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Stereochemistry of Nucleophilic Solvent Participation in the Decomposition of Diacyl Peroxides

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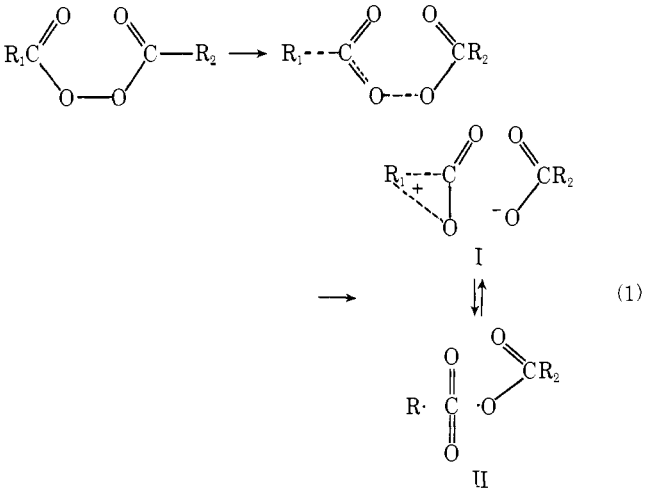
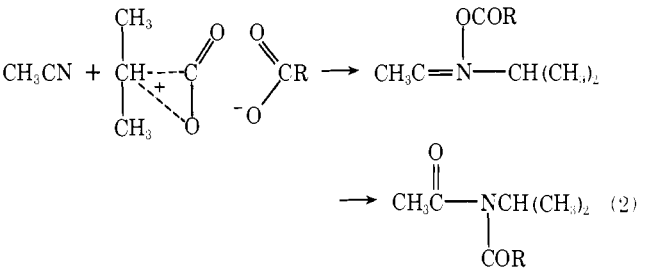
Abstract: Decomposition of (*S*)-(+)-*m*-chlorobenzoyl 2-methylbutanoyl peroxide in acetonitrile yields, among other products, *N*-acetyl-*N*-*m*-chlorobenzoyl-2-butylamine with 14.4% net inversion of configuration. Similar nucleophilic participation is observed in acetic acid and 2-butanol to yield 2-butyl acetate (14% net inversion) and di-2-butyl ether. In these solvents and in cyclohexane and CCl_4, carboxyl inversion product (*m*-chlorobenzoyl-2-butylcarbonate), on the other hand, is formed with retention of configuration. Decomposition of *cis*- and *trans*-4-*tert*-butylcyclohexylformyl *m*-chlorobenzoyl peroxide gives somewhat more complex stereochemical results, but again products involving solvent capture in acetonitrile, acetic acid, and 2-butanol show largely loss of original stereochemistry. Chemically induced dynamic nuclear polarization experiments with several peroxides show no evidence of polarization in any carbonyl-containing products. These results are discussed on the basis of a single rate-determining step in the polar and radical decompositions of diacyl peroxides and the lifetimes of intermediate ion radical pairs.

It is well established that the rapid decomposition of diacyl peroxides $R_1COO\text{-}OCOR_2$, in which one or both R's are secondary or tertiary alkyl, or a resonance stabilized fragment such as benzyl, involves a concerted scission of at least two bonds.[1] Further, decomposition rates are quite solvent dependent, increasing with solvent polarity, yields of scavengeable radicals are often very low, and both "radical" and "polar" products are produced, the best characterized of the latter being the carboxyl inversion product $R_1OCO\text{-}OCOR_2$. This dichotomy has often been discussed as arising from competing discrete radical and ionic decomposition paths, but, in 1970, we proposed[2] that all products could, as well, arise from a common rate-determining transition state, with partitioning into radical and ion pairs occurring at a later stage, with I going on to ionic products, and II either recombining (after



(1)

possible loss of another CO_2) or escaping from the solvent cage to yield scavengeable radicals. Whether I and II should be regarded as species in equilibrium or contributing resonance structures to a common species was not clear and is considered further in this paper. Although this interpretation has been frequently cited and has received some acceptance,[1] only a few[3] additional data have appeared which bear on its validity. An interesting feature of these decompositions is that, in acetonitrile, the solvent is able to capture the ion pair structure I,



(2)

to yield a mono- or diacylamine, sometimes as a major product,[2,3] e.g., with isobutyryl *m*-chlorobenzoyl peroxide (R = *m*-chlorophenyl). It is well established that, in a number of cases, the carboxyl inversion process gives a product, $R_1OCO\text{-}OCOR_2$ with clean retention of configuration at R_1.[1] It occurred to us that an investigation of the stereochemistry of products arising from acetonitrile trapping might give further insight into the nature and lifetime of the ion pair structure (I) and indicate how early in the decomposition process nucleophilic participation by acetonitrile becomes important.

This paper describes the result of our study, and also shows that other nucleophilic solvents are able to trap the ion pair (I).

Results

***m*-Chlorobenzoyl 2-methylbutanoyl peroxide** was chosen for most of our work because of its structural similarity to *m*-chlorobenzoyl isobutyryl peroxide which we had investigated previously and had shown to give good yields of diacylisopropylamine in acetonitrile.[2] The (*S*)-(+) enantiomer was prepared from (*S*)-(−)-2-methyl-1-butanol by oxidation of 2-methylbutanoic acid, conversion to the acid chloride, and re-

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Table I. Decomposition Rates of *m*-Chlorobenzoyl 2-Methylbutanoyl Peroxide (40 °C)

solvent	$k \times 10^4$, s^{-1}
cyclohexane	0.60 ± 0.02
CCl_4	1.32 ± 0.04
CH_3CN	17.2 ± 0.4
CH_3COOH	16.0 ± 0.7[a]
2-butanol	9.0 ± 0.6[a]

[a] Rate unchanged in presence of methyl methacrylate.

action with *m*-chloroperoxybenzoic acid. The peroxide was obtained as an oil, and, because of its instability and hazardous nature, was not purified further, but used directly after determination of purity by iodimetric titration. IR spectra indicated the presence of small amounts of *m*-chlorobenzoic acid and *m*-chlorobenzoyl anhydride as impurities.

Decomposition rates of the peroxide were determined at approximately 40 °C in several solvents, by carrying out the decompositions in polarimeter tubes and following the change in optical rotation. The data gave good first-order plots for two or more half-lives and measurements at several wavelengths were consistent. Results are summarized in Table I.

Decomposition rates are slightly faster than those of *m*-chlorobenzoyl isobutyryl peroxide ($k_{41°C} \times 10^5$ = 4.4 (CCl_4) and 103 (acetonitrile))[2] but show a similar solvent dependence. Decomposition rates in acetic acid and 2-butanol were unchanged in the presence of methyl methacrylate showing that the relatively fast rates arise from solvent polarity, as in the case of acetonitrile, and are not due to any induced decomposition such as is observed with benzoyl peroxide in alcohol solvents.[4]

Although we did not carry out complete product analyses, yields of major "polar" products are listed in Table II and are comparable to those observed with similar peroxides. Within our limits of experimental error, the carboxyl inversion products and ester obtained in cyclohexane and CCl_4 were formed with complete retention of configuration (see Experimental Section) as anticipated from literature results. The same was true for the small yield of carboxyl inversion product obtained in acetonitrile, although the determination was less precise.

In order to determine the enantiomeric composition of the acetyl-*m*-chlorobenzoyl-2-butylamine obtained in acetonitrile, authentic material of known stereochemistry was prepared via the sequence (R_1 = 2-butyl; R_2 = *m*-chlorophenyl).

$$R_1COCl \xrightarrow{NH_3} R_1CONH_2 \xrightarrow[KOH]{Br_2} R_1NH_2 \xrightarrow{R_2COCl} R_1NHCOR_2$$

$$\xrightarrow{PCl_5} R_1N(COR_2)(COCH_3) \xrightarrow{NaOAc} R_1N{=}C(Cl){-}R_2 \quad (3)$$

(*S*)-(+) acid chloride of 43% ee (enantiomeric excess) gave (*S*)-(+)-2-butylamine also of 43% ee; and, since subsequent steps did not involve the chiral center, the final product was assumed to have the same enantiomeric composition.

To determine the stereochemistry of the peroxide decomposition, (*S*)-(+) peroxide, ee 66.3%, was decomposed in acetonitrile and the diacylamine isolated by liquid column chromatography. Its purity was established as >99% by TLC, GC, and NMR and IR spectra. It proved to be (*R*)-(−) material with 9.6 ± 0.3 ee corresponding to a net *inversion* during reaction of 14.4 ± 0.4%.

The products observed in acetic acid and 2-butanol are of interest since 2-butyl acetate and di-2-butyl ether are the results expected from solvent trapping of the ion pair. Consistent with this, the 2-butyl acetate from (*S*)-(+) peroxide, ee 66.3%, was found to be (*R*-)-(−) material, ee 4.0%, corresponding to 6% net inversion. Since the di-2-butyl ether would be expected to be a mixture of diastereomers, its optical properties were not examined.

Table II. Products of Decomposition of (*S*)-(+)-*m*-Chlorobenzoyl 2-Methylbutanoyl Peroxide (66% ee)

solvent	products,[a] %	stereochemistry, % ee
cyclohexane	$R_1OCOOCOR_2$ (59)	*S* (66)
CCl_4	$R_2OCOOCOR_2$ (55), (85)[b]	*S* (66)
CH_3CN	$R_1OCOOCOR_2$ (36 ± 5)	*S* (66)
	$R_1N(COCH_3)COR_2$ (40 ± 5)	*R* (9.6) see text
CH_3COOH	R_1OCOCH_3 (33)	*R* (4.0)
	R_1COOR_2[c]	*S* (8)
	R_1OH (52)	*S* (66)
	Ac_2O (50)	
	chlorobenzene (1.5)	
	R_2COOH[c]	
2-butanol	$R_1OCOOCOR_2$ (~45)	*S* (66)
	R_1OR_1 (12)	ND
	chlorobenzene (1)	

[a] R_1 = 2-butyl; R_2 = *m*-chlorophenyl. [b] Two experiments, 0.1 and 0.03 M, respectively. [c] Not determined quantitatively.

Table III. Decomposition of 4-*tert*-Butylcyclohexylformyl *m*-Chlorobenzoyl Peroxides (40 °C)

solvent	$k \times 10^4$, s^{-1} cis	$k \times 10^4$, s^{-1} trans
cyclohexane	4.4	3.9
CCl_4	6.7 ± 0.1	6.5 ± 0.1
CH_3CN	59 ± 1	42 ± 1
2-butanol	44 ± 1	28 ± 1

The major products from the decomposition in acetic acid, 2-butanol and acetic anhydride, we believe arise from intermediate carboxyl inversion product via the sequence (R_1 = 2-butyl; R_2 = *m*-chlorophenyl).

$$R_1OCOOCOR_2 \xrightarrow{HOAc} R_1OH + CH_3CO\text{-}O\text{-}COR_2$$

$$\xrightarrow{HOAc} (CH_3CO)_2O + R_2COOH \quad (4)$$

Consistent with this, the 2-butanol was found to be (*S*)-(+) material with the same ee as the starting peroxide. Further, authentic carboxyl inversion product held at 40 °C in acetic acid was found to rapidly decompose into 2-butanol and acetic anhydride as indicated.

We also infer that a portion of the 2-butyl acetate found in our product arises from esterification of 2-butanol. Blank runs of acetic acid containing appropriate amounts of 2-butanol and acetic anhydride and treated in the same manner as the peroxide decomposition gave a small amount of 2-butyl acetate, corresponding to 7% of our observed yield. Since in an actual decomposition this would be (*S*)-(+) material, we obtain a corrected value of 14% net inversion for the ester arising from ion pair capture.

The small amount of 2-butyl *m*-chlorobenzoate, on the other hand, was found to contain a small ee (~8%) of (*S*)-(+) isomer and, apparently, is formed chiefly either from carboxyl inversion product or alcohol.

4-*tert*-Butylcyclohexylformyl *m*-chlorobenzoyl peroxide was chosen for further investigation because our earlier study[2] had yielded inconclusive results. A pure sample of the cis isomer was prepared by standard methods, as was also a mixture rich in the trans isomer (15:85 cis:trans). Decompositions in several solvents were followed by IR spectroscopy yielding the rate constants listed in Table III. Rates are higher and solvent effects slightly smaller than those in Table I.

Table IV. Products from 4-*tert*-Butylcyclohexylformyl *m*-Chlorobenzoyl Peroxide

solvent	products[a]	cis		trans	
		yield, %	cis:trans	yield, %	cis:trans
cyclohexane	R_1OH	45	100:0	10	60:40
	R_1OCOR_2	*b*	96:4	*b*	62:38
	$ROCOOCOR_2$	50	*b*	45	*b*
	R_2COOH	17		6	
CCl_4	R_1OH	42	100:0	25	62:38
	R_1OCOR_2	*b*	96:4	*b*	63:37
	$R_1OCOOCOR_2$	60	*b*	55	*b*
	R_2COOH	40		25	
CH_3CN	R_1OH	20	100:0	*b*	62:38
	R_1OCOR_2	40	84:16	30	52:48
	$R_1OCOOCOR_2$	30	*b*	30	*b*
	$R_1N(COCH_3)COR_2$	15	(0:100)[c]	12	(0:100)[c]
CH_3COOH	R_1OH	24	100:0	17	64:36
	R_1OCOR_2	2	85:15	3	29:71
	$ROCOCH_3$	5	42:58	7	32:68
2-butanol	R_1OH	27	95:5	20	55:45
	R_1OCOR_2	*b*	80:20	*b*	30:70
	$R_1OCOOCOR_2$	24	*b*	18	*b*
	R_2COOH	18		15	

[a] R_1 = 4-butylcyclohexyl; R_2 = *m*-chlorophenyl. [b] Not determined. [c] See text.

Major products of decompositions in several solvents are listed in Table IV. Carbonyl compounds were determined by IR spectroscopy using known standards. Cis–trans isomer ratios were in general determined by GC (gas chromatography). The alcohols can hardly be primary products in aprotic solvents, and they and at least part of the ester R_1OCOR_2 arise from pyrolysis of carboxyl inversion product during the analysis and thus reflect its stereochemistry. In the case of the imide, we were only able to prepare the trans isomer for reference. However, careful examination of reaction products by TLC and NMR spectroscopy indicated that both peroxides yielded predominantly the trans imide with no indication of more than traces of anything which might be the cis isomer.

The data of Table IV are discussed further below, but, overall, indicate that with these peroxides there is some loss of stereochemistry via the carboxyl inversion path as well as in solvent capture of intermediate ion pairs.

CIDNP Experiments. Chemically induced dynamic nuclear polarization (CIDNP) experiments provide an additional probe for the existence of radical pairs in chemical reactions. However, decomposition of *m*-chlorobenzoyl 2-methylbutanoyl peroxide in either acetonitrile or acetic acid in NMR tubes at 40 °C showed no signs of polarization of proton spectra. Since radical yields from this sort of peroxide are known to be low,[2] additional experiments were carried out with isobutyryl peroxide which gives higher radical yields. Again no polarization was observed at 68 °C in either acetonitrile or cyclohexane. In contrast, marked polarization was observed in CCl_4 for the multiplets of the 2-protons of propane, propylene, and 2-chloropropane, and also emission from $CHCl_3$. However, no polarization was observed for any of the carbonyl-containing products. These results are very similar to those reported by Kaptein[5] in hexachloroacetone; and, in fact, we have also confirmed his experiments.

Discussion

Our major findings are that other nucleophic solvents, acetic acid and 2-butyl alcohol, as well as acetonitrile are able to intercept intermediate ion pairs in the decomposition of *m*-chlorobenzoyl 2-methylbutanoyl peroxide; and that, in the first two cases, the imide and acetate produced respectively are formed with extensive racemization but small net *inversion*. On the other hand, the carboxyl inversion product forms with complete retention. The conclusion seems to be that the carboxyl inversion product arises early along the reaction path from a very tight ion pair, but in polar nucleophilic solvents the ion pair can separate with loss of CO_2 and react with solvent at a later stage in which stereochemistry has been largely lost. In fact, the amount of racemization is larger than has been noted previously in the solvolysis of *sec*-alkyl tosylates or halides,[6] perhaps because the CO_2 released facilitates the separation of the ion pair. Solvolyses typically also show some competing elimination. This was not examined here, but formation of propylene and butyric acid has been observed previously in the decomposition of isobutyryl peroxide in acetonitrile.[2]

Our results with *cis*- and *trans*-4-*tert*-butylcyclohexylformyl *m*-chlorobenzoyl peroxide similarly show extensive loss of stereochemistry in acetate and imide products in acetic acid and acetonitrile. In acetic acid, trans acetate is the major product from both isomers, but more is formed from the cis isomer, a result consistent with driving forces both for inversion and formation of the most stable isomer. On the other hand, we were able to detect only trans imide from either peroxide. It is possible that steric hindrance in the crowded cis structure precluded its formation both in the decomposition and in our attempts at independent synthesis. As a further complication, products formed via the carboxyl inversion path from the cis isomer show largely or entirely retention of configuration, while those from trans peroxide indicate a small net inversion. even after allowing for 15% cis impurity in the trans peroxide. As noted earlier, the *m*-chlorobenzoate esters probably arise by both paths and show intermediate results. It is worth noting that solvolyses of 4-*tert*-butylcyclohexyl tosylates also yield complicated results. Winstein and Holness[7] report that acetolysis of trans tosylate occurs with clean inversion, with cis tosylate giving both isomeric acetates plus extensive rearrangement.

We consider our stereochemical results at least consistent with the hypothesis of a single rate-determining step in the polar and radical paths of decomposition of this class of peroxides. On the other hand, had we observed clean inversion in the products arising from solvent capture, it would have implied strong nucleophilic participation and even covalent bond for-

mation at a very early stage in the reaction leading to polar products. If this occurred as early as the rate-determining transition state, two separate reactions paths would be indicated. It is of interest that a similar loss of stereochemistry was reported many years ago by Greene et al.[8] in the decomposition of *m*-bromobenzoyl peroxide in the presence of 4,4′-dimethoxystilbene. This reaction is first order to each reactant, gives an appreciable (10%) yield of scavengeable radicals, and occurs nine times as rapidly in acetonitrile as in benzene. The major products are the substituted stilbene dibenzoates and *cis*- and *trans*-stilbenes giving the same mixture of *dl* and meso isomers. These results also appear consistent with a one-path mechanism.

Very recently a paper by Taylor[3] has appeared which is also qualitatively consistent with our findings. They have investigated a series of acyl *m*-chlorobenzoyl peroxides (R = cyclobutyl, cyclopropylmethyl, and 3-butenyl) and found a small amount of typical carbocation rearrangement in their carbonyl inversion products, but much more among other ionic products. They also conclude that the latter arise from longer lived ion pairs as in our results.

While stereochemistry indicates something about the lifetime and separation of ion pairs in peroxide decompositions CIDNP experiments should throw light on the time scale and amount of separation over which ion and radical pairs are interconvertible since appreciable separation is required for the polarization process.[9] If the time scale is short and separation small, a resonance-structure formulation for the process seems appropriate, while if the separation is large the process is better treated as an equilibrium. We find no polarization in the polar products from our *m*-chlorobenzoyl peroxide. This may not be a good test, because of the low yield of radical products from this sort of peroxide, but isobutyryl peroxide and phenylacetyl peroxide[10] give similar results. In fact, as far as we know, polarization has rarely been reported in the carbonyl containing products from peroxide decompositions,[5,9] except in those cases where the peroxides plainly decompose by a simple one-bond scission into radicals, e.g., in the decomposition of benzoyl peroxide in tetrachloroethylene where the ^{13}C NMR spectrum of phenyl benzoate is polarized with a sign indication that it arises from cage recombination of phenyl and benzoyloxy radicals.[11] Here the failure to observe polarization is, of course, negative evidence, since a number of phenomena may prevent the observation of polarized spectra in processes in which radical sorting processes are, in fact, taking place.[9] Nevertheless, the result is consistent with the conclusion that, in our systems, any radical pair ion pair exchange is occurring in tight ion pairs with too short lives and too little separation for polarization to occur. However, the nature of the phenomena is evidently structure dependent. Lawler[12] has recently reported that, in the decomposition of *tert*-butylacetyl-*m*-chlorobenzoyl peroxide, although the carboxyl inversion product shows no NMR polarization, polarized 2-methyl-1-butene, 2-methyl-2-butene, and 1,1-dimethylcyclopropane, the consequences of what must be carbonium ion rearrangements, are also produced. Plainly the subject is complicated and additional work remains to be done.

Experimental Section

(*S*)-(+)-*m*-Chlorobenzoyl 2-Methylbutanoyl Peroxide. (*S*)-(−)-2-Methyl-1-butanol (Tridon Chemical Inc.), $[\alpha]_{546}^{20}$ −6.0 ± 1° (neat), was oxidized to (*S*)-(+)-2-methylbutanoic acid with $K_2Cr_2O_7$-H_2SO_4, and converted to acid chloride by reaction with $SOCl_2$ at −5 to 15 °C, following the procedure of Kharasch.[13] Yield of each step was approximately 50% and the product, bp 47–49 ° (127 Torr), had an optical rotation of $[\alpha]_{589}^{24}$ +11.2° (neat) corresponding to 66.3% ee ($[\alpha]_{589}^{24}$ for pure material reported as 17.2°).[13] It was found to undergo slow racemization on storage at room temperature, dropping to 43% ee in 11 months. The peroxide was prepared by reaction of the acid chloride with *m*-chloroperbenzoic acid in hexane-pyridine at −10 to −20 °C. Pyridine hydrochloride was removed; the solution washed with dilute HCl and $NaHCO_3$ and solvent removed under vacuo. The peroxide remained as an oil, purity by iodimetric titration 82.5%, and was stored at −78 °C until used. IR spectra indicated that the major impurities were *m*-chlorobenzoic acid and anhydride and NMR spectra were consistent with structure. Corrected for purity, optical rotation was $[\alpha]_{589}^{22}$ +11.8°. By comparison with reported rotations of a number of other derivatives of 2-methylbutanoic acid, it was estimated that the rotation of optically pure peroxide should be approximately +17°, so the observed value is in good agreement with the ee of the starting acid chloride (66.3%).

(*S*)-(+)-*N*-Acetyl-*N*-*m*-chlorobenzoyl-2-butylamine. (*S*)-(+)-2-Methylbutanoyl chloride, ee 43%, was converted to amide with aqueous NH_3 and rearranged to (*S*)-(+)-2-butylamine by treatment with NaOH–Br_2 using standard procedures. The amine was purified by fractional distillation, purity by NMR and IR >99%, $[\alpha]_{589}^{25}$ +2.53° (neat). Comparison with literature values[14] gave ee 43% as expected. The amine, dissolved in 10% NaOH, was treated with *m*-chlorobenzoyl chloride to yield amide, recrystallized from *n*-hexane–ethyl acetate, mp 66.5–67.5 °C, yield 94%. The amide (14 g) in cyclohexane (125 mL) was converted to imino chloride by addition of PCl_5 (16.3 g) refluxing for an hour and removing solvent in a rotary evaporator. The crude product was used directly to prepare the final amide by refluxing overnight with a stirred suspension (partially soluble) of sodium acetate in acetonitrile (170 mL). The reaction mixture was added to water, extracted with ether, and the imide purified by column chromatography on silica gel by using 20:1 CCl_4:ethyl acetate. The imide was a liquid, purity >99% by thin layer and GLC. It gave a correct analysis (C, H, N), an NMR spectrum consistent with its structure, and an IR showing carbonyl absorption at 1662 and 1704 cm^{-1}. Assuming 43% ee, its optical rotation was $[\alpha]_{26}^{589}$ +30.7° (neat) based on a measured density of 1.1561.

***cis*- and *trans*-4-*tert*-butylcyclohexylformyl *m*-chlorobenzoyl peroxides** were prepared from the corresponding acids (separated by fractional crystallization of their ammonium salts) via their acid chlorides as in the case of the 2-methylbutyryl peroxide above. Fractional crystallization gave pure cis acid and a trans-rich fraction which was converted to acid chloride and further epimerized by refluxing the acid chloride-$SOCl_2$ reaction mixture overnight. Hydrolysis of the acid chlorides and GLC analysis after silylation indicated that they were pure cis and 85:15 trans:cis. The peroxides were obtained as white solids, IR carbonyl peaks at 1802 and 1774 cm^{-1}, and were stored at −78 °C and used without further purification.

***N*-Acetyl-*N*-*m*-chlorobenzoyl-4-*tert*-butylcyclohexylamine.** The trans isomer was prepared from *trans*-4-*tert*-butylcyclohexylamine (obtained by the sodium-ethanol reduction of 4-*tert*-butylcyclohexanone oxime) by essentially the same procedure as the corresponding imide from *sec*-butylamine. It was purified similarly by column chromatography and obtained as a white crystalline solid, mp 95–98.5 °C with satisfactory analysis (C, H, N), an IR spectrum with major carbonyl bands at 1672 and 1712 cm^{-1}, and an NMR spectrum consistent with its structure. The corresponding cis amine was obtained by hydrogenation of the amine in acetic acid over platinum oxide, but, while the *m*-chlorobenzoylamide, mp 102–110 °C, was easily prepared, attempts to convert it to the corresponding imide were unsuccessful, presumably because of the latter's rather hindered structure.

Other reference compounds were prepared by standard methods. Esters of 4-*tert*-butylcyclohexanol were obtained from a mixture of the cis and trans alcohols and separated by preparative GLC. In addition it was found that *trans*-4-*tert*-butylcyclohexyl *m*-chlorobenzoate could be crystallized from the isomeric mixture in 50% ethanol, mp 82–83 °C. We find that cis-trans isomers in this series can, in general, be distinguished by their NMR spectra, the proton on C-1 in trans isomer appearing as a broader multiplet at higher field. In the case of the acetates, these appear at τ 0.05 and 5.42. The corresponding values for the *m*-chlorobenzoates are τ 4.75 and 5.15.

Attempts to prepare reference samples of the carboxyl inversion product of *m*-chlorobenzoyl 2-methylbutanoyl peroxide by reaction of *sec*-butyl chloroformate with *m*-chlorobenzoic acid in ether in the presence of triethylamine[2] were unsuccessful since the crystalline product proved to be *m*-chlorobenzoic anhydride. According, identification of this material in reaction mixtures was based on spectral properties.

Kinetic Experiments. Decompositions of *m*-chlorobenzoyl 2-methylbutanoyl peroxide were followed by optical rotation. All runs

gave good first-order plots over two or more half-lives and consistent results at different wavelengths. Results are summarized in Table I, and errors are standard deviations of the slopes of least-squares lines through the data.

Decompositions of *cis*- and *trans*-4-*tert*-butylcyclohexylformyl *m*-chlorobenzoyl peroxides were followed by IR spectroscopy. The peak at 1774 cm^{-1} corresponding to the peroxide was unsatisfactory due to interference by products, but good first-order plots were obtained by using product peaks at 1730 (ester) and 1659 cm^{-1} (imide) in acetonitrile, 1700 cm^{-1} (acid) in 2-butanol, and 1747 and 1751 cm^{-1} (carboxyl inversion product) in cyclohexane and CCl_4. Results are summarized in Table III.

Product Analysis: (*S*)-(+)-*m*-Chlorobenzoyl 2-Methylbutanoyl Peroxide. In Acetonitrile. Yields of imide were determined by GLC using a 6-ft 10% OV-1 column programmed at 10 °C/min from 50 to 250 °C with *o*-terphenyl as internal standard, calibrated against an authentic sample. To determine optical purity, the imide was separated by column chromatography, using the same techniques as in purification of reference material (see above). Optical rotation data were determined in acetonitrile, ethanol, and CCl_4 and compared with reference material, yielding the results given in the text. Carboxyl inversion product was determined by IR spectroscopy in CCl_4 by using the carbonyl peak at 1807 cm^{-1} and assuming the same ϵ per carbonyl as *m*-chlorobenzoic anhydride. The same technique was used to determine yields of carboxyl inversion product in other solvents. The optical purity of the carboxyl inversion product was estimated from the rotation of the product mixture as described below.

In Acetic Acid. Product distributions (Table II) were determined by GLC, using internal standards and authentic reference materials. Products were also collected by preparative GLC and optical rotations determined for 2-butanol and 2-butyl acetate. Comparison with literature values for pure materials gave the results cited in the text. No carboxyl inversion product was detected by IR. In freshly decomposed samples, authentic material (from a decomposition in CCl_4) was found to decompose completely in 3 h in acetic acid at 40 °C to 2-butanol and acetic anhydride.

Other Solvents. Di-2-butyl ether and chlorobenzene formed in 2-butanol were determined by GLC using authentic samples. Carboxyl inversion product was determined by IR carbonyl absorption. The same technique was used in cyclohexane and CCl_4. The conclusion that the carboxyl inversion product was formed with essentially complete retention of configuration in these solvents was based upon the optical rotation of the samples after reaction which agreed closely with that calculated based on carboxyl inversion product determined and the assumption of the same molar rotation as other *sec*-butyl esters.

Product Analysis: 4-*tert*-Butylcyclohexylformyl *m*-Chlorobenzoyl Peroxides. Esters and alcohols were determined by GLC analysis using a 10% OV-17 column, programmed at 3 °C/min starting at 100 °C with *n*-dodecane as an internal standard and retention times determined with authentic samples. This procedure gave good separation of cis-trans isomers. Total carboxyl inversion products were determined by IR absorption. Since they decompose to ester on GLC analysis, the composition of the observed esters indicates their stereochemistry.

Yields of imide formed in acetonitrile were determined by carbonyl absorption. TLC analysis of imide from both cis and trans peroxide yielded a single spot, R_f 0.25 with 10:1 CCl_4:ethyl acetate identical with that from authentic trans imide. Not more than traces of additional material which might correspond to the cis isomer could be detected. Similarly NMR spectra of reaction mixtures showed a single multiplet for C-1 with no indication of the second multiplet at lower field.

CIDNP experiments were carried out at 90 MHz, by conventional techniques.[10]

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References and Notes

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