H)$^+$. Anal. Calcd for $C_4H_8NO_3SF_3$: C, 23.19; H, 3.86; N, 6.76; S, 15.46; F, 27.54. Found: C, 22.94; H, 3.73; N, 6.49; S, 15.15; F, 26.95.

The trifylamide **6a** was converted to the oxamide **6** (yield, 99%) by the procedure described for 1. Vacuum distillation afforded pure **6**: bp 74–76 °C (0.5 mm); IR (liquid) 1740, 1720, 1420, 1320, 1200, 1160, and 1120 cm^{-1}; NMR ($CDCl_3$) δ 3.4 (s, 3 H), 3.7 (t, 2 H, J = 6 Hz), and 4.0 (t, 2 H, J = 6 Hz); mass spectrum (CI), m/e 461 (M + H)$^+$. Anal. Calcd for $C_{10}H_{14}N_2O_8S_2F_6$: C, 25.64; H, 2.99; N, 5.98; S, 13.68; F, 24.36. Found: C, 25.60; H, 3.11; N, 5.77; S, 13.92; F, 23.95.

***N,N'*-Bis(2-chloroethyl)-*N,N'*-bis(trifluoromethylsulfonyl)oxamide (7).** To a suspension of (2-chloroethyl)amine hydrochloride (5.80 g; 0.05 mol) and powdered 3A molecular sieves (15 g, from Linde Division, Union Carbide Corp.) in dichloroethane (100 mL) was added dropwise trifluoromethanesulfonyl chloride (5.3 mL; 0.025 mol) at room temperature under a nitrogen atmosphere. After the addition was completed, the mixture was stirred at 80 °C for 20 h. Filtration of the solid from the reaction mixture, followed by evaporation of the filtrate, gave 3.26 g (31%) of crude liquid product. Vacuum distillation of the liquid gave pure *N*-(2-chloroethyl)trifluoromethylsulfonamide (**7a**): bp 53–55 °C (0.5 mm); IR (liquid) 3310, 3150, 1420, 1370, 1220, 1200, and 1150 cm^{-1}; mass spectra (CI), m/e 212 (M + H)$^+$. Anal. Calcd for $C_3H_5NO_2SClF_3$: C, 17.06; H, 2.37; N, 6.64; S, 15.17; Cl, 16.59; F, 27.01. Found: C, 17.42; H, 2.51; N, 6.54; S, 15.38; Cl, 16.21; F, 26.79.

Oxalyl chloride (0.58 mL; 0.0067 mol) was added dropwise into a solution of **7a** (2.80 g; 0.013 mol) and "Proton Sponge" (1.44 g; 0.0067 mol, from Aldrich Chemical Co., Inc.) in methylene chloride (50 mL) at 0 °C under a nitrogen atmosphere. After the addition, the mixture was stirred at room temperature for 24 h. Solvent was evaporated, and the residue was treated with diethyl ether. The ethereal solution was dried over sodium sulfate. Evaporation of ether followed by the treatment of the residue with petroleum ether gave 2.55 g (80%) of crude product. Recrystallization of the crude product from petroleum ether afforded pure **7**: mp 71–73 °C; IR (CH_2Cl_2) 1720, 1400, 1360, 1320, 1230, 1160, and 1120 cm^{-1}; mass spectrum (CI), m/e 477 (M + H)$^+$. Anal. Calcd for $C_8H_8N_2O_6S_2Cl_2F_6$: C, 20.17; H, 1.68; N, 5.88; S, 13.45; Cl, 14.71; F, 23.95. Found: C, 20.05; H, 1.49; N, 5.92; S, 13.20; Cl, 14.98; F, 23.60.

***N,N'*-Bis(2-chloro-3-pyridyl)-*N,N'*-bis(trifluoromethylsulfonyl)oxamide (8).** To a suspension of 2-chloro-3-aminopyridine (5.14 g; 0.04 mol) and powdered 3A molecular sieves (10 g) in methylene chloride (60 mL) was added dropwise trifluoromethanesulfonic anhydride (3.4 mL; 0.02 mol) at 0 °C under a nitrogen atmosphere. After the addition was completed, the mixture was stirred at room temperature for 5 h, and then the solid was filtered. Filtrate was evaporated and treated with water to give 5.0 g (48%) of crude solid product. It was collected and recrystallized from cyclohexane to give pure *N*-(2-chloro-3-pyridyl)trifluoromethylsulfonamide (**8a**): mp 120–122 °C; IR (CH_2Cl_2) 3300, 1370, 1230, 1210, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 7.35 (m, 1 H), 8.0 (2 d, 1 H, J = 4 Hz), 8.35 (2 d, 1 H, J = 4 Hz), and 8.30 (s 1 NH); mass spectrum (EI), m/e 260 (M$^+$). Anal. Calcd for $C_6H_4N_2O_2SClF_3$: C, 27.69; H, 1.54; N, 10.77; S, 12.31; Cl, 13.46; F, 21.92. Found: C, 27.85; H, 1.41; N, 11.00; S, 11.95; Cl, 13.66; F, 21.50.

Oxalyl chloride (0.53 mL; 0.006 mol) was added dropwise into a stirring suspension of **8a** (2.61 g; 0.01 mol) and powdered 3A molecular sieves (5.0 g) in methylene chloride (75 mL) at 0 °C under a nitrogen atmosphere. The mixture was then heated to 60 °C, held there for 3 h, and then held at room temperature for 60 h. The reaction mixture was filtered, and the filtrate was evaporated to dryness. The resulting residue was extracted with diethyl ether, and the combined ethereal extracts were dried over sodium sulfate. Evaporation of the dried ethereal solution obtained 2.33 g (81%) of crude product. Recrystallization of the crude product from cyclohexane gave pure **8**: mp 104–106 °C; IR (CH_2Cl_2) 1750, 1730, 1420, 1360, 1220, and 1130 cm^{-1}; NMR ($CDCl_3$) δ 7.50 (m, 1 H), 8.10 (2 d, 1 H, J = 4 Hz), and 8.5 (m, 1 H); mass spectrum (EI), m/e 574 (M$^+$). Anal. Calcd for $C_{14}H_6N_2O_6S_2Cl_2F_6$: C, 29.27; H, 1.05; N, 9.76; S, 11.15; Cl, 12.20; F, 19.86. Found: C, 29.10; H, 1.14; N, 9.90; S, 10.89; Cl, 11.95; F, 19.40.

Registry No. 1, 71537-30-9; **1a**, 23384-04-5; **2**, 71537-31-0; **2a**, 23383-96-2; **3**, 71549-42-3; **3a**, 23384-20-5; **4**, 71537-32-1; **4a**, 23383-97-3; **5**, 71549-43-4; **5a**, 23383-95-1; **6**, 71537-33-2; **6a**, 65832-23-7; **7**, 71537-34-3; **7a**, 71537-35-4; **8**, 71537-36-5; **8a**, 58157-01-0; 4-chloroaniline, 106-47-8; trifluoromethanesulfonic anhydride, 358-23-6; oxalyl chloride, 79-37-8; 2,4-dichloroaniline, 554-00-7; 2,4,5-trichloroaniline, 636-30-6; 2,4,6-trichloroaniline, 634-93-5; 4-nitroaniline, 100-01-6; 2-methoxyethylamine, 109-85-3; 2-chloroethylamine hydrochloride, 870-24-6; 2-chloro-3-aminopyridine, 6298-19-7; trifluoromethanesulfonyl chloride, 421-83-0.

Transformation of Nitrimines to Acetylenes and Allenes. 1,3 Rearrangement of *N*-Nitroenamines to *C*-Nitro Compounds

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Nitrimines, prepared from ketoximes and nitrous acid, can be converted to acetylenes and allenes by treatment with excess acetic anhydride in the presence of pyridine at reflux. With 4-(dimethylamino)pyridine as catalyst, most fragmentations proceed at room temperature. Consecutive treatment of nitrimines with strong bases and aqueous acid allows their isomerization to the less stable *N*-nitroenamines which on storage revert to the parent nitrimines. Thermolysis of *N*-nitroenamines leads to α-nitroimines by 1,3 rearrangement or to the more stable 1-(alkylamino)-2-nitro-1-alkenes. The thermal rearrangement of nitrimines follows a different course and affords mainly nitronitriles by fragmentation.

In connection with other work on the chemistry of nitrimines we came across two distinct transformations which seem to be new and proceed in yields high enough to be of some preparative value. Nitrimines with neighboring methine, and particularly methylene groups, form salts with bases. For example, acidification of the salt derived from "pernitrosocamphor" (1) gave a crystalline tautomer, "isopernitrosocamphor", which on storage slowly returned to the more stable pernitrosocamphor.[1] The stable mod-

(1) Hantzsch, A.; Dollfuss F. E. *Ber. Dtsch. Chem. Ges.* **1902**, *35*, 226–65.

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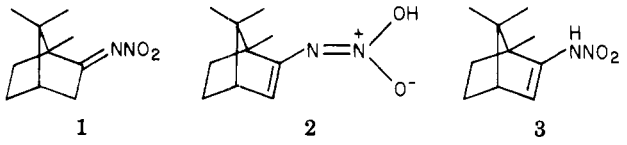

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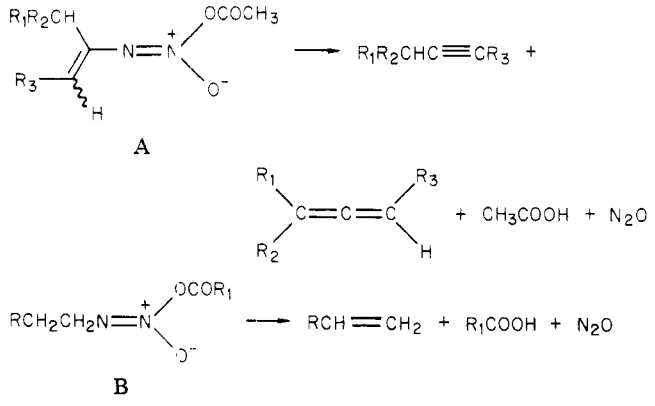
ification was correctly formulated as the nitrimine **1**, but the unstable form was assumed to be the "nitronic acid" **2** rather than the *N*-nitroenamine **3**. We have now prepared the tautomers of three other nitrimines, **4**, **5**, and **9**, and their formulation as *N*-nitroenamines is based on the following evidence. In agreement with earlier work,[2] methylation of pinacolone nitrimine (**22**) with methyl iodide in the presence of sodium methoxide gave the *N*-methyl-*N*-nitroenamine **25**, with ultraviolet absorption (all in isooctane) at 238 nm (ϵ 4900). The analogously prepared homologue **26** also absorbed at 238 nm (ϵ 3500). The tautomer **24** of *tert*-butyl-*n*-butylnitrimine **4**, available by consecutive treatments of **4** with potassium *tert*-butoxide and with aqueous sulfuric acid, exhibited absorption at 231 nm (ϵ 3400). All three compounds, **24**, **25**, and **26**, thus contain the same chromophore, and since the methyl derivatives **25** and **26** are *N*-methyl rather than *O*-methyl compounds (three proton singlets in their NMR spectra at δ 3.4 and 3.42), the tautomer of **4** must be the *N*-nitroenamine **24** rather than the "nitronic acid". Comparison of infrared spectra, which all exhibit the valence vibrations typical for the nitro group, led to the same conclusion.

In contrast to the N-alkylation of salts prepared by deprotonation of nitrimines, acylation of *N*-nitroenamines and nitrimines with acetic anhydride in the presence of a base seems to occur on oxygen. The resulting intermediates **A** decompose with elimination of nitrous oxide (identified by its infrared spectrum) and acetic acid to form acetylenes and allenes depending on the site of deprotonation. Support for intermediate A is provided by the decomposition of *N*-alkyl-*N*-nitroamides which leads to olefins, carboxylic acids, and nitrous oxide via the diazoxy ester B.[3] This new transformation was studied in some

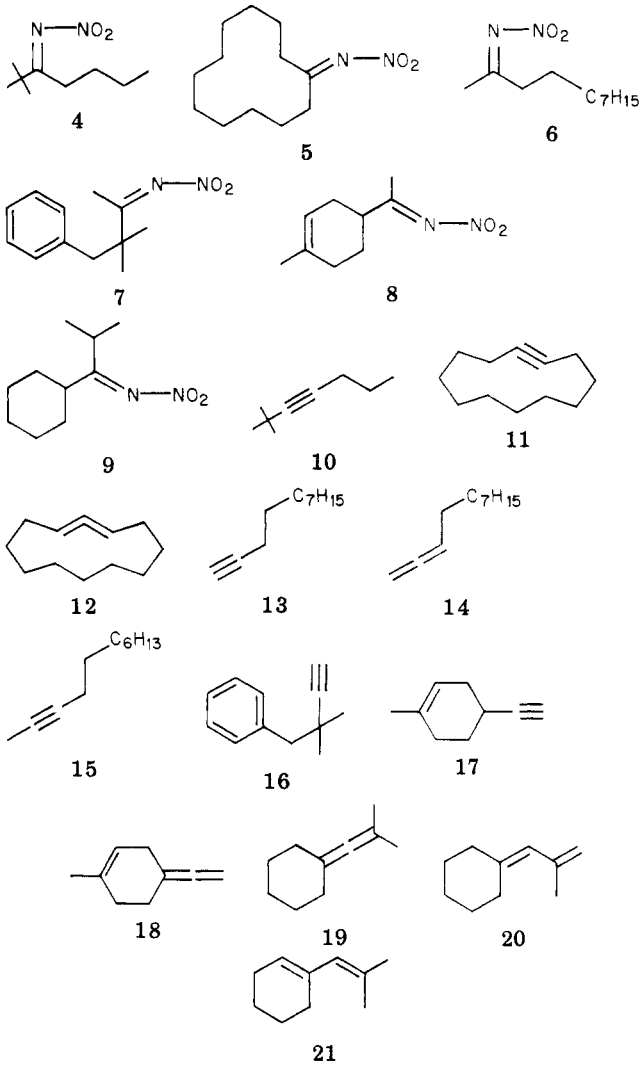


A

B

detail and the results are summarized in Table I (see Scheme I for the structures). With excess acetic anhydride as solvent, the reaction is performed at 100 °C with pyridine as the base. In the presence of even catalytic amounts of 4-(dimethylamino)pyridine[4] most fragmentations proceed at room temperature. The use of trifluoroacetic, rather than acetic, anhydride offers no advantage. This three-step procedure for the dehydration of ketones to acetylenes and allenes seems to be more general than that

Scheme I. Reactants and Products for Table I



using the Hofmann elimination of quaternized enamines,[5] and its scope probably compares favorably with methods going through vinyl ethers or vinyl sulfides.[6] It will only become as general as the intramolecular Wittig reaction of α-halo ketones or the dehydrohalogenation of geminal halides[6] after a more widely applicable method for the preparation of nitrimines has been discovered.

Efforts to purify *N*-nitroenamine **24** by gas–liquid chromatography failed and produced an isomer whose infrared and nuclear magnetic resonance spectra suggested the presence of the α-nitroimine **28**. An ultraviolet absorption spectrum displayed a low-intensity band at 345 nm (ϵ 290) which could only have been caused by the presence of approximately 2% of the tautomeric enamine. An analogous thermal rearrangement was observed with the *N*-methyl derivative **26** which was transformed to isomer **29**. Both α-nitroimines **28** and **29** were hydrolyzed over wet silica gel in benzene solution to the same α-nitro ketone **31**, identical with an authentic sample prepared from *tert*-butyl *n*-butyl ketone and propyl nitrate in the presence of potassium *tert*-butoxide. Compound **25**, derived from pinacolone, was also thermally unstable and afforded the *C*-nitro isomer, but this time in its enamine form **27** with ultraviolet absorption at 343 nm (ϵ 16000). Hydrolysis

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(3) White, E. H.; Grisley, D. W., Jr. *J. Am. Chem. Soc.* **1961**, *83*, 1191–6.
(4) Steglich, W.; Höfle, G. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 981.
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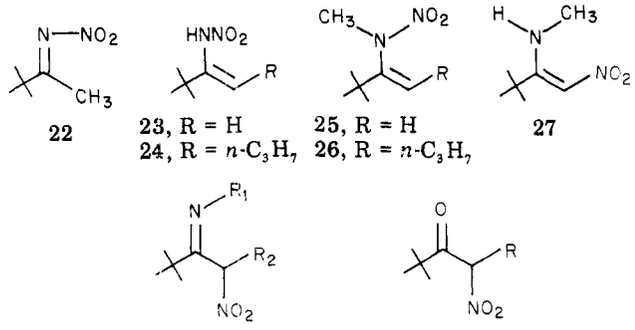
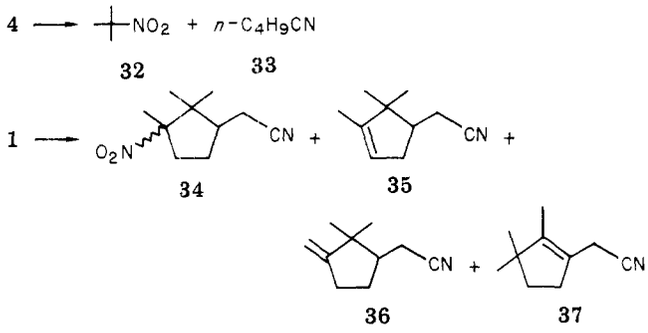


22 23, R = H 25, R = H 27
24, R = n-C_3H_7 26, R = n-C_3H_7

28, R_1 = H; R_2 = n-C_3H_7 30, R = H
29, R_1 = CH_3; R_2 = n-C_3H_7 31, R = n-C_3H_7

of **27** with aqueous oxalic acid gave ketone **30**, which, in agreement with data collected on other α-nitro ketones,[7] contained 10% enol in carbon tetrachloride as judged by nuclear magnetic resonance spectroscopy. The α-nitroimines **28** and **29** are the products initially formed in these thermal rearrangements, but the *C*-nitroenamines represent the more stable tautomers. In agreement with these observations, the compounds prepared by Feuer[8] from aldehyde imines and propyl nitrate in liquid ammonia with potassium amide and ammonium chloride (conditions leading to the thermodynamically more stable products) are all 1-(alkylamino)-2-nitro-1-alkenes. This efficient synthesis by necessity yields products with hydrogen attached to the C_1 carbon while the keto nitrimine rearrangement described in this paper affords homologues with alkyl substituents attached to this position. Other methods for the synthesis of α-nitroenamines are known, and their limitations have been enumerated.[8]

The pyrolysis of nitrimines was studied briefly; their behavior differs significantly from that of their tautomers. Nitrimine **4** on gas chromatography underwent fragmentation to 2-methyl-2-nitropropane (**32**) and valeronitrile (**33**). We also reexamined the thermolysis of camphor-



nitrimine (**1**) which was studied twice previously.[9,10] Interestingly, the major product (38%) isolated when the thermolysis was performed for 5 h in refluxing xylene was a mixture of epimeric nitronitriles **34**. One of these, with melting point 74–75 °C, is undoubtedly identical with a substance ($C_{10}H_{16}N_2O_2$, melting point 57 °C, typographical error?) reported by one investigator.[9] These nitronitriles were accompanied by the two campholenonitriles **35** and **36** (20 and 14%, respectively) which had been detected in both previous studies. Incidentally, the nitro derivative **34** is not a precursor of the two olefins **35** and **36** and was recovered unchanged when heated in xylene under the conditions leading to its creation. α-Campholenonitrile (**35**) and its isomer β-campholenonitrile (**37**), resulting from acid-catalyzed rearrangement, are produced from camphor oxime by "abnormal" Beckman rearrangement.[11] The thermolysis of nitrimines, which proceeds under neutral conditions, may thus be of use for cases in which the products formed initially in the Beckmann fragmentation undergo further, acid-induced changes.

Experimental Section

Vapor-phase chromatography was performed on a F&M 720 instrument. The following spectrometers and solvents were used: IR, Perkin-Elmer 247 ($CHCl_3$); NMR, Varian T-60 (CCl_4, Me_4Si as internal standard); UV, Perkin-Elmer Hitachi 200 (isooctane); mass spectrum, Varian Mat 44. Boiling points are not corrected. Microanalyses were performed by the Robertson Laboratory, Florham Park, NJ.

Nitrimine 4.[12] A separatory funnel was charged with a cold mixture of 30.1 g (0.19 mol) of 2,2-dimethyl-3-heptanone oxime in 200 mL of ether and 28 g (0.4 mol) of sodium nitrite in 150 mL of water. Cold 2 N sulfuric acid (175 mL) was added, and the funnel was immediately stoppered, rapidly inverted, and vented. The mixture was then shaken several times, and the aqueous layer was withdrawn and discarded. The ether layer was transferred to an Erlenmeyer flask and allowed to react for 5 h (gas evolution!). The solution was dried (Na_2SO_4), filtered, evaporated, and distilled to give 6.5 g of impure 2,2-dimethyl-3-heptanone, bp <30 °C (0.1 mm), and 23.4 g (66%) of **4**: bp 50–52 °C (0.1 mm); IR 1610, 1560, 1370, 1315 cm^{-1}; NMR δ 1.43 (s, 9), 0.8–2.6 (m, 9); UV 269 nm (ϵ 560). Anal. $C_9H_{18}N_2O_2$: C, H, N.

Nitrimines 5–9 were prepared similarly and had the following physical properties.

5: mp 60 °C (from hexane); IR 1620, 1570, 1360, 1320 cm^{-1}; NMR δ 1.2–1.9 (m, 18), 2.1–2.5 (m, 4). Anal. $C_{12}H_{22}N_2O_2$: C, H, N.

6: bp 85 °C (0.1 mm); IR 1630, 1580, 1360, 1325 cm^{-1}; NMR δ 0.90 (t, 3, J = 5 Hz), 1.0–1.7 (m, 14), 2.00 (s, 3), 2.1–2.4 (m, 2). Anal. $C_{11}H_{22}N_2O_2$: C, H, N.

7: bp 88 °C (0.1 mm); IR 1620, 1380, 1320 cm^{-1}; NMR δ 1.18 (s, 6), 1.92 (s, 3), 2.82 (s, 2), 6.9–7.3 (m, 5). Anal. $C_{12}H_{16}N_2O_2$: C, H, N.

8: bp 83 °C (0.1 mm); IR 1635, 1570, 1360, 1320 cm^{-1}; NMR δ 1.67 (s with fine splitting, 3), 2.03 (s, 3), 1.5–2.4 (m, 7), 5.40 (br, 1).

9: bp 70 °C (0.1 mm); IR 1620, 1570, 1370, 1320 cm^{-1}; NMR δ 1.18 (d, 3, J = 7 Hz), 1.21 (d, 3, J = 7 Hz), 1.0–2.8 (m, 11), 1.37 (septet, 1, J = 7 Hz). Anal. $C_{10}H_{18}N_2O_2$: C, H, N.

Transformation of Nitrimine 4. A stirred mixture of 1.86 g (10 mmol) of **4**, 6 mL (60 mmol) of acetic anhydride, and 2 mL (25 mmol) of pyridine was heated under nitrogen for 20 h at 100 °C. Water was added, and the mixture was extracted with three 10-mL portions of pentane. The combined extracts were washed with 5% sodium bicarbonate and dried (Na_2SO_4), and the solvent was removed through a Vigreux column at atmospheric pressure. Distillation of the residue at 10 mm into a dry ice cooled receiver flask afforded 0.80 g of **10** (65% yield), which was redistilled: bp 122–124 °C (760 mm) [lit.[13] bp 131–133 °C (680 mm)]; NMR δ 0.95 (t, 3, J = 7 Hz), 1.17 (s, 9), 1.2–1.4 (m, 2), 2.03 (t, 2, J = 6 Hz); mass spectrum, m/e (rel intensity) 124 (M^+, 12), 67 (100).

Transformations of nitrimines 5–7 were performed under the conditions given in Table I, and the reactions were worked up as described above. Separation of isomers was achieved by preparative VPC. The resulting products had the following spectra.

11:[14] IR (no C≡C stretching absorption); NMR δ 1.3–1.7 (m, 16), 1.9–2.3 (m, 4); mass spectrum, m/e (rel intensity) 164 (M^+, 2), 67 (100).

12:[14] IR 1960 cm^{-1}; NMR δ 0.9–1.7 (m, 14), 1.7–2.3 (m, 4), 4.6–5.0 (m, 2); mass spectrum, m/e (rel intensity) 164 (M^+, 2), 41 (100).

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(14) Ziegenbein, W.; Schneider, W. M. *Chem. Ber.* **1965**, *98*, 824–8.

Table I. Transformation of Nitrimines to Acetylenes and Allenes[a]

nitrimine	yield, %	mp or bp, °C (mm Hg)	transformation conditions: amt of reactant, equiv Ac$_2$O	py	*p*-Me$_2$N, py	temp, °C	time, h	yield, %	products (ratio)
4	66	50 (0.1)	6	2.5		100	20	65	**10**
			5		2.5	25	20	46	
			5	2.5		25	20	2	
5	52	60	5	2.5		100	2	76	**11/12** (81/19)
			5		0.5	30	24	71	(82/18)
6	47	78 (0.05)	5	2.5		100	5	28	**13/14/15** (31/20/49)
			5		0.5	25	24	22	(9/15/76)
7	33	95 (0.1)	5	2.5		100	4	71	**16**
			5		0.5	35	24	38	
8	40	63 (0.05)	5	2.5		100	6	52	**17/18** (80/20)
			5		0.5	35	24	18	(86/14)
9	32	75 (0.1)	5	2.5		100	48	22	**19/20/21** (8/19/73)

[a] See Scheme I for structures.

13:[15] IR 3340, 2140, 2120 cm^{-1}; NMR δ 0.90 (t, 3, J = 5 Hz), 1.1–1.6 (m, 14), 1.75 (t, 1, J = 2 Hz), 1.9–2.3 (m, 2).

14:[16] IR 1970 cm^{-1}; NMR δ 0.90 (t, 3, J = 6 Hz), 1.0–1.6 (m, 12), 1.7–2.2 (m, 2), 4.6 (m, 2), 5.0 (m, 1).

15:[15] IR (no C≡C stretching absorption); NMR δ 0.90 (t, 3, J = 6 Hz), 1.0–1.6 (m, 12), 1.75 (t, 3, J = 3 Hz), 1.8–2.2 (m, 2).

16: IR 3330, 2110, 1610 cm^{-1}; NMR δ 1.15 (s, 6), 1.95 (s, 1), 2.70 (s, 2), 7.15 (s, 5); mass spectrum, m/e (rel intensity) 143 (M − 15, 2), 57 (100). Anal. $C_{12}H_{14}$: C, H.

17: IR 3340, 2110, 1680 cm^{-1}; NMR δ 1.63 (s with fine splitting, 3), 1.87 (t, 3, J = 3 Hz), 1.4–2.6 (m, 7), 5.3 (br, 1); mass spectrum, m/e (rel intensity) 120 (M^+, 5), 40 (100). Anal. C_9H_{12}: C, H.

18: IR 1970, 1680 cm^{-1}; NMR δ 1.65 (s with fine splitting, 3), 1.9–2.4 (m, 4), 2.5–2.8 (m, 2), 4.5 (m, 2), 5.3 (br, 1); mass spectrum m/e (rel intensity) 120 (M^+, 4), 40 (100). Anal. C_9H_{12}: C, H.

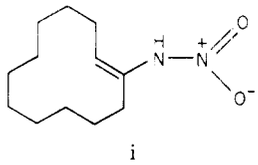
19:[17] IR 1970 cm^{-1}; NMR δ 1.65 (s, 6), 1.3–1.7 (m, 6), 1.8–2.1 (m, 4).

20:[18] IR 1970, 1650, 1635, 1600, 900 cm^{-1}; NMR δ 1.3–1.7 (m, 6), 1.80 (s, 3), 1.9–2.5 (m, 4), 4.65 (s, 1), 4.85 (s, 1), 5.40 (s, 1); UV 233 nm.

21:[18] IR 1650 cm^{-1}; NMR δ 1.4–1.7 (m, 4), 1.75 (s, 6), 1.8–2.2 (m, 4), 5.45 (br, 2); UV 232 nm.

Isomerization of Nitrimine 4. Potassium *tert*-butoxide (3.1 g, 27.5 mmol) in 15 mL of THF was added at 5–10 °C to a solution of 4.65 g (25 mmol) of **4** in 20 mL of THF. Stirring of the mixture was continued for 10 min at 5 °C, and then it was poured into cold water, and neutral parts were removed by extraction with ether. The aqueous layer was acidified with cold 2 N sulfuric acid, extracted with pentane, washed with water, dried (Na_2SO_4), and evaporated. Drying of the residue at 20 °C (0.1 mm) gave 3.78 g (81%) of **24**: IR 3000–3600, 1590, 1380, 1310 cm^{-1}; NMR δ 1.16 (s, 9), 0.7–2.2 (m, 7), 5.65 (t, 1, J = 7 Hz), 9.6 (br, 1); UV 231 nm (ϵ 3400); mass spectrum, m/e (rel intensity) 140 (M − 46, 9), 57 (100). Anal. $C_9H_{18}N_2O_2$: C, H, N.

Isomerization of Nitrimines 5 and 9 was carried out as above. The resulting tautomers i and ii, respectively, were not fully



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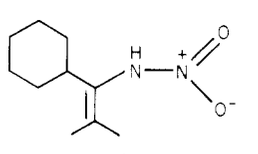

ii

characterized because of their unstability. They had the following spectral characteristics. i: IR 3000–3600, 1595, 1360, 1345, 1305 cm^{-1}; NMR δ 1.0–1.8 (m, 16), 1.9–2.5 (m, 4), 5.55 (t, 1, J = 8 Hz), 9.8 (br, 1). ii: IR 3000–3600, 1590, 1370, 1330 cm^{-1}; NMR 0.9–2.7 (m, 11), 1.70 (s, 3), 1.85 (s, 3), 9.7 (br, 1).

Transformation of *N*-Nitroenamine 24. An ice-cold solution of 1.86 g (10 mmol) of **24** in 5 mL (50 mmol) of acetic anhydride was treated with 1.2 mL (15 mmol) of pyridine. After being stirred for 2 h at 20 °C, the mixture was worked up as described for nitrimine **4** to yield 0.83 g (67%) of 2,2-dimethyl-3-heptyne (**10**).

Methylation of Nitrimine 4. To a solution of 0.14 g (6 mmol) of sodium in 10 mL of methanol were added 0.93 g (5 mmol) of **4** and 1 mL of iodomethane, and the mixture was heated at reflux for 6 h. After removal of the solvent in vacuo, water was added, and the mixture extracted with pentane, washed with water, dried (Na_2SO_4), and evaporated. Purification of the residue by silica gel chromatography afforded 0.46 g (46%) of **26**: bp 50 °C (0.1 mm); IR 1660, 1520, 1290 cm^{-1}; NMR δ 1.20 (s, 9), 0.8–2.0 (m, 7), 3.40 (s, 3), 5.55 (t, 1, J = 7 Hz); UV 238 nm (ϵ 5300); mass spectrum, m/e (rel intensity) 154 (M − 46, 15), 42 (100). Anal. $C_{10}H_{20}N_2O_2$: C, H, N.

Thermal Rearrangement of *N*-Nitroenamine 25. A solution of 0.50 g of **25**[2] in 5 mL of xylene under argon was heated at reflux for 2 min. The solvent was removed in vacuo, and the residue was crystallized from 10 mL of ether at −20 °C to give 0.17 g (34%) of **27**: mp 94 °C; IR 3000–3600, 1615, 1510, 1360 cm^{-1}; NMR δ 1.37 (s, 9), 3.28 (d, 3, J = 6 Hz), 6.63 (s, 1), 10.3 (br, 1); UV 237 nm (ϵ 2100), 343 (16 000); mass spectrum, m/e (rel intensity) 158 (M^+, 16), 56 (100). Anal. $C_7H_{14}N_2O_2$: C, H, N.

Hydrolysis of *C*-Nitroenamine 27. A mixture of 33 mg of **27**, 0.1 g of oxalic acid, 2 mL of water, and 1 mL of ether was stirred for 1 h at 20 °C. Ether was added, and the organic layer was separated, washed with water, and dried (Na_2SO_4). Evaporation left 22 mg of crude 2,2-dimethyl-4-nitro-3-butanone[19] (**30**), which was purified by VPC collection: IR 1735, 1570, 1380 cm^{-1}; NMR (keto form, 90%) δ 1.23 (s, 9), 5.42 (s, 2); NMR (enol form, 10%) 1.23 (s, 9), 6.82 (s, 1), 13.2 (br, 1); UV (EtOH) 230 nm (ϵ 600), 303 (140); NaOH added 234 (3500), 331 (16 100).

Thermal Rearrangement of *N*-Nitroenamines 24 and 26. VPC injection of **24** onto a 2-ft silicone rubber column at 140 °C (injector temperature 250 °C) resulted in the formation of α-nitroimine **28** as the major product. A pure sample was obtained by collection: IR 3000–3600, 1640, 1560, 1380 cm^{-1}; NMR δ 1.13 (s, 9), 0.8–2.7 (m, 7), 5.25 (dd, J = 5 and 9 Hz), 9.9 (br, 1); mass spectrum, m/e (rel intensity) 186 (M^+, 12), 41 (100); UV 285 nm (ϵ 170), 345 (290). Anal. $C_9H_{18}N_2O_2$: C, H, N.

***N*-Nitroenamine 26** rearranged under the same conditions mainly to the α-nitro compound **29**: IR 1660, 1550, 1370 cm^{-1}; NMR δ 1.17 (s, 9), 0.9–1.9 (m, 7), 3.17 (s, 3), 5.00 (dd, 1, J = 3 and 10 Hz); UV 251 nm (ϵ 680); mass spectrum, m/e (rel intensity) 158 (M − 42, 2), 42 (100). Anal. $C_{10}H_{20}N_2O_2$: C, H, N.

Hydrolysis of α-Nitroimines 28 and 29. A slurry of 38 mg of **28** and 2 g of moist silica gel (5% water) in benzene was stirred overnight at room temperature. It was filtered, washed with benzene, and evaporated to give 29 mg (76%) of nitro ketone **31**. An analytical sample was obtained by VPC collection: IR 1725, 1570, 1380, 1360 cm^{-1}; NMR δ 1.20 (s, 9), 0.9–2.5 (m, 7), 5.50 (dd,

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1, J = 5 and 9 Hz); UV (EtOH) 236 nm (ϵ 1800), 295 (150); NaOH added 230 (7500), 320 (2400). Anal. $C_9H_{17}NO_3$: C, H, N. These data were in agreement with those of a sample prepared by the action of propyl nitrate on 2,2-dimethyl-3-heptanone in the presence of potassium *tert*-butoxide.[20]

Similarly, α-nitroimine **29** led to the same nitro ketone **31** in 75% yield.

Thermolysis of Nitrimine 4. VPC injection of **4** onto a 6-ft silicone rubber column at 100 °C (injection port temperature 250 °C) produced two major products which were collected. They were identified as 2-methyl-2-nitropropane (**32**) and valeronitrile (**33**) by comparison of their spectra with those of authentic samples.

Thermolysis of Camphor Nitrimine (1).[9,10] A solution of 1 g of **1** in 15 mL of xylene under argon was heated at reflux for 5 h. The solvent was evaporated and the remaining oil separated by distillation into two fractions. The lower boiling fraction [0.32 g, bp <40 °C (0.1 mm)] consisted of nitriles **35** and **36** in 20 and 14% yield, respectively. They were separated by preparative VPC and had spectra identical with those published.[10] The higher boiling fraction [0.48 g, bp >40 °C (0.1 mm)] contained two epimers of **34** (38%). Separation was achieved by chromatography on silica gel with hexane–ethyl acetate (4:1) as eluant. Epimer A: bp 65 °C (bath temperature) (0.1 mm); IR 2250, 1540, 1390, 1360 cm^{-1}; NMR δ 0.78 (s, 3), 1.23 (s, 3), 1.63 (s, 3), 1.5–3.2 (m, 7). Anal. $C_{10}H_{16}N_2O_2$: C, H, N. Epimer B: mp 74–75 °C (from ether); IR 2250, 1540, 1390, 1350 cm^{-1}; NMR δ 0.90 (s, 3), 0.93 (s, 3), 1.55 (s, 3), 1.5–3.2 (m, 7). Anal. $C_{10}H_{16}N_2O_2$: C, H, N.

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Registry No. **1**, 31180-79-7; **4**, 71606-95-6; **5**, 71606-96-7; **6**, 71606-97-8; **7**, 71606-98-9; **8**, 71606-99-0; **9**, 71607-00-6; **10**, 29022-29-5; **11**, 1129-90-4; **12**, 1129-91-5; **13**, 2243-98-3; **14**, 56956-46-8; **15**, 60212-29-5; **16**, 65108-28-3; **17**, 31929-13-2; **18**, 71607-01-7; **19**, 20023-44-3; **20**, 71607-02-8; **21**, 62184-84-3; **24**, 71607-03-9; **25**, 71607-04-0; **26**, 71607-05-1; **27**, 71607-06-2; **28**, 71607-07-3; **29**, 71607-08-4; **30**, 35869-41-1; **31**, 71607-09-5; **32**, 594-70-7; **33**, 110-59-8; *cis*-**34**, 71607-10-8; *trans*-**34**, 71607-11-9; **35**, 15373-31-6; **36**, 15340-92-8; i, 71607-12-0; ii, 71607-13-1; 2,2-dimethyl-3-heptanone oxime, 71607-14-2; cyclododecanone oxime, 946-89-4; 2-undecanone oxime, 2158-28-3; 3,3-dimethyl-4-phenyl-2-butanone oxime, 71607-15-3; 1-(1-methylcyclohexene-4-yl)ethanone oxime, 71607-16-4; 1-cyclohexyl-2-methylpropanone oxime, 52247-05-9.

Fluorination with Xenon Difluoride. 21. Evidence for Free-Radical Intermediates in Trifluoroacetic Acid Catalyzed Fluorinations

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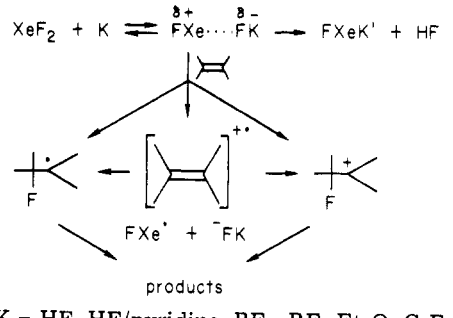
Trifluoroacetic acid catalyzed fluorination of styrene with xenon difluoride resulted in the formation of five products: 1-fluoro-1-phenyl-2-(trifluoromethyl)ethane (**2**), 1,2-difluoro-1-phenylethane (**3**), 1-(trifluoroacetoxy)-1-phenyl-2-(trifluoromethyl)ethane (**4**), 1-(trifluoroacetoxy)-1-phenyl-2-fluoroethane (**5**), and 1-fluoro-1-phenyl-2-(trifluoroacetoxy)ethane (**6**). The reaction with diphenylacetylene resulted in the formation of six products. The formation of fluoro radicals, trifluoromethyl radicals, and trifluoroacetoxy radicals, formed by decomposition of $FeXeOCOCF_3$, is suggested in order to explain the formation of products.

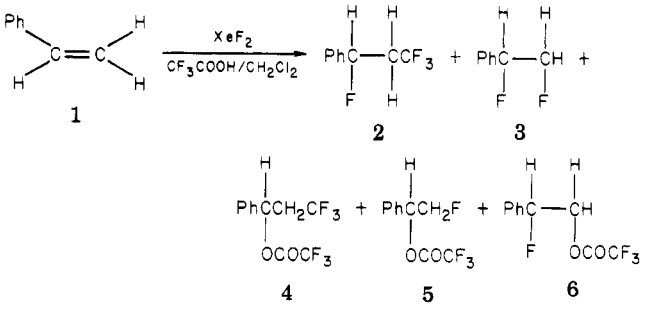
It has been demonstrated that xenon difluoride is a mild fluorinating agent for fluorination of alkenes, acetylenes, and aromatic and hetereoaromatic molecules; this topic has been recently reviewed.[1] It is known that the mechanism of fluorine addition to olefins with xenon difluoride depends on the following factors: the structure of the olefin, the catalyst used, solvent polarity, and temperature. The formation of β-fluoro carbonium ions, free-radical intermediates, or ion radicals has been suggested to explain the formation of products (Scheme I). It has been demonstrated that the following substrates are convenient catalysts for fluorination of olefins with xenon difluoride: hydrogen fluoride,[2] hydrogen fluoride–pyridine,[3] boron trifluoride[4] (for less reactive organic molecules), boron trifluoride etherate,[5] pentafluorothiophenol[6] (for sensitive organic molecules), trifluoroacetic acid,[7] and bromine.[8] We have already demonstrated[9] that trifluoroacetic acid catalyzed fluorination of *cis*- and *trans*-1-phenylpropene resulted in the formation of vicinal difluorides and fluoride trifluoroacetates, and the formation of β-fluoro carbonium ions was suggested. We now report that small changes in the structure of the olefin, e.g., styrene, dramatically change the course of the reaction with xenon difluoride in

Scheme I



K = HF, HF/pyridine, BF_3, $BF_3 \cdot Et_2O$, C_6F_5SH, CF_3COOH, Br_2

Scheme II



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