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

Conformational Effects on Diacyl Peroxide Decompositions[1]

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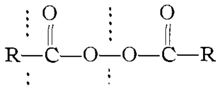
The diacyl peroxide of *cis*-4-*t*-butylcyclohexanecarboxylic acid decomposed, in carbon tetrachloride, about twice as fast as the *trans* isomer. The principal (~90%) organic product (in 1,1,2,2-tetrabromoethane) was *cis*-4-*t*-butylcyclohexyl *cis*-4-*t*-butylcyclohexanecarboxylate from the *cis*-peroxide, and the corresponding *trans–trans* ester from *trans*-peroxide. It is clear that C–C bond breaking (axial > equatorial) as well as O–O bond breaking is involved in the rate-determining step. The problem of free radical *vs.* cyclic mechanism for ester formation is discussed. 4-*t*-Butylcyclohexyl bromides (52–55% *trans*, 48–45% *cis*) were minor products from both peroxides. Improved syntheses of the pure isomeric acids and certain of their derivatives are given.

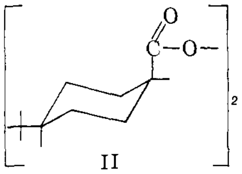
The initial step in the spontaneous decomposition of benzoyl peroxide has been demonstrated clearly to involve the formation of two benzoyloxy radicals by rupture only of the O–O bond, since these radicals could be scavenged by iodine and recovered totally in the presence of water as benzoic acid.[2] Similar experiments with acetyl peroxide[3] gave predominantly methyl iodide rather than acetic acid, suggesting that acetoxy radicals decompose to methyl radicals and carbon dioxide simultaneously with their formation, or nearly so.[3–5] Biscyclopropaneformyl peroxide[6] appears to be an intermediate case, cyclopropanecarboxylic acid and cyclopropyl iodide having been isolated from a similar experiment in nearly equal amounts. Kinetic evidence was presented[6] for C–C as well as O–O bond cleavage in the rate-determining step of certain aliphatic diacyl peroxide decompositions. Thus those peroxides which gave secondary radicals (for example, I, R = cyclohexyl) free of undue strain (*vide infra*) decomposed 20–30 times faster than those producing primary alkyl radicals (I, R = cyclopentylmethyl). Furthermore, when R (in I) was cyclopropyl or cyclobutyl, the peroxides decomposed abnormally slowly for a secondary R, a reflection of the strain or high energy of small ring free radicals. Resonance stabilization of R· has also been shown to be a factor in the decomposition rates of diacyl peroxides[7] and peresters.[8]



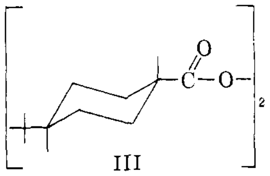
$$R-\overset{\overset{\textstyle O}{\|}}{C}-O-O-\overset{\overset{\textstyle O}{\|}}{C}-R$$

I

Although the evidence for C–C bond breaking in the cases referred to seems reasonable, one may raise the possible objection that the various alkyl groups have different electrical (especially inductive) effects which, if relayed to the O–O bond, might affect the decomposition rates in the observed fashion. It seemed worthwhile, therefore, to study two peroxides in which all electrical effects would be identical, yet in which some factor would influence the energy of the C–C bonds in question, but not affect the O–O bond energy. The diacyl peroxides related to *cis*- and *trans*-4-*t*-butylcyclohexanecarboxylic acids appeared to fulfil these requirements, with the possible exception of a small difference in a weak direct field effect; the C–C bonds in question would be axial or equatorial, respectively, provided that the *t*-butyl group were equatorial in each peroxide.[9–11] The C–C bond in II ought therefore to be the more strained, whereas the O–O bonds should be of equal energy content in the two peroxides. This paper describes the synthesis of peroxides II and III and their rates and products of decomposition under certain limited experimental conditions.



II



III

Results

Preparation of the Peroxides.—The preparation of 4-*t*-butylcyclohexanecarboxylic acids by hydrogenation of *p*-*t*-butylbenzoic acid has been described previously, procedures being modeled after the corresponding methyl and isopropyl compounds.[12] Platinum in acetic acid at low or high pressure gave[13] predominantly (70%) the *cis* isomer but the rather involved isolation procedure gave the pure product in only small yield. The *cis* isomer also appears to be formed predominantly (m.p. 111° given) in the hydrogenation of 1-*t*-butylcyclohexene-4-carboxylic acid in an unspecified manner.[14] The *trans*-acid has been obtained from high pressure (about 1500 p.s.i.) and temperature (200-225°) hydrogenation of an alkaline solution of 4-*t*-butylbenzoic acid over Raney nickel.[13,15] The method appears to be erratic, since difficulty was experi-

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[1] This work was supported by the National Science Foundation (NSF-G3289), whose financial assistance is appreciated.

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

[3] C. Walling and R. B. Hodgdon, Jr., unpublished results quoted in C. Walling "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 493.

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

[5] Alternatively, acetoxy radicals may react with iodine to give acetyl hypoiodite which may decompose to methyl iodide and carbon dioxide more rapidly than it hydrolyzes to acetic acid.

[6] H. Hart and D. P. Wyman, THIS JOURNAL, **81**, 4891 (1959).

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

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

[9] S. Winstein and N. J. Holness, *ibid.*, **77**, 5562 (1955).

[10] E. L. Eliel and R. S. Ro, *Chemistry & Industry*, 251 (1956); THIS JOURNAL, **79**, 5995 (1957); E. L. Eliel and C. A. Lukach, *ibid.*, **79**, 5986 (1957).

[11] E. L. Eliel and R. S. Ro, *ibid.*, **79**, 5992 (1957).

[12] R. G. Cooke and A. K. Macbeth, *J. Chem. Soc.*, 1245 (1939).

[13] Robert D. Stolow, Ph.D. thesis, University of Illinois, 1956. We are indebted to Professor Ernest L. Eliel for calling this thesis to our attention, and to Professor David Y. Curtin for additional details.

[14] K. Alder, K. Heimbach and E. Kuhle, *Chem. Ber.*, **86**, 1364 (1953). The procedure, judging from others which are described, may have used platinum and acetic acid.

[15] N. V. de Bataafsche Petroleum Maatschappij, British Patent 703,516 (1954); *C. A.*, **49**, 5522 (1955).

enced in repeating the hydrogenation after one successful run.[13] The *trans* isomer may also be obtained by isomerizing the *cis* under hydrogenation conditions favorable to the formation of *trans* product.[15]

We replaced the high pressure procedure for the *trans* isomer by a consistently successful low pressure method using 5% rhodium-on-charcoal. Work-up procedures were modified and details are given in the Experimental part for the preparation of pure *cis*-4-*t*-butylcyclohexanecarboxylic acid in 43% yield and the pure *trans* isomer in 34% yield from *p*-*t*-butylbenzoic acid. An additional 8% of pure *cis* isomer was isolated during the preparation of the *trans*-acid.

The acids were converted to acid chlorides with thionyl chloride. The *trans* isomer gave no difficulty; hydrolysis of distilled *trans*-acid chloride gave pure *trans*-acid. Product from distillation of *cis*-chloride also gave *trans*-acid on hydrolysis. Crude *cis*-chloride, however, obtained as a residue after removing the excess thionyl chloride at room temperature (vacuum), gave pure *cis*-acid on hydrolysis. The amides (*cis*, m.p. 161°; *trans*, m.p. 134-135°) and anilides (*cis*, m.p. 190-191°; *trans*, m.p. 133-135°) were prepared.

The peroxides II and III were obtained by reaction of the acid chlorides (crude *cis*, distilled *trans*) with sodium peroxide in moist ether near ice temperature. A portion of the chlorides hydrolyzed, and recovered acids were either pure *cis* or *trans*, showing no isomerization had occurred. The *cis*-peroxide II, though crystalline, was only about 75% pure (by iodometric titration[16]), contaminants being *cis*-acid anhydride. These impurities did not interfere with the kinetic measurements. *trans*-Peroxide III was obtained without difficulty in > 99% purity,[16] m.p. 89°.

Kinetics and Products.—The kinetic procedure was similar to that described in the previous paper[6] based on the decrease in intensity with time of the principal peroxide carbonyl band (5.65 μ) in the infrared. This band is distinctly removed from other possible interfering bands, namely anhydride (5.52 and 5.73 μ), ester (5.78 μ), mixed ester-anhydride (5.51 μ[17]) and acid (5.90 μ). Minor refinements are detailed in the Experimental part. The data are summarized in Table I, together with previous data[6] for I (R = cyclohexyl). Iodometric determination of the decomposition rate[16] gave values which agreed with those obtained by infrared analysis but had slightly larger limits of error (see footnote to Table I).

Although rates were measured in carbon tetrachloride, 1,1,2,2-tetrabromoethane was used for the product analysis, because pure *cis*- and *trans*-4-*t*-butylcyclohexyl chlorides have not yet been described, whereas the corresponding bromides have.[18] Only major products (carbon dioxide, *cis*- and *trans*-bromides and esters) were determined[19] but they accounted for over 90% of the products. The results are given in Table II.

TABLE I

DECOMPOSITION OF *cis*- AND *trans*-4-*t*-BUTYLCYCLOHEXANEFORMYL PEROXIDES (II AND III) IN CARBON TETRACHLORIDE

Peroxide	t, °C.	$k_1 \times 10^5$, sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$ cal./°
II	40.00	8.65 ± 0.35[a]		
	45.45	13.2 ± .41		
	50.70	23.5 ± .45	18.2 ± 0.6	−19.0
	50.70	22.6 ± 1.1		
III	40.00	4.25 ± .23		
	44.70	7.10 ± .38	19.5 ± 0.9	−16.1
	44.70	7.62 ± .55		
	49.80	11.4 ± .4[b]		
I (R = cyclohexyl)	35.0	2.87 ± .30		
	40.0	5.22 ± .30	26.1 ± 1.1	− 3.1
	40.0	5.29 ± .35		
	45.0	9.67 ± .5		

[a] Iodometric rate constant = $8.4 \pm 1.3 \times 10^{-5}$ sec.$^{-1}$.
[b] Iodometric rate constant = $11.9 \pm 0.6 \times 10^{-5}$ sec.$^{-1}$.

TABLE II

PRODUCTS FROM PEROXIDES II AND III DECOMPOSED IN 1,1,2,2-TETRABROMOETHANE AT 50.7° (MOLES OF PRODUCT/MOLE OF PEROXIDE DECOMPOSED)

Product	Peroxide II	Peroxide III
cis-4-*t*-Butylcyclohexyl bromide	0.051	0.013
trans-4-*t*-Butylcyclohexyl bromide	.062	.014
Ester[a]	.904	.90
Carbon dioxide	1.22	1.14

[a] *cis*-4-*t*-Butylcyclohexyl *cis*-4-*t*-butylcyclohexanecarboxylate from II and the corresponding *trans*–*trans* ester from III.

The geometry of the ester in each case was determined by comparison of its infrared spectrum with those of authentic samples of the four isomeric esters, each of which was prepared separately from the *cis*- or *trans*-acid chloride and *cis*- or *trans*-4-*t*-butylcyclohexanol[11] in pyridine. The esters were nearly pure *cis*–*cis* from II and *trans*–*trans* from III.[20]

Discussion

Winstein and Holness[9] and Eliel and Ro[10,11] employed the *t*-butyl group as a remote but compelling control over conformations of flexible cyclohexane derivatives; the reasonable assumption was made that the *t*-butyl group occupied an equatorial position in both *cis* and *trans* isomers of 4-*t*-butylcyclohexanols[9,11] and their half acid phthalates,[9] tosylates[9,10] and bromides.[18] The ionization constants of the acids, determined in 66% dimethylformamide,[13] are consistent with the view that in these compounds also, *t*-butyl is predominantly equatorial, even in the *cis* isomer.[21] If C–C bond breaking (or stretching) were important in diacyl peroxide decompositions, one would therefore antici-

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

(17) D. B. Denney, *ibid.*, **78**, 590 (1956).

(18) E. L. Eliel and R. G. Haber, *Chemistry & Industry*, 264 (1958).

(19) Carbon dioxide was determined gravimetrically. The esters were determined from quantitative infrared spectra of the crude reaction mixture. Distillation of the latter at 0.5 mm. gave distillate consisting of solvent and the *t*-butylcyclohexyl bromides, which were then also determined using quantitative infrared.

(20) The infrared spectra were identical with those of pure synthetic samples, but experiments with the synthetic mixtures showed that the limit of detectability of the other isomer (say, *trans*–*cis* ester in *cis*–*cis* ester) was about 10%.

(21) Models of the *cis*-acid show that if a "flexible" rather than "chair" conformation obtains, both large substituents have greater freedom of motion, but of course certain hydrogen–hydrogen interactions become less favorable. It is possible that in (*e*,*a*)-type molecules where both substituents are large, one may be obliged to consider these flexible conformations.

pate that II, with an axial C–C bond should decompose more rapidly than III (C–C equatorial), assuming that only ground state energy differences are important in radical formation. The observed rate ratio k_{cis}/k_{trans} was approximately 2 in the expected direction. This may be compared with the ratio of 3-4 observed for solvolysis of tosylates,[9] another presumably "spontaneous" process.[22]

One would like to conclude that a conformational effect on a free radical process has been demonstrated, and that it constitutes further evidence for C–C as well as O–O bond stretching in free radical aliphatic diacyl peroxide decompositions.[6] Unfortunately the matter is not quite so straightforward. The case rests very much on the as yet incompletely determined mechanism of ester formation, for II and III gave only minor amounts of products ascribable to radical attack on solvent molecules; the predominant product in each instance was ester (see Table II). Since ester accounted for 90% of the product,[23] the observed rate difference between *cis*-and *trans*-peroxides must arise predominantly from differences in the transition states for the ester-forming reaction. This may or may not be a free radical process.

Kharasch, Kuderna and Nudenberg[24] found that optically active α-methylbutyryl peroxide gave, in benzotrichloride, a 30–40% yield of optically active *sec*-butyl α-methylbutyrate with predominant retention of configuration in the alcohol portion.[25] Similar results were obtained by Greene[26] from the reaction of optically active hydratropoyl chloride with sodium peroxide, presumably *via* the diacyl peroxide as an intermediate.[27] Partial racemization was taken[26] as evidence for at least some (if not entire) radical path to ester, for if a cyclic mechanism[28] were exclusively operative, complete retention of optical purity would be expected. Partial rather than complete racemization is ascribed to recombination of alkyl and acyloxy radicals in a solvent cage before the alkyl radicals achieve a statistical orientation with respect to acyloxy radicals.[25,29]

Our results are consistent with those previously cited, but perhaps show greater stereospecificity. The spectra of crude ester obtained from the peroxide decompositions were virtually identical with *cis–cis* ester from *cis*–peroxide and *trans–trans* ester from *trans*-peroxide.[20] Most certainly, "free" radicals are not involved. The possibility, earlier considered and also rejected,[26] that stereospecificity is due to asymmetric induction in the recombination step is further mitigated against here, for there would seem to be little justification for equatorial $RCO_2\cdot$ to attack a free 4-*t*-butylcyclohexyl radical only equatorially, and an axial $RCO_2\cdot$ to attack only axially.[30] The low activation energies and large negative activation entropies (Table I) are consistent with a cyclic path.

cis- and *trans*-4-*t*-butylcyclohexyl bromides were produced in low yields in the decompositions; the composition of the bromide mixture was virtually independent of the geometry of the original peroxide, being about 45-48% *cis*. Thus 4-*t*-butylcyclohexyl radicals lose their stereochemical identity before reacting with solvent molecules. We obtained a somewhat higher proportion of *cis* isomer than arises in the Hunsdiecker reaction[30] but differences in solvent and temperature may account for the results.

It is plain, then, that our data argue for a conformational effect in a free radical process only to the extent that esters are formed from peroxides by a radical path, and that stereochemistry and energetics mitigate against such a path. Whatever the mechanism, there can be no doubt of considerable C–C bond stretching in the transition state, for the difference in rates of axial *vs.* equatorial peroxides was nearly as great as that observed for an SN1 process.[9] It would be desirable to use the approach described here with a reaction that is more cleanly free-radical in the rate-determining step.

Experimental[31]

cis-4-*t*-Butylcyclohexanecarboxylic Acid.[13]—A solution of 17.8 g. (0.1 mole) of 4-*t*-butylbenzoic acid in 125 ml. of glacial acetic acid was hydrogenated at room temperature and 50 p.s.i. initial pressure using 2.0 g. of platinum oxide. The theoretical volume of hydrogen was absorbed in 2 hours. After filtration from the catalyst and evaporation to dryness under vacuum (aspirator, with warming to about 50°) the solid residue was dissolved in 50 ml. of hot 95% ethanol and 50 ml. of hot water was added. Upon cooling, 15.9 g. of white crystals, m.p. 95–106°, was obtained. Infrared analysis showed this mixture to contain about 70% *cis*- and 30% *trans*-acid. It was boiled in 300 ml. of aqueous ammonia (1 part concentrated ammonia, 9 parts water) until all dissolved. Upon cooling, white needles separated from the solution. They were filtered, washed with aqueous ammonia, and the process repeated using 225 ml. of fresh aqueous ammonia. All mother liquors were saved. The crystals were dissolved in hot water, acidified with 6 *N* hydrochloric acid to congo red, left in the refrigerator for two hours, filtered and dried, yielding 3.7 g. of pure *cis*-acid, m.p. 117–118°. Mother liquors were combined and acidified with 6 *N* hydrochloric acid to recover the acid mixture. Repetition of this entire process gave another 3.0 g., m.p. 116–118°. A third treatment gave an additional 1.2 g., m.p. 116–118° (total recovery is 62% of the *cis*-acid present, and can only be improved by great patience in

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[22] The solvolysis case is complicated by the fact that it is probably not a simple carbonium ion process, since *cis* and *trans* isomers give different products. In "non-spontaneous" processes, such as SN2 displacement, k_{cis}/k_{trans} may be much larger.[10] It will be noted from a comparison of decomposition rates at 40° (Table I) that the unsubstituted peroxide decomposed at a rate intermediate between the pure axial (II) and pure equatorial (III) conformers. Indeed, one can calculate from these rates that I (R = cyclohexyl) exists about 80% in the equatorial conformation, a not unreasonable result.

[23] The solvent seems to influence the amount of ester produced. In preliminary experiments, I (R = cyclohexyl) gave about 74% ester in *sym*-tetrabromoethane at 50°, whereas in CCl_4 at 70° only 22–24% ester was obtained[6]; III gave about 50% ester in refluxing CCl_4. Since the C–Br bond should be *more* susceptible to radical attack than the C–Cl bond, this may be a reflection of a mass effect on the stability of solvent cages.

[24] M. S. Kharasch, J. Kuderna and W. Nudenberg, *J. Org. Chem.*, **19**, 1283 (1955).

[25] In fact, there was some loss of optical purity in *both* the acid and alcohol obtained from hydrolysis of the ester.

[26] F. D. Greene, THIS JOURNAL, **77**, 4869 (1955).

[27] Comparable results were obtained by D. F. DeTar and C. Weis, *ibid.*, **79**, 3045 (1957), for optically active β-phenylisobutyryl peroxide in carbon tetrachloride.

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

[29] O^{18} experiments with carbonyl labeled peroxides (M. A. Greenbaum, Ph.D. Thesis, Yale University, 1957) showed that the oxygens do not become equivalent in ester formation, and that carbonyl oxygen ends up predominantly as alcohol oxygen in the ester. A cyclic mechanism and induced decomposition ($R\cdot + (RCO_2)_2 \rightarrow RCO_2R + RCO_2\cdot$) were used to explain the data.

[30] We are indebted to Professor Eliel for his comments on this point, for the infrared spectra of pure *cis*- and *trans*-4-*t*-butylcyclohexyl bromides, and for a sample of the mixture of bromides obtained from the Hunsdiecker reaction on the silver salts of the corresponding acids.

[31] Microanalyses by Spang Microanalytical Laboratory, Ann Arbor, Mich., and Clark Microanalytical Laboratory, Urbana, Ill.

processing mother liquors). All fractions were recrystallized from hexane, m.p. 117–118° (lit. value[13] 117–118°). The infrared spectrum was identical with that recorded by Stolow.[13] Bands at 8.69 and 9.66 μ were used to analyze *cis–trans* mixtures.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.66; H, 10.86.

A solution of 0.5 g. of *cis*-acid and 0.6 g. of N,N'-dicyclohexylcarbodiimide in 10 ml. of tetrahydrofuran was left at room temperature for 4 hours. The precipitated dicyclohexylurea was filtered and the solvent evaporated. Heating the solid residue with 20 ml. of ether dissolved the small amount of anhydride (*vide infra*) present and left a white compound which, recrystallized from cyclohexane, melted at 176–177°. Elemental analysis and infrared spectrum (with distinctive bands at 5.89, 6.01 and 9.74 μ) were consistent with the structure N-*cis*-4-*t*-butylcyclohexanoyl-N,N'-dicyclohexylurea.

Anal. Calcd. for $C_{24}H_{41}O_2N_2$: C, 73.98; H, 10.61; N, 7.19. Found: C, 73.94; H, 11.12; N, 7.22.

***trans*-4-*t*-Butylcyclohexanecarboxylic Acid.**—4-*t*-Butylbenzoic acid (17.8 g., 0.1 mole) was suspended in 100 ml. of hot water and 4 g. (0.1 mole) of sodium hydroxide was gradually added to obtain a clear solution which was hydrogenated at 100° and 50 p.s.i. initial pressure using 4 g. of 5% rhodium-on-charcoal catalyst (Baker and Co., Newark, N. J.). The theoretical volume of hydrogen was absorbed in 5 hours. A sample of the crude product, obtained by acidifying a few drops of the solution, was checked *via* infrared to be certain that aromatic bands were absent. In some runs, hydrogen uptake ceased before the theoretical volume of hydrogen was absorbed; reaction could be completed only by filtering the spent catalyst and adding fresh catalyst.

The hot solution was filtered from catalyst and the sodium salt allowed to crystallize, yielding 6.7 g., m.p. above 225°. The salt was dissolved in 200 ml. of hot water and acidified with 6 *N* hydrochloric acid (to congo red) resulting in 5.0 g. of dry acid. Recrystallization from hexane gave 4.2 g., m.p. 174–174.5° (lit. values 174.5–175°[15] and 176–177°[13]). The infrared spectrum was identical with that recorded by Stolow,[13] and had analytically useful bands at 8.24, 8.45 and 9.58 μ.

Anal. Calcd. for $C_{11}H_{20}O_2$: C, 71.69; H, 10.94. Found: C, 71.58; H, 10.83.

The filtrate from the sodium salt was diluted to 200 ml. with water and acidified with 6 *N* hydrochloric acid, yielding another 8.9 g. of dry acid, m.p. 90–101°. Ammonia treatment as described for the *cis* isomer gave 1.5 g. of pure *cis*-acid, m.p. 116–118°. Conversion of the mother liquor to sodium salt and recrystallization from hexane as above gave another 2.1 g. of pure *trans*-acid.

Reaction of the *trans*-acid with N,N'-dicyclohexylcarbodiimide at room temperature, as described above for the *cis* isomer, gave a small amount of anhydride and N-*trans*-4-*t*-butylcyclohexanoyl-N,N'-dicyclohexylurea, m.p. 190° (from cyclohexane). The infrared spectrum showed distinctive bands at 5.89, 6.01, 8.79 and 9.59 μ.

Anal. Calcd. for $C_{24}H_{41}O_2N_2$: C, 73.98; H, 10.61; N, 7.19. Found: C, 73.53; H, 10.97; N, 7.20.

***cis*-4-*t*-Butylcyclohexanoyl Chloride.**—After the initial reaction between 3.68 g. (0.02 mole) of *cis*-4-*t*-butylcyclohexanecarboxylic acid and 2.3 ml. (0.03 mole) of thionyl chloride subsided, the solution was refluxed gently (steam-bath) for 90 minutes. Excess thionyl chloride was removed *in vacuo* at room temperature (30 minutes at <1 mm. pressure). The crude acid chloride (4.1 g.) was not further purified (since distillation caused isomerization) but identified by hydrolysis to pure *cis*-acid. *cis*-4-*t*-Butylcyclohexanoamide, from the acid chloride and concentrated ammonia, recrystallized from cyclohexane, melted at 161°.

Anal. Calcd. for $C_{11}H_{21}ON$: C, 72.10; H, 11.55; N, 7.63. Found: C, 72.19; H, 11.37; N, 7.62.

cis-4-*t*-Butylcyclohexanoanilide, recrystallized from absolute ethanol, melted at 190–191°.

Anal. Calcd. for $C_{17}H_{25}ON$: C, 78.71; H, 9.72; N, 5.40. Found: C, 78.80; H, 10.50; N, 5.51.

***cis*-4-*t*-Butylcyclohexanoic Anhydride.**—A mixture of 20 ml. of pyridine and *cis*-4-*t*-butylcyclohexanoyl chloride (freshly prepared from 0.92 g. of the acid and 0.6 ml. of thionyl chloride) was allowed to stand at room temperature for four hours. Ether was added and the solution washed successively with water, 6 *N* hydrochloric acid, 10% sodium carbonate solution and water. After drying over anhydrous magnesium sulfate and removal of the ether *in vacuo*, the residue was dissolved in petroleum ether (30–60°), filtered through a short column of alumina, the solvent removed *in vacuo*, and the residue recrystallized at low temperature from pentane, yielding 0.4 g., m.p. 119–119.5°. An about equal sample of anhydride and acid gave a mixed m.p. of 114–115.5°. The infrared spectrum was in accord with the anhydride structure and showed no free acid present (twin carbonyl bands at 5.52 and 5.73 μ, none at 5.90 μ).

Anal. Calcd. for $C_{22}H_{38}O_3$: C, 75.38; H, 10.93. Found: C, 75.33; H, 10.91.

trans-4-*t*-Butylcyclohexanoyl chloride was prepared as described above for the *cis* isomer, but distilled *in vacuo* yielding 3.6 g., b.p. 85° at 1 mm., 241° at atmospheric pressure, n^{25}_{D} 1.4706. Hydrolysis gave pure *trans*-acid. The acid chloride was converted to the amide, recrystallized from cyclohexane, m.p. 134–135°.

Anal. Calcd. for $C_{11}H_{21}ON$: C, 72.10; H, 11.55; N, 7.63. Found: C, 71.99; H, 11.07; N, 7.80.

The anilide, recrystallized from heptane, had m.p. 133–135°.

Anal. Calcd. for $C_{17}H_{25}ON$: C, 78.71; H, 9.72; N, 5.40. Found: C, 78.64; H, 9.64; N, 5.41.

Bis-*cis*-4-*t*-butylcyclohexanoyl Peroxide (II).—To a cold (−7 to −10°) stirred slurry of 0.63 g. (0.0082 mole) of sodium peroxide in 40 ml. of anhydrous ether there was added 3.03 g. (0.015 mole) of crude *cis*-4-*t*-butylcyclohexanoyl chloride and the reaction initiated by addition of 1–2 drops of water. The mixture was stirred at or below −5° for 4 hours during which the yellow color of sodium peroxide was replaced by precipitated sodium chloride. After this time, addition of several drops of ice-water caused no rise in temperature and 15 ml. of ice-water was slowly added. Layers were separated and the ethereal layer washed with 15 ml. of ice-water, 15 ml. of ice-cold 2% sodium carbonate and 15 ml. of ice-water, dried over anhydrous calcium chloride. The ether was evaporated by a stream of Dry Ice-cooled anhydrous nitrogen which blew at the surface causing rotational stirring of the solution, combined with aspirator suction, the pressure difference being equallized by a drying tube open to the air. After only 5 ml. of ether was left the crystalline peroxide was filtered by suction and dried in a pre-cooled vacuum desiccator in the refrigerator, yield 1.5 g. (55%). Iodometric titration[16] indicated a purity of 75.5%; infrared showed the impurities to be mainly *cis*-4-*t*-butylcyclohexanoic anhydride and ester, presumably *cis*-4-*t*-butylcyclohexyl *cis*-4-*t*-butylcyclohexanecarboxylate. A small sample of peroxide was recrystallized at low temperatures from pentane, m.p. 74–75°; the infrared spectrum of this sample did not contain anhydride or ester bands, but peaks at 8.62, 9.42 and 11.23 μ distinguished it from *trans*-peroxide.

Work-up of the alkaline and water washes gave some pure *cis*-acid.

Bis-*trans*-4-*t*-butylcyclohexanoyl Peroxide (III).—The procedure was the same as for the *cis* isomer, but greater stability allowed the reaction time to be shortened to 1 hour without loss in yield by keeping the temperature at 0 to +5°. The *trans*-peroxide, 1.65 g. (60%), was recrystallized from pentane and melted at 89°. Titration[16] showed >99% purity; the infrared spectrum was in accord with the structure, with bands at 9.33 and 10.75 μ not present in the *cis* isomer.

Four Isomeric 4-*t*-Butylcyclohexyl 4-*t*-Butylcyclohexanecarboxylates.—A mixture of 15 ml. of pyridine, 0.78 g. (0.005 mole) of the one isomer of 4-*t*-butylcyclohexanol[9,11] and one isomer of 4-*t*-butylcyclohexanoyl chloride (freshly prepared from 0.92 g. (0.005 mole) of the corresponding acid and 0.6 ml. of thionyl chloride) was allowed to stand at room temperature for 4 hours. Ether (35 ml.) was added and the solution washed successively with two 25-ml. portions of water, 25 ml. of 6 *N* hydrochloric acid, 25 ml. of 10% sodium carbonate solution and finally with two 25-ml. portions of water. After drying over anhydrous magnesium sulfate the ether was removed *in vacuo*. The two esters having mixed conformations solidified only on standing (vacuum desiccator); the other two came out of ether solution directly as solids. All four were recrystallized from hexane. Yields were about 0.5 g. of each. Physical constants, analytical data and infrared bands are given in Table III.

TABLE III

FOUR ISOMERIC 4-*t*-BUTYLCYCLOHEXYL 4-*t*-BUTYLCYCLOHEXANECARBOXYLATES[b]

Isomer	M.p., °C.	Carbon, %[a]	Hydrogen, %[a]
cis–cis	96–96.5	78.20	11.85
trans–cis	68–69	78.34	11.92
cis–trans	54.5–55.5	78.52	11.97
trans–trans	153–154	78.23	11.65

[a] Calcd. for $C_{21}H_{38}O_2$: C, 78.21; H, 11.88. [b] Infrared bands, carbon tetrachloride solution (s = strong, m = medium, w = weak, br = broad, sh = shoulder): *cis–cis* 6.75s, 6.89s, 7.16m, 7.32s, 7.47m, 7.67m-s, 8.1sh, 8.37s, 8.54s, 8.73s, 9.01m-s, 9.12m, 9.68s, 9.98m, 10.57m, 10.74m, 11.0w, 11.15m; *trans–cis*, 6.79s, 6.87s, 7.16m, 7.32s, 7.44m, 7.67m-s, 8.4–8.55s, br, 8.73s, 8.94m, 9.13m, 9.6–9.65sh, br, 9.8–9.95s, br, 10.33m, 10.85w, 11.07m; *cis–trans*, 6.79s, 6.87s, 7.16m, sh, 7.32s, 7.56m-s, 7.90m, sh, 8.05–8.15m-s, br, 8.37s, 8.6–8.65s, 8.80m, sh, 9.02m-s, 9.65–9.70s, 9.98m, 10.31–10.41w-m, 10.78w, 11.12m; *trans–trans*, 6.73, 6.78s, twin, 6.86s, 7.16m-s, 7.30s, 7.51m-s, 7.63m, 7.86m, 8.02s, 8.12m-s, sh, 8.36s, 8.53–8.62s, 8.79m-s, 8.93m, 9.01m, 9.13m-w, 9.56s, br, 9.73–9.77s, 10.32w, 10.92m, 11.06m, 11.57w.

Kinetic Procedure.—The apparatus and procedure was similar to that previously described.[6] Nitrogen, after purification through Fieser solution, saturated lead acetate, concentrated sulfuric acid and a calcium chloride drying tower, was saturated with the organic solvent at condenser-water temperature to eliminate evaporation losses during a run. Samples were taken with a hypodermic needle, with nitrogen flow stopped momentarily, transferred to a special tube[32] fitted with a standard Luer joint which matched the infrared cells, and cooled. The concentration of peroxide at different times was determined by infrared analysis and in some instances checked by iodometric titration. The 5.65 μ band of both II and III obeyed the Beer–Lambert law over the concentration range used, with ε 0.501 and 0.538 l. cm.$^{-1}$ mmole^{-1}, respectively. The first-order rate constants (Table I) were calculated in the usual way.

Product Studies.—The apparatus was the same as used in the kinetic studies except that the exit gases were passed through a cold trap (Dry Ice–dichloromethane), a tared Ascarite tube, a protective Ascarite tube and two drying tubes (magnesium perchlorate and Drierite). A weighed amount (1.5–2.5 mmoles) of peroxide was dissolved in about 45 ml. of 1,1,2,2-tetrabromoethane (purified by crystallization), cooled in an ice-bath, swept with dry nitrogen for 20 minutes, then decomposed in a nitrogen atmosphere at 50.7° for 8 hours (*cis*-peroxide) or 12 hours (*trans*-peroxide). Carbon dioxide was determined by weighing the Ascarite tube. The reaction mixture was combined with the cold trap contents, diluted to 50 ml. with solvent, and the amount of ester determined using infrared analysis (ε 0.373 l. cm.$^{-1}$ mmoles^{-1} at 5.78 μ). The solution then was carefully distilled at 0.5 mm. and the first fraction (56°) was analyzed for *cis*- and *trans*-4-*t*-butylcyclohexyl bromides using infrared (ε 0.0432 and 0.0321 l. cm.$^{-1}$ mmoles^{-1} at 11.68 and 12.28 μ for the *cis*- and *trans*-bromides, respectively). The second fraction contained no measurable quantity of bromides. After all the solvent was removed, the residue was dried *in vacuo* and a spectrum taken to determine the isomeric composition of the esters. Results are summarized in Table II.

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[32] This tube design was similar to one of D. F. DeTar and V. Gold described by D. F. DeTar and A. A. Kazimi, THIS JOURNAL, **77**, 3842 (1955).

EAST LANSING, MICH.

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Reactions of Hydrogen Peroxide. V.[1] Alkaline Epoxidation of Acrolein and Methacrolein

BY GEORGE B. PAYNE

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Acrolein and methacrolein have been converted to their respective epoxides, glycidaldehyde and α-methylglycidaldehyde, by the action of hydrogen peroxide at *p*H 8–8.5. These new epoxy aldehydes were obtained as distilled aqueous solutions free of acidic by-products in 68 and 79% yields, respectively. Corresponding yields of anhydrous products were 40 and 64%. Glyceraldehyde has been secured by an acid-catalyzed hydration of glycidaldehyde. Glycidonitrile, a new epoxy nitrile, was prepared from the acetate of glycidaldoxime by thermal deacetylation.

An early attempt to epoxidize simple α,β-unsaturated aldehydes by means of hydrogen peroxide under alkaline conditions was reported by Weitz and Scheffer[2] in their original study of the epoxidation of α,β-unsaturated ketones. They used a relatively large amount of caustic (as high as 40 mole % based on hydrogen peroxide) in attempts to epoxidize both cinnamaldehyde and crotonaldehyde, but observed only acidic products from both reactions.

Owing, perhaps, to Weitz and Scheffer's failure to obtain simple epoxidation, little other work appears to have been done in the past on the epoxidation of α,β-unsaturated aldehydes in general or on the simpler analogs in particular. Recently, however, there have been reports of the successful alkaline epoxidations of such materials as 1-benzoyl-5-formyl-1,2,2a,3-tetrahydrobenz(cd)indole[3] and 2,3-diphenylacrolein.[4] As an alternative method of preparing epoxy aldehydes, Schaer[5] has allowed some simple α,β-unsaturated aldehydes to react with sodium hypochlorite.

Glycidaldehyde.—In the present study it has been found possible to effect the epoxidation of even the most sensitive aldehyde such as acrolein[6] by carrying out the reaction under controlled *p*H conditions. For example, when acrolein was added dropwise at 25–30° to a dilute hydrogen peroxide solution maintained at *p*H 8–8.5 by the continuous addition of dilute sodium hydroxide solution, the acrolein was converted to glycidaldehyde (I) in yields of 75–85% as determined by titration for oxirane oxygen. Although the epoxidation could be carried out in the general *p*H range of 7–9.5, optimum yields were secured at 8–8.5. Acidic by-prod-

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[1] See G. B. Payne and P. H. Williams, *J. Org. Chem.*, **24**, 54 (1959), for paper IV of this series.

[2] E. Weitz and A. Scheffer, *Ber.*, **54B**, 2327 (1921).

[3] E. C. Kornfeld, *et al.*, THIS JOURNAL, **78**, 3087 (1956).

[4] H. E. Zimmerman, L. Singer and B. S. Thyagarajan, *ibid.*, **81**, 108 (1959).

[5] C. Schaer, *Helv. Chim. Acta*, **41**, 614 (1958).

[6] G. B. Payne, THIS JOURNAL, **80**, 6461 (1958).