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Reaction of Difluoramine with Some Allyl- and Cyclopropylcarbinylamines[1]

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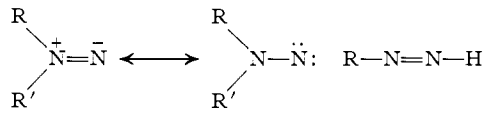
Difluoramine (HNF_2) converts diallylamine into N-allylpyrazoline. However, allylamine, crotylamine, cinnamylamine, and cyclopropylmethylcarbinylamine with difluoramine evolve N_2 and yield, respectively, propylene, butene-1, 3-phenylpropene, and pentene-2. The double bond migrations observed in the case of crotylamine and cinnamylamine and the ring opening in the reaction of cyclopropylmethylcarbinylamine are discussed in terms of cyclic alkyldiimide or azamine decompositions. These are contrasted with the Wolff–Kishner reduction.

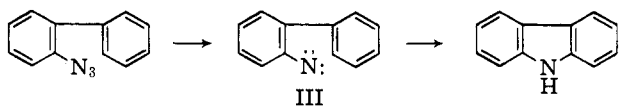
Intermediates I and II have been postulated to explain the behavior of difluoramine (HNF_2) as a deaminating agent toward primary and certain secondary amines.[2]



a I b II

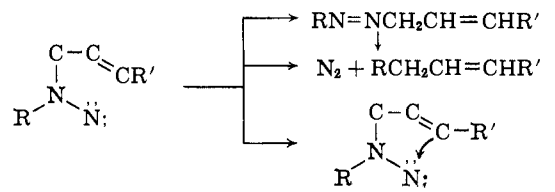
R′ = H or alkyl; R = alkyl

Resonance form Ib suggested that the terminal nitrogen atom might be susceptible to internal nucleophilic attack by a suitably arranged group. In view of the formation of carbazole from *o*-azidobiphenyl *via* intermediate III,[3] we treated diallylamine, allylamine,



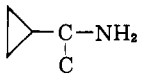
III

crotylamine, and cinnamylamine with difluoramine to see if the nitrogen atoms in intermediate IV could be captured by the double bond before decomposition to N_2 and hydrocarbons occurred. This latter process is the one generally observed with saturated primary and secondary amines.[2] If decomposition superceded, we hoped to ascertain whether double bond migration took place and so gain some insight into the nature of fragmentation or rearrangement of structure IV.



IVa, R = $CH_2CH{=}CH_2$, R′ = H
b, R = R′ = H
c, R = H, R′ = CH_3
d, R = H, R′ = C_6H_5

To compare the behavior of a cyclopropylcarbinylamine with the allylic examples, we included cyclopropylmethylcarbinylamine (V).



V

Results

Table I summarizes our results.

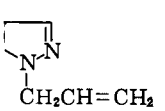
TABLE I

Starting amine	Products	Yield, %
Diallyl	N_2	4[a]
	$(CH_2{=}CHCH_2)_2$	Trace
	$C_6H_{10}N_2$	51[b]
Allyl	N_2	101[c]
	$CH_2{=}CHCH_3$	93[c]
Crotyl	N_2	80[c]
	$CH_2{=}CHC_2H_5$	52[c,d]
Cinnamyl	N_2	55
	$C_6H_5CH_2CH{=}CH_2$	
Cyclopropyl methylcarbinyl	N_2	40
	$CH_3CH{=}CHC_2H_5$	

[a] Based on $3R_2NH + HNF_2 = N_2 + R_2 + 2R_2\overset{+}{N}H_2\overset{-}{F}$. [b] Based on $3(C_3H_5)_2NH + HNF_2 = C_6H_{10}N_2 + 2(C_3H_5)_2\overset{+}{N}H_2\overset{-}{F}$. [c] Based on $3RNH_2 + HNF_2 = RH + N_2 + 2R\overset{+}{N}H_3\overset{-}{F}$. [d] After fractionation.

As indicated in Table I, reaction of diallylamine with difluoramine gives only traces of N_2 and biallyl although dibenzylamine under similar conditions gives N_2 and bibenzyl in high yields.[2] The main product from diallylamine is a mobile oil which was isolated by vacuum line fractionation followed by gas phase chromatography. Analyses established the formula as $C_6H_{10}N_2$, indicating that a nitrogen atom had been added to and a hydrogen atom lost from the starting amine.

Evidence summarized below allows the product to be formulated as N-allylpyrazoline (VI).



VI

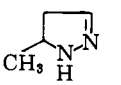
Its n.m.r. spectrum shows a signal at 6.8 p.p.m. (1 proton, vinyl hydrogen attached to C–N double bond[4]), a set of signals from 5.0 to 6.3 p.p.m. (3 protons) characteristic of the vinyl group, a doublet (2 protons) at 3.7 p.p.m. attributable to the methylene group adjacent to the C–C double bond, and a complex set of signals (4

(1) Presented in part at the Southeastern Regional Meeting of the American Chemical Society, Charlotte, N. C., Nov. 14–16, 1963.

(2) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *J. Am. Chem. Soc.*, **85**, 97 (1963).

(3) P. A. S. Smith and J. H. Hall, *ibid.*, **84**, 480 (1962); see also R. A. Abramovitch, Y. Ahmad, and D. Newman, *Tetrahedron Letters*, 752 (1961).

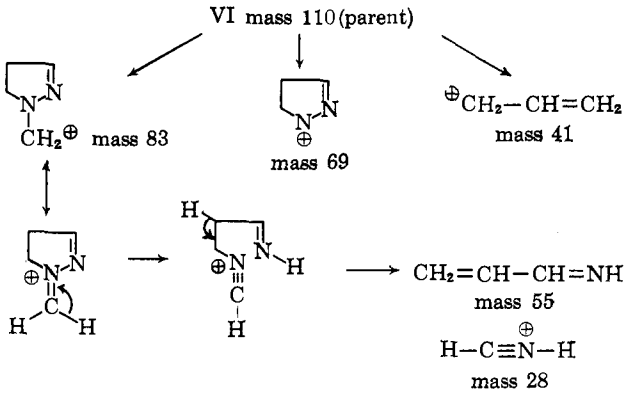
(4) In 5-methylpyrazoline (i) the vinylic proton resonates at 6.8 p.p.m., the ring methylene protons at 2–3 p.p.m.



i

protons) at 2.5–3.3 p.p.m. due to the ring methylene hydrogen atoms.[4] Bands in the infrared spectrum at 920 and 1640 cm.$^{-1}$ also indicate the presence of a terminal double bond.

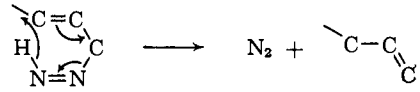
The main peaks in the mass spectrum correspond to mass numbers 110, 83, 69, 55, 41, and 28. These may be assigned according to the following fragmentation and rearrangement pattern.



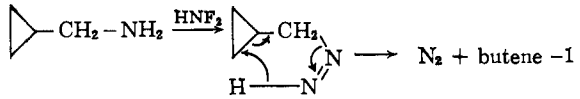
In contrast to diallylamine, the remaining amines in Table I, all primary, evolve N_2 in high yield and produce hydrocarbons as the major products. These were identified by infrared and mass spectrometry and in some cases by n.m.r. spectroscopy and gas phase chromatography.

Discussion

Formation of pyrazoline VI, probably arising through trapping of the nitrogen atoms in intermediate IVa,[5] adds support to the general scheme proposed for amine–difluoramine reactions[2] and illustrates that difluoramine may be used in some cases as a nitrogenating (nitrogen-adding) reagent. The fact that the primary amines in Table I discharge their nitrogen may mean that alkyldiimides II are produced directly in these examples, or that hydrogen migration in intermediates IVb–d occurs more rapidly than double bond attack on the electron deficient nitrogen atom. In any case, the double bond movements which occur in going from crotylamine to butene-1 and from cinnamylamine to 3-phenylpropene are remarkable, particularly the latter where deconjugation is involved. These results seem best accommodated by a cyclic, highly synchronous pathway.

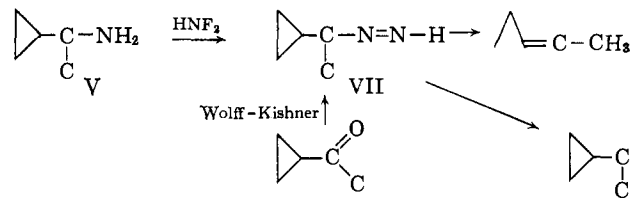


A modification of this process was suggested earlier as a possible explanation for the production of butene-1 from reductive deamination of cyclopropylcarbinylamine.[2]



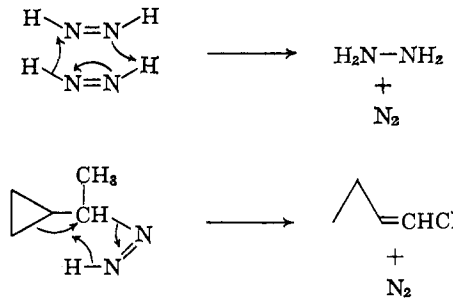
Since Table I shows that cyclopropylmethylcarbinylamine (V) yields pentene-2, olefin formation from cyclopropylcarbinylamines and difluoramine may be quite general.

In contrast, Wolff–Kishner reduction of cyclopropyl methyl ketone, which should involve the same diimide intermediate[6] VII as derived from amine V and HNF_2,[2] is reported to provide ethylcyclopropane.[7]

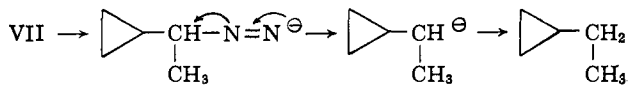


We repeated the Wolff–Kishner reaction and found, in agreement with the previous work,[7] that ethylcyclopropane is produced, free of isomeric olefins according to analysis of the n.m.r. spectra (see Experimental). We conclude, therefore, that although the difluoramine and Wolff–Kishner reactions may proceed through the same alkyldiimides (II), decomposition of these intermediates takes place by different paths.

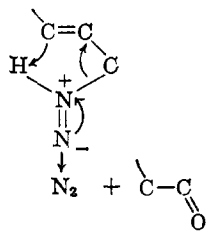
Since diimide disproportionates to nitrogen and hydrazine,[8] intermediate VII may tend to fragment similarly, reacting intramolecularly *via* the *cis* form to give olefin directly.



In the more basic medium of the Wolff–Kishner reduction proton removal from VII may compete with the above process and a nonisomerizing carbanion decomposition may become dominant.[9]



An equally acceptable alternative for possible intermediates IVb–d (and for those derived from the cyclopropylcarbinylamines) involves direct fragmentation into products without the necessity of rearrangement to alkyldiimides.



(5) As a referee pointed out, ring closure may occur as a result of attack by the double bond on the conjugate acid of intermediate IVa, *i.e.*, on the diazenium ion. Such ions are known to be highly electrophilic. See W. H. Urry, H. W. Kruse, and W. R. McBride, *J. Am. Chem. Soc.*, **79**, 6568 (1957).

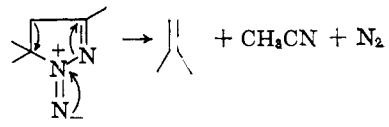
(6) D. J. Cram, M. V. Shayun, and G. R. Knox, *ibid.*, **84**, 1734 (1962).

(7) P. Pomerantz, A. Fookson, T. W. Mears, S. Rothberg, and F. L. Howard, *J. Research Natl. Bur. Standards*, **52**, 59 (1954). Also *methyl*-^{13}C-cyclopropane has been obtained through a Wolff–Kishner reaction: E. Renk, P. Shafer, W. H. Graham, R. D. Mazur, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 1987 (1961).

(8) F. Aylward and M. Sawistowska, *Chem. Ind.* (London), 484 (1962).

(9) D. J. Cram and J. S. Bradshaw, *J. Am. Chem. Soc.*, **85**, 1108 (1963), have observed that optically active alkyldiimides generated from several sources decompose with varying degrees of stereospecificity depending on the solvent and nature and concentration of the base employed.

This cyclic reorganization bears some resemblance to difluoramine-induced decomposition of 3,5,5-trimethylpyrazoline[2] which is believed to go through structure VIII or its equivalent.



VIII

Interestingly, Cram and Bradshaw[9] account for the influence of base on decomposition of R*NHNHTs by postulating formation of R^*N_2H at low base concentration and $\overset{*}{R}\overset{+}{N}H{=}\overset{-}{N}$ at high concentration. The distinguishing feature between Wolff–Kishner reduction and difluoramine deamination may be, therefore, the different behavior shown by alkyldiimides (intermediates in Wolff–Kishner) and the isomeric azamines, $\overset{+}{R}NH{=}\overset{-}{N}$ (intermediates in difluoramine deamination).

Experimental[10]

Caution: Difluoramine should be handled with care.

Diallylamine and Difluoramine.—Diallylamine (20 mmoles, Peninsular Chem. Research) was introduced into a vacuum system and degassed. Difluoramine[2] (5 mmoles) was then condensed in by means of a methylcyclohexane slush bath. While the stirred mixture was allowed to warm to room temperature, a total of 0.2 mmole of N_2 and a trace of biallyl were evolved. No further change was observed when the mixture was allowed to stand at 25° overnight. Volatile products were removed by pumping and the residue was taken up in water and ether. The combined ethereal solutions from three such reactions were concentrated and the residue was chromatographed in the gas phase. Chromatography at 100° using a 0.25 in. × 10 ft. column packed with silicone oil (Dow 710) on Fluoropak separated recovered starting amine from a product which analyses, n.m.r. and infrared and mass spectroscopy indicated was N-allylpyrazoline (VI). (see Results).

Anal. Calcd. for $C_6H_{10}N_2$: N, 25.4. Found: N, 25.5.

Cyclopropylmethylcarbinylamine (V).—Cyclopropyl methyl ketone (Aldrich Chemical Co.) was subjected to the Leuckart reaction using a procedure patterned after that described by Ingersoll[11] for converting acetophenone to α-phenylethylamine. From 26.8 g. of cyclopropyl methyl ketone, 92 g. of formamide, and 20.2 g. of ammonium formate, there was obtained 10.5 g. (39%) of cyclopropylmethylcarbinylamine, b.p. 55–58° (213 mm.), $n^{20.5}D$ 1.4240–1.4245. Bands at 1020 (cyclopropane ring) and 3020 $cm.^{-1}$ (cyclopropane hydrogen) in the infrared spectrum and signals at 0.65 and 0.42 p.p.m. in the n.m.r. spectrum showed that the small ring was still present.[12]

Anal. Calcd. for $C_5H_{11}N$: C, 70.52; H, 13.02; N, 16.45. Found: C, 70.06; H, 12.94; N, 16.62.

Deamination of Cyclopropylmethylcarbinylamine (V).—Amine V was treated with HNF_2 in a manner previously described for other primary amines.[2] The gases evolved consisted of N_2 and pentene-2 according to mass spectrum analysis.[13] The hydrocarbon was separated by vacuum line fractionation from N_2, excess amine, and salts and was condensed into a n.m.r. tube containing $DCCl_3$ and equipped with a Fischer–Porter Teflon-tipped needle valve. The valve was closed and the n.m.r. spectrum was obtained on the deuteriochloroform solution at 30°. Only vinyl, methylene, and methyl signals were observed consistent with a mixture of pentene-2[14] and pentane.

Wolff–Kishner Reduction of Cyclopropyl Methyl Ketone.—The directions of Pomerantz, *et al.*,[7] were followed. The n.m.r. spectrum of the product and that of a commercial sample of ethylcyclopropane (Columbia Organic Chemicals) were identical.

Deamination of Primary Olefinic Amines.—Allylamine, crotylamine,[15] and cinnamylamine were allowed to react with HNF_2 in the same general manner as described for amine V. Products (Table I) were separated by vacuum line fractionation and analyzed by gas phase chromatography, and infrared and mass spectrometry.

Acknowledgment.—This investigation was supported under Army Ord. Contract DA-01-021 ORD-11878. We are grateful to Mr. Kirt Keller for technical assistance, to Dr. Grover Paulett for mass spectral analyses, and to Mrs. Carolyn Haney for n.m.r. spectra.

(10) Boiling points are uncorrected. Infrared spectra were determined with a Perkin-Elmer Infracord spectrophotometer with a sodium chloride prism. Nuclear magnetic resonance spectra were obtained with either a Varian Associates, Model V-3000-B, high resolution spectrometer using a 40 Mc. probe or a Varian Associates A-60 spectrometer. A-60 spectra ($DCCl_3$ solutions, probe temperature 38°) were measured using TMS as internal standard. 40-Mc. spectra (probe temperature 30°) were measured from external TMS. Mass spectra were determined with a C.E.C. Type 21-620 mass spectrometer.

(11) A. W. Ingersoll, "Organic Syntheses," Coll. Vol. II, ed. by A. H. Blatt, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 503.

(12) Amine V has been prepared previously by reduction of methyl cyclopropyl ketoxime [M. S. Silver, M. C. Caserio, H. E. Rice, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 3671 (1961)]. We chose the Leuckart procedure because of our interest in isomerization which sometimes takes place under Leuckart conditions. This study will be published in another paper.

(13) Some pentane was also detected, but it was undoubtedly introduced with amine V. Pentane was used in the final extraction of V in the procedure outlined above and is difficult to remove completely from the amine. Since pentane contains no vinyl or cyclopropyl hydrogen atoms, it does not interfere with the n.m.r. analysis.

(14) No attempt was made to determine the *cis/trans* ratio. The authentic samples of pentene-2 used for n.m.r. and mass spectrum standards were obtained from Phillips Petroleum Co. (Pure Grade).

(15) J. D. Roberts and R. M. Mazur, *J. Am. Chem. Soc.*, **73**, 2517 (1951).