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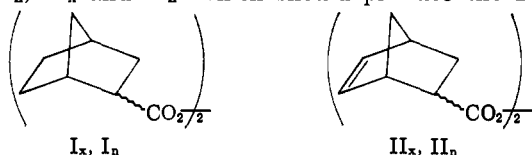
Decomposition of Diacyl Peroxides from *exo*- and *endo*-Norbornane-2-carboxylic Acids and *exo*- and *endo*-Norbornene-5-carboxylic AcidsBY HAROLD HART AND FRANK J. CHLOUPEK<sup>1</sup>

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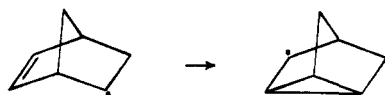
The decomposition rates and products of the crystalline diacyl peroxides referred to in the title ( $I_x$ ,  $I_n$ ,  $II_x$ ,  $II_n$ , respectively) have been studied in carbon tetrachloride. The observed rate difference for the saturated peroxides ( $I_x > I_n$  by 7–10-fold) shows that C–C bond stretching is important in the rate-determining step; the difference can be rationalized on steric grounds. The products from  $I_x$  and  $I_n$  are unexceptional. Even in dilute (0.05 *N*) solution,  $II_x$  and  $II_n$  are subject to induced decomposition which can be inhibited but not eliminated with a ten-mole excess of styrene. The major decomposition path for  $II_n$  involves *selective* attack of  $CCl_3$  radicals on  $C_2$  of the peroxide, producing lactone III, carbon dioxide and products from the norbornene-5-yl radical. A lactone is also formed, in lesser yield, from  $II_x$ .

## Introduction

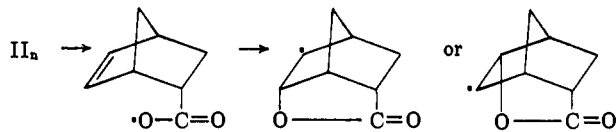
The decomposition of diacyl peroxides  $(RCO_2)_2$  is affected by the nature of the group R, since those peroxides in which R· is resonance stabilized<sup>2–4</sup> show accelerated decomposition. For example, 3-butenoyl peroxide initiates styrene polymerization at a rate >50-fold that of 2-butenoyl peroxide, presumably because of allylic stabilization of the transition state in the decomposition of the former. Part of this acceleration may arise from polar contributions<sup>5</sup> since the carbonium ions  $R^+$  are also resonance stabilized (benzyl,<sup>2</sup> allyl,<sup>3</sup> cyclopropylcarbinyl<sup>4</sup>). Because of the well established solvolytic accelerations in the 2-norbornyl<sup>6</sup> and 5-norbornenyl<sup>7</sup> systems, it seemed worthwhile on several counts to study the decomposition of diacyl peroxides  $I_x$ ,  $I_n$ ,  $II_x$  and  $II_n$ <sup>8</sup> which should produce the 2-nor-



bornyl and 5-norbornenyl radicals. If bridged radicals were formed, one might expect the *exo* isomers to decompose faster than their *endo* counterparts. One might also hope to find radical rearrangement products which, though uncommon in aliphatic systems, are known.<sup>9</sup> For example, II might lead to products with the nortricyclyl structure *via* radicals.



Finally there was the intriguing possibility that the double bond in II might act as an intramolecular trap for the acyloxy radical, particularly in  $II_n$  where the geometry would be favorable.



Accordingly, the four epimerically pure peroxides were

(1) National Science Foundation Cooperative Predoctoral Fellow, 1959–1961.

(2) P. D. Bartlett and J. E. Leffler, *J. Am. Chem. Soc.*, **72**, 3030 (1950).

(3) W. Cooper, *J. Chem. Soc.*, 3108 (1951).

(4) H. Hart and R. Cipriani, *J. Am. Chem. Soc.*, **84**, 3897 (1962).

(5) P. D. Bartlett and C. Rüdhardt, *ibid.*, **82**, 1756 (1960).

(6) S. Winstein and D. Trifan, *ibid.*, **71**, 2953 (1949); **74**, 1147 (1952);

J. D. Roberts, W. Bennett and R. Armstrong, *ibid.*, **72**, 3329 (1950); J. D. Roberts and W. Bennett, *ibid.*, **76**, 4623 (1954).

(7) J. D. Roberts, W. Bennett and R. Armstrong, ref. 6; S. Winstein,

H. M. Walborsky and K. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950).

(8)  $I_x$  and  $II_x$  refer to the *exo* isomers, and  $I_n$  and  $II_n$  to the *endo* isomers,

(9) J. A. Berson, C. J. Olsen and J. S. Walla, *ibid.*, **82**, 5000 (1960); **84**, 3337 (1962).

synthesized, and this paper describes their decomposition rates and products in carbon tetrachloride.<sup>10</sup>

## Results and Discussion

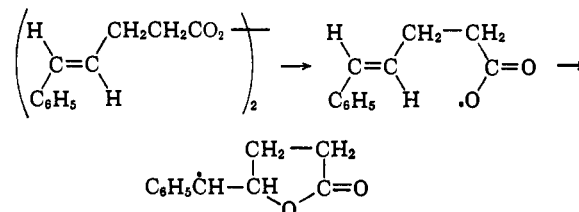
The peroxides were prepared from the corresponding acid chlorides and sodium peroxide in moist ether. Absence of epimerization at the acid chloride stage was established by hydrolysis of small samples to the starting acid. The peroxides were crystalline, obtained in 94–99% purity, and epimers could be distinguished by their melting points and infrared spectra.

**Kinetics.**—Decomposition rates were followed by iodometric titration<sup>13</sup> and also by infrared, following both peroxide disappearance and the appearance of certain products. Ampoules containing 0.05 *N* solutions of peroxide in carbon tetrachloride and sealed in a nitrogen atmosphere were heated for various time intervals, quenched and analyzed at the termination of the run. Experiments were made at 44.5°, 53.9° and 65.9°. First-order rate constants were determined by the Guggenheim method<sup>14</sup>; plots of  $\log(F_t - F_{t+\Delta})$ <sup>15</sup> against time gave excellent straight lines from whose least squares slopes  $k$  was calculated. Agreement between rate constants determined by different analytical methods was moderately good. The results are given in Table I.

Decomposition of the saturated peroxides  $I_x$  and  $I_n$  was not markedly altered by styrene; if the differences are significant there may in fact be a slight rate increase rather than the sharp decrease to be expected if induced

(10) Two pertinent papers appeared after the present work was completed. Bartlett and Pincock<sup>11</sup> found *t*-butyl *exo*-norbornane-2-percarboxylate to decompose 4.1 times faster than the *endo* isomer in chlorobenzene at 100° and concluded that this small rate difference probably did not represent anchimeric assistance; both esters decomposed more slowly than *t*-butyl cyclohexanepercarboxylate.

Lamb and co-workers,<sup>12</sup> in a kinetic study of the decomposition of *trans*-5-phenyl-4-pentenyl peroxide in a variety of solvents, concluded that the double bond participated as a neighboring group



Products have not yet been reported, but a lactone band at 5.7  $\mu$  is noted. This may be a particularly favorable case for the double bond to act as a radical trap, because the lactonic radical is benzylic.

(11) P. D. Bartlett and R. E. Pincock, *J. Am. Chem. Soc.*, **84**, 2445 (1962).

(12) R. C. Lamb, F. F. Rogers, Jr., G. D. Dean, Jr., and F. W. Voight, Jr., *ibid.*, **84**, 2635 (1962).

(13) L. Silbert and D. Swern, *ibid.*, **81**, 2364 (1959); L. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).

(14) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

(15)  $F_t$  and  $F_{t+\Delta}$  are volume of titrant or infrared absorbancy at times  $t$  and  $t + \Delta$ .

TABLE I  
RATE CONSTANTS FOR THE DECOMPOSITION OF *exo*- AND *endo*-NORBORNANE-2-CARBONYL PEROXIDES AND *exo*- AND *endo*-NORBORNENE-5-CARBONYL PEROXIDES IN CARBON TETRACHLORIDE (SEC.<sup>-1</sup> × 10<sup>5</sup>)

Peroxide <sup>a</sup>	<i>t</i> , °C.	<i>k<sub>t</sub></i> <sup>b</sup>	<i>k<sub>p</sub></i> <sup>b</sup>	<i>k<sub>a</sub></i> <sup>b</sup>	<i>k<sub>e</sub></i> <sup>b</sup>
I <sub>x</sub>	44.5	4.68 ± 1.00	5.63 ± 0.50	6.08 ± 0.88	
		*7.20 ± 0.58 <sup>c</sup>	*4.37 ± .18	*8.52 ± .52	
I <sub>n</sub>		0.61 ± .02	0.54 ± .04	0.59 ± .03	
		*0.91 ± .13	*0.64 ± .09	*0.87 ± .05	
II <sub>x</sub>		6.58 ± .52	7.42 ± .07		8.97 ± 0.85
		*2.58 ± .15	*3.92 ± .07		*3.83 ± 0.13
II <sub>n</sub>		6.30 ± .27	<sup>d</sup>		8.35 ± 1.02
		*2.22 ± .10			*2.27 ± 0.05
I <sub>x</sub>	53.9	20.5 ± 1.3	17.3 ± 0.8	18.0 ± 0.3	
		*16.0 ± 3.0	*19.5 ± 1.3	*27.0 ± 4.7	
I <sub>n</sub>		2.83 ± 0.17	3.00 ± 0.08	3.00 ± 0.35	
		*4.33 ± 0.13	*3.50 ± 0.13	*2.33 ± 0.30	
II <sub>x</sub>		12.1 ± 1.2	16.7 ± 2.0		25.5 ± 0.8
		*12.0 ± 0.6	*13.2 ± 1.2		*17.5 ± 2.8
II <sub>n</sub>		12.1 ± .7	<sup>d</sup>		13.8 ± 0.1
		*4.52 ± .28			*6.30 ± 0.32
I <sub>x</sub>	65.9	81.8 ± 7.7	86.0 ± 1.5	109.8 ± 15.2	
		*84.8 ± 1.7	*100.3 ± 6.3	*132.2 ± 12.0	
I <sub>n</sub>		12.5 ± 0.7	13.5 ± 0.7	12.7 ± 0.1	
		*12.8 ± 1.8	*13.3 ± 1.4	*16.3 ± 0.1	
II <sub>x</sub>		84.2 ± 1.7	84.2 ± 2.7		82.0 ± 0.2
		*71.0 ± 3.2	*62.0 ± 1.3		*68.5 ± 1.3
II <sub>n</sub>		71.8 ± 5.5	<sup>d</sup>		76.5 ± 2.7
		*23.7 ± 0.2			*27.2 ± 1.3

<sup>a</sup> The initial peroxide concentration was 0.05 *N* in all runs. <sup>b</sup> *k<sub>t</sub>* was determined by iodometric titration of undecomposed peroxide, *k<sub>p</sub>* by disappearance of the peroxide band at 5.65  $\mu$  in the infrared, *k<sub>a</sub>* and *k<sub>e</sub>* by appearance of acid (5.87  $\mu$ ) and ester (5.77  $\mu$ ) bands, respectively. <sup>c</sup> Those values marked with an asterisk were for decompositions carried out in the presence of 0.2 *M* styrene. <sup>d</sup> It was not possible to follow peroxide disappearance due to interference by a reaction product (lactone III).

decomposition were important.<sup>16</sup> I<sub>x</sub> decomposed 7 to 10 times faster than I<sub>n</sub>, the exact ratio depending upon the conditions. This is slightly larger than that comparable to the factor 4 observed by Bartlett and Pincock<sup>11</sup> for the corresponding *t*-butyl peresters; the variation in results may be a matter of temperature, the rate difference being smaller at the higher temperature needed to decompose the peresters. The slower rate for I<sub>n</sub> may reflect the fact that when the C<sub>2</sub>-C<sub>8</sub> bond stretches in the transition state (as C<sub>2</sub> approaches a trigonal structure) strain is relieved in I<sub>x</sub> but increased in I<sub>n</sub>, due to interaction with the *endo*-hydrogens on C<sub>5</sub> and C<sub>6</sub>. The rate difference can also be rationalized in terms of anchimeric assistance in I<sub>x</sub>, but in view of the results with II (*vide infra*) and the relatively small magnitude of the effect, when compared with solvolyses,<sup>6</sup> this seems unnecessary. Compound I<sub>n</sub> is also slower (by 2-4 fold) than either cyclohexane-carbonyl or cyclopentanecarbonyl peroxides.<sup>17</sup>

Both unsaturated peroxides undergo induced decomposition, even in 0.05 *N* solution, as shown by the rate diminution, particularly for II<sub>n</sub>, when styrene was added.<sup>18</sup> Even with a large styrene excess, induced decomposition was not entirely inhibited, as will be seen below from product studies. Without styrene, II<sub>x</sub> and II<sub>n</sub> decompose at nearly identical rates, approximately that of I<sub>x</sub>; with styrene, II<sub>x</sub> > II<sub>n</sub> by as much as 3 at higher temperatures. Once again the difference is very much smaller than that observed in related carbonium ion reactions<sup>7</sup> and, coupled with the absence of 3-chloronortricyclene among the products (*vide infra*), shows that double bond

participation does not contribute to the rate-determining step.

The activation parameters vary somewhat depending upon which method of following the reaction was used to evaluate the rates;  $\Delta E^\ddagger$  for I<sub>n</sub> is about 1.5-2 kcal. per mole higher than for I<sub>x</sub> (30.5 *vs.* 28.5), both peroxides having about the same  $\Delta S^\ddagger$  (+15 to +17 e.u.). Because of induced decomposition, activation parameters for the unsaturated peroxides probably do not have much theoretical significance. With styrene present, the mean value of  $\Delta E^\ddagger$  for II<sub>n</sub> was about 4-5 kcal. per mole less than for I<sub>x</sub>, the rate being made up by a more positive entropy for II<sub>x</sub> (about 15 e.u.).

**Products.**—The products were estimated by refluxing 0.022-0.025 *M* solutions of peroxide in carbon tetrachloride for three days, alone or in the presence of 0.2 *M* styrene. Carbon dioxide was determined gravimetrically, and carbonyl-containing products were estimated using their infrared absorptions, the extinction coefficients having been determined from independently prepared authentic samples. In larger scale experiments, many of the products were isolated and identified. The results appear in Table II.

The type and yield of products from the saturated peroxides (I<sub>x</sub>, I<sub>n</sub>) was normal for aliphatic peroxides.<sup>17,19</sup> The esters and acids retained their stereochemistry; *i.e.*, *exo*-2-norbornyl *exo*-norbornane-2-carboxylate and *exo*-norbornane-2-carboxylic acid were the only ester and acid isolated from I<sub>x</sub>, and only the corresponding *endo* isomers were obtained from I<sub>n</sub>.<sup>20</sup> The carbonyl

(19) D. F. De Tar and C. Weis, *J. Am. Chem. Soc.*, **78**, 4298 (1956).

(16) The increase may be due to a direct reaction between styrene and the peroxide; see J. C. Martin and E. H. Drew, *J. Am. Chem. Soc.*, **83**, 1232 (1961), and F. D. Greene, W. Adam and J. E. Cantrill, *ibid.*, **83**, 3461 (1961).

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

(18) The extreme susceptibility of unsaturated peroxides to induced decomposition was first noted by W. Cooper, *J. Chem. Soc.*, 2408 (1952), and more recently by Lamb.<sup>12</sup>

(20) At the suggestion of the referee, the "wrong" esters were prepared; *i.e.*, *endo*-2-norbornyl *exonorbornane*-2-carboxylate and the *exo-endo* ester. The melting points of the *exo-endo*- and *endo-exo*-esters (possible products from I<sub>x</sub>) were 120-121° and 113-115°, respectively; their mixture melting point was depressed, and their infrared spectra differed appreciably in the 9-10  $\mu$  region. It is not likely that the ester from I<sub>x</sub> contained over 10% of the alkyl stereoisomer. But the melting points of the *endo-endo*- and *exo-endo*-esters (possible products from I<sub>n</sub>) were nearly identical (109-110°

TABLE II

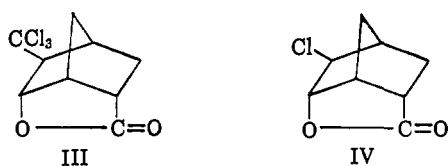
PRODUCTS FROM *exo*- AND *endo*-NORBORNANE-2-CARBONYL PEROXIDES AND *exo*- AND *endo*-NORBORNENE-5-CARBONYL PEROXIDES IN CARBON TETRACHLORIDE (72 HOURS AT 78°)

	I <sub>x</sub>	I <sub>n</sub>	II <sub>x</sub>	II <sub>n</sub>
mmoles of peroxide in 50 ml. of solvent	1.11	1.17	1.25	1.25
Products, mmoles per mmole of peroxide				
Carbon dioxide	1.59, 1.58 *1.50, *1.51	1.48, 1.47 *1.51, 1.50	1.11, 1.14 *1.22, 1.21	0.98, 0.95 *1.08, 1.06
Ester <sup>b</sup>	0.20, 0.21 * .25, .25	0.30, 0.29 * .23, .24	0.30, 0.29, 0.30 *0.42, 0.41, 0.38	0.18, 0.15, 0.25 *0.27, 0.26, 0.29
Acid <sup>c,d</sup>	.22, .23 * .30, .29	.12, .13 * .16, .16		
Lactone <sup>e</sup>			0.30, 0.30, 0.31 *0.33, 0.34, 0.34	0.80, 0.75, 0.78 *0.57, 0.50, 0.50
Av. % carbonyl accounted for	100.7 *102.5	94.7 *95.2	86.3 *97.6	97.2 *93.5
Av. % alkyl <sup>f</sup> accounted for	31.6 *40.2	35.7 *31.6	44.4 *57.0	58.4 *53.7

<sup>a</sup> Those values marked with an asterisk are for decompositions in the presence of 0.2 M styrene. <sup>b</sup> *exo*-2-Norbornyl *exo*-norbornane-2-carboxylate from I<sub>x</sub>, the corresponding *endo-endo* ester from I<sub>n</sub>, and analogous unsaturated esters from the unsaturated peroxides; included in the latter may be some ester in which the elements of carbon tetrachloride have added to the double bond(s). See ref. 20. <sup>c</sup> *exo*-Norbornane-2-carboxylic acid from I<sub>x</sub> and the analogous *endo*-acid from I<sub>n</sub>. <sup>d</sup> A 2-chloro-3-trichloromethyl-*exo*-norbornane-5-(or 6)-carboxylic acid was isolated from II<sub>x</sub>, but not estimated. <sup>e</sup> *exo*-2-Trichloromethyl-*endo*-3-hydroxy-*endo*-norbornane-5-carboxylic lactone from II<sub>n</sub>; the lactone from II<sub>x</sub> was different from this, was not identified, and was estimated assuming the same carbonyl extinction coefficient as for the lactone from II<sub>n</sub>. <sup>f</sup> *exo*-2-Chloronorbornane, a major isolated product from I<sub>x</sub> and I<sub>n</sub>, was not estimated but probably makes up most of the unaccounted for alkyl portion; similarly, a major isolated but unestimated product from II<sub>x</sub> and II<sub>n</sub> was 2,5(or 2,6)-dichloro-3-trichloromethylnorbornane. Traces of *exo*-5-chloronorbornene were also isolated from II<sub>x</sub> and II<sub>n</sub>.

portion of the peroxide was essentially quantitatively accounted for as carbon dioxide + ester + acid. The major (60–68%) unaccounted for fraction of the alkyl portion was undoubtedly present principally as *exo*-2-chloronorbornane, isolated in large scale experiments but not estimated quantitatively. The nature and amounts of products from I<sub>x</sub> and I<sub>n</sub> were not seriously altered by a large excess of styrene.

The unsaturated peroxides (II<sub>x</sub>, II<sub>n</sub>) behaved rather differently. The carbon dioxide yield was sharply reduced in comparison with the saturated peroxides, from about 75–78% to 49–55%, although the yield of ester or acid was not correspondingly increased. The crude reaction mixture from each peroxide showed a carbonyl band at 5.58 μ, possibly due to a lactone.<sup>22</sup> Work-up of the products from II<sub>n</sub> (see Experimental part for details) led to isolation of a crystalline lactone, m.p. 100–101°, which is assigned structure III on the basis of elemental analysis, infrared and n.m.r. spec-



trum (the latter was similar to that of authentic lactones containing I,<sup>23a</sup> Br<sup>23b</sup> or Cl<sup>24</sup> in place of the CCl<sub>3</sub> group) and extreme resistance of the halogens to hydrolysis (aliphatic trichloromethyl group<sup>25</sup>). The lactone was recovered from refluxing silver nitrate in 80% aqueous acetone, and from 4 hours at 100° with fuming and 107–109°, respectively) and their infrared spectra differed only in intensity of bands in the fingerprint region. Although a m.m.p. was depressed, it is quite possible that appreciable amounts of the isomer in which the alkyl portion had the inverted configuration may have gone undetected in the ester from I<sub>n</sub>.

(21) Cf. E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958); S. J. Cristol, J. R. Douglass, W. C. Firth, Jr., and R. E. Krall, *J. Org. Chem.*, **27**, 2711 (1962).

(22) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1958, p. 186.

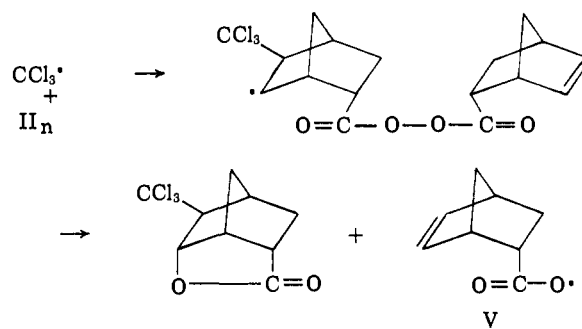
(23) (a) D. Ver Nooy and C. S. Rondestvedt, Jr., *J. Am. Chem. Soc.*, **77**, 3583 (1955); (b) J. D. Roberts, E. R. Trumbull, Jr., W. Bennett and R. Armstrong, *ibid.*, **72**, 3116 (1950).

(24) See Experimental part of this paper.

(25) R. Kh. Freidlina and Ye. I. Vasil'eva, *Doklady Akad. Nauk S.S.S.R.*, **100**, 85 (1955).

ing nitric acid, but was hydrolyzed in moderate yield to a crystalline lactonic acid by 80% aqueous sulfuric acid (100° for 6 hours). The *exo* configuration of the trichloromethyl group is not established but seems likely considering that it approximates a *t*-butyl group in size.

Formation of lactone III rather than IV shows that the lactone does not arise from intramolecular acyloxy radical trapping, as initially hoped for, but rather from induced decomposition, by attack of a CCl<sub>3</sub> radical on the peroxide molecule. The maximum lactone yield ought not to be greater than 50%, for rapid



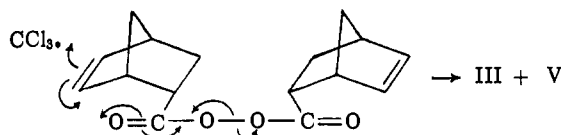
loss of carbon dioxide from the acyloxy radical V would be anticipated. The observed lactone yield was, in fact, not very much less than this (38–40%); indeed, if one corrects for the amount of ester, lactone is produced almost quantitatively according to this scheme.<sup>26</sup>

The yield of lactone decreased, as one would expect, by adding styrene. The norbornene double bond of the peroxide is, however, much more susceptible to radical attack than is that of styrene, for even with a 10-fold molar excess of styrene present the lactone was produced, though in reduced (25%) yield. Added norbornene was without effect on the decomposition rate or lactone yield; presumably it acts solely as a chain transfer agent.

One might argue that the maximum yield of III ought only to be 25%, since attack of a CCl<sub>3</sub> radical at C<sub>3</sub> or C<sub>2</sub> of the peroxide should be equally probable,

(26) The sum of mmoles of ester + lactone/mmmole of peroxide is 0.98, 0.90 and 1.03; see Table II.

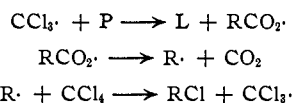
and attack at C<sub>3</sub> is unlikely to afford a lactone.<sup>27</sup> The >25% yield of III demonstrates, in fact, that attack at C<sub>2</sub> is preferred and suggests a lower energy transition state, possibly involving concerted radical attack, lactone formation and O-O bond cleavage.



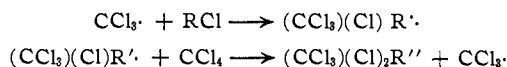
This possibility can be tested by O<sup>18</sup> labeling.

Radical V (if produced as a discrete entity) loses carbon dioxide in preference to other alternatives. The expected product of this process, 5-chloronorborene, was, however, obtained in only trace amounts (*exo* isomer from both II<sub>x</sub> and II<sub>n</sub>). In its place the CCl<sub>4</sub> addition product 2,5(or 2,6)-dichloro-3-trichloromethylnorborene was produced. Its yield was not determined, but in preparative experiments substantial quantities of identical polychlorinated material were isolated from II<sub>x</sub> and II<sub>n</sub>. There was no evidence for 3-chloronortricyclene, a possible radical rearrangement product, from either unsaturated peroxide.

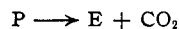
The major processes, then, which account nearly quantitatively for the products from II<sub>n</sub> may be summed up as two chain sequences



and



together with the competing non-chain reaction

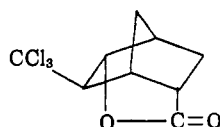


where P = peroxide, L = lactone III, R, R' and R'' are the appropriate bicyclic groups, and E = ester.

Surprisingly, a lactone was also produced during the decomposition of II<sub>x</sub>.<sup>28</sup> This lactone was not III, possibly arising from II<sub>n</sub> as an impurity in II<sub>x</sub>, for the lactone yield (15%) would require about 37% of II<sub>n</sub> as contaminant. The acid from which II<sub>x</sub> was prepared contained <2% of *endo*-acid (m.p., v.p.c. of methyl ester). Finally, conditions which lead easily to the sublimation and isolation of crystalline III from the decomposition products of II<sub>n</sub> failed to give a crystalline lactone from the crude products from II<sub>x</sub> (see Experimental for details).

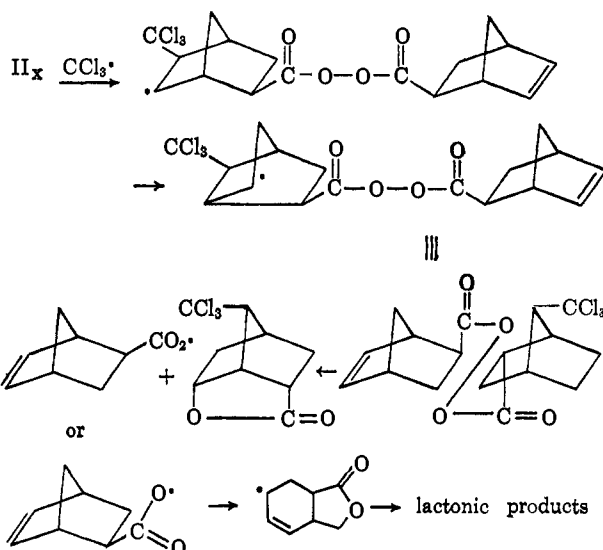
It would seem that a radical rearrangement may be necessary to rationalize a lactone from II<sub>x</sub>, since the stereochemistry for direct lactone formation is unfavorable. Two possibilities are

(27) The resulting lactone



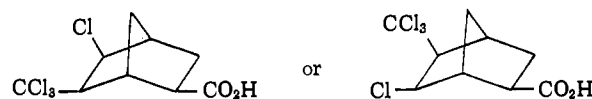
while structurally possible, is probably more strained than III and has not been isolated from II<sub>n</sub>.

(28) The possibility that the 5.58 μ band was not due to a lactone, but to *exo*-norborene-5-carbonyl chloride from which the peroxide was prepared, can be excluded because (a) the peroxide was carefully recrystallized before decomposition, (b) the intensity of the 5.58 μ band increased as decomposition proceeded, and (c) the amount of product with a 5.58 μ band was constant from different batches of peroxide.



the driving force in the latter case being relief of strain and formation of an allylic radical.<sup>29</sup> Unfortunately, attempts to isolate and identify the lactone from II<sub>x</sub> have thus far failed.

Finally, a crystalline acid VI corresponding to



VI

addition of carbon tetrachloride to *exo*-norborene-5-carboxylic acid was isolated (but not estimated) from II<sub>x</sub>.

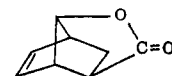
One concludes that anchimeric assistance, if involved at all, is not as important in the decomposition of the saturated peroxides I<sub>x</sub> and I<sub>n</sub> as it is in carbonium ion reactions, and that the double bond in II does not act as an intramolecular radical trap, but rather as a locus for induced decomposition, even in dilute solution and in competition with an excess of other olefin.

### Experimental<sup>30</sup>

**Preparation of the Acids and Acid Chlorides.**—*endo*-Norborene-5-carboxylic acid, m.p. 43–44°,<sup>31</sup> and *exo*-norborene-5-carboxylic acid, m.p. 43–44°,<sup>32</sup> were prepared and purified<sup>32</sup> by literature procedures. Although the acids have nearly identical melting points, small amounts of either admixed with the other caused liquefaction. *endo*-Norborene-2-carboxylic acid, m.p. 64–66°,<sup>11,31,32</sup> was obtained (94.5%) by hydrogenation of 0.616 mole of *endo*-norborene-5-carboxylic acid in 250 ml. of ethyl acetate over 0.5 g. of 5% Pd-C at room temperature and 50 p.s.i. (complete in 1 hour). *exo*-Norborene-2-carboxylic acid, m.p. 56–57°,<sup>11,32,33</sup> was similarly obtained (79%) from 0.29 mole of *exo*-norborene-5-carboxylic acid in 250 ml. of methanol with platinum oxide catalyst.

The corresponding acid chlorides were obtained (66–90%) from the acids and thionyl chloride in chloroform.<sup>34</sup> Lack of

(29) Since the yield of lactone from II<sub>x</sub> was not decreased by a large excess of styrene, the second alternative may be preferred. It should be noted that neither of these paths is sterically favorable with II<sub>n</sub>. A third alternative, abstraction of a hydrogen from C<sub>7</sub>, might lead to lactone, or derivatives thereof, without rearrangement.



(30) All microanalyses by Spang Microanalytical Laboratory, P. O. Box 1111, Ann Arbor, Mich. Melting points are uncorrected.

(31) K. Alder, G. Stein, M. Liebmann and E. Rolland, *Ann.*, **514**, 197 (1934).

(32) J. A. Berson and D. A. Ben-Efraim, *J. Am. Chem. Soc.*, **81**, 4083 (1959).

(33) K. Alder, K. Heimbach and R. Reubke, *Ber.*, **91**, 1516 (1958).

(34) W. R. Boehme, E. Schipper, W. G. Scharpf and J. Nichols, *J. Am. Chem. Soc.*, **80**, 5488 (1958).

epimerization of the acid chlorides was established by hydrolysis of a small sample.

**Preparation of the Peroxides.**—In a typical preparation, *endo-norbornene-5-carbonyl chloride* (0.624 g., 0.004 mole) was added to an ice-cold slurry of 0.156 g. (0.002 mole) of sodium peroxide and 40 ml. of ether. Water (2–4 drops) was added to the stirred mixture to initiate reaction, a temperature rise of 1–2° being observed. A few drops of water were added occasionally during the course of the reaction, which was judged complete after 5 hours, when the yellow sodium peroxide color was entirely replaced by white (sodium chloride). Ice-water (15 ml.) was then added, layers separated, the ether layer washed with ice-water, 5% sodium carbonate and ice-water and dried over magnesium sulfate. The residue after evaporation of the ether was taken up in pentane, dried (Drierite) and recrystallized at low temperature from pentane, yielding 0.48 g. (86%) of *endo-norbornene-5-carbonyl peroxide* (II<sub>n</sub>), m.p. 45–47° with gas evolution. Titration<sup>13</sup> indicated >99% purity.

By entirely analogous procedures, *exo-norbornene-5-carbonyl peroxide* (II<sub>x</sub>), m.p. 49.5–50.5°, *endo-norbornane-2-carbonyl peroxide* (I<sub>x</sub>), m.p. 87°, and *exo-norbornane-2-carbonyl peroxide* (I<sub>x</sub>), m.p. 55–56°, were obtained in 53, 60 and 72% yields with purities of 97, >99 and 94%, respectively.

**Peroxide Titration.**—The method of Silbert and Swern<sup>13</sup> was tested for applicability to diacyl peroxides by standardizing the same sodium thiosulfate solution against potassium iodate and against purified benzoyl peroxide using the following procedure. To an appropriate amount of benzoyl peroxide dissolved in carbon tetrachloride in a 125 ml. iodine flask there was added a small piece of Dry Ice to purge the oxygen. Acetic acid (5 ml.) containing 0.0005% ferric chloride hexahydrate, and 0.5 ml. of saturated aqueous sodium iodide were successively added, and the mixture allowed to stand in the dark for 25 minutes. Water (20 ml.) was added, and the magnetically stirred mixture was titrated with ca. 0.01 N sodium thiosulfate, 5 ml. of starch solution being added near the end as indicator. In one case, five determinations against potassium iodate gave an average normality of 0.01310 ± 0.00008; for the same solution standardized against benzoyl peroxide, an average normality of 0.01317 ± 0.00008 was obtained. The small difference may reflect either impurity in the benzoyl peroxide, error in the method, or both, but the method was sufficiently accurate for the present work, and was used both to estimate purity of the peroxides and to follow their thermal decomposition.

**Products from *endo-Norbornane-2-carbonyl Peroxide* (I<sub>n</sub>).**—A 0.05 N solution of I<sub>n</sub> in carbon tetrachloride (250 ml.) was refluxed for 24 hours, after which most of the solvent was removed at atmospheric pressure (maximum pot temperature 85°) through a 600 × 7 mm. vacuum jacketed tantalum wire spiral column. The pressure was then reduced to 11 mm. and distillate boiling to 80° was collected; gas chromatography showed a single peak, and the infrared spectrum of a collected sample was essentially identical with that of *exo-2-chloronorbornane*.

The pot residue was taken up in ether, extracted with 10% sodium hydroxide, dried (magnesium sulfate) and the residue after ether removal was sublimed at 100° and 10 mm. Recrystallization of the sublimate from pentane gave 0.12 g. of *endo-2-norbornyl endo-norbornane-2-carboxylate*, m.p. 106–108°, identical (m.m.p., infrared) with an authentic sample (*vide infra*). The alkaline extract, on acidification and work-up, gave *endo-norbornane-2-carboxylic acid*, m.p. 60–62° (identity by m.m.p., infrared).

***endo-2-Norbornyl endo-Norbornane-2-carboxylate.***—*endo-2-Hydroxynorbornane*, m.p. 144–145°,<sup>36</sup> was prepared by lithium aluminum hydride reduction of *endo-2-acetoxy-norbornane*<sup>36</sup> which itself was prepared by hydrogenation of *endo-5-acetoxy-norbornene*<sup>36</sup> in acetic acid with platinum. *endo-Norbornane-2-carbonyl chloride* (1.4 g., 8.7 mmoles) was added to *endo-2-hydroxynorbornane* (1.12 g., 9.4 mmoles) in 50 ml. of carbon tetrachloride. Pyridine (4 ml.) was added and the mixture refluxed for 2 hours, then poured onto 70 g. of ice. Ether extracts were washed successively with 3 N hydrochloric acid, 5% sodium carbonate and water. After removal of the solvent from the dried (magnesium sulfate) ether solution, the residue was sublimed (110° at 11 mm.), then recrystallized from pentane, yielding 1.3 g. (64%) of *endo-2-norbornyl endo-norbornane-2-carboxylate*, m.p. 109–110°;  $\epsilon$  for the 5.79  $\mu$  carbonyl peak was 470 l. mole<sup>-1</sup> cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>15</sub>H<sub>22</sub>O<sub>2</sub>: C, 76.88; H, 9.46. Found: C, 76.84; H, 9.47.

**Products from *exo-Norbornane-2-carbonyl Peroxide* (I<sub>x</sub>).**—The procedure was identical with that for I<sub>n</sub>. The alkyl halide had the same infrared spectrum as that from I<sub>n</sub>. The ester (0.15 g.), m.p. 118–119°, was identical (m.m.p., infrared) with authentic (*vide infra*) *exo-2-norbornyl endo-norbornane-2-carboxylate*. The acid, m.p. 50–52°, was *exo-norbornane-2-carboxylic acid* (m.m.p., infrared).

***exo-2-Norbornyl endo-Norbornane-2-carboxylate.***—*exo-2-Hydroxynorbornane*, m.p. 123–123.5°, prepared by the method of Bruson and Riener,<sup>36</sup> was esterified with *exo-norbornane-2-carbonyl chloride* as described above for the *endo-endo* ester. The product (64%), m.p. 120–121°, had an extinction coefficient for the 5.79  $\mu$  carbonyl band of 489 l. mole<sup>-1</sup> cm.<sup>-1</sup>.

*Anal.* Calcd. for C<sub>15</sub>H<sub>22</sub>O<sub>2</sub>: C, 76.88; H, 9.46. Found: C, 76.74; H, 9.41.

**Products from *endo-Norbornene-5-carbonyl Peroxide* (II<sub>n</sub>).**—Five grams of II<sub>n</sub> in 25 ml. of carbon tetrachloride was refluxed for 24 hours, after which the solvent was removed as with the saturated peroxides. The alkyl halide, isolated in very small yield by vacuum distillation followed by gas chromatography, was identified by infrared as *exo-5-chloronorbornane*. The residue contained ester (5.77  $\mu$ ), lactone (5.58  $\mu$ ) and polychlorinated material. It was taken up in a little ether, stirred with 10 ml. of 5% sodium carbonate containing a pellet of sodium hydroxide for 16 hours at room temperature, then extracted with ether. After drying (Drierite) and removal of the solvent, the residue still showed the ester (5.77  $\mu$ ) but not the lactone band. (Indeed, the ester was not appreciably hydrolyzed even after 1 hour reflux with 20% potassium hydroxide in aqueous dioxane.) The alkaline lactone-containing extract was discarded, as the lactone was more easily isolated by direct sublimation as described below.

The lactone-free fraction was distilled, yielding carbonyl-free polychlorinated hydrocarbon, b.p. 92–93° at 0.07 mm.

*Anal.* Calcd. for C<sub>6</sub>H<sub>9</sub>Cl<sub>5</sub>: C, 34.0; H, 3.2; Cl, 62.8. Found: C, 35.3; H, 3.7; Cl, 60.6.

Ester was not isolated directly from the remaining ester-containing residue but was reduced to the corresponding alcohols. The residue (ca. 3 g.) was dissolved in 25 ml. of anhydrous ether and added dropwise to 1.5 g. of lithium aluminum hydride in 50 ml. of ether. After 1 hour reflux followed by hydrolysis with 6 N hydrochloric acid and the usual work-up, there was obtained on distillation *endo-5-hydroxymethylnorbornane* (80–110° at 13 mm.), identified as its 3,5-dinitrobenzoate, m.p. 80–81°, m.m.p. and infrared spectrum identical with that of an authentic sample (*vide infra*). A small higher boiling fraction (110–150° at 13 mm.) gave an unidentified 3,5-dinitrobenzoate, m.p. 183–184°. The residue from this distillation gave a 3,5-dinitrobenzoate, m.p. 105–106°, which was identical with that prepared from *exo-5-hydroxynorbornane*, probably due to epimerization during the derivatization.

In another decomposition of II<sub>n</sub>, the residue after solvent removal was subjected directly to Hickman molecular distillation. After the polychlorinated hydrocarbon (*vide supra*) was removed, a white crystalline solid sublimed on the walls of the still. This was collected and recrystallized from ether; m.p. 100–101°. It showed a carbonyl band at 5.58  $\mu$ , and is assigned the structure (*exo?*)-2-trichloromethyl-*endo-3-hydroxy-endo-norbornane-5-carboxylic lactone* (III). Its n.m.r. spectrum was similar to those in which the trichloromethyl group was replaced by iodine,<sup>22</sup> bromine<sup>23</sup> or chlorine.

*Anal.* Calcd. for C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>Cl<sub>3</sub>: C, 42.35; H, 3.55; Cl, 41.65. Found: C, 42.60; H, 3.70; Cl, 41.71.

The lactone was recovered (94%) after 2 hours reflux with silver nitrate in 80% aqueous acetone, and also (>99%) after warming on a steam-bath with fuming nitric acid for 4 hours,<sup>23</sup> but hydrolyzed when 100 mg. was heated with 4 ml. of 80% sulfuric acid on a steam-bath for 6 hours. The chlorine-free acid (40 mg.), m.p. 119–120° after sublimation followed by recrystallization from pentane-ether, had lactone (5.58  $\mu$ ) and acid (5.87  $\mu$ ) carbonyl bands of nearly equal intensity. It is probably the 3,5-lactone of *endo-3-hydroxy-(exo?)2-endo-5-norbornane-dicarboxylic acid*; the small quantity and difficulty in purification gave a sample with only a moderately acceptable analysis.

*Anal.* Calcd. for C<sub>9</sub>H<sub>10</sub>O<sub>4</sub>: C, 59.35; H, 5.53. Found: C, 60.68; H, 6.15.

Attempts to synthesize lactone III by photochemical or benzoyl peroxide-catalyzed addition of bromotrichloromethane to *endo-norbornene-5-carboxylic acid* or its methyl ester led only to polymers.

***endo-5-Hydroxymethylnorbornane 3,5-Dinitrobenzoate.***—Methyl *endo-norbornene-5-carboxylate*<sup>23</sup> was reduced with lithium aluminum hydride in the usual fashion, giving *endo-5-hydroxymethylnorbornane*, b.p. 98–100° at 11 mm.,  $n_D^{25}$  1.4949, which, on refluxing with 3,5-dinitrobenzoyl chloride in carbon tetrachloride containing pyridine, gave the 3,5-dinitrobenzoate, m.p. 80–81° from pentane-ethyl acetate.<sup>37</sup>

(36) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, **67**, 723 (1945).

(37) After this work was completed, J. A. Berson, J. S. Wallia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff and D. Willner, *ibid.*, **83**, 3986 (1961), reported preparation of this alcohol from the corresponding acid by lithium aluminum hydride reduction, and derivatized it as the phenylurethane.

*Anal.* Calcd. for  $C_{15}H_{14}N_2O_6$ : C, 56.60; H, 4.40. Found: C, 56.56; H, 4.41.

*exo-2-Chloro-endo-3-hydroxy-endo-norbornane-5-carboxylic Lactone IV.*—*endo-Norbornene-5-carboxylic acid* (5 g., 0.0363 mole) was dissolved in a solution of 15 g. of sodium bicarbonate in 225 ml. of water. The magnetically stirred solution was cooled in an ice-bath and chlorine gas was passed in until the solution took on a green-yellow color. The mixture was then extracted with ether, and the ether layers washed successively with water, 10% sodium thiosulfate and water. After drying (calcium chloride) and evaporation of the ether, the residual oil was crystallized from pentane-ethyl acetate by cooling in Dry Ice. Recrystallization gave 3 g. (37%) of lactone, m.p. 75–76°.

*Anal.* Calcd. for  $C_8H_9O_2Cl$ : C, 55.65; H, 5.26; Cl, 20.56. Found: C, 55.01; H, 5.14; Cl, 21.92.

**Products from *exo-Norbornene-5-carbonyl Peroxide* (II<sub>x</sub>).**—A solution of 5 g. of the peroxide in 25 ml. of carbon tetrachloride was refluxed for 24 hours, then distilled as with the *endo*-isomer. Distillate collected up to 85° at 15 mm. contained, in addition to solvent, small amounts of the identical (infrared, retention time) alkyl halide obtained from II<sub>n</sub>. The residue showed both ester (5.77 μ) and lactone (5.58 μ) carbonyl bands, and was freed of lactone, as with the products from II<sub>n</sub>, by extraction with sodium carbonate and sodium hydroxide (the alkaline extracts in this case were saved and their work-up is described below). Distillation of the neutral material gave polychlorinated hydrocarbon (up to 160° at 1 mm.) identical, by infrared, with that from II<sub>n</sub>. The ester, collected between 160 and 220° at 1 mm., was reduced with lithium aluminum hydride as above. Distillation of the resulting alcohols gave *exo-5-hydroxymethylnorbornene*, identified as its 3,5-dinitrobenzoate, m.p. 96–98°. The pot residue gave *exo-5-hydroxynorbornene 3,5-dinitrobenzoate*, m.p. 104–105°. Mixture melting points and infrared spectra of these derivatives were identical with those of authentic samples (*vide infra*).

Acidification of the lactone extract gave a small amount of an acid, m.p. 176–177.5°, which is probably 4(or 5)-trichloromethyl-5(or 4)-chloronorbornane-2-carboxylic acid.

*Anal.* Calcd. for  $C_8H_9O_2Cl_4$ : C, 37.00; H, 3.45; Cl, 48.60. Found: C, 38.21; H, 3.85; Cl, 49.34.

No lactone was recovered, nor could any be isolated using the direct sublimation method, as with II<sub>n</sub>.

*exo-5-Hydroxymethylnorbornene 3,5-Dinitrobenzoate.*—The alcohol, prepared by lithium aluminum hydride reduction of the corresponding acid, had a b.p. of 94–95° at 11 mm.,  $n_D^{20}$  1.4972. The 3,5-dinitrobenzoate, prepared as above, gave colorless needles from pentane-ethyl acetate; m.p. 98–99°. <sup>37</sup>

*Anal.* Calcd. for  $C_{15}H_{14}N_2O_6$ : C, 56.60; H, 4.40. Found: C, 56.45; H, 4.27.

*exo-5-Hydroxynorbornene 3,5-Dinitrobenzoate.*—*exo-5-Hydroxynorbornene*,<sup>23</sup> m.p. 101.5–103.5°, converted to its 3,5-dinitrobenzoate as above, gave colorless needles from pentane-ethyl acetate; m.p. 104–105°.

*Anal.* Calcd. for  $C_{14}H_{12}N_2O_6$ : C, 55.26; H, 3.94. Found: C, 55.25; H, 3.98.

*endo-5-Norbornenyl endo-Norbornene-5-carboxylate.*—The ester, prepared in a manner analogous to the corresponding saturated ester, was obtained in 43.6% yield, m.p. 60.5–61°;  $\epsilon$  of the 5.77 μ band was 409 l. mole<sup>-1</sup> cm.<sup>-1</sup>.

*Anal.* Calcd. for  $C_{15}H_{16}O_2$ : C, 78.23; H, 7.88. Found: C, 77.97; H, 7.71.

*exo-5-Norbornenyl exo-Norbornene-5-carboxylate.*—The ester, prepared as above, was obtained in 48.3% yield, m.p. 72–73°;  $\epsilon$  of the 5.77 μ band was 473 l. mole<sup>-1</sup> cm.<sup>-1</sup>.

*Anal.* Calcd. for  $C_{15}H_{16}O_2$ : C, 78.23; H, 7.88. Found: C, 77.87; H, 7.74.

**Quantitative Estimation of the Decomposition Products.**—Decomposition for product estimation was carried out in a reaction flask equipped with a reflux condenser and a fritted-disk nitrogen inlet. Nitrogen, purified by passing successively through Fieser solution (two towers), saturated lead acetate, concentrated sulfuric acid and solid potassium hydroxide pellets, was presaturated with carbon tetrachloride. Following the reaction vessel in the train were an aniline trap (to remove phosgene), two Dry Ice traps, a tared Ascarite-Anhydron tube, a protective Ascarite-Anhydron tube and a Drierite tube.

For carbon dioxide determinations, the entire system including a 0.05 N peroxide solution in carbon tetrachloride was swept for 1 hour, after which the peroxide solution was refluxed for a minimum of 12 half-lives under continuous nitrogen sweep. Reflux was discontinued and the Dry Ice traps allowed to warm to room temperature. The tared Ascarite trap was weighed before and 30 minutes after reflux, the difference being taken as the weight of carbon dioxide liberated by the peroxide. The results are in Table II.

Carbonyl-containing products were determined by quantitative infrared analysis of the refluxed peroxide solutions. The extinction coefficients were determined on pure specimens of each compound. Those for the four esters were given with their preparation. The extinction coefficients for *endo*- and *exo*-norbornene-2-carboxylic acids are 505 and 499 l. mole<sup>-1</sup> cm.<sup>-1</sup>, respectively, and that for lactone III is 726 l. mole<sup>-1</sup> cm.<sup>-1</sup>. The latter value was also used to estimate the lactone from II<sub>x</sub>. All results are presented in Table II.

**Kinetic Procedure.**—The decomposition rates were followed by iodometric titration of remaining peroxide (the detailed procedure is given above), by disappearance of the 5.65 μ peroxide band, and by appearance of certain product bands in the infrared. A typical procedure follows. About 50 ml. of 0.05 N peroxide solution was purged of oxygen by bubbling purified (as in the carbon dioxide determinations described above) nitrogen through the solution for 15 minutes. The solution was then introduced with a hypodermic syringe as *ca.* 5-ml. samples into ten ampoules. The ampoules were 5-ml. Kimble Neutraglass, cleaned by immersion in hot concentrated sulfuric acid for 12 hours, rinsed 4 times with distilled water, once with acetone, and dried at 120° for 12 hours prior to use. The filled ampoules were sealed at -70°, placed in a metal cage and lowered in a mineral oil-bath controlled to 0.1°. Two minutes after immersion was taken as zero time. At various time intervals well suited to analysis by the Guggenheim method,<sup>14</sup> ampoules were removed, quenched in ice-water and stored at -70° until completion of the run, at which time 4-ml. aliquots were removed and titrated or analyzed by infrared techniques.

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