[CONTRIBUTION FROM THE KEDZIE CHEMICAL LABORATORY, MICHIGAN STATE UNIVERSITY]

The Effect of Ring Size on Diacyl Peroxide Decompositions[1,2]

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Cycloalkaneformyl (I_{3-7}) and cycloalkaneacetyl (II_{3-6}) peroxides were prepared and their products and rates of decomposition in carbon tetrachloride studied. A large variation in rate (10^2) was observed for type I peroxides, I_3 being remarkably slow. This is attributed to the difficulty with which a free-radical on a three-membered ring is produced. But the cyclopropyl radical, once formed, reacted with the solvent (giving cyclopropyl chloride) rather than isomerize to the more stable allyl radical. In anhydrous carbon tetrachloride containing iodine, I_3 gave mainly cyclopropyl iodide, but with water present, a 41% yield of cyclopropanecarboxylic acid was obtained (capture of acyloxy radicals by iodine). The ester from I_3 showed no alkyl rearrangement (cyclopropyl cyclopropanecarboxylate). Peroxides $II_{(4-6)}$ decomposed at about equal rates, and appreciably slower than corresponding peroxides $I_{(5-7)}$; the difference is attributed to the formation of primary rather than secondary alkyl radicals. All the rate data may be rationalized in terms of considerable C–C as well as O–O bond stretching in the transition state for radical peroxide decomposition. Peroxide II_3 was erratic in rate behavior, in most instances being remarkably fast. No product corresponding to abstraction of chlorine atoms from the solvent was detected, the major (85%) product being cyclopropylcarbinyl cyclopropanecarboxylate. Possible explanations are discussed.

Carbonium ions with a positive charge either directly on a cyclopropane ring, or on a carbon atom adjacent to one, exhibit distinctive chemical behavior.[3] For example, ions with the positive charge directly on the three-membered ring are reluctant to form when compared with equivalently substituted carbonium ions (slow acetolysis of cyclopropyl *vs.* isopropyl *p*-toluenesulfonate[4]) and give rearranged products (allyl acetate[4]). In contrast, reactions which involve cyclopropylcarbinyl ions proceed unusually rapidly[5–8]; they often, but not always,[6,8,9] give rearranged products. It was the initial purpose of this work to study similarly constituted (*i.e.*, cyclopropyl and cyclopropylcarbinyl) free radicals, to determine whether they are in any way remarkable.

Several reactions already described in the literature may involve these radicals as intermediates, and give some indication of the behavior to be anticipated. Photochemical chlorination[10] and vapor phase nitration[11] of cyclopropane gave good yields of chloro- and nitrocyclopropane, respectively. In these reactions, the intermediate cyclopropyl radical maintained its structural identity, and did not rearrange to the (presumably more stable) allyl radical. Brominative decarboxylation of silver cyclopropanecarboxylate to bromocyclopropane[12] may be another example.

But there are also several cases in which cyclopropyl radicals apparently rearrange to allyl radicals. Kolbe electrolysis[13] of potassium cyclopropanecarboxylate[14] is claimed to give allyl cyclopropanecarboxylate. Photolysis of methyl cyclopropyl ketone[15] gave, among products ascribable to initial alkyl–carbonyl cleavage, only structures related to allyl rather than cyclopropyl radicals.[16,17]

Trotman-Dickenson and Steacie showed that methyl radicals, generated from acetone photolysis, found it about equally difficult to remove a hydrogen atom from cyclopropane or benzene.[18] These results were confirmed by McNesby and Gordon[19] who found approximately 4 kcal./mole difference in activation energy for removing hydrogen atoms from cyclopropane and cyclopentane. Products from the former were structurally related to allyl, not cyclopropyl radicals.

There are fewer data on the cyclopropylcarbinyl radical. It presumably was an intermediate in the photochemical chlorination of methylcyclopropane where, at −20° in the liquid phase, cyclopropylcarbinyl chloride was obtained.[20] The vapor phase reaction (<100°) gave[5] in addition, considerable amounts of 4-chloro-1-butene[21] suggesting that rearrangements analogous to those observed with the corresponding carbonium ions may occur.[22] Stabilization of cyclopropylcarbinyl radicals by resonance was suggested by Overberger and Lebovits[23] when they observed that the azo-bis-nitrile from methyl cyclopropyl ketone decomposed in toluene

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[1] Taken in part from the Ph.D. thesis of Donald Paul Wyman, Michigan State University, 1957.

[2] Presented at the 133rd national Meeting of the American Chemical Society, San Francisco, Calif., April, 1958.

[3] For a general review, see E. Vogel, *Fortschr. chem. Forsch.*, **3**, 430 (1955).

[4] J. D. Roberts and V. C. Chambers, THIS JOURNAL, **73**, 5034 (1951).

[5] J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951).

[6] C. G. Bergstrom and S. Siegel, *ibid.*, **74**, 145 (1952).

[7] See A. Streitwieser, Jr., *Chem. Revs.*, **56**, 571 (1956), for a review and discussion.

[8] H. Hart and J. M. Sandri, THIS JOURNAL, **81**, 320 (1959).

[9] R. G. Pearson and S. H. Langer, *ibid.*, **75**, 1065 (1953).

[10] J. D. Roberts and P. H. Dirstine, *ibid.*, **67**, 1281 (1945).

[11] H. B. Hass and H. Shechter, *ibid.*, **75**, 1382 (1953).

[12] J. D. Roberts and V. C. Chambers, *ibid.*, **73**, 3176 (1951).

[13] See C. L. Wilson and W. T. Lippincott, *ibid.*, **78**, 4290 (1956), and C. G. Overberger and P. Kabasakalian, *J. Org. Chem.*, **21**, 1124 (1956), for recent discussions of the radical mechanism for Kolbe electrolysis.

[14] F. Fichter and H. Reeb, *Helv. Chim. Acta*, **6**, 450 (1923).

[15] J. N. Pitts and I. Norman, THIS JOURNAL, **76**, 4815 (1954).

[16] These products were 1-butene, propylene and diallyl. Only traces of cyclopropane were formed, and neither methylcyclopropane nor dicyclopropyl was detected. The reluctance with which cyclopropyl radicals form is illustrated by the major photolysis product, propenyl methyl ketone, in which the three-membered ring rather than the alkyl–carbonyl bond is broken. Dicyclopropyl ketone showed this effect even more (J. N. Pitts and R. W. Woolfolk, Abstracts of 133rd Meeting of the A.C.S., 1958, p. 4Q). Propylene, produced in very low yield, was the only significant hydrocarbon product, the major photolysis result being cyclopropyl propenyl ketone.

[17] Another example may be the mercury-photosensitized polymerization of cyclopropane; K. J. Ivin, *J. Chem. Soc.*, 2241 (1956).

[18] A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951).

[19] J. R. McNesby and A. S. Gordon, THIS JOURNAL, **79**, 825 (1957).

[20] H. C. Brown and M. Borkowski, *ibid.*, **74**, 1894 (1952).

[21] Some ring-chlorinated product was also obtained.

[22] Photochlorination of dicyclopropylmethane in carbon tetrachloride at −80° gave only 1-cyclopropyl-4-chloro-1-butene, another example of such rearrangement; H. Hart and D. P. Wyman, unpublished results.

[23] C. G. Overberger and A. Lebovits, THIS JOURNAL, **76**, 2722 (1954).

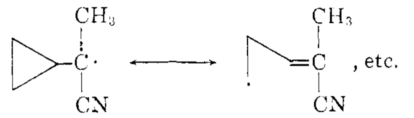
TABLE I

MAJOR PRODUCTS FROM THE DECOMPOSITION OF CERTAIN DIACYL PEROXIDES $(RCO_2)_2$ IN CARBON TETRACHLORIDE AT 70° (MOLES/MOLE OF PEROXIDE DECOMPOSED)[a]

Product \ Peroxide	I_3 Run 1	I_3 Run 2	I_6 Run 1	I_6 Run 2	II_3	II_6	Benzoyl peroxide
RCl	1.41	1.25	1.51	1.55	0.0[b]	1.32	1.27
CO_2	1.75	1.48	1.87	1.87	.88	1.77	1.725
RCO_2R	0.162	0.162	0.225	0.238	.85	0.30	0.255
RCO_2H	0.064	0.129	Small, not detd.		.0665	0.025	0.0155
Decomposition time, hr.	72	72	40	40	6	72	72
CO_2 accounted for, %	98.8	88.5	104.7	105.4	89.8	104.5	99.8
R-group accounted for, %	89.9	85.2	98.0	101.3	88.3	97.0	89.8

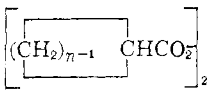
[a] 1–2 g. of peroxide was decomposed in 100 ml. of solvent. Results are corrected for undecomposed peroxide, for purity of the peroxide as determined iodometrically, and for any decomposition product already present (ester in II_3). [b] No evidence for any product with C–H bonds was obtained on distillation of 50 ml. of the reaction mixture through a Vigreux column, indicating the absence of cyclopropylcarbinyl, cyclobutyl or allylcarbinyl chlorides in the carbon tetrachloride distillate.

some 25x faster than that from methyl cyclopentyl ketone.



Unfortunately no product analysis has been reported for this decomposition.

In order to study more directly than previously cyclopropyl and cyclopropylcarbinyl radicals, we synthesized diacyl peroxides from cyclopropanecarboxylic and cyclopropaneacetic acids and studied their rates and products of decomposition in carbon tetrachloride. The results made it desirable to extend the range of peroxides, and the present paper includes data on the series of peroxides I and II.



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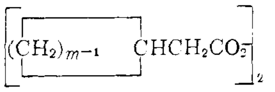


II

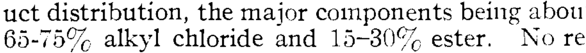
where $n = 3\text{-}7$ and $m = 3\text{-}6$. The results bear on the general mechanism of diacyl peroxide decomposition, as well as on the stability of small ring free radicals.

Results

Peroxides I_{3-7} and II_{3-6}[24] were prepared from the corresponding acid chlorides by reaction with sodium peroxide in moist ether. I_3 is a crystalline peroxide of remarkable stability; it can be stored in the pure state at room temperature for months without appreciable decomposition. Recrystallized from pentane, it melted at 79.2–80.0° and was melted, cooled and remelted about six times before decomposition was sufficiently extensive to prevent crystallization on cooling. I_6,[25] I_7, II_5 and II_6 were crystalline when stored in the freezer, but colorless liquids at room temperature. The remaining peroxides were not obtained crystalline. Purity of the peroxides, as determined by iodometric titration,[26] ranged from 88 to 99+%. One impurity known to be present in samples of I_6, I_7 and II_3 was the ester RCOOR corresponding to the peroxide $(RCO_2)_2$, carbonyl band at 5.75 μ, and was determined and corrected for in the kinetic experiments and product analyses. The most likely other impurity was a trace of solvent (ether) which was difficult to remove entirely.

Products of Decomposition.—Decomposition products in carbon tetrachloride were examined in some detail for I_3, I_6, II_3, II_6 and benzoyl peroxide. With the concentrations (about 0.1 *M*) and solvent used, induced decomposition was probably not very important (see kinetic section). The procedure for a typical product analysis is given in the Experimental part; most analyses were based on quantitative infrared. Each analysis was direct; none were by difference. Table I gives the significant results. In addition to the products shown, hexachloroethane was a major but undetermined product in each case except II_3. Phosgene was always produced in determined but insignificant amounts. Since the CO_2 balance was generally slightly higher than the alkyl (R) balance, some product containing the latter but not the former (such as R–R) may have gone undetected. This would appear quite reasonable, although such a product (dicyclopropyl) was carefully sought and not found among the products from I_3.[27]

Except for II_3, each peroxide gave a similar product distribution, the major components being about 65-75% alkyl chloride and 15-30% ester. No rearrangements of small ring radicals were observed; for example, I_3 gave only cyclopropyl chloride, the limit of detection of allyl chloride in the infrared being about 1-2%. The ester from I_3 was cyclopropyl cyclopropanecarboxylate (III), identical with an authentic sample synthesized from dicyclopropyl ketone[28] as shown.[29]



III

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[24] The Roman numerals correspond to bis-cycloalkaneformyl (I) and biscycloalkaneacetyl (II) peroxides (see formulas) and the subscripts to the values of *n* or *m*, which give directly the cycloaliphatic ring sizes. These symbols will be used throughout the paper in preference to the rather cumbersome names of these peroxides.

[25] Of the peroxides prepared during this work, only I_6 has been described previously. F. Fichter and W. Siegrist, *Helv. Chim. Acta*, **15**, 1304 (1932), prepared it from the acid anhydride and barium peroxide, found it to be a colorless liquid, and investigated certain of its decomposition products. W. Cooper, *J. Chem. Soc.*, 3106 (1951), reports a rate for its decomposition in styrene at 70°.

[26] C. G. Swain, W. H. Stockmayer and J. T. Clarke, THIS JOURNAL, **72**, 5426 (1950).

[27] Decomposition in a poorer radical transfer solvent (benzene) is being studied; R–R product should be more important here.

[28] H. Hart and O. E. Curtis, Jr., THIS JOURNAL, **78**, 112 (1956).

[29] W. D. Emmons and G. B. Lucas, *ibid.*, **77**, 2287 (1955).

Alkyl chlorides and esters from the other peroxides were also identified and determined by comparison of infrared spectra with those from authentic samples.

Peroxide II_3 was remarkable in that the only major product was the ester, cyclopropylcarbinyl cyclopropaneacetate; chlorine abstraction product (cyclopropylcarbinyl chloride or an isomer thereof) escaped detection. Comparison of carbon dioxide yield (88%) with ester yield (85%) indicates that the yield of chloride must have been less than 3%.[30]

Since the decomposition of I_3 was slow with respect to other peroxides of this series (*vide infra*), products obtained in the presence of a radical trap (iodine)[31] were investigated. In anhydrous carbon tetrachloride the principal product was cyclopropyl iodide, isolated in 66% yield but produced in about 85% yield, as determined from the infrared spectrum of the crude mixture.[32] Minor products were ester III, cyclopropanecarboxylic acid and cyclopropyl chloride. When 0.74×10^{-4} mole of I_3 was decomposed with a 10-fold excess of iodine in a shaken sealed tube containing 10 ml. of carbon tetrachloride and 2 ml. of water, 41% of the theoretical yield of cyclopropanecarboxylic acid was obtained. Other products were cyclopropyl iodide (45%), ester III (4%) and traces of phosgene. The amount of carbon dioxide was not determined. In other experiments, with perhaps less efficient stirring of the two-phase system, the yield of acid was slightly lower (all yields were determined by quantitative infrared).

Kinetics.—Rates of peroxide decomposition were followed by decrease with time in the intensity of the 5.65 μ band in the infrared, using 0.01–0.10 *M* solutions of peroxide in carbon tetrachloride. At these concentrations induced decomposition was anticipated to be[33] and found[34] negligible. Rate constants were calculated at each point from the equation

$$k_1 = \frac{2.3}{t} \log \frac{P_0}{P}$$

where P_0 = initial peroxide concentration and P = peroxide remaining at time t, or alternatively from the slopes of the least squares straight lines obtained when log P was plotted *vs.* t. In most cases, reactions were followed to about 40–60% completion, but in a few of the slow reactions, only initial rates (up to 20% decomposition) were measured. Data for a typical run are given in Table II and the results for the various peroxides at several temperatures are summarized in the Experimental part (Table IV). More useful for discussion purposes are the relative rates, either observed at or extrapolated to 70°, assigning a value of 1.00 to benzoyl peroxide, listed in Table III.

TABLE II

DECOMPOSITION OF BISCYCLOHEPTANEFORMYL PEROXIDE (I_7) IN CARBON TETRACHLORIDE AT 40° (P_0 = 15.47 × 10^{-3} *M*)

t, min.	$P \times 10^3$	$k_1 \times 10^3$, min.$^{-1}$
15	13.68	8.18
30	12.06	8.29
45	10.70	8.19
60	9.68	7.81
75	8.61	7.82
90	7.57	7.93

Av. $k_1 = 8.04 \pm 0.18 \times 10^{-3}$ min.$^{-1}$
or $13.4 \pm 0.30 \times 10^{-5}$ sec.$^{-1}$

TABLE III

RELATIVE RATES OF DECOMPOSITION OF SEVERAL DIACYL PEROXIDES IN CARBON TETRACHLORIDE AT 70°

Peroxide	Relative rate
Benzoyl	1.00[a]
I_3	0.44[b]
I_4	7.4
I_5	31.7[c]
I_6	60.3[d]
I_7	71.0[d]
II_3	[e]
II_4	2.8
II_5	1.8
II_6	2.6

[a] Our absolute value, using the same kinetic procedure as for the other peroxides, was 1.12×10^{-5} sec.$^{-1}$. [b] This value may have to be revised upward, to about 0.79, based on some recent measurements by Dr. H. H. Lau on a more refined apparatus. [c] Extrapolated from measurements at 40–55°. [d] Extrapolated from measurements at 35–45°. [e] Erratic results were obtained with different samples of peroxide; highest value would be about 1200, lowest about 23.

Discussion

The mechanism of diacyl peroxide decomposition was reviewed recently by Walling[35] who pointed up some of the as yet unsolved problems in this area. Our results may contribute more to these problems than to their solution, but they do indicate certain features of the reaction which must be rationalized by any satisfactory mechanism. Perhaps the most striking result is the rather large variation in decomposition rate with systematic variation of the alkyl group of the peroxide. Even neglecting II_3, whose kinetic behavior was erratic and will be discussed more fully below, a range of approximately 10^2 in rates was observed, mainly in type I peroxides. It is clear that the nature of R in $(RCO_2)_2$ markedly influences the decomposition rate, even when R is free of functionality (alkyl).[36]

The rate behavior of type II peroxides is most easily interpreted, for these rates are approximately

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[30] As indicated below, the kinetic behavior of II_3 was erratic. We are not certain at the moment whether a change in product pattern accompanies the different rate behavior, but infrared spectra of samples taken from our slowest kinetic run still show an unusually large ester yield. An attempt is being made to determine the cause of this variation in rate with peroxide sample, and to correlate it with any difference in product distribution.

[31] G. Hammond and L. M. Soffer, THIS JOURNAL, **72**, 4711 (1950).

[32] The low isolated yield was due to the proximity in boiling points of the iodide and solvent, coupled with the very large excess of the latter.

[33] D. F. DeTar and C. Weis, THIS JOURNAL, **78**, 4296 (1956).

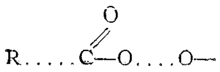
[34] Iodine did not depress the decomposition rate of I_3.

[35] C. Walling, "Free Radicals in Solution," John Wiley and Sons Inc., New York, N. Y., 1957, p. 474 ff.

[36] We do not believe the data are adequately explained by differences in inductive effects of the alkyl groups, relayed to the O–O bond even though there are fairly large changes in the inductive effects (as measured by σ^{*37}) of the alkyl groups employed. In a study of substituted benzoyl peroxides, Swain, Stockmayer and Clarke[26] found only a 7-fold variation in rate from *p,p'*-dimethoxy- to *p,p'*-dicyanobenzoyl peroxide.

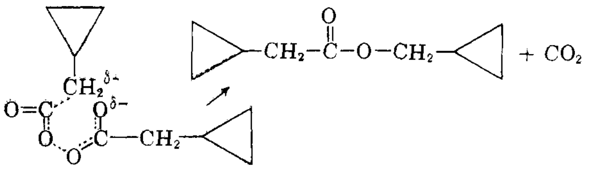
[37] R. W. Taft in M. S. Newman's "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 587 ff. For a value for the cyclopropyl group, which indicates that it is electron-withdrawing compared with methyl; see T. L. Brown, THIS JOURNAL, **80**, 6489 (1958).

independent of ring size (except for II$_3$ already noted) and comparable to those observed for acetyl, propionyl and *n*-butyryl peroxides[38]; presumably they are fairly typical of peroxides in which R is primary. Exceptions are phenylacetyl peroxide[39] and II$_3$, both of which are remarkably fast. Bartlett and Leffler found phenylacetyl peroxide to decompose as rapidly at 0° as benzoyl peroxide at 70°. They attributed the rapid rate to resonance stabilization of benzyl radicals produced in the decomposition, implying considerable R–C as well as O–O bond stretching in the transition state.



$\mathrm{R}\cdots\cdot\overset{\mathrm{O}}{\overset{/\!\!/}{\mathrm{C}}}\!-\!\mathrm{O}\cdots\mathrm{O}-$

This concept was placed on more firm ground by Bartlett and Hiatt[40] who found that systematic variation of the R group of *t*-butyl peresters, RCOOO-*t*-Bu, in such a manner as to increase the stability of the R radical produced gave increasing decomposition rates. Bartlett and Leffler[39] also noted that benzyl radicals from phenylacetyl peroxide failed to attack carbon tetrachloride molecules, at 0°, the major product being benzyl phenylacetate. There thus appear to be several similarities between phenylacetyl and cyclopropaneacetyl peroxides; decomposition rates are rapid and there is little attack on solvent molecules. Also, the erratic rate behavior of II$_3$ suggests the possibility of an acid-catalyzed decomposition, as was observed with phenylacetyl peroxide.[39] The rapid decomposition of II$_3$ may be due in part to such an ionic mechanism, particularly in view of the known stability of cyclopropylcarbonium ions[5–8]; thorough alkaline and water wash of the peroxide gave a sample which decomposed much more slowly, but still ten times faster than any other member of series II.[41] Resonance stabilization of the cyclopropylcarbinyl radical may be involved.[23] Alternatively, predominant ester formation in these cases may be due to appreciable carbonium ion character in a cyclic transition state leading directly to ester.[42]



A detailed study of peroxide II$_3$ is obviously warranted and is under way.

Whereas type II peroxides give primary free radicals, type I peroxides give secondary alkyl radicals. If cleavage of the O–O bond were the sole high energy process in the decomposition[38] no large rate effect would be anticipated, because small differences in inductive effects transmitted through saturated bonds are relatively unimportant. But if C–C bond stretching (as well as O–O bond stretching) were important in the transition state, one would anticipate faster rates for type I peroxides, since secondary alkyl radicals are generally more stable than primary alkyl radicals. As seen in Table III, all peroxides in this series (except I$_3$ discussed separately below) decomposed at faster rates than those of type II; for medium sized rings (I$_{5-7}$) the factor was about 20. This is taken as evidence for considerable C–C stretching in the transition state.[43]

Peroxides I$_4$ and I$_3$ decomposed at progressively slower rates than other members of this series; I$_3$ was even slower than series II peroxides, even though a secondary alkyl radical was produced. These slow rates can be rationalized in terms of I-strain[44] in small ring radicals, provided that the alkyl group has considerable radical character in the transition state (*i.e.*, C–C as well as O–O bond stretching). These results are consistent with series I peroxides being generally faster than those of series II.

The major product from I$_3$ was cyclopropyl chloride; cyclopropyl radicals therefore abstract a chlorine atom from carbon tetrachloride at 60–75° faster than they isomerize to allyl radicals. The alkyl group in ester III formed as a minor product in this decomposition also was not rearranged, which is quite different from the results obtained with Kolbe electrolysis,[14] but consistent with the known stereochemical differences in ester formation by the two reactions.[45]

Comparison of I$_3$ with benzoyl and acetyl peroxides is instructive. All three decompose at approximately the same rate; in anhydrous solvents containing iodine the major products are cyclopropyl iodide,[46] iodobenzene[31] and methyl iodide,[47] respectively. But in moist solvent containing iodine their behaviors differ markedly. Benzoyloxy radicals are the primary capturable radicals from benzoyl peroxide, since nearly quantitative yields of benzoic acid were obtained,[31] presumably by hydrolysis of initially formed benzoyl hypoiodite. But acetoxy radicals have not been similarly trapped; even in moist carbon tetrachloride containing iodine, methyl iodide (not acetic acid) was the major product.[48] Acetoxy radicals are thought to decompose almost simultaneously with their formation[47,48] to methyl radicals and carbon dioxide. The greater stability of benzoyloxy over acetoxy radicals has been attributed to conjugation between the electron systems of the carboxy radical and the benzene ring. We found bis-cyclopropaneformyl peroxide (I$_3$) to occupy an intermediate position; cyclopro-

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[38] J. Smid, A. Rembaum and M. Szwarc, THIS JOURNAL, **78**, 3315 (1956).

[39] P. D. Bartlett and J. E. Leffler, *ibid.*, **72**, 3030 (1950).

[40] P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

[41] We are indebted to Dr. Hans H. Lau for these experiments.

[42] Thus two paths for ester formation may be available, radica recombination and the cyclic path, the latter being particularly favorable when R accommodates carbonium ion character well. For further remarks on ester formation, see the following paper, H. H. Lau and H. Hart, THIS JOURNAL, **81**, 4897 (1959).

[43] An alternative explanation, involving a rapidly reversible equilibrium between peroxide and acyloxy radicals followed by a rate-determining loss of carbon dioxide from acyloxy radicals, discussed some time ago by C. C. Price, *Trans. N. Y. Acad. Sci.*, **44**, 351 (1943), seems not to be operative, at least with benzoyl and apocamphoy peroxides (M. A. Greenbaum, Ph.D. Thesis, Yale University, 1957).

[44] H. C. Brown, R. S. Fletcher and R. B. Johannesen, THIS JOURNAL, **73**, 212 (1951).

[45] J. Brenner and K. Mislow, *J. Org. Chem.*, **21**, 1312 (1956).

[46] Identity was established by conversion to the Grignard reagent and carbonation. Analysis made use of a very intense band at 8.08 μ. Details will be presented elsewhere.

[47] A. Rembaum and M. Szwarc, THIS JOURNAL, **77**, 3486 (1955).

[48] C. Walling and R. B. Hodgdon, Jr., unpublished results quoted in ref. 35, p. 493.

panecarboxylic acid and cyclopropyl iodide were formed in nearly equal amounts when the peroxide was decomposed in moist carbon tetrachloride and iodine.[49] Whether the greater stability of the cyclopropanoyloxy radical (compared with acetoxy) is due to conjugation between the carboxy electron system and the cyclopropane ring, or whether it is due to reluctance to form the cyclopropyl radical (with sp^2 bonding on the three-membered ring) cannot be determined at this point. The reactions of other members of these series in the presence of iodine, and their decomposition in poorer radical transfer solvents (such as benzene) is being studied.

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Experimental

Preparation of the Peroxides. A. Biscyclopropaneformyl Peroxide (I_3).—To a slurry of 6.9 g. (0.088 mole) of sodium peroxide and 45 ml. of ether there was added 18.5 g. (0.177 mole) of cyclopropanecarbonyl chloride (prepared by exchange with benzoyl chloride[50] in 73% yield, b.p. 113–115°[51]). Addition of 1–2 drops of water initiated the reaction, which proceeded sufficiently rapidly to cause reflux of the ether. When the reaction subsided, and addition of a drop of water no longer caused an increase in the temperature of the mixture, 25 ml. of water was added. The aqueous layer was basic to litmus. The ether layer was separated, dried over calcium chloride, and the ether evaporated to dryness in a stream of dry air. The crystalline residue was recrystallized from pentane, yielding 12.3 g. (83%) of peroxide, m.p. 79.2–80.0°. Iodometric titration[26] showed greater than 99% purity.

B. Biscyclopropaneacetyl Peroxide (II_3).—Differences from the above procedure were that smaller quantities were used, the reaction temperature was not allowed to exceed 2°, completion of the reaction was taken to coincide with disappearance of the yellow color of sodium peroxide, and the reaction was worked up with ice-water. In a typical experiment, from 0.86 g. (0.011 mole) of sodium peroxide and 3.9 g. (0.0213 mole) of cyclopropaneacetyl chloride (see below) in 10 ml. of ether there was obtained 1.83 g. (84%) of biscyclopropaneacetyl peroxide. The product was a clear colorless liquid, 84–86% pure by iodometric titration. Impurities (ascertained from infrared spectra) were solvent (ether) and cyclopropylcarbinyl cyclopropaneacetate.

C. The other peroxides were prepared by analogous procedures, except that the temperature was often allowed to reach 8–10°. Yields ranged from 78–91% and purity from 88–97%. I_6, I_7, II_5 and II_6 were crystalline when stored in the freezer, but liquids at room temperature. The others, except for I_3, were colorless liquids.

Apparatus and Procedure for Product Determination.—The decomposition vessel consisted of a 250-ml. thermostated flask which contained a gas inlet extending to the bottom of the flask, a cold finger condenser-type stopper, and a Graham condenser leading to a train for collecting exit gases. Anhydrous oxygen-free nitrogen was passed through the solution slowly throughout any experiment. The exit gases were led successively through a trap containing 30% aniline in carbon tetrachloride, two cold traps in a Dry Ice–isopropyl alcohol-bath, a tared U-tube containing Ascarite, and protective tubes containing Ascarite and anhydrone.

Phosgene was determined gravimetrically as diphenylurea isolated from the aniline trap. Carbon dioxide was also determined gravimetrically. All other determinations were accomplished using quantitative infrared, employing the base line technique.[52] Carbon tetrachloride for the decompositions and the infrared analyses was purified according to Fieser.[53]

In a typical decomposition, 1.898 g. of biscyclopropaneformyl peroxide (I_3) and 100 ml. of carbon tetrachloride were placed in the reaction vessel. After sweeping for 30 minutes with nitrogen at room temperature the mixture was heated for 72 hours at 70 ± 0.5°. The cooled solution was transferred to a 100-ml. volumetric flask (approximately 7 ml. was lost to the cold traps by evaporation) and diluted to volume. Quantitative infrared was then used to determine the amount of peroxide remaining (5.65 μ), the cyclopropyl cyclopropanecarboxylate (5.75 μ) and the cyclopropanecarboxylic acid (5.90 μ). The solution was then distilled at reduced pressure; after 10 ml. was collected, an infrared spectrum showed no further C–H bands in additional distillate. Clearly, all the cyclopropyl chloride had come over in the first 10 ml. of distillate which was diluted to 100 ml., and the cyclopropyl chloride determined quantitatively, using bands at 3.31 and 6.90 μ. Quantitative analyses of the residue from this distillation showed that no significant amount of the residual peroxide had decomposed during the process. Distillation of some of the carbon tetrachloride from the aniline trap, and rinsing of the cold traps gave an additional amount of cyclopropyl chloride, which was again determined quantitatively as above.

Carbon dioxide was determined by weighing the Ascarite-filled U-tube before and after the run.

Phosgene was determined by evaporating the remaining contents of the aniline trap to dryness *in vacuo*. The residue was washed with acid to remove the aniline, then dried, and the diphenylurea weighed. Hexachlorethane, also a decomposition product, was not estimated.

To establish qualitatively the structure of the ester produced, excess peroxide was destroyed with iodide and acid was removed by alkaline extraction. The residue had an infrared spectrum essentially identical with that of authentic cyclopropyl cyclopropanecarboxylate, as prepared below. (The hexachlorethane present did not interfere.)

Products from the other peroxides were determined in similar fashion, and are summarized in Table I.

Kinetic Procedure.—The same apparatus was used for kinetic measurements, except that the train for exit gases included only the Ascarite and anhydrone U-tubes. To remove aliquots for analysis, the nitrogen flow through the inlet tube was stopped, and the sample forced out of this tube by nitrogen pressure from the other end of the system. The kinetics were determined by following the disappearance of the peroxide carbonyl band (at 5.65 μ) in the infrared in 1-ml. aliquots. Results are given in Table IV.

Cyclopropaneacetic Acid.[54] A. 2-Cyclopropanethanol.—To cyclopropyllithium[55] prepared from 8 g. (1.13 g. atoms) of lithium and 50 g. (0.65 mole) of cyclopropyl chloride in 250 ml. of pentane and cooled to 0° in a flask equipped with a gas inlet tube, stirrer and a Dry Ice condenser, there was added over 0.5 hour 57.5 g. (1.3 moles) of gaseous ethylene oxide. The mixture was stirred in the cold for two more hours. Sufficient ice-cold 10% sulfuric acid was then added to make the solution acid to congo red, and the layers separated. The aqueous layer was saturated with salt and extracted twice with 100 ml. of ether. The combined organic fractions, after drying over anhydrous potassium car-

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[49] The observed stoichiometry and slow decomposition rate in this case might tempt one to revive the proposal of initial decomposition according to $(RCO_2)_2 \rightarrow R\cdot + RCO_2\cdot + CO_2$, but is more likely fortuitous.

[50] H. C. Brown, THIS JOURNAL, **60**, 1325 (1938).

[51] R. C. Fuson and F. N. Baumgartner, *ibid.*, **70**, 3255 (1948).

[52] W. R. Brode, "Chemical Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 245.

[53] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, Boston, Mass., 1955, p. 283.

[54] Authentic syntheses of this acid have been previously reported by L. I. Smith and S. McKenzie, *J. Org. Chem.*, **15**, 74 (1950), and by J. H. Turnbull and E. S. Wallis, *ibid.*, **21**, 663 (1956). The procedure reported here is more adaptable to a large scale.

[55] H. Hart and J. M. Sandri, *Chemistry & Industry*, 1014 (1956). We have recently developed a workable preparation of the Grignard reagent from cyclopropyl chloride; it serves equally as well as the lithium compound in this preparation (H. Hart and R. A. Cipriani, unpublished results).

TABLE IV

RATE CONSTANTS FOR DECOMPOSITION OF CERTAIN PEROXIDES AT SEVERAL TEMPERATURES ($k_1 \times 10^{-5}$, SEC.$^{-1}$)

Peroxide t, °C.	I_3[a]	I_4	I_5	I_6	I_7	II_3[b]	II_4	II_5	II_6
35				2.87	7.85				
40			1.50	5.22, 5.29	16.3, 13.4				
45			2.55	9.67	20.2				
50			4.96						
55			8.17, 7.85						
63	0.20								
65		5.15					1.37	1.48	1.27
70	0.44, 0.51, 0.58[c]	8.95, 6.63					2.13, 3.08	3.20, 3.20	2.75, 2.78
75		14.10					3.83	4.97	3.61
76	0.97								

[a] More recent runs made by Dr. Hans H. Lau indicate that these values should be revised upward to 0.44 at 64.5°, 0.93 at 70.4°, 1.18 at 72.4° and 2.31 at 77.8°. These changes do not affect the conclusions drawn from this work. [b] Values of 9.45 at 14° and 105.7, 97.5 at 25° were obtained by D. P. W. Very carefully purified samples gave values of 3.35 at 55.5° and 30.1 at 73° in the hands of Dr. Lau. [c] In this run, equimolar amounts of peroxide and iodine were present.

bonate and removal of the solvent, gave 32 g. (64%) of cyclopropane-ethanol, b.p. 135°, $n^{25}D$ 1.4327.[56]

Anal. Calcd. for $C_5H_{10}O$: C, 69.76; H, 12.54. Found: C, 69.87; H, 12.21.

B. Cyclopropaneacetaldehyde.—Cyclopropanethanol was catalytically dehydrogenated over a catalyst of copper and silver suspended on pumice described by Davies and Hodgson.[57] In a typical preparation, 15 g. (0.0175 mole) of cyclopropanethanol gave 9.0 g. (60%) of cyclopropaneacetaldehyde, b.p. 105–106°, $n^{25}D$ 1.4382, *p*-nitrophenylhydrazone m.p. 110–110.5°.

Anal. Calcd. for $C_{11}H_{13}N_3O_2$: C, 60.42; H, 5.95; N, 19.15. Found: C, 60.42; H, 5.62; N, 18.85.

Some unchanged alcohol and cyclopropaneacetic acid could also be recovered.

C. Cyclopropaneacetic Acid.—A tightly stoppered iodine flask containing 6 g. (0.071 mole) of cyclopropaneacetaldehyde, 35 g. (0.152 mole) of silver oxide and 25 ml. of water was shaken mechanically at room temperature for 12 hours, after which it was removed from the shaker and heated at 60° for one hour, then filtered. Ether washings of the silver and silver oxide were combined with four 150-ml. ether extracts of the aqueous layer, dried (calcium chloride) and the solvent removed. The residue gave 5.6 g. (79%) of cyclopropaneacetic acid, b.p. 90° at 15 mm., m.p. of *p*-bromophenacyl ester 83–83.5°.[54]

Cyclopropyl Cyclopropanecarboxylate.[29]—Peroxytrifluoroacetic acid from 10.8 ml. of 90% hydrogen peroxide, 100 ml. of methylene chloride and 67.6 ml. of bistrifluoroacetic anhydride was added to a suspension of 142 g. (1 mole) of disodium hydrogen phosphate in 22 g. (0.2 mole) of dicyclopropyl ketone[28] and 200 ml. of methylene chloride during 25 minutes. The solvent refluxed during the addition, and reflux was maintained for another hour by external heating. The solids were filtered and washed with 100 ml. of methylene chloride. After washing the organic layer with 10% sodium carbonate, water, and drying (magnesium sulfate), the solvent was removed by distillation, leaving a residue of 18.6 g., b.p. 60° at 15 mm. This proved to be a mixture of ester and unconverted ketone, approximately 60% the former, judging from the carbonyl intensities in the infrared.

Separation of the ester from the ketone was not readily accomplished by fractional distillation or chromatography on alumina, and the ketone was unreactive toward Girard T and P reagents.[58] Separation was finally accomplished by reaction with hydroxylamine. Typically, 9 g. of the ketone–ester mixture, 5 g. of hydroxylamine hydrochloride 10 ml. of pyridine and 15 ml. of absolute ethanol were refluxed for 1.5 hours, after which the pyridine and alcohol were removed *in vacuo*. Careful distillation of the residue at 40–20 mm. gave 5 g. of cyclopropyl cyclopropanecarboxylate, b.p. 163° at atmospheric pressure, 62° at 15 mm., $n^{25}D$ 1.4528, saponification equivalent 127 (calcd. 126).

Anal. Calcd. for $C_7H_{10}O_2$: C, 66.64; H, 8.05. Found: C, 66.95; H, 8.07.

Cyclopropylcarbinyl Cyclopropaneacetate.—A mixture of 20 ml. of pyridine, 2.4 g. (0.033 mole) of cyclopropylcarbinol and 4 g. (0.033 mole) of cyclopropaneacetyl chloride was allowed to stand at room temperature for two hours, then diluted with 50 ml. of ether. After washing with water, 6 *N* hydrochloric acid, 10% sodium carbonate and water, the organic layer was dried (magnesium sulfate) and distilled, yielding 4.1 g. (70%) of cyclopropylcarbinyl cyclopropaneacetate, b.p. 63–65° at 2 mm., $n^{25}D$ 1.4475.

Anal. Calcd. for $C_9H_{14}O_2$: C, 70.10; H, 8.75. Found: C, 69.83; H, 8.68.

Decomposition of Biscyclopropaneformyl Peroxide in the Presence of Iodine and Water.—A solution of 10 ml. of carbon tetrachloride containing 12.5 mg. (7.35×10^{-5} mole) of biscyclopropaneformyl peroxide and 0.2 g. (7.9×10^{-4} mole) of iodine was mixed with 2 ml. of water, sealed in a tube and heated at 75° for 65 hours. The contents were washed with sodium hydrosulfite to remove excess iodine, dried over calcium chloride, and analyzed quantitatively by infrared. The products were cyclopropyl iodide,[46] 11.1 mg. (45%), 5.16 mg. (41%) of cyclopropanecarboxylic acid and 0.36 mg. (4.3%) of cyclopropyl cyclopropanecarboxylate.

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[56] Attempted direct oxidation of 2-cyclopropanethanol (25 g., 0.29 mole) with potassium permanganate (61 g., 0.385 mole) in 1200 ml. of water for four hours at 0° and eight hours at room temperature gave, on work-up, 13 g. of acid which, on analysis, was shown to be a 50–50 mixture of cyclopropaneacetic and cyclopropanecarboxylic acids. This oxidation of a side-chain on the cyclopropane ring is noteworthy.

[57] R. R. Davies and H. H. Hodgson, *J. Chem. Soc.*, 282 (1943).

[58] Emmons and Lucas[29] encountered similar difficulties with methyl cyclopropyl ketone, but were able to purify the cyclopropyl acetate with a Girard reagent.