

ACTION OF ATOMIC FLUORINE ON *E*- AND *Z*-2-BUTENE

CARL L. BUMGARDNER* AND JAMES G. CARVER

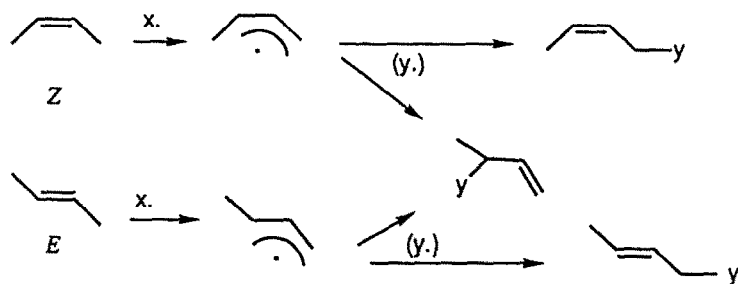
Department of Chemistry, North Carolina State University, Raleigh,
North Carolina 27695-8204 (U.S.A.)

SUMMARY

Irradiation of $N_2F_4(NF_2)$ with *E*- and *Z*-2 butene in the gas phase leads to addition of F and NF_2 across the double bond in a non-stereoselective manner and abstraction of H to give 2-butenyl radicals which interconvert rapidly before being trapped by NF_2 to yield *E*- and *Z*-1-difluoroamino-2-butene and 3-difluoroamino-1-butene. The configurational instability of the 2-butenyl radicals is attributed to the exothermicity of F atom abstraction. These results are contrasted with those of other workers who observed that in condensed phase reactions abstraction by *t*-butoxy radical leads to 2-butenyl radicals which are configurationally stable.

INTRODUCTION

Earlier work from our laboratory showed that photolysis of $N_2F_4(NF_2)$ [1] could be used as a convenient source of atomic fluorine [2,3]. The action of atomic fluorine generated in this manner on propene, 2-methylpropene and 1,1-difluoroethene was investigated [2,3] and the results found to be in gratifying agreement with studies of Rowland and co-workers who employed ^{18}F generated via nuclear recoil [4]. The regiochemistry of addition of atomic fluorine to these alkenes reflected the indiscriminate nature of F. Hydrogen atom abstraction reactions competed with addition in the case of propene and 2-methylpropene [3,4]. At low pressures unimolecular cleavage from vibrationally excited radical intermediates was observed [2,4]. Since abstraction of allylic-type hydrogen atoms from *E*- and *Z*-2-butene gives rise to 2-butenyl radicals which have a barrier to interconversion [5], we undertook a study of the action of atomic fluorine on the isomeric 2-butenes to see if this reactive hydrogen abstractor ($F\cdot$) would lead to products which retain the stereochemistry of the starting alkene.



Consequently mixtures of $\text{N}_2\text{F}_4(\text{NF}_2)$ with *E*- and with *Z*-2-butene were irradiated and the products examined. In this paper we report our results, which contrast with those reported earlier by Walling and Thayer [6] and by Cuthbertson *et al.* [7]. These workers observed that when *E*- and *Z*-2-butenyl radicals were generated via hydrogen abstraction by *t*-butoxy radical, final products retained the double bond configuration of the starting alkenes.

RESULTS

Irradiation of mixtures of *E*-2-butene and of *Z*-2-butene with $\text{N}_2\text{F}_4(\text{NF}_2)$ in the gas phase at various pressures was carried out in the manner previously described [3]. The reaction produced N_2F_2 , and minor amounts of SiF_4 , nitrogen oxides, and N_2 , identified by mass spectra, and a liquid mixture. This liquid fraction was purified by trap-to-trap distillation on the vacuum line followed by gas chromatography. The components were collected as eluted and were identified by ^1H and ^{19}F NMR, infrared, and mass spectra. Table I summarizes the NMR data.

Reactions carried out under low pressure conditions (total initial pressure 40 mm) also yielded a small amount of CH_3NF_2 , identified by its infrared and mass spectra [8], and 1-fluoropropene identified by its ^{19}F NMR [9] and mass spectrum. Product ratios were determined by NMR and gas phase chromatography and are recorded in Table II and III.

TABLE I

NMR Spectra of Products^a

Products	Chemical Shift ^b		Coupling Constant, Hz	
	¹ H, δ	¹⁹ F, δ		
$ \begin{array}{cccc} \text{a} & \text{b} & \text{c} & \text{d} \\ \text{CH}_3 & -\text{CH}- & \text{CH}- & \text{CH}_3 \\ & & & \\ & \text{F} & \text{NF}_2 & \end{array} $ 1	a 1.32 (d of d) b 4.80 (d of m) c 3.65 (m) d 1.24 (m)	-186.7 (m), -179.8 (m) + 49.3 (d)	J_{ab} 6.8 J_{bc} 6.8 ^c J_{cd} 7.2 $J_{b'c}$ 3.2 ^c J_{HaFb} 2.5 J_{HbFb} 49.2 J_{HdFc} 1.5	
$ \begin{array}{cccc} \text{a} & \text{b} & \text{c} & \text{d} \\ \text{CH}_2 = \text{CH} - & \text{CH} - & \text{CH}_3 \\ & & \\ & \text{NF}_2 & \end{array} $ 2	a, b multiplets centered at 5.1 c 4.10 (t of m) d 1.45 (d of t)	+42.5 (d)	J_{cd} 7.2 J_{HcF} 28 J_{HdF} 0.8	
$ \begin{array}{ccc} \text{a} & & \text{c} \\ \text{CH}_3 & & \text{H} \\ & \diagdown & / \\ & \text{C} = \text{C} & \\ & / & \diagdown \\ \text{b H} & & \text{d} \\ & & \text{CH}_2 - \text{NF}_2 \end{array} $ <i>E</i>-3	a 1.74 (d of d of t) b 5.89 (d of q of t) c 5.49 (d of t of q) d 3.95 (t of d of q)	+54.3 (t)	J_{ab} 6.4 J_{ac} 1.2 J_{ad} 1.0 J_{bc} 15.8 J_{bd} 0.8 J_{cd} 7.0 J_{HdF} 30	
$ \begin{array}{ccc} \text{a} & & \text{d} \\ \text{CH}_3 & & \text{CH}_2 - \text{NF}_2 \\ & \diagdown & / \\ & \text{C} = \text{C} & \\ & / & \diagdown \\ \text{b H} & & \text{c H} \end{array} $ <i>Z</i>-3	a 1.74 (d of d) b 5.89 (m) c 5.44 (m) d 4.12 (t of d)	+54.3 (t)	J_{ab} 6.9 J_{ac} 1.0 J_{cd} 7.0 J_{HdF} 29.7	

^a Elemental analyses and mass spectra were consistent with assigned structures.

^b Spectra were run as approx 5% volume solutions in DCCl₃ with probe temperature at 25°C. ¹⁹F chemical shifts are in parts per million downfield relative to FCCL₃ as external reference. Proton chemical shifts are in parts per million downfield relative to Si(CH₃)₄ as internal standard. Ratios of signals agreed with assigned structures.

^c 1:1 Diastomeric mixture.

TABLE II

Products from Photolysis of $\text{N}_2\text{F}_4(\text{NF}_2)$ with *E*- and *Z*-2-Butene.

Starting Alkene	Products	Yield ^a	Ratios, Molar	
			(2)+(3) (1)	(<i>E</i> -3) (<i>Z</i> -3)
<i>Z</i> -2-butene	1, 2, 3	50%	3.94	1.33 ± 0.15
<i>E</i> -2-butene	1, 2, 3	60%	3.68	1.44 ± 0.15

^aBased on the equations $2 \text{C}_4\text{H}_8 + 2 \text{N}_2\text{F}_4 = 2 \text{C}_4\text{H}_7\text{NF}_2 + 2\text{HF} + \text{N}_2\text{F}_2$ for substitution and $2 \text{C}_4\text{H}_8 + 2 \text{N}_2\text{F}_4 = 2 \text{C}_4\text{H}_8(\text{F})\text{NF}_2 + \text{N}_2\text{F}_2$ for addition. Reactant molar ratio of alkene to N_2F_4 3:2, 490 mm total initial pressure. Yield of N_2F_2 was essentially quantitative.

TABLE III

Ratio of *E*-3/*Z*-3 as Function of Pressure

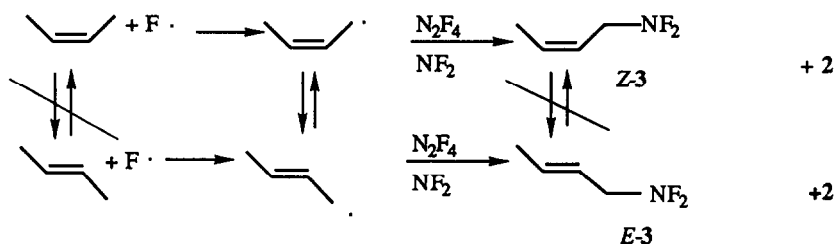
Starting Alkene	Total initial pressure, mm	<i>E</i> -3 <i>Z</i> -3 ± 0.15
<i>Z</i> -2-butene	490	1.33
<i>E</i> -2-butene	490	1.44
<i>Z</i> -2-butene	120	1.22
<i>Z</i> -2-butene	40	1.29
<i>E</i> -2-butene	40	1.22

The products *E*-3 and *Z*-3 were found to be stable under the reaction conditions and starting alkene recovered from partially completed reactions showed no isomerization.

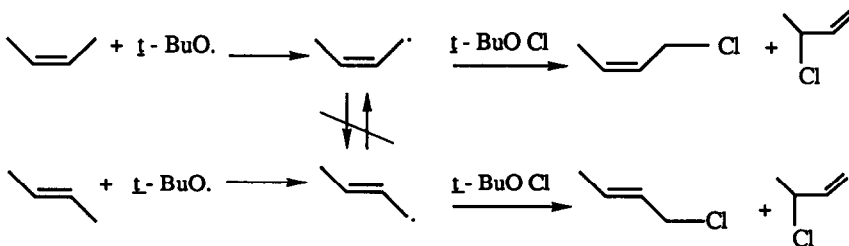
DISCUSSION

Results summarized in Tables II and III indicate that the stereochemical make-up of the product 3 is independent of the starting alkene; the same ratio of *E*-3/*Z*-3, within experimental

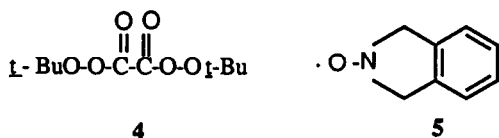
error, is obtained from either *Z*-2-butene or from *E*-2-butene. Since control experiments indicate that *E*-3 and *Z*-3 are stable (with respect to double bond isomerization) under the reaction conditions and that the starting alkenes do not undergo isomerization during reaction, we conclude that the intermediate 2-butenyl radicals are interconverting prior to trapping by $\text{N}_2\text{F}_4(\text{NF}_2)$.



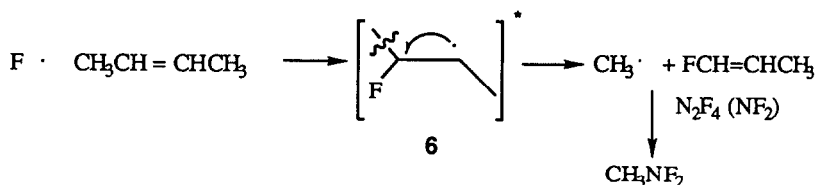
This finding contrasts with the photochlorination of the 2-butene (and similar alkenes) with *t*-butyl hypochlorite studied by Walling and Thayer [6]. These workers found that photolysis of *t*-butyl hypochlorite in the presence of neat alkene at 40°C gave substitution products which retained the stereochemistry of the starting alkene [6].



More recently Cuthbertson and co-workers [7] investigated the fate of the 2-butenes (neat) when exposed to *t*-butoxy radical derived from 4 in the presence of the nitroxyl trap 5.



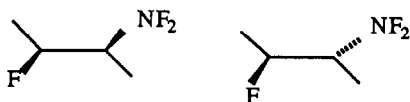
In this case also the 1-substitution product retained the starting alkene stereochemistry. The fact that our stereochemical results are at variance with the Walling and Cuthbertson studies may be attributed to the fact that our reaction takes place in the gas phase where vibrationally excited intermediates can play a role. Excitation of the intermediate 2-butenyl radicals under our conditions is not unreasonable since hydrogen abstraction by atomic fluorine is such an exothermic process. Although no significant change in the *E*-3/*Z*-3 ratio was observed when the pressure was varied (Table III), the cleavage products CH_3NF_2 and 1-fluoropropene were detected at the lower pressures. These fragments presumably arise via an excited intermediate resulting from atomic fluorine addition.



This type of β -scission has been previously noted in atomic fluorine reactions [2,4].

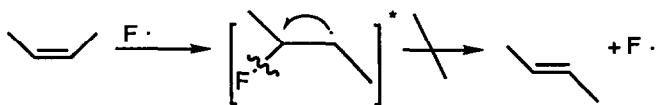
The insensitivity of the *E*-3/*Z*-3 ratio to pressure change (Table III) is probably due to the fact that the barrier to interconversion of the 2-butenyl radicals is much lower than that involved in methyl cleavage from intermediate 6. Fluorine-containing radicals are known to be more efficient storers of excess vibrational energy than similar hydrocarbon radicals [8].

The NMR data indicate that two diastereomeric adducts are obtained in about a 1:1 ratio from both *E*- and *Z*-2-butene.



This result points to non-selective stereochemistry of addition, an expected consequence for free radical addition in the gas phase. Cuthbertson *et al.* [7] reported similar findings for addition of *t*-butoxy radical and nitroxyl 5 across the double bond of *E*- and *Z*-2-butene.

Since no *cis-trans* isomerization of the starting 2-butene was observed, addition of atomic fluorine does not occur reversibly in these reactions on a time scale which would permit rotation about the C2-C3 bond in the intermediate.



In conclusion we find that 2-butenyl radicals generated from atomic fluorine and *E*- and *Z*-2-butene are not configurationally stable in the gas phase at ambient temperature.

EXPERIMENTAL

Caution: N_2F_4 and derivatives should be handled with care. The reactions and isolation operations were conducted routinely behind shields.

General

Proton nuclear magnetic resonance, fluorine nuclear magnetic resonance, infrared, and mass spectra were obtained using the following instruments, respectively: Varian HA-100 high-resolution spectrometer, Varian DA 60 high resolution spectrometer, Beckman-IR5A spectrophotometer, and either a Consolidated Model 620, Bendix Model 12 or Associated Electronics Model MS902 mass spectrometer.

Starting Materials

The *E*- and *Z*-2-butenes were obtained from Matheson and their purities checked by gas chromatography (GC, see below). Tetrafluorohydrazine of the (mole %) composition 99.3% N_2F_4 , 0.1% N_2O , 0.4% NO , 0.1% N_2 , 0.1% NF_3 , and 0.02% N_2F_2 was kindly supplied by the Redstone Research Laboratory, Rohm & Haas Co., Huntsville, AL.

Reaction of N_2F_4 with *E*- and *Z*-2-butene

The photolysis was carried out in an apparatus similar to that previously described using reactor volumes of 714 and 2240 ml [3]. The starting molar ratio of alkene to N_2F_4 was 3:2 and the initial pressure ranged from 490 to 40 mm at 25°C. After irradiation (0.5 to 3.0 h) the reaction mixture was passed over sodium fluoride pellets to remove HF and fractionated on the vacuum line

through traps at -86°C , -126°C , and -196°C . The less volatile fractions were further purified by gas chromatography (thermal conductivity cell, He carrier) using a 10 ft x 3/8 in column packed with 30% of QF-1 on 60/80 mesh Chromosorb P at 125°C and a 30 ft x 3/8 in column packed with 30% benzyl cyanide-silver nitrate on 60/80 mesh Chromosorb W at 60°C . The latter allowed *E*- and *Z*-3 to be separated. Products were collected as they eluted and were identified by NMR, IR, and mass spectra (Table I). Amounts recorded in Table II were determined by gas chromatography and NMR analysis. Infrared and mass spectra showed the more volatile fractions to be mixtures of recovered alkene (no isomerization by GC), *cis*- and *trans*- N_2F_2 , SiF_4 , and small amounts of nitrogen oxides and NF_3 . Occasionally small amounts of N_2 also were detected by mass spectrometry.

ACKNOWLEDGEMENT

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