A mixture of 10.5 g of IIb and 21 ml of ethylene oxide in 50 ml of glacial acetic acid was allowed to react for 16 hr at steam-bath temperature in a pressure flask. The reaction mixture was concentrated to one-half the original volume and made basic to litmus by the addition of 10% sodium hydroxide solution. An oily residue was deposited which crystallized on cooling and scratching, giving 7.0 g of product, mp 70–74°. Recrystallization from heptane afforded 5.8 g of product, mp 74–77°. A second recrystallization from *n*-pentane raised the melting point to 79–80° (lit.[6] mp 81–82°). A mixture melting point of the product with the authentic sample gave no depression, and their infrared spectra were identical, λ_{max}^{KBr} 5.86 μ (lactone C=O).

Preparation of IIIb from VIIIb.—A suspension of 4.0 g of VIIIb in 30 ml of concentrated ammonium hydroxide was heated in a Parr bomb at 180° for 6 hr. The reaction mixture was filtered and the aqueous layer was extracted with chloroform (three 75-ml portions). The combined chloroform fractions were dried over magnesium sulfate, filtered, and evaporated to dryness, giving 0.7 g of an oil. This material was allowed to react for 2 hr with 30 ml of thionyl chloride at ice-bath temperature and allowed to stand at room temperature for 16 hr. The excess thionyl chloride, was removed, leaving an oily residue. The residue was dissolved in 100 ml of water and the reaction mixture was filtered. The filtrate was brought to pH 2 with 10% HCl and washed with chloroform (two 50-ml portions). The water layer was basified with 10% sodium hydroxide solution and extracted with chloroform (two 100-ml portions). The combined chloroform extracts were dried over magnesium sulfate, filtered, and evaporated *in vacuo*. An oily residue crystallized on standing. Recrystallization from cyclohexane gave 0.1 g of IIIb, mp 91–95°. A mixture melting point with IIIb prepared from IIb gave no depression, and the infrared spectra of the samples were identical.

1-Benzyl-1,2,3,4-tetrahydro-5H-1,4-benzodiazepine-5-thione (XIa).—To a stirred suspension of 1.3 g of IVa in 10 ml of dry pyridine was added 1.3 g of phosphorus pentasulfide. The reaction mixture was heated under reflux for 2 hr, poured into 200 ml of boiling water, and cooled. An oil was deposited which crystallized on standing. Recrystallization from cyclohexane afforded 0.4 g of product: mp 119.5–120.5°, λ_{max}^{KBr} 3.18 μ (NH stretch) and 6.5 μ (S=CNH deformation).

Anal. Calcd for $C_{16}H_{16}N_2S$: C, 71.62; H, 5.96; N, 10.44; S, 11.95. Found: C, 71.66; H, 5.68; N, 10.67; S, 11.70.

1,2,3,4-Tetrahydro-1-methyl-5H-1,4-benzodiazepine-5-thione (XIb).—The product (0.7 g, mp 153–155°) was prepared, in the manner described for XIa, from 1.0 g of IVb and 1.0 g of phosphorus pentasulfide in 10 ml of dry pyridine. Recrystallization from ethanol afforded an analytical sample: mp 153.5–154°, λ_{max}^{KBr} 3.14 μ (NH stretch) and 6.62 μ (S=CNH deformation).

Anal. Calcd for $C_{10}H_{12}N_2S$: C, 62.45; H, 6.29; N, 14.57; S, 16.67. Found: C, 62.47; H, 6.11; N, 14.42; S, 16.70.

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Autoxidation of Octene-1 with *t*-Butyl Hydroperoxide and Metal Acetylacetonates

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In the course of studies exploring the usefulness of *t*-butyl hydroperoxide as an epoxidizing agent,[1] the effect of small quantities of metal acetylacetonates was noted.[2] The catalytic effect of the metal acetylacetonate–*t*-butyl hydroperoxide system was also observed in the polymerization of styrene.[3] Throughout these studies it was generally observed that the systems under investigation were sensitive to oxygen.[2,3] It is known that olefins in the presence of free-radical sources readily absorb oxygen[4–7] and that metals in the presence of peroxides promote the production of free radicals,[6–9] as well as reaction intermediates which are not so well defined.[2,7,8,10] The metal-catalyzed oxidation of many organic substances,[6,7,9,11,12] and decomposition of peroxides[6,7,9,13,14] have been frequently studied. It has also been shown that some metal acetylacetonates are oxidized by molecular oxygen at elevated temperatures.[15] This preliminary study is an effort to evaluate the metal acetylacetonate–*t*-butyl hydroperoxide system in terms of its ability to initiate autoxidation (Table I). Comparison of these results is made with earlier work[2,3] done under comparable conditions in which olefin epoxidation, styrene polymerization, and peroxide decompositions were studied (Table II).

Consideration of Tables I and II leads to the conclusion that Al(III), Zr(IV), Ni(II), Zn(II), and TiO(II) acetylacetonates have little or no effect on *t*-butyl hydroperoxide under the mild conditions of these experiments. *t*-Butyl hydroperoxide itself, in the absence of the acetylacetonates, exhibits no catalytic effect on the autoxidation of octene-1 under these conditions. It is also clear that all the other metals for which data are available promote autoxidation when the hydroperoxide to metal acetylacetonate ratio is balanced such that the peroxide decomposition rate is less than the oxygen absorption rate. It has been shown that under conditions of high metal concentrations or long time intervals a steady-state autoxidation rate is reached which is independent of initiator concentration.[16,17] The meaning of this steady state is that the peroxide produced in the autoxidation is the sole significant chain initiator. A zero rate of oxygen absorption might mean that oxygen is being produced as rapidly from peroxide decomposition as it is absorbed by substrate autoxidation. As in the case of metal acetylacetonate–*t*-butyl hydroperoxide initiated styrene polymerization[3] an optimal concentration range must exist for autoxidation initiation by the same system.

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TABLE I

AUTOXIDATION OF OCTENE-1[a] WITH *t*-BUTYL HYDROPEROXIDE[b]–METAL ACETYLACETONATE AND DECOMPOSITION OF *t*-BUTYL HYDROPEROXIDE[b] BY METAL ACETYLACETONATES *in vacuo* AT 30°

Metal	$(\Delta[O_2]/\Delta t) \times 10^6$ mole/l. sec	$(\Delta[\text{peroxide}]/\Delta t) \times 10^6$ mole/l. sec
Co(II)[c]	15.2	6.9
Co(II)[d]	0.0	360
Co(II)[o]	0.0	...
Mn(III)[e]	11.0	(2.0)[k]
Mn(III)[p]	0.0	...
Mn(II)[f]	6.3	(2.0)[k]
Mn(II)[n]	0.06	...
VO(II)[g]	5.5	3.3
Cr(III)[h]	3.3	2.2[l]
Cr(III)[d]	3.2	4.5
Cr(III)[n]	0.22	...
Co(III)[d]	3.2	0.7
Co(III)[n]	0.0	...
Fe(III)[d]	2.7	0.0[m]
Cu(II)[f]	2.6	(1.9)[k]
Zr(IV)[d]	1.2	0.0[m]
Al(III)[d]	0.6	0.0[m]
Ni(II)[f]	0.6	0.0[m]
Zn(II)[d]	0.0	0.0[m]
i	0.0	0.0[m]
j	0.0	...

[a] 5.2 *M* (no solvent). [b] 0.75 *M*. [c] 2.6×10^{-4} *M*. [d] 2.0×10^{-2} *M*. [e] 0.8×10^{-2} *M*. [f] 1.1×10^{-2} *M*. [g] 0.3×10^{-2} *M*. [h] 4.0×10^{-4} *M*. [i] No chelate. [j] No chelate, no hydroperoxide. [k] Data of ref 2. [l] (Chelate) = 8.0×10^{-4} *M*, (peroxide) = 0.36 *M*, (octene-1) = 2.6 *M*. [m] Negligible decomposition after 1 week. [n] 2.7×10^{-3} *M* (no *t*-butyl hydroperoxide). [o] 2.8×10^{-4} *M* (no *t*-butyl hydroperoxide). [p] 2.0×10^{-3} *M* (no *t*-butyl hydroperoxide).

TABLE II

REACTIVITIES OF METAL ACETYLACETONATES IN SEVERAL REACTIONS[a]

Metal	Hydroperoxide[b,c] decomposition	Olefin[c] epoxidation	Styrene[d] polymerization	Olefin[b] autoxidation	Chelate[e] autoxidation
Cr(III)	++	++	++(−)	++(−)	−
V(III)	+	++	−	Nd	++
VO(II)	+	++	−	++	Nd
Co(III)	+	+	++(−)	++	+
Co(II)	++(−)	+	−	++(−)	++
Cu(II)	+	+	++	+	+
Fe(III)	−	−	+	+	++
Mn(III)	+	+	Nd	++	++
Mn(II)	+	+	−	++	Nd
Ni(II)	−	−	−	−	++
Al(III)	−	−	−	−	−
TiO(II)	−	−	−	Nd	Nd
Zn(II)	−	−	−	−	Nd
Zr(IV)	−	−	−	−	−

[a] ++, very reactive; +, reactive; −, not reactive; ++(−), reactivity is concentration dependent; Nd, no data available. [b] This work. [c] Reference 2. [d] Reference 3. [e] Reference 15.

Whereas the presence of some of the metals suppressed the rate of polymerization of styrene even below that of the system containing only monomer and *t*-butyl hydroperoxide,[3] metal acetylacetonate promoted autoxidation may be inhibited or even eliminated by increasing the concentration of the chelate [see Co(II) or Cr(III) in Table I]. There are many cases cited in the literature in which metals act to promote autoxidation at low concentrations and to inhibit the same reaction at high concentrations.[9,16] There are several possible

$$\mathrm{M(acac)}_n + t\text{-BuOOH} = t\text{-BuOH} + 0.5\mathrm{O}_2 + \mathrm{M(acac)}_n \quad (1)$$

$$\mathrm{M(acac)}_n + t\text{-BuOOH} = \text{polar intermediates} \quad (2)$$

$$\mathrm{M(acac)}_n + t\text{-BuOOH} + \mathrm{RCH{=}CH_2} = \mathrm{R'OOC(CH_3)_3} \quad (3)$$

paths for the suppression of autoxidation. Reaction 1 indicates a process by which molecular oxygen is "catalytically" produced from hydroperoxide and thereby decreases the apparent rate of oxygen uptake.[13b,c,18–22] The reaction is often formulated as a multistep process in which the metal undergoes both oxidation and reduction reaction reactions with the peroxide.[6,7] In the present work, the production of oxygen has been observed in some of the metal acetyl acetonate–*t*-butyl hydroperoxide systems. Since under the conditions of these experiments the rate of oxygen evolution is appreciable, it is not possible from our limited data to determine the absolute efficiency of each metal in initiating autoxidation.

Reaction 2, indicating polar intermediates,[14,20,23] may play a role in olefin epoxidation,[2] hydroperoxide addition to a double bond,[20] ligand interchange,[13a,14,23] or in significantly controlling the catalytic activity of the initiator.[23] The significance of reaction 2 is implied by a strong rate retardation of the Co(II) acetylacetonate induced decomposition of *t*-butyl hydroperoxide in glacial acetic acid, a medium in which the complex intermediates of reaction 2 would be stabilized. *t*-Butyl hydroperoxide has been shown to be stable in 50% aqueous acetic acid in the presence of Co(II) acetate at 60°[13a] and although the hydroperoxide is decomposed by this same salt in *glacial* acetic acid, its rate of decomposition is retarded by dilution of the solvent with water,[24] which indicates inhibition *via* some sort of polar reaction. It is interesting to note that Richardson[13a] found no decomposition of *t*-butyl hydroperoxide in the presence of Co(III) ethylenediamine tetraacetate in 50% acetic acid (after 22 hr at 60°). However, Dean and Skirrow[24] observed that *t*-butyl hydroperoxide reacted several hundred times faster with Co(III) acetate than with the Co(II) salt in glacial acetic acid. In the present work no decomposition of *t*-butyl hydroperoxide was found in the presence of Co(III) acetylacetonate in octene-1 after 19 hr at 30°. However, 10% decomposition was observed after 48 hr and 58% of the hydroperoxide had disappeared after 3 weeks. The importance of reaction 2 is also suggested by the striking color changes which occur in many of these systems [Co(II), VO(II), Cr(III), etc.] as the reaction proceeds, indicating either a ligand exchange[13a,14,23] or alteration in the oxidation state of the metal[23] or the ligand.[25] Reactions 2 may either retard the decomposition reaction or consume peroxide.

Reaction 3 indicates a nonchain process[18,20] which reduces the effectiveness of the *t*-butyl hydroperoxide–

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metal acetylacetonate in initiating the autoxidation of the olefin. The most frequently proposed mechanism consists of the formation of radicals *via* some sort of "redox" reaction between the metal and the hydroperoxide and the subsequent addition of the radicals to the olefin.[7,18,20]

Table II offers a comparison of certain related reactions involving metal acetylacetonates. There seems to be some general correlation in the ability of the various metals to act as initiators; however, there is apparently no connection between this property and the ease of autoxidation of the chelates themselves.[15] The work of Arnett and co-workers[15,26,27] has shown that these compounds exhibit extraordinary catalytic and inhibiting properties toward each other in autoxidation reactions in which the ligands themselves are involved, and that small structural changes in the chelate part of the molecule have marked but unsystematic effects on these same reactions. These authors have also shown that autoxidation of these compounds is inhibited in the presence of usual free-radical sources and not affected by usual inhibitors of autoxidations.

Based on these observations and our own preliminary findings, it is difficult to predict the behavior of the metal acetylacetonate complexes under various experimental conditions. However, it is clear that the ligand itself plays a significant role[15,23,26] and reagents which are capable of altering the ligand–metal interactions will alter the transformations that are possible. For example, when the ligand portion of the molecule is varied, the catalytic properties are altered in a way which cannot be predicted by the oxidation state of the ligand itself.[25] Detailed kinetic studies are underway in this laboratory for several metal acetylacetonate–*t*-butyl hydroperoxide–olefin systems.

Experimental Section

Chemicals.—Octene-1 was Phillips research grade (99.9 mole %), distilled prior to use (bp 120–121°). *t*-Butyl hydroperoxide was obtained from Wallace and Tiernan Inc. (Lucidol Division) as *t*-butyl hydroperoxide-90 and further purified by distilling off the lighter impurities under vacuum. Iodometric titration indicated >95% hydroperoxide. The metal acetylacetonates (McKenzie Chemical Corp.) were recrystallized from acetone. Cr(III) acetylacetonate was dissolved in benzene and precipitated with petroleum ether (bp 30–60°).[28] Oxygen (Matheson) was used without further purification.

Kinetics.—Oxygen absorption measurements were carried out in jacketed Pyrex cells. Temperature was maintained at 30 ± 0.1° by running thermostated water through the jacket. Stirring was accomplished by means of a magnetic stirrer with a Teflon-coated stirring bar. A small test tube containing molecular sieve (Fisher, Type 4A) was suspended in the cell to remove heavy, gaseous products which might interfere with the measurement of oxygen uptake.[15] The volume of oxygen was read at specified times and converted to the volume at STP. Volume of oxygen absorbed was plotted against time, and the rates reported are taken from the slopes of the linear portions of these graphs. No oxygen was picked up over a period of 5.5 hr, in the absence of metal acetylacetonate, by a solution of *t*-butyl hydroperoxide in octene-1. In the absence of the *t*-butyl hydroperoxide oxygen absorption was comparatively negligible (Table I). The production of gaseous products was observed in the absence of an oxygen atmosphere. Even in the presence of oxygen for some of the experimental conditions of Table I an initial gas-producing period was detected. For the system *t*-butyl hydroperoxide–Cr(III) acetylacetonate in diphenyl ether (no octene, no oxygen) under an atmosphere of nitrogen the evolved gas was shown to be oxygen by absorption in alkaline pyrogallol.[29]

The autoxidation cell was cleaned between runs by soaking in a solution of $K_2Cr_2O_7$ plus concentrated H_2SO_4, washing successively with water, benzene, acetone, methanol, and drying in a stream of air passed through a column of molecular sieve.

t-Butyl hydroperoxide decomposition studies were carried out in the absence of oxygen. Reactants were degassed several times and sealed, *in vacuo*, in new Carius tubes. The tubes were thermostated at 30 ± 0.1° and removed at intervals. The remaining peroxide was determined iodometrically.[1]

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Rearrangement of 1,1,1,2-Tetraphenylethane to 1,1,2,2-Tetraphenylethane by Means of Phenylsodium[1]

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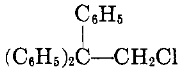
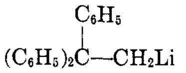
1,1,1,2-Tetraphenylethane underwent a 1,2 shift of a phenyl group to form 1,1,2,2-tetraphenylethane on treatment with phenylsodium in decane–heptane at 90–100°. This appears to be the first example of such a rearrangement in which the initial carbanion was generated by an acid–base reaction.

Although a few anionic 1,2-phenyl migrations from carbon to carbon within a saturated system to form a saturated product have been reported,[2] the initial carbanion has previously been generated only by the action of an alkali metal on a halide; for example, halide I converted by means of lithium metal to initial carbanion I′, which rearranged to form the more stable carbanion II.



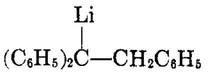
$(C_6H_5)_2C(C_6H_5)-CH_2Cl$

I



$(C_6H_5)_2C(C_6H_5)-CH_2Li$

I′



$(C_6H_5)_2C(Li)-CH_2C_6H_5$

II

Such a rearrangement has now been realized in which the initial carbanion was generated by an acid–base reaction. Thus, 1,1,1,2-tetraphenylethane (III) was rearranged by phenylsodium in decane–heptane at 90–100° to form 1,1,2,2-tetraphenylethane (IV); presumably hydrocarbon III was converted initially to carbanion III′, which rearranged to carbanion IV′ (Scheme I).

Interestingly, this rearrangement was facilitated by the presence of sodium *t*-butoxide which appeared to enhance the activity of the organosodium compounds. This observation is similar to that of Benkeser and Crimmins who found that sodium *t*-butoxide greatly enhances the reactivity of *n*-amylsodium toward metalation of *t*-butylbenzene.[3]

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