Structure and Reactivity of Bis(iodozincio)methane in Tetrahydrothiophene

Seijiro Matsubara,* Yuhei Yamamoto, Kiitiro Utimoto

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606-8501, Japan Fax: 75-753-4863; E-mail: matsubar@mc.kyoto-u.ac.jp Received 24 June 1999

Abstract: Addition of tetrahydrothiophene (THT) to a THF solution of bis(iodozincio)methane modified the stability and reactivity: EXAFS analysis indicated that THT stabilizes bis(iodozincio)methane in a monomeric structure; the species reacts with acyl chlorides to give 1,3-diketones.

Key words: zinc, 1,3-diketone, dimetal, THT, EXAFS

The high synthetic potential of gem-dimetallic reagents has been extensively studied,¹ but any study for controlling the reactivity by adding ligand or solvent has not been examined. Recently we reported a preparation of bis(iodozincio)methane (1), 1,1-bis(iodozincio)ethane,^{1f} and bis(bromozincio)methyltrimethyl-silane^{1h} from the corresponding gem-dihalides by Pb-catalyzed reaction with zinc in THF. These reagents realized the following transformations; olefination of carbonyl compounds,^{1f} three component coupling by connection of two different electrophiles on the dimetallated carbon.^{1g,h} 1,3-Diketones were produced by the direct reaction with acyl cyanides.² A use of acyl chloride instead of acyl cyanides lead to the reaction of acyl chloride with THF, which afforded 4-iodobutyl ester, as acyl chlorides react faster with THF than 1 in THF (Scheme 1).³ An appropriate solvent, activating 1 will proceed the reaction of 1,3-diketone formation. Among the examined solvents, tetrahydrothiophene (THT) showed the reasonable activation and characteristic function for the stabilization of **1**.



Scheme 1

To the dizinc reagent **1** in THF (2.0 mmol, 0.4 M), prepared from diiodomethane with zinc in THF according to the reported procedure, ^{1e,f} was added 5 ml of tetrahydrothiophene (THT)⁴ at 25 °C. The mixture was stirred for 10 min. At the same temperature, benzoyl chloride (2.0 mmol) in THF (1.0 ml) was added dropwise. The resulting solution was stirred for 2 h at the same temperature. An aqueous work-up afforded 1,3-diketone **3a** in 98% yield, and the formation of **2a** was not observed. The results using various acyl chlorides are shown in Table 1.





 Table 1
 Preparation of 1,3-Diketones by the Reaction of Acyl Chloride with Bis(iodozincio)methane (1) in THF–THT ^a

Entry	R	3a-f	2a-f ^c
1	Phenyl	98%b	<1%
2	2-Furan	96	<1
3	2-Thiophene	82	<1
4	2-Naphtyl	71	23
5	(E)-2-phenylethenyl	58	34
6	(E)-1-propenyl	52	32

^aacyl chloride (2.0 mmol), bis(iodozincio)methane (0.4 M THF solution, 2.0 mmol), and THT (5 ml) were used. ^bIsolated yields. ^cWithout THT, **2** is formed quantitatively without forming **3** in all cases.

In entries 4–6, the reactions afforded the 1,3-diketones **3** with accompanying 2 that is formed from THF and acyl chloride. This problem was overcome by removing THF from the reagent. To a THF solution of 1 (0.4 M, 2.0 mmol), THT (7.5 ml) was added and stirred for 5 min. The mixture was concentrated in vacuo at 0 °C until a half volume of the mixture was removed. An selective evaporation of THF from the mixture, owing to the difference of boiling points, gave a THT solution of 1 that was free from THF.⁵ One may think that a concentration of 1 in THF in vacuo before an addition of THT will offer a simple procedure, but the removal of THF without adding THT afforded the solid which would not been dissolved into THF and THT. A direct concentration from 1 in THF caused a structural change which may produce the polymeric compound as being discussed later in the text. A treatment of 2-naphthoyl chloride with thus obtained THT solution of 1 gave 1,3-diketone 3d in 86% yield and did not afford 2d. The ¹H NMR spectra of 1 in THF-THT implies an effective coordination of THT to the dizinc compound. A methylene proton signal of 1 in THF appears at -1.12 ppm (20 °C) were shifted to -0.90 ppm by an addition of THT. A THT solution of **1** also gave a signal at – 0.90 ppm (20 °C). Thus, the shift of the signal was not effected by the existence of THF. It shows that THT coordinate 1 more effectively than THF.

The aliphatic carboxylic acid chloride was also treated with 1 in THT as shown in Scheme 3. In this case, 1,3-diketone was obtained along with the formation of vinyl ester.





The difference of reactivity depending on the solvent can be explained by a coordination to zinc, which may lead to the change of the reagent structure itself. The possibility of a contribution of Schlenk equilibrium should be considered (Scheme 4). The equilibrium would not be discussed not only by eq 1 in Scheme 4 but also by eq 2, as the dimetallic structure of **1** induces polymeric structure like $IZn-(-CH_2Zn-)_n-I$ (5) or cyclic compound 6. A removal of solvent from a THF solution of 1 gave a white solid as described above. The solid would not dissolve into THF or THT. A treatment of benzoyl chloride with a THT dispersion of the solid gave a THF derivative 2a, and did not afford 1,3-diketone 3a. A concentration in vacuo could not remove THF which coordinates to 1 unless THT was added. The solid can undergo methylenation of aldehyde even though it was reacted as a THF dispersion. Various other solvents, DMI, CS₂, 1,2-dichloroethane, pyridine, DMF, and DMSO, were examined to dissolve the solid. Among them, DMSO showed a reasonable solubility. A spectra of ¹H NMR of its DMSO solution showed a sharp singlet at -1.8 ppm. The solid was considered to be a polymeric dizinc species (5 or 6). The solid was also obtained by heating **1** in THF at 80 °C for 5 h. A removal of solvent from 1 in THF-THT gave also the white solid. The solid is soluble in THF and THT; ¹H NMR spectra of its THF solution showed a methylene signal at -0.90 ppm (20 °C) that is identified with 1 in THT. So an addition of THT stabilize the structure of 1. An extended X-ray absorption fine structure (EXAFS) spectroscopy of these reagent was measured to get any information about structure.^{6,7} This measurement showed 1 in THT exists with keeping the high homogeneity. The Schlenk equilibrium of 1 in THT may incline to $CH_2(ZnI)_2$ in eq 1 (Scheme 4).



Scheme 4

LETTER

Downloaded by: Rutgers University. Copyrighted material

The structural study about *gem*-dizinc compound in solvent has just begun and is now undergoing. But, a reasonable activation of 1 by adding THT make the 1,3-diketone preparation from acyl chloride possible and effect also to the structure of 1 in solution.

We thank Prof. Satohiro Yoshida, Dr. Tsunehiro Tanaka, and Mr. Takashi Yamamoto (Department of Molecular Engineering, Graduate School of Engineering, Kyoto University) for the EXAFS measurement at Spring 8 and helpful discussions. This work was supported by a Grantin-Aid for Scientific Research on Priority Areas (No.10132227 and 10208208), from The Ministry of Education, Science, Sports, and Culture.

References and Notes

- (1) a) Marek, I.; Normant, J.-F. Chem. Rev. 1996, 96, 3241.
 b) Knochel, P.; Normant, J.-F. Tetrahedron Lett. 1986, 27, 4427 and 4431. c) Nakamura, E.; Kubota, K.; Sakata, G. J. Am. Chem. Soc. 1997, 119, 5457. d) Bertini, F.; Grasselli, P.; Zubiani, G.; Cainelli, G. Tetrahedron 1970, 26, 1281; van de Heisteeg, B.J.J.; Schat, M.A.; Tinga, G.; Akkerman, O.S.; Bickelhaupt, F. Tetrahedron Lett. 1986, 27, 6123. e) Takai, K.; Kakiuchi, T.; Utimoto, K. J. Org. Chem. 1994, 59, 2671.
 f) Matsubara, S.; Mizuno, T.; Otake, Y.; Kobara, M.; Utimoto, K.; Takai, K. Synlett 1998, 1369. g) Utimoto, K.; Toda, N.; Mizuno, T.; Kobata, M.; Matsubara, S.; Otake, Y.; Morikawa, T.; Utimoto, K. Synlett 1998, 1315.
- (2) Matsubara, S.; Kawamoto, K.; Utimoto, K. Synlett 1998, 267.
- (3) Zinc(II) halide containing the reagent may assists the ring opening of THF as Lewis acid. In reference 2, the preparation of 1,3-diketone in the presence of Pd catalyst is shown.
- (4) Freshly distilled Tetrahydrothiophene (drying over LiAlH₄ under an Ar atmosphere) was used; bp. 119 °C. A reaction of CH₂I₂, PbCl₂, and Zn in THT did not afford 1. Other solvents, such as ether, DME, and 1,4-dioxane were also examined as a solvent for the preparation of 1. Only the reaction in 1,4-dioxane afforded 1 in 8% yield, and the reactoins in ether and DME did not give 1.
- (5) A measurement of ¹H nmr of reagent did not show the signal from the proton based on THF.
- (6) A Structural study of organozincate by EXAFS: Uchiyama, M.; Kameda, M.; Mishima, O.; Yokoyama, N.; Koike, M.; Kondo, Y.; Sakamoto, T. J. Am. Chem. Soc., **1998**, 120, 4943.
- (7) In Figure 1 and 2, (I) EXAFS spectra of 1 in THF, (II) the DMSO solution of the residue obtained by a removal of THF from 1 in THF, and (III) 1 in THT, are shown. Comparison of spectrum implies the species in is much more homogenic than (I) and (II). So in (III) the dimetal species takes a simple structure like CH₂(ZnI)₂ in a momomeric form.



k³-Weighted EXAFS spectra at Zn K-edge; (I) **1** in THF (0.1 M), (II) **5** in DMSO (0.1 M), and (III) **1** in THT (0.1 M).

Figure 1



Fourier transform of the EXAFS spectra of (I) **1** in THF (0.1 M), (II) **5** in DMSO (0.1 M), and (III) **1** in THT (0.1 M).

Figure 2

Article Identifier: 1437-2096,E;1999,0,09,1471,1473,ftx,en;Y13799ST.pdf