

Preliminary communication

NOVEL REACTIONS OF SUBSTITUTED 1-AZA-4-OXOBUTADIENES (α -IMINOKETONES) WITH DIORGANOZINC REAGENTS. SELECTIVE ETHYL TRANSFER IN THE $\text{Et}_2\text{Zn}/t\text{-BuN}=\text{C}(\text{H})-\text{C}(\text{Me})=\text{O}$ SYSTEM AND X-RAY CRYSTAL STRUCTURE OF $[\text{EtZn}(\text{Et})(t\text{-Bu})\text{NC}(\text{H})=\text{C}(\text{Me})\text{O}]_2$

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(Received April 6th, 1982)

Summary

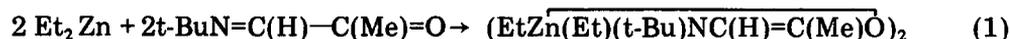
The 1/1 reaction of Et_2Zn with *N*-*t*-butyliminopropanone ($t\text{-BuN}=\text{C}(\text{H})-\text{C}(\text{Me})=\text{O}$) leads to quantitative formation of dinuclear $[\text{EtZn}(\text{Et})(t\text{-Bu})\text{NC}(\text{H})=\text{C}(\text{Me})\text{O}]_2$ via ethyl transfer within the unstable $\text{Et}_2\text{Zn}(t\text{-BuN}=\text{C}(\text{H})-\text{C}(\text{Me})=\text{O})$ complex. An X-ray structure determination has shown the product to have a dinuclear structure involving a N,O-chelate bonded $[\text{Et}(t\text{-Bu})\text{NC}(\text{H})=\text{C}(\text{Me})\text{O}]^-$ mono-anionic ligand and a central four membered Zn_2O_2 ring formed by intermolecular Zn—O coordination. Hydrolysis of this zinc complex gives a quantitative yield of *N*-*t*-butyl-*N*-ethylamino propanone, which upon reaction with Et_2Zn reforms the dinuclear zinc complex.

1,4-Diaza-1,3-butadienes ($\text{RN}=\text{C}(\text{H})-\text{C}(\text{H})=\text{NR}$) are known to interact with metal centres in a variety of ways [1]. Recent observations indicate that, depending on the coordination mode, one electron transfer from the metal to the neutral $\text{N}=\text{C}-\text{C}=\text{N}$ skeleton can take place. When followed by selective transfer of a one electron ligand R' (e.g. H or alkyl) this produces the mono-anionic ligand $[\text{R}(\text{R}')\text{N}-\text{C}(\text{H})=\text{C}(\text{H})-\text{NR}']^-$ [2]. Use of reactions of 1,4-diaza-1,3-butadienes with either organo-zinc or -aluminum reagents provides straightforward syntheses of new classes of 1,2-iminoaminoethane and 1,2-diaminoethene molecules [3].

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We have now extended these investigations to reactions of molecules containing the N=C—C=O moiety, since these are attractive starting materials for the synthesis of more complex organic skeletons containing two different hetero atoms. A few such conversions were already known, e.g. ethyl *N*- α -methylbenzyl iminoacetate can be converted by Fe₂(CO)₉ and PhCH₂Br into α -amino acids [4], while, in contrast, Grignard reagents give both C- and N-alkylated products [5]. We now report that with Et₂Zn as reagent *N*-*t*-butyliminopropanone can be selectively converted into the *N*-alkylated product.

Addition of a 1.5 *M* hexane solution of Et₂Zn to a hexane solution containing an equimolar amount of *t*-BuN=C(H)—C(Me)=O (1), at -100°C, resulted in almost quantitative formation of the new organozinc complex 2 (80% isolated yield).



The ¹H and ¹³C NMR spectra of 2 revealed the formation of a Et(*t*-Bu)NC(H)=C(Me)O bidentate monoanion N,O-chelate bonded to an EtZn moiety. The ¹H NMR spectrum (RT, C₆D₆) showed one singlet for the *t*-Bu group (δ 1.14 ppm) while the NCH=C proton appeared in the olefinic region as a singlet (δ 4.16 ppm). The CH₂ protons of the NEt group are diastereotopic (δ 2.06 and 2.79 ppm, ²*J*(HH) 12.0 Hz) pointing to coordination of the Et(*t*-Bu)N group to zinc, thus making the N atom a stable chiral centre. The ¹³C NMR spectrum of 2 (RT, C₆D₆) was consistent with the presence of a EtZn($\overline{\text{Et}}$)(*t*-Bu)NC(H)=C(Me)O unit, showing, for example, two different olefinic C atoms (δ 104.6 and 160.0 ppm) and two ethyl C resonance patterns (EtZn δ 1.8, 12.4 ppm; EtN δ 13.3, 45.0 ppm).

Cryoscopic molecular weight determinations showed that 2 is dimeric in benzene. This contrasts with the monomeric nature of EtZn($\overline{\text{Et}}$)(*t*-Bu)NC(H)=C(H)N*t*-Bu [2].

In order to establish the N,O-chelate bonding as well as the nature of the bridge bonding giving rise to the dimeric structure an X-ray structure of 2 was carried out*.

Crystals of 2 (C₁₁H₂₃NOZn)₂ grown from pentane are triclinic with space group *P* $\bar{1}$, *Z* = 1 and unit cell dimensions of *a* 7.57(1), *b* 8.82(2), *c* 11.14(1) Å, α 102.6(1), β 91.8(1), γ 114.4(2)°. A whole sphere of reflections up to θ = 20° was collected in the ω -scan mode using Zr-filtered Mo-*K* α -radiation (λ 0.71069 Å). The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares techniques. Hydrogen atoms were introduced at calculated positions and refined in the riding or rigid rotator mode with one overall isotropic temperature ** factor.

*Atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, Great Britain. Any request should be accompanied by a full literature citation for this communication.

**The non-hydrogen atoms were refined with anisotropic thermal parameters. Convergence was reached at *R* = 0.089 (*R*_w = 0.085) for 1051 reflections and $w^{-1} = (\sigma^2(F) + 0.001 F^2)/3.09$. The structure determination and refinement was carried out on an in-house ECLIPSE S/230 mini-computer with a locally adapted and modified version of the SHELX 76-package (G.M. Sheldrick) named ILIAS. All derived geometry calculations and illustrations were carried out with the programs of the EUCLID-package [8] of the CYBER-175 of the University of Utrecht.

The molecular geometry of the $(\text{EtZn}(\overline{\text{Et}})(\text{t-Bu})\text{NC}(\text{H})=\text{C}(\text{Me})\text{O})_2$ dimer is shown in Fig. 1, together with some relevant bond distances and bond angles

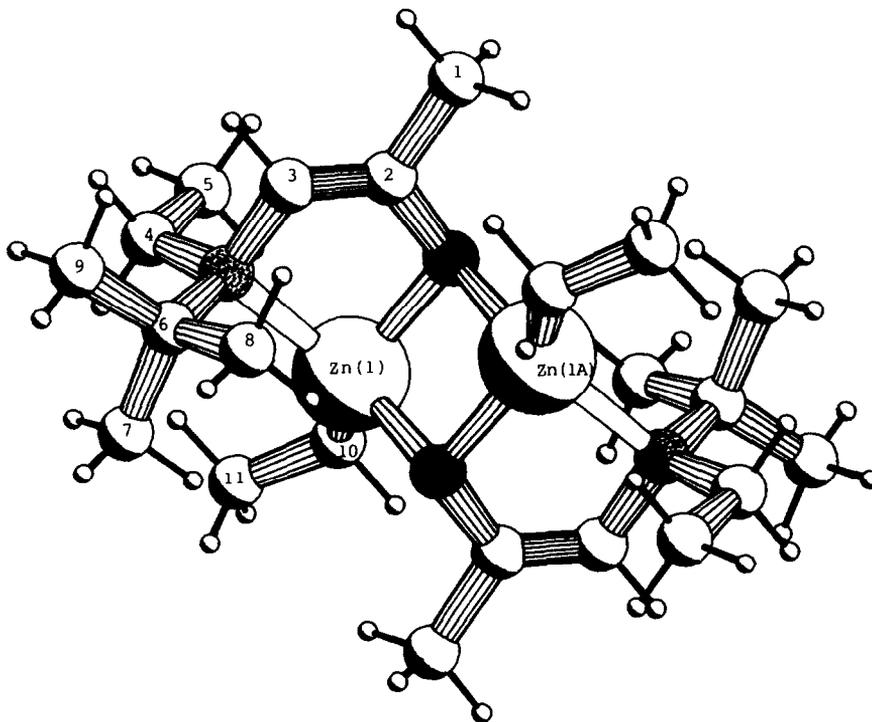


Fig. 1. PLUTO drawing of $(\text{EtZn}(\overline{\text{Et}})(\text{t-Bu})\text{NC}(\text{H})=\text{C}(\text{Me})\text{O})_2$. Full black spheres represent oxygen and dotted spheres nitrogen. Some relevant distances (Å) and bond angles ($^\circ$) are: Zn(1)—Zn(1A) 3.069(3), Zn(1)—O(1) 2.02(1), Zn(1)—O(1A) 2.12(1), Zn(1)—N(1) 2.21(2), O(1)—C(2) 1.40(2), N(1)—C(3) 1.43(2), C(2)—C(3) 1.27(3); O(1)—Zn(1)—O(1A) 84.2(5), O(1)—Zn(1)—N(1) 82.8(5), O(1)—Zn(1)—C(10) 130.5(7), O(1A)—Zn(1)—N(1) 114.3(6), O(1A)—Zn(1)—C(10) 112.0(6), N(1)—Zn(1)—C(10) 124.9(7), Zn(1)—N(1)—C(4) 109.(1), Zn(1)—N(1)—C(6) 113.(1), Zn(1)—N(1)—C(3) 102.(1), C(3)—N(1)—C(6) 112.(2), N(1)—C(3)—C(2) 123.(2), Zn(1)—O(1)—C(2) 109.(1), Zn(1A)—O(1)—C(2) 116.(1), Zn(1)—O(1)—Zn(1A) 95.8(5).

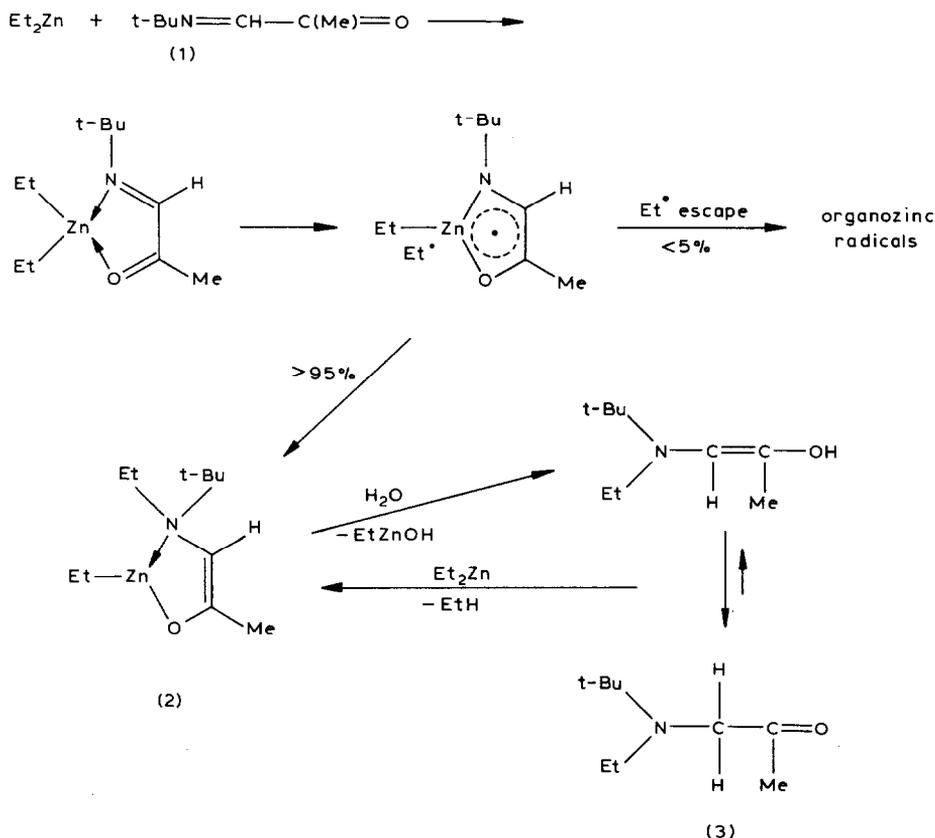
The structure consists of two $\text{EtZn}(\overline{\text{Et}})(\text{t-Bu})\text{NC}(\text{H})=\text{C}(\text{Me})\text{O}$ moieties which are linked by intermolecular Zn—O coordination. Association of organozinc alkoxides via formation of four membered Zn_2O_2 rings is a general phenomenon, cf. structure of $(\text{RZnOR})_4$ [6]. The present dinuclear structure is very similar to that proposed for $[\text{HZnOCH}_2\text{CH}_2\text{NMe}_2]_2$ by analogy to $[\text{HZnN}(\text{Me})\text{CH}_2\text{CH}_2\text{NMe}_2]_2$ [7].

The dimeric compound **2** does not react further with N-donor ligands such as pyridine, indicating that the dimeric association is very stable.

The reaction described leads to exclusive formation of the N-alkylated product **2** paralleling the N-alkylation reaction found for the $\text{Et}_2\text{Zn}/\text{R-DAB}$ system. However, the product formation in the $\text{R}_n\text{M}/\alpha$ -iminoketone system is strongly dependent on the metal, the nature of R, the substituents on the α -iminoketone and the solvent used. For example, reaction of $\text{t-Bu}_2\text{Zn}$ and **1** results exclusively in a C-alkylation product which after hydrolysis produces $\text{t-BuN}=\text{C}(\text{H})\text{C}(\text{Me})(\text{t-Bu})\text{OH}$. Understanding of these reactivity patterns requires knowledge of the complexes

formed during initial stages of the reaction. In the case of the $\text{Et}_2\text{Zn}/t\text{-BuN}=\text{C}(\text{H})-\text{C}(\text{Me})\text{O}$ system there is a transient red colouration of the solution during the addition of Et_2Zn , and so we assume that the initial step is the formation of a 1/1 complex containing a σ, σ' -N,O-chelate bonded iminoketone. Furthermore we observe that the **2** formed has exclusively the *cis*-configuration at the olefinic bond, whereas the alternative N or O monodentate coordination of the $\text{N}=\text{C}-\text{C}=\text{O}$ system in the *trans*-conformation would lead to both *cis*- and *trans*-products.

Monitoring of the ESR spectra of the reaction mixture indicates that the formation of **2** is accompanied by the production of trace amounts of a stable organozinc radical. However, in contrast to the easy assignment of the ESR spectra of the stable $\text{EtZn}(\text{R-DAB})$ radicals formed in the $\text{Et}_2\text{Zn}/\text{R-DAB}$ reactions [3b, c] these complex ESR spectra could not be readily interpreted. Nevertheless, production of a stable organozinc radical indicates that the $\text{Et}_2\text{Zn}/t\text{-BuN}=\text{C}(\text{H})-\text{C}(\text{Me})=\text{O}$ and $\text{Et}_2\text{Zn}/t\text{-BuN}=\text{C}(\text{H})-\text{C}(\text{H})=\text{N}(\text{t-Bu})$ reactions probably have the same mechanism. First a single electron transfer produces the $[\text{EtZn}(\text{t-Bu})\text{NC}(\text{H})\text{C}(\text{Me})\text{O}]^{\cdot-}$ Et^{\cdot} pair, and this is followed by trapping of the Et^{\cdot} at the N centre (see Scheme 1). A trace amount of the Et radicals escapes from the solvent cage giving rise to an EtZn radical complex (cf. ref. 3):



SCHEME 1.

An important observation is the nearly quantitative formation of *N*-*t*-butyl-*N*-ethylamino propanone (3)* on hydrolysis of 2 with H₂O in CH₂Cl₂. Upon treating 3 with Et₂Zn, 2 and ethane are produced quantitatively. The consequences of these findings and the further reactions of the zinc complex of the 2-aminovinyl oxy anion (deprotonated enol form of 3) are now under study.

Acknowledgement. The X-ray data were kindly collected by Dr. A.J.M. Duisenberg. These investigations were supported in part by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organisation of Pure Research (ZWO) (A.L.S.).

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*B.p. 110°C/0.5 mmHg. ¹H NMR (RT, CDCl₃) δ(Et) 0.92t (3H), 2.49q (2H); δ(*t*-Bu) 0.97s (9H); δ(CH₂) 2.13s (3H); δ(CH₂) 3.06s (2H) ppm.