80–92°, in 99% yield. The optical rotation was $[\alpha]^{32}\text{D}$ +28.1° corresponding to 89% 3α- and 11% 3β-cholestanyl acetate.[3] In a second run, a value of $[\alpha]^{30}\text{D}$ + 26.4° corresponded to 80% of the 3α isomer.

Reduction of Norcamphor with Alkoxyaluminum Dichlorides.—In a typical experiment, isopropoxyaluminum dichloride was prepared as described earlier from 5 g. (0.0375 mole) of aluminum chloride in 40 ml. of ether, 10 ml. of 1 *M* ethereal $LiAlH_4$ (0.01 mole), and 2.4 g. (0.04 mole) of isopropyl alcohol in 10 ml. of ether. The chilled solution was brought to room temperature and, after hydrogen evolution ceased, 3.3 g. (0.03 mole) of norcamphor in 20 ml. of ether was added with stirring (10 min.) and the solution was refluxed for 0.5 hr. It was then cooled and worked up in the usual way and the residue was analyzed for residual norcamphor, *exo*-norborneol, and *endo*-norborneol as described earlier. The results of this experiment and similar ones employing cyclopentanol and cyclohexanol instead of isopropyl alcohol are entered in Table II. The *exo–endo* ratio of the alcohols was 23.8:76.2 with isopropyl alcohol, 8.8:91.2 with cyclopentanol, and 16.8:83.2 with cyclohexanol.

When isobornyloxyaluminum dichloride was used as reducing agent, analytical difficulties arose because of overlap of the *exo*-norborneol and camphor peaks in the gas chromatogram. Fortunately, there was no residual norcamphor in this case (*cf.* Table II), so the product was treated with an excess of lithium aluminum hydride which reduced the camphor to borneol and isoborneol, whereupon gas chromatographic analysis could be effected as described before, indicating 96.5% *endo* and 3.5% *exo* isomer.

Miscellaneous Reductions. 4-*t*-Butylcyclohexanone and Isobornyloxymagnesium Bromide.—To the Grignard reagent prepared from 11 g. (0.1 mole) of ethyl bromide and 2.4 g. (0.1 g.-atom) of magnesium in 80 ml. of dry ether was slowly added a solution of 15.4 g. (0.1 mole) of isoborneol in 50 ml. of dry ether with cooling and stirring until gas evolution ceased. The apparatus was then set for downward distillation, 180 ml. of dry benzene was added, and the solvent was distilled through a Vigreux column until the overhead temperature reached 70°. To the homogeneous solution was then added 5.1 g. (0.033 mole) of 4-*t*-butylcyclohexanone in 10 ml. of benzene. The solution was stirred for 3 hr. at room temperature and then decomposed with water and dilute acid. The benzene layer was separated, washed with water, dried, and concentrated. The gas chromatogram of the product indicated very little camphor (less than 5% of the original isoborneol), large amounts of unchanged 4-*t*-butylcyclohexanone and isoborneol, and only traces of 4-*t*-butylcyclohexanol, indicating that little reduction had occurred.

When the reaction was repeated with 2 hr. of reflux, some reduction occurred. The extent of oxidation to camphor now was about 20% and the extent of reduction to 4-*t*-butylcyclohexanol about 22%. The alcohol portion was largely *trans* isomer (81%) with but 19% *cis*.

4-*t*-Butylcyclohexanone and Aluminum Isobornyl Oxide.—Redistilled aluminum tri-*t*-butoxide (14 g., 0.17 mole) was dissolved in 100 ml. of dry toluene and heated to reflux. Part of the toluene (20 ml.) was allowed to distil to entrain any free *t*-butyl alcohol that might have been present. Isoborneol (5.1 g., 0.033 mole) was then added and the solution was refluxed for 4 hr. The apparatus was then set for downward distillation and two portions of 25 ml. of solvent were removed. The first portion was found, by gas chromatography using isopropyl alcohol as an internal standard, to contain 2.52 g. (0.034 mole) of *t*-butyl alcohol, whereas the second portion was free of *t*-butyl alcohol. Thus, the theoretical amount of *t*-butyl alcohol was evolved, though it is not clear whether the alkoxide formed was of the type $ROAl(O\text{-}t\text{-}Bu)_2$ or a mixture of $(RO)_3Al$ and $Al(O\text{-}t\text{-}Bu)_3$ and possibly even $(RO)_2Al(O\text{-}t\text{-}Bu)$ where R = isobornyl. To the remaining solution was added 2.5 g. (0.0165 mole) of 4-*t*-butylcyclohexanone in 30 ml. of toluene and the mixture was stirred at room temperature for 1 hr. An aliquot of the reaction mixture (10 ml.) was worked up and analyzed at this stage but only about 10% camphor was formed; the proportion of *cis*- and *trans*-4-*t*-butylcyclohexanol in the small amount of reduced product formed was 70:30. The solution was then boiled for 0.5 hr. This virtually completed the reduction but, apparently, also produced considerable equilibration, since now the ratio of *cis*- to *trans*-4-*t*-butylcyclohexanol was 1:2.

Acknowledgment.—We gratefully acknowledge support of this work under National Science Foundation Grant GP-2096. 4-*t*-Butylcyclohexanone was generously donated by the Dow Chemical Company. We are indebted to Dr. Jean-Claude Richer for preliminary experiments on the mixed hydride reductions of camphor and norcamphor.

Synthesis of 1-Olefins and α-Substituted Allylic Compounds by Free-Radical Addition of Acetylene[1]

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α-Substituted allyl alcohols, amines, esters, and ketones were produced when the appropriate substrate was added to acetylene in a free-radical reaction initiated by di-*t*-butyl peroxide. 1-Olefins were produced when isoparaffins or cycloparaffins underwent reaction. Products were identified from physical properties, including infrared and n.m.r. spectra. The reaction was carried out in a high-pressure 1-l. autoclave at 140°. Acetylene partial pressure was maintained at 100 to 200 p.s.i. during reaction. Isoparaffins, cycloparaffins, and compounds containing a functional group underwent reaction. At the conditions employed, acetylene addition took place at the secondary hydrogen of cycloparaffins, at tertiary hydrogen, or at hydrogens adjacent to an activating group. The yield of monoadduct based on di-*t*-butyl peroxide increased as the amount of peroxide used was decreased.

Free-radical additions to acetylene which produce new carbon–heteroatom bonds are well known. The literature on these reactions has been reviewed by Stacey, *et al.*[2] However, the addition of radicals to acetylene to form carbon–carbon bonds has not been studied extensively. Bartok and Lucchesi[3] reported 3-methyl-1-butene as a product of the radiation-initiated addition of propane to acetylene. Schluback, *et al.*,[4] prepared 2,5-hexanedione by the addition of acetylaldehyde to acetylene initiated by benzoyl peroxide. The competitive addition of methyl radicals to acetylene and ethylene was studied by Gazith and Szwarc[5] who found that the addition of methyl radicals to acetylene has a slightly higher activation energy than the addition to ethylene, and that the rate of addition is about 30 times

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TABLE I

EXPERIMENTAL CONDITIONS AND PRODUCT YIELD

					Heating schedule		Monoadduct					
Addend	Addend, g.	DTBP, g.	N_2, p.s.i.	Total pressure, p.s.i.g.	Hr.	°C.		Wt., g.	B.p., °C.	n^{20}_D	$\frac{\text{Moles}}{\text{mole of DTBP}}$	Residue, g.
2,3-Dimethylbutane	425	58.8	75	300	^{a}		3,3,4-Trimethyl-1-pentene	35.7	107	1.4134	0.80	85
	439	39.2	75	300	^{a}		3,3,4-Trimethyl-1-pentene	26.7			0.89	71
Cyclopentane	480	59.0	0	260	22	140	Vinylcyclopentane	35.3	97.7	1.4357	0.93	99
	514	19.8	0	280	21	140	Vinylcyclopentane	30.4			2.50	45
Cyclohexane	461	48.5^{b}	100	300	4	130	Vinylcyclohexane	35.8	129	1.4546	1.20	84
					4	140						
Ethyl ether	454	58.8	0	300	9^{c}	140	3-Ethoxy-1-butene	8.0	77.2	1.3882	0.20	71
Methyl isopropyl ketone	521	38.9	100	250	10^{c}	148	3,3-Dimethyl-1-penten-4-one	15.5	129.5		0.52	. . .
Methyl isobutyrate	499	19.6	100	240	8^{c}	145	Methyl dimethylvinylacetate	22.0	126.6	1.4162	1.30	45
n-Butylamine	477	39.5	0	230	5.5	140	3-Amino-1-hexene	20.2	114	. . .	0.74	. . .
Methyl alcohol	513	60.5	0	300	5^{c}	140	Allyl alcohol	6.4	. . .	. . .	0.27	13
Ethyl alcohol	509	58.7	0	300	5^{c}	140	3-Butene-2-ol	16.6	96.2	1.4142	0.57	124
	546	19.6	0	300	5^{c}	140	3-Butene-2-ol	20.4			2.10	38
Isopropyl alcohol	507	58.6	0	300	5^{c}	140	2-Methyl-3-buten-2-ol	52.0	95.6	1.4168	1.50	181
	545	18.7	0	300	5^{c}	140	2-Methyl-3-buten-2-ol	37.0			3.70	54
	561	7.8	0	300	2.3^{c}	140	2-Methyl-3-buten-2-ol	35.0			7.70	26
	562	2.2	0	290	5^{c}	140	2-Methyl-3-buten-2-ol	15.9			12.00	7

[a] 3 hr. at 125°, 4 hr. at 135°, and 6 hr. at 145°. [b] 7.1 g. of di-*t*-butyl peroxide was recovered from the products. [c] The acetylene valve was closed and heating was continued for about 17 hr. to decompose residual peroxide.

as fast as the rate of abstraction of hydrogen from isooctane.

In the present study, the addition of free radicals to acetylene in the liquid phase was explored. Acetylene partial pressures of 100 to 200 p.s.i. were employed. Paraffins, cycloparaffins, and compounds containing a functional group underwent reaction, di-*t*-butyl peroxide (DTBP) being the initiator employed. The products were 1-olefins and α-substituted allylic compounds containing the original functional group.

Discussion

The reaction proceeds through a free-radical chain sequence initiated by the thermal decomposition of the added peroxide. The di-*t*-butyl peroxide decomposes[6-8] by first-order kinetics to yield *t*-butoxy and methyl radicals. These radicals abstract hydrogen from the substrate, present in large excess, to form a new radical, *t*-butyl alcohol, and methane.

The new radical may choose to react in any of a number of ways, depending on its concentration and stability. At proper conditions of low concentration and sufficient stability, reaction to the desired adduct may be made the major reaction taking place. In this case the radical adds to acetylene to form a new vinyl radical. This, in turn, abstracts hydrogen from the substrate to form the stable monoadduct, and to regenerate the substrate radical, which can then continue the reaction. However, the substrate radical may also add to another radical, producing dimers or polymers and terminating the chain, or it may decompose or add to a product olefin to form saturated products. In addition, the vinyl radical formed by addition to acetylene may add a second molecule of acetylene. Thus, there are many paths to side products, and numerous products are formed.

It was of interest to determine the range of radical stabilities useful in this reaction under the conditions chosen. Only a trace of monoadduct was obtained in the reaction of neopentane and acetylene at 140°. It may be that primary hydrogen was not abstracted, although the *t*-butoxy radical would appear to be sufficiently energetic.[8] Nevertheless, we did not find any evidence in this study that primary hydrogens were attacked. Generally, the reaction is quite selective to tertiary hydrogen.

On the other hand, a small but identifiable yield of C_9 olefins was obtained using *n*-heptane as a substrate. Secondary hydrogen abstraction appears thus to be borderline at our conditions. Good product yields were obtained from cyclopentane, cyclohexane, and some isoparaffins, as well as compounds containing hydrogen adjacent to an activating group. Such radicals thus represent optimum stability at our conditions. The cycloparaffins represent a special case. All of the hydrogens are identical and only one monoadduct can be formed. In addition, it has been shown[9] that the hydrogens of cyclohexane are considerably more reactive to *t*-butoxy radicals than aliphatic secondary hydrogens.

At 140° or somewhat higher, the radicals formed from the larger isoparaffins tend to decompose. Thus, only a small amount of the monoadduct was obtained from 2,4-dimethylpentane, large amounts of isobutane being formed. In addition, at temperatures above 150°, increasing amounts of propylene and 2-methyl-2-butene were formed from 2,3-dimethylbutane.

Thus, the free-radical addition of hydrocarbons or monofunctional organic compounds to acetylene offers an opportunity to produce a wide variety of 1-olefins or α-substituted allylic compounds containing the original functional group. The reaction appears to be quite general, and hinges in a particular case on the generation of a free radical in the right stability range at the conditions employed.

In Table I are listed the experimental conditions used and the results obtained in this work. This survey was exploratory, and the conditions and yields are probably not optimum. A large excess of addend was employed, and acetylene concentration was held reasonably constant by continuous addition of acetylene during the first 5 or 6 hr. of the run. The composition of the higher boiling products was not determined.

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For the nonhydrocarbons, attack was at the hydrogen adjacent to the functional group. When these hydrogens were primary, product yield tended to be small at our conditions. Thus, only a small amount of monoadduct was obtained from acetone. The yield was somewhat better from methanol. Edwards and Mayo[10] compared the relative reactivities of acetone, methyl acetate, and methyl benzoate for hydrogen abstraction with methyl radicals and found them to be 1, 52, and 0.15. Thus, product yield would be expected to vary with the electrophilic properties of the functional group. The secondary hydrogens of ethyl ether, *n*-butylamine, and ethanol likewise show some spread in reactivity, the ether being the least active. The remaining compounds investigated contain a tertiary hydrogen adjacent to the functional group. The yield of monoadduct was generally good for these compounds.

A large yield of by-products boiling above the monoadduct was observed in most cases. As shown by the series of runs on isopropyl alcohol, much of this residue was due to the large amount of DTBP used. Thus, reducing the peroxide from 59 to 2.2 g. reduced the yield of heavy products from 3.5 to 0.44 g./g. of monoadduct. The larger amounts of peroxide were employed in order that sufficient monoadduct would be available for characterization and other tests.

Assuming that two free radicals are formed per molecule of peroxide decomposed, the isopropyl alcohol series shows that the number of molecules of monoadduct formed per initiating free radical (chain length) increased from less than one, to about six as peroxide concentration was decreased from 4.7 to 0.16 moles/100 moles of alcohol. Side products are, of course, decreased as chain length increases.

Experimental Section

Commercial cylinder acetylene was employed in this work. Part of the acetone was removed by passing under pressure through an ice trap. Pure grade hydrocarbons were employed, and 2,3-dimethylbutane was distilled immediately before use to remove inhibitor and any peroxide present. Other chemicals were reagent grade.

The procedure employed is described below using the first run in the isopropyl alcohol series as an illustration.

Isopropyl alcohol (650 ml., 507 g., 8.5 moles) and 75 ml. (58.6 g., 0.402 mole) of di-*t*-butyl peroxide were placed in a 1-l., high pressure autoclave equipped with a magnetically driven stirrer and a rupture disk set to release at 1000 p.s.i.g. The autoclave was closed and flushed free of air by addition of nitrogen to 500 p.s.i.g. followed by venting to atmospheric pressure. This was repeated three times and resulted in some loss of the more volatile reagents. The autoclave was then flushed once by adding acetylene to 100 p.s.i.g. and venting to atmospheric pressure to remove nitrogen. Acetylene was then added to 100 p.s.i.g., and the reactor was heated to 140°. The reaction was run at this temperature for 5–6 hr. with continuous addition of acetylene to maintain a pressure of 280–300 p.s.i.g. on the autoclave. At the end of this time the acetylene was shut off and heating was continued overnight to decompose residual peroxide.

The reaction temperature was limited to 120–150° by the use of di-*t*-butyl peroxide as initiator. The half-life ranges from 19 to 1 hr. over this temperature range.[8] In the runs with 2,3-dimethylbutane and cyclohexane, the reaction was started at a low temperature and the temperature was increased during the run in an effort to obtain a relatively constant rate of radical production. However, the results were about the same as obtained when running at a constant temperature of 140°; so this procedure was adopted. While the reaction was essentially complete at the end of 6 hr. at 140°, the removal of any unreacted peroxide was difficult. With a boiling point of 111° not only can it contaminate the monoadduct, but it can also collect in the distillation flask and cause polymerization of the product olefin. For this reason heating was usually continued overnight to destroy remaining peroxide. Some monoadduct may have been lost during this period.

Acetylene partial pressures of 100–200 p.s.i. with total pressures as high as 300 p.s.i. were used in this work. Since this entails some hazard, work was done in a barricaded cell. Generally, acetylene can be used at pressures up to 400 p.s.i. in equipment providing good heat removal if no surface-to-surface distance is more than 1 in. Larger vessels can be used if the acetylene is diluted. Thus, Reppe[11] reports the use of a 2:1 acetylene–nitrogen mixture at 20–25 atm. as a regular operating procedure. In the present work, when the substrate developed ~100 p.s.i. of vapor pressure at operating temperature, it was considered safe to use acetylene without additional diluent. For less volatile materials, 100 p.s.i. of nitrogen was employed as shown in Table I.

After heating overnight, the reactor was cooled to room temperature by an air blast. Residual acetylene was vented and the reactor was opened. The liquid products were transferred to a flask and distilled at 50-mm. pressure to an overhead temperature of 100°, the product being collected in an ice-cooled receiver. This fraction had a normal boiling range of 50–150° and contained unreacted isopropyl alcohol, *t*-butyl alcohol, and the monoadduct. The heavy residue remaining in the flask weighed 181 g. The 50–150° fraction was redistilled in a fractionating column containing 15 to 20 equilibrium stages, and 52.0 g. of 2 methyl-3-buten-2-ol, b.p. 95.5–95.7°, was obtained.

In reactions of hydrocarbons yielding water-insoluble products, the reaction mixture was extracted with water to remove acetone and *t*-butyl alcohol. This avoided the possible formation of azeotropes during fractionation of the product.

The overhead fraction from the vacuum distillation was also analyzed by gas chromatography. This provided a check on yield determined as above, or could be used to determine yield in duplicate runs.

Product Identification

Infrared spectra were obtained in all cases, and these showed the strong absorption bands characteristic of vinyl hydrogen. N.m.r. spectra were obtained in some cases. A Varian Associates V4300C spectrometer operating at 60 Mc. was employed. Resonance positions, given in τ units, are for the pure liquid unless otherwise stated. Tetramethylsilane was used as an internal reference.

Vinylcyclohexane, vinylcyclopentane, and allyl alcohol were identified by comparison of physical properties and infrared spectra with those of authentic reference samples.

3,3,4-Trimethyl-1-pentene had b.p. 106°, $n^{20}\mathrm{D}$ 1.4140 (lit.[12] b.p. 105°, $n^{20}\mathrm{D}$ 1.4144). Upon hydrogenation 1.0 mole equiv. of hydrogen was absorbed to produce 2,3,3-trimethylpentane, identified by comparison of the infrared spectrum with that of an authentic sample.

3-Ethoxy-1-butene had b.p. 77.2°, $n^{20}\mathrm{D}$ 1.3891 (lit.[13] b.p. 76.6°, $n^{23}\mathrm{D}$ 1.3882). The n.m.r. spectrum shows three groups of peaks in the ratio of 3:3:6. The first group, in the τ 4–5 region, is a typical ABCX pattern of a vinyl group attached to a carbon with only one hydrogen. The second group consists of two complex overlapping patterns in the τ 6.5 region characteristic of hydrogen adjacent to oxygen. The third group, centered at τ 8.9, consists of an overlapping doublet and triplet and is assigned to the two methyl groups.

3,3-Dimethyl-1-penten-4-one had b.p. 129.5°. The n.m.r. spectrum of a 25% solution in carbon tetrachloride shows an ABC pattern for a vinyl group attached to a completely substituted carbon in the τ 4–5 region. There are, in addition,

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two single peaks, one at τ 8.0, equivalent to three hydrogens, from the methyl group on the carbonyl, and the other at τ 8.8, equivalent to six hydrogens, from the dimethyl group β to the carbonyl and the double bond.

Anal. Calcd. for $C_7H_{12}O$: C, 74.9; H, 10.8. Found: C, 74.9; H, 10.6.

Methyl dimethylvinylacetate had b.p. 126.6°, $n^{20}D$ 1.4162. The n.m.r. spectrum shows an ABC pattern for a vinyl group attached to a completely substituted carbon in the τ 4–5 region. There are two other single peaks, one at τ 6.4, equivalent to three hydrogens, from the methoxy group, and the other at τ 8.8, equivalent to six hydrogens, from the dimethyl group β to the carbonyl and the double bond.

Anal. Calcd. for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found: C, 66.4; H, 9.7.

3-Amino-1-hexene had b.p. 114°. The n.m.r. spectrum shows an ABCX pattern in the τ 4–5 region for the vinyl groups attached to a tertiary carbon. A broad, unresolved resonance at τ 6.8, equivalent to one hydrogen, is in the region expected for the single hydrogen α to both the double bond and the amino group. A complex methylene resonance, equivalent to four hydrogens, occurs at τ 8.6. A methyl resonance is present at τ 9.0. The amino group is identified with a single peak, equivalent to two hydrogens, which occurs at τ 8.8 in the pure liquid, shifting to 9.0 for a 25% solution in carbon tetrachloride.

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Generation of Free Radicals through Organic Oxidation–Reduction Systems

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The oxidation–reduction reaction between alkyl hydroperoxides, acyl and aroyl peroxides, and organometallic compounds such as manganous acetylacetonate and ferrocene as a means of generation of free radicals in organic solvents at ambient temperatures was studied. The radical nature of these reactions was indicated by the initiation of vinyl polymerization and the chain addition of sodium bisulfite, mercaptans, and ethyl α-bromoacetate to olefins.

The interaction between hydrogen peroxide and ferrous ion known as Fenton's[2] reagent affords a unique method to generate hydroxy free radicals in aqueous solution at low temperature. This reaction involves a complicated sequence of transformations and can be simplified as a one-electron transfer process whereby one hydroxy radical is reduced to hydroxide ion and ferrous ion is oxidized to ferric ion.

$$Fe^{2+} + HOOH \longrightarrow Fe^{3+} + HO^- + HO$$

This reaction has been extensively studied[3] and expanded[4] through the years. Different oxidizable metal ions including some organometallic ions have been used with various organic hydroperoxides and acyl peroxides. Enormous development has been achieved in the field of low-temperature emulsion polymerization in the past 20 years.[5] The use of organometallic compounds instead of inorganic metal salts in the oxidation–reduction systems has the advantage that the reaction can be carried out in organic solutions instead of either in aqueous or emulsion systems, thus polymerization in bulk can be carried out at ambient temperature range. Uri[6] indicated that the presence of very low concentrations of ferrous and cuprous phthalocyanine catalyzed the autoxidation of linoleic acid. Lowell[7] reported that ferrocene reacted with benzoyl peroxide to initiate free-radical chain reactions, and Konish and Namba[8] polymerized vinyl chloride with lauroyl peroxide and ferrous caproate as the oxidation–reduction couple.

Systems which involve oxidation–reduction cleavage of chemical bonds other than oxygen–oxygen have been proposed by Evans and Baxendale and their coworkers on the cleavage of oxygen–nitrogen bond in hydroxylamine with titanous ion[9] and on the bromine–bromine bond cleavage with ferrous ion.[10] Both systems have induced vinyl polymerization and the radical nature of such systems was well established. The oxidation–reduction cleavage of the sulfur–sulfur bond in aryl and cyclic alkyl disulfides by organometallic compounds and amines was reported recently.[11] Reduction of phenylmercuric cation whereby phenyl free radical[12] is produced, and of triethyllead cation leading to the formation of ethyl radical[13] constitute examples of oxidation–reduction cleavage of chemical bonds between carbon and metals.

In this paper we wish to report some more additional findings on the oxidation–reduction cleavage of acyl peroxide and alkyl hydroperoxides with organometallic compounds in organic solvents.

Results and Discussion

We noticed that the electron-transfer process between organic acyl peroxides or hydroperoxides with organometallics is almost a general reaction. In addition to the oxidizable metal phthalocyanines and metallocenes, metal chelates such as acetylacetonates with metal at lower valency state which can be oxidized further by a one-electron transfer mechanism interact with acyl peroxides and alkyl hydroperoxides whereby a free radical is generated in organic solvent at or below room temperatures. The radical nature of this reac-

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