Polyfluoroalkyl Derivatives of Nitrogen. Part 49.[1] Ene Reactions of Trifluoronitrosomethane: Formation of *N*-Trifluoromethylhydroxylamines

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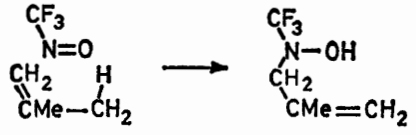
Trifluoronitrosomethane is a versatile and reactive enophile, forming *N*-alkenyl-*N*-trifluoromethylhydroxylamines, by transfer of allylic hydrogen to oxygen and bonding of olefinic carbon to nitrogen, with the olefins: propene, [1-^{2}H]propene, but-1-ene, (*E*)-but-2-ene, 2-methylpropene, (*Z*)-pent-2-ene, 2-methylbut-1-ene, 2-methylbut-2-ene, (*Z*)-4-methylpent-2-ene, 2,3-dimethylbut-2-ene, cyclopentene, cyclohexene, 1-methylcyclohexene, β-pinene, and allyl bromide, chloride, and cyanide. Cyclo-octa-1,5-diene gives an ene-adduct, while the initial ene-adduct from cyclohexa-1,4-diene undergoes rapid Diels–Alder addition of further trifluoronitrosomethane. Cyclohepta-1,3,5-triene undergoes Diels–Alder addition by way of its bicyclo[4.1.0]hepta-2,4-diene isomer. Acetylacetone gives the compound $CF_3{\cdot}N(OH){\cdot}CH(CO{\cdot}CH_3)_2$. In these ene reactions, nitrogen becomes bonded to the least substituted carbon atom. At −78 °C, the following relative rates of reaction were observed:

Z-MeCH:CHMe:	*E*-MeCH:CHMe:	$Me_2C{:}CH_2$:	MeCH:CH_2:	EtCH:CH_2
170	21	14	1.5	1.0

The hydroxylamines are easily oxidised to nitroxides, and those from the compound $CF_3{\cdot}N(OH){\cdot}CMe_2{\cdot}CMe{:}CH_2$ and its reduction product, $CF_3{\cdot}N(OH){\cdot}CMe_2{\cdot}CHMe_2$, are stable; their ^{1}H n.m.r. spectra have been examined.

SINCE our report that trifluoronitrosomethane undergoes ready reaction with 2-methylpropene (Scheme 1),[2] a number of 'ene' reactions of nitroso-compounds have been described. Nitrosobenzene reacts with 2,3-dimethylbut-2-ene to give a hydroxylamine, easily

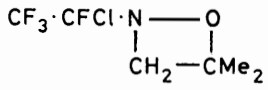


SCHEME 1

oxidised to a nitroxide.[3] Fairly stable *N*-pentafluorophenylhydroxylamines are formed from pentafluoronitrosobenzene and the olefins 2,3-dimethylbut-2-ene, 2-phenylpropene, and methyl methacrylate.[4] With polyfluoronitrosoalkanes, the area is a little confused. The nitroso-compounds $R_F{\cdot}CFCl{\cdot}NO$ ($R_F = CF_3$ or $CF_2{\cdot}NO_2$) react with propene and with isobutene to give unstable adducts, hydrolysed to, for example, the hydroxylamine $CF_3{\cdot}CO{\cdot}N(OH)CH_2{\cdot}CMe{:}CH_2$, but it was suggested that the initial adduct was an oxazetidine (1), largely on the basis of a ^{1}H n.m.r. spectrum of poor quality.[5] Ginsberg and his co-workers have described on a number of occasions reactions of trifluoronitrosomethane with unsaturated compounds, with an emphasis on electron-transfer reactions and e.s.r. studies.[6-9] The adducts with methyl methacrylate, and with propene and isobutene, are of the 'ene'-type (2; R = CO_2Me, H, or Me),[9] but those of allyl compounds $CH_2{:}CH{\cdot}CH_2X$ (X = Cl, Br, $SiCl_3$, or NCS) were given an isomeric structure (3) rather than (4), largely on the basis of an e.s.r. signal observed during the reaction, ascribable to the fragment $CF_3{\cdot}N(\dot{O}){\cdot}CH$.[8,9]

We have studied the reactions of trifluoronitrosomethane with various hydrocarbon olefins, which give adducts of the 'ene'-type, and disagree with the structure (3) ascribed to the adducts of allyl compounds. We have made a few relative rate studies, and have investigated the e.s.r. spectra of a number of nitroxides, readily produced by oxidation of the initial hydroxylamines, and of the corresponding saturated hydroxylamines.

The terminal olefins propene and but-1-ene readily gave adducts (4; X = H or Me), the latter largely as the



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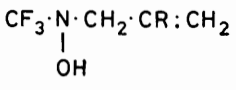

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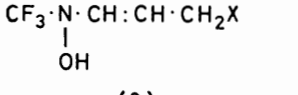

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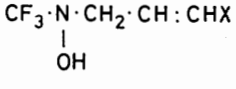

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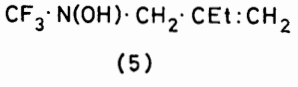

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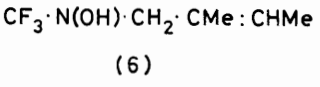

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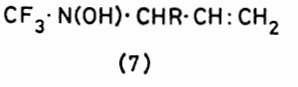

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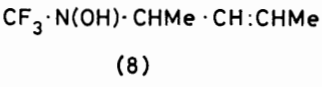

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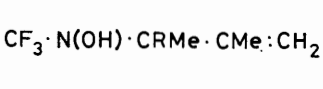

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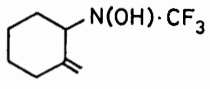


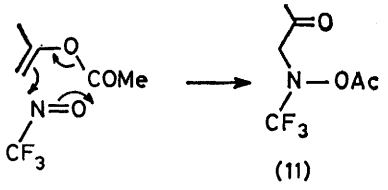
(10)

trans-isomer. 2-Methylbut-1-ene gave a 55 : 45 mixture of adducts (5) and (6) and [1-^{2}H]propene gave (7; R = D). So far as internal olefins were concerned, (*E*)-but-2-

ene gave the expected (7; R = Me) and (*Z*)-pent-2-ene gave equal amounts of (7; R = Et) and (8), resulting from transfer of a hydrogen from a CH_3 group and a CH_2 group, respectively. With (*Z*)-4-methylpent-2-ene, where the choice is between a CH and a CH_3 group, only (7; R = Pr^i) from attack at the latter was formed. Cyclo-pentene and -hexene gave the expected ene-adducts.

With 2-methylbut-2-ene, adduct (9; R = H) from attack at the least substituted olefinic carbon resulted, and 2,3-dimethylbut-2-ene gave adduct (9; R = Me). With 1-methylcyclohexene, only the least substituted olefinic carbon was attacked, and the major product (10) (80%) resulted from transfer of a methyl group hydrogen. No rearrangement of carbon skeleton was observed in the ene reaction with β-pinene.

The allyl compounds $CH_2{:}CH{\cdot}CH_2X$ (X = Cl, Br, or CN) reacted much less readily than unsubstituted olefins,

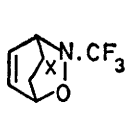


(11)

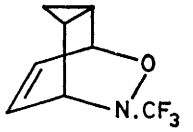
SCHEME 2

but gave isomeric mixtures of adducts (4). The initial propene adduct appeared to give [4; X = $N(OH){\cdot}CF_3$], as the *Z*-isomer. Reaction with isopropenyl acetate occurred fairly readily and resulted in a mixture of the expected ene-product and *O*-acetylhydroxylamine (11), possibly by the $[2\pi + 2\pi + 2\sigma]$ transition state in Scheme 2.

Cyclohexa-1,4-diene gave the adduct (12) apparently resulting from Diels–Alder addition of nitroso-compound to the initial ene-adduct. For comparison, rapid Diels–Alder addition occurred to cyclohexa-1,3-diene. Ene-



(12) X = $N(OH){\cdot}CF_3$



(13)

reaction occurred with cyclo-octa-1,5-diene. With cyclohepta-1,3,5-triene, the possibility presented itself of $[6\pi + 2\pi + 2\sigma]$ addition to give a cyclohepta-2,4,6-trienylhydroxylamine; however, instead (13) was formed by Diels–Alder addition to its bicyclo[4.1.0]hepta-2,4-diene isomer.

Acetylacetone gave a product $CF_3{\cdot}N(OH){\cdot}CH(COCH_3)_2$ formally derived by ene-reaction of the enol tautomer. A recent e.s.r. spectroscopic study of the reactions of trifluoronitrosomethane with 1,3-diketones described the initial formation of nitroxide radicals derived from hydroxylamines of this type.[10]

Limited studies of reactions of simple olefins at −78 °C gave the following relative rates (*k*, but-1-ene = 1.0):

(*Z*)-MeCH:CHMe	(*E*)-MeCH:CHMe	$Me_2C{:}CH_2$
170	21	14
$MeCH{:}CH_2$	$EtCH{:}CH_2$	
1.5	1.0	

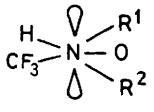
At −35 °C, cyclopentene reacted five times faster than cyclohexene.

Thus alkyl substitution increases the rate of attack at the double bond, (*Z*)-but-2-ene being the most reactive olefin, the nitrogen becomes attached to the least substituted olefinic carbon atom, and where competition is possible, methyl group hydrogens are transferred about as readily as methylene group hydrogens, whereas a methine group transfers its hydrogen much less readily. An allylic hydrogen is always transferred, and the reaction with β-pinene goes without rearrangement. Electron-withdrawing substituents at the allylic carbon reduce considerably the ease of reaction. Trifluoronitroso-methane appears to be one of the most reactive of enophiles, and the direction of addition is understandable if the nitrogen is the more electrophilic centre. An analogy may perhaps be drawn with singlet oxygen,[11] but the nitroso-compound shows more selectivity,[12] not surprisingly in view of its polar character.

Nitroxide Formation and E.S.R. Studies.—Ginsberg and his co-workers have reported the formation during the reactions of trifluoronitrosomethane with olefins of nitroxide radicals, and indeed used the observed hyperfine structure in their e.s.r. spectra as a basis for assigning structures to the resultant hydroxylamines, largely on the basis of the presence or absence of coupling to α-hydrogens.

We have observed in a qualitative fashion the formation of nitroxides during the reaction, by e.s.r. spectroscopy. The same nitroxides could be detected by subsequent oxidation of the product hydroxylamines by potassium permanganate and acetic acid, or by simple air oxidation of a benzene solution of the hydroxylamine. Presumably, the nitroxides observed during the reaction are produced by trifluoronitrosomethane oxidation of these hydroxylamines. The unsaturated hydroxylamines could readily be reduced by hydrogen in the presence of a palladium catalyst, and the resultant saturated hydroxylamines readily produced the signal of a nitroxide also. With one exception, nitroxides with α-hydrogens were not obtained in high concentration. Oxidation of a benzene solution of the cylohexa-1,4-diene adduct (12) produced a bright reddish purple solution (e.s.r. spectrum:[13] 12-line multiplet with $a_N \simeq a_F =$ 10.5, a_H 5.5 G) which however, faded rapidly upon concentration, or in contact with air. The nitroxides from cyclopentene and cyclohexene also appeared as 12-line multiplets. The appearance of hyperfine coupling to α-hydrogens was not general, however. It was shown by the nitroxide from (9; R = H) ($a_F \simeq a_N = 11.4$; $a_H = 4.5$ G) but not resolved for that from (7; R = Pr^i)

($a_F \simeq a_N = 11.7$ G), or from the saturated hydroxylamines $CF_3{\cdot}N(OH){\cdot}CHMe{\cdot}CHMe_2$ ($a_F = a_N = 11.6$ G) or $CF_3{\cdot}N(OH){\cdot}CHEt{\cdot}CHMe_2$ ($a_F = a_N = 11.9$ G). If the nitroxides are near planar at the nitrogen atom, then hyperconjugative delocalisation can only occur if the adjacent hydrogen is not located in the nodal plane of the orbital carrying the unpaired electron.[14] Thus in conformation (14), only a small coupling would be expected. Coupling is observed when $R^1 = Me$ and $R^2 = CMe{:}CH_2$ but not when $R^1 = CHMe_2$ and $R^2 = CH{:}CH_2$, Me, or Et, where the bulky isopropyl group is present. Thus the absence of coupling is not indicative of the absence of α-hydrogens. Ginsberg and his co-workers concluded that the adducts of allyl compounds contained the $CF_3{\cdot}N(OH){\cdot}CH{:}$ grouping since a coupling to one hydrogen was observed in a nitroxide formed during the course

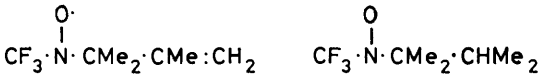


(14)

of the reaction. We find that the products of these reactions are mixtures of *cis*- and *trans*-isomers, whose n.m.r. spectra indicate the isomeric structure (4) rather than (3).

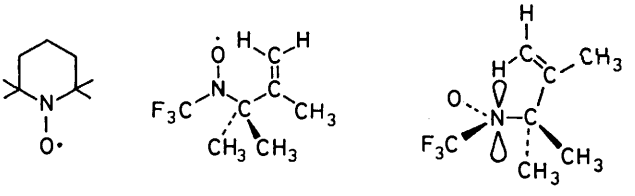
The hydroxylamine from 2,3-dimethylbut-2-ene (9; R = Me) and its reduced product $CF_3{\cdot}N(OH){\cdot}CMe_2{\cdot}CHMe_2$ both contain no α-hydrogens, and consequently gave rather stable nitroxides upon oxidation with silver(II) oxide, as deep red liquids. Nitroxide (15) gave a rather broad e.s.r. spectrum ($a_F \simeq a_N = 11.3$ G), and showed $\lambda_{max.}$ *ca.* 500 and 227 nm (ε 2 090 in hexane), parameters similar to those of (16) ($a_F \simeq a_N = 12.2$ G), $\lambda_{max.}$ 506 and 232 nm (ε 1 800).

The ^1H n.m.r. spectra (at 35° C, neat liquid) of the two radicals (15) and (16) showed substantial contact shifts. The saturated nitroxide showed three bands,



(15) (16)

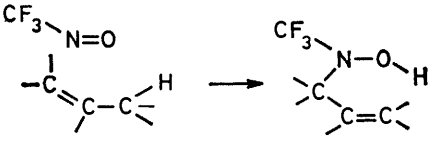
assigned on the basis of their estimated intensities, at 0.6 p.p.m. to low field (2 CH_3), and 14.3 (CH) and 17.0 p.p.m. (2 CH_3) to high field of the corresponding absorptions of the parent hydroxylamine, equivalent [15] to hyperfine couplings of +0.02, −0.56, and −0.66 MHz (+8, −200, and −240 mG). The spectrum of (15) showed a low-field band at +11.7 (:CH) and, apparently, overlapping high-field bands at −1.4 (2 CH_3), −7.5 (CH_3), and −16.0 p.p.m. (:CH), relative to (9), corresponding to hyperfine couplings of +0.45, −0.06, −0.29, and −0.62 MHz (+160, −20, −105, and −230 mG). A number of aliphatic nitroxides have been studied by n.m.r. spectroscopy. In di-t-butyl nitroxide $a_H = 0.11$ G,[16] and it is tempting to suggest that in (16), the coupling constant of least magnitude is due to coupling to the more remote methyls. The coupling constants in (15) are more problematical, and the substantial couplings of opposite sign involving the olefinic protons are unusual. Alteration of sign of the hyperfine coupling constants for protons attached to adjacent carbons has been observed for a number of cyclic



(17) (18) (19)

nitroxides, *e.g.* (17).[17] Perhaps a substantial contribution from conformation (18) or (19) would account for the observations.

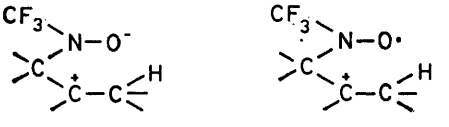
The Mechanism of the Ene Reactions of Trifluoronitrosomethane.—All the above results can be accommodated by a concerted mechanism (Scheme 3) which is, however, somewhat affected by polar effects, in that the nitrogen becomes bonded to the more nucleophilic carbon. The absence of rearrangement in the reaction with β-pinene argues against any zwitterionic intermediate such as



SCHEME 3

(20), or any other in which a positive charge resides on the hydrocarbon portion. A non-concerted mechanism which involves the formation by hydrogen transfer to the nitroso-compound of an allyl fragment as an intermediate, either as an ion or radical, also appears untenable since the evidence is that the nitrogen also becomes bonded to an olefinic carbon and not to one that was originally allylic. The suggestion of an oxazetidine as an intermediate [5] appears unlikely and the postulate by Russian workers of the involvement of ion radicals (21) is based upon doubtful e.s.r. evidence and a misidentification of the products of allyl compounds.

The rate-determining formation of a diradical in the reactions of nitroso-compounds with olefins has recently

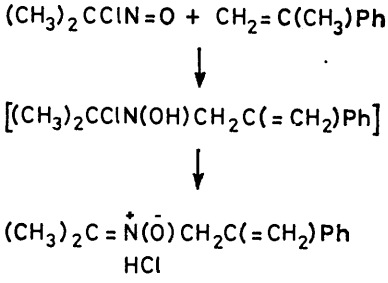


(20) (21)

received support, largely on the basis of e.s.r. spectroscopic studies of nitroxide formation during the reaction of 2,4,6-trichloronitrosobenzene with olefins.[18] However, no study was made of the products of these reactions, and the evidence is therefore doubtful.

α-Chloronitroso-compounds, particularly α-chloro-

nitrosoadamantane, undergo ene reaction with olefins, but here, it appears that the initial hydroxylamines are unstable, and eliminate hydrogen chloride to form a nitrone salt (Scheme 4).[19]



SCHEME 4

The ease of the ene reactions of the strongly electrophilic trifluoronitrosomethane, and its regiospecificity, offer promise in synthesis. The chemistry of the novel nitroxides (15) and (16) will be reported elsewhere.[20]

EXPERIMENTAL

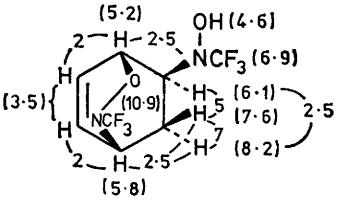
I.r., ^1H, and ^{19}F n.m.r. (trifluoroacetic acid as external reference, with positive shifts to low field), mass, and e.s.r. spectra were obtained with a Perkin-Elmer spectrophotometer model 21, a Perkin-Elmer R10 (60 and 56.46 MHz) instrument, an A.E.I. MS/2H spectrometer (electron beam energy 70 eV), and a Decca Radar Ltd. spectrometer (Type XI instrument operating at 9 270 ± 1 MHz; 100 kHz field modulation, phase-sensitive detection), respectively.

Trifluoronitrosomethane was obtained by the pyrolysis of trifluoroacetyl nitrite,[21] and the hydrocarbon olefins were high quality commercial samples, purified by g.l.c. where necessary.

Ene reactions (see Table) were carried out in tapped ampoules, using equimolar amounts of reactants (5—20 mmol). They were readily monitored by loss of the blue colour of the nitroso-compound. The product *N*-trifluoromethylhydroxylamines, which were isolated by fractional condensation *in vacuo*, were colourless liquids which decomposed fairly readily at room temperature, with the liberation of hydrogen fluoride and the formation of intractable polymeric material.

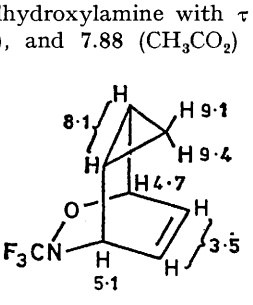
In the relative rate studies, the excess of olefin was analysed by g.l.c. (silver nitrate–ethylene glycol at room temperature).

Reactions of Trifluoronitrosomethane.—(*a*) *With* N-*allyl*-N-*trifluoromethylhydroxylamine.* Reaction at room temperature for 15 h gave an unstable, highly viscous, product, which could not be analysed because of decomposition, but which ^1H n.m.r. spectroscopy indicated to be (*Z*)-1,1,1,7,7,7-hexafluoro-2,6-dihydroxy-2,6-diazahept-3-ene with τ 3.9 and 4.0 (20 H), 4.4 (:CHN, J_{cis} 6 Hz), 5.3 (:CHC, $J_{CH.CH_3}$ 7 Hz), and 6.4 (CH_2N, AB-type m).



SCHEME 5

(*b*) *With isopropenyl acetate.* Reaction at room temperature for 4 h gave a product, identified by i.r. and n.m.r. spectroscopy as a 1 : 1 mixture of *N*-trifluoromethyl-*N*-2-acetoxyprop-2-enylhydroxylamine with τ 2.38 (OH), 4.97 (:CH_2), 6.03 (CH_2), and 7.88 (CH_3CO_2) and *O*-acetyl-*N*-acetonyl-*N*-trifluoromethylhydroxylamine, with τ 6.3 (CH_2), 7.77 (CH_3COC), and 7.88 (CH_3CO_2).



SCHEME 6

(*c*) *With acetylacetone.* A mixture of acetylacetone (5.0 g,

Reactions of trifluoronitrosomethane with olefins

Olefin	Conditions (°C/time)	Yield (%)	Adduct	Molecular formula	Found C	Found H	Found N	Found F	Found *M*	Required C	Required H	Required N	Required F	Required *M*
CH_2=CHMe	−78/3 d	90	(4; X = H)	$C_4H_6F_3NO$	33.9	4.4	9.7		141.0388	34.0	4.3	9.9		141.0400
CH_2=CHEt	−78/7 d	83	(4; X = Me)	$C_5H_8F_3NO$	38.6	5.4	8.9	36.4	155.0566	38.7	5.2	9.0	36.8	155.0557
(*E*)-CHMe=CHMe	−78/1 h	87	(7; R = Me)	$C_5H_8F_3NO$	38.5	5.1	8.8	36.5	155.0557	38.7	5.2	9.0	36.8	
CH_2=CMe_2	−78/16 h	87	(2; R = Me) [a]	$C_5H_8F_3NO$	see ref. 2					38.7	5.2	9.0	36.8	
(*Z*)-CHMe=CHEt	−78/15 min	96	*b*	$C_6H_{10}F_3NO$	42.6	6.0	8.4		169.0722	42.6	5.9	8.3		169.0713
CH_2=CMeEt	−78/30 min	97	*c*	$C_6H_{10}F_3NO$	42.6	5.9	8.3		169.0722	42.6	5.9	8.3		
CHMe=CMe_2	−78/1 h	95	(9; R = H)	$C_6H_{10}F_3NO$	42.7	5.7	8.4		169.0715	42.6	5.9	8.3		
(*Z*)-CHMe=CHPr^i	−78/20 min	93	(7; R = Pr^i)	$C_7H_{12}F_3NO$	45.9	6.5	7.6		183.0871	45.9	6.6	7.7	31.2	183.0870
Me_2C=CMe_2	*d*	96	(9; R = Me)	$C_7H_{12}F_3NO$	46.1	6.6	7.8	31.4		45.9	6.6	7.7	31.2	
Cyclopentene	−78/8 d	90		$C_6H_8F_3NO$	43.2	5.1	8.1	34.0		43.1	4.8	8.4	34.2	
Cyclohexene	0/16 h	89		$C_7H_{10}F_3NO$	46.3	5.5	8.0	31.1		46.5	5.5	7.7	31.5	
1-Methylcyclohexene	25/1 h	91	*e*	$C_8H_{12}F_3NO$	49.5	6.3	6.9	29.3	195.0867	49.3	6.2	7.2	29.2	195.0870
β-Pinene	25/30 min	95		$C_{11}H_{16}F_3NO$	56.5	7.0	6.0		235.1185	56.2	6.8	6.0		235.1183
CH_2=$CHCH_2Cl$	25/24 h	58	*f*	$C_4H_5ClF_3NO$	27.7	3.0	7.9			27.4	2.8	8.0		
CH_2=$CHCH_2Br$	25/15 h	33	*g*	$C_4H_5BrF_3NO$	22.1	2.3	6.4			21.8	2.3	6.4		
CH_2=$CHCH_2CN$	25/30 h	96	*h*	$C_5H_5F_3N_2O$	36.4	3.1	17.2		166.0342	36.2	3.0	16.9		166.0353
Cyclohexa-1,3-diene	25/1 h	100	(12; X = H)	$C_7H_8F_3NO$	47.0	4.6	7.6	31.5	179.0561	46.9	4.5	7.8	31.8	179.0557
Cyclohexa-1,4-diene	25/1 h	97	(12) [i]	$C_8H_8F_6N_2O_2$	34.7	2.9	10.1	40.8		34.6	2.9	10.1	41.0	
Cyclo-octa-1,5-diene	25/20 min	30	*j*	$C_9H_{12}F_3NO$	51.9	6.0	6.6		207.0864	52.2	5.8	6.8		207.0870
Cycloheptа-1,3,5-triene	*k*	47	(13) [l]	$C_8H_8F_3NO$	50.4	4.3	7.1			50.3	4.2	7.3		

[a] Gave an O-*acetyl derivative* (35%) (Found: C, 42.8; H, 5.2; N, 7.1. $C_7H_{10}F_3NO_2$ requires C, 42.6; H, 5.1; N, 7.1%) with acetic anhydride–pyridine. [b] 1:1 Mixture of (7; R = Et) and (8). [c] 55 : 45 Mixture of (5) and (6). [d] Trifluoronitrosomethane added in four portions at −78 °C. [e] 2 : 8 Mixture of *N*-trifluoromethyl-*N*-2-methylcyclohex-2-enylhydroxylamine and *N*-trifluoromethyl-*N*-2-methylenecyclohexylhydroxylamine (10). [f] 3 : 1 Mixture of *Z*- and *E*-isomers. [g] 1 : 1 Mixture of *Z*- and *E*-isomers. [h] 1 : 2 Mixture of *Z*- and *E*-isomers. [i] Liberating trifluoronitrosomethane when heated *in vacuo*, and the n.m.r. parameters of Scheme 5 confirmed by spin decoupling. [j] 85 : 4 : 11 Mixture of three isomers by ^{19}F n.m.r. spectroscopy. [k] Warmed from −196 °C to room temperature. [l] With the τ values of Scheme 6.

50 mmol) and trifluoronitrosomethane (0.76 g, 7.7 mmol), after being allowed to react for 3 h at room temperature, gave unchanged trifluoronitrosomethane (0.07 g, 0.7 mmol) and acetylacetone, and a yellow liquid residue, which from carbon tetrachloride gave N-*trifluoromethyl*-N-*diacetylmethylhydroxylamine* (1.38 g, 6.9 mmol, 97%) (Found: *M*, 199.045 5. $C_6H_8F_3NO_3$ requires *M*, 199.044 4) as a solid which rapidly darkened, τ 1.9 (OH), 5.3 (CH), and 7.7 (2 CH_3), δ_F 7.6 p.p.m.

Catalytic Hydrogenation of N-*Trifluoromethylhydroxylamines.*—(*a*) N-*Trifluoromethyl*-N-1,1,2-*trimethylprop*-2-*enylhydroxylamine*. The title hydroxylamine (9.17 g, 50.1 mmol) in diethyl ether (20 ml) was hydrogenated at atmospheric pressure in the presence of 5% Pd–C (0.5 g). When one molar equivalent of hydrogen had been absorbed, fractionation *in vacuo* yielded N-*trifluoromethyl*-N-1,1,2-*trimethylpropylhydroxylamine* (7.60 g, 41.1 mmol, 82%) (Found: C, 45.7; H, 7.7; N, 7.5. $C_7H_{14}F_3NO$ requires C, 45.4; H, 7.6; N, 7.6%), as a liquid which condensed at 0 °C.

(*b*) N-*Trifluoromethyl*-N-2-*methylprop*-2-*enylhydroxylamine*. The title hydroxylamine was similarly hydrogenated at 0 °C, to give, after separation by g.l.c. (2-m PEGA at 150 °C), N-*trifluoromethyl*-N-2-*methylpropylhydroxylamine* (35%) (Found: *M*, 157.072 8. $C_5H_{10}F_3NO$ requires *M*, 157.071 4).

In a similar manner the *N*-1,2-dimethylprop-2-enyl- and *N*-1-isopropylprop-1-enyl-hydroxylamines were reduced.

Spectra and Structure of the N-*Trifluoromethylhydroxylamines.*—Analytical, mass, and i.r. spectral data usually confirmed the molecular formulae and suggested their identity as *N*-trifluoromethylhydroxylamines. For the most part, the ^1H and ^{19}F n.m.r. spectra then completed the identification, the compounds showing the expected absorptions. It was noted that progressive replacement of hydrogens by alkyl groups at the carbon attached to nitrogen resulted in a low-field shift of the CF_3 absorption; the following ranges were observed: $CF_3{\cdot}N{\cdot}CH_2$, 2.2—3.8; $CF_3{\cdot}N{\cdot}CHR$, 7.2—8.9; and $CF_3{\cdot}N{\cdot}CR_2$, 13.2—15.4 p.p.m. In a few cases, it was not immediately clear which of the groupings N·C=C·C or N·C·C=C were present, namely, the products of reaction with the allyl compounds $CH_2{:}CH{\cdot}CH_2$-X [where X = Br, Cl, CN, or $N(OH){\cdot}CF_3$]. In each case, however, the presence of $CF_3{\cdot}N{\cdot}CH_2$ groups was indicated, and the olefinic proton coupling constants were consistent with the presence of a CH:CHX group [$^3J_{cis}$ 8, 12, and 6 Hz, respectively for X = Cl, CN, or $N(OH){\cdot}CF_3$ and $^3J_{trans}$ 16, 17, and 15 Hz, respectively for X = Cl, CN, or Me] with magnitudes in rough accord with expectations.[22]

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