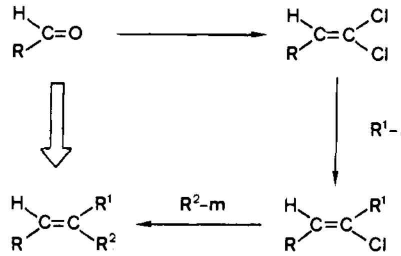
Scheme I



organozinc reagents to give the corresponding substituted (*Z*)-chloroethenes in high yields, showing the wide applicability of the reaction (entries 2–4 and 6–10). Significantly, trichloroethene underwent selective monoarylation similarly at the expected position[8] to give 1-substituted (*Z*)-1,2-dichloroethenes[9] in moderate to excellent yields (entries 11–13).

The following two points deserve comment. (1) The presence of the substituent R in dichloro olefin skeletons was essential for the regio- and stereoselective monocoupling, since parent 1,1-dichloroethene itself produced a comparable amount (ca. 25% yield) of diarylation product and no reaction took place with 1,1-dichloro-2,2-diphenylethene. The significant effect exerted by the vicinal-cis substituent R may be steric, since the electronically different groups, such as alkyl, aryl, heteroaryl, and chlorine, are equally effective. Thus, the chlorine atom cis to hydrogen is preferentially replaced to produce monocoupling product stereoselectively and further reaction is retarded owing to the steric effect of vicinal-cis substituent. (2) A further important point is that the present success depended upon choice of [$PdCl_2$(dppb)] as a catalyst,[10] because the use of the conventional [$PdCl_2(PPh_3)_2$] catalyst resulted mainly in the formation of diarylation products,[11] even when 1 equiv of Grignard reagent was used. The amazing ligand effect strongly suggested that the latter complex would be effective for further coupling reactions.

The subsequent reaction of thus obtained monohalo olefins with Grignard reagents in the presence of [$PdCl_2(PPh_3)_2$] as a catalyst indeed gave trisubstituted olefins stereoselectively (entries 1, 3, 7, and 8). The preparation of opposite stereoisomers **4** and **5** was readily attained from the same starting dihalide **3** by merely changing the order of the treatment of two Grignard reagents (entries 7 and 8). Since 1,1-dichloro-1-alkenes are readily obtainable from aldehydes by dichloromethylenation,[12] the present method has opened a new, general transformation of aldehydes to unsymmetrically trisubstituted olefins in a stereoselective manner (Scheme I), showing the synthetic superiority over the Wittig olefination reaction which has almost no ability toward such a transformation.[13,14]

Acknowledgment. We thank Professor Emeritus M. Kumada and Professor Y. Ito for valuable discussion and encouragement and S. Kawano for partial experimental assistance. This research was partially supported by Scientific Research Fund of Kyoto Pharmaceutical University (A.M.).

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(7) The Pd or Ni complex catalyzed cross-coupling reaction of orgnozinc reagents with organic halides was first reported by Negishi and co-workers.[2a]

(8) The present result is quite interesting, because it had been well documented that the oxidative addition of trichloroethene to [$M(PPh_3)_4$] (M = Pd or Ni) occurs at the monosubstituted position: Fitton, P.; McKeon, J. E. *J. Chem. Soc., Chem. Commun.* **1968**, 4. Johnson, F. G.; Lewis, J.; Jones, J. D.; Taylor, K. A. *J. Chem. Soc., Dalton Trans.* **1974**, 34. Carvajal, J.; Muller, G.; Sales, J.; Solans, X.; Miravitlles, C. *Organometallics* **1984**, *3*, 966. Coupling reactions of trichlorethene induced by the same complexes have also been known to occur at the monosubstituted position in contrast to the present results: Moritani, I.; Fujiwara, Y.; Danno, S. *J. Organomet. Chem.* **1971**, *27*, 279. Ratovelomanana, U.; Linstrumelle, G.; Normant, J. F. *Tetrahedron Lett.* **1985**, *26*, 2575.

(9) The structure of (*Z*)-1,2-dichloro-1-phenylethene was fully characterized by comparing retention times on GLC and spectral data with those of authentic samples of all three regio- and stereoisomers.

(10) Comparable results were obtained with [$PdCl_2$(dppf)], dppf = 1,1′-bis(diphenylphosphino)ferrocene, while [$PdCl_2$(dppp)] and [$PdCl_2$(dppe)], dppp = 1,3-bis(diphenylphosphino)propane and dppe = 1,2-bis(diphenylphosphino)ethane, showed less efficiency. For understanding of the relationship between structure and catalytic activity of bidentate phosphine–palladium complexes, see: Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.

(11) The reaction of **1** with the phenyl Grignard reagent (1 equiv) under ether reflux for 2 h in the presence of [$PdCl_2(PPh_3)_2$] (1 mol%) gave a mixture of triphenylethene (33%), diphenylchloroethene (3%), and recovered **1** (50%).

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Theoretical Study of Structures and Relative Energies of Isomeric Metalated Acetaldoximes, Models for Metalated Oxime Ethers

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Received September 15, 1986

The regioselective formation of a new carbon–carbon bond in the α-position to a carbonyl group is one of the fundamental reactions of modern synthetic organic chemistry.[2] Metalated enolate equivalents derived from N-derivatives of carbonyl compounds,[3] $R_1R_2C{=}NX$, such as imines,[4-6] hydrazones,[7-11] oximes,[11-17] and oxime ethers,[18-22] have been used for such regioselective reactions. A remarkable preference for the formation of the syn-configured[23] enolate intermediate is generally observed. The role of aggregated intermediates in these reactions is still not

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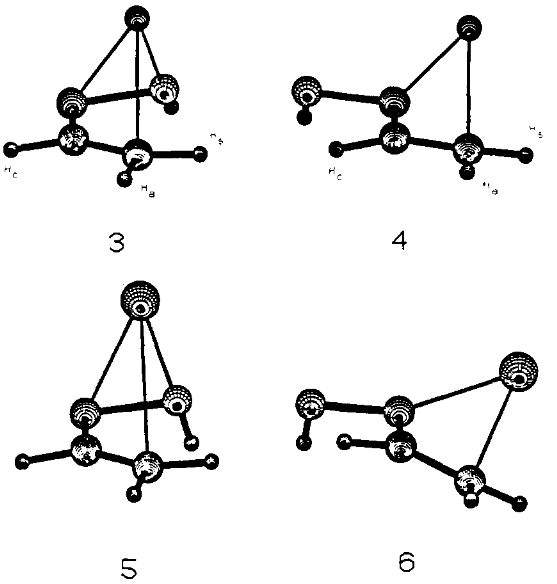
Table I. Bond Lengths (Å) Involving the Gegenion for Compounds **3**–**6**

molecule	M–C(C)	M–C(N)	M–N	M–O
3	2.502	2.254	1.979	1.781
4	2.270	2.198	1.871	2.544
5	3.051	2.634	2.238	2.018
6	2.591	2.544	2.029	3.419



3 4

5 6

Figure 1. Molecular models of the *ab initio* structures of the metalated oximes **3**–**6**.

settled;[10] most recent discussions have assigned a primary role to monomeric metalated species. We report ab initio structures[24] and syn-preference energies[25] (SPE) of the isomeric anions of acetaldoxime and their monomeric lithium and sodium derivatives as models of metalated oxime ethers. Several important conclusions have resulted. The importance of chelation of the gegenion by the hydroxy O in the syn isomers manifests itself in short cation–O distances. Short contacts between the gegenion and the N are found in both geometrical isomers, whereas the distances between the gegenion and the carbanionic carbon are surprisingly long. The metalated derivatives are best described as ion pairs. The SPE is greater for the ion pairs than for the free carbanions and greater for the sodium than for the lithium ion pairs; that is, the theoretical results suggest that increased regioselectivity may be achieved with larger cations.

Energies and structures of the syn and anti isomers respectively of the isolated (C_s) acetaldoxime anions **1** and **2**, their lithiated derivatives (C_1) **3** and **4**, and the sodium derivatives (C_1) **5** and **6** are given in the supplemental material. Table I summarizes the major structural parameters involving the cations. Molecular model type drawings of **3**–**6** are shown in Figure 1.

Li^+ assumes bridging positions that result in formal η^4- and η^3-coordination in **3** and **4**, respectively. A number of reasonable structures with lithium in the plane of the ligand were also studied. All were found to have one imaginary frequency; such structures are transition structures for interconversion of enantiomers corresponding to **3** and **4**. Structure **3** contains a characteristic triangular arrangement formed by Li^+ bridging the NO bond.

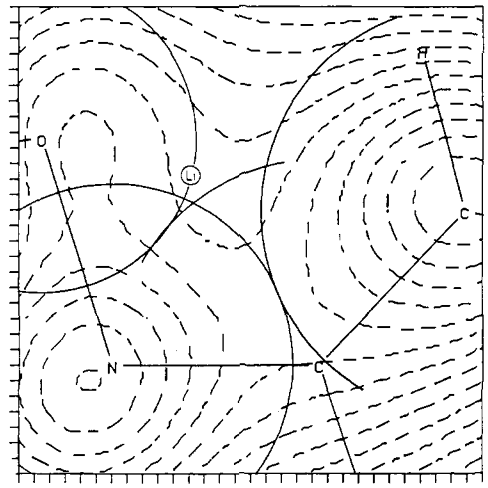


Fig Contour map of the electrostatic potential with polarization cor of the acetaldoxime anion **1**. Contour levels start at −0.34 au wit el spacing of 0.01. The electrostatic potential in the plane para and separated by 1.5 Å from the molecular plane is displayed. The ion marked by Li is that of the lithiated structure with the ligand xed as **1**.

The short distances between Li^+ and the heteroatom(s) indicate the dominant role of the heteroatom(s) in the determination of the position of the cation, whereas the LiC contact is less important. Although the LiC distance becomes significantly shortened in **4**, due to the lack of oxygen chelation, the Li^+ bridges in a highly unsymmetrical fashion. The tendency of the gegenion to assume a position close to the heteroatom(s) is enhanced for Na^+ compared to Li^+. In **5** the increase in bond lengths between the heteroatoms and sodium compared to lithium (Δ(M–O) = 0.24 Å, Δ(M–N) = 0.26 Å) is less than the difference in the ionic radii of the two alkali metals (0.35 Å), whereas the opposite is true for the carbon–metal bond (Δ(M–C) = 0.56 Å). Similarly, in **6** the sodium–nitrogen bond is only lengthened by 0.16 Å compared to **4**, whereas the carbon–metal bond is lengthened by twice that amount. Replacement of Li^+ by Na^+ does not give simple changes in bond distances. Sodium assumes an equilibrium position in **5** in which the ONNa and the ONC planes are almost perpendicular, resulting more in a η^2-coordination of the NO bond rather than a η^4-face-coordination.

The electrostatic potential of **1** and **2** is especially revealing. Figure 2 shows the electrostatic potential of **1** including polarization correction[26] for a plane parallel to the molecular plane of the ligand and at a z value approximately that of the lithium. The circles drawn correspond to the closest normal approach of lithium to the ligand atoms (O, 1.8 Å; N, 1.9 Å; C, 2.0 Å). The maximum electrostatic stabilization consistent with these distances is found at a point close to the actual position of lithium optimized for the fixed ligand **1** (marked Li in Figure 2). Similar agreement is found for the anti case (Figure 3, supplemental material). These close agreements provide compelling evidence for the essentially ionic nature of the bonds to lithium in compounds **3** and **4**.[27] Preliminary results show comparable agreement for sodium.

Further evidence for the dominance of ion pair interactions stems also from the relaxation pattern within the ligand. Upon ion pair formation, the atoms H_a and H_c (see Figure 1 for definition) are moved out of the NCC plane and toward the gegenion, whereas H_s is moved still farther away from the cation. This relaxation pattern is similar to that found in allyllithium.[29] The

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[24] Structure optimizations are with the 3-21+G basis set, resulting from augmenting the standard 3-21G basis set (Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939) with sets of single-diffuse functions (Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comp. Chem.* **1983**, *3*, 294) on all negatively charged atoms (C,N,O).

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orientation of the hydroxy group is especially instructive. In **3** and **5** this group is slightly bent away from the gegenion and the HO bond is directed in such a way as to allow for the best lone pair orientation. Cation-dependent differences are seen in **4** and **6**. In **4** the OH group is moved toward the Li^+, much like H_a, allowing for a maximum orientation of the pseudo-π-density toward the cation as well as an optimum cation-induced polarization of the O lone pairs. In **6**, however, the OH group is bent toward the opposite face of the ligand, away from Na^+. Due to the larger size of sodium it necessarily needs to assume a position in closer proximity to the N lone pair, as compared to **4**, and the orientation of this lone pair becomes dominant.

The 6-31+G*/3-21+G SPE is 2.6 kcal mol^{-1} for the isolated anions. Ion pair formation increases the SPE to 3.2 kcal mol^{-1} for Li^+ and 7.0 kcal mol^{-1} for Na^+. These results suggest that bases with larger cations may achieve increased regioselectivity.

Extensions of the present work to ketoximes and studies of solvation and aggregation effects at the ab initio level are in progress. Preliminary results for the ketoximes show no major differences from the aldoxime results presented here. Preliminary results for lithioacetaldoxime show that the incorporation of one molecule of water solvating lithium is not accompanied by large changes in structure and that significant conclusions will not be changed.

Acknowledgment. This research was supported in part by NIH Grant GM-30369.

Supplementary Material Available: Tables of bond lengths and angles and energies for **1–6** and contour map of the electrostatic potential of **2** (5 pages). Ordering information is given on any current masthead page.

Stereospecific Oxygenation of 3-Adamantylidenetricyclo[3.2.1.$0^{2,4}$]octane: Singlet Oxygen vs. Electron-Transfer Oxygenations[1]

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Much attention has been drawn to singlet oxygen ($^1O_2$) and electron-transfer oxygenations of electron-rich olefins.[2] Electron-transfer reactions (i.e., Foote-type[3–5] and Barton-type[6–9] oxygenations) giving products once thought to be characteristic of singlet oxygen[2,10,11] are topics of great current interest. We already reported that a stereochemical oxidation of di-*tert*-butylbi(bicyclo[3.3.1])non-9-ylidenes can act as a useful tool for distinction between $^1O_2$ and Barton-type oxygenations of hindered olefins,[12] Accordingly, a reliable molecule that may serve as a diagnostic test for distinguishing between $^1O_2$ and electron-transfer (both Foote-type and Barton-type) oxygenations is clearly desirable for mechanistic studies of oxygenation reactions. This report describes stereospecific oxygenation of 3-adamantylidenetricyclo[3.2.1.$0^{2,4}$]octane (**1**),[13] which constitutes a superior mechanistic probe for distinguishing between $^1O_2$ and electron-transfer oxygenations, and the results obtained from dye-sensitized photooxygenation of **1**.

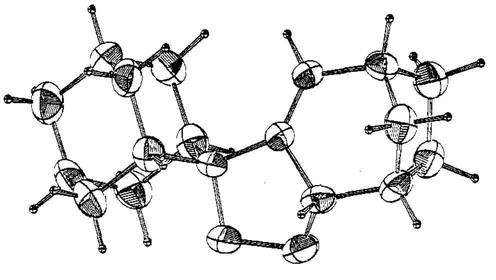


Figure 1. ORTEP drawing of **3a**.

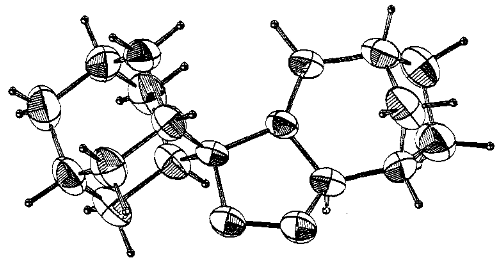
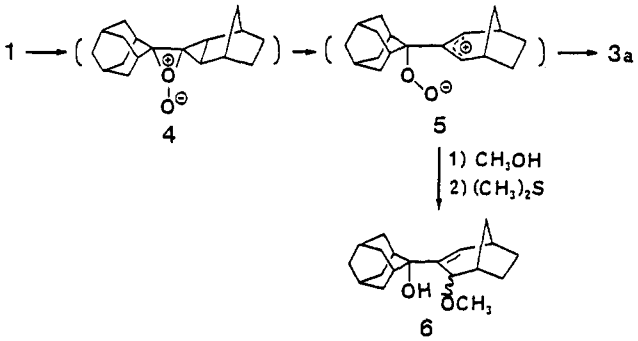


Figure 2. ORTEP drawing of **3b**.

Scheme I



Oxidation of **1**[14] with 1,4-dimethylnaphthalene endoperoxide[15]

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