Stereochemistry of the Reactions of Molecular Oxygen with 1,4-Dimethylcyclohexyl and 2-Methylnorbornyl Radicals Generated from Isomeric Sources[1]

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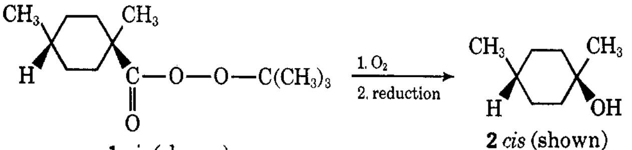
The *cis* and *trans* isomers of 1-(carbo-*t*-butylperoxy)-1,4-dimethylcyclohexane undergo thermal decomposition at 60° in cumene at essentially the same rates (*cis* isomer, $\Delta H^{\ddagger} = 27.5$ kcal/mol, $\Delta S^{\ddagger} = 5.1$ eu; *trans* isomer, $\Delta H^{\ddagger} = 27.8$ kcal/mol, $\Delta S^{\ddagger} = 5.8$ eu). The products, *cis*- and *trans*-1,4-dimethylcyclohexane, 1,4-dimethylcyclohexene, and 4-methylmethylenecyclohexane, formed from the 1,4-dimethylcyclohexyl radical are the same from both precursors. In the presence of oxygen in 1,2-dimethoxyethane or in a Freon solvent, both the *cis* and *trans* peresters gave identical yields (after reduction) of 58% *trans*- and 42% *cis*-1,4-dimethylcyclohexanol at oxygen pressures from 1 to *ca.* 600 atm. In cumene at 75°, *exo*-2-(carbo-*t*-butylperoxy)-2-methylnorbornane decomposes 6.7 times faster than its *endo* isomer ($\Delta H^{\ddagger} = 27.9$ kcal/mol, $\Delta S^{\ddagger} = 6.3$ eu, and $\Delta H^{\ddagger} = 30.3$ kcal/mol, $\Delta S^{\ddagger} = 9.3$ eu, respectively). The products resulting from 2-methyl-2-norbornyl radicals are essentially the same from either isomeric source; the same ratio of 2-methyl-2-norbornyl *exo*- and *endo*-hydroperoxides (85:15) is formed from either perester in the presence of oxygen at pressures up to *ca.* 600 atm. These results suggest that the same intermediate free radical is formed directly in a planar configuration from these isomeric perester sources. Relative rates of both decomposition and product formation are consistent with involvement of torsional effects and a planar radical center.

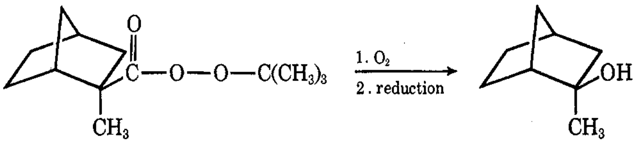
It has become well accepted that the most generally stable configuration of alkyl free radicals is planar. The most compelling data leading to this conclusion are from physical chemical measurements (esr results);[2] however, some of the chemical data (product study results) have been interpreted to indicate nonplanar configurations for intermediate radicals.[3,4] While planar configurations seem the preferred arrangement, it is also possible that most unconjugated free radicals may be initially formed in a nonplanar state. Initial radical centers may retain (for only a very short time) the tetrahedral configuration of their precursors. Physical measurements, like esr spectra, would yield no information about such metastable initial states, and stereochemical products studies would indicate nonplanar radicals only when some further reaction rapidly intercepts the initial radical. From two different isomeric sources of radicals, the products could be different if the radicals were first formed in different configurations (or conformations) and, second, if they were rapidly swept up by a trapping agent. These conditions were clearly obtained in some stereospecific reactions of isomeric 9-decalyl radicals.[5] When generated from *cis* and *trans* perester decompositions and treated quickly with the highly effective trapping agent oxygen, decalyl radicals have a "memory" of their origin which may be due to configurational differences at C-9[5a] and/or conformational differences in the rings.[5b]

To find out if such initially different radicals may also be shown to exist in other systems, we have generated 1,4-dimethylcyclohexyl radicals and 2-methylnorbornyl radicals in solution each from two different isomeric sources (**1** *cis* and *trans*, **2** *cis* and *trans*). In the presence of oxygen, hydroperoxides are formed which may be reduced to alcohols for analysis to show the existence of any stereospecific reactions. Oxygen was built up to high concentrations by use of pressures up to 600 atm.



1 *cis* (shown)
1 *trans*

2 *cis* (shown)
2 *trans*

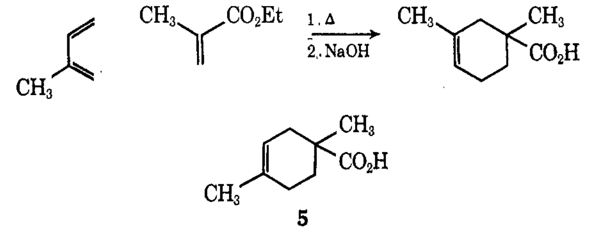


3 *exo* (shown)
3 *endo*

4 *exo* (shown)
4 *endo*

Results

1,4-Dimethylcyclohexyl System.—The *cis*- and *trans*-1,4-dimethylcyclohexane carboxylic acids, *cis*-**1**-CO_2H and *trans*-**1**-CO_2H, required for preparations of the isomeric peresters, were prepared by Diels–Alder reaction of methyl methacrylate with isoprene.[6] After hydrolysis of the esters, separation of the solid 1,4 acid from the liquid 1,3 isomer was by crystallization. Hydrogenation of the methyl ester of pure 1,4 acid **5** then gave a 62:38 mixture of *trans*-**1** and *cis*-**1** esters. This



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[1] Research sponsored by the U. S. Air Force Office of Scientific Research, the Petroleum Research Fund administered by the American Chemical Society, and the National Research Council of Canada.

[2] R. W. Fessenden, *J. Phys. Chem.*, **71**, 74 (1967); M. Karplus and G. K. Fraenkel, *ibid.*, **35**, 1312 (1961); R. W. Fessenden and R. H. Schuler, *ibid.*, **39**, 2147 (1963), and references therein.

[3] W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., New York, N. Y., 1966, p 30.

[4] (a) F. D. Greene, C. Chu, and J. Walia, *J. Amer. Chem. Soc.*, **84**, 2463 (1962); *J. Org. Chem.*, **29**, 1285 (1964). (b) F. G. Bordwell, P. S. Lanis, and G. S. Whitney, *ibid.*, **30**, 3764 (1965). (c) W. O. Haag and E. I. Heiba, *Tetrahedron Lett.*, 3679 (1965).

[5] (a) P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Amer. Chem. Soc.*, **87**, 2590 (1965); (b) F. D. Greene and N. N. Lowry, *J. Org. Chem.*, **32**, 875 (1967).

[6] I. N. Nazkrov, A. I. Kuznetsova, and N. V. Kuznetsov, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **8**, 1362 (1959); I. N. Nazkrov, A. I. Kuznetsova, and N. V. Kuznetsov, *J. Gen. Chem. USSR*, **25**, 75 (1955).

tentative assignment of *cis* and *trans* structures to these esters comes from the expectation[7] that the *trans* isomer, with a carbomethoxy group predominately in an axial (less accessible) position,[8] would have a shorter retention time on glpc analysis. Separation of these esters by preparative glpc, followed by hydrolysis, gave *trans*-**1** acid, mp 46.5–47°, and *cis*-**1** acid, bp 148–150 (19–21 mm). The isomeric peresters were then prepared by the reaction of the corresponding acid chlorides with the sodium salt of *t*-butyl hydroperoxide.

The stereochemical assignment of *cis* and *trans* structures, based at first on glpc retention times of esters, is supported by the nmr spectra of isomeric esters, acids, acid chlorides, and peresters. In all cases the isomer assigned to the *trans* series (axial carbonyl function) showed two broad downfield peaks at τ 7–8 not present in the spectra of the *cis* isomers. This feature apparently arises from deshielding of the axial protons at C-3 and C-5 by the C-1 carbonyl function. In addition, it is interesting to note that, just as *cis*-1,4-dimethylcyclohexane has a higher refractive index than its *trans* isomer,[9] the *cis* isomer of ester, acid chloride, and perester had the higher refractive index.

Rates of thermal decomposition of the 1,4-dimethylcyclohexyl peresters were determined in cumene solution. Variation of concentration or addition of inhibitors produced no change in the observed first-order rate constants (see Table I). Although the *cis* perester consistently gave a slightly greater rate constant than the *trans* isomer, the decomposition rates and activation parameters are essentially identical.

TABLE I

RATES OF DECOMPOSITION OF 1-(CARBO-*t*-BUTYLPEROXY)-*cis*- AND -*trans*-1,4-DIMETHYLCYCLOHEXANES IN CUMENE

Perester	Temp, °C	Concn, *M*	$k_1 \times 10^5$, sec^{-1}
cis[a]	60.0	0.0441	7.52
		0.0444[c]	7.74
	70.0	0.0433	26.6
		0.0435[d]	26.6
	80.0	0.0441	84.9
		0.447	85.7
trans[b]	60.0	0.169	6.83
		0.0365	6.93
		0.0359	25.2
		0.353	25.7
		0.0417	77.9
		0.0407[d]	79.6

[a] $\Delta H^{\ddagger}$ = 27.5 kcal/mol, $\Delta S^{\ddagger}$ = 5.07 eu. [b] $\Delta H^{\ddagger}$ = 27.8 kcal/mol, $\Delta S^{\ddagger}$ = 5.75 eu. [c] Contains 0.009 *M* 2,5-di-*t*-butylhydroquinone. [d] Contains 0.10 *M* 2,6-di-*t*-butyl-4-methylphenol as inhibitor.

The products of decomposition of *cis* and *trans* peresters in degassed cumene at 60° were also identical within experimental error of the glpc analysis (Table II). In glyme, under 1 atm of oxygen, the products after $LiAlH_4$ reduction were *cis*- and *trans*-1,4-dimethylcyclohexanol and the two olefins, 1,4-dimethylcyclohexene and 4-methylmethylenecyclohexane. In the presence of 1 (or more) atm of oxygen pressure the intermediate free radicals are diverted from hydrogen atom transfer from the solvent and no *cis*- or *trans*-1,4-dimethylcyclohexane was formed.

TABLE II

PRODUCTS OF DECOMPOSITION OF 1-(CARBO-*t*-BUTYLPEROXY)-*cis*- AND -*trans*-1,4-DIMETHYLCYCLOHEXANES IN CUMENE AT 60°

Product	Mol of product/mol of perester *cis*	Mol of product/mol of perester *trans*
Carbon dioxide (by pressure)	0.96	0.90
(by weight)	0.91	0.91
t-Butyl alcohol	0.87	0.78
cis- and *trans*-1,4-dimethylcyclohexane	0.31 (17% *cis*) (83% *trans*)	0.36 (18% *cis*) (82% *trans*)
4-Methylmethylenecyclohexane	0.16	0.18
1,4-Dimethylcyclohexene	0.14	0.15

At higher than 1 atm of oxygen the solvent that was used was a 25:1 (v/v) mixture of Freon TF and glyme, respectively. This mixed solvent was chosen because of the stability of the Freon in the presence of high pressures of oxygen,[10] and the glyme served as a good source of hydrogen atoms. From this solvent the product hydroperoxides were reduced to alcohols by catalytic hydrogenation prior to analysis. The hydrogenation procedure was checked by comparing the results of hydrogenation of half of a decomposition solution with those obtained by reduction of the other half with triphenylphosphine. There was no change in the *cis*/*trans* product ratio. Also the stability of the product hydroperoxides at the temperature of the product runs was shown by putting half of a decomposition solution back in the heated bomb under oxygen for an additional 40 hr. Again there was no change in the *cis*/*trans* alcohol ratio nor in total yield of alcohol (45–60% after reduction, transfer, and concentration of the solutions before analysis). Table III summarizes the

TABLE III

PRODUCTS OF THERMAL DECOMPOSITION OF 1-(CARBO-*t*-BUTYLPEROXY)-*cis*- AND -*trans*-1,4-DIMETHYLCYCLOHEXANES IN THE PRESENCE OF OXYGEN

Perester	Temp, °C	O_2 pressure, atm	1,4-Dimethylcyclohexanols % *trans*	1,4-Dimethylcyclohexanols % *cis*
trans	60 ± 0.2	1[a]	59	41
	70 ± 5	51	60[b]	40[b]
			60	40
		310	59	41
			58[c]	42[c]
	60 ± 5	610	58	42
cis	60 ± 0.2	1[a]	58	42
	60 ± 5	51	59	41
	70 ± 5	290	56	44
	60 ± 5	580	57	43

[a] In glyme, and reduced with $LiAlH_4$; all others in Freon TF–glyme (25 ml:1 ml) and hydrogenated except as noted. [b] After twice the usual decomposition time (stability check). [c] Reduced with triphenylphosphine.

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[7] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," John Wiley & Sons, Inc., New York, N. Y., 1965, p 177. For a specific example of configurational assignment by glpc to 4-methylcyclohexanecarboxylate esters, see E. L. Eliel, H. Haubenstock, and R. V. Acharya, *J. Amer. Chem. Soc.*, **83**, 2351 (1961).

[8] The predominate conformations of the 1,4-dimethylcyclohexyl carbonyl compounds (**1**) are likely those with the C-4 methyl group equatorial; see the example of 1,4-dimethylcyclohexanol reported by J. J. Vebel and H. W. Goodwin, *J. Org. Chem.*, **33**, 3317 (1968). *trans*-**1** compounds would then have a predominately C-1 axial carbonyl function.

[9] See ref 7, p 172.

[10] Underwriter's Laboratories Report MH-3072, "The Comparative Life, Fire and Explosion Hazards of Freon-113," 1941; see also *Chem. Eng. News*, **43** (24), 41 (1965).

relative yields of alcohols from the 1,4-dimethylcyclohexyl peresters from various runs under different pressures of oxygen. From 1 to 610 atm, the yields of *cis* alcohol to *trans* alcohol (42% *cis*, 58% *trans*) were independent of oxygen pressure.

2-Methyl-2-norbornyl System.—The 2-methylnorbornyl peresters (*exo*-**3** and *endo*-**3**) were prepared from the known acid chlorides and sodium *t*-butyl peroxide. Good first-order decomposition of the *exo* isomer occurred in cumene, but the *endo* isomer gave an increasing rate (and some scattered points) after one or two half-lives. However, a sample of *endo* perester especially freed from traces of acid chloride gave, at high perester concentration, a good first-order kinetic plot and a rate constant the same as found at low concentrations. As shown in Table IV the *exo* isomer decomposes about seven times faster than *endo* isomer.

TABLE IV

RATES OF DECOMPOSITION OF *exo*- AND *endo*-2-(CARBO-*t*-BUTYLPEROXY)-2-METHYLNORBORNANES IN CUMENE

Perester	Temp, °C	Concn, M	$k_1 \times 10^5$, sec^{-1}
exo[a]	60.0	0.0333	7.78
	65.0	0.0314	14.4
	70.0	0.0340	27.5
		0.0316[c]	28.2
	75.0	0.0320	48.9
	80.0	0.0339	89.3
		0.165	90.6
endo[b]	75.0	0.0319	7.35
	80.0	0.0309	13.9
	85.0	0.0319	26.4
	90.0	0.0328	48.1
		0.159	45.9
	95.0	0.0322	84.1

[a] $\Delta H^{\ddagger}$ = 27.9 kcal/mol, $\Delta S^{\ddagger}$ = 6.31 eu. [b] $\Delta H^{\ddagger}$ = 30.3 kcal/mol, $\Delta S^{\ddagger}$ = 9.33 eu. [c] Contains 0.10 *M* 2,6-di-*t*-butyl-4-methylphenol as inhibitor.

As with the cyclohexyl peresters, the products of decomposition of isomeric norbornyl peresters in degassed cumene were the same from both sources (Table V).

TABLE V

PRODUCTS OF DECOMPOSITION OF *exo*- AND *endo*-2-(CARBO-*t*-BUTYLPEROXY)-2-METHYLNORBORNANES IN CUMENE AT 60°

Product	Mol of product/mol of perester *exo*	Mol of product/mol of perester *endo*
Carbon dioxide (by pressure)	0.97	1.02
(by weight)	0.96	1.00
t-Butyl alcohol	0.78	0.86
exo- and *endo*-2-methylnorbornane	0.36 (7% *exo*) (93% *endo*)	0.39 (13% *exo*) (87% *endo*)
2-Methyl-2-norbornene	0.12	0.14
2-Methylenenorbornane	0.19	0.24

The percentages of *exo*- and *endo*-2-methyl-2-norbornanols formed in the presence of various pressures of oxygen are given in Table VI. After reduction of the product solutions by hydrogenation the 2-methyl-2-norbornanols were the only products analyzed, although numerous other unidentified peaks appeared in the glpc tracings. Many of these compounds undoubtedly arise from oxidation of the solvent. The yields of alcohols were only 15–25%; however, their ratio was found to be independent of oxygen pressure and was the same from either *exo* or *endo* perester (85:15 with *endo*-2-methyl-2-norbornanol, *i.e.*, *exo* OH group, the major isomer).

TABLE VI

PRODUCTS[a] OF THERMAL DECOMPOSITION OF *exo*- AND *endo*-2-(CARBO-*t*-BUTYLPEROXY)-2-METHYLNORBORNANES IN THE PRESENCE OF OXYGEN

Perester	Temp, °C	O_2 pressure, atm	2-Methyl-2-norbornanols % *endo*-methyl	2-Methyl-2-norbornanols % *exo*-methyl
exo	65 ± 0.2	1[b]	85[c]	15
	60 ± 0.5	280	85[c]	15
			85	15
	70 ± 5	600	84	16
endo	65 ± 0.2	1[b]	85	15
	60 ± 0.5	270	86	14
			87[c]	13
	70 ± 0.5	560	84	16

[a] After hydrogenation. [b] In glyme; all other runs in Freon TF (25 ml)–glyme (1 ml). [c] Analyzed before concentration by distillation of the solvent.

Discussion

The high yields of CO_2 and the absence of carbonyl-containing products from the four peresters studied here indicated that the formation of alkyl radical, CO_2, and *t*-butoxy radical occurs directly (in one step) from the peresters. For formation of tertiary free radicals from peresters this is the expected mechanism,[11] and the rates and activation parameters of the peresters are similar to those of known peresters decomposing by such a concerted path. It is the structure of the initial radical that is the question of special interest here. Lorenz, Rüchardt, and Schacht[12] have presented kinetic studies of cycloalkyl peresters which suggest that, at the transition state for decomposition, the radical sites remain nonplanar. As it is also known that there is relatively little preference for planarity in free alkyl radicals,[13] there could be an initial state after the transition state in which the radical remains in a nonplanar configuration. With 9-decalyl radicals the conversion of a nonplanar radical center to a planar state can occur only with concomitant movement of part of the ring system in a manner similar to a chair–chair interconversion.[5a] Any questions concerning possible restraints on a pure configurational change of the radical center were blurred out by the requirements for this conformational change. With the isomeric 2-methylnorbornyl and 1,4-dimethylcyclohexyl radical sources (**1** and **3**) no complex conformational changes are necessary to produce a planar radical center; a methyl group need only move into a plane with other atoms attached to the radical center. Although an extremely efficient radical trap at high pressures was used in our attempt to intercept this movement, it is perhaps surprising to few that no stereospecific trapping was obtained. Since oxygen trapping did not succeed in demonstrating a "memory" of origin on the part of these alkyl radicals, it seems unlikely that any external trapping agent would be able to do so.

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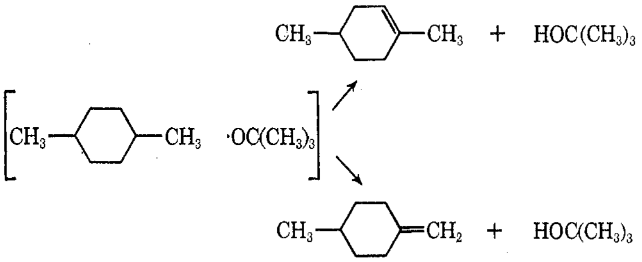
(11) P. D. Bartlett and R. R. Hiatt, *J. Amer. Chem. Soc.*, **80**, 1398 (1958).

(12) P. Lorenz, C. Rüchardt, and E. Schacht, *Tetrahedron Lett.*, 2787 (1969).

(13) *Cf.* L. F. Humphrey, B. Hodgson, and R. E. Pincock, *Can. J. Chem.*, **46**, 3099 (1968), and references therein.

9-Decalyl radicals therefore remain unique as a case in which isomeric initial cyclohexyl radicals have been proven. It seems this difference is not due to any innate hesitancy on the part of initial radical centers in becoming planar, but is due to a lag in obtaining a conformationally more stable state in the cyclic ring system. Indeed, it has been suggested that the decalyl radical center may be formed in a planar state from both *cis* and *trans* peresters even though conformational differences in the rings still remain.[5b] In this regard, evidence for two conformationally different 9-decalyl cations, both with planarity at the 9 atom, has recently been presented.[14]

Stereospecific trapping of isomeric radicals by an *internal* agent (*i.e.*, reaction of geminate caged radicals) may account for formation of different products from isomeric radical sources.[15] With 1,4-dimethylcyclohexyl radical reacting with *t*-butoxy radical as a caged pair, the same ratio of olefins is formed from either *cis* or *trans* source. If the newly formed radicals retain any individual structural features similar to the original peresters, this individualism does not last even long enough to give different products within the cage. As movement of only a methyl group is sufficient to make the radicals planar, it is probable that radicals from isomeric sources are made identical, if not at the transition state, immediately thereafter.



A movement of the groups of the 2-methylnorbornyl peresters during the development of the transition states is consistent with their relative rates of decomposition. For the *endo* compound, Schleyer's[16] suggestion of a destabilizing torsional effect as the *exo* methyl group sweeps past the bridgehead hydrogen atom may account for the slower rate of reaction of this isomer. The *exo* perester reacts faster as the movement of the 2-methyl (*endo*) group does not eclipse it with the bridgehead C–H bond.[17]

The products of reaction of the radicals can also be rationalized on the basis of a torsional effect. In the reaction of cyclohexyl radicals, a favoring of axial attack on R· (planar) would be expected to promote formation of *trans* product.[18] For hydrogen atom transfer, 83% *trans* and 17% *cis* 1,4-dimethylcyclohexane was formed. As expected,[18a] the less selective reagent oxygen gave a more statistical 58% *trans* and 42% *cis* product. In the norbornyl case the greater torsional effects present would strongly favor *exo* attack of reagent;[16] the percentage found for H transfer from cumene was 94% *exo* approach yielding *endo*-2-methylnorbornane (Table V), and, for reaction with oxygen, 85% *exo* attack yielding 2-methyl-*exo*-2-norbornanol (Table VI).

In summary, the radicals from the tertiary peresters studied here are probably formed directly in a planar state and these give nonstereospecific products. The restraints present in more complicated cyclic systems (which give rise to memory effects in 9-decalyl radicals) seem to be just barely sufficient to give stereospecific trapping by a highly reactive external reagent. It seems that a relatively slow conformation change of the ring system accounts for the existance of two very short-lived decalyl radicals. Whether such a property can be attained by some complex acyclic system remains to be seen, but it is clear that restraints more incumbering than the movement of a simple methyl group must be present.

Experimental Section[19]

Materials.—Cumene was stirred with concentrated sulfuric acid, then refluxed over sodium for 24 hr, and distilled through a Vigreux column, taking a center cut with bp 152–152.2° at 761 mm. Freon TF (1,1,2-trichloro-1,2,2-trifluoroethane) was supplied by Du Pont and used without further purification, or stirred over and distilled from magnesium sulfate, bp 47.4–47.5° at 757 mm. Glyme (1,2-dimethoxyethane) was refluxed over and distilled from sodium through a Vigreux column. The distillate was treated with lithium aluminum hydride and distilled, bp 85° at 756 mm. Petroleum ether (bp 30–60°) was treated with concentrated sulfuric acid and then distilled from sodium. Fractions with several different boiling points were used.

1,4-Dimethyl-3-cyclohexene-1-carboxylic Acid (5).—The distilled product (258 g) from the Diels–Alder reaction[6] of isoprene and methyl methacrylate was refluxed for 1.5 hr with 340 ml of 40% aqueous sodium hydroxide. The solution was cooled and acidified with 360 ml of 12 *N* hydrochloric acid; the product was extracted into ether. The ether solution was dried and evaporated and the residual oil was cooled to 5° to crystallize. After filtration and recrystallization from methanol–water at about −5°, the yield of white crystals, mp 64.5–66° (lit.[6] mp 62–63°), was 73.0 g. Analysis by glpc of the methyl ester (from ethereal diazomethane) showed that the 1,3-dimethyl isomer was absent.

Separation of 1-Carbomethoxy-*cis*- and -*trans*-1,4-dimethylcyclohexanes.—1-Carbomethoxy-1,4-dimethylcyclohex-3-ene (30.8 g) from the corresponding acid plus ethereal diazomethane was hydrogenated at room temperature and pressure in 100 ml of 95% ethanol using 3.0 g of 10% palladium on charcoal as catalyst. Hydrogen consumption ceased at the theoretical value. Analysis by glpc, after filtration and evaporation of the ethanol, indicated 62% *trans* ester (1-CO_2CH_3) and 38% *cis* ester (1-CO_2CH_3). No unsaturated starting material was detected by glpc.

The *cis* and *trans* esters were separated by preparative-scale glpc (500-μl samples) on a Model A-700 "Autoprep" fitted with a 10-ft Carbowax 20M on 60–80 mesh Chromosorb W column at 150° and a flow rate of 63 cc/min. The *cis* and *trans* isomers were separated by 10–11 min under these conditions. Collection was 80% efficient, and 20.3 g of *trans* ester ($n^{20}{}_D$ 1.4405) and 13.7 g of *cis* ester ($n^{20}{}_D$ 1.4459) were obtained. Efficiency of the separation was checked by reinjection on a 6-ft TCEP or 10-ft Carbowax 20M column, and both isomers were found to be >99% pure. These glpc-collected samples were used without further purification.

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[14] A. F. Boschung, M. Grisel, and C. A. Grob, *Tetrahedron Lett.*, 5169 (1968). See also R. E. Hornish, G. Liang, and R. C. Fort, Jr., Abstracts, the 158th National Meeting American Chemical Society, New York, N. Y., Sept 1969, ORGN-2.

[15] *Cf.* E. M. Kosower, "An Introduction to Physical Organic Chemistry," Johns Wiley & Sons, Inc., New York, N. Y., 1968, p 352–359; E. I. Heiba and R. M. Dessau, *J. Amer. Chem. Soc.*, **89**, 2238 (1967); H. M. Walborsky and C. Chen, *ibid.*, **89**, 5499 (1967); M. J. S. Dewar and J. M. Harris, *ibid.*, **91**, 3653 (1969).

[16] P. von R. Schleyer, *ibid.*, **89**, 699, 701 (1967).

[17] Decompositions of peroxy compounds leading to norbornyl radicals have relative *exo*/*endo* rates of *ca.* 4–10; (a) P. D. Bartlett and R. E. Pincock, *ibid.*, **84**, 2445 (1962); (b) H. Hart and F. J. Chloupek, *ibid.*, **85**, 1155 (1963); (c) P. D. Bartlett and J. M. McBride, *ibid.*, **87**, 1727 (1965).

[18] See for example (a) F. R. Jensen, L. H. Gale, and J. E. Rodgers, *ibid.*, **90**, 5793 (1968); (b) C. L. Osborn, T. V. Van Auken, and D. J. Trecker, *ibid.*, **90**, 5806 (1968).

[19] Further details can be obtained from the Ph.D. Thesis of W. Schindel, University of British Columbia, 1968, available on microfilm through the National Library of Canada, Ottawa.

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found (*cis* isomer): C, 70.29; H, 10.74. Found (*trans* isomer): C, 71.00; H, 11.03.

***trans*-1,4-Dimethylcyclohexanecarboxylic Acid.**—1-Carbomethoxy-*trans*-1,4-dimethylcyclohexane (15.0 g) was heated and stirred for 21 hr with 45 ml of 40% aqueous sodium hydroxide to which had been added 6 ml of ethanol. The precipitated salt was collected by filtration, washed with ether, and dissolved in hot water and the carboxylic acid was generated with concentrated hydrochloric acid. The white solid (13.5 g) was recrystallized from methanol–water (recovery of 88%), mp 46.5–47°.

***cis*-1,4-Dimethylcyclohexanecarboxylic Acid.**—The *cis* acid was prepared by refluxing 8.0 g of 1-carbomethoxy-*cis*-1,4-dimethylcyclohexane with 25 ml of 40% aqueous sodium hydroxide and 3.0 ml of ethanol for 4 hr. After acidification and extraction the product was distilled, bp 148–150° at 19–21 mm, with 85% yield. Koch and Haaf[20] reported synthesizing both 1,4-dimethylcyclohexanecarboxylic acids (mp 35° for one isomer, bp 143° (20 mm) for the other), but did not specify which isomer was *cis* and which was *trans*.

***trans*-1,4-Dimethylcyclohexanecarbonyl Chloride.**—Reaction of 10 g of *trans* acid with 30 ml of thionyl chloride at room temperature for 15 hr, followed by 2 hr of refluxing, yielded 9.8 g (88%) of colorless liquid, bp 88–89° (14 mm) or 30.5–31° (1.3–1.5 mm), $n^{20}\mathrm{D}$ 1.4605.

Anal. Calcd for $C_9H_{15}ClO$: C, 61.89; H, 8.66; Cl, 20.29. Found: C, 61.99; H, 8.53; Cl, 20.50.

***cis*-1,4-Dimethylcyclohexanecarbonyl Chloride.**—*cis*-1,4-Dimethylcyclohexanecarboxylic acid (10.0 g) with thionyl chloride, as with the *trans* isomer above, gave the corresponding acid chloride, bp 89.5–90° (12.5 mm). The yield was 10.4 g (93%), $n^{22}\mathrm{D}$ 1.4673 or $n^{22.5}\mathrm{D}$ 1.4670.

Anal. Calcd for $C_9H_{15}ClO$: C, 61.89; H, 8.66; Cl, 20.29. Found: C, 61.95; H, 8.41; Cl, 20.63.

1-(Carbo-*t*-butylperoxy)-*trans*-1,4-dimethylcyclohexane (1).—To a stirred suspension of 4.0 g of sodium *t*-butylperoxide in 50 ml of anhydrous ether at 0° was added dropwise over 20 min 5.0 g of *trans*-1,4-dimethylcyclohexanecarbonyl chloride in 10 ml of dry ether. After stirring for 4 hr at 0°, 20 ml of distilled water was added and stirring was continued for 15 min. Then 50 ml of purified petroleum ether (30–60°) was added, the water layer was separated off, and the organic phase was washed with two 10-ml portions of cold 10% sulfuric acid, five 10-ml portions of 10% sodium carbonate, five 10-ml portions of distilled water, and one 20-ml portion of brine. The solvent was removed by rotary evaporation at about 15–20°, and the resulting oil taken up in 50 ml of purified petroleum ether (40–41°) and washed well with distilled water and once with brine to remove the *t*-butyl hydroperoxide present. Drying over magnesium sulfate, followed by thorough rotary evaporation, gave 5.30 g (81%) of a clear, colorless oil with $n^{20.5}\mathrm{D}$ 1.4470.

Anal. Calcd for $C_{13}N_{24}O_3$: C, 68.38; H, 10.59. Found: C, 67.93; H, 10.46.

1-(Carbo-*t*-butylperoxy)-*cis*-1,4-dimethylcyclohexane (1).—This perester was prepared from 5.0 g of the corresponding *cis* acid chloride (XVI) and 4.1 g of sodium *t*-butylperoxide in a manner analogous to the *trans* isomer. The yield was 5.5 g (84%) of very pale yellow liquid with $n^{20.5}\mathrm{D}$ 1.4501. A second preparation gave $n^{20}\mathrm{D}$ 1.4496.

Anal. Calcd for $C_{13}H_{24}O_3$: C, 68.38; H, 10.59. Found: C, 68.56; H, 10.47.

The above are typical preparations, and more perester was prepared in a similar fashion when needed. One preparation of the *cis* perester showed a weak to medium peak at 1810 cm^{-1} in the ir spectrum (possibly anhydride). Some preparations indicated unreacted acid chloride was present (infrared spectrum), and this was removed by putting the perester back to stir with more sodium salt. The peresters were stored at −10 to −15°. Neither compound crystallized.

***exo*- and *endo*-2-methyl-5-norbornene-2-carboxylic acids** were separated by the iodolactonization procedure of Rondestvedt and Ver Nooy.[21] Hydrogenations then gave the *exo* acid (**3**), mp 51.3–52° (lit. mp 50.5–51.6°,[22] 52–53° [23]), and the *endo* acid (**3**) mp 96.0–96.2° (lit. mp 92–93°,[23] 97.5–98.5°).[24] The observed and reported nmr spectra were in agreement, and the methyl esters (from etheral diazomethane) of our samples showed the absence of isomeric impurities. The acid chlorides were prepared by reaction of the acids with thionyl chloride.

***exo*-2-(Carbo-*t*-butylperoxy)-2-methylnorbornane (*exo*-3).**—A stirred suspension of 2.5 g of sodium *t*-butyl peroxide in 40 ml of anhydrous ether was cooled to 0°. Over a 15-min period, 3.5 of 2-methylnorbornane-2-*exo*-carbonyl chloride in 10 ml of dry ether was then added from a dropping funnel. Half an hour later, 0.5 g of sodium *t*-butyl peroxide was added, and finally, after 3 hr, another 0.2 g of sodium salt was added. After a total time of 4 hr at 0° the reaction mixture was filtered; the salts and paper filter were washed well with dry ether. The ether solution was then extracted with one 10-ml portion of water, two 10-ml portions of 10% sulfuric acid, four 10-ml portions of 10% sodium carbonate, two 10-ml portions of distilled water, and one 10-ml portion of brine, dried over magnesium sulfate, and rotary evaporated at ~20° to yield 4.32 g of liquid containing *t*-butyl hydroperoxide (as shown by the infrared spectrum). This crude product was taken up into 50 ml of pentane, washed 10 times with 10-ml portions of distilled water, and dried over magnesium sulfate, and the solvent was rotary evaporated as above. The last traces of solvent were removed by pumping down to 1–3 mm at room temperature for a short time. The colorless oil (3.77 g, 82%) had $n^{19.5}\mathrm{D}$ 1.4674. A second preparation gave perester with $n^{19.5}\mathrm{D}$ 1.4675 in 87% yield.

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.15; H, 9.75.

***endo*-2-(Carbo-*t*-butylperoxy)-2-methylnorbornane (*endo*-3).**—The preparation of the *endo* perester from the acid chloride was identical with that of the *exo* perester. The yield was 4.14 g (90%) of clear, colorless perester, $n^{19.5}\mathrm{D}$ 1.4652. Perester, with $n^{19.5}\mathrm{D}$ 1.4650, was obtained in 88% yield from a second preparation.

Anal. Calcd for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.09; H, 9.76.

Authentic samples of the alcohols *cis*- and *trans*-**2** and *exo*- and *endo*-**4**, and various olefins were prepared for glpc comparison with product solutions. Addition of methylmagnesium iodide to 4-methylcyclohexanone gave 46% *trans* alcohol **2**, mp 71.5–72° (lit.[25] 72.5°), and 54% *cis* alcohol **2**, a liquid at room temperature (lit.[25] mp 24°). Pure samples of each isomer were obtained by glpc. 1,4-Dimethylcyclohexane was prepared by action of phosphorous oxychloride in pyridine on *cis* and *trans* alcohol **2**. 4-Methylmethylenecyclohexane was prepared by the procedure of Greenwald, *et al.*,[26] and obtained pure by glpc. *cis*- and *trans*-1,4-dimethylcyclohexanes were separated from a commercial mixture by glpc and identified by refractive indices.

2-Methyl-*endo*-2-norbornanol (*endo*-**4**), mp 31.5–33.0° (lit.[27] mp 32.5–32°), was obtained by Grignard reaction with norcamphor. The isomer (*exo*-**4**), mp 80–80.7 (lit. mp 82–82°), was obtained by the procedure of Brown.[28] 2-Methyl-2-norbornene and 2-methylenenorbornane, prepared by dehydration of **4**, were separated by glpc and identified by their nmr and infrared spectra. A mixture of 84% *endo*- and 16% *exo*-2-methylnorbornane was prepared by hydrogenation of the mixture of olefins obtained by dehydration of 2-methyl-2-norbornanol.

Kinetic studies[19] were carried out by infrared analysis of individual sealed samples as previously described.[29] A Perkin-Elmer Model 137-B spectrophotometer was used with matched 0.523-mm sodium chloride cells.

Product studies[19] in degassed cumene were carried out as previously described.[29]

Product Studies at High Oxygen Pressures.—The general procedure was as follows. The desired perester, 0.50 g, was dissolved in 25 ml of Freon TF, 1 ml of glyme was added, and the solution was placed in the glass liner of a steel, high-pressure

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bomb (50 ml in volume) supplied by the Parr Instrument Co. The apparatus was flushed several times with oxygen, and oxygen was then introduced into the bomb at the desired pressure, making a rough allowance for the increase in pressure on raising the temperature. The bomb was then heated, without agitation, to 60 or 70° by means of a custom-made heating mantle for the desired length of time, measuring the temperature (±5°) by a thermocouple. The pressure fluctuated somewhat (±5-15%), especially at the higher pressures, and values reported are "averages." The bomb was then allowed to cool to room temperature before slowly releasing the oxygen. Because of possible explosions, strict safety precautions (special explosion-proof rooms, remote control of the bomb at all times, etc.) and proper equipment are mandatory.

The products from decompositions using Freon TF were reduced by hydrogenation. In a typical reduction, the solution from the decomposition was transferred, along with ether or Freon TF washings, from the bomb to the glass bottle of a Parr hydrogenator. Catalyst, 0.50 g of 10% palladium on charcoal, was added, and hydrogenation carried out for about 1.5 hr at ambient temperature and an initial hydrogen pressure of approximately 50 psi. The catalyst was removed by filtration, and the solution concentrated by distillation at atmospheric pressure through a 4-4.5-cm column (packed length) filled with perforated stainless steel plates, followed by pumping down twice to *ca.* 180 mm on a rotary evaporator. Concentration was necessary since the solvent interfered with glpc analysis on the standard 0.25-in.-diameter columns when large samples (necessitated by the dilute nature of the solution) were injected. Products were not fractionated by this concentration procedure as shown by the consistency of the results in various runs.

Solutions were analyzed by glpc using Varian-Aerograph A-90-P and Perkin-Elmer Model 226 gas chromatographs. Products were identified by peak enhancement on addition of authentic compounds. Yields were obtained by comparison of peak areas with those obtained from standard samples. Separation of *exo* and *endo* alcohols **4** was by use of a 150 ft × 0.01 in. (i.d.) Quadrol capillary column. Other separations were accomplished by various standard columns.[19]

Registry No.—1,4-Dimethylcyclohexyl radical, 24151-68-6; 2-methylnorbornyl radical, 24212-34-8; *trans*-1,4-dimethylcyclohexanecarboxylic acid, 24097-70-9; *cis*-1,4-dimethylcyclohexanecarboxylic acid, 24097-71-0; *trans*-1,4-dimethylcyclohexanecarbonyl chloride, 24097-72-1; *cis*-1,4-dimethylcyclohexanecarbonyl chloride, 24097-73-2; *cis*-**1**, 24097-65-2; *trans*-**1**, 24097-66-3; *cis*-**1**-CO_2CH_3, 23250-42-2; *trans*-**1**-CO_2CH_3, 23059-38-3; *exo*-**3**, 24162-40-1; *endo*-**3**, 24097-69-6.

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Kinetics of the Reverse Diels-Alder Dissociation of Substituted Dicyclopentadienes

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The kinetics of the dissociation of dicyclopentadienes substituted with alkyl and ester groups were measured. The effects of these groups on the kinetics of the dissociation are described. The dimer of *t*-butylcyclopentadiene was prepared and found to be 1,4-di-*t*-butyltricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene.

Although kinetics of the dissociation of dicyclopentadiene have been the subject of a number of studies,[2] there is very little information in the literature on the dissociations of substituted dicyclopentadienes. In a previous communication from this laboratory,[3] the kinetics of the dissociation of dicyclopentadiene (**1**) and the methyl esters of dicyclopentadienemonocarboxylic acid (4-carbomethoxytricyclo[5.2.1.$0^{2,6}$]-deca-3,8-diene, **2**) and dicyclopentadienedicarboxylic acid (4,9-dicarbomethoxytricyclo[5.2.1.$0^{2,6}$]deca-3,8-diene, **3**) were reported.

Reactive dienophile trapping agents removed the monomer as it was formed and allowed measurement of the dissociation reaction without interference from the dimerization reaction. These dissociations followed first-order kinetics with respect to the dimer[4] and were independent of the nature or concentration of the trapping agent.[3]

The previous kinetic measurements had been made by a novel and rapid technique using a differential scanning calorimeter,[3] and this technique was extended to other substituted cyclopentadiene dimers which were available. This communication reports the results of these measurements.

Results

The kinetics of the dissociation reactions were measured with the differential scanning calorimeter, which measures directly the rate of absorption or evolution of heat in the sample as its temperature is being raised at a controlled rate. Liquid samples, such as the solution samples used in the present work, are in a layer of 1 mm or less thickness and are in good thermal contact with the heating and temperature sensing elements of the instrument. Problems of thermal gradients within the samples are therefore largely eliminated in these measurements.

Since the samples are in the form of solutions of reagents, such as are used in more conventional kinetic measurements, the recent criticisms[5] of the use of thermoanalytical methods to obtain kinetic data do not apply to the present measurements.

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