green was observed. Samples were collected at different temperatures during the period of contact with the alkali metal. The esr spectra of all samples collected at temperatures from −65 to 0° in THF and −55 to 0° in DME were identical. Each spectrum indicated the presence of two different radicals in the solution. One of these radicals was easily identified as the naphthalene radical anion from the values of the hyperfine splitting constants and the relative line intensities. The other radical is difficult to analyze because of the broad lines and the overlap of some of them with those due to the naphthalene radical anion. The second radical is believed to be the di(1-naphthyl)phosphine oxide, sulfide, or selenide–alkali metal adduct.

The esr spectrum of the sample at room temperature was typical of that of the naphthalene radical anion. The expected lines were very well characterized. In addition, there were present other broad lines of very low intensities compared to those observed in the spectra of the samples taken at lower temperatures. This suggests that the concentration of the second radical present together with the naphthalene radical anion is lower at room temperature than at low temperature. This occurs because of the conversion of the second radical to the dinegative anion at the higher temperature. Also, the radical has been permitted to remain in contact with the alkali metal for a longer time.

Reactions of Tris(1-naphthalene)phosphine Oxide, Sulfide, and Selenide with Lithium in THF and DME. It has been mentioned that lithium behaves differently than the other alkali metals in its reactions with some phosphine compounds. The reaction of the three tris(1-naphthyl)phosphine chalcogenides with lithium in both THF and DME proceeded similarly. The color of the reaction solution was purple throughout the temperature range studied, from −65° in THF and in DME from −55° to room temperature. The esr spectra of all samples taken from this reaction were identical. This spectrum was identified as that of the **1,1′**-binaphthyl radical anion. This means that a carbon–phosphorus bond was cleaved to produce the naphthyl radical which then undergoes dimerization to binaphthyl. This, in turn, is reduced with lithium to produce the 1,1′-binaphthyl radical anion. No other radical was observed in the spectra.

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Pair Production and Cage Reactions of Alkyl Radicals in Solution

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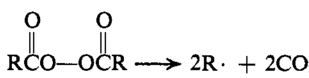
Abstract: Aliphatic diacyl peroxides undergo homolysis on ultraviolet irradiation at 30° to a pair of alkyl radicals and 2 mol of carbon dioxide. The quantum yield for carbon dioxide formation is 2 (2537 Å) and independent of the structure of the alkyl groups. The alkyl radicals are generated in sufficiently high steady state concentrations to enable the esr spectra of a variety of transient alkyl species to be recorded with excellent signal-to-noise ratios. The disproportionation and combination of alkyl–alkyl radical pairs formed in this manner are studied in various solvents and the results compared to those obtained in the gas phase. The cage processes of alkyl–alkyl radical pairs are delineated. The esr study of the rearrangement of cyclopropylmethyl and ω-hexenyl radicals indicates that the cage combination is fast and only those alkyl radicals which diffuse from the solvent cage are observed. In contrast to the thermolytic decomposition of diacyl peroxides, little or no esters are formed in the photolytic process.

Homolytic decomposition of diacyl peroxides has been used extensively as a source of alkyl and aryl radicals.[1] In most cases the decomposition has been induced thermally. However, diacyl peroxides



$$\mathrm{R\overset{\displaystyle O}{\overset{\|}{C}}O{-}O\overset{\displaystyle O}{\overset{\|}{C}}R} \longrightarrow 2\mathrm{R}\cdot + 2\mathrm{CO_2}$$

in which the alkyl group can readily sustain a cationic charge are prone to undergo ionic decomposition *via* carboxy inversion, especially in polar solvents.[2]

We recently showed that photolysis of a diacyl peroxide at low temperatures constitutes a convenient and versatile method of generating a specific alkyl radical in solution for electron spin resonance studies.[3]

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(1) See A. G. Davies, "Organic Peroxides," Butterworth and Co., Ltd., London, 1961; E. Hawkins, "Organic Peroxides, Their Formation and Reactions," E. and F. Spon Ltd., London, 1961; C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957; W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., New York, N. Y., 1966.

(2) (a) F. D. Greene, H. S. Stein, C. C. Chu, and F. M. Vane, *J. Amer. Chem. Soc.*, **86**, 2081 (1964); (b) C. Walling, H. N. Moulden, J. H. Waters, and R. C. Neuman, *ibid.*, 87, 518 (1965); (c) H. Hart and D. Wyman, *ibid.*, 81, 4891 (1959); (d) J. K. Kochi, *ibid.*, **85**, 1958 (1963); (e) R. C. Lamb and J. R. Sanderson, *ibid.*, **91**, 5034 (1969); (f) S. Oae, T. Kashiwagi, and S. Kozuka, *Chem. Ind.* (London), 1964 (1965); (g) D. B. Denney and N. Sherman, *J. Org. Chem.*, 30, 3760 (1965); (h) D. S. Tarbell, *Accounts Chem. Res.*, **2**, 296 (1969).

(3) J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969); R. O. C. Norman, *Chem. Soc., Spec. Publ.*, **No. 24** (1970).

The quality spectra, with excellent signal-to-noise ratios, were indicative of high steady state concentrations of alkyl radicals. Aside from the efficient production of alkyl radicals by this method, little is known about the chemical consequences of the photolysis of diacyl peroxides.[4,5] The pertinent objectives of this study are (1) to show that the photolysis of diacyl peroxides in solution at ambient temperatures occurs with high quantum yields, (2) to relate the electron spin resonance results to the formation of high steady state concentrations of alkyl radicals, (3) to distinguish between heterolytic and homolytic processes, and (4) to study the reactions of a series of alkyl radical pairs in solution, *e.g.*, cage reactions, radical–solvent reactions, and disproportionation–combination ratios.

The photochemistry of the diacyl peroxides is in itself also very interesting. The nature of the electronic states participating in the photolysis, however, remains uncertain at this juncture since we were primarily interested in the chemistry of the "dark-reactions" subsequent to homolysis.

Results

Diacyl peroxides have continuous and weak absorption bands in the ultraviolet region commencing at about 2800 Å (Table I). Irradiation at 2537 Å for the photolysis could be conveniently supplied by a low-pressure mercury resonance lamp. Product studies were carried out in quartz tubes sealed with gas-tight rubber serum caps. Oxygen was removed by entrainment with helium. In typical cases, irradiation of a 0.05 *M* solution of diacyl peroxide in a hydrocarbon solvent required approximately 1 hr for completion at 30°. The course of the photolysis could be quantitatively followed by the evolution of carbon dioxide which was conveniently determined by gas chromatography using the internal standard method.

Table I. Ultraviolet Absorption of Diacyl Peroxides in *n*-Hexane

Peroxide	ϵ, M^{-1} cm^{-1} [a]
Acetyl	47[b]
Propionyl	50
n-Butyryl	59
Isobutyryl	54
2-Methylbutyryl	62

[a] At 2537 Å. [b] In cyclohexane; see ref 4.

Photolysis of Primary Diacyl Peroxides. The photolysis of diacyl peroxides in which the alkyl group is primary was examined in *n*-pentane (Table II) and in decalin (Table III) solutions. In both solvents 2 mol of carbon dioxide was formed from each mole of diacyl peroxide. Greater than 90% of the alkyl moiety was accounted for as alkane, alkene, and dimer (last column, Tables II and III). Less than 1% of the esters (RCO_2R) were found, and no carboxylic acid (RCO_2H) was detected by gas chromatography. However, the photolysis of acetyl peroxide in acetonitrile solutions produced approximately 3% of methyl acetate in addition to methane, ethane, and carbon dioxide (Table II). The thermal decomposition of the primary diacyl peroxides under these conditions was nil.

$$RCO_2O_2CR \longrightarrow 2CO_2 + [RH, R(-H), R-R] \qquad (1)^{6}$$

Table II. Photolysis of Diacyl Peroxides in *n*-Pentane at 2537 Å and 30°

RCO_2O_2CR		Products, mmol				
R =	Amt, mmol[a]	CO_2,[b] %	RH	R(–H)	R–R × 2[c]	ΣR·/CO_2
Ethyl	0.27	89	0.08[d]	0.025[e]	0.32[f]	0.93
n-Propyl	0.29	91	0.09[g]	0.03[h]	0.36[i]	0.89
n-Butyl	0.29	90	0.09[j]	0.03[k]	0.38[l]	0.96
n-Propyl + *n*-butyl[m]	0.29	93	0.08[n]	0.02[o]	0.40[p]	0.93
Methyl	0.42[q]	95	0.34[r]	0.013[s]	0.33[d]	0.87

[a] Dissolved in 5 cc of pentane, all experiments run in duplicate. [b] Assuming $(RCO_2)_2 \rightarrow 2R\cdot + 2CO_2$. [c] Equivalent to mmoles of R·. [d] Ethane. [e] Ethylene. [f] *n*-Butane, ~0.02 mmol of a mixture of 3-ethylpentane, 3-methylhexane, and *n*-heptane, approximate ratio (25:4:1), was also found. [g] Propane. [h] Propylene. [i] *n*-Hexane. [j] *n*-Butane. [k] Butene-1. [l] *n*-Octane. [m] An equimolar mixture of *n*-butyryl and *n*-valeryl peroxides. [n] 0.04 mmol of propane + 0.04 mmol of *n*-butane. [o] ~0.01 mmol of propylene and ~0.01 mmol of butene-1. [p] A mixture of the two symmetrical dimers, *n*-hexane (0.075 mmol), *n*-octane (0.075 mmol), and the unsymmetrical dimer, *n*-heptane (0.055 mmol); [q] Dissolved in 10 cc of acetonitrile, experiments in duplicate. [r] Methane. [s] Methyl acetate.

Table III. Photolysis of Diacyl Peroxides in Decalin at 2537 Å and 30°

RCO_2O_2CR		Products, mmol				
R =	Amt, mmol[a]	CO_2, %[b]	RH	R(–H)	R–R × 2[c]	ΣR·/CO_2
Ethyl	0.29	90	0.18[d]	0.015[e]	0.26[f]	0.88
n-Propyl	0.29	93	0.18[g]	0.02[h]	0.28[i]	0.89
n-Butyl	0.29	90	0.22[f]	0.02[j]	0.24[k]	0.92
Ethyl + *n*-propyl[l]	0.29	88	0.19[m]	0.02[n]	0.28[o]	0.96
n-Propyl + *n*-butyl[p]	0.29	88	0.20[q]	0.02[r]	0.24[s]	0.90

[a] Dissolved in 5 cc of decalin, all experiments were run in duplicate. [b] Assuming the stoichiometry $(RCO_2)_2 \rightarrow 2R\cdot + 2CO_2$. [c] Equivalent to mmoles of R·. [d] Ethane. [e] Ethylene. [f] *n*-Butane. [g] *n*-Propane. [h] Propylene. [i] *n*-Hexane. [j] Butene-1. [k] *n*-Octane. [l] Equimolar mixture of propionyl and *n*-butyryl peroxides. [m] 0.09 mmol of ethane + 0.10 mmol of propane. [n] ~0.01 mmol of ethylene + ~0.01 mmol of propylene. [o] 0.07 mmol of *n*-butane + 0.07 mmol of *n*-hexane + ~0.003 mmol of *n*-pentane. [p] An equimolar mixture of *n*-butyryl and *n*-valeryl peroxide. [q] 0.09 mmol of propane + 0.11 mmol of *n*-butane. [r] ~0.01 mmol of propylene + ~0.01 mmol of butene-1. [s] 0.06 mmol of *n*-hexane + 0.06 mmol of *n*-octane + ~0.002 mmol of *n*-heptane.

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(4) The photolysis of acetyl peroxide was examined by O. J. Walker and G. L. Wild, *J. Chem. Soc.*, 1133 (1937).

(5) The photosensitized decompositions of diacyl peroxides have also been reported. (a) C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, **87**, 3413 (1965); (b) V. A. Krongauz and I. N. Vasil'ev, *Kinetika i Kataliz* (USSR), **4**, 67, 204 (1963); (c) T. Nakata, K. Tokumaru, and O. Simamura, *Tetrahedron Lett.*, 3303 (1967). (d) The photolysis of ketone peroxides has recently been postulated to proceed *via* rearrangement to a diacyl peroxide followed by subsequent homolysis [P. R. Story, D. D. Denson, C. E. Bishop, B. C. Clark, Jr., and J. C. Farine, *J. Amer. Chem. Soc.*, **90**, 818 (1968)]; (e) J. Bevington and T. Lewis, *Trans. Faraday Soc.*, **54**, 1340 (1958); (f) C. Luner and M. Szwarc, *J. Chem. Phys.*, **23**, 1978 (1955); (g) F. G. Moses (Ph.D. Dissertation, California Institute of Technology, Pasadena, Calif., 1967). We wish to thank Professor George Hammond for sending us a copy of this thesis. (h) N. S. Kardash and V. A. Krongauz, *Teor. Eksp. Khim.*, **1**, 796 (1965). (i) W. F. Smith, Jr., *Tetrahedron*, **25**, 2071 (1969). (j) A. T. Koritskii, A. V. Zubhov, and Ya S. Lebedev, *Dokl. Akad. Nauk SSR*, **185**, 1312 (1969).

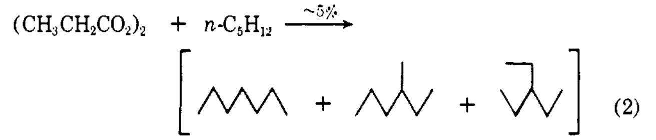
(6) Except for carbon dioxide, the reaction is not balanced; for stoichiometry see Tables II–VI.

Table IV. Photolysis of Isobutyryl, 2-Methylbutyryl, and Pivaloyl Peroxides at 2537 Å and 30°

$RC(=O)OOC(=O)R$ R =	Amt, mmol[a]	Solv	Products, mmol CO_2, %[b]	RH	R(-H)	R-R × 2[c]	$\Sigma R\cdot/CO_2$
Isopropyl	0.26	Dec	94	0.16[d]	0.11[e]	0.18[f]	0.92
sec-Butyl	0.25	Dec	90	0.12[g]	0.10[h]	0.18[i]	0.91
sec-Butyl	0.25	Pen	86	0.10[g]	0.09[j]	0.18[i]	0.86
t-Butyl[n]	0.25	Pen	86	0.17[k]	0.18[l]	0.05[m]	0.93

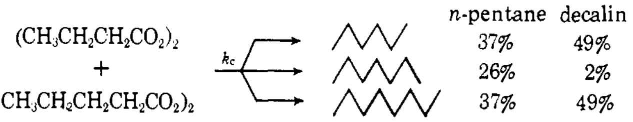
[a] Dissolved in 5 cc of decalin or *n*-pentane, all experiments run in duplicate. [b] Assuming $(RCO_2)_2 \rightarrow 2R\cdot + 2CO_2$. [c] Equivalent to mmoles of R·. [d] Propane. [e] Propylene. [f] 2,3-Dimethylbutane. [g] *n*-Butane. [h] A mixture of butene-1, *trans*-butene-2, and *cis*-butene-2 in the ratio 5.5:3.2:1. [i] 3,4-Dimethylhexane. [j] Butene-1, *trans*-butene-2, and *cis*-butene-2 in the ratio 5:3:1. [k] Isobutane. [l] Isobutene. [m] 2,2,3,3-Tetramethylbutane. [n] Photolysis carried out at 5°.

The photolysis of propionyl peroxide in *n*-pentane produced approximately 5% of a mixture of all three isomeric heptanes from the combination of ethyl radicals and the three possible pentyl radicals derived from the solvent.[7]



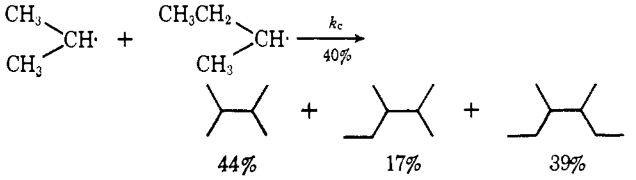
(2)

More than 50% of the alkyl moiety was accounted for as dimer when photolyses were carried out in pentane solution. The yields of dimer were slightly less in decalin solution. However, photolysis of an equimolar mixture of *n*-butyryl and *n*-valeryl peroxides in *n*-pentane (Table II) afforded not only the two symmetrical dimers (*n*-hexane and *n*-octane) but also a substantial amount of unsymmetrical dimer (*n*-heptane). Contrariwise, in decalin solutions the unsymmetrical dimer was formed only in insignificant amounts.



Photolysis of Secondary and Tertiary Diacyl Peroxides. Isobutyryl and 2-methylbutyryl peroxides were studied as sources representative of secondary radicals (isopropyl and *sec*-butyl). In hydrocarbon solvents, the competing thermal reactions accounted for less than 5% of the photochemical decomposition. Good yields of carbon dioxide were obtained together with the respective alkanes, alkenes, and alkyl dimers (Table IV). 2-Methylbutyryl peroxide afforded a mixture of isomeric butenes, butene-1, *trans*- and *cis*-butene-2 in the ratio 5:3:1, respectively. Only a trace (<0.01 mmol) of isopropyl isobutyrate was formed from isobutyryl peroxide under these conditions. Similarly, *sec*-butyl 2-methylbutyrate could not have been an important product from 2-methylbutyryl peroxide.

An equimolar mixture of isobutyryl peroxide (0.025 *M*) and 2-methylbutyryl peroxide (0.025) was also photolyzed in decalin solution. Unlike primary radicals, the unsymmetrical dimer, 2,3-dimethylpentane, was formed in significant amounts from the secondary radicals.

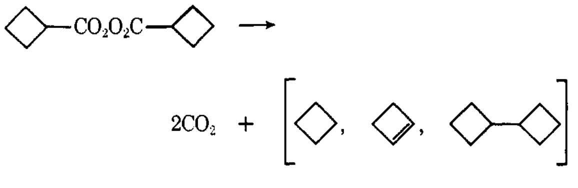


Pivaloyl peroxide could not be prepared as a pure compound due to its facile heterolytic rearrangement.[2d] The peroxide was therefore prepared in pentane solution and used *in situ*. Even at 5° the thermal decomposition (eq 3) corresponded to approximately

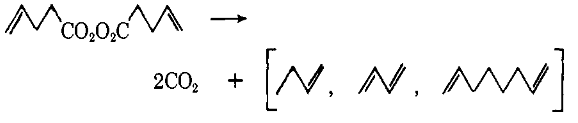
$$[(CH_3)_3CCO_2]_2 \longrightarrow (CH_3)_2C{=}CH_2 + CO_2 + (CH_3)_3CCO_2H \quad (3)$$

10% of the photochemical reaction. The results presented in Table IV were corrected for isobutylene and carbon dioxide produced in the dark reaction.

Photolysis of Homoallylic and Cyclopropylcarbonyl Peroxides. The cyclobutyl moiety remained intact during photolysis of cyclobutanecarbonyl peroxide since only cyclobutane, cyclobutene, and dicyclobutyl were observed.[8] Similarly, allylacetyl peroxide produced only products (1-butene, 1,3-butadiene, and 1.7-octadiene) derived from the allylcarbinyl group.



(4)[6]



(5)[6]

Only cyclopropylacetyl peroxide of the homoallylic analogs led to rearranged hydrocarbon products. It is significant that the unrearranged cyclopropylmethyl moiety survived only in the coupled products (4-pentenylcyclopropane and 1,2-dicyclopropylethane). Neither methylcyclopropane nor methylenecyclopropane[9a] was found.

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[7] If it is assumed that ethane only arose by disproportionation and by attack on the pentane solvent, the amount of the latter may be estimated by subtracting the yield of ethylene from ethane. From Table II, we calculate that 11% of the ethyl radicals generated pentyl radicals which were roughly equally partitioned between self-reaction and reaction with ethyl radicals.

[8] A trace of butene-1 was also observed.

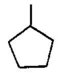
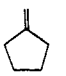
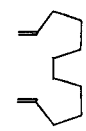
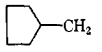
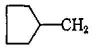
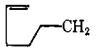
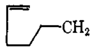
[9] (a) This alkene may not have been stable under reaction conditions. (b) The cage disproportionation of a substituted cyclopropyl radical in carbon tetrachloride has been observed (2%) although no alkene was isolated (H. M. Walborsky and C. J. Chu, *J. Amer. Chem. Soc.*, **89**, 5499 (1967).

Table V. Photolysis of Cyclopropylcarbonyl, Allylacetyl, Cyclopropylacetyl, and Cyclobutylcarbonyl Peroxides at 2537 Å and 30°

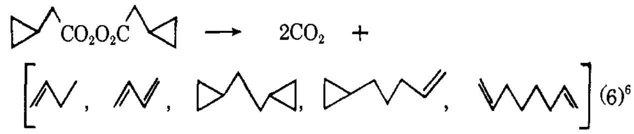
RCO_2O_2CR			Products, mmol					
R =	Amt, mmol[a]	Solv	CO_2, %[b]	RH	R(-H)	R-R × 2[c]	RCO_2R	$\Sigma R\cdot/CO_2$
Cyclopropyl	0.24	Dec	89	0.13[d]	*e*	0.14[f]	0.02[g]	0.68
Cyclopropyl	0.23	Pen	83	0.16[d]	*e*	0.10[f]	<0.01	0.69
3-Butenyl (homoallyl)	0.25	Dec	94	0.18[h]	<0.01	0.24[j]	<0.001	0.90
3-Butenyl (homoallyl)	0.27	Pen	92	0.10[h]	~0.01	0.26[j]	<0.001	0.74
Cyclobutyl	0.25	Dec	94	0.13[k]	0.05[l]	0.20[m]	<0.001	0.81
Cyclobutyl	0.26	Pen	92	0.10[k]	0.05[l]	0.22[m]	<0.001	0.77
Cyclopropylcarbinyl	0.25	Dec	80	0.10[n]	<0.001[i]	0.20[o]	0.02[p]	0.80
Cyclopropylcarbinyl	0.25	Pen	86	0.09[n]	0.001[i]	0.24[q]	0.01[p]	0.82

[a] Dissolved in 5 cc of decalin or *n*-pentane, all experiments were run in duplicate. [b] Assuming $(RCO_2)_2 \rightarrow 2R\cdot + 2CO_2$. [c] Equivalent to mmoles of R·. [d] Cyclopropane. [e] No cyclopropene was found but a trace of propylene was found. [f] Bicyclopropyl. [g] Cyclopropyl cyclopropanecarboxylate. [h] Butene-1. [i] Butadiene, unstable under the reaction conditions. [j] 1,7-Octadiene. [k] Cyclobutane. [l] Cyclobutene, trace of butene-1 was also found. [m] Bicyclobutyl. [n] No methylcyclopropane was found, represents the yield of rearranged product butene-1. [o] A mixture of 1,7-octadiene, 4-pentenylcyclopropane, and 1,2-dicyclopropylethane in the per cent ratio 5:27:68. [p] Cyclopropylmethylcyclopropyl acetate. [q] A mixture of 1,7-octadiene, 4-pentenylcyclopropane, and 1,2-dicyclopropylethane in the ratio 41:15:44.

Table VI. Photolysis of 6-Heptenoyl and Cyclopentylacetyl Peroxides at 2537 Å and 30°

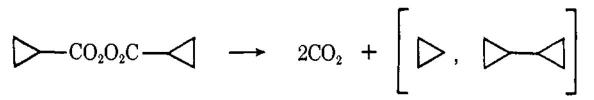
RCO_2O_2CR				Products, mmol[c]					
R =	Amt, mmol[a]	Solv	CO_2[b]						$\Sigma R\cdot$[d]$/CO_2$
	0.25	Pen	96	0.09	0.008	0.36	0	0	0.95
	0.25	Nuj	94	0.08	<0.005	0.36	0	0	0.90
	0.25	Pen	96	0.09	0.005	0.20	0.014	0.15[e]	0.95
	0.25	Nuj	100	0.09	0	0	0	0.34[f]	0.94

[a] 5 ml of *n*-pentane or Nujol (~0.05 *M*), run in duplicate. All yields in mmoles. [b] Percentage yield based on peroxide charged. [c] Dimer yields multiplied by two. [d] ΣR is the sum of all alkyl products. [e] In addition to <0.005 mmol each of hexene-1 and 1,5-hexadiene. [f] In addition to 0.02 mmol of hexene-1 and 0.02 mmol of 1,5-hexadiene.



(6)[6]

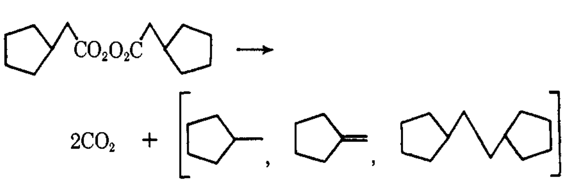
Good yields of carbon dioxide were also obtained from the photolysis of cyclopropanecarbonyl peroxide. Cyclopropane and dicyclopropyl were the principal hydrocarbon products, and only insignificant amounts (<1%) of propylene were detected. The formation of cyclopropene is uncertain due to its instability under



(7)[6]

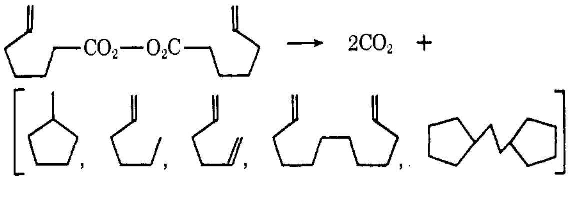
reaction conditions, but the rather poor material balance (last column, Table V) indicates that it may have been a product.[9b] A trace of cyclopropanecarboxylic acid and less than 5% cyclopropyl cyclopropanecarboxylate were also found.

Photolysis of 6-Heptenoyl and Cyclopentylacetyl Peroxides. The photolysis of 6-heptenoyl and cyclopentylacetyl peroxides proceeded in a manner analogous to other primary acyl peroxides. Only cyclopentylmethyl products (methylcyclopentane and 1,2-dicyclopentylethane together with traces of methylenecyclopentane) were formed (Table VI) from cyclopentylacetyl peroxide as given in eq 8. On the other hand,



(8)[6]

6-heptenoyl peroxide afforded methylcyclopentane as well as 1-hexene and 1,5-hexadiene. The dimeric product was exclusively 1,11-dodecadiene. No 6-cyclopentylhexene-1 or 1,2-dicyclopentylethane was detected when 6-heptenoyl peroxide was photolyzed in mineral oil (Nujol). Photolysis of 6-heptenoyl peroxide in



(9)[6]

n-pentane generated the same products, albeit in different yields. The most notable change due to solvent, however, was the formation of significant amounts of 1,2-dicyclopentylethane and 6-cyclopentylhexene-1 largely at the expense of 1,11-dodecadiene in the less viscous pentane medium (Table VI).

Discussion

The photochemically induced decomposition of each mole of diacyl peroxide at 2537 Å results cleanly in the liberation of 2 mol of carbon dioxide with a quantum yield Φ_{CO_2} of 2 (see Experimental Section). Two equivalents of the alkyl moiety are accounted for as alkane, alkene, and alkyl dimer in excellent yields (Tables II–VI).

We postulate that these products arise from the homolysis of the diacyl peroxide into two alkyl radicals

$$\mathrm{RCO_2O_2CR} \longrightarrow \mathrm{2R\cdot + 2CO_2} \qquad (10)$$

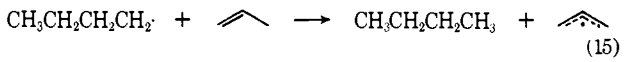
and two molecules of the carbon dioxide.[10] The alkyl radicals may be diverted to products *via* bimolecular reaction with themselves or with solvent.

$$\begin{tikzcd} & \mathrm{RR} \quad (11) \\ \mathrm{R\cdot + R\cdot} \arrow[ur, "k_c"] \arrow[dr, "k_d"'] & \\ & \mathrm{RH + R(\text{-}H)} \quad (12) \end{tikzcd}$$

$$\mathrm{R\cdot + SH} \longrightarrow \mathrm{RH + S\cdot} \qquad (13)$$

$$\mathrm{R\cdot + S\cdot} \longrightarrow \mathrm{RS + [RH, SH, R(\text{-}H), S(\text{-}H)]} \qquad (14)$$

Most of the alkyl radicals could be accounted for among the products of reactions 11, 12, and 13. The products of reaction 14 with the solvent were not examined in detail except in the case of propionyl peroxide in *n*-pentane. In that instance only 4–5% of the ethyl radicals resulted in cross-dimerization products (14) with the three possible pentyl radicals (eq 2). The absence of significant attack on *n*-pentane is supported by studies of the electron spin resonance spectra obtained during photolysis in other solvents. For example, under conditions in which the esr spectrum of the *n*-butyl radical was obtained (with high signal-to-noise ratios) from the photolysis of *n*-valeryl peroxide in propylene, we were unable to observe a significant spectrum of the allyl radical.[3] The latter does not mean that *n*-butyl radicals generated during the photolysis do not react with propylene. The rate



(15)

of hydrogen transfer to produce an adequate steady-state concentration of allyl radicals, however, must be slow compared to other processes.[21]

Disproportionation and Combination of Alkyl Radicals. The relative rates of disproportionation (12) and combination (11) were determined from the yields of alkene and alkyl dimer. These values of k_d/k_c listed in Table VII were based on the assumption that alkene only arose by disproportionation, and that alkyl dimer resulted from combination of alkyl radicals.[22] The disproportionation–combination ratios of alkyl radicals have not been extensively measured in solution, although it has been generally assumed that these ratios are the same in solution as they are in the gas phase. Indeed, the comparisons of k_d/k_c given in Table VII for gas phase and solution processes do show striking agreement.[23] The difference in activation energies for disproportionation and combination is sufficiently small to warrant comparing these results obtained at slightly different temperatures.

The values of k_d/k_c for alkyl radicals were normalized by dividing through by the number of β-hydrogen atoms available for disproportionation. These ratios (listed in the last column of Table VII) are quite consistent among primary radicals at a value of 0.06, for secondary radicals at 0.2, and for tertiary radicals at 0.8. The increase of the normalized value of k_d/k_c in the order tertiary > secondary > primary reflect factors in the disproportionation process which involve

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(10) Our inability to detect significant amounts of products attributable to other intermediates, however, does not preclude their transient existence. For example, a simple homolysis into two acyloxy radicals could be followed by a rather rapid decarboxylation.[11-13] Alternatively, a two-bond or three-bond homolysis is also possible.[14] The formation of ester (methyl acetate) from the thermal decomposition of diacetyl peroxide has been attributed to a cage recombination of acyloxy and alkyl radicals. Except in isolated cases we have been unable to find any significant amounts of esters or carboxylic acids among the products of photolysis although they are stable under the reaction conditions. We found significant yields of ester only from acetyl, cyclopropanecarbonyl, and cyclopropylacetyl peroxides. The latter is known to undergo facile carboxy inversion to afford esters, due no doubt to the enhanced stability of the cyclopropylmethyl cation.[15,16] However, the thermal stability of cyclopropanecarbonyl peroxide precludes the possibility that cyclopropyl cyclopropanecarboxylate was formed by a similar heterolytic process.[16] This ester was most likely formed *via* a cage combination of cyclopropyl and cyclopropanecarboxy radicals. Indeed, the yield of ester decreased on changing the solvent from decalin to the less viscous pentane (*vide infra*).[17] Cyclopropanecarboxy radicals are longer lived than other acyloxy radicals and thus more likely to be trapped.[16,18] A similar process probably also pertains to methyl acetate from acetyl peroxide, which was only photolyzed in acetonitrile solutions (Table II). If acyloxy radicals are primary intermediates in the photolysis as these data suggest, their combination with alkyl radicals appears to be slower than those involved in thermolysis.[19] Alternatively, esters found in the thermal decomposition of diacyl peroxides may have also arisen *via* a competing heterolytic route (carboxy inversion) not involving acyloxy radicals.[20]

(11) The rate constant for fragmentation of acetoxy radicals to carbon dioxide and methyl radical has been estimated as 1.6×10^9 sec^{-1} at 60° with an activation energy of 6.6 kcal/mol.[12] The rate of decarboxylation of the higher homologs may be even faster.

(12) W. Braun, L. Rajenbach, and F. R. Eirich, *J. Phys. Chem.*, **66**, 1591 (1962).

(13) It would be interesting to carry out the photolysis in cyclohexene and related compounds in an attempt to trap any acyloxy intermediates similar to those found by J. C. Martin, J. W. Taylor, and E. H. Drew in their thermolytic studies [*J. Amer. Chem. Soc.*, **89**, 129 (1967); see also H. J. Shine, J. A. Waters, and D. M. Hoffman, *ibid.*, **85**, 3613 (1963)].

(14) *Cf.* the thermal decomposition of diacyl peroxides: D. F. DeTar and R. C. Lamb, *ibid.*, **81**, 122 (1959).

(15) Carboxy inversion is inferred from the work of H. Hart and K. Cipriani, *ibid.*, **84**, 3698 (1962).

(16) H. Hart and D. Wyman, *ibid.*, **81**, 4891 (1959).

(17) For a discussion of cage ester (methyl acetate) from the thermolysis of acetyl peroxide, see M. Levy, M. Steinberg, and M. Szwarc, *ibid.*, **76**, 5978 (1954);[12] (b) J. W. Taylor and J. C. Martin, *ibid.*, **89**, 6904 (1967); (c) T. Koenig and R. Cruthoff, *ibid.*, **91**, 2562 (1969).

(18) G. Grieg and J. C. Thynne, *Trans. Faraday Soc.*, **63**, 1369, 2197 (1967).

(19) The difference (~80 kcal/mol) between the energy of the incident light (~110 kcal/mol) and the bond energy of the peroxy linkage (~30 kcal/mol) may be partly converted to kinetic energy in the fragments. Other studies have indicated, however, that the excess energy is rapidly dissipated (L. Herk, M. Feld, M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 2998 (1961); O. Dobis, J. M. Pearson, and M. Szwarc, *ibid.*, **90**, 278 (1968).

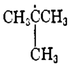
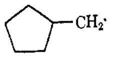
(20) (a) In the thermal decomposition of acetyl peroxide the route to methyl acetate by carboxy inversion was ruled out by the observation that the anhydride is too stable to be an intermediate (F. D. Greene, footnote 40, ref 17b). (b) Both methyl acetate and methyl acetyl carbonate are photolytically stable under our conditions.

(21) Especially in view of the greater stability and hence longer lifetime of allyl compared to *n*-butyl radicals.

(22) This ignores formation of alkene by disproportionation with solvent-derived radicals. The excellent material balance obtained in these photolyses indicates that cross-combination with radicals derived from solvent was not very important (see, *e.g.*, Tables II and III).

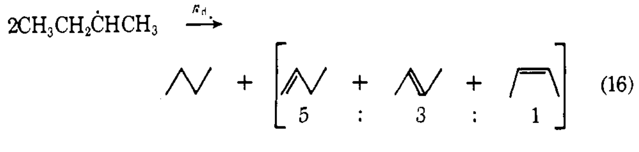
(23) The values for isopropyl and *t*-butyl radicals in the gas phase are variable and differ from our values.

Table VII. Disproportionation to Combination Ratios (k_d/k_c) for Alkyl Radicals in Solution at 30°

Alkyl radical	Solvent	k_d/k_c	Gas-phase value[a]	$k_d/k_c(n)$[b]
$CH_3CH_2\cdot$	*n*-Pentane	0.15	0.14	0.05
$CH_3CH_2\cdot$	Decalin	0.12	0.14	0.04
$CH_3CH_2CH_2\cdot$	*n*-Pentane	0.15	0.16	0.075
$CH_3CH_2CH_2\cdot$	Decalin	0.13	0.16	0.065
$CH_3CH_2CH_2CH_2\cdot$	*n*-Pentane	0.14	0.14[c]	0.07
$CH_3CH_2CH_2CH_2\cdot$	Decalin	0.13	0.14[c]	0.065
$CH_3\dot{C}HCH_3$	Decalin	1.2	0.65, 1.09[d]	0.20
$CH_3CH_2\dot{C}HCH_3$	*n*-Pentane	1.0	2.3, 1.5, 0.94	0.20
$CH_3CH_2\dot{C}HCH_3$	Decalin	1.1		0.22
	*n*-Pentane	0.45		0.11
	Decalin	0.50		0.12
 $CH_3\dot{C}(CH_3)CH_3$	*n*-Pentane	7.2[g]	4.5, 2.3[e], 7.4,[f] 3.2, 4.4, 3.2[i]	0.80
$CH_2{=}CHCH_2CH_2CH_2CH_2\cdot$	Nujol	0.12	0.14	0.06
	Nujol	<0.1	0.075[e,h]	<0.1

[a] J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 115 (1961), unless stated otherwise. [b] n = number of available β-hydrogen atoms. [c] W. E. Morganroth and J. G. Calvert, *J. Amer. Chem. Soc.*, **88**, 5387 (1966). [d] J. Bradley, H. W. Melville, and J. C. Robb, *Proc. Roy. Soc.* (London), **236A**, 339 (1956). [e] J. O. Terry and J. H. Futrell, *Can. J. Chem.*, **46**, 664 (1968). [f] H. M. Frey, *Proc. Chem. Soc.* (London), 385 (1959). [g] This value may be too large due to insufficient correction for the formation of isobutylene by the ionic reaction. [h] Value for isobutyl radical [D. H. Slater, S. S. Collier, and J. G. Calvert, *J. Amer. Chem. Soc.*, **90**, 268 (1968)]. [i] D. G. L. James and R. D. Suart, *Trans. Faraday Soc.*, **65**, 183 (1969).

more than simple statistical ones.[24] This is also shown by the intramolecular comparisons possible with the *sec*-butyl radical.[25a] The ratio of *cis*- and *trans*-butene-2 is close to a thermodynamic value, but the formation of butene-1 is apparently favored more by

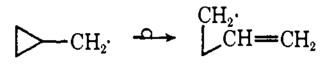


(16)

statistical rather than thermodynamic considerations.[25b] The diminished value of k_d/k_c for cyclobutyl radical may also reflect the increased strain in cyclobutene. We were unfortunately unable to obtain a value for the cyclopropyl radical.

The values of k_d/k_c obtained in various solvents are the same (within experimental error) for a number of alkyl radicals. Since the magnitudes of the cage reactions of alkyl radicals are different in these solvents (*vide infra*), we conclude that the relative rates of disproportionation and combination of alkyl radicals in the solvent cage are essentially the same as those free in solution.[26,27]

Rearrangements of Alkyl Radicals Examined by Esr. Rearrangement of the alkyl group during photolysis of diacyl peroxides is also consistent with the alkyl radicals as intermediates. Thus, in agreement with other studies[28,29] we observed no significant rearrangement of the cyclopropyl, cyclobutyl, or allylcarbinyl groups from photolysis of their respective diacyl peroxides. The cyclopropylmethyl radical, on the other hand, is known to rearrange rapidly to allylcarbinyl radical and the rate constant has been estimated to be greater than 10^8 sec^{-1}.[30] In the photochemical decomposition of



(17)

cyclopropylacetyl peroxide in decalin or pentane neither methylcyclopropane nor methylenecyclopropane was found. Only butene-1 and the three possible dimers from a mixture of cyclopropylmethyl and allylcarbinyl radicals resulted. The yield of dimer (1,7-octadiene) from the rearranged allylcarbinyl radical is significantly less in decalin than in pentane (Table VI). In decalin almost all of the dimeric products are formed in a cage process whereas in pentane much of the coupling takes place in bulk solution (*vide infra*). Based on the yields of products we estimate that the cage combination of cyclopropylmethyl radicals in decalin proceeds roughly five times faster than the rearrangement (eq 17).

The esr spectrum obtained during photolysis of cyclopropylacetyl peroxide varies dramatically with temperature.[31b] At −150° only the spectrum of the cyclopropylmethyl radicals is observed, whereas at

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(24) Compare J. A. Kerr and A. F. Trotman-Dickenson, *Progr. Reaction Kinetics*, **1**, 107 (1961); J. O. Terry and J. H. Futrell, *Can. J. Chem.*, **45**, 2327 (1967); J. N. Bradley, *J. Chem. Phys.*, **35**, 748 (1961).

(25) (a) The reported values for reactions in the gas phase are similar although variable.[24] (b) The composition based on thermodynamic equilibration is 2% butene-1, 23% *cis*-butene-2, and 75% *trans*-butene-2. For a discussion of factors involved in butene formation, see J. K. Kochi, *J. Amer. Chem. Soc.*, **85**, 1958 (1963).

(26) For a discussion of cage and solution combination processes, see H. P. Waits and G. S. Hammond, *ibid.*, **86**, 1915 (1964); S. F. Nelson and P. D. Bartlett, *ibid.*, **88**, 143 (1966).

(27) The effect of solvents on k_d/k_c, however, is not completely clear. Thus, A. P. Stefani, [*ibid.*, **90**, 1694 (1968)] has recently shown a correlation between k_d/k_c and the internal pressure of the solvent for ethyl radicals generated photochemically from azoethane. His values of k_d/k_c in the gas phase, however, varied little from those measured in hydrocarbon solutions. Only in the more polar solvents was the disproportionation process favored. On this basis we doubt whether it is possible to make a distinction between effects due to changes in internal pressure of the solvent or changes in solvation of the alkyl radical.

(28) See following paper, R. A. Sheldon and J. K. Kochi, *ibid.*, in press.

(29) (a) C. Walling, "Molecular Rearrangements," Vol. 1, P. De-Mayo, Ed., Interscience Publishers, New York, N. Y., 1963, p 440; (b) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Amer. Chem. Soc.*, **91**, 1877, 1879 (1969).

(30) Based on the rate of the isocholesteryl–cholesteryl radical rearrangement: D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968).

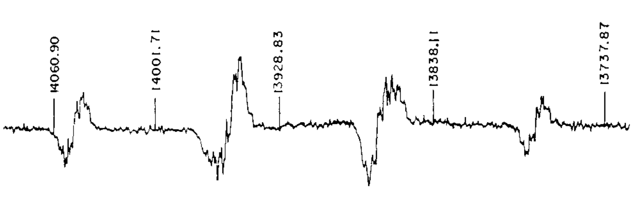


Figure 1. The esr spectrum of the cyclopentylmethyl radical from the photolysis of cyclopentylacetyl peroxide at −90°. The proton nmr field markers are in kHz.

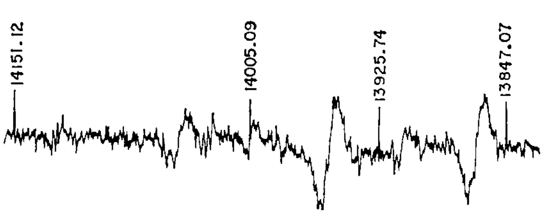


Figure 3. The high-field portion of the esr spectrum obtained from the photolysis of 6-heptenoyl peroxide at −35°.

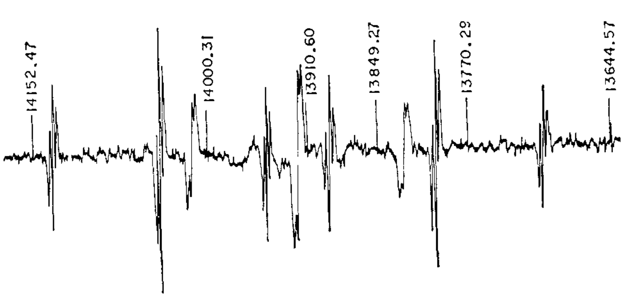


Figure 2. The esr spectrum of the ω-hexenyl radical from the photolysis of 6-heptenoyl peroxide at −90°.

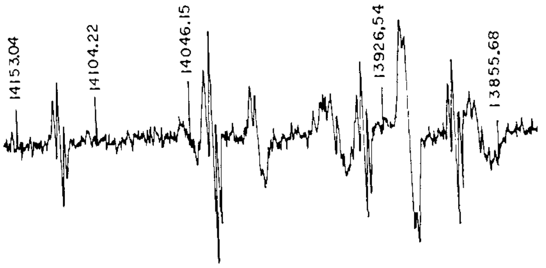
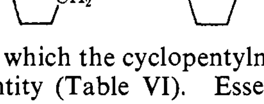


Figure 4. The high field portion of the esr spectrum obtained from the photolysis of 6-heptenoyl peroxide at −65°.

−100° or higher temperatures only the spectrum of the allylcarbinyl radical is apparent. Since the cyclopropylmethyl moiety is retained in the dimeric products at temperatures as high as 30°, we conclude that only those alkyl radicals which diffuse from the solvent cage are observed by this technique.

The competition can be shown more unequivocally with ω-hexenyl radicals which undergo rearrangement to cyclopentylmethyl radicals at a rate (10^5 sec^{-1} at 25°) several orders of magnitude slower than the rearrangement of cyclopropylmethyl radical. The photolysis of cyclopentylacetyl peroxide produces only methylcyclopentane, methylenecyclopentane, and 1,2-dicyclo-



(18)

pentylethane, in which the cyclopentylmethyl group has retained its identity (Table VI). Essentially the same results are obtained in mineral oil and in *n*-pentane. The esr spectrum of the cyclopentylmethyl radical during photolysis of cyclopentylacetyl peroxide is shown in Figure 1.

On the other hand, the photolysis of the isomeric ω-heptenoyl peroxide in mineral oil afforded methylcyclopentane, hexene-1, and hexadiene-1,5. Among dimeric products only 1,11-dodecadiene was found. In pentane solutions, however, two additional isomers, 1,2-dicyclopentylethane and 7-cyclopentylheptene-1, were derived from ω-hexenyl radicals as well as cyclopentylmethyl radicals. The yields of the rearranged products formed in pentane solution corresponded to the combination of alkyl radicals in the bulk solution (*i.e.*, noncage) determined by an alternative method (*vide infra*). These conclusions are also supported by esr studies. If the photolyses of ω-heptenoyl peroxide are carried out at less than −90° only the spectrum of ω-hexenyl radical is observed (Figure 2). At higher temperatures ($> -35°$) only the spectrum of cyclopentylmethyl radicals is observed (Figure 3), and at intermediate temperatures the spectra of both species are obtained (Figure 4). Product studies carried out at 30° show the predominance of cyclopentylmethyl fragments derived by processes occurring in the bulk solution. The absence of lines in the esr spectrum due to the ω-hexenyl radical at these temperatures despite the formation of the dimer, 1,11-dodecadiene, supports the conclusion that the lifetimes of radical pairs in the cage are significantly shorter than those in the bulk solution.

The principal difference between the results obtained with cyclopropylmethyl radical and ω-hexenyl radical lies in the rates of rearrangement. The rate of rearrangement of ω-hexenyl radical to cyclopentylmethyl radical is sufficiently slow (10^5 sec^{-1}) that cage combination leads only to 1,11-dodecadiene. The rearranged dimers (7-cyclopentylheptene-1 and 1,2-dicyclopentylethane) only arise from combination of radicals in the bulk solution. However, the spontaneous rearrangement of cyclopropylmethyl radical to allylcarbinyl radical proceeds at a much faster rate ($>10^8$ sec^{-1}) and it competes with the cage combination process. With both ω-hexenyl and cyclopropylmethyl radicals the slower reactions in bulk solution proceed only from the rearranged cyclopentylmethyl and allylcarbinyl species, respectively.[29b,31]

Cage Reactions of Alkyl Radicals. When solutions of equimolar mixtures of two diacyl peroxides are photolyzed in decalin, high yields of the two symmetrical dimers are obtained (Table III). The yield of the unsymmetrical dimer is minor. On the other hand, in pentane almost as much unsymmetrical dimer is formed as the respective symmetrical dimers (Table II). We ascribe the results in decalin to the almost exclusive combination of alkyl radicals formed in pairs in the

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(31) If we assume that the lifetime of an alkyl radical pair in the cage is less than 10^{-7} sec only a very small number of ω-hexenyl and cyclopropylmethyl radicals may be involved in noncage processes. Compare (b) T. Koenig and M. Deinzer, *J. Amer. Chem. Soc.*, 90, 7014 (1968); (c) T. Koenig, *ibid.*, 91, 2558 (1969); (d) R. M. Noyes, *Progr. Reaction Kinetics*, 1, 131 (1961); (e) the esr studies were carried out at lower temperatures than the product studies, but the principal features of the two should be the same.

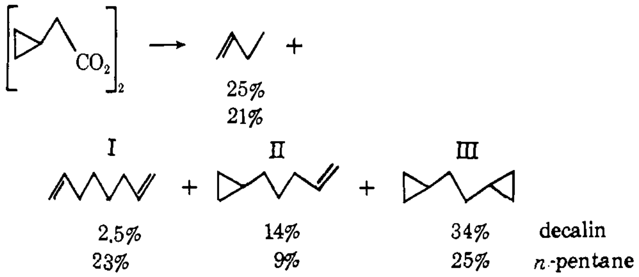
solvent cage.[32] The extensive scrambling in the less viscous pentane solvent is attributed to further dimerization of free alkyl radicals in bulk solution.[33] The percentage of dimers formed in the cage can be calculated according to eq 20. The latter is based

$$(RCO_2)_2 + (R'CO_2)_2 \longrightarrow [\underset{x}{R{-}R} + \underset{y}{R{-}R'} + \underset{z}{R'{-}R'}] \quad (19)$$

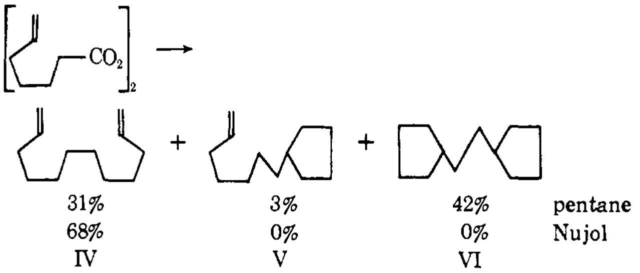
$$\text{cage dimer } (\%) = \frac{x + z - y}{x + z + y}(100) \quad (20)$$

on the assumption that the rate constants for dimerization and cross-combination of similar alkyl radicals are the same. The invariance of the quantum yield for carbon dioxide formation with structure (see Experimental Section) is taken as an indication that alkyl radicals are formed at the same rate from photolysis of an equimolar mixture of peroxides. Furthermore, the quantum yield of two for carbon dioxide formation indicates that there is little or no primary recombination of acyloxy radicals. We calculate from the data in Table III that 96% of the dimers from the photolysis of propionyl and *n*-butyryl peroxides in *decalin* are formed in the cage. The same result (95%) is obtained from a study of a mixture of *n*-butyryl and *n*-valeryl peroxides. The latter pair of peroxides in the less viscous *pentane* solvent generates 46% of the dimers by a cage process. The total cage reaction[34a] is obtained from the yield of cage dimer after correction for the small amount of disproportionation (Table VII). In decalin we estimate that 46–53% of the primary alkyl radicals[36b] react within the cage, whereas in pentane 34% are so involved. Of the alkyl radicals which diffuse from the cage, approximately three times as many abstract hydrogen from decalin than from *n*-pentane.[35] The difference is attributed to the better hydrogen donor properties of decalin. The noncage combination of alkyl radicals is higher in *n*-pentane than in decalin partly for the same reason.

An alternative approach to evaluating the cage process can be considered from the spontaneous rearrangement of the cyclopropylmethyl radical. If we assume that the rearrangement ($k \sim 10^8$ sec^{-1}) competes effectively with the rate of diffusive displacement,[33b-d] then cyclopropylmethyl products II and III only arise within the cage. We calculate on this simple basis that 48 and 34% of the alkyl radicals in decalin and pentane, respectively, are reacting within the solvent cage. These values agree remarkably well with those estimated above.



The rearrangement of ω-hexenyl radical (18) is at least 10^3 times slower than that of the cyclopropylmethyl radical.[32] If we assume at the other extreme that the cage combination and the diffusion of ω-hexenyl radicals are much faster than rearrangement,[33] only ω-hexenyl products IV and V are cage dimers. The results are similar to those obtained from the cyclopropylmethyl radical if correction is made for the disproportionation of the ω-hexenyl radical. Thus, 34% of the primary alkyl radicals in pentane react by a cage process, and the percentage increases to 76% in mineral oil (Nujol).[36]



The geminate combinations of primary alkyl radicals calculated by these largely independent procedures are highly consistent (±5%) despite the rather crude approximations made. Thus, in pentane approximately 35% of the primary alkyl radicals react by a cage process, and in the more viscous decalin solvent the geminate combination constitutes 50% of the reactions of the alkyl radicals.

The percentage of dimers arising from the cage reactions of secondary alkyl radicals is slightly less than it is for primary radicals. In decalin, for example, we calculate from eq 20 that only 66% of the dimers arise by cage combination in contrast to 95% for primary radicals. The difference may be attributed either to slower rates of combination of secondary radicals[37] or more likely to the increased probability of combination outside the cage. Since the combination of radicals outside the cage must compete with hydrogen abstraction from the solvent, the more stable secondary alkyl radicals will suffer less diversion than the primary radicals.

In decalin solutions the alkyl dimer from primary radicals arises almost exclusively (95%) by geminate combination (*vide supra*). We employ the dimer

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[32] The definition of a cage which we use here is an operational one based on combination of alkyl radicals derived from the same parent (diacyl peroxide); (b) under these conditions we cannot distinguish a cage combination of radicals from a multicentered concerted decomposition of the peroxide to yield dimer and two carbon dioxides directly; (c) the nonradical path to formation of ethane from the photolysis of azomethane has also been discussed at length and discounted [J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1962, p 462 ff]; (d) the absence of scrambling in the photolysis of azoalkanes has also been shown (R. K. Lyons and D. H. Levy, *J. Amer. Chem. Soc.*, **83**, 4290 (1961)).

[33] There is no interchange of acyloxy groups in the peroxides under these conditions.

[34] (a) By definition the *cage dimer* is that percentage of all dimers which is formed by geminate combination. The *cage reaction* (%) is obtained from the yield of the cage dimer plus twice a fraction (k_d/k_c) due to disproportionation. The yield of cage dimer includes a factor of 2 and the cage reaction is based on each alkyl radical and has a theoretical limit of 100; (b) depending on the pair of peroxides studied.

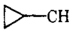
[35] From the data in Table III, approximately 30% of the alkyl radicals react with decalin to afford alkane and decalyl radicals. The material balance indicates that only a small portion of the alkyl radicals are unaccounted for by reaction with decalyl radicals.

[36] In the photolysis of *t*-butyl peresters the cage reaction increases from pentane (27%) to decalin (45%) to Nujol (75%) in the same manner.[28]

[37] See, however, rate constants for combination of secondary and tertiary radicals: S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, **91**, 986 (1969); **90**, 1659 (1968); D. J. Carlsson and K. U. Ingold, *ibid.*, **90**, 7047 (1968); (b) differences in solvation between primary and secondary radicals should be minor.

yields (together with a correction for disproportionation) to assess the cage processes for several alkyl radicals listed in Table VIII. The values given for the secondary radicals were corrected for the noncage dimerization. The efficiencies of the cage reactions determined in this manner show little variation with structure of the alkyl radical. We tentatively conclude, therefore, that the cage combination of radicals is not affected by the stability of the radical.[38]

Table VIII. Cage Reactions of Alkyl–Alkyl Radical Pairs in Decalin from the Photolysis of Diacyl Peroxides

Alkyl radical	Cage reaction,[a] %
$CH_3CH_2\cdot$	55
$CH_3CH_2CH_2\cdot$	57
$CH_3CH_2CH_2CH_2\cdot$	51
$CH_2{=}CHCH_2CH_2\cdot$	49[b]
	50[b]
$CH_3\dot{C}HCH_3$	54
$CH_3CH_2\dot{C}HCH_3\cdot$	57
	61
	33[c]

[a] Calculated from 200(dimer + alkene)/CO_2. [b] Does not include 1,3-butadiene, value low. [c] Does not include cyclopropene; value low; see text.

Our results clearly do not delineate the primary photochemical processes involved in the pair production of alkyl radicals from the photolysis of diacyl peroxides. For example, the spin multiplicity of the geminate alkyl radicals is unknown,[39] although we judge from their chemical behavior that the ensemble represents a normal distribution of spin pairing obtained by other methods.[40] Furthermore, the highly efficient cage combination of alkyl radicals separated by two molecules of carbon dioxide is rather unexpected. These and other questions merit further study.[41]

Experimental Section

Pentane (Nanograde, Mallinckrodt Chemical Co.) was used without further purification. **Decalin** (Eastman Organic Chemicals) was redistilled before use. **Bicyclopropyl** was prepared from butadiene, methylene iodide, and zinc–copper coupling using the LeGoff procedure[42] and had bp 76° (lit. 76°).[43] Other cyclopropyl compounds prepared by the LeGoff procedure were **1,2-dicyclopropylethane**, bp 133–134° (lit.[44] 128–129°); *n*-**pentylcyclopropane**, bp 125–126° (lit.[44] 128–129°). **Cyclopropyl cyclopropanecarboxylate** was prepared from dicyclopropyl ketone and trifluoroperacetic acid and had bp 66° (17 mm) (lit.[18] 62° (15 mm)). Other esters were prepared by reaction of the corresponding alcohols and acid chlorides. Authentic samples of **1,11-dodecadiene, 1,2-dicyclopentylethane,** and **7-cyclopentylheptene-1** were prepared previously[45] by electrolysis of 6-heptenoic acid. A small sample of **bicyclobutyl** for comparison of gas chromatographic retention time was prepared from cyclobutylmagnesium bromide and silver bromide in tetrahydrofuran; it was not isolated. Acid chlorides were obtained by treatment of the corresponding carboxylic acid with thionyl chloride and their purity could be determined by conversion to the methyl ester which was analyzed for isomers by gas chromatography. **2-Methylbutyric acid** was prepared by carbonation of *sec*-butylmagnesium bromide free of the isomeric impurities.

Diacyl peroxides were prepared by the following general procedure. A solution of pyridine (158 ml, 2 mol) in ether (50 ml) was cooled to −10° and 30% hydrogen peroxide (62.5 ml, 0.55 mol) was added at such a rate that the temperature did not exceed 10°. The mixture was rapidly stirred so that the two-phase system was finely dispersed. The acid chloride (1 mol) was then added dropwise, maintaining the temperature between −5 and −10°. The mixture was then stirred for 2 additional hr at 0° and carefully neutralized with a chilled 10% sulfuric acid solution. Ether (100 ml) was added and the peroxide extracted (throughout this and subsequent operations the temperature was not allowed to rise above 0°). The aqueous layer was extracted further with pentane. The ether and pentane extracts were combined, washed with chilled 10% sulfuric acid, 10% aqueous sodium carbonate, and finally with water. The solution was dried over anhydrous sodium sulfate and concentrated on a rotary evaporator, first at aspirator pressures, and then the final traces of solvent removed on a vacuum pump. The yield of peroxide was 90–95%. The purity of the product was estimated by isometric titration using the method of Silbert and Swern.[46] All the peroxides studied were >95% pure by titration except for pivaloyl which was not isolated because of its thermal instability.

Photolysis of Diacyl Peroxides. The photolyses were carried out in a Rayonet RPR-100 photochemical reactor (The Southern New England Ultraviolet Co.). Sixteen 2537-Å region lamps were employed. Aliquots (5 ml) of a 0.05 *M* solution of the diacyl peroxide were transferred from a standard flask to 15 × 1.5 cm quartz tubes. The solution, and the free space above the solution, were purged of oxygen by sweeping with a slow stream of helium for 5–10 min. After the tube was sealed tightly with a rubber septum, it was placed in the photochemical reactor which maintained an ambient temperature of 30 ± 1°. The tubes were rotated using a Rayonet MGR-100 merry-go-round. The progress of the reaction could be followed by carbon dioxide evolution and, in general, the reactions were complete in approximately 1 hr. It was shown, for the case of propionyl peroxide, that using four lamps and photolyzing for 4 hr, instead of 16 lamps for 1 hr, had no effect on the product distribution.

Analytical Procedures. When the reactions were complete a small aliquot of gas was removed and immediately analyzed qualitatively. The tubes were then cooled in liquid nitrogen and known amounts of marker (internal standard) were added. The tubes were allowed to warm to room temperature with vigorous agitation and analyzed by gas chromatography. Mixtures containing known amounts of products and markers were analyzed in the same way to obtain calibration factors. Pressure was then released from the tubes and the mixtures analyzed quantitatively for higher boiling products.

Gas chromatographic analyses of gaseous products were performed on instruments equipped with thermal conductivity detectors. Other analyses were performed on instruments with flame ionization detectors. The following are the conditions used in determining yields of products (product, marker, column, temperature): carbon dioxide, ethylene, 2-ft Porapak Q, room temperature; methane, ethylene, 2-ft Porapak Q, room temperature; ethylene, ethane, 2-ft Porapak Q, room temperature; propane, isobutane, 15-ft 30% Dowtherm on firebrick, room temperature;

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[38] Diffusion, however, is probably the most important factor to be considered, but in our study the limited variation in size of the alkyl fragments was insufficient to assess the importance of this factor. See, for example, J. Smid and M. Szwarc, [*J. Amer. Chem. Soc.*, **78**, 3322 (1956); 83, 3004 (1961)], who reported that only 6% of the methyl radicals dimerized under conditions in which 35–40% of the ethyl radicals combined or disproportionated from the thermolysis of diacyl peroxides. Other factors are also involved [M. Chakravorty, J. M. Pearson, and M. Szwarc, *ibid.*, **90**, 283 (1968)].

[39] We hope to apply the technique of chemically induced dynamic nuclear polarization developed by G. L. Closs [*ibid.*, **91**, 4552 (1969); G. L. Closs and A. D. Trifunac, *ibid.*, **91**, 4554 (1969)] to this problem; (b) G. S. Hammond and J. R. Fox [*ibid.*, **86**, 1918 (1964)] showed that the cage effects in the thermal and photochemical (3660 Å) decomposition of azobisisobutyrate were the same; (c) see also S. F. Nelson and P. D. Bartlett, *ibid.*, **88**, 143 (1966), and R. D. Burkhart and J. C. Merrill, *J. Phys. Chem.*, **73**, 2699 (1969).

[40] In the limited number of cases which have been examined in detail, the efficiency of the cage reaction of alkyl radicals generated by thermolysis compare favorably with those obtained photolytically in this study.[38] See also D. F. DeTar and C. Weis, *J. Amer. Chem. Soc.*, **79**, 3041 (1957); J. E. Guillet and J. C. Gilmer, *Can. J. Chem.*, **47**, 4405 (1969); K. R. Kopecky and T. Gillan, *ibid.*, **47**, 2371 (1969).

[41] Scavenger studies and the production of diradicals from the photolysis of cyclic acyl peroxides are in progress.

[42] E. LeGoff, *J. Org. Chem.*, **29**, 2048 (1964).

[43] C. Overberger and G. Halek, *ibid.*, **28**, 867 (1963).

[44] H. E. Simmons and R. Smith, *J. Amer. Chem. Soc.*, **81**, 4256 (1959).

[45] J. Kochi and T. Bethea, *J. Org. Chem.*, **33**, 75 (1968).

[46] L. Silbert and D. Swern, *Anal. Chem.*, 30, 385 (1958).

propylene, isobutane, 12-ft 30% Dowtherm on firebrick, room temperature; isobutane, *n*-butane, 15-ft 30% Dowtherm on firebrick, room temperature; isobutylene, *n*-butane, 15-ft 30% Dowtherm on firebrick, room temperature; cyclopropane, propane, 15-ft 30% Dowtherm on firebrick, room temperature; cyclobutane, *cis*-butene-2, 15-ft 30% Dowtherm on firebrick, room temperature; cyclobutene, *cis*-butene-2, 15-ft 30% Dowtherm on firebrick, room temperature; butene-1, *cis*-butene-2, 15-ft 30% Dowtherm on firebrick, room temperature; *cis*-butene-2, isobutane, 15-ft 30% Dowtherm on firebrick, room temperature; *trans*-butene-2, isobutane, 15-ft 30% Dowtherm on firebrick, room temperature; methylcyclopropane, *cis*-butene-2, 15-ft 30% Dowtherm on firebrick, room temperature; *n*-pentane, *n*-hexane, 12-ft SF 96, 90°; *n*-heptane, *n*-octane, 12-ft SF 96, 90°; 3-methylhexane, *n*-octane, 12-ft SF 96, 90°; 3-ethylpentane, *n*-octane, 12-ft SF 96, 90°; 1-hexene, cyclohexane, 12-ft SF 96, 85°; methylcyclopentane, cyclohexane, 12-ft SF 96, 85°; methylenecyclopentane, cyclohexane, 12-ft SF 96, 85°; 2,2,3,3-tetramethylbutane, *n*-octane, 12-ft SF 96, 90°; bicyclobutyl, *n*-octane, 12-ft SF 96, 130°; 1,6-hexadiene, cyclohexane, 12-ft SF 96, 85°; 3,4-dimethylhexane, *n*-octane, 12-ft SF 96, 90°; 2,3-dimethylbutane, *n*-heptane, 12-ft SF 96, 90°; bicyclopropyl, *n*-heptane, 12-ft SF 96, 90°; bicyclobutyl, *n*-octane, 12-ft SF 96, 130°; 1,2-dicyclopropylethane, *n*-octane, 12-ft SF 96, 130°; *n*-pentylcyclopropane, *n*-octane, 12-ft SF 96, 130°; 1,7-octadiene, *n*-octane, 12-ft SF 96, 130°; 1,2-dicyclopentylethane, dodecane, 3-ft SF 96, 125°; 1,11-dodecadiene, bicyclohexyl, 3-ft SF 96, 125°; 7-cyclopentylheptene-1, bicyclohexyl, 3-ft SF 96, 125°; ethyl propionate, *sec*-butyl acetate, 12-ft didecyl phthalate, 100°; isopropyl isobutyrate, isopropyl *n*-butyrate, 12-ft didecyl phthalate, 100°; cyclopropyl cyclopropanecarboxylate, *n*-propyl *n*-butyrate, 4-ft Chromosorb 101, 200°; cyclopropylcarbinyl cyclopropylacetate, cyclobutyl cyclobutanecarboxylate, 12-ft SF 96, 155°; cyclopropanecarboxylic acid, 4-ft Chromosorb 101, 200°. Many of the products were analyzed by gas chromatography on more than one type of column.

Analysis of Cyclopropylacetyl Peroxide Reaction Mixture. Gas chromatographic analysis of the mixture showed the presence of 1,7-octadiene, 1,2-dicyclopropylethane, and a peak tentatively identified as 5-cyclopropylpentene-1. An aliquot was diluted with an equal volume of methanol, 5% palladium on charcoal as catalyst was added, and the mixture was hydrogenated. The peak tentatively assigned to 5-cyclopropylpentene-1 disappeared and this coincided with the appearance of *n*-pentylcyclopropane (*n*-octane was also formed by reduction of 1,7-octadiene).

Quantum Yield Measurement. Aliquots (3 ml) of a 0.1 *M* solution of diacyl peroxide were transferred from a standard flask to 10 × 1 cm quartz tubes. The solutions were degassed with a slow stream of helium and the tubes tightly sealed with rubber septa. The solutions were photolyzed in a merry-go-round apparatus (F. G. Moses Co., Wilmington, Del.) which maintained an ambient temperature of 28° in the reaction cell. Aliquots (3 ml) of degassed 0.5 *M* aqueous chloracetic acid solutions were photolyzed at the same time as the diacyl peroxide solutions. The reaction was allowed to proceed to about 5% conversion, approximately 20 min. The yield of carbon dioxide, from the diacyl peroxide, was determined by gas chromatography. The yield of chloride ion from the chloracetic acid solutions was determined using a specific chloride ion electrode. A value of 0.34 was used for the quantum yield of chloride ion from the chloracetic acid actinometer at 28°.[47] There was negligible dark reaction for the diacyl peroxides studied under these conditions. A low-pressure mercury lamp was used as the light source and the quartz tubes were covered with aluminum foil except for the windows being irradiated. Solutions >2 *M* in diacyl peroxide were thermally unstable at room temperature.

Quantum Yields. The quantum yields for carbon dioxide were measured for some representative diacyl peroxides listed in Table IX. The values of Φ_{CO_2} at 2537 Å were close to 2 and varied little with the structure of the alkyl group. The latter could also be established by photolyzing mixtures of several diacyl peroxides. The quantum yield for carbon dioxide formation increased slightly with concentration due probably to induced decomposition, but the problem was not severe at moderate concentrations. No significant difference in Φ_{CO_2} was found in changing the viscosity of the solvent from *n*-pentane to decalin to mineral oil (Nujol).

Table IX. Quantum Yields for Carbon Dioxide Formation from Diacyl Peroxides at 2537 Å and 28°

Diacyl peroxide	Concn, *M*	Solvent	Φ_{CO_2}
Propionyl	0.10	Pentane	2.0
Propionyl	0.10	Decalin	2.1
Propionyl	0.10	Nujol	2.0
n-Butyryl	0.10	Decalin	2.1
n-Butyryl	0.30	Decalin	2.1
n-Butyryl	1.0	Decalin	2.2
n-Butyryl	3.0[a]	Decalin	2.9
n-Valeryl	0.10	Decalin	2.0
Isobutyryl	0.10	Decalin	2.1
Cyclopropanecarbonyl	0.10	Decalin	2.0
2-Methylbutyryl	0.10	Decalin	2.1

[a] A 3 *M* solution of butyryl peroxide in decalin was thermally rather unstable.

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(47) (a) R. Smith, P. Leighton, and W. Leighton, *J. Amer. Chem. Soc.*, **61**, 2299 (1939); (b) L. Thomas, *ibid.*, **62**, 1879 (1940).