to its entrance to the reactor. The reactor was completely enclosed in an electrical furnace and the temperature measured by means of thermocouples placed within the furnace immediately adjacent to the reactor coil. The exit line from the reactor was passed through a series of cold traps cooled in the order −80, −130, and −196°. In practice the organic materials from the reactor were always collected in the −80° trap while excess or unreacted tetrafluorohydrazine and other volatile gases were collected in the −196° trap. The reactions were initiated by first flushing the system at a given temperature with helium and, while maintaining the helium flow at the desired level, both tetrafluorohydrazine and cyclopentene flows were started. For instance at a reactor temperature of 250° and a constant helium flow of 25 ml/min, tetrafluorohydrazine was introduced at the rate of 140 ml/min and cyclopentene at 0.2 ml/min. The reaction was continued for 50 min with the helium flow being continued for an additional 15-min period. The −80° trap contained the major part of the organic materials. These materials were transferred from the trap into another series of cold traps cooled to −80, −130, and −196° in order to ensure removal of any dissolved tetrafluorohydrazine. After opening to the air, the contents of the trap were transferred to a distillation assembly and the products isolated by distillation. From this reaction there were obtained 2.05 g of A, 0.96 g of B, and 1.05 g of C whose physical properties were identical with those previously described. This represents ~25% conversion of cyclopentene into products and increased the relative yield of A to ~50%.

In another reaction 6.8 g (100 mmol) of deaerated cyclopentene was condensed through a glass manifold into an evacuated 1-l. stainless-steel cylinder fitted with pressure gauge and valve. Tetrafluorohydrazine, 10.4 g (100 mmol), was condensed into the cylinder, the valve closed, and the cylinder allowed to warm to ambient temperature (30°). After standing for a period of 48 hr the contents of the cylinder were removed and collected in a series of cold traps cooled in the order −80, −130, and −196°. The −196° trap was found to contain 1.87 g (18 mmol) of tetrafluorohydrazine and a trace of cyclopentene. The −80° trap contained 14.9 g of liquid residue. Distillation of this residue gave 0.75 g (6.3%) A, 2.5 g (14.5%) of B, and 9.3 g (54%) of C. This was one instance where the ratio of the bis isomers was decidedly different.

Tetrafluorohydrazine–Cyclohexene Reaction.—Reactions of tetrafluorohydrazine with cyclohexene were conducted under similar conditions employing the three experimental techniques. For instance, when a solution of 5.8 g (71 mmol) of cyclohexene in 30 ml of methylene chloride contained in the glass Aerosol tube was heated to 90° for 2 hr under 330–160-psi tetrafluorohydrazine pressure the products isolated by fractional distillation were 3(difluoramino)cyclohexene (D), bp 45° (24 mm), $n^{20}D$ 1.4138, 1.08 g (11.5%); a mixture of isomeric bis(difluoramino)-cyclohexanes [E, bp 56° (12 mm), $n^{20}D$ 1.4099, $d^{25}{}_4$ 1.305, 5.06 g (38%), and F, bp 58° (11 mm), $n^{20}D$ 1.4123, $d^{25}{}_4$ 1.337, 5.64 g (42%)]. The infrared spectrum of D showed strong N–F absorption in the 800–1000-cm^{-1} region. Its F^{19} nmr spectrum displayed a doublet at ϕ −43.6 and −43.1 typical of the $>CHNF_2$ group. Vinyl proton absorption was noted in the H^1 nmr spectrum at τ 3.8–4.2.

Anal. Calcd for $C_6H_9F_2N$: C, 54.14; H, 6.77; F, 28.57; N, 10.53. Found for D: C, 53.97; H, 6.61; F, 27.8; N, 10.91.

The identity of products E and F as being *cis–trans* isomers was based on similar data. Their infrared spectrum displayed strong absorption in the 800–1000-cm^{-1} region typical of N–F compounds. The fluorine resonance of the two isomers occurred as a typical ABX pattern.

Anal. Calcd for $C_6H_{10}F_4N_2$: C, 38.71; H, 5.38; F, 40.86; N, 15.05. Found for E: C, 38.51; H, 5.49; F, 40.56; N, 15.51. Found for F: C, 38.96; H, 5.41; F, 40.93; N, 15.69.

In a similar reaction conducted at 30° the products were D (7%), E (39%), and F (43%).

When the reaction was conducted in the flow reactor under the following conditions [200°, helium (25 ml/min), N_2F_4 (140 ml/min), cyclohexene (0.2 ml/min), time, 50 min], 7.69 g of liquid was collected in the −80° trap. Distillation gave 5.8 g of cyclohexene, bp 83°, 1.95 g of 3-(difluoramino)cyclohexene (D), and 0.69 (E) and 1.46 g (F) of the bis(difluoramino)cyclohexanes. This represents a conversion of approximately 26% under these experimental conditions with a ratio of the mono- to bis(difluoramines) of close to 1:1.

The reaction of 8.2 (100 mmol) of cyclohexene with 15.42 g (148 mmol) of tetrafluorohydrazine in a 1-l. stainless-steel cylinder at 30° for 4 hr gave 0.15 g of D, 3.16 g of E, and 8.73 g of F. This ratio of products was similar to that found in the case of cyclopentene.

Tetrafluorohydrazine–Cyclooctene.—When 5.5 g (50 mmol) of cyclooctene in 30 ml of methylene chloride was treated with tetrafluorohydrazine (350–150 psi) at 90° for 6 hr in a glass Aerosol tube the only products isolated was a mixture of the *cis–trans*-bis(difluoramino)cyclooctenes which were not separated. There was no evidence for the presence of the mono(difluoramino)-

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[21] All boiling points are uncorrected.

[22] F. A. Johnson, C. Haney, and T. E. Stevens, *J. Org. Chem.*, **32**, 466 (1967).

cyclooctene. The isomers, 10.62 g (67%), were isolated by distillation: bp 50° (0.85 mm); n^{20}_D 1.4342; d^{25}_4 1.265. The presence of the two isomers in a ratio near 1:1 was established by gas chromatography using a 5-ft Dow Corning silicone 11 on Fluoropak column. The F^{19} nmr spectrum of the mixture showed the typical ABX pattern.

Anal. Calcd for $C_8H_{14}F_4N_2$: C, 44.86; H, 6.54; F, 35.51; N, 13.08. Found: C, 44.20; H, 6.62; F, 35.60; N, 14.42.

Registry No.—Tetrafluorohydrazine, 10036-47-2; fraction A, 16666-28-7; fraction B (*cis*), 16666-34-5; fraction C (*trans*), 16666-35-6; fraction D, 16666-29-8; fraction E (*cis*), 14182-81-1; fraction F (*trans*), 16666-31-2; *cis*-1,2-bis(difluoramino)cyclooctane, 16666-32-3; *trans*-1,2-bis(difluoramino)cyclooctane, 16666-33-4.

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The Addition of N,N-Dichloro Carbamates to Conjugated Dienes

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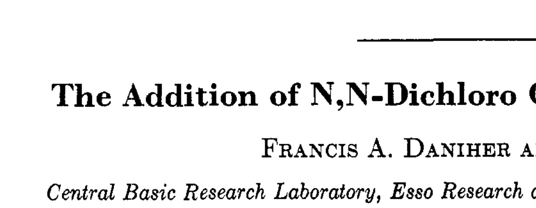
The addition of N,N-dichloro carbamates (methyl, isopropyl, and bisethylene glycol) to a series of conjugated dienes (butadiene, isoprene, 2,3-dimethyl-1,3-butadiene, chloroprene, and piperylene) has been found to give high yields of the corresponding N-chloro-ω-chlorocrotyl carbamates. The mode of addition of these pseudohalogens has been shown to be primarily 1,4 with minor amounts of other adducts also being formed. The N-chloro function of the adducts can be reduced in high yield with sodium sulfite to give the corresponding carbamates. Spectral data pertinent to the proof of structures are presented. A possible mechanism for the addition is discussed.

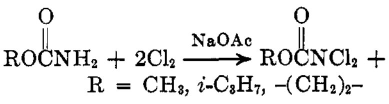
The addition of the pseudo-halogen, N,N-dichlorourethan, to a number of olefins has been reported.[2,3] The reaction is reported to give anti-Markovnikov adducts with terminal olefins.[2] With the isomeric-2-butenes[3c] and *trans*-3-hexene[2] mixtures of the *erythro* and *threo* isomers are formed. The initial adducts β-chloro-N-chloro carbamates were not isolated but were reduced to the β-chloroethyl carbamates with either sodium bisulfite[2] or potassium iodide followed by thiosulfate solution.[3]



$$RCH{=}CHR' + C_2H_5O\overset{O}{\overset{\|}{C}}NCl_2 \longrightarrow RCH(Cl)CH(R')N(Cl)\overset{O}{\overset{\|}{C}}OC_2H_5 \longrightarrow RCH(Cl)CH(R')NH\overset{O}{\overset{\|}{C}}OC_2H_5$$

As part of a continuing study in this laboratory[4] of the chemistry of unsaturated hydrocarbons, the reaction of N,N-dichloro carbamates with a series of conjugated dienes has been examined.

The particular N,N-dichloro carbamates employed were methyl,[5] isopropyl, and a novel difunctional species, N,N,N',N'-tetrachloroethylene glycol biscarbamate. These materials were prepared in fair to good yields by chlorination of the corresponding carbamate in aqueous sodium acetate solution.[2]



$$RO\overset{O}{\overset{\|}{C}}NH_2 + 2Cl_2 \xrightarrow{NaOAc} RO\overset{O}{\overset{\|}{C}}NCl_2 + 2HCl$$

$$R = CH_3,\ i\text{-}C_3H_7,\ \text{-}(CH_2)_2\text{-}$$

Results

The addition reactions could be performed in a number of ways. The N,N-dichloro carbamate could be added dropwise to a cooled solution of the diene or vice versa. With gaseous butadiene it was found to be particularly advantageous simply to distil the material, after dilution with nitrogen, into a chilled solution of the N,N-dichloro carbamate. Removal of the solvent afforded near quantitative yields of monoadduct.

The crude products were analyzed by a combination of gas chromatography (gc) and nuclear magnetic resonance spectroscopy (nmr). The products were then further purified by distillation *in vacuo*. The yields of analytically pure product along with pertinent physical data are recorded in the Experimental Section. The nmr parameters of the adducts are tabulated in Table I.

The reduction of the N-chloro group of the adducts could be effected in good yield with sodium sulfite to give the corresponding crotyl carbamates. The nmr parameters of these materials are tabulated in Table I.

An examination of the infrared and nmr spectra of the N-chloro adducts and their corresponding reduction products clearly indicate that the principal mode of addition is 1,4. As an example, the infrared spectrum of the butadiene adduct shows strong absorptions for the *trans*-disubstituted double bond. In the nmr spectra, the chemical shift of the CH_2Cl grouping was essentially the same in the N-chloro adduct and its corresponding reduction product. On the other hand, the chemical shift of the CH_2–N group was very sensitive to changes in chemical environment. Upfield shifts of the magnitude of 0.4–0.5 ppm were observed for this signal upon reduction of the N-chloro group ($-CH_2-NCl- \rightarrow CH_2-NH-$). Further substantiation of this assignment is found in the fact that this signal appears as a doublet (J = 5–7 Hz) in the reduction product due to NH–CH< coupling.[6] Exchange of the amide proton with

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