reflections were measured according to the ω technique (Mo Kα, graphite monochromator), using a scan range of 1° and a scan speed between 0.5 and 24.0 deg min^{-1} as a function of the intensities of the reflections. In the range between $3.0° \leq 2\theta \leq 55.0°$ all reflections hkl with $F > 3\sigma(F)$ were applied for the structure determination. For the evaluation the SHELXTL System on an Eclipse S250 at the Max-Planck-Institut für Festkörperforschung was employed. All structures were solved by the direct phase determination. The parameters of the complete structures could be refined by anisotropic least-squares cycles to the given R values. The positions of the hydrogen atoms were calculated geometrically and considered isotropically in all refinements. Special X-ray operations and results are listed in Table IV. We have omitted the presentation of the structure factors, which can be obtained upon request.

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Mechanisms of the π-Electron Steric Effect

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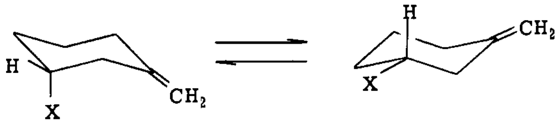
Abstract: Replacement of a β-CH$_2$ in methoxycyclohexane by C═CH$_2$ produces an increased proportion of the equatorial conformer in a nonpolar medium. We previously suggested that this change resulted from an electrostatic repulsion between the axial 3-methoxy group and the exocyclic C═CH$_2$ structure. We now observe that exocyclic C═C(CH$_3$)$_2$ yields the opposite result, an increased proportion of the axial 3-methoxy conformer. The presence of methyl on the exocyclic double bond reduces or eliminates the C═CX$_2$ dipole. These observations are consistent with the earlier suggestion that this π-electron steric effect results from dipole–dipole interactions. The corresponding 3-methoxy C═CCl$_2$ and C═CBr$_2$ systems, however, also exhibit an increased proportion of the axial conformer. In the halogen systems, either the dipolar interaction has changed sign as the result of an unexpected alteration of intervector angles or an alternative attractive mechanism such as an n–π^* orbital interaction has become important. The orbital interaction would be favored by the lower LUMO's of the halogenated double bond.

We recently reported the functional equivalent of a π-electron steric effect on the conformational equilibria of 3-substituted 1-(*exo*-methylene)cyclohexanes (eq 1).[2] In this system, one of the cyclohexane CH$_2$ groups, with its axial proton, has been replaced by C═CH$_2$. Because the mutual repulsion between the axial substitutent X and the syn-axial ring protons is a substantial factor in determining axial/equatorial equilibrium constants in cyclohexane, one might expect that removal of one such axial proton would increase the proportion of the axial conformer. The 3-alkyl ketone effect in 3-substituted cyclohexanones has been interpreted in these terms.[3] We found that 3-alkyl-1-methylenecyclohexanes behave in a similar fashion.[2] Replacement of a CH$_2$ group of cyclohexane with C═O or C═CH$_2$ increases the proportion of the axial alkyl conformer.



(1)

The cyclohexanone studies did not examine polar substituents at the 3-position.[3] In our methylenecyclohexane study, we were able to examine OH, OCH$_3$, and SCH$_3$, among others. Surprisingly, the effect of the exo-methylene group on these substituents was opposite to that on the alkyl groups. Replacement of the CH$_2$ of cyclohexane by C═CH$_2$ brought about a large decrease in the proportion of the 3-axial isomer. These observations were made in the almost nonpolar solvent CF$_2$Cl$_2$, in which intramolecular interactions should achieve the greatest importance. We attributed the decreased axial population to a repulsive interaction between the 3-axial substituent and the 1-C═CH$_2$ group.[2] Through-bond orbital interactions should have caused the opposite result (increased axial population), so we attributed our observations to electrostatic rather than orbital interactions. These interactions could involve the dipole of the 3 substituent and either the dipole or the quadrupole of the C═CH$_2$ group. Calculations suggested that both mechanisms could contribute.[2]

Examination of the same equilibrium in a polar, hydrogen-bonding solvent (CHFCl$_2$) showed an appreciable increase in the axial population. Solvation partially insulates the 3 substituent from the C═CH$_2$ group, thereby decreasing the repulsive electrostatic interaction that had served to disfavor the axial conformer. With this effect substantially reduced, the proportion of axial conformer is actually larger than in cyclohexyl, as in the 3-alkyl ketone effect. Thus in a polar solvent, the effect originally expected is realized, although it does not reflect the true intramolecular interactions. Solvent effects on conformational equilibria have been thoroughly studied.[4a] In cyclohexyl systems such as methoxycyclohexane solvent effects are opposite to what we observed in the *exo*-methylenecyclohexanes, since polar solvents decrease the proportion of the axial cyclohexyl conformer.[4b]

The exact nature of the intramolecular effects observed in CF$_2$Cl$_2$ was not clear.[2] Although we favored simple electrostatic interactions, they were not fully defined. Because electrostatic calculations are fraught with uncertainties in these systems, we

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(1) (a) This work was supported by the National Science Foundation (Grant Nos. CHE77-08384 and CHE79-05542); (b) Fellow of the African-American Institute, 1975–1979.

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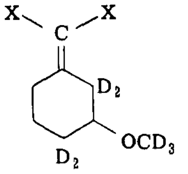
Table I. Spectral and Kinetic Parameters for Exo-Disubstituted Methylenecyclohexanes in CF_2Cl_2 at 90 MHz

compd	subst	T_c, K	$\Delta\nu$, ppm	J, Hz	k_c,[a] s^{-1}	$\Delta G_c^{\ddagger}$,[b] kcal/mol
5	CH_3	117	1.17	12.4	243	5.4 ± 0.2[c]
6	Br	105	1.17	12.4	244	4.8 ± 0.2
7	Cl	113	1.11	12.8	233	5.2 ± 0.2[d]
8	CN	143			(167)[e]	(6.7)[f]

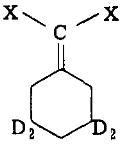
[a] $k_c = \pi(6J^2 + \Delta\nu^2)^{1/2}/(2)^{1/2}$. [b] $\Delta G^{\ddagger} = RT_c\,(23.76) + \ln\,(T_c/k_c))$. [c] Lit.[6] 5.8. [d] Lit.[6] 5.4. [e] Calculated from $\Delta G^{\ddagger}$. [f] Interpolated from a plot of the methyl rotation barrier for substituted *cis*-propenes vs. $\Delta G^{\ddagger}$ for ring reversal in exo-substituted methylenecyclohexanes, given in ref 13.

decided on an experimental approach. In our original investigation,[2] we held the structure of the exo-methylene group constant and varied the substituent at the 3-position. In order to clarify the nature of the 1,3-repulsive interaction, we now have examined a series in which the 3 substituent is held constant and the electronic nature of the exo-methylene group is varied. Alteration of its dipolar properties may yield an interpretable pattern in the axial/equatorial ratios.

Consequently, we have prepared a series of 3-methoxy-1-methylenecyclohexanes, in which the hydrogens on the exo-methylene group have been replaced by CH_3, Br, Cl, or CN. These substituents vary from electron donating to electron withdrawing, so that, within the series, the dipole of the methylene group is altered in either direction from that of $C{=}CH_2$. Axial/equatorial equilibrium constants were measured below the coalescence temperature for ring reversal by direct integration of the 3-proton resonance, geminal to methoxyl. Clarification of the spectrum was obtained by deuteration of the 2, 4, and OCH_3 positions. The synthetic goals for the study therefore were **1**–**4**. In addition, we prepared and examined the analogous systems without the methoxy group (**5**–**8**) for purposes of comparison.



	X
1	CH_3
2	Br
3	Cl
4	CN



	X
5	CH_3
6	Br
7	Cl
8	CN

Results

In order to have a better understanding of the ring reversal process as a function of exo substitution, we prepared the ring-unsubstituted series **5**–**8** by the procedures given in Scheme I.[5] These preparations also provided practice for the more important 3-methoxy series, **1**–**4**. Bernard and St. Jacques[6] studied ring reversal in the undeuterated versions of **5** and **7**. We wanted to supplement the series with **6** and **8** and to obtain more accurate ring reversal barriers through deuteration at the 3- and 5-positions. This pattern of deuteration provides clear and simple $A_2 \rightarrow AB$ spectra for the 2,6 and the 4 protons. In order to introduce the deuterium atoms, we cyclized 1,5-dibromopentane-*2,2,4,4-d_4*[7] by treatment with methyl methylthiomethyl sulfoxide followed by hydrolysis.[8] Reaction of the resulting ketone with CBr_4 and triphenylphosphine in dry benzene gave the dibromide **6**,[9] which was converted to the isopropylidene **5** on treatment with dimethylcopperlithium. Reaction of the ketone with the anion of diethyl 1-chloromethanephosphonate in the presence of CCl_4 led to the dichloride **7**.[10] The Knoevenagel reaction of the ketone with malonitrile gave the dinitrile **8**.[11]

Ring reversal studies of **5**–**8** were carried out in CF_2Cl_2 at 90 MHz. The two-peak room-temperature spectrum for each compound evolved into a pair of overlapping AB quartets below the coalescence temperature T_c. The dinitrile **8** precipitated from solution close to the coalescence temperature, so that the slow exchange $\Delta\nu$ could not be obtained for this compound. For the remaining three compounds, $\Delta G^{\ddagger}$ could be calculated from J, $\Delta\nu$, and T_c by the usual equations (Table I). Bernard and St. Jacques[6] found a linear relationship between the barrier to methyl rotation for substituted *cis*-propenes and $\Delta G^{\ddagger}$ for ring reversal in exo-substituted methylenecyclohexanes. Our data for the three points for CH_3, Br, and Cl, together with the literature value for the parent methylenecyclohexane,[12] also gave a linear plot.[13] Use of this correlation provides an approximation to the ring reversal barrier for the dinitrile **8**, which is given in Table I.

In order to provide deuteration at the 2 and 4 positions of **1**–**4**, we prepared 2-cyclohexen-1-one by modifications of earlier procedures.[2] Addition of CD_3OD under acidic (D^+) conditions yielded 3-methoxy-d_3-cyclohexanone-*2,2,4,4-d_4*, which was converted to the deuterated 3-methoxy-1-methylenecyclohexanes **1**–**4** by the same procedures as described above for **5**–**8**.

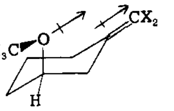
Proton spectra of **1**–**4** were taken in $CHFCl_2$ at 90 MHz and in CF_2Cl_2 at 270 MHz.[13] Again the dinitrile (**4**) came out of solution in the vicinity of the coalescence temperature. Equilibrium constants for **1**–**3** were obtained by direct integration at the low-temperature extreme. The free energies of activation were obtained from coalescence methods. These data are given in Table II.

Discussion

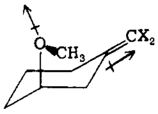
Questions concerning the overall conformation of the ring and of the axial/equatorial chemical shift difference have been examined previously and will not be discussed again here.[2,12] The ring assumes a slightly flattened chair shape, and the axial resonance is always at higher field than the equatorial resonance.

In order to assess the importance of electrostatic interactions, it is necessary to assign directions to the dipoles within the *exo*-methylenecyclohexane system. The dipole of the $C{=}CX_2$ group naturally lies close to the axis of the double bond, bisecting the CX_2 bond angle. For $C{=}CH_2$, the negative end of the dipole should point toward the CH_2, analogous to the dipole of isobutylene. (We follow the organic chemistry convention that the dipole points from the positive to the negative pole.) For $C{=}C(CH_3)_2$, there should be little or no dipole, since the methyl groups nearly symmetrize the double bond (compare isobutylene, μ = 0.50 D, with tetramethylethylene, μ = 0.0 D). Finally for $C{=}CCl_2$ and $C{=}CBr_2$, the dipole should point toward the halogens. The early work of Rogers[14] clearly showed that the dipole of the $C{=}CX_2$ is dominated by inductive rather than resonance effects.[5]

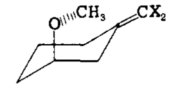
The dipole of the 3-methoxy group also requires examination, since the group can exist as three rotamers for each ring form. In our analysis, we assume that the group dipole approximately bisects the CH_3–O–CH bond. If X in CX_2 is not electron donating, then the dipole of the double bond points toward CX_2. The rotamers for the axial form are then given by structures **9**. Of



9a



9b



9c

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[5] Scheme I, discussion of the relative contributions of induction and resonance to the $C{=}CX_2$ dipole, discussion of the dipole–quadrupole interaction, Table III, and further experimental details are found in the archival version of this paper.

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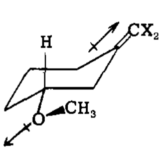
Table II. Spectral, Kinetic, and Equilibrium Parameters for Exo-Disubstituted 3-Methoxy-1-methylenecyclohexanes

solvent	compd	subst	T_c, K	$\Delta G_c^{\ddagger}$,[a] kcal/mol	$\Delta\nu$,[b] ppm	T,[c] K	K[d]	$-\Delta G°$,[e] kcal/mol
CF_2Cl_2[f]	1	CH_3	150	6.8	0.68	120	2.2 ± 0.1	0.19 ± 0.01
	2	Br			0.54	120	1.05 ± 0.05	0.01 ± 0.01
	3	Cl			0.56	120	1.35 ± 0.1	0.07 ± 0.01
		H[g,h]	173	8.3[i]	0.52	158	14.2 ± 0.9	0.80 ± 0.02
$CHFCl_2$[g]	1	CH_3	120	5.65	0.64	107	1.50 ± 0.1	0.08 ± 0.01
	2	Br	101	4.75	0.53	96	1.25 ± 0.1	0.04 ± 0.005
	3	Cl	115	5.4	0.57	105	1.50 ± 0.1	0.08 ± 0.01
		H[h]	181	8.7[i]	0.58	153	1.45 ± 0.05	0.11 ± 0.01

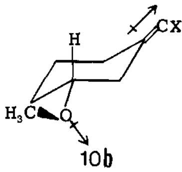
[a] Calculated from $k_c = \pi\Delta\nu/(2)^{1/2}$ and $\Delta G^{\ddagger} = RT_c(23.76 + \ln(T_c/k_c))$. [b] Axial/equatorial separation. [c] Temperature of equilibrium constant K. [d] Equatorial/axial. [e] $\Delta G° = -RT \ln K$. [f] Except as noted, data from 270 MHz. [g] Data from 90 MHz. [h] Reference 2. [i] The values of $\Delta G^{\ddagger}$ in Table III of ref 2 were miscalculated from the correct values of k_c given in the same table; the correct values are about 2 kcal/mol lower, as seen by the figures given here.

these, **9c** must contribute very little, since the interaction with the ring is analogous to the interaction of an axial methyl with two other axial carbons. Thus the molecule exists as a mixture of **9a** and **9b**. The interdipole angle for **9b** is close to 90°, so that this conformer contributes minimally to any electrostatic interactions. The interaction in **9a** is repulsive for X = H. Since **9a** contributes the only significant interaction between the dipoles, we can conclude that the axial conformer is destabilized by a repulsive dipole–dipole interaction.[15]

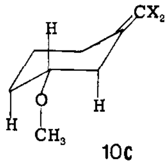
Structures **10** illustrate the analogous rotamers for the equatorial form.



10a



10b



10c

Again, form **10c** can be disregarded, and **10b**, in which the angle is about 90°, should exhibit little dipole–dipole interaction. Although dipolar interactions in **10a** are attractive, the distance between the dipoles is relatively long. We conclude that the interaction in the equatorial conformer is weakly attractive. Consequently, as we concluded before,[2] the dipole–dipole interaction for $C{=}CH_2$ should destabilize the axial form and stabilize the equatorial form. Earlier calculations showed that the interaction is feasible in magnitude.[2,15]

Replacement of the double-bond hydrogens with methyl ($C{=}CH_2 \rightarrow C{=}C(CH_3)_2$) should reduce the alkene bond moment to close to zero and nullify the repulsive dipole–dipole interaction between the axial 3-methoxy substituent and the double bond in **9a**. The conformational result would be an increase in the proportion of axial methoxyl for $C{=}C(CH_3)_2$, compared to $C{=}CH_2$. Reference to Table II shows that indeed the equatorial preference is lowered from 0.80 kcal/mol for $C{=}CH_2$ to 0.19 for $C{=}C(CH_3)_2$ in the noninteracting solvent CF_2Cl_2. These results are consistent with a dipole–dipole interaction in the parent compound ($C{=}CH_2$) that is nearly nullified in the methyl-substituted compound. Direct comparison of the isopropylidene case with monosubstituted cyclohexyl indicates that replacement of CH_2 in cyclohexyl by $C{=}C(CH_3)_2$ eliminates one repulsive syn-axial interaction but, unlike $C{=}CH_2$, does not introduce an even stronger repulsive polar effect. For the polar solvent $CHFCl_2$, there is a further, small reduction in $\Delta G°$ to 0.08, as a result of a residual polar interaction, inaccuracy in the measurements, or a solvent effect that has no relation to the exo-methylene group (*A* values exhibit small solvent effects of this magnitude).

The presence of halogen on the double bond considerably increases the bond dipole in the direction of the halogens[5] and consequently should increase the repulsive interaction between the 3-axial substituent and the exocyclic double bond. Examination of Table II shows that the reverse takes place. Introduction of chlorine or bromine on the double bond reduces the axial/equatorial free energy from 0.80 to 0.07 or 0.01 kcal/mol, respectively, in the noninteracting solvent CF_2Cl_2. Since the free energy difference for methoxycyclohexane is 0.55 kcal/mol, the replacement of CH_2 in a monosubstituted cyclohexane by $C{=}CCl_2$ or $C{=}CBr_2$ increases the axial proportion.

If the electrostatic explanation is operative for the halogen systems, there must be a change in the sign of the interaction. This is possible if the angle between either dipole and the interdipole vector decreases below the magic angle (54.7°), as might happen if the halogens push the center of the $C{=}CX_2$ dipole much further from the ring. Because this center cannot be accurately defined, this possibility cannot be tested. On the other hand, the electrostatic mechanism could be operative for $C{=}CH_2$ but an alternative mechanism for the halogenated cases.

Whereas there is a dearth of mechanisms that provide the required repulsive interaction (favoring the equatorial form) between axial methoxyl and $C{=}CH_2$ (electrostatics being one such), there are several electronic mechanisms that provide the reverse. Through-bond interactions,[17] for example, should favor the axial form. The arrangement between the axial substituent and the exocyclic double bond is very similar to a gauche conformation, which is favored by highly polar substituents. Through-space electronic interactions, such as the $n \rightarrow \pi^*$ transition that has frequently been invoked to explain transannular interactions between amine and carbonyl functionalities,[18] should occur preferentially in the axial form.

The through-space interaction depends on the ability of the 3-axial oxygen lone pair to donate electrons to the lowest unoccupied molecular orbital (LUMO) of the double bond. Electron withdrawal commonly lowers the energy of the LUMO, making it more able to interact with the nonbonding electrons on oxygen. Thus the LUMO of benzene (1.15 eV) is lowered on halogen substitution (Cl, 0.75; Br, 0.70 eV).[19] Similarly, electron donation raises the LUMO energy, cf., ethylene (1.78 eV), *cis*-butene (2.22), and tetramethylethylene (2.27).[19]

One possible explanation that satisfies all the experimental observations, then, invokes both electrostatic and orbital interactions. In the unsubstituted case ($C{=}CH_2$), the double bond LUMO is too high for the axial-favoring orbital interaction to be important. Consequently, the electrostatic repulsion between the axial 3-methoxy group and the exocyclic double bond ($C{=}CH_2$) brings about a greater equatorial preference than that

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(15) Rigorous dipole and quadrupole[16] calculations on **9** and **10** are subject to serious limitations. The center of the C—O dipole, the center of the $C{=}CX_2$ dipole, and the role of oxygen and halogen lone pairs are not easily specified, as would be necessary in a quantitative calculation. These considerations make it almost impossible to specify the angle between the dipoles and the interdipole vector. The oxygen lone pairs could not be disregarded under any circumstances. Experimental measurement for dipole moments would not be useful, because it is not possible to obtain the moments of both conformational components (**9**, **10**) in a mobile equilibrium without the use of anchors. Consequently, we have decided that the qualitative electrostatic approach is least subject to criticism.

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observed in the monosubstituted cyclohexane.[2] Introduction of the methyl group on the double bond ($C{=}C(CH_3)_2$) raises the LUMO even further but reduces or eliminates the electrostatic interaction, so that the presence of only one axial hydrogen opposing the axial methoxyl results in a larger proportion of the axial conformer. Because of the higher LUMO, the orbital interaction is even less important than in the $C{=}CH_2$ case. On the other hand, halogen substitution ($C{=}CCl_2$, $C{=}CBr_2$) reduces the energy of the LUMO sufficiently that electron donation can take place between the 3-axial substituent and the $C{=}CX_2$ bond, thereby bringing about a net stabilization and increased population of the axial conformer. Although we cannot distinguish between the electrostatic and orbital mechanisms for $C{=}CX_2$ (X = Cl, Br), the interaction in either case is opposite to that of $C{=}CH_2$. Solvent effects in the halogenated cases are small but consistent with an attractive interaction. Thus the change in ΔG° from CF_2Cl_2 to $CHFCl_2$ is −0.2 kcal/mol for Cl and −0.03 for Br; i.e., the more polar solvents decrease the axial proportion. Little can be made of these small differences, except that the solvent effect appears to be opposite to that observed for the $C{=}CH_2$ systems.

Summary and Conclusions

Examinations of exo-substituted 3-methoxy-1-methylenecyclohexanes provides a reasonable definition of the mechanism of the interaction between a polar substituent at the 3-axial position and the exo double bond. In the exo-unsubstituted case ($C{=}CH_2$), the interaction is repulsive and the proportion of axial conformer is reduced (ΔG° = 0.80 kcal/mol in CF_2Cl_2, compared to 0.55 for methoxycyclohexane).[2,20] That this interaction is primarily electrostatic can be demonstrated by substitution for the exo hydrogens, which alters the polarity of the double bond. Symmetrization through methyl substitution ($C{=}C(CH_3)_2$) reduces or nullifies the dipole of the double bond. As a result, the equatorial preference for the 3-methoxy group is greatly reduced, from 0.80 to 0.19 kcal/mol in CF_2Cl_2. Since the *A* value for methoxyl is 0.55 kcal/mol, the replacement of CH_2 in cyclohexane by $C{=}C(CH_3)_2$ brings about a net increase in the population of the 3-axial conformer. That the electrostatic interaction has been greatly reduced in the $C{=}C(CH_3)_2$ system is further demonstrated by the small change in conformational preference between CF_2Cl_2 and $CHFCl_2$ (from 0.19 to 0.08 kcal/mol). We had previously observed that the solvent effect was quite large for $C{=}CH_2$ (0.80 in CF_2Cl_2 to 0.11 in $CHFCl_2$), which was consistent with a reduction in the electrostatic repulsion through solvation in the polar, hydrogen-bonding solvent $CHFCl_2$.

These observations support the existence of a strong dipole–dipole interaction between the axial 3-methoxy substituent and the exo-methylene ($C{=}CH_2$) group. This repulsion is reduced by use of highly polar solvents or by replacement of $C{=}CH_2$ by $C{=}C(CH_3)_2$. The dipole–quadrupole interaction provides a less satisfactory explanation.[5] Whereas methyl substitution on the exo double bond reduces the dipole, it increases the quadrupole.[16] Had the dipole–quadrupole interaction been dominant, we would have expected a decreased proportion of the axial conformer.

In the exo-halogenated cases ($C{=}CCl_2$, $C{=}CBr_2$), the interaction appears to be attractive and the proportion of axial conformer is increased. The dipole–dipole mechanism can accommodate this result only if there is a major change in intervector angles (**9a**) caused by displacement of the center of negative charge in the $C{=}CX_2$ bond. Alternatively, the electron-withdrawing groups on the double bond may elicit a different mechanism such as an attractive n–π* orbital interaction analogous to transannular interactions observed in cyclic amino ketones.

Experimental Section

Infrared spectra were measured on Beckman IR-10 and Perkin-Elmer 283 spectrometers. Routine ^{1}H nuclear magnetic resonance (NMR) spectra were recorded on Varian Associates T-60 and Hitachi Perkin-Elmer R-20B 60-MHz spectrometers. The low-temperature NMR spectra were measured on Bruker HFX-90 (90-MHz) and Bruker HX-270 (270-MHz) spectrometers.[21] Carbon-13 spectra were recorded on a Varian CFT-20 spectrometer. The ^{13}C shifts are collected in Table III.[5] Mass spectra were obtained on Consolidated Electrodynamics Corp. 21-104 and Hewlett-Packard 583A mass spectrometers. Analytical and preparative vapor-phase chromatography was performed on a Hewlett-Packard Model 700 laboratory chromatograph. Elemental analyses were performed by Micro-Tech Laboratories, Inc., Skokie, Il.

1,5-Dibromopentane-*2,2,4,4-d*$_4$ was prepared by our earlier pathway.[7]

Cyclohexanone-*3,3,5,5-d*$_4$ was prepared according to the procedure of Ogura and co-workers.[5,8]

(Dibromomethylene)cyclohexane-*3,3,5,5-d*$_4$ (6). A mixture of 1.00 g (9.8 mmol) of cyclohexanone-*3,3,5,5-d*$_4$, 12.0 g (48.4 mmol, Aldrich) of triphenylphosphine, and 7.7 g (23.25 mmol, Aldrich) of CBr_4 in 150 mL of dry benzene was stirred at reflux under N_2 for 15 h.[9] The mixture was cooled to room temperature, the solid material was removed by filtration, and the filtrate was concentrated in vacuo. The greenish liquid residue was chromatographed on 30 g of alumina, eluted with hexane/ether. The liquid product was further purified by distillation to yield 1.8 g (78%) of the desired compound at 80 °C (1 mm): NMR (CCl_4) δ 1.55 (s, 2, γ-CH_2), 2.45 (s, 4, α-CH_2); IR (film) 1625 ($C{=}C$) cm^{-1}; mass spectrum (70 eV), *m/e* 258 (M^+), 256 ($M^+ - 2$), 260 ($M^+ + 2$). Anal. (undeuterated) Calcd for $C_7H_{10}Br_2$: C, 33.10; H, 3.99; Br, 62.92. Found: C, 33.22; H, 3.91; Br, 63.13.

(Dichloromethylene)cyclohexane-*3,3,5,5-d*$_4$ (7). Anhydrous LiCl (0.8 g, 19.6 mmol) was dissolved in 40 mL of dry THF under a N_2 atmosphere. Butyllithium (4.7 mL, 9.8 mmol) was added to the mixture at 0 °C. The reaction flask was cooled to −78 °C (dry ice/acetone bath), and 1.83 g (9.8 mmol) of diethyl chloromethanephosphonate in 10 mL of THF was added.[10] After 10 min of constant stirring, CCl_4 (1.5 g, 9.8 mmol) in 5 mL of THF was added, followed by 1.0 g (9.8 mmol) of cyclohexanone-*3,3,5,5-d*$_4$ in 5 mL of THF. The mixture was further stirred at −78 °C for 2 h and then slowly brought to room temperature. It was hydrolyzed by addition of 40 mL of H_2O. The two layers were separated, and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed. The remaining liquid was sent through an alumina column eluted with hexane. The collected crude product was distilled to give 1.2 g (78%) of the desired colorless compound at 40–44 °C (2.5 mm) (lit.[17] 70 °C (8.0 mm)). The sample was further purified by preparative gas chromatography on a 6 ft by $^1/_4$ in. column packed with 10% Carbowax 20 M on chromosorb W 60/80: NMR (CCl_4) δ 1.6 (s, 2, γ-CH_2), 2.4 (s, 4, α-CH_2); IR (film) 1630 ($C{=}C$) cm^{-1}; mass spectrum (70 eV), *m/e* 169 (M^+). Anal. (undeuterated) Calcd for $C_7H_{10}Cl_2$: C, 50.95; H, 6.10; Cl, 42.90. Found: C, 51.83; H, 6.40; Cl, 41.90.

Isopropylidenecyclohexane-*3,3,5,5-d*$_4$ (5). According to the procedure by Posner,[9] an ethereal solution of dimethylcopperlithium was prepared at 0 °C under N_2 from 12.6 g (67.1 mmol) of cuprous iodide and 60 mL (124 mmol, 2.06 M solution in ether) of methyllithium in 100 mL of ethyl ether. To this solution was added 1.8 g (6.98 mmol) of (dibromomethylene)cyclohexane-*3,3,5,5-d*$_4$ (**6**) in 5 mL of ether. The reaction mixture was then brought slowly to room temperature and stirred for 15 h. Methyl iodide (5 mL) was added, and the reaction mixture was stirred for 1 h. The mixture was then poured into 200 mL of saturated aqueous NH_4Cl. The solid material was removed by filtration, and the aqueous layer was extracted with ethyl ether (4 × 50 mL). The combined ether layers were washed with brine, dried ($MgSO_4$), filtered, and concentrated. Distillation gave 0.7 g (76%) of the desired product: bp 40 °C (1 mm). Further purification by vapor-phase chromatography (see compound **7**) gave the final product: NMR ($CDCl_3$) δ 1.5 (s, 2, γ-CH_2), 1.65 (s, 6, CH_3), 2.10 (s, 4, α-CH_2); IR (film) 1650 ($C{=}C$) cm^{-1}; mass spectrum (70 eV), *m/e* 128 (M^+). Anal. (undeuterated) Calcd for C_9H_{16}: C, 87.00; H, 12.98. Found: C, 86.68; H, 13.23.

(Dicyanomethylene)cyclohexane-*3,3,5,5-d*$_4$ (8) was prepared from 0.45 g (4.4 mmol) of cyclohexanone-*3,3,5,5-d*$_4$ and 0.30 g (4.4 mmol) of malonitrile:[5] bp 128 °C (2.5 mm) (lit.[10] 85–90 °C (1.0 mm)); NMR (CCl_4) δ 1.70 (s, 2, γ-CH_2), 2.65 (s, 4, α-CH_2); IR (film) 2960 (CH), 2210 ($C{\equiv}N$), 2140 (CD), 1640 ($C{=}C$) cm^{-1}.

3-Methoxy-*d*$_3$-cyclohexan-1-one-*2,2,4,4-d*$_4$ was prepared by modifications of our earlier procedure:[2,13] bp 70–74 °C (3 mm); NMR ($CDCl_3$) δ 1.7–2.7 (m, 4, CH_2), 3.6–3.8 (br s, 1, CH); IR (film) 2060, 1700 ($C{=}O$), 1125 (CO) cm^{-1}.

3-Methoxy-*d*$_3$-1-(dibromomethylene)cyclohexane-*2,2,4,4-d*$_4$ (2) was prepared from 3-methoxy-*d*$_3$-cyclohexan-1-one-*2,2,4,4-d*$_4$ (0.9 g, 7.4 mmol), CBr_4 (5.8 g, 17.5 mmol), and triphenylphosphine (9.2 g, 35 mmol) according to the above procedure for the compound lacking me-

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thoxyl (**6**). The yield was 0.8 g (40%): bp 115–117 °C (1.2 mm); NMR ($CDCl_3$) δ 1.0–2.05 (m, 4, CH_2), 3.25 (br s, 1, CH); IR (film) 2970 (CH), 2200, 2060 (CD), 1650 (C=C) cm^{-1}; mass spectrum (70 eV), *m/e* 290 (M^+), 288 ($M^+ - 2$), 292 ($M^+ - 2$). Anal. (undeuterated) Calcd for $C_8H_{12}OBr_2$: C, 33.83; H, 4.25. Found: C, 34.26; H, 4.18.

3-Methoxy-*d*$_3$-1-(dichloromethylene)cyclohexane-*2,2,4,4-d*$_4$ (3). To 0.4 g (10.4 mmol) of LiCl in 40 mL of dry THF at −78 °C was added 2.5 mL (5.2 mmol) of butyllithium under N_2. After 8 min of stirring, diethyl chloromethanephosphate (0.97 g, 5.2 mmol) was added, followed by 0.8 g (5.2 mmol) of CCl_4 and 0.7 g of 3-methoxy-d_3-cyclohexan-1-one-*2,2,4,4-d*$_4$ (5.2 mmol). The product was isolated as described for the compound lacking methoxyl (**7**). The crude yield was 2.6 g (50%). The pure compound was isolated by vapor-phase chromatography on a 5 ft × $^1/_4$ in. column, 20% Carbowax 20-M Chromosorb P 60/80: NMR (CCl_4) δ 0.7–2.8 (m, 4, CH_2), 3.2 (br s, 1, CH); IR (film) 2940 (CH), 2200, 2060 (CD), 1630 (C=C) cm^{-1}; mass spectrum (70 eV), *m/e* 201 (M^+), 167 ($M^+ - 34$). Anal. (undeuterated) Calcd for $C_8H_{12}OCl_2$: C, 49.25; H, 6.20. Found: C, 49.55; H, 6.26.

3-Methoxy-*d*$_3$-1-(isopropylidene)cyclohexane-*2,2,4,4-d*$_4$ (1). An ethereal solution of dimethylcopperlithium was prepared from 8.55 g (45 mmol) of cuprous iodide, 49 mL (83.25 mmol, 1.7 M solution in ethyl ether) of methyllithium, and 1.3 g (4.72 mmol) of 3-methoxy-d_3-1-(dibromomethylene)cyclohexane-*2,2,4,4-d*$_4$ as described for the compound lacking methoxyl (**5**).[5] The crude yield was 0.7 g (93%). The compound was purified by vapor-phase chromatography (see compound **3**): NMR (CCl_4) δ 1.1–2.3 (m, 4, CH_2), 1.67 (s, 6, CH_3), 3.1 (br s, 1, CH). Anal. (undeuterated) Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 76.63; H, 11.64.

3-Methoxy-*d*$_3$-1-(dicyanomethylene)cyclohexane-*2,2,4,4-d*$_4$ (4) was prepared from 0.35 g (2.55 mmol) of 3-methoxy-d_3-cyclohexan-1-one-*2,2,4,4-d*$_4$ and malononitrile (0.17 g, 2.55 mmol):[5] 0.3 g (64%); bp 139–140 °C (0.7 mm); NMR (CCl_4) δ 1.6–2.0 (m, 2, CH_2), 3.4 (br s, 1, CH); IR (film) 2940, 2890 (CH), 2240 (C≡N), 2200, 2060 (CD), 1670 (C=C) cm^{-1}; mass spectrum (10 eV), *m/e* 183 (M^+).

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Supplementary Material Available: The archival version of this paper includes Scheme I, discussions of the relative contributions of induction and resonance to the C=CX_2 dipole and dipole–quadrupole interactions, Table III, and further experimental details (13 pages). Ordering information is given on any current masthead page.

Stereochemistry and Mechanisms of Reactions of Dioxygen Complexes with Organic Electrophiles as Studied by Use of Chiral Reagents and Isotopic Labeling

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Abstract: From reactions of PtO_2L_2 (L = PPh_3, $P(c\text{-}C_6H_{11})_3$) with 1 mol of triphenylmethyl bromide or benzoyl bromide the corresponding (alkylperoxo)platinum(II) complexes $L_2PtBr(OOR)$ (**1a**, L = PPh_3, R = CPh_3; **1b**, L = $P(c\text{-}C_6H_{11})_3$, R = CPh_3; **2**, L = PPh_3, R = COPh) were isolated, which were well characterized by elemental analysis and IR spectroscopy. The complex **1a,b** or **2** was treated with another mole of organic halides to give the corresponding dialkyl peroxides ($Ph_3COOCPh_3$, PhC(O)OOC(O)Ph) in good yields. Thus, the stepwise mechanism proposed previously for "metal-assisted peroxidations" was verified. A similar reaction of $PtO_2(PPh_3)_2$ with an optically active (*S*)-(−)-α-phenethyl bromide produced a peroxoplatinum(II) complex, $PtBr(OOCH(CH_3)Ph)(PPh_3)_2$ (**3**), which gave upon acidolysis (*R*)-(+)-α-phenethyl hydroperoxide. Reductive cleavage of **3** with $NaBH_4$ gave (*R*)-(+)-α-phenethyl alcohol. Hence, it can be concluded that the reaction of PtO_2L_2 with organic halides proceeds via the S_N2-type transition state. From the IR ^{18}O isotopic shifts the O–O stretching band was assigned for the products from the reactions of PtO_2L_2 with acetone (**4**), benzophenone (**5**), 1,1-dicyano-2-methylpropene (**8**), and tetracyanoethylene (**9**). The ^{18}O IR study also shows that the peroxy bond involved in these products is derived from PtO_2L_2. The reaction product $\overline{\mathrm{PtO(CH_3OOC)C{=}CO}}\mathrm{(COOCH_3)L_2}$ (**10a**, L = PPh_3; **10b**, L = $P(c\text{-}C_6H_{11})_3$) obtained from PtO_2L_2 and $CH_3OOCC{\equiv}CCOOCH_3$ was also studied by ^{18}O isotopic IR and ^{13}C NMR spectra. Acidolysis of **10b** gave dimethyl dihydroxymaleate in a good yield. Thus it was established that the reaction of an electrophilic acetylene with PtO_2L_2 results in the O–O bond cleavage.

Reactivities of the η^2-dioxygen ligand of low-valent later transition-metal complexes have received considerable investigations.[1] The nature of the $M(\eta^2\text{-}O_2)$ bonding was a subject of several theoretical studies.[2] These studies on $M(\eta^2\text{-}O_2)L_2$ (M = Ni, Pd, Pt) indicate that a considerable charge is transferred to the O_2 ligand. This is reflected in the facile reactions of $M(\eta^2\text{-}O_2)L_2$ (M = Ni, Pd; L = *t*-BuNC) with various electrophiles as we reported previously.[3] One of the nucleophilic reactions of $M(\eta^2\text{-}O_2)L_2$ is the "metal-assisted peroxidation" reaction[3] (eq 1).

$$2RX + Ni(O_2)(t\text{-}BuNC)_2 \rightarrow NiX_2(t\text{-}BuNC)_2 + ROOR \qquad (1)$$

A closely related reaction is the formation of hydrogen peroxide from acidolysis of $M(\eta^2\text{-}O_2)L_2$ (e.g., M = Ni, Pt; L = PPh_3).[4-6] The mechanisms of these peroxidation reactions still remain to be elucidated.

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