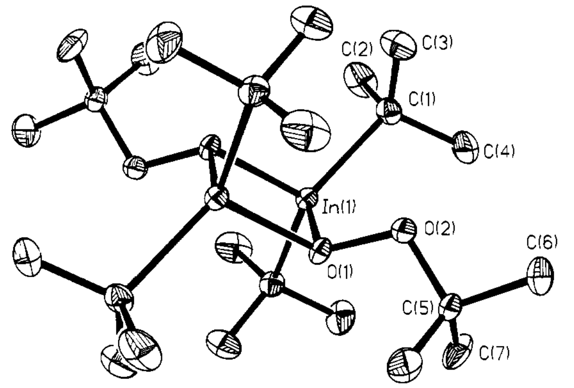


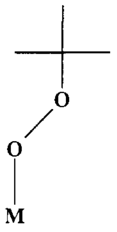
Figure 1. The molecular structure of $[(t\text{-Bu})_2In(OO\text{-}t\text{-Bu})]_2$. Thermal ellipsoids are shown at the 50% probability level, and hydrogen atoms are omitted for clarity.

N-oxide.[8] Attempts to synthesize **1** by the reaction of $In(t\text{-Bu})_3$ with t-BuOOH have, however, failed.

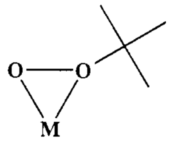
$$In(t\text{-Bu})_3 + O_2 \rightarrow \underset{\mathbf{1}}{(t\text{-Bu})_2In(OO\text{-}t\text{-Bu})} \tag{2}$$

Compound **1** is moisture sensitive, but is stable indefinitely under an oxygen atmosphere. No reaction is observed between **1** and Lewis bases, e.g., pyridine. The IR spectrum of **1** exhibits a moderate absorption at 870 cm^{-1} attributable to the characteristic (O–O) peroxidic stretching vibration.[1]

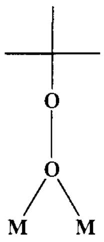
Alkylperoxo moieties are known to act as monodentate (η^1) (I), bidentate (η^2) (II), and bridging (μ_2) (III) ligands to transition metals.[9] Since the existence of dimers involving bridging alkoxides is a common feature in group 13 chemistry,[10] it would, therefore, be logical to expect the alkylperoxo group in **1** to ligate in a similar fashion. The μ_2-bridging mode of coordination of the *tert*-butyl peroxide group and the dimeric nature of **1** in the solid state have been confirmed by X-ray crystallography.[11]



(I)

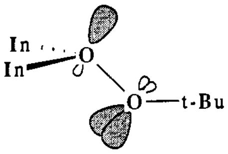


(II)



(III)

The molecular structure of **1** is shown in Figure 1. The molecule exhibits overall C_{2h} symmetry with the two indium atoms lying on the 2-fold axis and the alkylperoxo groups on the mirror plane. The In(1)–O(1) distance [2.191 (2) Å] and In(1)–O(1)–In(1a) angle [105.2 (1)°] are similar to those found for other In_2O_2 cores,[6,12] and the In(1)–C(4) bond length [2.199 (4) Å] is in the region previously observed for In–C bonds (2.09–2.25 Å).[11] The peroxo O(1)–O(2) bond distance of 1.484 (4) Å is close to that found for free alkyl hydroperoxides and alkyl peroxides coordinated to transition metals.[9,13] The *tert*-butylperoxo ligand is orientated so as to minimize lone-pair repulsion on the oxygen atoms (IV). A similar *tert*-butyl peroxide geometry was found in the X-ray structural study of the related complex $[(Cl_3CCO_2)Pd(OO\text{-}t\text{-Bu})]_4$.[13]



(IV)

The stability of **1** toward further oxidation is unexpected in view of the highly reactive nature of previously reported organoindium compounds toward dioxygen.[14] We propose that this stability is due to the steric hindrance of the *tert*-butyl groups and the strength of the In_2O_2 core, precluding both further attack by O_2 and oxygen transfer from the peroxide to other In–C bonds.

Acknowledgment. Financial support of this work is provided by the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grant No. 20082-G5), the National Science Foundation (Grant No. DMR-86-14003), and ICI Wilton Materials Research Center, U.K. We thank Dr. Joseph W. Ziller and Dr. Simon G. Bott for assistance with the X-ray crystallography.

Supplementary Material Available: Tables of atomic positional and isotropic equivalent thermal parameters, anisotropic thermal parameters, and bond distances and angles for **1** (2 pages); listing of observed and calculated structure factors for **1** (11 pages). Ordering information is given on any current masthead page.

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(8) The reaction of $In(t\text{-Bu})_3$ with pyridine *N*-oxide yields $[(t\text{-Bu})_2In(O\text{-}t\text{-Bu})]_2$ as the major product, which reacts slowly with excess pyridine *N*-oxide to give small quantities of **1**.

(9) Mimoun, H. *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A., Eds.; Pergamon: Oxford, 1988; Vol. 6, Chapter 1.

(10) Bradley, D. C. *Adv. Chem. Ser.* **1959**, *No. 23*, 10.

(11) Crystal data for $[(t\text{-Bu})_2In(OO\text{-}t\text{-Bu})]_2$: monoclinic, $C_{2/m}$, $a = 16.745$ (10) Å, $b = 11.453$ (9) Å, $c = 9.173$ (4) Å, $\beta = 117.16$ (4)°, $V = 1565$ (2) Å^3, $Z = 8$, D(calcd) = 1.350 g cm^{-3}, λ (Mo Kα) = 0.71073 Å (graphite monochromator), $T = -80$ °C. A Nicolet R3m/V diffractometer, equipped with an LT-1 low-temperature device, was used to collect 2973 reflections (4° $< 2\theta <$ 65°) on a colorless crystal 0.24 × 0.30 × 0.36 mm. Of these, 2865 were independent, and 2540 observed $[F_o > 6\sigma F_o]$. Lorentz and polarization corrections were applied to the data. The In atom was located by direct methods. Standard difference map techniques were used to find the remaining non-hydrogen atoms. All In, O, and C atoms were refined anisotropically. The hydrogen atoms were included as idealized contributions. $R = 0.030$, $R_w = 0.037$, final residual = 1.12 e Å^{-3}. All computations used SHELXTL-PLUS: Sheldrick, G. Nicolet XRD, Madison, WI, 1987.

(12) Cleaver, W. M.; Ziller, J. W.; Barron, A. R., unpublished results.

(13) Mimoun, H.; Charpentier, R.; Mitscher, A.; Fischer, J.; Weiss, R. *J. Am. Chem. Soc.* **1980**, *102*, 1047.

(14) Tuck, D. G. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 1, Chapter 7.

Evidence for Formation of Gaseous Methyl Radicals in the Decomposition of Methoxide on Oxygen-Precovered Mo(110)

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Received May 22, 1989

Evidence of the unprecedented formation of gaseous methyl radicals from adsorbed methoxide is presented in this study. Previously, surface methoxide has been found to either form formaldehyde or decompose to CO and H_2. The observation of methyl radicals during decomposition of methanol on Mo(110) precovered with atomic oxygen is of significance to the study of the partial oxidation of methane over metal oxide catalysts, since the observed decomposition pathway of methanol is analogous to the reverse of methane oxidation. Methyl radicals, produced from methane reaction over metal oxide catalysts,[1,2] evolve into the gas phase to form C_2 products or react on the catalyst to produce surface methoxide ions. Methyl radical formation is attributed solely to the direct abstraction of H from methane whereas ad-

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(1) Driscoll, D. J.; Martir, W.; Wang, J.-X.; Lunsford, J. H. *J. Am. Chem. Soc.* **1985**, *107*, 58.

(2) Liu, H.-F.; Liu, R.-S.; Liew, K. Y.; Johnson, R. E.; Lunsford, J. H. *J. Am. Chem. Soc.* **1984**, *106*, 4117.

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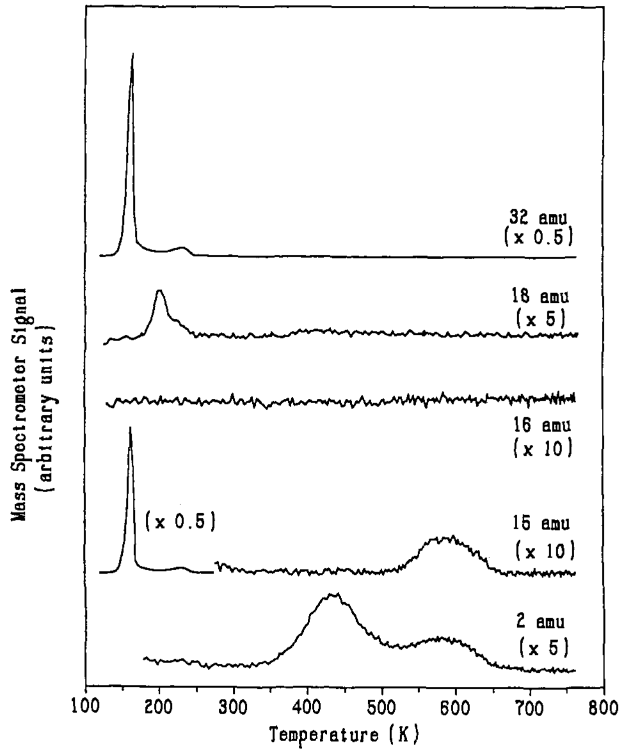

Figure 1. Temperature-programmed reaction data obtained after saturation exposure of Mo(110) precovered with 0.33 monolayers of atomic oxygen to methanol. The sample was exposed to methanol at a crystal temperature of 120 K, and a heating rate of 15 K/s was used during temperature-programmed reaction data collection.

sorbed CH_3O is thought to form methanol, formaldehyde, and combustion products. In our work, gaseous methyl radical is formed from methoxide decomposition, but on oxygen-precovered Mo(110) only, not clean Mo(110).

Two separate ultrahigh vacuum chambers with base pressures of 1×10^{-10} Torr, described previously,[3,4] were used in these experiments. The Mo(110) crystal was cleaned in oxygen at 1200 K to remove carbon and flashed to ~1800 K to remove oxygen. The oxygen overlayer was formed as described previously[5] and had a coverage of 0.33 monolayers. Methyl radical formation is observed over a wide range of oxygen precoverages (0.15–0.5 monolayers). Methanol was adsorbed at a crystal temperature of 120 K.

Figure 1 shows temperature programmed reaction data obtained after adsorption of methanol multilayers onto oxygen-precovered Mo(110). All masses between 2 and 120 amu were monitored, and no masses above 32 amu (methanol parent) were observed. The sharp peak appearing at 160 K in the 32- and 15-amu spectra[6] is attributed to the sublimation of methanol multilayers since this peak grows indefinitely in intensity with methanol exposure. Above 160 K, molecular methanol desorbs over a range of temperatures, ending in a resolvable peak at 240 K. This methanol arises from molecular desorption since surface deuterium is not incorporated into these peaks. Concurrent with molecular methanol desorption is the formation of gaseous water (18 amu) in a peak centered at ~220 K. Since only $H_2{}^{18}O$ is formed from the reaction of methanol on an ^{18}O overlayer and only H_2O from CD_3OH, this water must arise from reaction of oxygen in the overlayer with the alcoholic proton.

Reaction of CD_3OH shows that the O–H bond is broken first, with H_2 formed in the leading edge of the dihydrogen peak. Some C–D bond cleavage occurs by ~425 K to form deuterium-containing dihydrogen isotopes in the falling edge of the lower temperature peak. The higher temperature dihydrogen peak (590 K) is derived from C–D(H) bond breaking only since it contains only deuterium in the reaction of CD_3OH. The water formed in small amounts around 400 K probably arises from reaction of surface-bound hydrogen atoms with the oxygen overlayer, since water is formed after adsorbing hydrogen atoms on an oxygen overlayer at this temperature.[5]

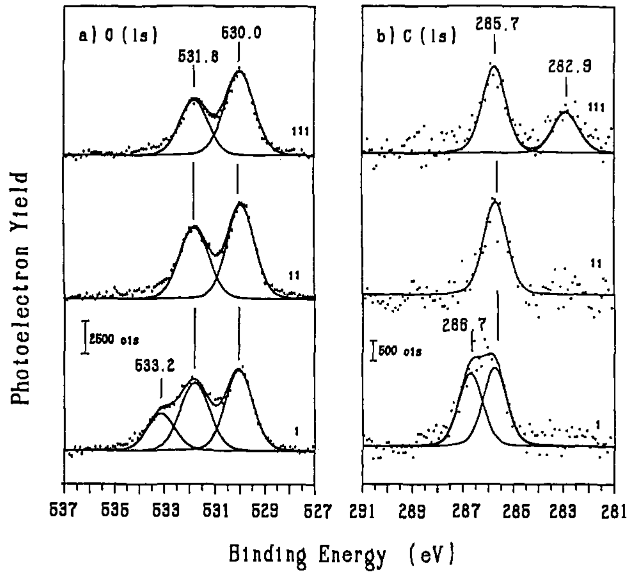

Figure 2. X-ray photoelectron spectra obtained for (a) O(1s) and (b) C(1s) regions after annealing a saturation exposure of methanol on oxygen-precovered Mo(110) to (*i*) 185 K, (*ii*) 300 K, and (*iii*) 500 K. Data for the O(1s) and C(1s) regions were collected in the same experiments. The clean Mo(110) C(1s) spectrum has been subtracted from the C(1s) spectra shown since molybdenum exhibits photoemission in this region.

Concurrent with the formation of the higher temperature dihydrogen is the detection of gaseous methyl radicals with *m/e* 15 amu. This peak does not appear in spectra collected at masses higher than 15 amu, including 31 amu.[7] Reaction of CH_3OH to 500 K, followed by cooling and adsorption of CD_3OH at 120 K, produces CD_3 and CH_3, with the majority of the signal intensity being at 18 and 15 amu. There is no evidence for isotopic mixing in the methyl radicals, on the basis of good agreement with fragmentation patterns of CH_3OH and CD_3OH obtained in separate experiments.

X-ray photoelectron spectroscopy was used to characterize the methoxide intermediate on the surface. X-ray photoelectron data collected after annealing methanol multilayers to 185, 300, and 500 K is shown in Figure 2. After annealing to 185 K, two carbon-containing species are detected: molecular methanol with binding energies of 533.2 eV (O(1s)) and 286.7 eV (C(1s)) and methoxide with binding energies of 531.8 and 285.7 eV. Photoemission from the oxygen overlayer is observed at 530.0 eV in the O(1s) region at all annealing temperatures. After annealing to 300 K, a temperature where methanol desorption is complete but below the onset of dihydrogen formation, only atomic oxygen and methoxide are detected (Figure 2, ii). The C(1s) methoxide binding energy, 285.7 eV, agrees well with that reported for methoxide on Pd(111), 285.9 eV,[8] and the O(1s) binding energy of 531.8 eV is also close to that observed for phenoxide on oxygen-precovered Mo(110), 531.6 eV.[5]

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(3) Friend, C. M.; Serafin, J. G. *J. Chem. Phys.* **1988**, *88*, 4037.
(4) Roberts, J. T.; Friend, C. M. *J. Am. Chem. Soc.* **1986**, *108*, 7204.
(5) Serafin, J. G.; Friend, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 4233.
(6) Methanol fragments to 15 amu in the mass spectrometer.

(7) Data collected in another vacuum chamber in our lab did show the formation of some 16 amu at the same temperature as 15 amu although 15 amu was still the most intense ion observed. Intensity at 16 amu is attributed to reaction of gaseous methyl radical with hydrogen atoms on the liquid nitrogen cooled shield surrounding the mass spectrometer on the basis of the fact that, during reaction of CD_3OH in the chamber where 16 amu is observed, *only* CD_3 (18 amu) and CD_3H (19 amu) are observed, *not* CD_4 (20 amu). This is clear evidence for a background reaction since a surface reaction should produce CD_4.

(8) Levis, R. J.; Zhicheng, J.; Winograd, N. *J. Am. Chem. Soc.* **1988**, *110*, 4431.

Both temperature-programmed reaction and X-ray photoelectron data indicate that methoxide is the intermediate that gives rise to gaseous methyl radicals. After annealing to 500 K, a temperature near the onset of methyl radical formation, methoxide (285.7 eV) is the majority surface species. A species with a C(1s) binding energy of 282.9 eV is also present; this binding energy is the same as that of atomic carbon detected after annealing to 750 K, a temperature past all dihydrogen formation. The intensity of the 282.9-eV peak increases after annealing from 500 to 750 K by 20–60%. Adsorbed methyl would be expected to have a binding energy around 284 eV, on the basis of comparison with C(1s) data for other hydrocarbon species on Mo(110),[9-11] and to undergo strong irreversible bonding with molybdenum atoms. Formation of a significant amount of low-temperature dihydrogen during temperature-programmed reaction agrees with the presence of atomic carbon at 500 K. Also, high-temperature dihydrogen and methyl radical are formed with similar kinetics during temperature-programmed reaction above 500 K, supporting reaction of a common intermediate (methoxide) to form both products and in agreement with the observed increase in the 282.9-eV peak intensity after annealing to 750 K. Thus we assign the low binding energy species present at 500 K to atomic carbon or a partially dehydrogenated fragment. Since no reversible C–H bond activation is observed during reaction of coadsorbed CD_3O and CH_3O, the lower binding energy species cannot give rise to methyl radical via C–H bond formation. Only reaction of *methoxide* to gaseous methyl radical and high-temperature dihydrogen in a competing reaction pathway is consistent with these results.

Acknowledgment. This work was supported by the Department of Energy, Basic Energy Sciences, Grant No. DE-FG02-84ER13289.

Registry No. Mo, 7439-98-7; CH_3O, 3315-60-4; O, 7782-44-7; CH_3OH, 67-56-1; CH_3, 2229-07-4.

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[9] Liu, A. C.; Friend, C. M. *J. Chem. Phys.* **1988**, *89*, 4396.

[10] Roberts, J. T.; Friend, C. M. *J. Chem. Phys.* **1988**, *88*, 7172.

[11] Serafin, J. G.; Friend, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 6019.

Phosphonium Ion Fragmentations Relevant to Organophosphonate Biodegradation

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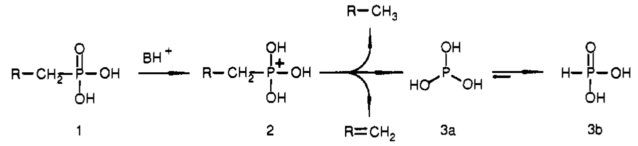
Microbial degradation of organophosphonates **1** via carbon to phosphorus (C–P) bond cleavage has prompted a rapid expansion in chemical literature[1,2] relevant to the biodegradation. However, the chemistry of organophosphonates under reducing conditions, particularly in regard to C–P bond cleavage, is still largely unknown. This report examines the single-electron and hydride reduction of organophosphonates and organotrineopentoxyphosphonium[3] trifluoromethanesulfonates **4a–e** (Table I) structurally related to organophosphonium ion **2** (Scheme I). A tremendous difference in reactivity of reductants with organophosphonium ions relative to organophosphonates has been discovered. This leads to the suggestion (Scheme I) of possible phosphonium ion **2** intermediacy during organophosphonate biodegradation. Phosphonium ion **2** reduction or eliminative cleavage of the organophosphonium C–P bond could produce alkanes and alkenes along with phosphite **3a**.

Scheme I



Scheme II

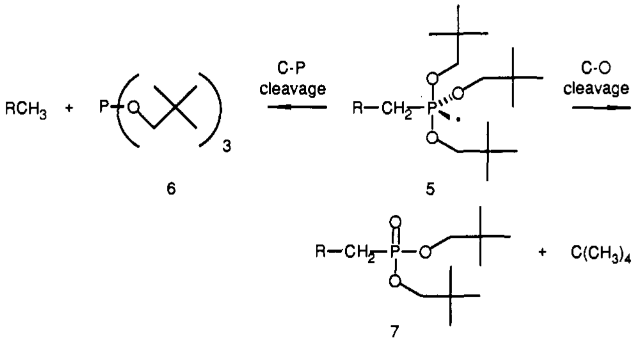
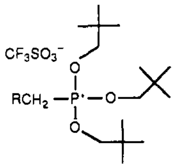
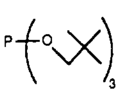
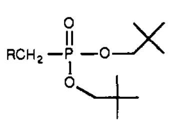


Table I[a]

 **4**	RCH_3 ($R = CH_2$) % yield	 %yield	 %yield
a, R = H	1	2	91
b, R = CH_3	1	3	89
c, R = CH_3CH_2	1.1 (0.02)	4	89
d, R = $CH_2{=}CH$	6	22	70
e, R = C_6H_5	24	35	58

[a] A tetrahydrofuran solution of naphthalene radical anion was added dropwise to organophosphonium ions **4a–e** in tetrahydrofuran under nitrogen at room temperature. Addition was continued until a green color persisted. Volatiles (C1–C3) were analyzed by gas chromatography fitted with alumina F1 or Carbosphere columns. Solution components were separated by gas chromatography fitted with an OV-101 column. Gas chromatography yields were determined relative to an internal standard. Products were identified by coinjection and comparison of ^{31}P NMR chemical shifts with those of authentic samples.

Neither hydrocarbons nor phosphorus-containing products resulting from C–P bond cleavage are observed during naphthalene radical anion reactions with organophosphonate diesters. In contrast, addition of naphthalene radical anion to organotrineopentoxyphosphonium ions leads to instantaneous reaction with complete loss of starting phosphonium ion. Hydrocarbon[4] as well as phosphorus-containing products indicative of C–P bond cleavage (Table I) are observed.[5] The hydrocarbons[6] formed during C–P bond cleavage are reminiscent of the carbon fragments formed during *Escherichia coli* degradation of organophosphonates. Notably, *E. coli* degradation of propylphosphonic acid leads to

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[1] (a) Cordeiro, M. L.; Pompliano, D. L.; Frost, J. W. *J. Am. Chem. Soc.* **1986**, *108*, 332. (b) Frost, J. W.; Loo, S.; Cordeiro, M. L.; Li, D. *J. Am. Chem. Soc.* **1987**, *109*, 2166. (c) Avila, L. Z.; Loo, S. H.; Frost, J. W. *J. Am. Chem. Soc.* **1987**, *109*, 6758. (d) Avila, L. Z.; Frost, J. W. *J. Am. Chem. Soc.* **1988**, *110*, 7904.

[2] Shames, S. L.; Wackett, L. P.; LaBarge, M. S.; Kuczkowski, R. L.; Walsh, C. T. *Bioorg. Chem.* **1987**, *15*, 366.

[3] (a) Colle, K. S.; Lewis, E. S. *J. Org. Chem.* **1978**, *43*, 571. (b) Hudson, H. R.; Rees, R. G.; Weekes, J. E. *J. Chem. Soc., Chem. Commun.* **1971**, 1297.

[4] Propene formation could be due to eliminative C–P bond cleavage or alkyl radical disproportionation. The absence of products resulting from alkyl radical combination which competes with alkyl radical disproportionation suggests that propene arises primarily from eliminative C–P bond cleavage. Naphthalene dianion is probably functioning as the base. See ref 7a.

[5] The difference in hydrocarbon and trineopentylphosphite yield is likely a consequence of naphthalene radical anion trapping of alkyl radical. See: (a) Shafer, S. J.; Closson, W. D.; van Dijk, J. M. F.; Piepers, O.; Buck, H. M. *J. Am. Chem. Soc.* **1977**, *99*, 5118. (b) Garst, J. F. *Acc. Chem. Res.* **1971**, *4*, 400.

[6] Ethene is also produced during single-electron reduction of **4b**. However, an undetermined proportion of the ethene is coming from tetrahydrofuran decomposition. No propene is generated during decomposition of tetrahydrofuran. See: Carnahan, J. C., Jr.; Closson, W. D. *J. Org. Chem.* **1972**, *37*, 4469.