occurs when the rings are rotated 50.7° out of the reference plane. This result is in reasonable accord with that (45°) of a previous calculation.[4b]

Supplementary Material Available. A listing of the final atomic parameters and of the observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-73-7019.

Conformational Dynamics of Alkoxydiarylboranes[1]

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Abstract: The low-temperature ^1H-nmr spectra of several alkoxydiarylboranes are shown to be consistent with three alternatives: the molecules adopt propeller conformations, and stereoisomerization is slow on the nmr time scale; the molecules adopt propeller conformations with rapid stereoisomerization by means of one-flip pathways; the molecules adopt perpendicular conformations with slow stereoisomerization. Stereoisomerization phenomena observed at elevated temperatures are discussed in terms of flip mechanisms, and pathways which involve the flipping of aryl groups only are found to have lower activation energies than those which also involve flipping of the alkoxy group. An analysis of the isomerization processes reveals restricted rotation about the B–O bond, and arguments are presented which suggest that conjugative effects between boron and oxygen play a significant role in the stereochemistry of alkoxyarylboranes.

In conjunction with a stereochemical study of triarylboranes,[3] we have examined the temperature-dependent nmr spectral behavior of alkoxydiarylboranes. Reports concerning restricted rotation about boron–nitrogen[4a–c] and boron–oxygen[4d] bonds suggest that π-bonding between boron and oxygen,[5] as well as other conjugative and steric interactions, might be expected to play a significant role in the stereochemistry of alkoxydiarylboranes. The present paper reports the results of our investigation and provides a basis for understanding the major stereochemical features of these systems.

Ground-State Geometry of Alkoxydiarylboranes

Since this study deals with stereoisomerism due to restricted rotation about the B–C and B–O bonds in alkoxydiarylboranes, the conformation of these compounds may be defined, for our purposes, in terms of the orientations of three planes (the *ligand planes*), *i.e.*, the planes of the two aryl rings and the B–O–C plane, with respect to the plane defined by the two carbon atoms and the oxygen atom bonded to boron (the *reference plane*). For a given ligand plane, there are two unique orientations: the ligand plane may be perpendicular to the reference plane (case I), or the ligand plane may coincide with the reference plane (case II).[6] In addition to these two special cases, there are an infinite number of intermediate orientations.

At present, there are no X-ray structural data available in the literature for alkoxydiarylboranes. Solid state and solution studies of hindered triarylboranes demonstrate that these compounds have a propeller-like conformation in the ground state, in which the sense of twist of all three groups is the same.[3] Similarly, an X-ray analysis of $(Mes)_2BN{=}C(C_6H_5)_2$ shows that the mesityl rings are rotated out of the C–B–C plane.[7] By analogy, it might be tentatively postulated that in the ground state, alkoxydiarylborane molecules also adopt a propeller conformation (Figure 1).[8]

9-Anthrylmesitylmethoxyborane (1)

If it is assumed that **1** has a propeller conformation in the ground state, four stereoisomers (two diastereomeric *dl*-pairs) are possible, labeled A, $\bar{A}$, B, and $\bar{B}$ in Figure 2. The methoxy methyl group resides near the anthryl group in A and $\bar{A}$, and near the mesityl group in B and $\bar{B}$. It is apparent that each stereoisomer has two diastereotopic *o*-methyl groups, as well as one *p*-methyl group and one methoxy group. Thus, in the absence of accidental isochrony, the ^1H-nmr spectrum

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[2] NATO Fellow, 1972–1973, on leave of absence from the University of Catania, Catania, Italy.

[3] J. F. Blount, P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, **95**, 7019 (1973).

[4] (a) D. Imbery, A. Jaeschke, and H. Friebolin, *J. Org. Magn. Resonance*, **2**, 271 (1970), and references cited therein; (b) P. A. Barfield, M. F. Lappert, and J. Lee, *Trans. Faraday Soc.*, **64**, 2571 (1968); (c) R. L. Wells, H. L. Paige, and C. G. Moreland, *Inorg. Nucl. Chem. Lett.*, **7**, 177 (1971); (d) G. F. Lanthier and W. A. G. Graham, *Chem. Commun.*, 715 (1968).

[5] (a) G. L. Lewis and C. P. Smyth, *J. Amer. Chem. Soc.*, **62**, 1529 (1940); (b) H. A. Skinner and N. B. Smith, *J. Chem. Soc.*, 3930 (1954); (c) C. A. Coulson, *Acta Crystallogr.*, **17**, 1086 (1964); (d) C. A. Coulson and T. W. Dingle, *Acta Crystallogr., Sect. B*, **24**, 153 (1968); (e) D. R. Armstrong and P. G. Perkins, *J. Chem. Soc. A*, 123 (1967).

[6] A more general and rigorous definition of case II geometry is that for a given ligand, the normal to the ligand plane which passes through the atomic center bonded to boron lies in a plane which is perpendicular to the reference plane and which contains boron and the atom bonded thereto.

[7] G. J. Bullen and K. Wade, *Chem. Commun.*, 1122 (1971).

[8] Any alkoxydiarylborane in the propeller conformation is necessarily asymmetric. The probability that the angles of twist of the three ligand planes, relative to the reference plane, are not all different, even on the time average (*e.g.*, on the nmr time scale, in solution), is therefore vanishingly small.

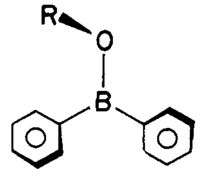

Figure 1. An alkoxydiphenylborane in the propeller conformation.

of a mixture of $A\bar{A}$ and $B\bar{B}$ in an achiral solvent should display eight distinguishable methyl signals.

Interconversions of stereoisomers of **1** can be interpreted in terms of an extension of the flip mechanisms postulated by Kurland, *et al.*, for triarylcarbonium ions.[9,10] In each of these mechanisms, zero, one, two, or all three of the ligand planes "flip," *i.e.*, rotate through planes perpendicular to the reference plane (case I above), while the remaining ligand planes rotate through orientations coplanar with the reference plane (case II orientations).[6] These general mechanisms will be called zero-, one-, two-, and three-flips, respectively. The effects of interconversions by these mechanisms among the stereoisomers of **1** are listed in Table I and may be summarized by the statement that flips which include the methoxy group result in diastereomerizations, whereas those which do not result in enantiomerizations. Also listed are the methyl groups whose environments are exchanged by each pathway.

Table I. Stereoisomerization Pathways for 9-Anthrylmesitylmethoxyborane (**1**) in the Propeller Conformation

Flip pathway[a]	Resulting isomerizations[b]	Resulting site exchanges[b]			
Zero-flip	$A \rightleftarrows \bar{A}$, $B \rightleftarrows \bar{B}$	$(a\bar{a})$	$(c\bar{c})$	$(e\bar{e})$	$(g\bar{g})$
		$(b\bar{b})$	$(d\bar{d})$	$(f\bar{f})$	$(h\bar{h})$
[1]-flip	$A \rightleftarrows \bar{B}$, $B \rightleftarrows \bar{A}$	$(a\bar{e})$	$(b\bar{f})$	$(c\bar{g})$	$(d\bar{h})$
		$(e\bar{a})$	$(f\bar{b})$	$(g\bar{c})$	$(h\bar{d})$
[2]-flip	$A \rightleftarrows \bar{A}$, $B \rightleftarrows \bar{B}$	$(a\bar{b})$	$(c\bar{c})$	$(e\bar{f})$	$(g\bar{g})$
		$(b\bar{a})$	$(d\bar{d})$	$(\bar{e}f)$	$(h\bar{h})$
[3]-flip	$A \rightleftarrows \bar{A}$, $B \rightleftarrows \bar{B}$	$(a\bar{a})$	$(c\bar{c})$	$(e\bar{e})$	$(g\bar{g})$
		$(b\bar{b})$	$(d\bar{d})$	$(f\bar{f})$	$(h\bar{h})$
[1,2]-flip	$A \rightleftarrows \bar{B}$, $B \rightleftarrows \bar{A}$	$(a\bar{f})$	$(b\bar{e})$	$(c\bar{g})$	$(d\bar{h})$
		$(f\bar{a})$	$(e\bar{b})$	$(g\bar{c})$	$(h\bar{d})$
[1,3]-flip	$A \rightleftarrows \bar{B}$, $B \rightleftarrows \bar{A}$	$(a\bar{e})$	$(b\bar{f})$	$(c\bar{g})$	$(d\bar{h})$
		$(e\bar{a})$	$(f\bar{b})$	$(g\bar{c})$	$(h\bar{d})$
[2,3]-flip	$A \rightleftarrows \bar{A}$, $B \rightleftarrows \bar{B}$	$(a\bar{b})$	$(c\bar{c})$	$(e\bar{f})$	$(g\bar{g})$
		$(b\bar{a})$	$(d\bar{d})$	$(f\bar{e})$	$(h\bar{h})$
[1,2,3]-flip	$A \rightleftarrows \bar{B}$, $B \rightleftarrows \bar{A}$	$(a\bar{f})$	$(b\bar{e})$	$(c\bar{g})$	$(d\bar{h})$
		$(f\bar{a})$	$(e\bar{b})$	$(g\bar{c})$	$(h\bar{d})$

[a] Numerals in brackets identify the ligands which flip during the conversion: 1 = methoxy, 2 = mesityl, 3 = 9-anthryl. [b] For significance of letters, see Figure 2.

The experimental results obtained for **1** may now be discussed using the analysis presented above as a guide. At −86°, the 60-MHz ^{1}H-nmr spectrum of a solution of **1** in CS_2 includes two methoxy resonances at δ^{TMS} 3.94 and 3.58 ppm in a ratio of intensities of 0.1 :1. The mesityl methyl groups appear as three signals at δ^{TMS} 2.71, 2.19, and 1.48 ppm, with intensities of 1 :1.29 :1, respectively. The observation of two methoxy signals provides conclusive evidence for the presence of two diastereomers in solution. If we call the more abundant diastereomer **1a**, and the less abundant **1b**, then **1a** has a methoxy resonance at δ 3.58 and three mesityl methyl resonances at 2.71, 2.19, and 1.48 ppm (*i.e.*, all methyl groups are accounted for), whereas **1b** has a methoxy resonance at δ 3.94 and apparently isochronous mesityl methyl signals at 2.19 ppm.

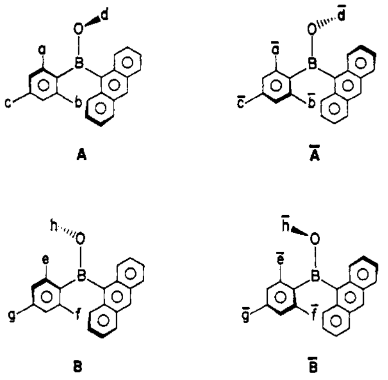

Figure 2. Stereoisomers of 9-anthrylmesitylmethoxyborane (**1**) in the propeller conformation. The mesityl methyl group environments are designated by lower case letters. Barred letters or numerals denote enantiomeric relationships.

If we assume a rigid propeller conformation for **1** in the ground state, then **1a** must correspond to either $A\bar{A}$ or $B\bar{B}$, and **1b** to the remaining diastereomer, with the accidental isochrony indicated above. However, Table I indicates several other possibilities, involving the time averaging of methyl proton resonances, which are also consistent with the spectrum at −86°. The zero-flip and the [3]-flip exchange only enantiotopic groups, and therefore cannot be detected by the nmr experiment described above. The zero-flip would involve large steric repulsions in the transition state, relative to the other flip mechanisms, and may therefore be safely ruled out. Similarly, the [3]-flip of $B\bar{B}$ would involve, in the transition state, repulsive steric interactions between the methoxy group and one of the *o*-methyl groups, since both would be forced into the reference plane. However, the [3]-flip of $A\bar{A}$ would not suffer from any such interactions, and the rapid interconversion of A and $\bar{A}$ by the [3]-flip may thus be a possible isomerization pathway at −86°. Furthermore, although the [2]-flip exchanges the *o*-methyl groups of a given diastereomer, and thus can be ruled out for **1a** at −86°, the rapid interconversion of enantiomers of **1b** on the nmr time scale by the [2]-flip is consistent with the spectrum, since the *o*-methyl groups of this diastereomer are apparently isochronous.[11] The [2]-flip of $A\bar{A}$ would involve unfavorable steric interaction between the methoxy group and the anthryl group in the transition state, whereas the [2]-flip of $B\bar{B}$ would necessitate no such interactions. Thus, if one identifies **1a** and **1b** with $A\bar{A}$ and $B\bar{B}$, respectively, enantiomerization of $A\bar{A}$ (**1a**) by the [3]-flip and of $B\bar{B}$ (**1b**) by the [2]-flip, assumed rapid on the nmr time scale at −86°, is consistent with the spectrum at this temperature, as well as with reasonable energetic constraints. The

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(9) R. J. Kurland, I. I. Schuster, and A. K. Colter, *J. Amer. Chem. Soc.*, **87**, 2279 (1965).

(10) D. Gust and K. Mislow, *ibid.*, **95**, 1535 (1973).

(11) The [2,3]-flip of **1b** is also consistent with the spectrum, but it is difficult to rationalize the required large difference in activation energies between the [2,3]-flips of $A\bar{A}$ and $B\bar{B}$.

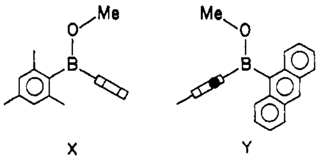

Figure 3. Two perpendicular conformations of 9-anthrylmesitylmethoxyborane (**1**). In X the 9-anthryl group is perpendicular to the plane of the figure, whereas in Y the mesityl group is perpendicular to this plane.

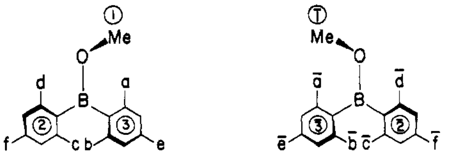

Figure 4. Dimesitylmethoxyborane (**2**) in the propeller conformation. The mesityl methyl group environments are designated by lower case letters. The numerals identify the ligands which may flip during stereoisomerizations (see Table II).

effective time-average geometries for the structures undergoing rapid isomerization are depicted in Figure 3: X represents the time-average structure for the [3]-flip of $A\bar{A}$, and Y the corresponding structure for the [2]-flip of $B\bar{B}$.

None of the evidence excludes the alternative possibility that X and Y are not time-average geometries, but represent the ground states of **1a** and **1b**, respectively. The molecules in this case adopt conformations in which one aryl group is perpendicular to the reference plane, and the other two ligands are in case II orientations.

In summary, the nmr spectrum of **1** at −86° is in agreement with three reasonable alternative interpretations: (1) the molecules adopt propeller conformations (Figure 2) with slow interconversion of all stereoisomers on the nmr time scale, (2) the molecules adopt propeller conformations with rapid interconversion of enantiomers by means of the appropriate one-ring flips, or (3) the compound exists in the ground state in two diastereomeric perpendicular conformations (Figure 3), with slow interconversion of stereoisomers on the nmr time scale. The presently available data do not allow a rigorous choice among these three alternatives.

As the sample of **1** is warmed, the resonances at δ 2.71 and 1.48 ppm broaden, and finally coalesce at −62°, while the methoxy group resonances remain sharp. This coalescence phenomenon must correspond to the exchange of the *o*-methyl groups of **1a**. The Gutowsky–Holm equation[12] was employed to derive a rate constant at the coalescence temperature, and this value was used to calculate an Eyring free energy of activation for the exchange process of $\Delta G^{\ddagger}_{-62} =$ 10.1 kcal/mol.

On the assumption that **1** exists in the propeller conformation in the ground state, there are only two mechanisms which will exchange the *o*-methyl groups of a given diastereomer (**1a**) without accompanying interconversion of diastereomers, *i.e.*, the [2]-flip and the [2,3]-flip (Table I). The preceding statement is applicable regardless of whether or not the rapid one-flip discussed above is also taking place, *i.e.*, it is true for both possibilities (1) and (2) above.

The stereoisomerization pathways described above for the propeller conformations as expressed in terms of transition states and permutations of groups are equally applicable to the perpendicular conformations, when the proper degeneracies are considered. Thus, for example, if the ground-state conformation of **1a** can be represented by X (possibility (3)), the two diastereotopic *o*-methyl groups are exchanged either by a rotation of the mesityl ring by π radians, or by such a rotation concurrent with the rotation of the anthryl group by π radians. The transition states for these two processes, however, are identical with those for the [2,3]-flip and the [2]-flip for the propeller conformation, respectively.[13]

In summary, the coalescence of *o*-methyl groups observed for **1a** is attributable to either the [2]-flip or the [2,3]-flip, regardless of whether **1a** is a noninterconverting enantiomeric pair, a pair of enantiomers (A and $\bar{A}$) which are rapidly interconverting by the [3]-flip, or a single perpendicular structure (X) in the ground state.

When the sample of **1** is warmed to −24°, the methoxy signals coalesce to a broad singlet. Further heating sharpens the signals, and at *ca.* 37° the methoxy and *o*-methyl groups appear as sharp singlets at $\delta_{CS_2}^{TMS}$ 3.62 and 2.14 ppm, respectively. Analysis[14] yields $\Delta G^{\ddagger}_{-24} = 13.7$ kcal/mol for the conversion of **1a** to **1b**, and $\Delta G^{\ddagger}_{-24} = 12.6$ kcal/mol for the conversion of **1b** to **1a**. Table I indicates that the four mechanisms which are compatible with such a coalescence, corresponding to interconversion of diastereomers, are the [1]-, [1,2]-, [1,3]-, and [1,2,3]-flips. Of these mechanisms, the [1]-flip would be expected to have a higher activation energy than the other three because of large steric repulsions in the transition state; however, the nmr data do not allow rigorous exclusion of any one of the four alternatives.

Dimesitylmethoxyborane and Related Compounds

Dimesitylmethoxyborane (**2**), in the propeller conformation, exists as a *dl*-pair (Figure 4). Each enantiomer has four diastereotopic *o*-methyl groups, two diastereotopic *p*-methyl groups, and a methoxy group. Operation of any one of the eight flip mechanisms results in enantiomerization, but the effects on the nmr spectrum of rapid enantiomerization by each mechanism are not the same. Table II lists the methyl groups which are exchanged by rapid interconversion of enantiomers on the nmr time scale by means of each mechanism. Since the [1,2]- and [1,3]-flips are enantiomeric, and therefore occur at the same rate in an

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[12] H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

[13] In general, for all of the alkoxydiarylboranes discussed in this paper, it can be asserted that although the overall motions of the ligands during interconversions by the flip mechanisms will necessarily be different for the propeller and the perpendicular ground-state conformations, the transition states (and/or high-energy intermediates) as well as the permutations of groups achieved by the mechanisms will be identical when degeneracies are taken into account. Thus although the remaining interconversion processes to be discussed below will be described in terms of flip mechanisms, it is understood that the detailed motions of the ligands cannot be determined unambiguously without knowledge of the ground-state conformations. An analogous ambiguity in mechanisms has been noted for the stereoisomerizations of perpendicular and helical conformations of diaryl ethers and analogous molecules.[10]

[14] H. Shanan-Atidi and K. H. Bar-Eli, *J. Phys. Chem.*, **74**, 961 (1970).

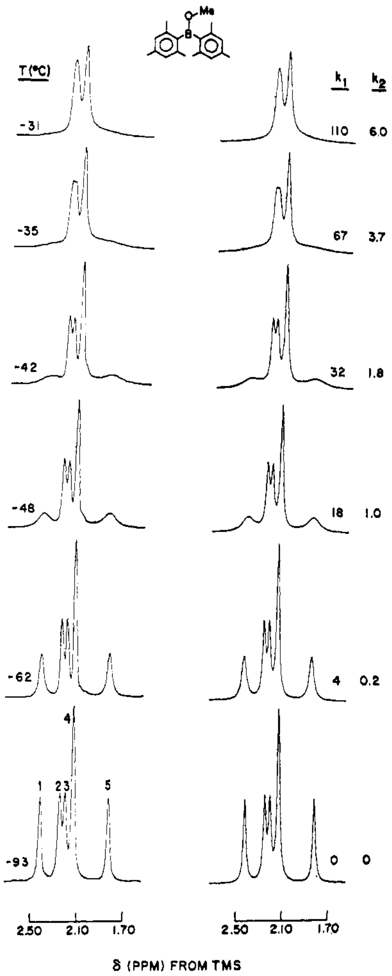

Figure 5. The 60-MHz ^{1}H-nmr spectrum of the mesityl methyl groups of dimesitylmethoxyborane (**2**) at various temperatures (left), and the matching calculated spectra (right) based on the [2,3]-flip (k_1) plus the [1,2]- and [1,3]-flip (k_2) mechanisms.

achiral solvent, the effects of these two mechanisms upon the nmr spectrum have been considered together.[15]

At −93°, the 60-MHz ^{1}H-nmr spectrum of the mesityl methyl groups of **2** features five resonances at $\delta_{\mathrm{CS}_2}^{\mathrm{TMS}}$ 2.40 (signal 1), 2.23 (2), 2.19 (3), 2.12 (4), and 1.82 (5) ppm, with a ratio of intensities of *ca.* 1:1:1:2:1, respectively (Figure 5). Thus, the six methyl groups of **2** are accounted for. In order to decide which of these resonances correspond to *o*-methyl groups and which to *p*-, the low-temperature nmr spectra of two similar compounds were examined. At −57°, the ^{1}H-nmr spectrum of bis(2,6-dimethylphenyl)methoxyborane features three resonances at $\delta_{\mathrm{CS}_2}^{\mathrm{TMS}}$ 2.46, 2.17, and 1.88 ppm, with a ratio of intensities of 1:2:1, respectively. The spectrum of bis(4-methoxy-2,6-dimethylphenyl)methoxyborane at −77° includes aryl methyl resonances at $\delta_{\mathrm{CS}_2}^{\mathrm{TMS}}$ 2.41, 2.12, and 1.81 ppm, in a ratio of 1:2:1. Since the resonances reported for these two compounds necessarily represent *o*-methyl groups, we assume that the corresponding methyl resonances in the closely analogous compound **2** also arise from *o*-methyl groups. Thus, for **2**, signals 1, 4, and 5 represent *o*-methyl groups, and resonances 2 and 3 arise from *p*-methyl groups.

Table II. Enantiomerization Pathways for Dimesitylmethoxyborane (**2**) in the Propeller Conformation

Flip pathway[a]	Resulting site exchanges[b]		
Zero-flip	$(a\bar{a})$	$(b\bar{b})$	$(c\bar{c})$
	$(d\bar{d})$	$(e\bar{e})$	$(f\bar{f})$
[1]-flip	$(a\bar{d})$	$(b\bar{c})$	$(e\bar{f})$
	$(d\bar{a})$	$(c\bar{b})$	$(f\bar{e})$
[2]-flip	$(a\bar{a})$	$(c\bar{d})$	$(e\bar{e})$
	$(b\bar{b})$	$(d\bar{c})$	$(f\bar{f})$
[3]-flip	$(a\bar{b})$	$(c\bar{c})$	$(e\bar{e})$
	$(b\bar{a})$	$(d\bar{d})$	$(f\bar{f})$
[1,2]- and [1,3]-flips	$(a\bar{d}b\bar{c})$		$(e\bar{f})$
	$(c\bar{a}d\bar{b})$		$(f\bar{e})$
[2,3]-flip	$(a\bar{b})$	$(c\bar{d})$	$(e\bar{e})$
	$(b\bar{a})$	$(d\bar{c})$	$(f\bar{f})$
[1,2,3]-flip	$(a\bar{c})$	$(b\bar{d})$	$(e\bar{f})$
	$(c\bar{a})$	$(d\bar{b})$	$(f\bar{e})$

[a] Numerals in brackets identify the ligands which flip during the conversion (see Figure 4). The flips refer to the enantiomer with unbarred ligand designations. [b] For significance of letters, see Figure 4. The site exchange $(a\bar{d}b\bar{c})$ signifies that the methyl group is carried from environment a into $\bar{d}$, etc.

The spectrum at −93° is consistent with the propeller conformation for **2** and with slow enantiomerization on the nmr time scale only if two of the *o*-methyl resonances are accidentally isochronous (signal 4). The zero-flip exchanges only enantiotopic groups (Table II), and would therefore again require accidental isochrony in order to be compatible with the spectrum. Alternatively, the spectrum is also consistent with enantiomeric propeller conformations which are rapidly interconverting by [2]- or [3]-flips (Table II); either one of these mechanisms would result in the coalescence of two of the four ortho group signals to yield a pattern consistent with the one observed. However, as in the case of **1**, the zero-flip and the [2]-flip are both expected to be unfavorable for steric reasons when compared to the [3]-flip. Therefore, a propeller ground-state geometry with rapid enantiomerization by the [3]-flip remains a reasonable rationalization of the nmr results at −93°. As in the case of **1**, a perpendicular ground state, corresponding to the effective time-average geometry for the rapid [3]-flip, is also consistent with the experimental results. Thus, the nmr results for **2**, as well as those for **1**, can be reconciled with three alternative interpretations of the low-temperature spectra.[16]

In an attempt to distinguish between a helical conformation with slow enantiomerization on the nmr time scale and a perpendicular conformation, at least on the time average, bis(2,6-dimethylphenyl)isopropoxyborane was prepared and its nmr spectrum investigated. In the helical conformation the two isopropyl methyl groups would be diastereotopic, and could thus give rise to two doublets in the ^{1}H-nmr spectrum. However, at −73° the 60-MHz ^{1}H-nmr spectrum of this compound featured only one sharp doublet for the isopropyl methyl groups, and three resonances for the

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(15) The results of rapid enantiomerization by the [1,2]- and [1,3]-flips may be determined in the same manner as those for the corresponding flips of the topologically analogous dimesityl-1-(2-methylnaphthyl)borane.[3] The effects of interconversion by means of each of the other six pathways may be readily determined by an examination of the idealized transition-state geometry for the process in question.

(16) The above analysis shows that the [2,3]-flip of **2** is not consistent with the low-temperature spectrum of this compound (Table II). This result supplies additional support for our conclusion that the [2,3]-flip of **1** is probably not occurring rapidly on the nmr time scale at −86°.

aromatic methyl groups at $\delta^{\mathrm{TMS}}_{\mathrm{CS_2}}$ 1.88, 2.20, and 2.51 ppm, with a ratio of intensities of 1:2:1, respectively. This observation is in accord with a time average perpendicular conformation, but a helical conformation with accidental isochrony cannot be excluded.

When a sample of **2** is warmed to $-62°$, signals 1 and 5 broaden noticeably, and further warming results in the coalescence of resonances 1, 4, and 5, and also of resonances 2 and 3 (Figure 5). At *ca.* 37°, the spectrum consists of two sharp peaks at $\delta^{\mathrm{TMS}}_{\mathrm{CS_2}}$ 2.20 and 2.12 ppm, in a ratio of 1:2. The coalescence of the *p*-methyl group peaks (2 and 3) indicates flipping of the methoxy group, whereas coalescence of *o*-methyl group resonances (1 and 5) reflects flipping of the aryl groups (Table II).

There is only one interconversion pathway which exchanges the four *o*-methyl groups of **2** as well as the two *p*-methyl groups: the enantiomeric [1,2]- and [1,3]-flips. However, calculated nmr line shapes[17] for this process were not consistent with the experimental spectrum. In the calculated spectrum, the *p*-methyl group resonances coalesce much more rapidly, relative to the *o*-methyl group signals, than they do in the experimental spectrum.[18] Therefore, more than one exchange process must be taking place. These pathways must involve a lower energy process which causes the coalescence of only the *o*-methyl group signals (1 and 5), and a higher energy pathway which also results in coalescence of the *p*-methyl group resonances (2 and 3).

There are three pathways consistent with the lower-energy process when the apparent isochrony in the spectrum is taken into account: the [2]-flip, the [3]-flip, and the [2,3]-flip (Table II). These pathways involve flipping of only the mesityl rings. The higher energy process must involve flipping of the methoxy group, *i.e.*, it can be explained by the [1]-flip or the [1,2,3]-flip, in combination with the lower energy process, or by the combination of enantiomeric [1,2]- and [1,3]-flips as mentioned above. It might be argued that the [1]-flip and the [2]-flip would require higher activation energies than the other pathways listed above on the basis of steric crowding in the transition states, but a decision among the other alternatives is less obvious.

A complete line-shape analysis[17] of the variable-temperature nmr spectrum of **2** based upon a combination of the [2,3]-flip and the enantiomeric [1,2]- and [1,3]-flips was carried out. A satisfactory fit to the experimental spectrum at five temperatures was obtained using a rate ratio of [1,2]- and [1,3]-flips (k_2) to [2,3]-flips (k_1) of $k_2/k_1 = 0.055$ for the entire range of temperatures studied (Figure 5). The rate data obtained were used to calculate $\Delta G^{\ddagger}_{-35} = 11.8$ kcal/mol for the lower energy coalescence of the *o*-methyl groups (flipping of the aryl groups) and $\Delta G^{\ddagger}_{-35} = 13.2$ kcal/mol for the higher energy process involving coalescence of the *p*-methyl groups (flipping of the methoxy group). Line-shape calculations do not distinguish among the various possible combinations of mechanisms and the calculated free energies of activation are independent of the particular combination chosen.

As was reported above, bis(2,6-dimethylphenyl)-methoxyborane and bis(4-methoxy-2,6-dimethylphenyl)methoxyborane also have nmr spectra which feature nonequivalent *o*-methyl groups in the low-temperature limit.[19] In each case, the *o*-methyl group signals coalesce to a singlet as the temperature is raised. Isomerism and isomerization processes in these molecules may be analyzed in a manner analogous to that described for **2**. By employing the Gutowsky–Holm equation[12] and the Eyring equation, free energies of activation for the exchange of the *o*-methyl groups at their coalescence temperatures were calculated to be $\Delta G^{\ddagger}_{-31} = 12.0$ kcal/mol and $\Delta G^{\ddagger}_{-27} = 12.2$ kcal/mol, respectively, for the two compounds.

Restricted Rotation about B–O Bonds

The results obtained for **1** and **2** demonstrate that in the low-temperature limit, rotation about the B–O bonds is significantly restricted on the nmr time scale. Evidence for this derives from the coalescence phenomena observed at higher temperatures. Rapid exchange of two mesityl *o*-methyl groups of **1** with concurrent observation of two diastereotopic methoxy groups was noted. Similarly, rapid exchange of two *o*-methyl groups of **2** was observed with simultaneous nonequivalence of *p*-methyl groups. Since in both cases the barriers to flipping of the aryl groups are significantly lower than the barriers to interconversion of the methoxy or *p*-methyl groups, the hypothesis of unrestricted rotation about the B–O bonds is rendered untenable.[20]

Both steric and electronic effects are expected to contribute to the magnitude of barriers to stereoisomerization of alkoxydiarylboranes. The fact that the barrier to flipping of the mesityl group in **1** is *ca.* 3 kcal/mol lower than that of the less bulky methoxy group (Table III) suggests that (p–p)π conjugation between boron and oxygen plays an important role in determining the magnitude of the barriers observed

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(17) The computer program employed was adapted from one developed by M. Saunders (see M. Saunders in "Magnetic Resonance in Biological Systems," A. Ehrenberg, B. G. Malmström, and T. Vänngård, Ed., Pergamon Press, New York, N. Y., 1967, p 85). We are grateful to Professor Saunders for providing us with a copy of his program. Chemical shift assignments for the *o*-methyl groups were made in a manner analogous to that described for dimesityl-1-(2-methylnaphthyl)borane.[3]

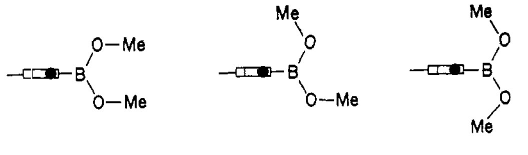
(18) The [1]-flip or the [1,2,3]-flip also might be consistent with the observed spectrum at 37°, if the time-average resonance arising from the coalescence of signals 1 and 5 were accidentally isochronous with signal 4. However, line-shape analysis[17] shows that these two mechanisms give calculated spectra which suffer from the same defect as those for the [1,2]- and [1,3]-flips.

(19) The *p*-methoxy groups of bis(4-methoxy-2,6-dimethylphenyl)-methoxyborane also give rise to anisochronous signals in the low-temperature limit. However, activation parameters were not calculated for the coalescence of these signals because of the small chemical shift difference and the presence of an interfering resonance from the methoxy group bonded to boron.

(20) Molecular association in solution does not enter as a complicating factor, since **1**, **2**, bis(2,6-dimethylphenyl)methoxyborane, and bis(4-methoxy-2,6-dimethylphenyl)methoxyborane were all shown to be monomeric in benzene solution. Furthermore, trimesitylborane, another sterically congested borane, has been shown not to form complexes with ammonia or sodium alkoxides,[21] and sterically crowded aminoboranes are also monomeric in solution.[22] The ^{1}H-nmr spectra of **1** and **2** in the presence of Eu(fod)$_3$ were determined at ambient temperatures. No shift of the methoxy or methyl group signals was observed. Under the same conditions, the spectrum of bis(4-methoxy-2,6-dimethylphenyl)methoxyborane showed significant downfield shifts. The shift was greatest for the *p*-methoxy group signal.

(21) H. C. Brown and V. H. Dodson, *J. Amer. Chem. Soc.*, **79**, 2302 (1957).

(22) G. E. Coates and J. G. Livingstone, *J. Chem. Soc.*, 4909 (1961).



3a 3b 3c

Figure 6. Schematic representation of conformations of mesityldimethoxyborane (3). The mesityl group is perpendicular to the plane of the figure.

in these systems.[23] The same effect is seen in **2**, where the higher energy process also corresponds to the flipping of the methoxy group, while the lower energy pathway involves flipping of only the aryl groups.[25,26]

Boron–oxygen π bonding will necessarily influence not only the magnitudes of rotational barriers about the B–O bond itself, but indirectly also the magnitudes of barriers to rotation about the B–C bonds of alkoxydiarylboranes. An indication of the magnitude of this "second order" effect was obtained from observations on two alkyldiarylboranes. Ethyldimesitylborane shows only a single nmr resonance for the protons of the *o*-methyl groups of the mesityl rings even at −100°. The ^{1}H-nmr spectrum of isopropyldimesitylborane at −98° features resonances for the *o*-methyl groups at $\delta_{CS_2}^{TMS}$ 1.94, 2.08, and 2.43 ppm, in a ratio of 1:2:1, respectively. The two outer signals broaden as the temperature is raised, and coalesce at −85°. The free energy of activation for this process, which presumably involves the flipping of mesityl groups, is only $\Delta G^{\ddagger}_{-85}$ = 9.3 kcal/mol (calculated using the Gutowsky–Holm equation[12] and the Eyring equation). Alkyldiarylboranes are at least as sterically encumbered about the boron atom as are the alkoxydiarylboranes, yet the latter have significantly higher barriers to flipping of the aryl groups (Table III). Although this comparison is by no means rigorous, it does suggest that B–O conjugation does much to raise barriers to rotation about B–C bonds in the systems studied.[27]

Table III. Activation Energies for the Stereoisomerization of Arylmethoxyboranes

Compound	Aryl group flip[a] $\Delta G^{\ddagger}_T$	T, °C	Methoxy group flip[a] $\Delta G^{\ddagger}_T$	T, °C
9-Anthrylmesitylmethoxyborane (1)	10.1[b]	−62	13.7[d] 12.6[e]	−24 −24
Dimesitylmethoxyborane (2)	11.8[c]	−35	13.2[c]	−35
Bis(2,6-dimethylphenyl)methoxyborane	12.0[b]	−31		
Bis(4-methoxy-2,6-dimethylphenyl)methoxyborane	12.2[b]	−27		
Mesityldimethoxyborane (3)			9.4[b]	−88

[a] See text for a precise description of the process observed in each case. [b] Calculated from rate constants obtained at coalescence by the method of Gutowsky and Holm.[12] T = coalescence temperature (T_c). [c] Calculated from rate constants obtained by total line-shape analysis.[17] [d] More to less stable diastereomer; calculated at $T = T_c$.[14] [e] Less to more stable diastereomer; calculated at $T = T_c$.

As an extension of the preceding work, the conformational dynamics of mesityldimethoxyborane (**3**) were briefly investigated. At −100°, the 60-MHz ^{1}H-nmr spectrum of **3** features one signal for the *p*-methyl group of the mesityl ring at $\delta_{CS_2}^{TMS}$ 2.22 ppm, one signal for the two *o*-methyl groups (δ 2.15 ppm), one resonance for the ring protons (δ 6.63 ppm), and two methoxy group signals at $\delta_{CS_2}^{TMS}$ 3.35 and 3.57 ppm in a 1:1 ratio of intensities. Although we may only speculate on the ground-state geometry of **3**, it seems reasonable to suggest that the ligand planes of the methoxy groups will lie approximately in the reference plane, in order to maintain maximum conjugation with boron. This will result in three possible arrangements, illustrated by structures **3a**, **3b**, and **3c** in Figure 6. In structures **3a** and **3c**, the methoxy groups are homotopic whereas in **3b** they are diastereotopic. Therefore, barring accidental isochronies and fortuitous equalities in populations, structure **3b** is the only one of the three which is consistent with the spectrum at −100°. In addition, if the ground-state or effective time-average conformation of the mesityl group is perpendicular to the reference plane, then the observation of only one *o*-methyl signal and one signal for the two ring protons is accounted for.

Upon warming the sample, the methoxy signals broaden, and coalesce at −88°. From this coalescence temperature and the chemical shift difference in the absence of exchange (13 Hz), the rate constant was estimated using the Gutowsky–Holm equation.[12] The Eyring equation was then employed to derive the free energy of activation for the exchange process $\Delta G^{\ddagger}_{-88}$ = 9.4 kcal/mol. The mechanism for this process involves flipping of the methoxy groups, and could conceivably be concerted. Alternatively, the exchange mechanism might involve either **3a** or **3c** as relatively high energy intermediates. The information available does not allow us to differentiate among these possibilities. The barrier lowering for the flipping of the methoxy groups in **3** as compared to the alkoxydiarylboranes discussed above (Table III) is probably due not only to a lessening of steric hindrance, but also to a competitive effect between the two methoxy groups in conjugation with the boron. Similar behavior has been noted for diaminoboranes.[4a]

We recognize that the stereoisomerizations which have been described above as involving rotations about the boron–oxygen bond might conceivably involve linear inversion ("lateral shift") instead; the two

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[23] *Ab initio* calculations[24] indicate that the rotation barriers increase in the order CH_3–BH_2 < Ph–BH_2 < HO–BH_2 < H_2N–BH_2. According to Mulliken population analysis, the order parallels that of increasing B–X π-bonding, which is roughly three times as great in HO–BH_2 as in phenylborane.

[24] J. A. Pople, P. v. R. Schleyer, and J. D. Dill, unpublished work. We thank J. D. Dill for providing us with these results, and for helpful discussions.

[25] If the activation parameters obtained for **1** and **2** are compared (Table III), it is seen that while the barriers for the pathways which include flipping of the methoxy group are quite similar (*ca.* 13 kcal/mol), the barrier for the aryl ring flip in **1** (10.1 kcal/mol) is nearly 2 kcal/mol lower than that for the corresponding process in **2** (11.8 kcal/mol). This observation suggests that steric repulsions in the transition states may increase when anthryl is replaced by mesityl as a ligand.

[26] The barriers to rotation about the boron–oxygen bond reported here are significantly higher than those reported in the literature[4d] for dimethylborinic anhydride (8.6 ± 0.5 kcal/mol) and methoxydimethylborane (8.5 ± 0.3 kcal/mol).

[27] Meissner and Staab[28] recently observed restricted rotation of the aryl groups in a series of aryl-*n*-butoxy(2,4,6-tri-*tert*-butylphenyl)boranes, for which a perpendicular conformation analogous to X was assumed. In contrast to the work reported here, these investigators obtained no evidence for restricted rotation of the alkoxy group. However, in line with the above discussion of second order effects, it is conceivable that conjugative effects between boron and oxygen also contribute significantly to the barriers to rotation about B–C bonds observed by Meissner and Staab.

[28] B. Meissner and H. A. Staab, *Justus Liebigs Ann. Chem.*, **753**, 92 (1971).

mechanisms are permutationally indistinguishable. However, calculations[29] indicate that the minimum energy of activation for linear inversion in isoelectronic alkoxycarbonium ions is *ca.* 17 kcal/mol for a "full" double bond, and that a decrease in double bond character increases this barrier. Substituted boric and boronic acids have π-bond orders of much less than 1,[5d] and boron forms weaker π bonds with oxygen than with nitrogen.[5b] Since the barriers reported above are considerably lower than 17 kcal/mol and furthermore are lower than the unarguably rotational barriers observed for aminoboranes,[4a–c] our assumption that these barriers are best described as rotation seems justified. Further support for this conclusion is provided by *ab initio* calculations[24] which indicate that rotation is energetically more favorable than linear inversion for BH_2OH.

It is interesting to compare the barriers to stereoisomerization found here for alkoxyboranes with those for the isoelectronic carbon compounds. The barriers to stereoisomerization (by either rotation or linear inversion) of protonated aldehydes and ketones and related substances are relatively sensitive to electronic effects,[30] and therefore meaningful comparisons are difficult. However, it has been reported[31] that the ^{1}H-nmr spectrum of protonated 2,2′,6,6′-tetramethylbenzophenone features nonequivalent methyl group resonances at $-10°$ ($\Delta\nu = 6$ Hz) which coalesce at *ca.* 15°. This coalescence was ascribed to rotation about the C–O bond. The Gutowsky–Holm equation[12] and the Eyring equation may be used to estimate an activation energy of $\Delta G^{\ddagger}_{15} = 15.2$ kcal/mol from these data. Protonated 2,2′-dimethylbenzophenone, a compound with fewer bulky ortho substituents, shows similar behavior, and an activation energy of $\Delta G^{\ddagger} = 13.6$ kcal/mol was reported[31] for the interconversion of methyl groups. On the other hand, the barrier for methoxy group rotation in **2**, which has four *o*-methyl groups, is only *ca.* 13 kcal/mol.

Similarly, the barrier for stereoisomerization of methyldimethoxycarbonium ion was reported[32] to be *ca.* 15 kcal/mol, and both experimental results[30,33] and calculations[29] indicate that the analogous barrier for protonated carboxylic acids is also on the order of 11–15 kcal/mol. By comparison, the barrier to site exchange of the methyl groups in dimethoxymesitylborane (**3**) is only 9.4 kcal/mol.

Although the differences in activation energies between the boron and carbon compounds reported above are not large, and generalizations based upon comparisons such as these are by no means rigorous, the results are nevertheless at least consistent with the hypothesis that the π-bond order of the B–O bond in alkoxyboranes is somewhat lower than that of the C–O bond in the analogous carbon compounds. Parallel conclusions have been drawn for aminoboranes and their carbon analogs.[34]

As was noted in the preceding paper,[3] the barriers to aryl group rotation in triarylcarbonium ions are higher than those in triarylboranes whose aryl groups have comparable steric requirements. The same relationship evidently obtains for protonated diaryl ketones and the analogous methoxydiarylboranes, although it would appear that the energy differences in these systems are comparatively minor.

Experimental Section[35]

Mesityldimethoxyborane (3) was prepared by the method of Staab and Meissner.[36] The ^{1}H-nmr spectrum featured absorptions at $\delta_{CS_2}^{TMS}$ 2.13 (6 H, s, CH_3), 2.18 (3 H, s, CH_3), 3.45 (6 H, s, OCH_3), and 6.62 (2 H, s, aromatic H).

9-Anthrylmesitylmethoxyborane (1). A solution of 9-bromoanthracene (2.70 g, 10.5 mmol) in 50 ml of anhydrous ether was converted to the organolithium compound by treatment with *n*-butyllithium (10.5 mmol, 4.8 ml of a 2.2 *M* solution in hexane, Alfa Inorganics). Mesityldimethoxyborane[36] (2.0 g, 10.5 mmol) dissolved in 15 ml of ether was added dropwise to the solution of the lithium reagent at room temperature, with stirring. After heating at reflux for 30 min, the mixture was poured onto crushed ice, the organic layer was diluted with chloroform, separated, and dried ($MgSO_4$), and the solvent was removed by distillation at reduced pressure. The crude product was recrystallized from 80:20 methanol–acetone to yield 2.1 g (59%) of pale yellow plates, mp 109–110°. The ^{1}H-nmr spectrum featured absorptions at $\delta_{CS_2}^{TMS}$ 2.14 (6 H, s, CH_3), 2.20 (3 H, s, CH_3), 3.62 (3 H, s, OCH_3), 6.71 (2 H, s, aromatic H), 7.30 (4 H, m, aromatic H), 7.90 (4 H, m, aromatic H), and 8.32 (1 H, s, aromatic H). Mass spectral analysis was consistent with the assigned structure; exact mass, 338.18385 (calcd, 338.18419).

Anal. Calcd for $C_{24}H_{23}BO$: C, 85.22; H, 6.85; B, 3.20; mol wt, 338. Found: C, 85.37; H, 6.78; B, 3.35; mol wt (osmometry), 341.

Dimesitylmethoxyborane (2). A solution of fluorodimesitylborane[21] (3.0 g, 11.2 mmol) dissolved in 40 ml of methanol was refluxed for 10 min under nitrogen. The excess methanol was removed by distillation under reduced pressure, and the product was recrystallized from methanol to yield 2.91 g (93%) of white needles, mp 75–76°. The ^{1}H-nmr spectrum featured absorptions at $\delta_{CS_2}^{TMS}$ 2.12 (12 H, s, CH_3), 2.20 (6 H, s, CH_3), 3.64 (3 H, s, OCH_3), and 6.62 (4 H, s, aromatic H). Mass spectral analysis was consistent with the assigned structure; exact mass, 280.199603 (calcd, 280.199837).

Anal. Calcd for $C_{19}H_{25}BO$: C, 81.44; H, 8.99; B, 3.86; mol wt, 280. Found: C, 81.26; H, 8.94; B, 3.81; mol wt (osmometry), 277.

Bis(2,6-dimethylphenyl)methoxyborane, mp 91–92°, was prepared in a manner analogous to that described for **2** from bis(2,6-dimethylphenyl)fluoroborane[37] and methanol (89% yield). The ^{1}H-nmr spectrum featured resonances at $\delta_{CS_2}^{TMS}$ 2.18 (12 H, s, CH_3), 3.68 (3 H, s, OCH_3), and 6.88 (6 H, m, aromatic H). The mass spectrum showed the parent ion at *m/e* 252; exact mass, 252.168387 (calcd, 252.168539).

Anal. Calcd for $C_{17}H_{21}BO$: C, 80.97; H, 8.39; B, 4.29; mol wt, 252. Found: C, 80.74; H, 8.13; B, 4.10; mol wt (osmometry), 256.

Bis(2,6-dimethylphenyl)isopropoxyborane, mp 87–88°, was prepared (72% yield) in a manner analogous to that described for **2** from bis(2,6-dimethylphenyl)fluoroborane[37] and isopropyl alcohol. The ^{1}H-nmr spectrum featured resonances at $\delta_{CS_2}^{TMS}$ 1.23 (6 H, d, $^3J_{HH} = 6.2$ Hz, $CH(CH_3)_2$), 2.20 (12 H, s, CH_3), 4.34 (1 H, heptet, $^3J_{HH} = 6.2$ Hz, $CH(CH_3)_2$), and 6.89 (6 H, m, aromatic H). The

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(35) Elemental analyses and molecular weight determinations by osmometry (in benzene) were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Unless otherwise specified, ^{1}H-nmr spectra were recorded on a Varian A-60A spectrometer at ambient probe temperature (*ca.* 37°) and refer to *ca.* 20% solutions in CS_2, with tetramethylsilane (TMS) as internal reference. Mass spectra were obtained on an AEI MS-9 high-resolution mass spectrometer with an ionizing voltage of 70 eV. All reactions which involved the use of organometallic compounds as reagents or intermediates were carried out under a high-purity nitrogen atmosphere. Melting points were measured in a Thomas-Hoover apparatus and are corrected.

(36) H. A. Staab and B. Meissner, *Justus Liebigs Ann. Chem.*, **753**, 80 (1971).

(37) P. J. Grisdale, J. L. R. Williams, M. E. Glogowski, and B. E. Babb, *J. Org. Chem.*, **36**, 544 (1971).

mass spectrum showed the parent ion at *m/e* 280; exact mass, 280.199867 (calcd, 280.199837).

Anal. Calcd for $C_{19}H_{25}BO$: C, 81.44; H, 8.99; B, 3.86. Found: C, 81.70; H, 9.23; B, 3.97.

Hydroxybis(4-methoxy-2,6-dimethylphenyl)borane. Magnesium turnings (1.00 g, 41.5 mmol) and 70 ml of dry tetrahydrofuran were placed in a three-necked flask equipped with a dropping funnel, mechanical stirrer, condenser, and nitrogen inlet. After heating this mixture at reflux for 5 min, a solution of 4-methoxy-2,6-dimethylbromobenzene (9.0 g, 41.5 mmol) in 50 ml of tetrahydrofuran was added dropwise. The solution was heated to reflux during the addition period (*ca.* 1 hr) and for 30 min after addition was complete. The resulting brown solution was cooled to −10°, and a solution of boron trifluoride etherate (2.8 ml, 22.0 mmol) in 30 ml of anhydrous ether was added dropwise over a period of 15 min. When addition was complete, the pale yellow solution was refluxed for 15 min and then poured onto crushed ice containing 5% HCl. The organic material was extracted with ether and dried ($MgSO_4$), and the solvent was distilled at reduced pressure. The resulting white solid was recrystallized from carbon tetrachloride to yield 4.0 g (65%) of the desired product, mp 121–123°. The ^1H-nmr spectrum showed absorptions at $\delta_{CS_2}^{TMS}$ 2.13 (12 H, s, CH_3), 3.63 (6 H, s, OCH_3), 5.97 (1 H, s, OH), and 6.33 (4 H, s, aromatic H). The mass spectrum featured the parent ion at *m/e* 298; exact mass, 298.174221 (calcd, 298.174016).

Anal. Calcd for $C_{18}H_{23}BO_3$: C, 72.50; H, 7.77; B, 3.63. Found: C, 72.33; H, 7.53; B, 3.90.

Bis(4-methoxy-2,6-dimethylphenyl)methoxyborane, mp 76–77°, was prepared from hydroxybis(4-methoxy-2,6-dimethylphenyl)borane and methanol in 89% yield in a manner similar to that described for the preparation of **2**. The ^1H-nmr spectrum featured absorptions at $\delta_{CS_2}^{TMS}$ 2.14 (12 H, s, CH_3), 3.63 (3 H, s, $BOCH_3$), 3.66 (6 H, s, $ArOCH_3$), and 6.50 (4 H, s, aromatic H). Mass spectral analysis showed the parent ion at *m/e* 312; exact mass, 312.189560 (calcd, 312.189666).

Anal. Calcd for $C_{19}H_{25}BO_3$: C, 73.09; H, 8.07; B, 3.46; mol wt, 312. Found: C, 73.12; H, 8.14; B, 3.73; mol wt (osmometry), 310.

Ethyldimesitylborane. A solution of ethylmagnesium bromide (14.0 mmol) in ethyl ether was added dropwise to an ether solution of fluorodimesitylborane[21] (2.1 g, 7.8 mmol), with stirring. After refluxing for 10 min, the reaction mixture was poured onto crushed ice, and the organic layer was separated and dried ($MgSO_4$). The solvent was removed by distillation at reduced pressure. The crude product was recrystallized from methanol to yield 1.93 g (88%) of white needles, mp 77–78°. The ^1H-nmr spectrum showed absorptions at $\delta_{CS_2}^{TMS}$ 1.00 (3 H, m, CH_2CH_3), 1.77 (2 H, m, CH_2CH_3), 2.13 (12 H, s, CH_3), 2.18 (6 H, s, CH_3), and 6.63 (4 H, s, aromatic H). The mass spectrum featured the parent ion at *m/e* 278; exact mass, 278.220756 (calcd, 278.220573).

Anal. Calcd for $C_{20}H_{27}B$: C, 86.33; H, 9.78; B, 3.89; mol wt, 278. Found: C, 86.23; H, 9.79; B, 4.06; mol wt (osmometry), 277.

Isopropyldimesitylborane, mp 92–93°, was prepared in 70% yield by a procedure analogous to that described for ethyldimesitylborane, The ^1H-nmr spectrum featured resonances at $\delta_{CS_2}^{TMS}$ 1.05 (6 H, d, $^3J_{HH}$ = 7.1 Hz, $CH(CH_3)_2$), 2.12 (12 H, s, CH_3), *ca.* 2.15 (1 H, m, $CH(CH_3)_2$), 2.19 (6 H, s, CH_3), and 6.65 (4 H, s, aromatic H). The mass spectrum showed the parent ion at *m/e* 292.

Anal. Calcd for $C_{21}H_{29}B$: C, 86.30; H, 10.00; B, 3.70. Found: C, 86.14; H, 9.90; B, 3.74.

Dnmr Measurements. ^1H-nmr spectra were recorded on a Varian A-60A spectrometer equipped with a variable-temperature accessory. Temperature measurements were based on the chemical-shift separation of the protons of a methanol sample, and utilized the temperature-shift correlation of Van Geet.[38] Temperatures are believed to be accurate to ±2°, although within a given series of measurements smaller differences (*ca.* ±0.5°) are considered significant. Saturation of nmr signals was avoided. Dnmr samples were *ca.* 25% v/v solutions with *ca.* 5% v/v TMS. Samples were sealed under vacuum in precision thin-wall nmr tubes. The line-shape analyses[17] were performed on an IBM 360/91 computer equipped with a Calcomp plotting accessory.

The line-shape analyses were carried out as described previously.[3] The frequency assignments for the *o*-methyl groups of **2** are ambiguous, since several distinct assignments all give identical calculated spectra which match the experimental spectra. One arbitrary set of static parameters which produced a satisfactory fit to the experimental spectra was: $a = 2.40$, $b = 1.82$, $c = d = 2.12$, $e = 2.23$, and $f = 2.19$ ppm, for the combination of the [2,3]-flip plus the [1,2]- and [1,3]-flips (see Figure 4 for significance of letters).

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Conformations and Rotation Barriers in Allylcarbinyl Radicals by Electron Spin Resonance

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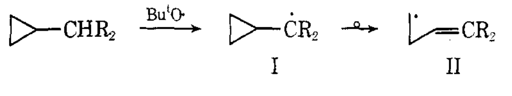
Abstract: Allylcarbinyl and 1,1,3-trimethylallylcarbinyl radicals are derived from methylcyclopropane and 1,1,2,2-tetramethylcyclopropane, respectively, by hydrogen abstraction followed by rearrangement of the corresponding cyclopropylcarbinyl intermediate. The isomeric tetramethylcyclopropyl radicals can be generated independently and shown not to be intermediates, and they do not undergo ring opening to allyl radicals. The conformations of allylcarbinyl radicals are deduced from their esr spectra. The pronounced selective line broadening observed in the spectrum of the 1,1,3-trimethylallylcarbinyl radical is attributed to hindered rotation about the C_β–C_γ bond and analysis of the line shape using the relaxation matrix theory affords a barrier of 3.5 kcal mol^{-1}. Rotation barriers in alkyl radicals are discussed in the light of methods used to extract information from esr data.

Electron spin resonance studies of alkyl radicals derived from a variety of alkylcyclopropanes were reported previously in preliminary form.[1] It was shown that cyclopropylcarbinyl radicals I are readily formed from the hydrocarbons by hydrogen atom abstraction with *tert*-butoxy radicals generated photochemically from di-*tert*-butyl peroxide. These radicals undergo spontaneous rearrangement at temperatures higher than about −100° to afford allylcarbinyl radicals II according to eq 1. Thus, temperature is an important factor in the observation of the esr spectrum



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[1] (a) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *J. Amer. Chem. Soc.*, **91**, 1877 (1969); (b) *ibid.*, **91**, 1879 (1969).