(*trans*-4-methyl-2-pentene yields *trans* epoxide; *cis* 4-methyl-2-pentene yields *cis* epoxide exclusively). Epoxide yields fall with increasing catalyst concentration, long reaction times, higher temperatures, and the presence of oxygen. The temperature dependence of the rate of hydroperoxide disappearance for the four best catalysts is shown in Table III. The data at early reaction times for peroxide disappearance are best described by

TABLE III

EXPERIMENTAL ACTIVATION ENERGY FOR *t*-BUTYL HYDROPEROXIDE DECOMPOSITION IN OCTENE-1 CATALYZED BY METAL ACETYLACETONATES[a]

Metal	E_a, kcal./mole[b]
Cr(III)	23
VO(II)	15
MoO_2(II)	12
V(III)	9

[a] At 25–120°. [b] E_a is 21 kcal./mole for the uncatalyzed decomposition. See ref. 1.

$$-\,d[t\text{-BuOOH}]/dt = k[t\text{-BuOOH}][\text{metal}(C_3H_7O_2)_n]^{1/2}$$

The effect of olefin structure on epoxide yield by this reaction is paralleled by the epoxidation yields in the absence of metal chelate,[1] best yields being obtained for the most highly substituted olefin (Table II).

On the basis of these observations it seems reasonable to describe the reaction course as involving a peroxidic intermediate complex with the metal acetylacetonate which is especially favorable for epoxidation. At higher temperatures and/or long reaction times decomposition of complex may compete with epoxide formation, *t*-butyl alcohol (produced inevitably as a by-product) may complex preferentially, the metal may be oxidized to an unfavorable oxidation state,[2] or the epoxide may be destroyed by the metal.[2,3] Stereospecificity and structural effects favor a polar mechanism.[1] The effects of oxygen[4] and the kinetic equations make a free-radical chain process a possible mechanism.

Although yields and rates of epoxide formation are consistently better from *t*-butyl hydroperoxide–metal acetylacetonate systems than from *t*-butyl hydroperoxide alone (*e.g.*, Table II), the rates, yields, and convenience on a preparative scale cannot compete with methods using peracids. The possibility of epoxidation in acid-sensitive systems is a conceivable advantage over peracid epoxidation.

Experimental

Chemicals.—Olefins were Phillips pure grade, distilled prior to use. *t*-Butyl hydroperoxide (Lucidol) was distilled to greater than 90% purity as determined by iodometric analysis. McKenzie metal acetylacetonates from freshly opened containers were used without purification.

Kinetics and Preparative-Scale Experiments.—Kinetics,[1] Tables I and III, were carried out in new glass carius tubes, degassed and thermostated at temperatures of 25–120 ± 0.02°. Remaining peroxide was determined iodometrically. Epoxide yield was measured gas chromatographically (Perkin-Elmer Model 154C) using a column containing diisodecyl phthalate on Celite (Perkin-Elmer A column). The metal acetylacetonates interfered neither with the iodometric analysis of peroxide nor with epoxide analysis. The column deteriorated somewhat more rapidly in the course of these experiments than in earlier ones[1] in which metal acetylacetonates were absent, as evidenced by poor baselines probably due to bleeding of the ester substrate.

In preparative-scale experiments olefin, *t*-butyl hydroperoxide, and metal acetylacetonate were allowed to react at temperatures ranging from ambient to the reflux temperature of the olefin under a nitrogen atmosphere[4] for 2 hr. to 2 weeks. Epoxides isolated by fractional distillation at reduced pressure through a spinning-band column had infrared, mass spectra, and boiling points identical with authentic samples. Yields in cases where all or nearly all *t*-butyl hydroperoxide was consumed were less than quantitative.

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(2) R. Stewart, "Oxidation Mechanisms," W. A. Benjamin, New York, N. Y., 1964.

(3) W. Sager, *J. Am. Chem. Soc.*, **78**, 4970 (1956).

(4) The system olefin–Cr$(C_5H_7O_2)_3$–*t*-BuOOH absorbs oxygen rapidly at room temperature. No epoxide is detected under conditions identical with Table I. The nature of this reaction has not yet been investigated. *Cf.* M. Mendelsohn, E. Arnett, and H. Freiser, *J. Phys. Chem.*, **64**, 660 (1960); E. Arnett, H. Freiser, and M. Mendelsohn, *J. Am. Chem. Soc.*, **84**, 2482 (1962); E. Arnett and M. Mendelsohn, *ibid.*, **84**, 3821, 3824 (1962).

Free-Radical Addition of Perfluoroalkylnitriles to Propylene

G. J. JANZ, N. A. GAC, A. R. MONAHAN, AND W. J. LEAHY

Rensselaer Polytechnic Institute, Department of Chemistry,
Troy, New York

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A kinetic study for the reaction of CF_3CN and ethylene at 400–440° has shown[1] that this may be classed as a free-radical telomerization, with the formation of $CF_3CH_2CH_2CN$ and $CF_3(CH_2CH_2)_2CN$ as principal addition products. The prospect of two isomeric 1:1 addition compounds arises in this reaction with an unsymmetrical olefin, such as propylene. The present Note reports some experiments undertaken with propylene and CF_3CN and $CF_3CF_2CF_2CN$, respectively, particularly to investigate the nature and composition of the 1:1 addition products. The results are considered briefly relative to the kinetics of the mechanism for CF_3CN–ethylene reaction advanced elsewhere[1] in detail.

Experimental

The reactants, C_3H_6 (99% minimum purity; Matheson Co., Inc.), CF_3CN, and C_3F_7CN (95% minimum purity; b.p. −64 and −5°, respectively; Peninsular Chemresearch, Inc.) were vacuum degassed (−195°) prior to use. The purity of all samples was checked by gas chromatographic analysis.

The reactants were premixed in the desired amounts in a suitable, all-glass manifold system at room temperature, and transferred to the reaction flask using conventional vacuum gas transfer techniques. The latter consisted simply of a 5-l. flask heated with a Glas-Col mantle.

Two series of experiments were undertaken with each nitrile and propylene to accumulate sufficient addition product for analytical characterization. The initial ratio of reactants, pressure, and temperature in these two series of experiments were as follows: C_3H_6 and CF_3CN, mole ratio (nitrile to olefin) 3.3:1.0; total initial pressure, 700–720 mm.; reaction temperature, 400 ± 2°; duration (three experiments), 20, 24, and 50 hr., respectively; C_3H_6 and C_3F_7CN, mole ratio (nitrile to olefin) 5.0:1.0; total initial pressure, 700 mm.; reaction temperature, 420°; duration (four experiments), 20, 22, 24, and 25 hr. No attempt was made in these experiments to estimate yields or conversions.

A third set of experiments was made with CF_3CN and propylene to ascertain yields. The results are shown in Table I.

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(1) N. A. Gac and G. J. Janz, *J. Am. Chem. Soc.*, **86**, 5059 (1964).

TABLE I

Temp., °C.	Time, hr.	Mole ratio of CF_3CN/C_3H_6	Initial charge, g.	Yield g.	Yield Wt. %[a]
410	17	1:1	6.4	3.31	52
404	23	10:1	6.61	0.73	72
404	26	10:1	11.36	1.0	67
408	20	5:1	9.77	1.8	72
411	24	10:1	10.41	1.2	72
420	4	10:1	10.06	1.2	80

[a] Based on the assumption of 100% olefin conversion.

For the ethylene–CF_3CN system under comparable conditions,[2] the yields fall in the range, 60–70 wt. % (also based on 100% olefin conversion).

The fractions corresponding to the 1:1 addition product were separated by gas chromatographic techniques (Beckman GC-2 chromatograph; 6- and 12-ft. columns with di-*n*-decyl phthalate on C-22 firebrick packing, at 130 and 160°). The gas chromatograms did not show a resolution for two isomeric compounds for the 1:1 addition product of C_3H_6 and CF_3CN; however, for C_3H_6 and C_3F_7CN, the gas chromatogram indicated that the 1:1 addition product was a mixture of two compounds, with one in large excess (*i.e.*, 97%). Aliquots of the 1:1 addition products thus isolated were examined by microelemental analysis, infrared spectroscopy (Perkin-Elmer Model 21, NaCl optics), and H^1 and F^{19} n.m.r. spectral analysis.[3a]

Microelemental[3b] analyses are as follows.

Anal. Calcd. for $CF_3(C_3H_6)CN$: C, 43.80; H, 4.38; N, 10.20. Found: C, 43.55; H, 4.29; N, 10.02.

Anal. Calcd. for $C_3F_7(C_3H_6)CN$: C, 35.46; H, 2.55; N, 5.91. Found: C, 35.67; H, 2.59; N, 6.12.

TABLE II

N.M.R. SPECTRA FOR THE $CF_3(C_3H_6)CN$ AND $C_3F_7(C_3H_6)CN$ FRACTIONS SEPARATED BY GAS CHROMATOGRAPHY FROM THE PRODUCTS OF THE $CF_3CN–C_3H_6$ AND $C_3F_7CN–C_3H_6$ ADDITION REACTIONS

Structure	H¹ chemical shifts[a] —CH δ_e mult.	—CH₂— δ_d mult.	—CH₃ δ_f mult.	Spin–spin coupling[b] J_{HH} J_{de}	J_{ef}	J_{df}	J_{HF} J_{ad} or J_{cd}
$\underset{a}{CF_3}\underset{d}{CH_2}\underset{e}{\overset{CN}{C}}H\underset{f}{CH_3}$ (87%)	2.95 sextet	2.4 complex	1.33 doublet	7	7	...	c
$\overset{a}{CF_3}\overset{e}{\underset{CH_3}{CH}}—\overset{d}{CH_2}—CN$ (11%)	Too low in relative intensity to be resolved and interpreted						
$\underset{a}{CF_3}\underset{b}{CF_2}\underset{c}{CF_2}\underset{d}{CH_2}\underset{e}{\overset{CN}{C}}H\underset{f}{CH_3}$	3.02 sextet	2.35 complex	1.33 doublet	7	7	...	c

Structure	F¹⁹ Chemical Shifts[d] —CF₃ ϕ_a mult.	—CF₂— ϕ_b mult.	—CF₂— ϕ_c mult.	Spin–spin coupling[b] J_{FF} J_{ab}	J_{bc}	J_{ac}	J_{FH} J_{ad}
$\underset{a}{CF_3}\underset{d}{CH_2}\overset{CN}{C}HCH_3$ (89%)	65.2 triplet	...	...	...	...	...	10.6
$\overset{a}{CF_3}\overset{d}{\underset{CH_3}{CH}}—CH_2—CN$ (11%)	73.8 doublet	...	...	...	...	...	7.5
$CF_3CF_2CF_2CH_2\overset{CN}{C}HCH_3$	81.5 triplet	128.2 singlet	114.9 multiplet	<2	<2	14.5	c

[a] In p.p.m. downfield from TMS internal references. [b] In c.p.s. [c] Not interpreted. [d] In p.p.m. from $CFCl_3$ internal reference.

Results

N.m.r. Spectra.—The fraction for which the microelemental analyses confirmed the empirical formula, $C_5H_6F_3N$, was found to consist of two components by F^{19} n.m.r. analysis. Two chemical shifts (relative to $CFCl_3$ internal standard) were observed, a triplet at ϕ 65.2, confirming CF_3 adjacent to a methylene carbon, and a doublet at ϕ 73.8, indicating a CF_3 adjacent to a methynyl carbon. The relative signal intensities show the former to be 89% of this two-component mixture. The H^1 n.m.r. analysis for this aliquot confirms the structure of the component in excess in this mixture to be $CF_3CH_2CH(CN)CH_3$. Thus a doublet at 1.33 p.p.m. (relative to TMS as internal reference) and a sextet at 2.95 p.p.m. were observed, consistent with a CH_3 adjacent to a methynyl carbon and a CH adjacent to both CH_3 and CH_2 groups, respectively. The complete structural analysis of the spectrum for the minor component in this mixture was not possible owing to the low relative intensities of the chemical shifts. The n.m.r. spectral data for the $C_7H_6F_7N$ fraction (confirmed by microelemental analysis) similarly show the component in large excess (97%) to have the structure $CF_3CF_2CF_2CH_2CH(CN)CH_3$. The n.m.r. spectra for these new fluoroorganics are described in Table II.

Infrared Spectra.—In the two samples (*i.e.*, $C_5H_6F_3N$ and $C_7H_6F_7N$, respectively), absorption at 2245 and 2262 cm.$^{-1}$ confirmed the nitrile group (*cf.* perfluoronitriles[4] 2275 ± 1cm.$^{-1}$). Bands at 1320, 1197–1113, and

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[2] G. J. Janz and J. J. Stratta, *J. Org. Chem.*, **26**, 2169 (1961).

[3] (a) We are indebted to C. W. Wilson, III, and L. O. Moore, Union Carbide Co., Research Laboratory, South Charleston, W. Va., for the n.m.r. spectra; (b) Schwartzkopf Microanalytical Laboratories, Woodside, N. Y.

[4] D. G. Weiblen, "Fluorine Chemistry," Vol. 2, Academic Press Inc., New York, N. Y., 1954.

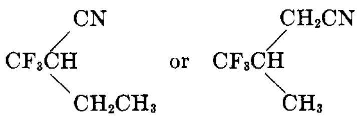
at 1339, 1176, and 1145 cm.$^{-1}$, respectively, are in accord with the literature values,[5] 1321 ± 9, 1179 ± 7, and 1140 ± 9 cm.$^{-1}$ for the CF_3 symmetrical and antisymmetrical deformation modes. Similarly, bands in the 1230–1287- and 3000-cm.$^{-1}$ regions for each sample confirmed[6] the presence of the C–F and C–H stretching modes.

The CF_2 symmetrical and antisymmetrical stretching modes have been well characterized[7] as 1125 ± 10 and 1181 cm.$^{-1}$ in a series of pentafluoroethylhalides. In the $C_7H_6F_7N$ fraction, bands are observed at 1119 and 1198 cm.$^{-1}$, respectively.

Discussion

While the microelemental analyses of the 1:1 addition products from propylene with CF_3CN and $CF_3CF_2CF_2CN$, confirm the empirical formulas, $C_5H_6F_3N$ and $C_7H_6F_7N$, respectively, the n.m.r. spectra (and chromatographic analyses for $C_7H_6F_7N$) clearly show that these are two component mixtures in each case. The compounds, $CF_3CH_2CH(CN)CH_3$ and $CF_3CF_2CF_2CH_2CH(CN)CH_3$ are present in large excess (*i.e.*, 89 and 97%), in these mixtures. The predominance of these two compounds is strong support for the viewpoint[1] that $\dot{C}F_3$ is the chain initiator in the propagation cycle of this free-radical reaction. The thermally initiated reactions of perfluoroalkylnitriles with propylene correspond closely, in this respect, with those reported elsewhere[8] for CF_3I and monoolefins.

The results are inadequate for the exact structural characterization of the second component observed in the 1:1 addition fractions. It can nevertheless be inferred (microelemental analysis, infrared spectra, and F^{19} magnetic resonance spectrum) that for the CF_3CN-propylene product two structures are probable.



I II

The presence of this second component in much smaller amounts may thus be attributed to abnormal radical additions of the perfluoroalkylnitriles with propylene. Disappearance of CN radicals in the presence of olefins has been observed[9]; in the present systems this is also a possible route to the formation of an (isomeric) 1:1 addition product.

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[5] R. R. Randle and D. M. Whiffen, *J. Chem. Soc.*, 1371 (1955).

[6] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958.

[7] O. Risgin and R. C. Taylor, *Spectrochim. Acta*, **12**, 1036 (1958).

[8] R. N. Hazeldine and B. R. Steel, *J. Chem. Soc.*, 1193 (1953).

[9] D. E. Paul and F. W. Delby, *J. Chem. Phys.*, **37**, 592 (1962).

Nitrile Oxides. III. Reduction of Nitrile Oxides to Nitriles[1]

CHRISTOPH GRUNDMANN AND HANS-DIETER FROMMELD

Mellon Institute, Pittsburgh, Pennsylvania

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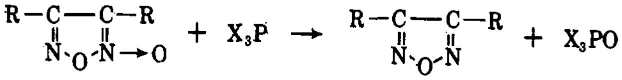
The reduction of benzonitrile oxide and triphenylacetonitrile oxide to the corresponding nitriles has been achieved by means of zinc dust and acetic acid or tin and hydrochloric acid.[2] In other cases, however, these methods have failed because of side reactions, *e.g.*, addition of the acid to the nitrile oxide with formation of a hydroxamic acid derivative which is no more reduced to the nitrile.[3]

A generally applicable method for the conversion of nitrile oxides (I) into nitriles (II) in excellent yields under very mild conditions was found in the reduction with trivalent phosphorus compounds, especially trialkyl- or triarylphosphines and trialkyl phosphites, as shown in eq. 1. The reduction of the semipolar

$$\underset{\text{I}}{R{-}C{\equiv}N{\rightarrow}O} + X_3P \longrightarrow \underset{\text{II}}{R{-}C{\equiv}N} + X_3PO \qquad (1)$$

$\geqslant N{\rightarrow}O$ group to $\geqslant N$ by trivalent phosphorus compounds is generally known,[4–8] although the ease of reduction depends to a large extent on the nature of the groups attached to nitrogen; *e.g.*, triphenylphosphine does not reduce pyridine and quinoline N-oxides or aromatic nitro groups.[4a] The dimers of nitrile oxides, the furoxans (III, 1,2,5-oxadiazol-2-oxides), are easily deoxygenated to the corresponding furazans (IV, 1,2,5-oxadiazoles),[5,6,8] although claims to the contrary have been made.[7] Reduction of III to IV has been achieved with aliphatic or aromatic tertiary phosphines as well as with trialkyl phosphites (eq. 2).



III IV (2)

For our purpose, we found the lower aliphatic trialkyl phosphites, *e.g.*, trimethyl or triethyl phosphite, especially suitable, since any excess of the reagent is almost instantly hydrolyzed by dilute mineral acids and the trialkyl phosphates formed during the reaction are water soluble, thus rendering the isolation of the nitrile very convenient.[9] The nitriles were identified by analysis and mixture melting point with an authentic sample. In the cases where the nitrile was not known, it was also

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[1] Second communication: C. Grundmann and J. M. Dean, *Angew. Chem.*, **76**, 682 (1964); *Angew. Chem., Intern. Ed. Engl.*, **3**, 585 (1964).

[2] H. Wieland, *Ber.*, **40**, 1672 (1907); H. Wieland and B. Rosenfeld, *Ann.*, **484**, 241 (1930).

[3] C. Grundmann, unpublished.

[4] (a) L. Horner and H. Hoffmann, *Angew. Chem.*, **68**, 473 (1956); there is also a review of the literature; (b) L. Horner and E. Jürgens, *Ber.*, **90**, 2184 (1957); L. Horner, L. Hockenberger, and W. Kirmse, *ibid.*, **94**, 290 (1961).

[5] C. Grundmann, *ibid.*, **97**, 575 (1964).

[6] A. S. Bailey and J. M. Evans, *Chem. Ind.* (London), 1424 (1964).

[7] J. H. Boyer and S. E. Ellzey, Jr., *J. Org. Chem.*, **26**, 4684 (1961).

[8] T. Mukaiyama, H. Nambu, and M. Okamoto, *ibid.*, **27**, 3651 (1962).

[9] In case of water-soluble nitriles, one would for the same reasons, preferably employ, for instance, triphenylphosphine.