of magnesium in 300 ml. of tetrahydrofuran. This was added to 170 ml. of methyl borate in 640 ml. of ether with stirring below −65°. The mixture was acidified with 550 ml. of 3 *M* hydrochloric acid, extracted with butanol and ether (1:1), and distilled to yield 270 g. (75%) of dibutyl α-styreneboronate, b.p. 98° (0.4 mm.).

Anal. Calcd. for $C_{16}H_{25}BO_2$: C, 73.86; H, 9.68; B, 4.15. Found: C, 73.65; H, 9.80; B, 4.10.

Dibutyl 1-Phenylethaneboronate. Hydrogenation of 26 g. of dibutyl α-styreneboronate in 100 ml. of butanol at 2–3 atm. over 0.05 g. of 10% palladium-on-charcoal catalyst yielded 23–25 g. of dibutyl 1-phenylethaneboronate, b.p. 80–83° (0.1 mm.), d^{25} 0.910, $n^{25}D$ 1.4709.

Anal. Calcd. for $C_{16}H_{27}BO_2$: C, 73.29; H, 10.38; B, 4.12. Found: C, 73.09; H, 10.31; B, 4.12.

Bisdemethylbrucine. The nitric acid treatment[12] of pure brucine sulfate required a catalytic amount of sodium nitrite[22] to start the reaction. We used sodium bisulfite (instead of sulfur dioxide) for the reduction and found it necessary to keep the mixture below 10–15° to avoid tar formation.

Resolution of Dibutyl 1-Phenylethaneboronate. The crude bisdemethylbrucine salt worked as well as the more elaborately prepared hydrochloride.[12] It was necessary to carry out all operations under nitrogen. A solution of 42 g. of bisdemethylbrucine sulfate in 420 ml. of near-boiling water was mixed with 37 g. of dibutyl 1-phenylethaneboronate in 840 ml. of cool 95% ethanol, then treated with 14 g. of sodium bicarbonate. Crystals separated on cooling. The filtrate was concentrated under vacuum to about half its volume, diluted with 2–3 volumes of water, and treated with 30 ml. of hydrochloric acid. Extraction with four ~300-ml. portions of 1:5 butanol–ether followed by distillation yielded 5.5–6 g. of dibutyl 1-phenylethaneboronate, $[\alpha]^{23}D$ +4 to +5°. The crystalline demethylbrucine derivative was recrystallized repeatedly from 65% ethanol–water, then treated with 0.5 *M* hydrochloric acid and extracted and distilled as described for the other enantiomer. After three recrystallizations, 4.7 g. of dibutyl 1-phenylethaneboronate was obtained, $[\alpha]^{23}D$ −7.4°. Eight recrystallizations led to 1.9 g. of product, $[\alpha]^{23}D$ −10.4°.

1-Phenylethylmercuric Chloride. A solution of 1.20 g. of sodium chloride, 1.00 g. of mercuric chloride, and 0.30 g. of sodium acetate in 8 ml. of water, 5 ml. of glycerol, and 3 ml. of acetone was mixed with a (slightly cloudy) solution of 0.65 g. of dibutyl 1-phenylethaneboronate in the same quantities of solvents. Crystallization began within 0.5 hr. at 23°. The yield of 1-phenylethylmercuric chloride after 24 hr. was 0.36 g. (53%), m.p. 116–118°. In set 5, Table I, the sodium acetate was replaced by 0.13 g. of sodium hydroxide and 0.53 g. of *p*-nitrophenol and the product was isolated after 12 hr. The analytical sample was recrystallized from acetone, m.p. 118–119°.

Anal. Calcd. for C_8H_9ClHg: C, 28.16; H, 2.66; Cl, 10.39; Hg, 58.79. Found: C, 28.25; H, 2.74; Cl, 10.12; Hg, 58.72.

1-Phenylethyl Bromide. Dropwise addition of 0.9 g. of bromine in 6 ml. of pyridine to 1.5 g. of 1-phenylethylmercuric chloride in 5 ml. of pyridine at ~−60° followed by addition of 20 ml. of hexane and 20 ml. of water, then further extraction with hexane below −5°, yielded 0.45–0.5 g. (42–47%) of 1-phenylethyl bromide, b.p. 46–48° (1 mm.), shown to be free of 1-phenylethyl chloride by n.m.r. comparison with authentic samples and by elemental analysis.

Anal. Calcd. for C_8H_9Br: C, 51.92; H, 4.90; Br, 43.18. Found: C, 52.18; H, 4.87; Br, 43.43.

1-Phenylethanol was prepared from optically active dibutyl 1-phenylethaneboronate by treatment with alkaline hydrogen peroxide[7b] and distilled, yield 64–77%.

(22) H. Leuchs, H. Seeger, and K. Jaegers, *Ber.*, 71, 2023 (1938).

The Stereochemistry of 9-Decalyl Free Radicals

Paul D. Bartlett, Richard E. Pincock, John H. Rolston, W. G. Schindel, and L. A. Singer

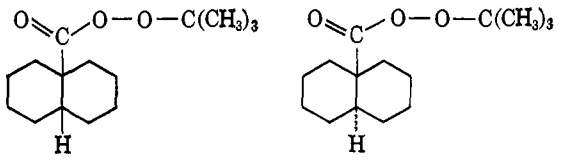
Contribution from the Departments of Chemistry of Harvard University, Cambridge, Massachusetts 02138, and of the University of British Columbia, Vancouver 8, British Columbia. *Received March 11, 1965*

cis- and trans-9-carbo-t-butylperoxydecalins undergo thermal decomposition in cumene at 50° at identical rates and with direct formation of decalyl radicals, carbon dioxide, and t-butoxy radicals. The products, cis- and trans-decalins, 1,9- and 9,10-octalins, formed from decalyl radicals in various degassed solvents, are the same from either perester. In the presence of oxygen at 1 atm. in cyclohexane or 1,2-dimethoxyethane, cis- and trans-9-decalyl hydroperoxides are formed (10% cis, 90% trans from either perester). This same ratio of hydroperoxides is also obtained from trans perester at 600 atm. of oxygen, while at high pressures from cis perester more cis hydroperoxide is formed (e.g., at 545 atm. of oxygen in 1,2-dimethoxyethane, 70% cis, 30% trans). The results show that two different 9-decalyl radicals exist; one a short-lived (ca. 10^{-8}–10^{-9} sec.) radical from cis source which changes into the same radical obtained from trans source but yields cis product on reaction with oxygen, and the other a more stable radical from trans source which yields both cis and trans products on reaction with oxygen. The products obtained indicate a nonplanar arrangement of bonds at C-9 for the initial radical from cis source and a coplanar arrangement of bonds at C-9 for the more stable radical from both sources.

Introduction

A reaction which involves an intermediate free alkyl radical usually results in a mixture of products arising from nonstereospecific reactions at the radical center. Thus generation of a radical at the single asymmetric center of an optically active compound leads to racemic products,[1,2] while stereoisomeric compounds give identical mixtures from either isomer.[3] Such lack of stereospecificity is interpretable either in terms of a planar arrangement of the atoms attached to the radical center, or in terms of a nonplanar radical which inverts configuration faster than it otherwise reacts. Both of these possibilities result in loss of structural features which would lead to specific products, so a choice between planar and nonplanar structures for the intermediate free radicals involved cannot be made. Although radicals constrained to a nonplanar state, as at the bridgehead of a small bicyclic ring system,[4] seem to be formed less readily than related unconstrained radicals, and physical measurements on simple free alkyl radicals indicate a planar arrangement as the most stable state,[5] it is possible that a nonplanar configuration exists in some flexible systems when radicals are initially formed.

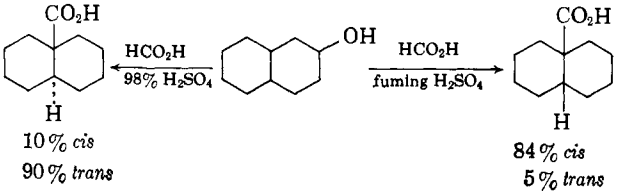
To obtain information concerning the possible existence of radicals which have a short stereochemical "memory" of their origin, a highly reactive scavenging agent is required, one able to react with radicals even before conversion to planar or inversion to isomeric nonplanar radicals occurs. Observation of different products from two isomeric sources would then directly indicate the presence of two isomeric radicals and make possible an estimate of their lifetimes. Since molecular oxygen is known[6] to have an extremely high rate of reaction with alkyl radicals, we have investigated the stereochemistry of the reaction of oxygen with radicals generated from two isomeric compounds. We report here a study of the reactions of 9-decalyl radicals generated from *cis*- and *trans*-9-carbo-*t*-butylperoxydecalins (*cis*-I and *trans*-I). These compounds are convenient since the radicals are formed from the peresters at low temperatures (*ca.* 50°), the product hydroperoxides are stable under the reaction conditions, and the stereochemical results are readily determined by analysis of the known *cis*- and *trans*-9-decalols obtained by the reduction of the hydroperoxides.



cis-I *trans*-I

Results

cis- and *trans*-9-decalincarboxylic acids were prepared by carbonylation of the 9-decalyl cation generated from decahydro-2-naphthol.[7] Kinetic control of product formation leads predominantly to *trans* isomer while equilibrium control favors the *cis* isomer.[8] Recrystallization of the acid mixtures or preparative gas phase



chromatographic separation of their methyl esters followed by hydrolysis gave the pure acids; *trans* m.p. 134°, *cis* m.p. 122°. Reaction of the corresponding acid chlorides with the sodium salt of *t*-butyl hydroperoxide gave the peresters *cis*-I and *trans*-I as oils which were purified by chromatography on Florisil.

The results of kinetic studies, followed by measurement of the rate of loss of perester carbonyl absorption at 5.67 μ in cumene, are shown in Table I. Both isomers decompose at about the same first-order rate and show no appreciable increase in rate constant with higher concentrations of perester. The rates of decomposition are about eight times greater than that of *t*-butylperoxy trimethylacetate which is known to undergo decomposition with direct formation of tertiary radicals.[9]

Table I. Rates of Decomposition of *cis*- and *trans*-9-Carbo-*t*-butylperoxydecalins in Cumene

Perester	Temp., °C.	Concn., *M*	$k_1 \times 10^5$ sec.$^{-1}$
cis[a]	45.0	0.0546	3.64
	55.0	0.0586	13.9
		0.646	14.3
	65.0	0.0686	46.7
		0.0612	46.7
		0.634	49.0
trans[b]	45.0	0.0592	3.76
	55.0	0.0558	14.5
		0.629	14.8
	65.0	0.0581	49.0
		0.0576	47.5
		0.620	50.3

[a] $\Delta H^* = 26.6$ kcal., $\Delta S^* = 4.7$ e.u. [b] $\Delta H^* = 26.4$ kcal., $\Delta S^* = 4.2$ e.u.

The products of decomposition of either perester in degassed cumene are carbon dioxide (greater than 90% yield), *t*-butyl alcohol (*ca.* 80%), acetone, *cis*- and *trans*-decalins, 1,9- and 9,10-octalins, and dicumyl. The

(1) (a) H. C. Brown, M. S. Kharasch, and T. H. Chao, *J. Am. Chem. Soc.*, **62**, 3435 (1940); (b) W. von E. Doering, M. Farber, M. Sprecher, and K. B. Wiberg, *ibid.*, **74**, 3000 (1952); (c) J. T. Gruver and J. G. Calvert, *ibid.*, **80**, 3524 (1958); (d) F. D. Greene, *ibid.*, 81, 2688 (1959); (e) D. B. Denney and W. F. Beach, *J. Org. Chem.*, **24**, 108 (1959); (f) H. J. Dauben, Jr., and L. L. McCoy, *J. Am. Chem. Soc.*, 81, 5404 (1959); (g) for a stereospecific radical reaction involving a bridged radical intermediate see P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963).

(2) For radicals formed from diacyl peroxide decompositions see F. D. Greene, H. P. Stein, C. C. Chu, and F. M. Vane, *ibid.*, **86**, 2080 (1964), and references therein.

(3) See, *e.g.*, S. J. Cristol, J. R. Douglas, W. C. Firth, Jr., and R. E. Krall, *J. Org. Chem.*, **27**, 2711 (1962); F. D. Greene, C. C. Chu, and J. Walia, *ibid.*, **29**, 1285 (1964).

(4) M. S. Kharasch, F. Englemann, and W. H. Urry, *J. Am. Chem. Soc.*, **65**, 2428 (1943); P. D. Bartlett and F. D. Greene, *ibid.*, **76**, 1088 (1954); see also ref. 2.

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

(6) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 418, 436.

(7) H. Koch and W. Haaf, *Ann.*, **618**, 251 (1958).

(8) R. E. Pincock, E. Grigat, and P. D. Bartlett, *J. Am. Chem. Soc.* 81, 6332 (1959).

(9) P. D. Bartlett and D. M. Simons, *ibid.*, **82**, 1753 (1960).

Table II. Products of Thermal Decomposition of *cis*- and *trans*-9-Carbo-*t*-butylperoxydecalins in Various Degassed Solvents at 50°

Perester	Concn., *M*	Solvent	Products, % Decalins *cis*-	Decalins *trans*-	Octalins 1,9-	Octalins 9,10-	Total octalins
trans	0.338	Cumene	66	34	81	19	42
cis	0.337	Cumene	66	34	83	17	39
cis	0.280	Cumene[a]	82	18	50	50	36
trans	0.356	Cyclohexane	84	16	79	21	45
cis	0.401	Cyclohexane	83	17	76	24	43
cis	0.444	Cyclohexane[b]	85	15	48	52	35
trans	0.244	Isooctane	85	15	80	20	44
cis	0.381	Isooctane	81	19	78	22	41
cis	0.323	Toluene	84	16	80	20	30
cis	0.304	Chloroform	63	37	43	57	69

[a] Contains 0.56 *M p*-thiocresol. [b] Contains 0.89 *M p*-thiocresol.

decalyl-derived products in various degassed solvents as determined by vapor phase chromatography are shown in Table II. Either *cis* or *trans* perester gives the same mixture of hydrocarbons in each solvent. Although the relative yields of the products change slightly with solvent, *trans*-decalin predominates over *cis*-decalin and 1,9- over 9,10-octalin.

In the presence of oxygen at atmospheric pressure the formation of decalins is totally suppressed; the products are *cis*- and *trans*-9-decalyl hydroperoxides[10] and the two octalins. For analysis by v.p.c. the decalyl hydroperoxides present in the product solutions were reduced with lithium aluminum hydride to the known *cis*- and *trans*-9-decalols. The effect of oxygen pressure on the products was studied in cyclohexane containing pyrogallol and in 1,2-dimethoxyethane. As shown in Table III the relative yield of *cis*-9-decalol from *cis* perester

Table III. Products[a] of Thermal Decomposition of *cis*- and *trans*-9-Carbo-*t*-butylperoxydecalins in the Presence of Oxygen at 50°

Perester	Solvent	O_2 pressure, atm.	Products,[b] % 9-Decalols *trans*-	9-Decalols *cis*-	Octalins 1,9-	Octalins 9,10-
cis	Cyclohexane[c]	1	87	13	73	27
trans		1	89	11	79	21
cis		3.5	84	16	74	26
trans		3.5	93	7	..	..
cis		95	63	37	73	27
trans		95	89	11	68	32
cis	1,2-Dimethoxyethane	1	85	15	66	32
trans		1	91	9	57	43
cis		146	61	39	..	..
cis		340	46	54	63	37
cis		545	30	70	53	47
trans		600	87	13	59	41

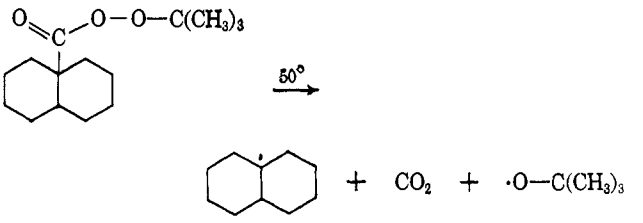
[a] After lithium aluminum hydride reduction. [b] Estimated possible error in percentages is ±5%. [c] Containing pyrogallol as an oxidation inhibitor for solvent.

increases with pressure from 15% *cis* at 1 atm. to 70% *cis* at 545 atm., while the relative yield of *cis*- and *trans*-decalols from *trans* perester remains unchanged from 1 to 600 atm. (*ca.* 90% *trans* and 10% *cis*-9-decalols). The absolute yield of octalins decreases slightly with increasing pressure but still remains about 20% at 500–600 atm. of oxygen in 1,2-dimethoxyethane.

(10) The presence of the uncharacterized compound, *cis*-9-decalyl hydroperoxide, among the many products of autoxidation of *cis*- and *trans*-decalins has been established by F. Jaffe, T. R. Steadman, and R. W. McKinney, *J. Am. Chem. Soc.*, 85, 351 (1963).

Discussion

The products of thermal decomposition of *cis*- and *trans*-I establish these peresters as efficient sources of decalyl radicals, while their high rates of decomposition show that decalyl radicals are formed by direct, rate-determining loss of carbon dioxide. Since the activation parameters for decomposition of the two



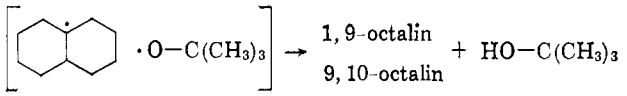
peresters are the same, the transition states in the decompositions differ energetically (and probably structurally) to the same extent as do the peresters themselves. It is possible then that newly formed radicals also retain, at least momentarily, structural features similar to those of the original peresters.

Hydrogen atom transfer to decalyl radicals from various hydrocarbon solvents or from *p*-thiocresols is not fast enough to distinguish any difference in radicals as formed from the two sources and the same amounts of *cis*- and *trans*-decalins (Table II) are formed from either perester.[11] The variation in the ratio of *cis*/*trans* decalins among the solvents may reflect steric effects in the ability of different solvents to approach the two sides of decalyl radicals during the hydrogen atom transfer (see below).

The octalin products, which arise by hydrogen atom transfer from decalyl radicals, are also identical from the two sources, and the ratio of 1,9- to 9,10- isomers found in most solvents is near 4:1.[12] The two octalins are formed to the extent of 20% even in the presence of high concentrations of oxygen (see Table III), and under these conditions must arise from the cage reaction of decalyl radicals with *t*-butoxy radicals.

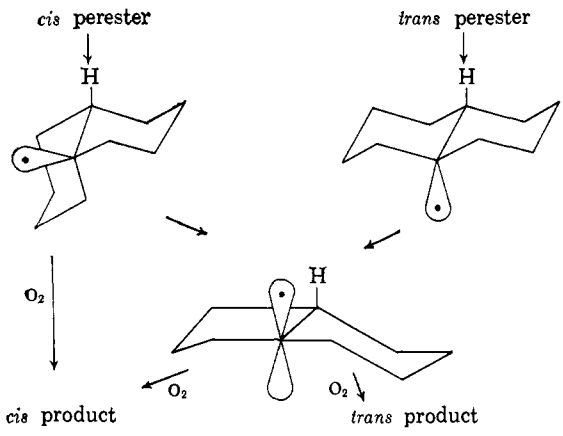
(11) Isomerization of the two decalins after their formation cannot proceed to any appreciable extent under the conditions used. See R. M. Roberts and J. J. Madison, *ibid.*, 81, 5839 (1959).

(12) The ratios of octalins found in degassed solvents are probably the kinetically controlled initial product ratios, but some later isomerization is possible, especially in the presence of *p*-thiocresol.



As expected from the high rate of the reaction of oxygen with alkyl radicals, the presence of oxygen even at 1 atm. is sufficient to eliminate completely the formation of decalins by hydrogen atom transfer from solvent. All of the decalyl radicals which escape the cage reaction with *t*-butoxy radicals react with oxygen to give decalylperoxy radicals which in turn obtain hydrogen atoms from the solvent or from added pyrogallol to form the two 9-decalyl hydroperoxides. Oxygen in low concentration (*i.e.*, at 1 atm.) gives the same ratio of *cis*- to *trans*-9-decalols from both peresters; the reaction with oxygen under these conditions is not fast enough to indicate any difference in decalyl radicals from the two isomeric sources. However, at high pressures the greatly different relative yields of *cis* and *trans* hydroperoxides from *cis* and *trans* sources directly shows that two different 9-decalyl radicals are initially formed in decomposition of the two peresters. The difference persists long enough for the radicals to escape the cage disproportionation reaction, but not long enough to give significantly different products in reaction with oxygen at low pressures.

Two different decalyl radicals which have nonplanar radical centers and react as shown below do not directly account for the results. If *cis* radical from *cis* perester is captured by reaction with oxygen before inversion to *trans* radical, then *trans* radical from *trans* perester should also be more efficiently captured by oxygen at high pressures before conversion to *cis* radical. However, the ratio of *cis* to *trans* product from *trans* perester is unchanged by a variation of oxygen pressure of 1 to 600 atm. As *cis* product from *trans* source is observed to the invariant extent of 10% at all pressures of oxygen, the above scheme does not fit the results.[13]



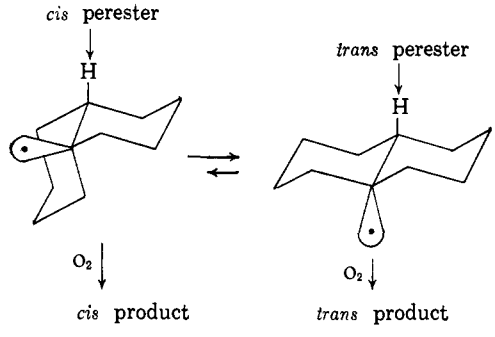
A reaction scheme which accommodates the available data involves the radicals shown below. Initial nonplanar radicals are quickly converted to a planar radical which reacts to form both *cis* and *trans* products. The initial radicals have conformations which are similar to the conformations of the parent peresters.

(13) A direct pressure effect, which would favor *cis* product due to its smaller molar volume, may be involved in modifying the ratio of products formed at high pressures. At the pressures used, however, this effect must be small and the change of oxygen concentration with pressure a much more important factor.

If a radical with coplanar bonds at C-9 retains, as is indicated by models, a near-chair form for both rings, an initial radical from *trans* perester may be readily converted to planar radical with only a slight flexing of its structure, while *cis* radical requires an inversion of one of its chair-form rings. This process can be slow relative to the times involved in trapping by oxygen at high concentrations. With low concentrations of oxygen the radicals from *cis* perester have time to reach the planar stage before reacting.

The planar arrangement around C-9 of the more stable decalyl radical accounts for formation of both *cis* and *trans* products from *trans* source at all oxygen pressures and is consistent with evidence[5] that planar radical structures are most stable. A planar decalyl radical giving predominant *trans* product (*i.e.*, 85% *trans* and 15% *cis*) on reaction with oxygen is analogous to a planar decalyl cation giving predominant *trans*-9-decalylcarboxylic acid (90% *trans* and 10% *cis*) in the carbonylation reaction.[8] The similar steric requirements of oxygen and of carbon monoxide lead to similar products. The important difference exists that carbonylation of the cation is reversible, while no reversal is known of the oxygenation of the radical. More bulky reactants should favor *cis* product, as is consistent with the greater relative yields of *cis*-decalin (Table II) on hydrogen atom transfer from cumene and chloroform to decalyl radicals.

The existence of at least two structurally different 9-decalyl radicals in decomposition of 9-decalyl peresters shows that the formation of a single planar radical is not a necessary condition for radical formation by perester decomposition[14] and suggests that the existence of short-lived structurally isomeric radicals might be more general. It is likely, however, that this requires constraints other than those arising from the bonds directly to the free-radical center. In the formation of products, the evidence is that isomeric radicals can be



stereochemically important only in very fast reactions, such as the reaction with oxygen or in radical–radical cage reactions.[14,15]

The rate constants for conformational interconversion of the two forms of 9-decalyl radical, and for the reaction of either form with oxygen, are uncertain by several orders of magnitude. However, the ratio between these two rate constants can be estimated by the following considerations.

(14) Two stereoisomeric decalyl radicals *both* with coplanar arrangements of the atoms attached to C-9 do not seem to be likely candidates for the two radicals required. Models suggest that planarity of the bridgehead carbon bonds at C-9 allows only very slight conformational differences elsewhere in the chair-form ring system.

(15) K. B. Wiberg and G. Foster, *J. Am. Chem. Soc.*, 83, 423 (1961).

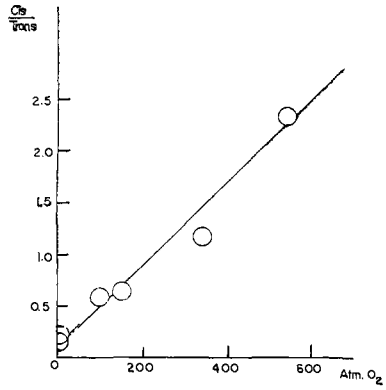
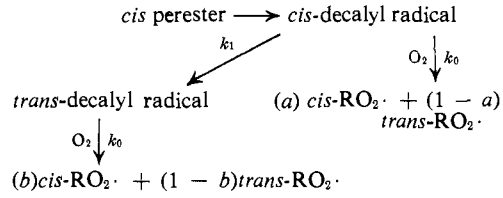


Figure 1. *cis*/*trans* ratio of 9-decalyl hydroperoxide produced from *cis*-9-carbo-*t*-butylperoxydecalin as a function of oxygen pressure: first three points, cyclohexane solvent; last three points, dimethoxyethane solvent.

In the sequence



let x = [*cis*-decalyl radical] and y = [*trans*-decalyl radical] and assume that O_2 reacts with both conformations with the same rate constant, k_0.
Then

$$(dy)/(dt) = k_1x - k_0y[O_2]$$

applying the steady-state approximation yields

$$y = \frac{k_1}{k_0[O_2]}x$$

Then

$$\frac{d(cis\text{-}RO_2\cdot)}{d(trans\text{-}RO_2\cdot)} = \frac{ak_0[O_2]x + bk_0[O_2]y}{(1-a)k_0[O_2]x + (1-b)k_0[O_2]y}$$

Substituting for y

$$\frac{d(cis\text{-}RO_2\cdot)}{d(trans\text{-}RO_2\cdot)} = \frac{a + b\dfrac{k_1}{k_0(O_2)}}{(1-a) + (1-b)\dfrac{k_1}{k_0(O_2)}}$$

Since this expression is constant throughout any run it is also equal to r, the *cis*/*trans* ratio in the product. Now

$$r(1-a) + \frac{rk_1(1-b)}{k_0(O_2)} = a + \frac{bk_1}{k_0(O_2)}$$

For the probable case that $a = 1$, this becomes

$$rk_1(1-b) - bk_1 = k_0(O_2)$$

or

$$r = \frac{k_0(O_2)}{k_1(1-b)} + \frac{b}{1-b} \qquad (1)$$

Figure 1 shows a plot of the data in two solvents according to eq. 1. The plot is a line of slope 0.0040 atm.$^{-1}$. The average value of b from Table II is 0.1. Using this and the solubility of oxygen in cyclohexane at 25°[16] yields the result that

$$\frac{k_0}{k_1} = 0.9 \times 0.0040/0.012$$
$$= 0.3 \text{ l./mole}$$

Thus if we could establish either the rate constant for conformational change of *cis*- → *trans*-9-decalyl radical, or the rate constant for oxygenation of this radical, we should know the other value. A rate constant of about 3×10^6 sec.$^{-1}$ can be estimated for the chair–chair interconversion of the cyclohexane conformers at 50° from n.m.r. evidence.[17] Although much the same forces are involved in the chair–chair interconversion in *cis*-decalin, this change has been found to be faster than in cyclohexane and not to be measurable by the same means.[18] Moreover, the absence in the radical of one of the rigid tetrahedral carbon atoms of the decalin molecule can only reduce further the barrier to conformational interconversion. Thus the value of k_1 must be considerably greater than 3×10^6 sec.$^{-1}$. No upper limit on its value is available since even the diffusion-controlled cage reaction between decalyl and *t*-butoxy radicals leading to octalins fails to distinguish between *cis*- and *trans*-decalyl radicals.

Similar uncertainty prevails with respect to the value of k_0. Its lower limit is about 3×10^7 l./mole sec., and it may be much greater.[19]

Experimental

cis-9-Decalincarboxylic Acid. A representative preparation was as follows. To 415 g. of 98% sulfuric acid was added 200 g. of 30% fuming sulfuric acid and the solution was cooled to *ca.* 10°. About 3 ml. of 88% formic acid was added and the rapidly stirred solution was cooled to 5°. After 5 min., 46 g. of 88% formic acid and 50 g. of decahydro-2-naphthol (or its acetate ester) were added from two dropping funnels over 0.5 hr. The solution should foam greatly during the additions. After stirring at *ca.* 0° for 0.5 hr. longer, the solution was poured on ice. The oil, which soon crystallized, was dissolved in ether and extracted into 10% sodium carbonate solution. Acidification of the aqueous layer gave 47 g. (80%) of 9-decalincarboxylic acid which was largely *cis* by qualitative infrared comparisons.[8] After three recrystallizations from acetone, 7.0 g. was obtained which melted at 121.8–123° (lit. 122.0–122.3[23] and 123–124°[7]).

(16) The Ostwald coefficient of oxygen in cyclohexane at 25° is 0.282, A. B. McKeown and R. R. Hibbard, *Anal. Chem.*, 28, 1490 (1956), corresponding to 0.0126 *M*/atm. partial pressure of oxygen; the value in diethyl ether at 20° is 0.017 *M* per atm.: F. Fischer and G. Pfleiderer, *Z. anorg. allgem. Chem.*, **124**, 61 (1922); *Chem. Abstr.*, 17, 7 (1923). Assuming Henry's law there should be 7.56 *M* oxygen in cyclohexane under oxygen at 600 atm. at 25°.

(17) F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *J. Am. Chem. Soc.*, **82**, 1256 (1960); **84**, 386 (1962).

(18) W. B. Moniz and J. A. Dixon, *ibid.*, **83**, 1671 (1961).

(19) The rate of reaction of oxygen with tetralyl radicals[20] at 25° is 6.76×10^7 l. mole^{-1} sec.$^{-1}$, with α-phenylalkyl radicals[21] from styrene 3×10^7 l. mole^{-1} sec.$^{-1}$. With simple alkyl radicals the reaction is very fast[22] and may be diffusion controlled (*i.e.*, a rate constant of *ca.* 10^{10} l. mole^{-1} sec.$^{-1}$).

(20) C. H. Bamford and M. J. S. Dewar, *Proc. Roy. Soc.* (London), **A198**, 252 (1949).

(21) A. A. Miller and F. R. Mayo, *J. Am. Chem. Soc.*, 78, 1017 (1956).

(22) G. A. Russell in "Peroxide Reaction Mechanisms," J. O. Edwards, Ed., Interscience Publishers, Inc., New York, N. Y., 1962, p. 107.

trans-9-Decalincarboxylic Acid. Method I. To 600 g. of 98% sulfuric acid at 0° was added about 3 ml. of 88% formic acid. When the rapidly stirred solution became foamy with evolution of carbon monoxide, 50 g. of decahydro-2-naphthol (or acetate) and 100 g. of 88% formic acid was added from two dropping funnels over 3 hr. During the addition the temperature was less than 5° and the mixture continued to foam. Work-up as for the *cis* acid gave 50 g. (85%) of solid acid, predominantly *trans*. After three recrystallizations from acetone, 7.5 g. was obtained with m.p. 134.5–135.5° (lit.[7] 134.6–135.7°).

Method II. The methyl esters of mixtures of the 9-decalyl acids were prepared by treatment with diazomethane in ether. Pure esters were obtained from mixtures containing predominantly one isomer by preparative gas phase chromatography using a 5-ft. Apiezon J on firebrick column at 210° with 600-μl. repetitive shots.

The pure acids were obtained by hydrolysis of the chromatographically pure esters. Hydrolysis of the *trans* ester, which proceeds more slowly than with the *cis* isomer, was as follows. Methyl *trans*-9-decalincarboxylate (17.5 g.), shown to be free from *cis* isomer by v.p.c., in 80 ml. of 95% ethanol containing 23 g. of potassium hydroxide, was refluxed 96 hr. Evaporation of ethanol under vacuum, addition of ether, and extraction with 5% potassium hydroxide solution separated 6.8 g. of *trans* acid from 9.3 g. of recovered ester.

cis-9-Decalincarbonyl Chloride. *cis*-9-Decalincarboxylic acid, 10 g., was added in small portions over 0.5 hr. to 30 g. of stirred thionyl chloride. The solution was allowed to stand at room temperature for 17 hr. and then heated on a steam bath for 1 hr. Distillation at 114–120° (6 mm.) gave 9.9 g. of acid chloride, $n^{26.5}$D 1.5051.

trans-9-Decalincarbonyl Chloride. *trans*-9-Decalincarboxylic acid with thionyl chloride, as with the *cis* isomer above, gave its acid chloride, b.p. 105–112° (8 mm.), $n^{26.5}$D 1.4998. This compound crystallized slowly on standing at room temperature. The infrared spectra of the two acid chlorides are strikingly different; the *trans* isomer has two carbonyl bands at 5.54 and 5.60 μ (evidently due to Fermi resonance) and four strong bands at 10.45, 11.08, 12.1, and 13.7 μ, while the *cis* isomer has a single carbonyl band at 5.58 μ and many bands in the "fingerprint" region not possessed by the *trans* isomer.

9-Carbo-t-butylperoxy-cis-decalin. The sodium salt of *t*-butyl hydroperoxide was prepared by dropwise addition of 25 g. to 150 ml. of a cold 20% sodium hydroxide solution. The crystals formed were collected and washed with acetone. The salt was then dried at 55° under vacuum for 13 hr.

To 7 g. of sodium *t*-butylperoxide suspended in 50 ml. of cold ether was added 7 g. of *cis*-9-decalincarbonyl chloride in 20 ml. of ether. The mixture was stirred for 3 hr. at room temperature, 10 ml. of water was added, and the two-phase mixture was stirred rapidly for 15 min. in order to hydrolyze unreacted acid chloride. Pentane was added and the organic layer washed with cold solutions of 10% sulfuric acid, 10% sodium carbonate, and water. The organic phase was dried and evaporated at low temperature. The residue was taken up in pentane and washed several times with water to remove *t*-butyl hydroperoxide. After drying and evaporation, 6.4 g. of *cis* perester was obtained. After purification by chromatography on Florisil to remove traces of hydrocarbon impurities formed in the preparation, n^{20}D 1.4810.

Anal. Calcd. for $C_{15}H_{26}O_3$: C, 70.82; H, 10.30. Found: C, 70.95; H, 10.53.

9-Carbo-t-butylperoxy-trans-decalin. A mixture of 3 g. of sodium *t*-butylperoxide and 5 g. of *trans*-9-decalincarbonyl chloride in 50 ml. of ether was rapidly stirred at room temperature for 8.5 hr. Water was added and the ether layer was washed with cold 10% sulfuric acid, then dried and evaporated under vacuum. To hydrolyze excess acid chloride the residue was stirred at 0° for 7 hr. with 5 ml. of pyridine and 5 ml. of water. Pentane was added and the organic phase was washed with 10% sulfuric acid, 10% sodium carbonate, and water. After drying with magnesium sulfate, the pentane was evaporated at low temperature to leave 2.3 g. of a clear oil. Samples of *trans* perester prepared this way were free from acid chloride, but contained some hydrocarbon decomposition products formed during the long preparation. These were removed by chromatography on Florisil, with elution by petroleum ether (b.p. 35–57°) followed by ethyl ether, to yield *trans* perester, n^{20}D 1.4750.

Anal. Calcd. for $C_{15}H_{26}O_3$: C, 70.82; H, 10.30. Found: C, 70.80; H, 10.13.

Kinetic Procedure. The rates of decomposition of the *cis* and *trans* peresters in cumene were obtained by use of the infrared analytical method previously described.[24]

Product Analyses. Analysis of the hydrocarbons formed in degassed solvents was by v.p.c. on a Ucon LB-55X column at 100° or on a 6-ft. Carbowax 20-M on acid-washed 60–80 Chromosorb W column at 105°. The order of elution was *trans*-decalin, *cis*-decalin, 1,9-octalin, and 9,10-octalin. These were identified by comparison of retention times with those of authentic decalins and with the components of an octalin mixture prepared by dehydration of decahydro-2-naphthol with phosphoric acid.[25] 1,9- and 9,10-octalins were collected and identified by their infrared and n.m.r. spectra.

Analysis of the *cis*- and *trans*-9-decalols was also carried out with the above-mentioned v.p.c. columns or on a 20% Apiezon J firebrick column at 135°. The 9-decalols are easily resolved and the relative amounts determined by the ratio of areas of the chromatographic traces. Authentic *trans*-9-decalol was prepared by reduction of *trans*-9-decalyl hydroperoxide and *cis*-9-decalol by oxidation of *cis*-decalin.[15]

Product Study Runs. Runs in the presence of oxygen were carried out in cyclohexane with added pyrogallol and in 1,2-dimethoxyethane (distilled from lithium aluminum hydride). The general procedure was as follows. The perester, *ca.* 1.00 g., was dissolved in 30 ml. of 1,2-dimethoxyethane and placed in the glass

(23) W. G. Dauben and J. B. Rogan, *J. Am. Chem. Soc.*, **79**, 5002 (1957).

(24) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *ibid.*, **82**, 1762 (1960).

(25) A. S. Hussey, J. Sauvage, and R. H. Baker, *J. Org. Chem.*, **26**, 256 (1961).

liner of a steel, high-pressure bomb. After introduction of oxygen, the bomb was warmed, with suitable protection from possible explosions, to 50–55° for 24 hr. and then allowed to cool to room temperature before slowly releasing the oxygen. The solution was evaporated down to a residual oil. This was dissolved in 20 ml. of anhydrous ether and reduced with excess lithium aluminum hydride at room temperature. After addition of water, the ether layer was dried and evaporated. The residue was analyzed by v.p.c. as described above. When cyclohexane was used the solution was filtered free from suspended pyrogallol before evaporation and hydride reduction. The decomposition of the peresters was shown to be complete by absence of carbonyl absorption in the initial product mixture and absence of *cis*- or *trans*-9-decalylcarbinols in the reduced products. In 1,2-dimethoxyethane the weight of crude products corresponded to 70–80% yields of hydroperoxides.

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The Stereochemistry of the Pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradecanes and -dienes. Norbornene and Norbornadiene Dimers

Donald R. Arnold, David J. Trecker,[1] and Earl B. Whipple

Contribution from the Union Carbide Research Institute, Tarrytown, New York.
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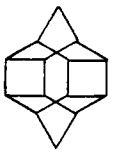
Six of the possible twelve stereoisomeric pentacyclo[8.2.1.1^{4,7}.0^{2,9}.0^{3,8}]tetradecanes and -dienes have been prepared, separated, and characterized. The structural assignments were made largely on the basis of a detailed study of the n.m.r. spectra.

The importance of the stereochemistry of a reaction product as a probe into the mechanism for its formation has been adequately demonstrated in the past. This is particularly true for norbornene where the double bond has one side (*exo*) less hindered than the other (*endo*) by virtue of strong steric shielding by the *endo* hydrogens on the ethylene bridge. Thus, reagents prefer to approach norbornene from the *exo* side.[2] The purpose of this work was to determine the stereochemistry of the norbornene and norbornadiene dimers. With this knowledge in hand it is possible to reflect upon the mechanism of the reactions for their formation. It should be noted that the stereochemistry of some of these isomers has been erroneously assigned[3a,b] and several times quoted[3c,d] in the recent past.

There are six possible stereoisomeric structures for a dimer of norbornene or norbornadiene, corresponding to three ways of specifying two possible configurations (*exo* or *endo*) in each of two norbornane fragments[4] and two independent choices of juncture (*cis* or *trans*) to the four-membered ring; these are shown in rough projection formulas in Table I. All of the structures have a plane of symmetry; in addition **1**, **2**, **4**, **5**, **7**, **8**, **10**, and **11** have a twofold axis. The point groups are as indicated in the table.

On the basis of molecular models and calculations reported below, structures **7**, **10**, and **11** are expected to be highly strained in order to relieve nonbonded repulsions between protons at 13, 14, or 5, 6, and 11, 12. The situation is more favorable in **12** since the opposing groups do not lie in the same plane, and possibly in **8** and **9** where the interactions involve π-electrons.

Pertinent to the possible existence of **8** is the isolation of a saturated norbornadiene dimer for which structure **13** is proposed.[3b,6] This structure could have **8** as a precursor.



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Preparation of Dimers. The arguments that follow demonstrate that the stereochemistry of the dimers which have been prepared to date is that of structures **1** through **6** (Table I). The reactions used for the preparation of these dimers are summarized in eq. 1–7.[7] In addition, treatment of norbornadiene with phenyllithium is reported[8] to give a dimer (m.p. 33°) which

(1) Research and Development Department, Chemicals Division, Union Carbide Corp., South Charleston 3, W. Va.

(2) E. J. Corey, R. Hartmann, and P. A. Vatakencherry, *J. Am. Chem. Soc.*, **84**, 2611 (1962), and references therein.

(3) (a) C. W. Bird, R. C. Cookson, and J. Hudec, *Chem. Ind.* (London), 20 (1960); (b) C. W. Bird, D. L. Colinese, R. C. Cookson, J. Hudec, and R. O. Williams, *Tetrahedron Letters*, 373 (1961); (c) D. Scharf and F. Korte, *ibid.*, 821 (1963); (d) G. N. Schrauzer and S. Eichler, *Ber.*, **95**, 2764 (1962).

(4) Structures in which the cyclobutane ring is fused *trans* on the norbornane would be highly strained. There are several examples of a six-membered ring fused to a four-membered ring by a *trans* juncture but only a few examples of a five-membered ring fused to a four-membered ring by a *trans* juncture, and then only when the five-membered ring is flexible.[5]

(5) J. Meinwald, J. J. Tufariello, and J. J. Hurst, *J. Org. Chem.*, **29**, 2914 (1964).

(6) D. M. Lemal and K. S. Shim, *Tetrahedron Letters*, 368 (1961).

(7) We wish to thank Professor R. C. Cookson for providing samples of dimers **2** and **5**.

(8) G. Wittig and J. Otten, *Tetrahedron Letters*, 601 (1963).