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O$_2$ Insertion and Epoxidation

First Structurally Authenticated Zinc Alkylperoxide: A Model System for the Epoxidation of Enones**

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It is over 150 years since the high reactivity of zinc alkyl species towards oxygen was noted by Frankland in his pioneering studies on dialkyl zinc compounds, R_2Zn.[1] Since then the interaction of zinc alkyl complexes with O_2 has been of continuous interest from the fundamental and practical point of view as well as an ubiquitous side reaction in the preparation and handling of organozinc compounds.[2] In 1890 Demuth and Meyer[3] postulated for the first time the formation of the alkylperoxide [EtZnOOEt] as the result of the insertion of an O_2 molecule into the Zn–C bond. On the other hand, the most spectacular application of the reaction of zinc alkyl complexes with O_2 is the epoxidation of enones, where the alkylperoxide [ZnOOR] species is prepared in situ and acts as an efficient epoxidizing reagent.[4,5] Recently, there has also been an increased interest in various radical addition reactions initiated by the R_2Zn/O_2 system.[6] However, despite the long history of studies on the reaction of organozinc compounds with dioxygen, there have been no reports of the structurally authenticated zinc alkylperoxide; controlling and understanding the reactivity of zinc alkyl complexes with dioxygen is a demanding task. It should be also noted that the structural data for main-group metal alkylperoxides are very limited because of the high reactivity and often low stability of this group of compounds.[7]

Our recent studies have been directed towards designing main-group complexes as model species for investigations of the relationship between the molecular geometry and reactivity or other property of interest.[7a,b,8] Thus, investigations on the reactivity of aluminum alkyl species with molecular oxygen have shown that the key feature in the oxygenation reaction is the O_2 attack on the four-coordinate metal center, followed by an insertion of O_2 into the Al–C bond to generate an Al–OOR moiety.[7a,b] As an extension of these studies we turned our attention to the design of zinc alkyl complexes as model species with which a better understanding of dioxygen activation by organometallic compounds could be gained. The

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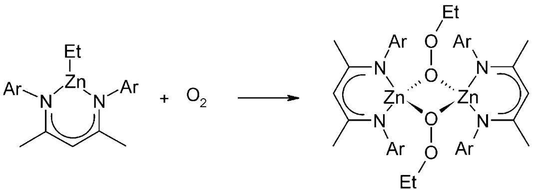
choice of ligand, 2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-diisopropylphenyl)imino]-pent-2-ene (BDI-H), was dictated by the recent successful use of such bulky β-diketiminates in the stabilization of unique main-group metal species[9] and of well-defined single-site catalysts.[10] We report herein the synthesis and structural characterization of the zinc alkylperoxide derived from the insertion of dioxygen into the Zn−Et bond, and the high reactivity of the resulting compound in the epoxidation of enones.

The reaction of $[Et_2Zn]$ with BDI-H leads to the well-defined three-coordinate complex [(BDI)ZnEt] (**1**).[10b,c] When the toluene solution of **1** was exposed to an excess of dry dioxygen at 0 °C for approximately 5 min. and then stored at −20 °C, a white crystalline precipitate of $[\{(BDI)ZnOOEt\}_2]$ (**2**) deposited in good yield [Eq. (1)].[11] The room temperature ^{1}H NMR spectrum of the final mixture reveals the presence of an ethyl group bound to oxygen and the lack of the Zn−Et group, which implies the complete oxygenation of the Zn−C bond [Eq. (1)]. The IR spectrum of **2** exhibits a moderate absorption at 854 cm^{-1} attributable to the characteristic peroxidic $\tilde{\nu}$(O−O) stretching vibration.



(1)

Ar = 2,6-diisopropylphenyl

The molecular structure of **2** was determined by a single-crystal X-ray diffraction (Figure 1).[12] Most notably, the structure reveals **2** to be a dinuclear aggregate with monomeric {(BDI)ZnOOEt} units joined by the μ_2-bridging ethylperoxide groups. The central $\{ZnN_2O_2\}$ core in **2** has a similar structure to that observed for recently characterized alkoxides $[\{(BDI)ZnOR\}_2]$ (where R = Me, *i*Pr).[10a,b,e] The molecule has crystallographic C_i symmetry and the geometry about the zinc centers is distorted tetrahedral. The six-membered ZnNCCCN ring adopts a sofa conformation, and the zinc atom is displaced 0.532(2) Å out of the almost flat ligand plane. The Zn–Zn separation is 3.179 Å and Zn1−O1 and Zn1−O1′ bonds (1.971(1) and 2.044(1) Å) all are slightly larger than those in the alkoxide compounds $[\{(BDI)ZnOR\}_2]$. This observation correlates well with both the relatively wide Zn1-O1-Zn1′ angle (104.69(6)°) and narrow O1-Zn1-O1′ angle (75.31(6)°) when compared to the related values in the alkoxide $\{Zn_2O_2\}$ cores.[10a,b,e] The peroxo O1−O2 bond of 1.451(2) Å is close to that found for alkylperoxides coordinated to main-group metal centers and transition-metals.[7,13] While the bridging oxygen atom in the alkoxides $[\{(BDI)ZnOR\}_2]$ is planar, the oxygen atom of the ethylperoxo group in **2** shows the expected pyramidal stereochemistry.[14] The ethylperoxo ligand is oriented in an eclipsed–staggered conformation, to minimize lone-pair repulsion on the oxygen atoms. It should be noted that the relative orientation of this ligand with respect to the central $\{Zn_2O_2\}$ ring (the torsion angles for COOZn1 and COOZn1′ are 167.3(1) and −57.3(2)°) is distinct from that observed for other compounds containing μ_2-bridging alkylperoxide groups, all of which are essentially perpendicular to the central core.[7d,f,14,15] However, a detailed inspection of the molecular structure of **2** indicates that a complex system of weak intramolecular hydrogen bonds plays a substantial role in the determination of the molecular shape (Figure 1). The analysis of intramolecular contacts shows a pair of C−H···π interactions between the C18 and C27′ methyl groups and the proximal aryl ring of adjacent ligand (the intermolecular H···(ring centroid) contacts are 2.85 and 2.96 Å) as well as the C−H···O interaction between the C27′ methyl groups and the ethylperoxide oxygen atom (C-H27A′···O2 2.67 Å).[16] The orientation of the *i*Pr groups in the 2,6-diisopropylphenyl substituents also indicates the presence of intramolecular C−H···N interactions between the *i*Pr group methine hydrogen atoms and the nitrogen atoms (2.41–2.50 Å). Therefore we presume that although the structure of the central core is dictated by the strong Zn−O bonds, the observed conformational preferences in **2** result from the cooperative non-covalent interactions.[17]

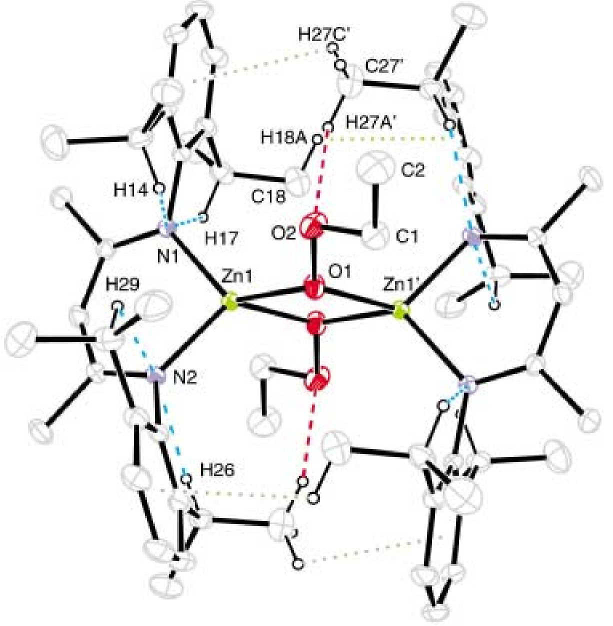
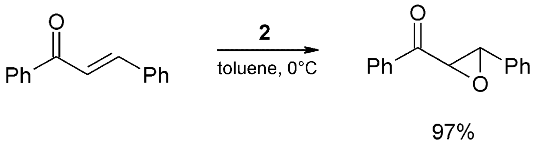


Figure 1. The molecular structure of **2**. Thermal ellipsoids are set at 40% probability, and only selected hydrogen atoms are shown for clarity.

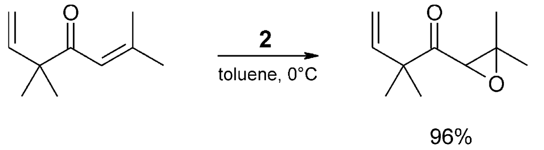
The epoxidation of electron-deficient olefins remains a challenging task in organic chemistry[5] and, as we mentioned above, zinc alkylperoxides are very promising reagents for this process. Thus, we assume that compound **2** may be a useful model compound for the epoxidation of enones. Indeed, the epoxidation of *trans*-chalcone revealed that **2** is a highly reactive oxidizing reagent, the reaction being complete in several minutes at 0 °C, to give the *trans*-epoxide in very good yield [Eq. (2)]. For comparison, epoxidation of chalcone with an Et_2Zn/O,N-H/O_2 system (where O,N-H =



(2)

aminoalcohol as the auxiliary ligand) was completed after 16 h under similar conditions.[4b]

Furthermore, despite the high reactivity of **2** towards enones, the regio- and chemoselective epoxidation of artemisia ketone is feasible as illustrated in Equation (3). Thus, **2** is highly selective for the electron-deficient alkene unit in the presence of β-functionalized unconjugated alkene. Based on these initial studies we anticipate that using **2** will allow the epoxidation of a wide range of enones.



(3)

Further studies on the interaction of zinc alkyl complexes with dioxygen and the reactivity of zinc alkylperoxides are in progress along with developing the epoxidation of enones.

Experimental Section

2: A stirred solution of [(BDI)ZnEt] (1.02 g, 2 mmol) in toluene (5 cm^3) was cooled to 0 °C, then an excess of dry dioxygen (1 atm) was introduced. After 5 min the excess of O_2 was removed (the reaction mixture was cooled to −78 °C, then the system was purged with nitrogen using a vacuum/nitrogen line). The mixture was stored at −20 °C and white crystalline product deposited; yield: 90 %. ^{1}H NMR (400 MHz, C_6D_6): $\delta = 1.02$ (t, $J = 6.8$ Hz, 6H, OCH_2CH_3) 1.15 (d, $J = 7.0$ Hz, 24H, $CH(CH_3)_2$), 1.20 (d, $J = 7.0$ Hz, 24H, $CH(CH_3)_2$), 1.66 (s, 12H, CCH_3), 3.31 (m, 8H, $CH(CH_3)_2$), 3.84 (q, $J = 6.8$ Hz, 4H, OCH_2CH_3), 4.88 (s, 2H, CH), 7.12 ppm (m, 16H, Ar); IR (Nujol): $\tilde{\nu} =$ 1547 (m), 1526 (s), 1462 (s), 1436 (s), 1407 (s), 1317 (s), 1265 (m), 1253 (m), 1235 (w), 1180 (m), 1160 (w), 1137 (w), 1107 (w), 1100 (w), 1058 (w), 1036 (w), 1022 (w),937 (w), 854 (w), 796 (m), 760 (m), 729 (m), 694 (w), 638 (w), 563 (w), 529 cm^{-1} (w); elemental analysis (%) calcd for $C_{62}H_{92}N_4O_4Zn_2\cdot 0.95$ toluene: C70.21, H 8.54, N 4.75; found: C 70.12, H 8.56, N 4.78.

Epoxidation of enones: To a stirred solution of **2** (2 mmol) in toluene (5 cm^3) was added the corresponding enone (1.9 mmol) at 0 °C and the reaction mixture was stirred for 15 min and the crude mixture was analyzed by ^{1}H NMR. Then the solution was treated with KF (3.5 g, 60 mmol) and water (1.2 mL, 67 mmol). The organic products formed were extracted with ethyl ether and the conversion was analyzed by liquid chromatography (HPLC) and ^{1}H NMR. Additionally, the α,β-epoxyketones were isolated by flash chromatography.

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