

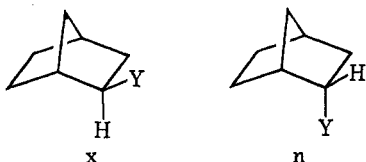
Stereoselectivity in Free Radicals of the Norbornyl Type*

PAUL D. BARTLETT, GARRY N. FICKES, FREDERIC C. HAUPT, AND ROGER HELGESON

Converse Memorial Laboratory, Harvard University, Cambridge, Massachusetts 02138

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One of the most dramatic examples of dissimilar behavior of closely related stereoisomers has been observed in the *exo*- and *endo*-2-substituted norbornanes (x and n). In ionizing systems, where Y is a sulfonate



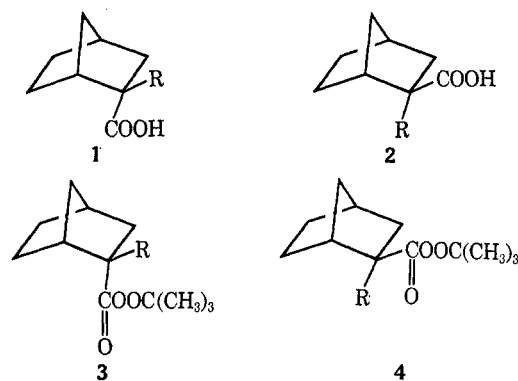
or carboxylate group, the *exo* isomer is often a thousand times as reactive as the *endo* in ionization and is formed by recombination of the ions with a kinetic preference of the same order of magnitude. Since at equilibrium x is favored over n in such cases by a factor of only four or five, much interest has been attached to the structural and mechanistic factors entering into this strong kinetic selectivity.

In contrast to the norbornyl cation, the norbornyl free radical appears from previous work to have only mild stereoselectivity responding to the bulk of the attacking reagent.¹⁻¹⁴ The preference for attack to give one configuration is modified or even reversed by adjacent *exo* or *endo* substituents in the ring.

Our work was undertaken in order to apply the free-radical criterion uniformly, with the precision allowed by vapor phase chromatography, to a related set of

secondary and tertiary norbornyl and apobornyl radicals with the widest possible range of atom donors. The norbornyl radical is expected to be stereochemically similar to the charge-localized or "classical" structure for the much-studied norbornyl cation, and the steric effects in reactions of the latter should be reflected also in the former.

Sources of Norbornyl Radicals. The principal sources of the norbornyl radicals used were the *endo* and *exo* peresters **3** and **4**, prepared according to standard general methods. In the decomposition of these peresters it was repeatedly found that identical products resulted from **3** and **4** in all experiments in fluid media (a contrary result in a rigid glass is described in the next section). In view of this identical behavior of the *exo*- and *endo*-peresters, some experiments were performed on a mixture of **3d** and **4d** (R = Cl), without separating the geometrical isomers.



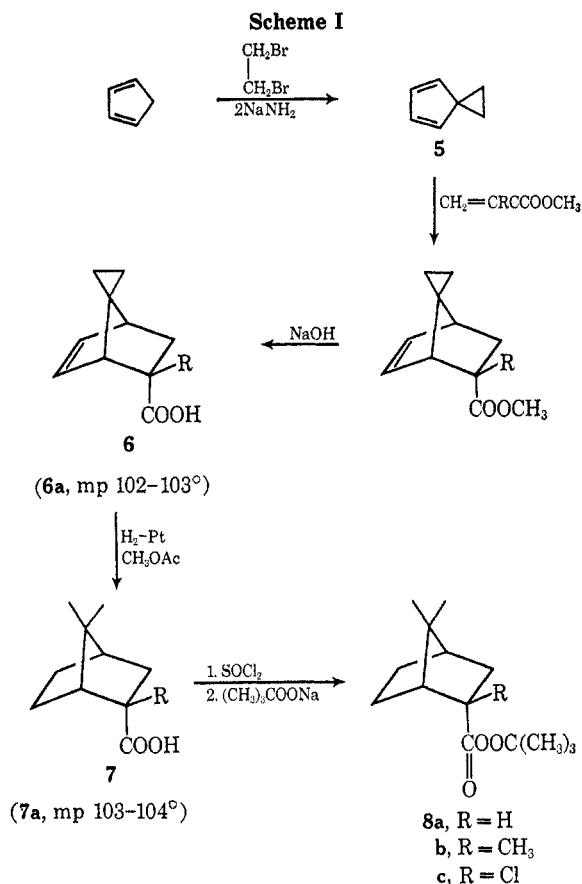
a, R = H; b, R = CH₃; c, R = C₆H₅; d, R = Cl

Scheme I shows the method employed for the synthesis of the *endo*-apobornyl perester **8a**, the *endo* orientation being apparently complete for the addition of methyl acrylate to spiroheptadiene (homofulvene, **5**). The addition of methyl methacrylate to homofulvene gave a mixture of *endo* and *exo* products which was made into a stereoisomeric mixture of peresters, **8b** and **9b**, R = CH₃, and this mixture was used as a free-radical source.

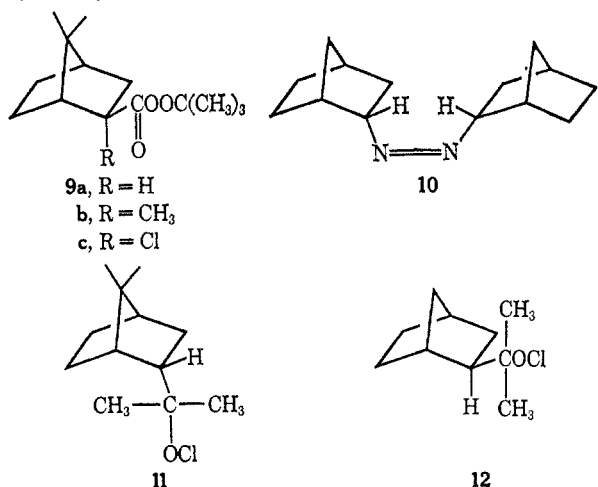
In addition to the peresters, several other sources were used for norbornyl radicals in various experiments: 2-azonorbornane (**10**), 2-apobornyl dimethylcarbinyl

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- (1) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).
- (2) S. J. Cristol, L. K. Gastan, and T. Tiediman, *J. Org. Chem.*, **29**, 1279 (1964).
- (3) S. J. Cristol, J. R. Douglass, W. C. Firth, and R. E. Krall, *ibid.*, **27**, 2711 (1962).
- (4) S. J. Cristol and L. K. Gastan, *ibid.*, **26**, 280 (1961).
- (5) S. J. Cristol, J. R. Douglass, W. C. Firth, and R. E. Krall, *J. Amer. Chem. Soc.*, **82**, 1829 (1960).
- (6) J. A. Berson, C. J. Olsen, and J. S. Walia, *ibid.*, **84**, 3337 (1962).
- (7) S. J. Cristol and T. W. Russell, quoted by D. J. Davies and S. J. Cristol, *Advan. Free-Radical Chem.*, **1**, 174 (1965).
- (8) S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2182 (1961).
- (9) E. Tobler and D. J. Foster, *ibid.*, **29**, 2839 (1964).
- (10) E. Tobler, D. E. Battin, and D. J. Foster, *ibid.*, **29**, 2834 (1964).
- (11) M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 4293 (1965).
- (12) N. A. LeBel, P. D. Beirne, E. R. Kerger, J. C. Powers, and P. M. S. Subramian, *ibid.*, **85**, 3199 (1963).
- (13) H. Kwart and J. L. Nyce, *ibid.*, **86**, 2601 (1964).
- (14) C. L. Osborne, T. V. VanAuken, and D. J. Trecker, *ibid.*, **90**, 5806 (1968).



hypochlorite (**11**), and *exo*-2-norbornyldimethylcarbinyl hypochlorite (**12**). The 2-norbornyl and 2-apobornyl radicals were also produced by the lead tetraacetate oxidation of the corresponding carboxylic acids, and some experiments were performed on the direct chlorination of norbornane.



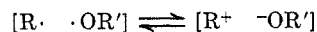
Direct Comparison between Ionic and Free-Radical Recombination. In many common free-radical reactions the principal products are not formed by direct recombination of two free radicals but by the reaction of a free radical with a molecule in a homolytic displacement reaction or atom transfer. In most of the cases to be reported in this study a chlorine atom or hydrogen atom is captured by a free radical of the norbornyl type from a solvent, and this process is not directly comparable with an ionic S_N1 displacement in which a nucleophile recombines directly with the carbonium ion. It is

possible, however, to conduct the decomposition of a carbo-*t*-butylperoxynorbornane in such a way that some norbornyl *t*-butyl ethers are found which result from the direct reunion of norbornyl and *t*-butoxy radicals. When either *endo*- or *exo*-2-carbo-*t*-butylperoxynorbornane (**3a** or **4a**) was heated in benzene solution at 80° for 60 hr about 12% of the product was a mixture of *exo*- and *endo*-2-*t*-butoxynorbornane. The *exo/endo* ratio in each case was 1.65. That this product was formed by direct combination of free norbornyl and *t*-butoxy radicals and not by a cage effect was shown by the fact that chlorine-containing solvents able to donate a chlorine atom to the norbornyl radical reduced the amount of ether formed or eliminated it altogether. In *t*-butyl chloride as solvent, ethers and chlorides were formed in a 1:1 ratio and in carbon tetrachloride as solvent in a 1:6 ratio, while a solvent of benzyl or *p*-methoxybenzyl chloride reduced the ether formation to zero. The *exo* and *endo* *t*-butyl ethers were separated on a 5% Zonyl E7 column when the ethers were free from chlorides.

Solvolysis of *exo*-norbornyl tosylate in *t*-butyl alcohol containing potassium *t*-butoxide yielded *exo*-2-*t*-butoxynorbornane unmixed with its *endo* isomer (preparative vpc, nmr, mass spectrum) and having properties identical with those reported by Nickon and Werstiuk.¹⁵

It has been shown previously¹⁶ that even when a cage effect in homolytic decomposition is very small in fluid media the effect can be enhanced by carrying out the reaction in a medium of greatly increased viscosity. Stereospecific decomposition of *meso*-, *dl*-, and optically active azo compounds has been achieved by using this principle in its extreme form and carrying out photodecompositions in frozen solvents.¹⁷ Peresters **3a** and **4a** were separately dissolved in EPA mixture, frozen at 77°K, and irradiated for 10 hr through quartz with a 450-W Hanovia lamp. On warming and vpc separation of the products the *endo* perester **3a** was found to have produced the *t*-butyl ethers in an *exo/endo* ratio of 0.33, while the *exo* perester **4a** gave a ratio of 14. Thus we have further examples of the increased probability of radical pairs reacting together in their original relative positions when in a frozen medium, of the very low selectivity between *exo* and *endo* modes of combination when the radicals are free in a fluid medium, and of the high selectivity shown by ion pairs of the corresponding structures in solution. These results are summarized in Table I.

Incidentally, these experiments show that whatever may be the favored direction of electron transfer in a radical pair which is interconvertible with an ion pair



(15) (a) A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3915 (1967). (b) It is not known how small the amount of *endo* ether in the ionic product must have been to escape detection. In the products of acetolysis, the *exo/endo* ratio of 2810 at 78.46° corresponds to a $\Delta\Delta F^\ddagger$ of 5.5 kcal between *exo* and *endo* coupling. Direct comparison with the radical coupling result of Table I would suggest that only about 0.34 kcal, or 6%, of the $\Delta\Delta F^\ddagger$ in the ionic case is steric.

(16) R. Hiatt and T. G. Traylor, *ibid.*, **87**, 3766 (1965).

(17) P. D. Bartlett and J. M. McBride, *Pure Appl. Chem.*, **15**, 89 (1967).

Table I
Direct Combination of Norbornyl and *t*-Butoxy
Radical Pairs and Ion Pairs

Source	Solvent	Temp, °C	<i>exo</i> -NbOC ₄ H ₉ / <i>endo</i> -NbOC ₄ H ₉
3a (<i>endo</i>)	Benzene	80	1.65
4a (<i>exo</i>)	Benzene	80	1.65
3a (<i>endo</i>)	EPA ^a	-196	0.33
4a (<i>exo</i>)	EPA ^a	-196	14.00
<i>exo</i> -Norbornyl tosylate + (CH ₃) ₃ COK	(CH ₃) ₃ COH	Reflux	Only <i>exo</i> detected

^a EPA, 5:5:2 (v/v) ether-isopentane-ethanol: G. N. Lewis and M. Kasha, *J. Amer. Chem. Soc.*, **66**, 2115 (1944).

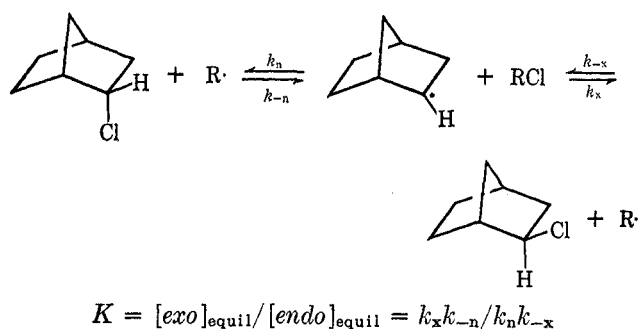
the two types of pairs do not become equivalent in reaction and therefore the transfer of a single electron within the pair must not occur until such an advanced stage of approach that combination of the pair is assured. A reservation concerning this conclusion is that the radical and ionic experiments were not performed in the same solvent; it has previously proved difficult to work with peresters in alcoholic solvents because of the ease of transesterification.

Rates of Decomposition of the Norbornane Peresters.

The rates of decomposition in cumene of peresters **3a-c** and **4a-c** were determined by periodic sampling of 0.05 *M* solutions and determination of the carbonyl absorption at 5.66 μ .¹⁸ The peresters showed good first-order behavior through the three half-lives followed. Table II shows the half-lives at 60° of these six peresters and the activation parameters for four of them, and includes also the comparable data on the closely related acyclic peresters, *t*-butylperoxy isobutyrate, pivalate, and α -phenylisobutyrate, previously reported. Table III shows a number of ways of comparing the rate constants of related peresters to show the effect of *exo* or *endo* configuration, the effect of an R group at position 2 when in the *endo* or *exo* configuration, and the effect of the norbornane ring in comparison to the most nearly related open chain structure. These data may be compared with summaries previously made of the effects of these characteristics on the rates of ionization of norbornyl esters (Table IV). As has been commented previously,^{19,20} the *exo/endo* rate ratio in **3** and **4** is of the same order of magnitude as the equilibrium ratio instead of two orders of magnitude greater as in the case of ionic dissociations. The kinetic preference for the decomposition of the *exo* perester over the *endo* is increased 50% by a methyl group at C₂ and about threefold by a phenyl group, while the actual decomposition rate of **3** is increased 54 times by methyl and 1200 times by phenyl. As shown by the last column in Table III, the acyclic perester in each case is between four and six times as reactive at 60° as the *endo*-norbornyl perester.

Behavior toward Chlorine Atom Donors. A number of chlorinations were carried out in which the norbornyl free radical abstracts a chlorine atom from a variety of

Scheme II



$$K = [exo]_{\text{equil}}/[endo]_{\text{equil}} = k_x k_{-n}/k_n k_{-x}$$

solvents. In these cases the product is formed in a reaction identical in type with the much studied chain transfer in polymerization. In the same way as in the ionization of *exo*- and *endo*-norbornyl ionogens and the nucleophilic capture of the norbornyl cation,²¹ considerations of microscopic reversibility show a relation between the rates of atom capture by a norbornyl radical on the *exo* and *endo* sides, the *exo/endo* equilibrium of the product, and the relative chlorine-donor activities of the *exo* and *endo* isomers of the product. These relations are summarized in Scheme II. As a practical matter the use of chlorine-donating solvents is applicable to the unsubstituted norbornyl radical, but not to the tertiary ones, since under the conditions of the analysis and of some of the reactions the tertiary chlorides are unstable. The experiments are advantageously carried out by using a large excess of the chlorine atom donor as solvent, in which case a kinetically determined product mixture is obtained and reversibility of the reaction is rendered unimportant by the great excess of RCl. It is clear from the equation, however, that the values of k_x/k_n determined from the product ratios under these irreversible conditions may be combined with any measurement of the equilibrium constant between *exo*- and *endo*-norbornyl chlorides to yield a value for the ratio k_{-x}/k_{-n} of the rate constants of *exo*- and *endo*-norbornyl chlorides donating Cl to the solvent radical in question.

To determine the *exo/endo* equilibrium constant, *exo*- and *endo*-norbornyl chlorides were separately equilibrated in sealed test tubes with concentrated hydrochloric acid and zinc chloride, in a procedure similar to one used by Greene and Lowry²² for *cis*- and *trans*-9-chlorodecalins. At 80° a composition consisting of 80% *exo*- and 20% *endo*-norbornyl chloride was reached from the *exo* side in 225 hr and from the *endo* side in 142 hr. The composition was determined by vapor phase chromatography.

As a check on the assumption that the product is determined in the reaction step between the free radical and the chlorine donor the results in carbon tetrachloride were compared with three different starting

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

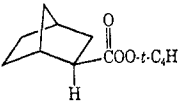
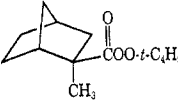
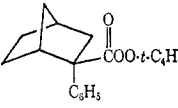
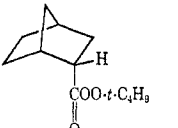
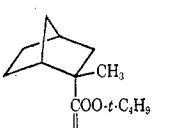
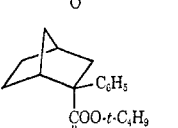
(19) P. D. Bartlett and J. M. McBride, *ibid.*, **87**, 1727 (1965).

(20) P. D. Bartlett and R. E. Pincock, *ibid.*, **84**, 2445 (1962).

(21) H. L. Goering and C. B. Schewene, *ibid.*, **87**, 3516 (1965).

(22) F. D. Greene and N. N. Lowry, *J. Org. Chem.*, **32**, 875 (1967).

Table II
Decomposition Half-Lives for Several Peresters at 60°

No.	Compd	$t_{1/2}$, min at 60°	ΔH^\ddagger	ΔS^\ddagger	k_R/k_H
4a (<i>exo</i>) ^a		13,200	30.9	6	1
4b (<i>exo</i>)		151	27.8	5.9	87
4c (<i>exo</i>)		3-4			3800
3a (<i>endo</i>) ^a		61,800	32.8	9	1
3b (<i>endo</i>)		1,140	29.8	7.8	54
3c (<i>endo</i>)		51			1200
	(CH ₃) ₂ CHCO ₂ - <i>t</i> -C ₄ H ₉ ^b	9,700	31.8	9.4	1
	(CH ₃) ₂ CCO ₂ - <i>t</i> -C ₄ H ₉ ^c	300	30.0	11.1	32
	(CH ₃) ₂ (C ₆ H ₅)CCO ₂ - <i>t</i> -C ₄ H ₉ ^d	12	26.1	5.8	810

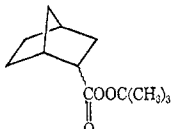
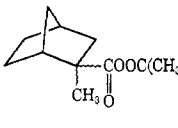
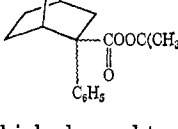
^a Data from P. D. Bartlett and J. M. McBride, *J. Amer. Chem. Soc.*, **87**, 1727 (1965). ^b Data from P. D. Bartlett and L. B. Gortler, *ibid.*, **85**, 1864 (1963). ^c Data from P. D. Bartlett and D. M. Simons, *ibid.*, **82**, 1753 (1960). ^d Data from P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958).

materials: norbornane initiated by benzoyl peroxide, azonorbornane (**10**) decomposed by photolysis, and 2-carbo-*t*-butylperoxynorbornane pyrolyzed. The *exo/endo* ratios in the products were 42 ± 2 , 44 ± 2 , and 42 ± 2 , respectively. The photolysis was carried out at 30°, the other reactions at 80°.

Experiments were carried out to determine whether in the runs showing low and high k_x/k_n ratios the product composition was shifting with time. In the direct chlorination of norbornane with molecular chlorine the products after 1, 3, 5, and 20 hr showed *exo/endo* ratios of 2.6, 2.3, 2.3, and 2.5, respectively. In the experiment with sodium trichloroacetate as chlorine source these ratios after 2, 6, and 20 hr were 30, 29, and 26, respectively. Thus, no drift with time was detected which would in any way account for the large differences in selectivity observed in Table V.

The purpose of the experiment with sodium trichloroacetate was to see whether any of the incidental properties of an ionic medium were of influence in determining the stereoselectivity in the reaction of the norbornyl free radical. This chlorination was carried out in the comparatively ionizing solvent acetic acid, and the only source of chlorine for the free radical was the solvated trichloroacetate anion. The result of this experiment,

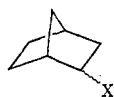
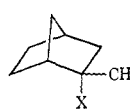
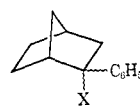
Table III
Rates of Decomposition of Peresters at 60°

Perester	k_{exo}/k_{endo}	k_{exo}^R/k_{exo}^H	k_{endo}^R/k_{endo}^H	$k_{exo}/k_{acyclic}$	$k_{endo}/k_{acyclic}$
	4.7	(1)	(1)	0.73	0.16
	7.6	87	54	2.0	0.26
	~15	3800	1200	3-4	0.24

which showed two-thirds of the selectivity characteristic of carbon tetrachloride, indicates that neither an ionizing medium nor a negative charge on the donor with its attendant solvation plays any decisive role in determining the stereoselectivity of the radical.

The Apobornyl Radical. The apobornyl radical was of special interest because its *endo* derivatives are known to be slightly favored at equilibrium over the

Table IV
exo/endo Rate Ratios in Homolytic and Ionic Cleavages

Ring system	X	Ionization Solvent	Temp, °C	<i>k_{exo}/k_{endo}</i>	Perester decomposition, X = CO ₂ C(CH ₃) ₃	
					Temp, °C	<i>k_{exo}/k_{endo}</i>
	OCOCH ₃	CH ₃ COOH	24.9°	1480 ^a	60	4.7
			78.5°	629 ^a		
	OCOC ₆ H ₄ - <i>p</i> -NO ₂	60% dioxane	25	580 ^b	60	7.6
			75	95 ^c		
	OCOC ₆ H ₄ - <i>p</i> -NO ₂	60% dioxane	25	260 ^b	60	~15
			75	118 ^c		

^a Reference 21. ^b H. C. Brown, *Chem. Brit.*, **2**, 230 (1966). ^c H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Amer. Chem. Soc.*, **86**, 1248 (1964). ^d S. Ikegami, D. L. Vander Jagt, and H. C. Brown, *ibid.*, **90**, 7124 (1968).

Table V
Stereoselectivity of the Norbornyl Radical with Chlorine Donors
(Notation of Scheme II)

RCl	Temp, °C	<i>k_x/k_n</i>	<i>k_{-x}/k_{-n}</i>	Method
(CH ₃) ₃ CCl	80	2	0.5	<i>c</i>
Cl ₂	80	2.5	0.6	<i>a</i>
C ₆ H ₅ CH ₂ Cl	80	6	1.5	<i>c</i>
LiCl + Pb(OCOCH ₃) ₄	80	6	1.5	<i>d</i>
<i>exo</i> -Norbornyldimethyl- carbinyl chloride	80	6	1.5	<i>e</i>
<i>p</i> -CH ₃ OC ₆ H ₄ CH ₂ Cl	80	7	1.8	<i>c</i>
(CH ₃) ₃ COCl	40	7	1.8	<i>f</i>
HCCl ₃	Room	14	3.6	<i>b</i>
CH ₂ Cl ₂	Room	16.5	4.1	<i>b</i>
SO ₂ Cl ₂	40	18	4.5	<i>a</i>
Cl ₃ CCOONa	80	28	7	<i>a, g</i>
CCl ₄	80	42	10.5	<i>a-c</i>

^a Chlorination of norbornane. ^b Photolysis of 2-azonorbornane. ^c Thermolysis of perester. ^d Pb(OCOCH₃)₄ on norbornanecarboxylic acid with LiCl. ^e Thermal decomposition of *exo*-2-norbornyldimethylcarbinyl hypochlorite. ^f AIBN-initiated in benzene; norbornane used. ^g Acetic acid solvent, benzoyl peroxide, initiator, 0.5 *M* norbornane.

exo, and the free-radical selectivities should therefore serve as a critical test of whether there is a steric effect favoring *exo* atom capture or whether this effect now favors reactions on the *endo* side.

Table VI shows a set of experiments to test the occurrence of molecular rearrangements such as beset all ionic reactions of apobornyl and camphenyl compounds. The first experiment showed both Wagner-Meerwein and 6,2 rearrangement increasing in amount with the duration of the experiment. Inclusion of pyridine in the solvent so reduced the rearrangement products that it was suspected that the amount still present might have been formed during the vpc analysis. The conditions finally adopted, those of the last line of Table VI, gave clean mixtures of apobornyl (*endo*) and apoisobornyl (*exo*) chlorides without any rearrangement products. These results show that the apobornyl radical is entirely stable against this type of rearrangement during its lifetime and that the rearrangements observed were probably due in part to traces of hydrogen

chloride and in part to reaction on the hot surface of a metal injection port in the vapor chromatographic apparatus.

Experiments using these precautionary conditions showed no significant difference in the *exo/endo* ratio of the chlorides produced in carbon tetrachloride from thermal decomposition of the perester at 80 or 100° or from photodecomposition at 30°. Table VII summarizes the results with a series of chlorine donors.

The value of the *exo/endo* equilibrium constant between apoisobornyl and apobornyl chlorides cannot be determined conveniently by the same method used for *exo*- and *endo*-norbornyl chlorides because under any ionic equilibration conditions there is rapid rearrangement of the ring system. However, it is noted that the *exo/endo* equilibrium constant for norbornyl chloride is very close to that for norborneol (4.0), and for purposes of evaluating the rate ratios in both directions in Table VII we have taken the equilibrium constant between apoisoborneol (*exo*) and apoborneol (*endo*) as being equal to 0.59, the value found for the alcohols by Howe, Friedrich, and Winstein.²³

Products of the 2-Methylnorbornyl Radical. The decomposition of *exo*- and *endo*-2-methyl-2-carbo-*t*-butylperoxynorbornanes (**3b** and **4b**) in cumene at temperatures from 60 to 90° gave mixtures which could be separated on a 100-ft Ucon polar capillary column operating at 25° into five hydrocarbons with retention times from 7.4 to 12.2 min, along with *t*-butyl alcohol and small amounts of acetone. The results from the *exo* and *endo* peresters were identical within the experimental uncertainty. The hydrocarbons were identified as methylnortricyclene (**17**), 2-methylnorbornene (**13**), *exo*- and *endo*-2-methylnorbornanes (**15** and **16**), and 2-methylenenorbornane (**14**) in order of increasing retention times. After this demonstration that the configuration of the perester is without influence upon the product composition, we used *exo* and *endo* peresters and mixtures of the two interchangeably as sources for

(23) R. Howe, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, **87**, 380 (1965).

Table VI
Decomposition of 8a in CCl₄

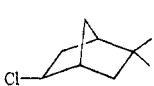
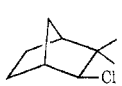
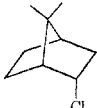
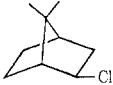
Conditions	Products, %			
				
80°, 24 hr	3.0	4.6	32.3	60.0
80°, 115 hr	13.5	16.9	36.4	33.0
100°, 38 hr	14.9	12.3	41.0	31.8
100°, 4:1 CCl ₄ -pyridine				
1 hr	0.4	3.4	36.6	59.6
6 hr	0.6	3.0	38.6	56.7
100°, 20 hr	0	0	27.3	72.7
Na ₂ CO ₃ (glass injection port, 75°)				

Table VII
Stereoselectivities of Apobornyl Radicals with Various Chlorine Donors

Donor	Reaction time, hr		$-k_x/k_n$		$-k_{-x}/k_{-n}$	
	Thermal	Photo	Thermal, 80°	Photo, 30°	Thermal, 80°	Photo, 30°
C ₆ H ₅ CH ₂ Cl	12	16	0.6	0.6	1.0	1.0
(CH ₃) ₃ CCl	16	22	1.0	0.9	1.7	1.5
Tetrachlorocyclopropene	24	10	1.2	1.3	2.0	2.2
CHCl ₃	26	20	1.8	1.7	3.0	2.9
CH ₃ OCH ₂ Cl		20		1.8		3.0
N-Chlorosuccinimide ^a	16		1.8		3.0	
(CH ₃) ₃ SiCl		24		1.9		3.2
<i>endo</i> -Apobornyl dimethylcarbinyl hypochlorite ^b				2.2		3.7
Pb(OCOCH ₃) ₄ + LiCl on <i>endo</i> -carboxylic acid	0.1		2.3		3.9	
Cl ₃ CCOONa-CH ₃ COOH	10		2.5		4.2	
CCl ₄	20	4	2.6	2.6	4.4	4.4
Hexachlorocyclopentadiene	24	10	3.3	3.5	5.6	5.9
2,4-(NO ₂) ₂ C ₆ H ₃ SCl ^a	24		3.4		5.8	

^a In benzene as solvent. ^b 0.5 M in CCl₄.

the 2-methylnorbornyl radical. The hydrocarbon products were identified by preparation of authentic samples and comparison of their vpc retention times with those in the product mixtures and, in the case of methylnortricyclene, a comparison of its mass spectrum with that of an authentic sample and by contrast with a sample of 1-methylnorbornane.

Table VIII shows that added thiols have the effect of diminishing the amounts of olefins in the product, the methylnorbornene being more sensitive to this effect than the methylenenorbornane. It is not known whether the thiols operate by addition to the double bond with the formation of a less volatile product (addition to methylnorbornene being known to be faster than to methylenenorbornane)²⁴ or by rapid scavenging of the *t*-butoxy radical which may otherwise be responsible for hydrogen abstraction from some of the norbornyl radicals. The former interpretation seems to be favored by the fact that the methylnortricyclene product remains unaffected by the addition of thiol whereas it

must also owe its origin to hydrogen abstraction from the free radical. The fact that chloroform used as a solvent for this reaction produces a smaller effect in the same direction is also consistent with the hypothesis that the unsaturated products are being removed by addition of solvent to the double bond by a free-radical mechanism.

Berson and coworkers^{25,26} pointed out that as one possibility a bornyl radical might lead to a tricyclene by way of a carbene formed by α -hydrogen abstraction. The present example shows that a tricyclene can be formed where the absence of α -hydrogen on the free radical makes such a mechanism unavailable.

Tri-*n*-butyltin hydride, 1.5 M in benzene, was the only agent capable of reducing the amount of methylnortricyclene in the product below 1%. In the presence of this agent 98% of the products consisted of *exo*- and *endo*-2-methylnorbornanes. If this result is due to removal of methylnorbornyl radicals by hydrogen donation competing with all other modes of reaction, it supports the view that tin hydrides are among the most active of all hydrogen atom donors. Undiluted thiophenol, considered²⁷ a somewhat better donor toward a substituted cyclooctenyl radical than trimethyltin hydride, gave 96.8% 2-methylnorbornanes accompanied by 3.1% methylnortricyclene as the only other identified product. This suggests that tributyltin hydride may actually be able to attack methylnortricyclene during a reaction in which R₃Sn· radicals are formed.

Equilibration of *exo*- and *endo*-2-methylnorbornanes with 1-methylnorbornane was accomplished by Belikova, Platé, and Sterin²⁸ by means of sulfuric acid. The slow equilibration at 50° resulted in a mixture containing 5% *endo*-2-methyl-, 25% *exo*-2-methyl-, and 70% 1-methylnorbornane, corresponding to an *exo/endo* equilibrium constant of 5 at 50°, very close to that observed for the equilibration of 2-norbornyl chloride. By heat-

(25) J. A. Berson and C. J. Olsen, *J. Amer. Chem. Soc.*, **84**, 3178 (1962).

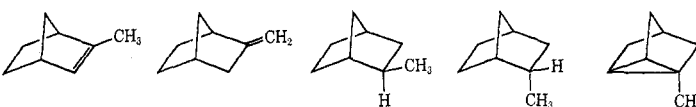
(26) J. A. Berson, C. J. Olsen, and J. S. Walia, *ibid.*, **84**, 3337 (1962).

(27) H. Kuivila, *Accounts Chem. Res.*, **1**, 302 (1968).

(28) N. A. Belikova, A. F. Platé, and K. H. E. Sterin, *J. Gen. Chem. USSR*, **34**, 128 (1964).

(24) E. S. Huyser and R. M. Kellogg, *J. Org. Chem.*, **30**, 3003 (1965).

Table VIII
Effect of H Solvents and Thiols on Olefin and Paraffin Formation from 4b



Solvent	Thiol	(CH ₃) ₃ COH	13	14	15	16	17
Cumene	None	32.8	11.0	20.8	4.1	29.2	2.1
Cumene	None	35.4	10.8	19.3	3.8	28.7	1.6
Cumene	p(0.5) ^a	37.2	0	Trace	4.5	56.0	2.3
Cumene	p(0.9) ^a	33.7	0	0	3.3	41.1	1.9
Cumene	t(1.2) ^a	33.1	0.8	13.5	3.0	47.2	2.0
C ₆ H ₅ Cl	p(0.8) ^a	58.5	0.1	3.8	2.7	32.7	1.9
C ₆ H ₅ Cl	t(1.2) ^a	28.1	0.4	12.3	3.3	53.0	2.9
CHCl ₃	None	66.1	2.4	6.9	4.0	14.1	

^a p = *n*-C₁₂H₂₅SH; t = *t*-octanethiol.

Table IX
Stereoselectivity of the 2-Methylnorbornyl Radical toward
Hydrogen Donors

Donor	Solvent	Temp, °C	Time, hr	<i>k_x/k_n</i> ^c	<i>k_{-x}/k_{-n}</i>
CHCl ₃	CHCl ₃	70	7	3.6	14
<i>p</i> -CH ₃ C ₆ H ₄ Br	Benzene	75	8	5.7	23
<i>p</i> -(CH ₃) ₂ C ₆ H ₄	Neat	75	8	6.2	25
<i>p</i> -CH ₃ C ₆ H ₄ CN	Benzene	75	8	6.6	26
<i>p</i> -CH ₃ C ₆ H ₄ OCH ₃	Neat	75	8	7.3	29
	Neat ^b	30	4	6.9	28
C ₆ H ₅ CH(CH ₃) ₂	Neat	70	<i>a</i>	7.8	31
	Neat ^b	30	4	7.1	28
<i>n</i> -(C ₄ H ₉) ₃ SnH	Benzene	75	8	8.1	32
<i>n</i> -C ₁₂ H ₂₅ SH	C ₆ H ₅ Cl	70	<i>a</i>	12.2	49
<i>n</i> -C ₁₂ H ₂₅ SH	Benzene	70	<i>a</i>	12.4	50
<i>p</i> -NH ₂ C ₆ H ₄ SH	Benzene	75	8	12.8	51
<i>t</i> -C ₈ H ₁₇ SH	Benzene or cumene or chloro- benzene	75	8	16.2	65
<i>p</i> -NO ₂ C ₆ H ₄ SH	Benzene	75	8	16.1	64
<i>p</i> -BrC ₆ H ₄ SH	Benzene	75	8	16.2	65
C ₆ H ₅ SH	Benzene	75	8	16.8	67

^a At end of kinetic run. ^b Photodecomposition of azo-2-methylnorbornane. ^c *k_x/k_n* refers to attack at the *exo* position, leading to *endo*-methylnorbornane.

ing with 10% palladium on carbon at 250° we brought *endo*- and *exo*-2-methyl norbornanes into a 40:60 equilibrium without structural isomerization. Interpolation between the temperatures of these two measurements by means of an Arrhenius plot indicates a value of 4 for the *exo/endo* equilibrium constant at 75°. We have chosen this value, which is identical with the equilibrium constant of the chlorides, to use in converting our observed *k_x/k_n* ratios into *k_{-x}/k_{-n}*.

Table IX summarizes the *exo/endo* selectivities observed with various hydrogen donors. These ratios are reported as the ratios between attack at the *exo* and *endo* positions by the hydrogen donor. It will be noted that in this reaction the favored *exo* attack by H donor yields the unfavored *endo*-methylnorbornane.

Products of the 2-Chloronorbornyl and 2-Chloroapobornyl Radicals. Decomposition of the peresters 3d and 4d at 60° and of 8c and 9c at 80° in the presence of various hydrogen atom donors yielded the *exo/endo* ratios listed in Table X, where again *k_x/k_n* is the ratio of attack by the solvent delivering hydrogen to the *exo*

and *endo* positions of the 2-chloro radical, and *k_{-x}/k_{-n}* is the ratio of rates of removal of hydrogen from those positions in the norbornyl and apobornyl chlorides by the solvent radical. From methylene chloride to ethyl mercaptan the chloronorbornyl radicals exhibited a six-fold range of *exo/endo* selectivity, this range being only 2.5-fold in the case of the 2-chloroapobornyl radical.

Products of the 2,7,7-Trimethylnorbornyl Radical. The radical from the peresters 8b and 9b yielded a series of selectivity ratios covering a threefold range from chloroform to the thiols; the results are given in Table XI. With these radicals the calculated selectivities in reactions of the 2-methylapocamphanes and 2-chloroapocamphanes with the trichloromethyl, benzyl, and cumyl radicals are slightly in favor of attack at the *endo* position.

Stereochemistry of the Norbornyl Radical. Since a free radical is electronically intermediate between a carbonium ion, which is trigonally hybridized and coplanar, and a carbanion, which uses tetrahedral orbitals, there has been some question as to how closely the free radical resembles the carbonium ion geometrically.²⁹ The balance of evidence from vibrational³⁰⁻³² and electron spin resonance spectra³³ favors a planar structure for free radicals. Bridgehead free radicals are much more easily generated from certain sources than the corresponding carbonium ions,³⁴⁻³⁷ however, it has been pointed out that this is a function of the reaction used to generate the free radical,³⁸ and hence applies to cer-

(29) For a review see W. A. Pryor, "Free Radicals," McGraw-Hill Book Co., Inc., New York, N. Y., 1966, Chapter 3.

(30) G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956).

(31) G. Herzberg, *Ann. Rev. Phys. Chem.*, **9**, 357 (1958).

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(33) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

(34) T. Wilder and A. Winston, *J. Amer. Chem. Soc.*, **75**, 5370 (1953).

(35) F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963).

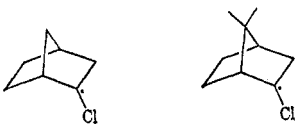
(36) D. E. Applequist and L. Kaplan, *J. Amer. Chem. Soc.*, **87**, 2194 (1965).

(37) R. C. Fort, Jr. and P. von R. Schleyer, *Advan. Alicyclic Chem.*, **1**, 337 (1966).

(38) C. Rüchardt and A. Oberlinner, private communication. This conclusion means that reactions such as the decomposition of *exo*- and *endo*-peresters, in which bond breaking at C-2 is developed to an unknown and perhaps small extent at the transition state, may not provide a good measure of steric effects at the 2 position of the norbornyl system. For this reason the rate comparisons of Table IV are not as significant as those involving direct radical or ionic coupling (Table I).

Table X

Stereoselectivity of 2-Chloronorbornyl and 2-Chloroapobornyl Radicals toward Hydrogen Donors



Donor	k_x/k_n	k_{-x}/k_{-n}	k_x/k_n	k_{-x}/k_{-n}
CHCl ₃	3	12	1.0	0.6
CH ₂ Cl ₂	2	8		
C ₆ H ₅ CH ₃	5	20	1.2	0.7
C ₆ H ₅ CH(CH ₃) ₂	7	28	1.5	0.9
1,4-Cyclohexadiene	5	20	2.0	1.2
C ₂ H ₅ SH	12	48	2.5	1.5

tain (but not all) transition states, not to the radicals themselves. Thus the 2-norbornyl radical, while deformable at C-2, presumably has an energy minimum with the hydrogen atom at C-2 in the plane with C-2 and its adjoining carbon atoms, a geometry identical with that of the "classical" norbornyl cation.

Since a free radical does not have the electron deficiency that leads to three-center bonding, it is not to be expected that a norbornyl free radical will show any tendency to assume a bridged structure analogous to the nonclassical norbornyl cation. Hence, regardless of one's interpretation of the reactions and structure of the norbornyl cation, one may expect the norbornyl free radical to be a close stereochemical analog of the classical norbornyl cation, except in one important respect. The formation and separate existence of any carbonium ion are critically dependent on solvation by an ionizing solvent. The solvation required by a free radical is so much less critical that the radical cannot be a suitable stereochemical model for the cation in any reaction where the hindrance is only hindrance to solvation.

Three facts stand out in connection with the stereoselectivities of the norbornyl radicals. (1) The radicals, both in rate of formation from *exo* and *endo* peresters and in the ratio of stereoisomers formed on reaction, are less selective than the carbonium ions by factors from one to three orders of magnitude. (2) Regardless of the position of equilibrium between *endo* and *exo* products, there is a preference for atom capture in the *exo* position amounting to a factor up to ten times the equilibrium constant. (3) This factor is not constant, but varies characteristically with the nature of the agent from which the atom is captured. We shall assume that by the use of free radicals rather than carbonium ions we have excluded any role of nonclassical bridging in this selectivity and shall examine the nature of the effects accordingly.

Three kinds of steric effects have been discussed in connection with *exo/endo* selectivity. First, there is the sum total of the attractive and repulsive interactions operating on a group in the *exo* and *endo* positions, arising from the *endo* hydrogens at C-3, C-5, and C-6 and from the *exo* hydrogen at C-3 and *syn*-C-7. These effects determine the equilibrium constant between *exo* and *endo* derivatives, whose value in the present cases lies between 0.5 and 4. If such forces were to be responsible for ionic kinetic ratios 500 times the equilib-

Table XI

Stereoselectivity of the 2,7,7-Trimethylnorbornyl Radical toward Hydrogen Donors^a

Donor	k_x/k_n	k_{-x}/k_{-n}
CHCl ₃	1.0	0.6
CH ₃ C ₆ H ₅	1.3	0.8
(CH ₃) ₂ CHC ₆ H ₅	1.5	0.9
1,4-Cyclohexadiene	1.9	1.1
<i>n</i> -C ₄ H ₉ SH	2.9	1.7
<i>t</i> -C ₄ H ₉ SH	3.1	1.8
C ₆ H ₅ SH	3.0	1.8

^a Mixed *exo* and *endo* peresters heated about 24 hr at 80°.

rium ratios, such as are seen in the behavior of carbonium ions, there must be a great amplification of their force as they operate on the transition states rather than the ground states of the molecules. It has been proposed³⁹ that such an amplification might arise from the fact that an ion on its way into or out of the molecule must pass closer to the hindering atoms than it ever comes in the ground state of the molecule (Figure 4 of ref 39). This hypothesis acquires special attractiveness from the observation⁴⁰ that certain reactions requiring the symmetrical approach of a reagent equidistant from C-2 and C-3 are hindered on the *exo* side by a *syn* substituent at C-7.

The second steric hypothesis calls attention to the essential role of solvation in any ionization process. Here the kinetic amplification is sought in the need for solvent molecules to surround the leaving group, or to continue the solvation of the entering group until it reaches a point within bond-forming distance of C-2. This version of the steric hypothesis has the advantage of predicting that *exo/endo* selectivities should be greater in ionic than in free-radical reactions, as observed.

However, both of these steric explanations fail in an important respect. Neither one provides for kinetic effects to operate in the *opposite direction* from the equilibrium effects; yet there are dramatic examples,^{41,42} notably among apocamphyl arylsulfonates, where because of hindrance at C-7 the *endo* derivatives are favored over the *exo* at equilibrium, but the kinetic selectivity favors *exo* by an even larger margin than in norbornyl analogs.

The third steric effect is a specialized one which, it appears, accommodates the direction and range of magnitude of the *exo/endo* selectivities of the free radicals. This is the "torsional" effect arising from the unsymmetrical staggering of the hydrogen atoms at C-1 and C-2 of the norbornane ring.⁴³ In the light of this effect, an entering group may form a bond with a classical cation or free radical at C-2 from the *exo* side without any atom at C-2 passing the position of maximum eclipsing repulsion from the bridgehead hydrogen at C-1; approach from the *endo* side, however, must

(39) *E.g.*, H. C. Brown, *Chem. Brit.*, 205 (1966).

(40) H. C. Brown and J. H. Kawakami, *J. Amer. Chem. Soc.*, **92**, 201 (1970).

(41) R. Howe, E. C. Friedrich, and S. Winstein, *ibid.*, **87**, 380 (1965).

(42) A. Colter, E. C. Friedrich, N. J. Holness, and S. Winstein, *ibid.*, **87**, 378 (1965).

(43) P. von R. Schleyer, *ibid.*, **89**, 699, 701 (1967).

force the hydrogen atom at C-2 up past the full barrier to its new *exo* position. Schleyer has predicted that the maximum effect of this kind for reaction at C-2 alone will be roughly of the order of 1 kcal. The effect will operate universally in favor of entrance or departure of groups at the *exo* side in the norbornyl ring system, regardless of the position of the *exo/endo* equilibrium.

The dependence of the selectivities upon the donor molecule is not predicted in the original consideration of the torsional effect, and requires special discussion. It is natural to consider first the possibility that the bulkiest atom donors are the most subject to steric effects and might show the highest *exo* preference. Not much of a correlation of the results can be achieved on this basis. The two most similarly shaped chlorine donors, *t*-butyl chloride and carbon tetrachloride, are at opposite ends of the scale of *exo/endo* selectivities. Tributyltin hydride, though branched near the reaction site, is a less selective hydrogen donor than *n*-dodecyl mercaptan, and cumene is slightly less selective still.

Neither is it true that the vigorous atom donors are always more, or always less, selective than the weak ones. Molecular chlorine, a powerful atom donor, and benzyl chloride, a weak one, both show low selectivities, one a little below and the other a little above the equilibrium value. Especially unfruitful is an attempt to correlate the selectivities with thermochemical bond-strength values. What does emerge is the fact that, with chlorine donation, the greatest *exo/endo* selectivities are seen in the reaction of the norbornyl radical with atom donors of *intermediate* vigor: carbon tetrachloride is a selective donor, chlorine and *t*-butyl chloride are both unselective ones. Further consideration shows that, though not predicted, this result is in complete accord with the postulated nature of the torsional effect. The point of maximum torsional barrier in the *endo* reaction is that at which the hydrogen atom at C-2 is exactly eclipsed with that at C-1 as bond formation progresses. The torsional effect will not be the main obstacle to reaction, and hence the exact degree of eclipsing at the transition state will be determined by factors inherent in the reactants and products. A maximum torsional effect will be seen only in those cases, if any, in which the transition state and the point of maximum eclipse coincide. In general a series of donor molecules may spread into a spectrum in which some will yield transition states before, some at, and some after the point of maximum torsional barrier.

In an extension of the Hammond postulate,⁴⁴ we might speculate that the location of the transition state along the reaction coordinate (near the starting materials or far from them) would be determined by the degree of exothermicity of the process. However, the situation in which the Hammond postulate is so generally successful is one involving very exothermic or very endothermic reactions. In contrast some of the atom transfers from molecule to free radical here are

approximately thermoneutral, and the transition state lies about midway between starting materials and products. In this case other factors are more important than exothermicity in determining the location of the transition state along the reaction coordinate. Two of these factors are the degree of ionic contribution to the transition state and the possible role of d orbitals, which (as in the case of hydrogen transfers to or from sulfur) may be important in determining reaction rate, height of the transition state barrier, and steepness of climb of energy along the reaction coordinate. No single recognized property of the donors affords a simple correlation with the *exo/endo* selectivities, but it seems reasonable that the combined effect of the above factors may shift the transition state enough relative to the position of maximum torsional barrier to produce the changes in selectivity.

In the case of hydrogen donors the mercaptans, which have very high chain-transfer constants in free-radical polymerization, yield *exo/endo* selectivities as great as four times the equilibrium ratio. However, tributyltin hydride, a hydrogen donor of comparable activity, shows a selectivity only half as great.

This brings up the question of possible polar contributions to the transition-state structure as a contributor to rate, barrier height, and selectivity in atom-transfer reactions. The transition state in hydrogen transfer from a mercaptan must favor more cationic character in the accepting radical than in the case of a metallic hydride, resulting in a more polar transition state in the former case. It was with such ideas in mind that we included hexachlorocyclopentadiene and tetrachlorocyclopropene among the chlorine donors investigated. The former, donating chlorine from a strongly anionic fragment, is almost three times as selective (Table VII) toward the apocamphyl radical as the latter donor, whose residue differs in being strongly cationic. That there are other factors as important as polarity, or more so, is indicated by the fact that molecular chlorine is highly unselective.

Conclusions

The moderate preference of free radicals of the norbornyl type for reacting in atom-transfer reactions at the *exo* rather than the *endo* position and the dependence of this selectivity upon the atom donor involved are consistent with a basically steric origin of the effects. Comparison of these effects with the much larger selectivities in reactions of the corresponding norbornyl cations leaves in the latter a presumably nonsteric factor of greater magnitude than the steric. This extra factor is the domain of σ delocalization or bridged-ion effects.^{45,46}

This work was supported by the National Institutes of Health, the National Science Foundation, and the Petroleum Research Fund, administered by the American Chemical Society.

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(44) G. S. Hammond, *J. Amer. Chem. Soc.*, **77**, 334 (1955).