night. After the addition of still more ammonium hydroxide (150 ml.) followed by a 2-hr. reflux, the solution was concentrated to near dryness under reduced pressure and chilled. The gray crystalline precipitate was collected, washed with water, and dried *in vacuo:* yield 78.3 g. (82%), m.p. 182–184° (lit.[6] m.p. 163°). Recrystallization of a small sample from ethanol provided white crystals (melting point unchanged) for analysis.

Anal. Calcd. for $C_3H_9N_3S$: C, 30.23; H, 7.61; N, 35.25; S, 26.91. Found: C, 30.08; H, 7.40; N, 34.70; S, 26.8.

2-Hydrazino-2-thiazoline Hydrobromide (IVa).—A mixture of thiosemicarbazide (13.7 g., 0.150 mole), 2-bromoethylamine hydrobromide, and 2-propanol (400 ml.) was heated under reflux for 5 hr. The resulting mixture was filtered hot to remove ammonium bromide, and the filtrate was allowed to cool slowly. The solid that precipitated was collected, dried *in vacuo*, and recrystallized from ethanol (220 ml.) to yield IVa as white needles, 10.4 g. (35%), m.p. 167–168°, $\tilde{\nu}_{\max}^{\mathrm{KBr}}$ 1670 cm.$^{-1}$ (s, C=N).

Anal. Calcd. for $C_3H_7N_3S \cdot HBr$: C, 18.18; H, 4.07; N, 21.21. Found: C, 18.37; H, 4.22; N, 21.27.

2-Hydrazino-2-thiazoline picrate was prepared from IVa in ethanol and recrystallized from methanol as fine yellow needles, m.p. 203–204° dec.

Anal. Calcd. for $C_9H_{10}N_6O_7S$: C, 31.24; H, 2.91; N, 24.27; S, 9.24. Found: C, 31.40; H, 3.07; N, 24.00; S, 9.3.

Acetone (0.4 ml.) was added to a solution of IVa (495 mg., 2.50 mmoles) in water (5 ml.). When exothermic reaction ceased, the solution was warmed slightly and then evaporated to dryness under reduced pressure. Recrystallization of the residue from ethanol (10 ml.) gave 383 mg. (64%) of vacuum-dried **acetone (2-thiazolin-2-yl)hydrazone hydrobromide (V)** as a white crystalline solid, m.p. 210–212°.

Anal. Calcd. for $C_6H_{11}N_3S \cdot HBr$: C, 30.25; H, 5.20; N, 17.65. Found: C, 30.57; H, 5.18; N, 17.56.

2-Hydrazino-2-thiazoline hydrochloride was recrystallized from ethanol and melted at 185–187° dec., $\tilde{\nu}_{\max}^{\mathrm{KBr}}$ 1675 cm.$^{-1}$ (s, C=N).

Anal. Calcd. for $C_3H_7N_3S \cdot HCl$: C, 23.45; H, 5.25; Cl, 23.07. Found: C, 23.76; H, 5.29; Cl, 22.5.

2-(2,2-Dimethylhydrazino)-2-thiazoline (IVb Free Base).—A stirred mixture of Ib (11.9 g., 0.100 mole), 2-bromoethylamine hydrobromide (20.5 g., 0.100 mole), and 2-propanol (100 ml.) was heated under reflux for 5 hr. Complete solution resulted as the mixture was gradually heated, but precipitation of ammonium bromide began shortly after reflux temperature was reached. The reaction mixture was filtered hot, ammonium bromide (6.49 g., vacuum dried) being removed. The filtrate was evaporated to dryness under reduced pressure. Extraction of the viscous semisolid residue first with acetonitrile and then with chloroform left additional ammonium bromide (2.15 g.) making the total yield 88%. Evaporation of the combined filtrates *in vacuo* gave crude IVb as a yellow, viscous oil, which eventually solidified to a gummy solid (21.1 g., 93%), $\tilde{\nu}_{\max}^{\mathrm{KBr}}$ 1640 cm.$^{-1}$ (s, C=N). The **picrate** was prepared from crude IVb in ethanol and recrystallized from ethanol as yellow needles, m.p. 205° dec. (Kofler Heizbank).

Anal. Calcd. for $C_{11}H_{14}N_6O_7S$: C, 35.29; H, 3.77; N, 22.45; S, 8.56. Found: C, 35.21; H, 3.89; N, 22.11; S, 8.4.

A solution of crude IVb (3.65 g., 16.2 mmoles) and (ethylenedinitrilo)tetraacetic acid (0.35 g.) in 2 *N* sodium hydroxide (26 ml.) was heated at 90° for 2 hr., cooled, and brought to pH 8 with 48% hydrobromic acid (4 ml.). The solution was then extracted continuously with ether for 3.5 hr. in a liquid–liquid extractor (225-ml. volume). Evaporation of the ether left 1.88 g. (79%, 73% from Ib) of IVb free base as a white crystalline solid.

For analysis a small sample was recrystallized from hexane with 87% recovery, m.p. 113–115°.

Anal. Calcd. for $C_5H_{11}N_3S$: C, 41.34; H, 7.63; S, 22.08. Found: C, 41.35; H, 7.48; S, 22.2.

Acknowledgment.—The authors are indebted to Dr. W. J. Barrett and his associates in the Analytical Chemistry Section of Southern Research Institute for the analytical and spectral data reported, and to Dr. W. C. Coburn, Jr., and Mrs. Martha Thorpe for interpretations of the infrared and p.m.r. spectra, respectively.

Metal Acetylacetonate Catalyzed Epoxidation of Olefins with *t*-Butyl Hydroperoxide

NORMAN INDICTOR

Department of Chemistry, Brooklyn College,
Brooklyn, New York

AND WILLIAM F. BRILL

Petro-Tex Chemical Corporation, FMC Research and
Development Center, Princeton, New Jersey

Received January 27, 1965

In the course of efforts to explore the usefulness of *t*-butyl hydroperoxide as an epoxidizing agent for olefins,[1] the effect of small quantities of metal acetylacetonates was noted. Table I sets forth results obtained with 2,4,4-trimethyl-1-pentene. It is noteworthy that the Cr(III), MoO_2(II), VO(II), and V(III) compounds gave quantitative yields of epoxide. In the absence of metal acetylacetonates no reaction occurred under the stated conditions. The metal-catalyzed epoxidation is general for hydrocarbon olefins (see Table II), and appears to be stereospecific

TABLE I

EPOXIDE FORMATION IN THE SYSTEM *t*-BUTYL HYDROPEROXIDE[a]–2,4,4-TRIMETHYL-1-PENTENE–METAL ACETYLACETONATE[b]
(at 25° *in vacuo*)

Metal	*n*	Remaining hydroperoxide, %	Epoxide, %[c]
Cr	3	47[d]	100
V	3	60[e]	100
VO	2	56[e]	100
MoO_2	2[f]	83[d]	100
Co	3	75[d]	30
Cu	2	67[d]	25
Co	2	52[d]	20
Mn	3	53[g]	15
Mn	2	56[g]	15
Al	3	100[d]	. . .
Fe	3	100[d]	. . .
Mg	2	95[g]	. . .
Ni	2	100[e]	. . .
TiO	2	95[e]	. . .
Zn	2	90[e]	. . .
Zr	4	90[e]	. . .

[a] About 2.0 *M*. [b] 4×10^{-4} *M*. [c] Based on reacted hydroperoxide. [d] After 4 days. [e] After 7 days. [f] At 60° in octene-1. [g] After 5 days.

TABLE II

EFFECT OF OLEFIN STRUCTURE ON EPOXIDE YIELD IN *t*-BUTYL HYDROPEROXIDE EPOXIDATION THE IN PRESENCE AND ABSENCE OF CHROMIUM(III) ACETYLACETONATE

Olefin	Uncatalyzed epoxide,[a] %	Catalyzed epoxide,[a] %
Octene-1	5–10	5–53
4-Vinylcyclohexene	10–20[b]	13–60[b]
Octene-2	25–40	42–78
2,4,4-Trimethyl-1-pentene	40–50	28–100

[a] Based on reacted hydroperoxide. Lower values represent yields at 60° or higher, long reaction times, high metal chelate concentration. See ref. 1. [b] Mono ring epoxide only.

---

(1) W. F. Brill and N. Indictor, *J. Org. Chem.*, **29**, 710 (1964). See also references cited therein.

(*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.

---

[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

Received November 23, 1964

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.

---

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