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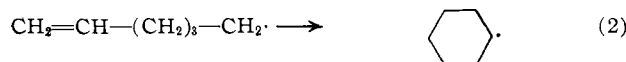
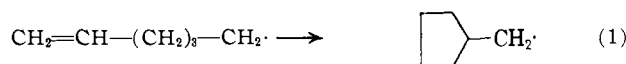
Organic Peroxides. II. The Mechanism of the Thermal Decomposition of 6-Heptenoyl Peroxide in Toluene. The Rearrangements of the 5-Hexenyl Radical¹BY ROBERT C. LAMB,² PAUL WAYNE AYERS, AND MYRON K. TONEY³

RECEIVED APRIL 17, 1963

Kinetics and products of the thermal decomposition of 6-heptenoyl peroxide in toluene indicate that its initial cleavage is typical of saturated diacyl peroxides, *i.e.*, there is no neighboring group effect of the double bond, and little if any radical-induced decomposition. 1-Hexene, 1,5-hexadiene, 5-hexenyl 6-heptenoate, 1,11-dodecadiene, and 6-heptenoic acid are formed in the decomposition in pure toluene, and the same products are formed in similar amounts in toluene solutions containing excess galvinoxyl. Since the stable radical has no effect on the decomposition rate, these products are formed in cage reactions of radicals. 6-Heptenoyl peroxide is a good source of 5-hexenyl radicals in toluene, which eventually lead to the formation of methylcyclopentane and cyclohexane in the products. Two possible mechanisms of formation of these products are discussed, one of which involves classical radical additions to the double bond; the other involves the formation of an intramolecular complex between the radical site and the double bond in the 5-hexenyl radical.

Introduction

The reactions of the 5-hexenyl radical have been studied in the gas phase, first by Arai, Sato, and Shida in the mercury-sensitized photolysis of cyclohexane,⁴ and, more recently, by Gordon and Smith in the photolysis of cyclohexane-acetone-*d*₆ mixtures between 154–440°.⁵ Among the several reactions of the 5-hexenyl radical which were reported by these authors, two of particular importance to this work are the rearrangements of the 5-hexenyl radical to the cyclopentyl methyl radical (1), and to the cyclohexyl radical (2).



The purpose of the present work was to generate the 5-hexenyl radical in solution by decomposing 6-heptenoyl peroxide. The use of a diacyl peroxide invites the usual complicating cage reactions and the possibility of radical induced decomposition. In addition, if double bonds are present in the peroxide molecule, the possibility arises for an intramolecular reaction between the double bond and the peroxide linkage.⁶ Other, more subtle reactions are conceivable, and as we shall show, one of these probably occurs in the decomposition of 6-heptenoyl peroxide in carbon tetrachloride.

Results and Discussion

The results of the necessary adjunct kinetics experiments are listed in Table I. Although these experiments are not highly accurate, all of the decompositions are first order within experimental error. The logarithms of the rate constants for the decompositions of 6-heptenoyl peroxide in toluene do not give a linear 1/*T* plot; hence a good estimate of the activation energy cannot be obtained from the data. The important points which are established by the kinetics experi-

ments are: (a) Comparison of the rates of decomposition of heptanoyl and 6-heptenoyl peroxides in toluene at 77° shows that there is *no group participation by the double bond in the decomposition of 6-heptenoyl peroxide.* (b) Neither galvinoxyl nor hydrogalvinoxyl have an appreciable effect upon the rate of decomposition of 6-heptenoyl peroxide under the conditions used. This means that neither of these scavengers reacts directly with the peroxide, and also that there is little if any radical-induced decomposition of 6-heptenoyl peroxide in toluene alone.

TABLE I
KINETICS OF DECOMPOSITION OF 6-HEPTENOYL PEROXIDE^a

<i>P</i> ₀ ^b	Medium	No. of samples	<i>T</i> , °C.	<i>t</i> _{1/2} (IR), ^c min.	<i>t</i> _{1/2} (iodometric), min.
0.03	Toluene	8	70	216.4	
.03	Toluene	9	70		230.5
.01	Toluene	9	77		107.9
.03	Toluene-0.06 <i>M</i> galvinoxyl	6	77	103.6	
.04	Toluene	7	85	40.1	
.03	Toluene-0.04 <i>M</i> hydrogalvinoxyl	4	85	39.9	

KINETICS OF DECOMPOSITION OF HEPTANOYL PEROXIDE

0.03	Toluene	7	77	92.8	
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^a All runs obey the first-order law through at least 2 half-lives.^b Approximate initial molar peroxide concentration. ^c Infrared band at 1777 cm.⁻¹ used to follow peroxide disappearance.

Table II gives several products which have been identified in the thermal decompositions of 6-heptenoyl peroxide in various media, and also the C-6 hydrocarbon products which are formed in decompositions of cyclopentylacetyl and cyclohexaneformyl peroxides.⁷

The products listed in the first entry of Table II represent about 86% of the R-groups originally present in the peroxide. At least two other products are detectable by v.p.c. which have not been fully identified. One of these products has a retention time near that of 1,11-dodecadiene, and is believed to be another C-12 hydrocarbon. The other product is not formed in the presence of either galvinoxyl or hydrogalvinoxyl, nor is it formed when the peroxide is decomposed in isooctane. Therefore, it is probably a ring or side chain substitution product of a C-6 radical on toluene. The two unidentified

(1) This work was supported by the National Science Foundation. The paper is taken for the most part from the thesis of Paul Wayne Ayers, presented in partial fulfillment of the requirements for the Master of Science degree, August, 1962. The paper was read in part at the Southeastern Regional Meeting of the American Chemical Society, Gatlinburg, Tenn., Nov. 1, 1962.

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(3) NDEA Fellow, University of Georgia, 1961–present.

(4) S. Arai, S. Sato, and S. Shida, *J. Chem. Phys.*, **33**, 1277 (1960).(5) A. S. Gordon and S. R. Smith, *J. Phys. Chem.*, **66**, 521 (1962).

(6) (a) R. C. Lamb, F. F. Rogers, Jr., G. C. Dean, Jr., and F. W. Voigt, Jr., *J. Am. Chem. Soc.*, **84**, 2635 (1962), which is paper I in this series. Apologetically, we report that there are mistakes in the names of two authors of this paper (Messrs. Dean and Voigt), which are corrected here; (b) J. C. Martin and E. H. Drew, *ibid.*, **83**, 1232 (1961); (c) F. D. Greene, W. Adam, and J. E. Cantrell, *ibid.*, **83**, 3461 (1961); (d) M. M. Martin and D. C. De Jongh, *ibid.*, **84**, 3526 (1962).

(7) The 6-heptenoic acid from which the peroxide was made was prepared by the carbonation of the Grignard reagent obtained by treatment of 1,2,6-tribromohexane with magnesium (ref. 18). This synthesis was shown belatedly to give 6-heptenoic acid which is contaminated with a 3–5% impurity of cyclopentylacetic acid. The data reported in entries 1, 3, 5, 7, and 8 in Table II were determined in experiments in which the peroxide used had been synthesized from impure 6-heptenoic acid. The peroxide samples which gave the data in entries 2, 4, and 6 were prepared from a 6-heptenoic acid sample from which the cyclopentylacetic acid had been carefully removed (see Experimental section).

TABLE II^a
 PRODUCTS OF SOME PEROXIDE DECOMPOSITIONS AT 77°

Entry	Peroxide	Medium	1-Hexene and 1,5-hexadiene	Methyl-cyclopentane	Cyclohexane	Cyclohexene	1,11-Dodecadiene	6-Heptenoic acid	5-Hexenyl 6-heptenoate	Bibenzyl
1	6-Heptenoyl 0.099 M	Toluene	0.120 ^b (0.04)(0.08)	0.940	0.026	0.008	0.196	0.046	0.098	0.252
2	6-Heptenoyl, 0.093 M	Toluene	0.155	.900	.030	.006	.202	n.d.	.100	0.260
3	6-Heptenoyl, 0.101 M	Toluene-0.36 M galv.	.122	.005	.003	.001	.188	n.d.	.090	0
4	6-Heptenoyl, 0.102 M	Toluene-0.16 M galv.	.130	.005	tr.	tr.	n.d.	n.d.	n.d.	0
5	6-Heptenoyl, 0.088 M	Toluene-0.10 M hydrogalv.	.225	.008	.005	tr.	0.200	n.d.	0.094	0
6	6-Heptenoyl, 0.094 M	Toluene-0.16 M hydrogalv.	.220	.006	tr.	tr.	n.d.	n.d.	n.d.	0
7	6-Heptenoyl, 0.11 M	Toluene-50% cumene	.160	.800	0.030	tr.	n.d.	n.d.	n.d.	...
8	6-Heptenoyl, 0.094 M	Isooctane	.129	.860	n.d.	n.d.	0.193	n.d.	0.092	...
9	Cyclohexane-formyl, 0.01 M	Toluene	0	0	0.440	0.300	n.d.
10	Cyclopentyl-acetyl, 0.093 M	Toluene	tr.	0.950	.042	.042	n.d.
11	Cyclopentyl-acetyl, 0.093 M	Toluene-0.14 M galv.	tr.	.020	.042	.042	0
12	Cyclopentyl-acetyl, 0.093 M	Toluene-0.17 M hydrogalv.	tr.	.330	.042	.042	0

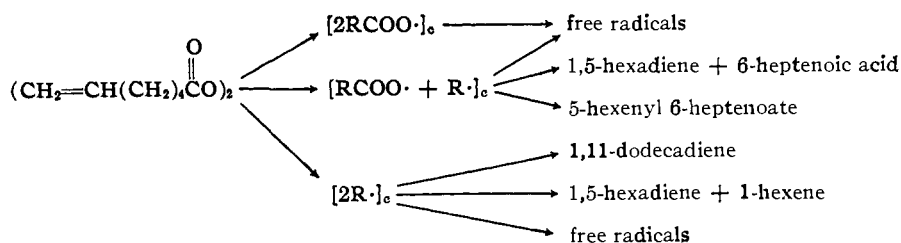
^a Yields are reported in moles of product per mole of peroxide. Abbreviations used: galv. = galvinoxyl; hydrogalv. = hydrogalvinoxyl; tr. = trace; n.d. = not determined, although known to be present (also see ref. 7). ^b 1-Hexene and 1,5-hexadiene could not be separated completely by v.p.c. under the conditions used; therefore the sum of the two yields is given. In the first entry, the approximate yields of 1-hexene and 1,5-hexadiene are entered under the total yield.

products could not account for more than 5% of the R-groups originally present in the peroxide. Also, small traces of substances which have retention times identical with those of 1,4-cyclohexadiene and benzene are formed in the decomposition of 6-heptenoyl peroxide in toluene.

The volatile products which are formed in the presence of the efficient scavenger, galvinoxyl,⁸ are those which, on the basis of the known chemistries of similar peroxides,⁹ one would have predicted to be the cage reaction products in the decomposition of 6-heptenoyl peroxide

tion reactions involving the cyclohexyl radical and other radicals in the solution. It should be noticed that traces of methylcyclopentane, cyclohexane, and cyclohexene are formed even in the presence of galvinoxyl, which could indicate that the galvinoxyl fails to capture all of the free radicals which escape cage reactions.

That methylcyclopentane and cyclohexane are formed in radical reactions which occur after the rate-determining peroxide homolysis is shown by the fact that the labile hydrogen atom source, hydrogalvinoxyl, drastically lowers the yields of methylcyclopentane and cyclo-

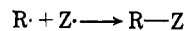
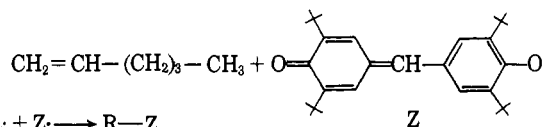
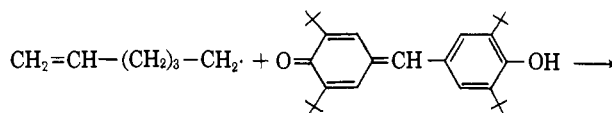


Brackets with subscript c indicate solvent cages; R = 5-hexenyl

The above scheme suggests that, in the decomposition of 6-heptenoyl peroxide in toluene, the sum of the yields of 6-heptenoic acid and 1-hexene should equal the yield of 1,5-hexadiene, so long as these products are formed in cage reactions only. This condition is essentially satisfied by the data, since the yields of these products are approximately the same in pure toluene and in toluene-galvinoxyl. The sum of the yields of 6-heptenoic acid and 1-hexene also approximates the yield of 1,5-hexadiene, as the mechanism requires. This means that essentially all the 1-hexene is formed in cage reactions.

The classical mechanism for the formation of the cyclic C-6 hydrocarbons in the decomposition of 6-heptenoyl peroxide would be in terms of reactions 1 and 2, and subsequent reactions of the cyclic radicals. Thus according to this mechanism methylcyclopentane and cyclohexane would be formed mainly by the abstraction of hydrogen from the methyl group in toluene by the cyclopentylmethyl and cyclohexyl radicals, respectively, and cyclohexene is formed in disproportiona-

tion reactions involving the cyclohexyl radical and other radicals in the solution. It should be noticed that traces of methylcyclopentane, cyclohexane, and cyclohexene are formed even in the presence of galvinoxyl, which could indicate that the galvinoxyl fails to capture all of the free radicals which escape cage reactions.



R· is any reactive radical in solution, and Z· is galvinoxyl

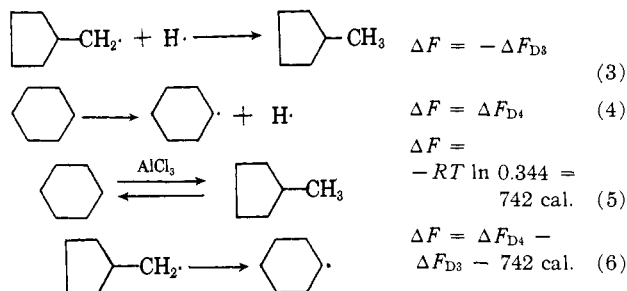
The reversibilities of the radical cyclization processes were tested by decomposing cyclopentylacetyl and cyclohexaneformyl peroxides in toluene at 77°, and analyzing the C-6 hydrocarbon products. The decomposition of cyclohexaneformyl peroxide gives only hydrocarbons with six-membered rings, therefore reaction 2 is not significantly reversible under the conditions used.

(8) (a) P. D. Bartlett and T. Funahashi, *J. Am. Chem. Soc.*, **84**, 2596 (1962); (b) G. M. Coppinger, *ibid.*, **79**, 501 (1957); (c) M. S. Kharasch and B. S. Joshi, *J. Org. Chem.*, **22**, 1435 (1957).

(9) (a) D. F. DeTar and C. Weis, *J. Am. Chem. Soc.*, **78**, 4296 (1956); **79**, 3041 (1957); (b) D. F. DeTar and R. C. Lamb, *ibid.*, **81**, 122 (1959); (c) D. F. DeTar and D. V. Wells, *ibid.*, **82**, 5839 (1960).

Cyclopentylacetyl peroxide, on the other hand, gives both 1-hexene and the two six-membered ring products. On the surface, this fact would appear to indicate that reaction 1 is reversible.¹⁰ However, when the same peroxide is decomposed in toluene containing galvinoxyl, the aforementioned products are formed in similar yields, although the yield of methylcyclopentane is reduced by a factor of 50 in the presence of galvinoxyl. It was shown by v.p.c. that the traces of materials which have retention times identical with those of 1-hexene, cyclohexene, and cyclohexane were not present as impurities in the toluene. Furthermore, a substantial quantity of toluene was added to the peroxide samples used in experiments 10, 11, and 12, and the toluene was removed by vacuum distillation below room temperature just before the peroxide was used in these experiments. It is most unlikely, therefore, that the traces of 1-hexene, cyclohexane, and cyclohexene were present as impurities in the peroxide samples. It can only be concluded that traces of these hydrocarbons are formed in decomposition of cyclopentylacetyl peroxide in toluene by a nonradical path. The data indicate that reaction 1, like reaction 2, is not significantly reversible in toluene at 77°.

It is difficult to justify the large yield of methylcyclopentane in the decomposition of 6-heptenyl peroxide in toluene in terms of reactions 1 and 2. For example, it is known that cyclohexane is slightly more stable than methylcyclopentane at 77°, since the equilibrium constant (using AlCl₃ catalyst) is 0.344,¹¹ and all that is required to make ΔF_6 (reaction 6, below) negative is the likely condition that ΔF_{D_4} be less positive than ΔF_{D_3}



In addition, Hart and Wyman have shown that cyclohexanecarboxyl peroxide decomposes 34 times as rapidly in carbon tetrachloride at 70° as cyclopentylacetyl peroxide, again an indication that the cyclohexyl radical is more stable than the cyclopentylmethyl radical.¹² Obviously, if reactions 1 and 2 do constitute steps in the mechanism of formation of the cyclic hydrocarbons, the rates of these reactions do not follow a linear free energy relationship.

The preference of the 5-hexenyl radical to cyclize to give cyclopentylmethyl rather than cyclohexyl would not have been anticipated from the gas-phase work of Gordon and Smith.⁵ In the pyrolyses of cyclohexane-acetone-*d*₆ mixtures, methylcyclopentane (*d*₀ and *d*₁) appears first at 298°, although reaction 2 is presumably reversible (hence 5-hexenyl radicals are present in the system) at temperatures considerably below this. Gordon and Smith assigned values of 12 ± 2 and 8 kcal., respectively, for *E*_a (1) and *E*_a (2).

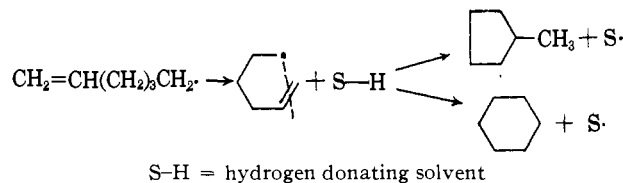
The difference in the behavior of the 5-hexenyl radical in the gas phase and in toluene does not appear to be explicable in terms of complex formation between

(10) These data led us to report at the Gatlinburg meeting (ref. 1) that reaction 1 not only is reversible but completely equilibrates in toluene at 77°, a statement which we must now retract.

(11) A. L. Glasebrook and W. G. Lovell, *J. Am. Chem. Soc.*, **61**, 1717 (1939).

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

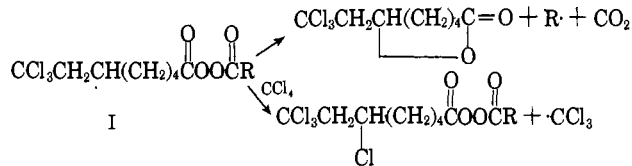
the 5-hexenyl radical and toluene. The product distribution in the decomposition of 6-heptenyl peroxide in toluene differs little from the product distribution in the decomposition in isooctane, with which radical complex formation is not to be expected (compare entries 1, 2, and 8 in Table II). It is possible that in solution at low temperatures, intramolecular complex formation occurs between the free radical site and the double bond in the 5-hexenyl radical, and that the formation of this complex is not kinetically important at higher temperatures in the gas phase



The formation of the intraradical complex would have to be assigned a low activation energy, perhaps less than 5 kcal. Also, inasmuch as the two hydrocarbon products differ little in thermodynamic stability, the steric requirements in the transition states of the two reactions in which hydrogen is transferred from the solvent to carbon 6 and carbon 5 in the self-complexed 5-hexenyl radical would determine the yields of methylcyclopentane and cyclohexane.

This mechanism, which requires discarding reactions 1 and 2 altogether in favor of a common precursor for cyclohexane and methylcyclopentane, should be considered tentative pending further work. It is similar in some respects to the mechanism which has been used by Walling and Padwa to explain the olefin inhibition of the chlorination of cyclohexane by *tert*-alkyl hypochlorites.¹³ These authors have shown that alkoxy radicals of formula R-C(CH₃)₂-O· form complexes with olefins which subsequently decompose into R·, acetone, and olefin, the decomposition (and the inhibition of cyclohexane chlorination) being most effective when R- is benzyl.

Preliminary work on the decomposition of 6-heptenyl peroxide in carbon tetrachloride indicates that the reaction is not simple in this solvent. The kinetics of the decomposition of the peroxide at 70° were determined iodometrically on a 0.03 *M* solution. During the first half-life (205 min.), the reaction appears to be greater than first order. The second half-life is much longer (430 min.), and the reaction is first order during the second half-life. The infrared spectrum of a sample which had been heated for 300 min. showed that little or no unsaturation was left in the peroxide or products, as evidenced by the disappearance of the 6.1- μ peak. This indicates that the identity of the peroxide is altered in the early part of the reaction, very probably by addition of the elements of carbon tetrachloride to the double bonds. The adduct radical formed when the trichloromethyl radical adds to the terminal double bond in 6-heptenyl peroxide probably has the choice of displacing at the peroxide linkage within the molecule (which amounts to radical induced decomposition—hence higher order kinetics in the early part of the reaction), or reacting with carbon tetrachloride (altering the identity of the peroxide)



(13) C. Walling and A. Padwa, *ibid.*, **84**, 2845 (1962); **85**, 1593 (1963).

(In structure I, R- may be 5-hexenyl or 5,7,7,7-tetrachloroheptyl, depending upon whether the elements of carbon tetrachloride were previously added to the other double bond in the molecule).

It should be noted that intramolecular reactions between radical site and the peroxide linkage have been observed in decompositions of dialkyl peroxides.¹⁴

According to this scheme, the kinetics observed during the second "half-life" (determined iodometrically) are due entirely to bis-(6,8,8,8-tetrachlorooctanoyl) peroxide. While the mechanism is rather speculative, the evidence suggests rather strongly that 6-heptenoyl peroxide is a poor source of 5-hexenyl radicals in carbon tetrachloride.¹⁵

Experimental¹⁶

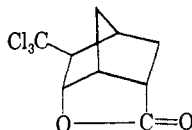
Many of the chemicals used in the work are commercially available.¹⁷ Solvents used were reagent grade and were distilled through a 4-ft. vacuum-jacketed column which was packed with glass helices.

6-Heptenoic Acid.—The synthesis of this acid in three steps from 1,2,6-hexanetriol has been described.¹⁸ However, it was found belatedly that this synthesis gives 6-heptenoic acid which is contaminated with a 3–5% impurity of a substance with a v.p.c. retention time identical with that of cyclopentylacetic acid (using a 6 ft. × 0.25 in. column packed with 30% Silicone 550-Dimer Acid mixture on Neutraport-S).⁷ Since v.p.c. showed that simple vacuum distillation effects no purification of the mixture, purification was effected by transforming the 6-heptenoic acid into 6,7-dibromoheptanoic acid, recrystallization of the latter, and regenerating the 6-heptenoic acid with zinc dust. In particular, bromine was added to 6-heptenoic acid (50 g., 0.39 mole) in 200 ml. of anhydrous ether until the color of bromine persisted.¹⁹ The ether was removed, and the residue was dissolved in about 3 l. of low boiling petroleum ether. A small amount of insoluble oily residue was discarded. The dibromoacid was recrystallized from the petroleum ether at –10°, filtered, and the recrystallization repeated. The yield of dibromoacid, m.p. 23–25°, was 100 g. (0.33 mole).

The dibromoacid was dissolved in 200 ml. of anhydrous ether, and added by dropping funnel into a flask containing 100 ml. of anhydrous ether and zinc dust (26 g., 0.4 mole). The reaction was started by warming the flask with warm water. After the addition of dibromoacid was complete, the reaction mixture was refluxed for 2 hr. The ether solution was decanted from the excess zinc and washed with cold, dilute hydrochloric acid. The acid was then extracted into cold, dilute sodium hydroxide solution, the latter was reacidified, and the crude 6-heptenoic acid was extracted again into ether. The ether was removed, and the 6-heptenoic acid was distilled (b.p. 70–72° at 0.5 mm.). The yield was 32 g. (0.25 mole), or 64% of theory, based on the original impure 6-heptenoic acid; neut. equiv. 128.4, 128.5 (calcd. 128.2); n_D^{20} 1.4391 (reported²⁰ n_D^{14} 1.4404). Complete removal of the original impurity was indicated by v.p.c.

(14) H. E. De La Mare and F. F. Rust, *J. Am. Chem. Soc.*, **81**, 2691 (1959), and literature cited therein.

(15) After this manuscript was submitted, an article appeared by Hart and Chloupek which has an important bearing upon this mechanism. It was found that in the decomposition of the diacyl peroxide of *endo*-norbornene-5-carboxylic acid in carbon tetrachloride at 78°, the following lactone is formed in 40% yield



The authors proposed that this lactone is formed by the induced decomposition of the diacyl peroxide by the trichloromethyl radical. This is completely analogous to the mechanism suggested above for the induced decomposition of 6-heptenoyl peroxide in carbon tetrachloride. Cf. H. Hart and F. J. Chloupek, *J. Am. Chem. Soc.*, **85**, 1155 (1963).

(16) Infrared spectra were recorded with Perkin-Elmer Models 421 and 137 spectrophotometers. A Beckman GC-2 gas chromatograph (equipped with fraction collector) was used for the v.p.c. work. The recorder used was a modified Sargent MR recorder (equipped with disk integrator) which has a 1-sec. pen response.

(17) Cyclopentylacetic acid and 5-hexen-1-ol were obtained from K and K Laboratories, Jamaica, N. Y. 6-Bromo-1-hexene and 1,6-dibromohexane were obtained from Columbia Organic Chemicals Co., Columbia, S. C.

(18) R. C. Lamb and P. W. Ayers, *J. Org. Chem.*, **27**, 1441 (1962); correction, *ibid.*, **27**, 4718 (1962).

(19) N. A. Khan, *Org. Syn.*, **32**, 104 (1952).

(20) P. A. Gaubert, R. P. Linstead, and H. H. Rydon, *J. Chem. Soc.*, 1971 (1937).

6-Heptenoyl Chloride.—Excess phosphorus pentachloride was added to 6-heptenoic acid (45 g., 0.35 mole). The phosphorus oxychloride was removed with a rotating evaporator, and the 6-heptenoyl chloride distilled, b.p. 30–35° near 1 mm. The yield was 30 g. (51%).

The diacyl peroxides used were prepared by the standard method of adding ether solutions of the acid chlorides to ice-water slurries containing excess sodium peroxide. Each of the peroxides was found to be better than 95% pure by iodometric titration.

5-Hexenyl 6-Heptenoate.—6-Heptenoyl chloride (9 g., 0.05 mole) was added to a mixture of 5-hexen-1-ol (5 g., 0.05 mole) and 15 ml. of pyridine. The mixture was refluxed for about 5 min., cooled, and extracted with water to remove the pyridine and its salt. The organic layer was separated, and after drying with sodium sulfate, it was purified by v.p.c. using column E, described below. *Anal.*²¹ Calcd. for C₁₂H₂₂O₂: C, 74.24; H, 10.55. Found: C, 74.19; H, 10.71.

1,11-Dodecadiene was prepared by coupling the Grignard reagent of 1,6-dibromohexane with allyl bromide, by the method described by Petrov and Chel'tsova.²²

Galvinoxyl and hydrogalvinoxyl were synthesized by methods which have been described by Coppinger.^{5b}

Product Analyses.—All products were analyzed by v.p.c. except for 6-heptenoic acid. The acid was extracted with sodium bicarbonate solution from the mixture obtained when 6-heptenoyl peroxide was decomposed in pure toluene, and, after isolation, the acid was titrated with standard sodium hydroxide solution for quantitative estimation. The infrared spectrum of an acid sample so obtained was identical with that of the 6-heptenoic acid sample from which the peroxide had been prepared.

The following v.p.c. columns were used in this work: A, 12 ft. × 0.25 in. column packed with Flexol 8N8 Plasticizer on C-22 firebrick (Beckman No. 70132); B, 12 ft. × 0.25 in. column packed with 30% Silicone 550 on C-22 firebrick; C, 6 ft. × 0.25 in. column, packed as in B; D, 6 ft. × 0.25 in. column, packed with 40% Apiezon M on Neutraport-S; E, 80 in. × 5/8 in. preparative column, packed as in D. The fraction collector was used in conjunction with this column.

The procedure for the product analysis for the decomposition of 6-heptenoyl peroxide in pure toluene will be described. 1,11-Dodecadiene, 5-hexenyl 6-heptenoate, and bibenzyl were isolated from a residue which was obtained from the decomposition of the peroxide in pure toluene, after the acid had been removed with base and the toluene and lower boiling materials had been removed by distillation. Column E was used for the isolation of these products, whose infrared spectra were identical with those of authentic samples. Also, methylcyclopentane was isolated by v.p.c. using a preparative column similar to E whose length was 10 ft. The latter was accomplished by first separating the entire C-6 fraction from a decomposition mixture, then the methylcyclopentane was isolated from the remainder of the C-6 fraction.

The other products were identified qualitatively by comparison of retention times with those of authentic samples (both in excess toluene) on two or more of the above columns. Columns A and B were used for the C-6 hydrocarbons.

Several columns were used attempting to separate 1-hexene from 1,5-hexadiene in excess toluene. Columns packed with diethylene glycol succinate, Carbowax 1000, β,β'-oxydipropionitrile, and the columns described above were tried. None of these gave satisfactory separation, but partial separation was obtained with the DEGS column.

Quantitative estimation of products was accomplished by comparison of peak areas with those of authentic samples, both determined in dilute solution in toluene. Column A was used for the C-6 hydrocarbons; column D was used for the other products.

The products of decomposition of 6-heptenoyl peroxide, in media other than pure toluene, and the products of the decompositions of cyclopentylacetic and cyclohexanecarbonyl peroxides were analyzed similarly by v.p.c. No products were actually isolated from these decompositions.

The data in each entry of Table II are average values obtained from two or more decompositions, except for the data obtained with 6-heptenoyl peroxide which was made from the acid sample from which the impurity had been removed.⁷ Several v.p.c. determinations were carried out on each decomposition and the yields averaged.

Acknowledgment.—We are indebted to the National Science Foundation for Grants NSF-G11277 and NSF-G24910 under which this work was conducted. In addition, we wish to express appreciation to Mr. Wm. Walter for synthesis of the galvinoxyl and hydrogalvinoxyl samples, and to Mr. Jas. G. Pacifici for the synthesis of the sample of cyclohexanecarbonyl peroxide.

(21) Performed by Galbraith Laboratories, Knoxville, Tenn.

(22) D. Petrov and M. A. Chel'tsova, *Bull. acad. sci. URSS, Classe sci. Chim.*, 267 (1940).