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Mini Review

Bis(iodozincio)methane — preparation, structure, and reaction

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Abstract

Bis(iodozincio)methane was prepared from diiodomethane and zinc in the presence of a catalytic amount of lead. The compound showed a high potential as an organic synthetic reagent. The reaction with carbonyl compounds proceeded to give methylenated products. The reagent also reacted with a couple of electrophiles. A structural study was also examined.

Keywords: Dimetal; Zinc; Palladium; Titanium; EXAFS

1. Introduction

Reaction of *gem*-dimetallic reagents has attracted considerable attention as versatile reagents in organic synthesis [1]. As doubly nucleophilic species, they have been treated with electrophiles to form a couple of new bonds. The *gem*-dimetallic reagents have been also used for the Wittig-type olefination reaction of carbonyl compounds. Although they possess potential utility for organic transformation, only a few examples of the selective synthesis have been reported.[1] It is assumed that the reactivity and selectivity of the reagents largely depend on the metals. We focused on the corresponding zinc derivatives, as the availability and convenience of organozinc compounds in organic synthesis are well recognized [3]. The corresponding *gem*-dizinc compounds showed high characteristic performance in organic transformation beyond our imagination. Here we summarize our recent work on the simplest *gem*-dizinc species, bis(iodozincio)methane.

2. Preparation of *gem*-dizinc compounds

The preparation of *gem*-dimetal compounds has been achieved by the following three methods: (1) A double deprotonation from the methyl or methylene carbon, which connects with an electron-withdrawing group [4], (2) a regioselective carbometalation to alkenylmetal compound as well as a double hydrometalation to alkyne [5], (3) a halogen–metal exchange of *gem*-dihaloalkane [6]. For the preparation of the simplest *gem*-dizinc compound, *gem*-dizinciomethane, only the third method could be applied. Following the methylenation of aldehydes and ketones with CH_2X_2–Zn–$TiCl_4$–Pb by Utimoto and Takai [7], we tried to prepare a series of *gem*-dizinc compounds from $RCHX_2$–Zn–Pb as shown in Scheme 1 [8]. The reaction temperature is crucial for the yield of *gem*-dizinc compounds. The best yields of each *gem*-dizinc compound in THF solution were obtained at the following reaction temperature: CH_2I_2 (**2a**, 0°C, 60%) [8a], CH_3CHI_2 (**2b**, 20°C, 30%) [8a], $PhMe_2SiCHBr_2$ (**2c**, 80°C, 80%) [8b], $Et_3GeCHBr_2$ (**2d**, 80 °C, 30%) [8c], and $(RO)_2BCHBr_2$ (**2e**, 80°C, 70%) [8d]. These yields were calculated by ^{1}H-NMR spectra using 2,2,3,3-tetramethylbutane as an internal standard.

2.1. Preparation of bis(iodozincio)methane (2a) [8a]

A mixture of Zn (25 mmol), diiodomethane (1.0 mmol), and $PbCl_2$ (0.01 mmol) in THF (2.0 ml) was sonicated for 1 h in an ultrasonic cleaner bath under Ar. To the mixture, diiodomethane (10 mmol) in THF

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[1] For an example of *E*-selective olefin syntheses, see Ref. [2].

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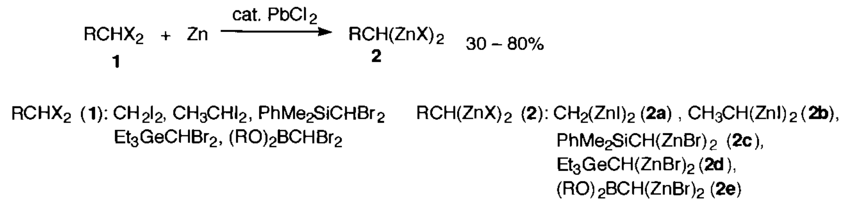
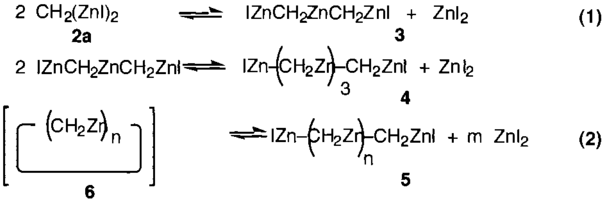


Scheme 1.

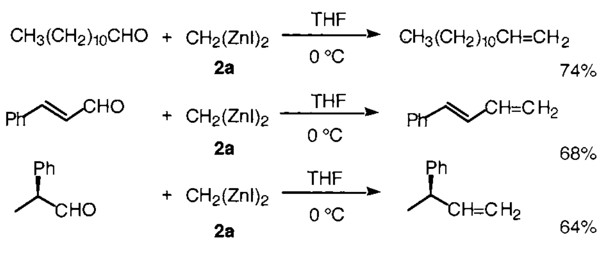
(20 ml) was added dropwise over 15 min at 0°C with vigorous stirring. The mixture was stirred for 2 h at 0°C. After the stirring was stopped, the reaction vessel was stood undisturbed for several hours. Excess zinc was separated by sedimentation. ^{1}H-NMR spectra of the obtained supernatant showed a broad singlet at -1.2 ppm at 0°C, which corresponded to the methylene proton of **2a**. The supernatant was used for the further reaction as a solution of **2a** in THF (0.5–0.6 M). Bis(iodozincio)methane in THF can be kept unchanged at least for a month in the sealed reaction vessel.

3. Structure of bis(iodozincio)methane

The structure of bis(iodozincio)methane (**2a**) in THF is not so simple, as the possibility of a contribution of Schlenk equilibrium of bis(iodozinciomethane) should be considered (Scheme 2) [9]. The equilibrium would be discussed not only by Eq. (1) but also by Eq. (2), as the dimetallic structure of **2a** induces a polymeric structure such as a linear compound **5** or cyclic compound **6**. Removal of the solvent from the THF solution of **2a** in vacuo gave a white solid **7**. The solid **7** would not dissolve into THF. During the concentration, the structure had changed. Various other solvents, DMI (1,3-dimethyl-2-imidazolidinone), CS_2, 1,2-dichloroethane, pyridine, DMF, and DMSO, were examined to dissolve the solid **7**. Among them, DMSO promoted reasonable solubility. The solid **7** was also obtained by heating **2a** in THF at 80°C for 5 h. The solid was considered to be a polymeric dizinc species (**5** or **6**). An addition of tetrahydrothiophene (THT) changed the situation dramatically. After an addition of the same volume of THT to the THF solution of **2a**, the resulting mixture was concentrated in vacuo to half the volume. In this procedure, THF was removed selectively, and a THT solution of **2a** was obtained. The further concentration also gave a white solid. This solid is soluble in THF. An extended X-ray absorption fine structure (EXAFS) spectroscopy of these solutions (**2a** in THF, **7** in DMSO, and **2a** in THT) was measured to get some information regarding the structure [9,10]. The measurement showed **2a** in THT exists while maintaining high homogeneity, whereas the spectrum of **7** in DMSO showed an effect from the polymeric species such as **5** and **6**. The Schlenk equilibrium of **2a** in THT may incline to $CH_2(ZnI)_2$ in Eq. (1), and a concentration or heating of **2a** in THF causes a formation of the polymeric species **5** or **6** [12].[2]



Scheme 2.



Scheme 3.

4. Methylenation of aldehydes, ketones, and esters with bis(iodozincio)methane

Wittig reagents [13], *gem*-dimetalloalkanes [14], Schrock type metal–carbene complexes [15], Tebbe complex [16] and dialkyltitanocenes [17] are commonly used for olefination of aldehydes and ketones. Reagent systems composed of $RCHX_2$-Zn-$TiCl_4$ [7] were also successfully applied to such olefination, where *gem*-dimetaloalkanes were assumed as the reactive species of olefination. To develop an effective reagent for methylenation of aldehydes and ketones, reaction of bis(iodozincio)methane (**2a**) was examined [8a].

Treatment of aldehyde with **2a** gave the corresponding methylenated product as shown in Scheme 3. Even

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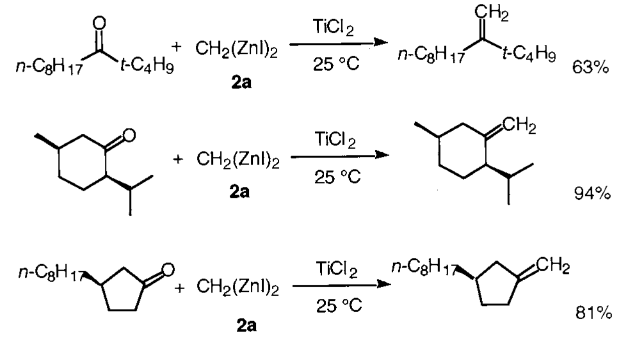
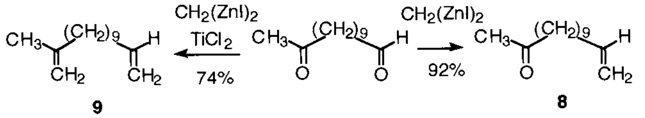
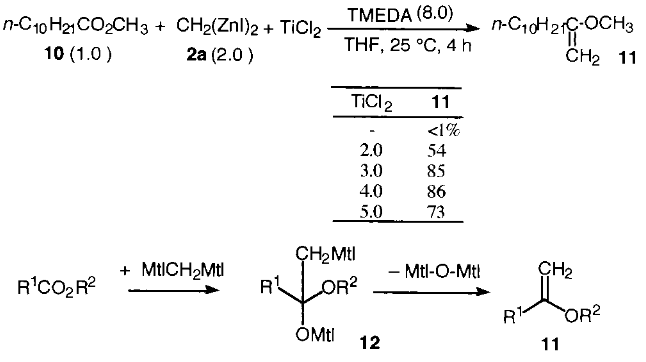
[2] The Nysted reagent [11] is commercially available from Aldrich Co. In preparation of the Nysted reagent, it was reported that dibromomethane was treated with a zinc–lead couple or zinc activated with hydrochloric acid in THF at 80°C. This is also a white solid which is dispersed in THF, and would not solve into THF, DMF, and DMI.



Scheme 4.



Scheme 5.



$TiCl_2$	**11**
-	<1%
2.0	54
3.0	85
4.0	86
5.0	73

Scheme 6.

with α,β-unsaturated enal, 1,2-addition proceeded selectively to give a diene. The reaction with (*S*)-2-phenylpropanal converted it into the corresponding alkene without racemization.

Reactions of **2a** with ketones proceeded sluggishly. Addition of a stoichiometric amount of $TiCl_2$ accelerated the reaction (Scheme 4). Even a sterically hindered or easily enolizable ketone was also converted into the corresponding alkene. The use of $TiCl_4$ instead of $TiCl_2$ was also effective, but required an excess amount of **2a**. One molar equivalent of **2a** was consumed to reduce $TiCl_4$ into $TiCl_2$ at the beginning of the reaction.

Chemoselective methylenation of a keto aldehyde, 11-oxododecanal, with **2a** was examined with or without $TiCl_2$: the reaction with two molar equivalents of **2a** with the keto aldehyde gave 1-tridecen-2-one (**8**) in 92% yield without any methylenation of the ketone, whereas it was converted into 2-methyl-1,12-tridecadiene (**9**) in 74% yield by treatment with two molar equivalents of **2a** in the presence of two molar equivalents of $TiCl_2$ (Scheme 5).

4.1. $TiCl_2$-mediated methylenation of ketone [8a]

To $TiCl_2$ (0.48 g, 4.0 mmol) was added THF (8 ml) at −40°C under Ar. The mixture was stirred for 10 min at 20°C. To the obtained dispersion was added $CH_2(ZnI)_2$ (**2a**, 4.0 mmol) in THF at 20°C and the resulting mixture was stirred for 5 min. Ketone (4.0 mmol) in THF (4 ml) were added dropwise to the resulting mixture at 0°C. The mixture was stirred for 1 h at 20°C. To the mixture was added ether (16 ml). The resulting mixture was filtered through a celite column and washed with ether (20 ml). The filtrate was concentrated. The product was isolated with a short silica-gel column chromatography.

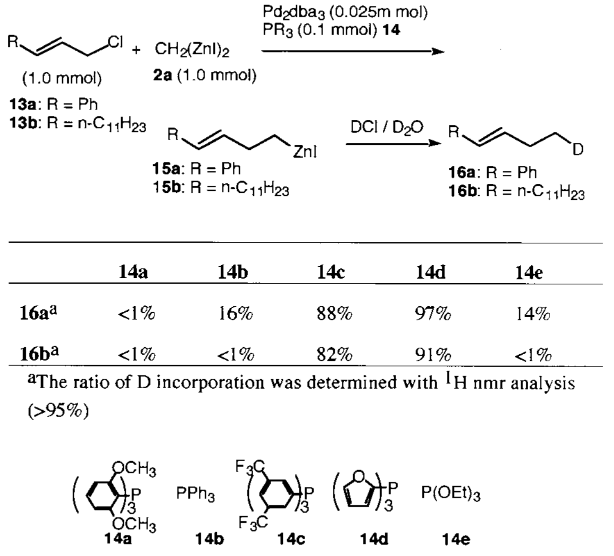
Methylenation of the carbonyl group of esters is still a challenging problem. Only a few reagents were effective for methylenation of esters: the Tebbe reagent and a titanocene methylene complex showed high performance for the methylenation of esters [16]. Some other titanium-mediated reagents offered a useful alkylidenation of esters [18], but did not work well for methylenation of esters. A reagent consisting of **2a**–$TiCl_2$–TMEDA was examined for the methylenation of methyl *n*-undecanoate (**10**) as shown in Scheme 6 [19]. The reaction condition using two molar equivalents of **2a**, four molar equivalents of $TiCl_2$, and eight molar equivalents of TMEDA to ester, gave the best result. A reaction of **2a** with **10** and $TiCl_2$ in the absence of TMEDA did not afford **11**, although the starting material was completely consumed. Treatment of the reaction mixture with 1 M HCl(aq.) instead of the non-aqueous work-up described above afforded 2-dodecanone in 68% yield. This fact may imply the reaction proceeds stepwisely via **12** in Scheme 6. An elimination of metal oxide from the adduct **12** will lead to the formation of **11**. In the absence of TMEDA, the elimination may be slow and hydrolysis of **12** gave a methyl ketone. TMEDA may play a role for acceleration of the elimination of metal oxide. Although the structural information of the reactive species formed by **2a** and $TiCl_2$ is not clear, we assume that transmetalation from **2a** to titanium plays an important role. The possibility of the formation of a titanium carbene complex from **2a**–$TiCl_2$–TMEDA cannot be ruled out. This method was applicable to other carboxylic acid esters.

4.2. Methylenation of carboxylic acid ester [19]

To a suspension of $TiCl_2$ (4.0 mmol) in THF (10 ml), **2a** (2.0 mmol, 0.4 M in THF) and TMEDA (8.0 mmol) were added at 25°C. The mixture was stirred for 3 min and became a deep reddish–brown solution. A solution of **10** in THF (1.0 ml) was added and the whole was stirred for 4 h. The resulting mixture was diluted with ethyl acetate (20 ml) and hexane (20 ml), and passed

$$CH_2(ZnI)_2 + D_2O \xrightarrow[-35\ °C]{THF} CH_2D(ZnI) + D_2O \xrightarrow[0\ °C]{THF} CH_2D_2$$

Scheme 7.



	14a	14b	14c	14d	14e
16a[a]	<1%	16%	88%	97%	14%
16b[a]	<1%	<1%	82%	91%	<1%

[a]The ratio of D incorporation was determined with ^1H nmr analysis (>95%)

Scheme 8.

through a short celite and alumina column (ICN Alumina B, Grade III). Concentration in vacuo gave **11** in 86% yield.

5. Stepwise reaction of bis(iodozincio)methane with two different electrophiles

5.1. Sequential coupling of bis(iodozincio)methane with organic halides

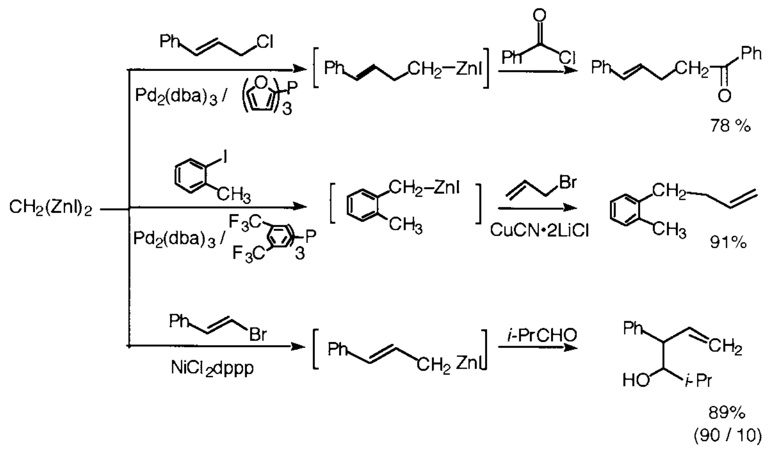
The structure of bis(iodozincio)methane, which possesses double nucleophilic sites on one carbon, has a possibility to react with two different electrophiles sequentially. It will act as a molecular hinge which connects two molecules. It was found that reactivity of one C–Zn bond of bis(iodozincio)methane was much higher than that of methylzinc in the reaction with water or iodine (Scheme 7) [5a,20]. These results indicated the possible use of the two C–Zn bonds separately. A stepwise reaction of *gem*-dimetallic compounds with two different electrophiles under palladium catalysis was examined as follows (Scheme 8) [20].

Allyl chloride **13** (1.0 mmol) was treated with **2a** (1.0 mmol) in the presence of $Pd_2dba_3·CHCl_3$ (0.025 mmol) and a phosphine ligand (0.1 mmol) in THF for 30 min. The resulting mixture was quenched with $DCl–D_2O$. Combinations of applied allyl chlorides, ligands, and yields of coupling products are summarized in Scheme 8. As can be seen from the Scheme 8, excellent results were obtained by ligand tuning; phosphine ligands, having an electron-withdrawing group, such as tris[3,5-bis(trifluoromethyl)phenyl]phosphine (**14c**) and tris(2-furanyl)phosphine (**14d**), gave excellent results [21].

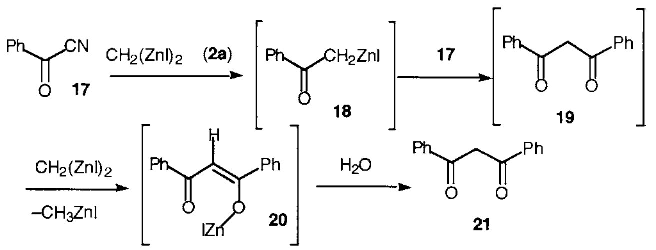
As the intermediate of the sequential coupling reaction (**15**) still has a carbon–zinc bond, it can be used as a nucleophile in the reaction with allyl halides and acyl halides instead of quenching with $DCl–D_2O$. In Scheme 9, the sequential coupling reactions of bis(iodozincio)methane with two types of organic halides are summarized. In the case of the coupling with a bromoalkene, a nickel catalyst was more effective than a palladium catalyst.

5.1.1. Sequential coupling reaction [20]

To a mixture of $Pd_2dba_3·CHCl_3$ (0.025 g, 0.025 mmol) and tris(2-furanyl)phosphine (**14d**, 0.023 g, 0.1 mmol) was added THF (2 ml). The mixture was stirred for 5 min at 20°C. To the mixture, a solution of cinnamyl chloride (**13a**, 0.15 g, 1.0 mmol) in THF (1 ml) and a THF solution of bis(iodozincio)methane (**2a**, 0.5 M, 2 ml, 1.0 mmol) were added subsequently at the same temperature. The resulting mixture was stirred for

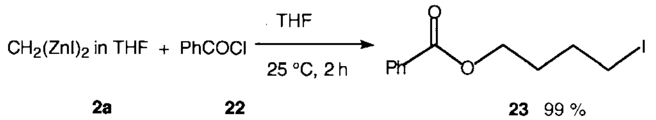


Scheme 9.

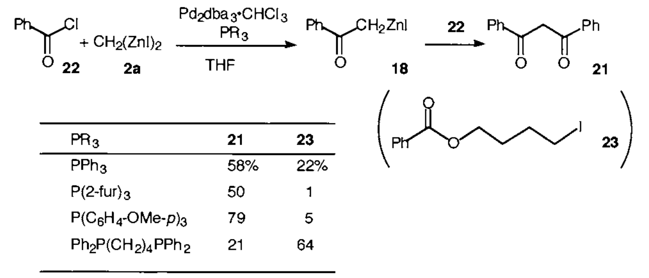


17	2a	21
2.0 mmol	1.0 mmol	44 %
2.0	1.5	59
2.0	2.0	90

Scheme 10.

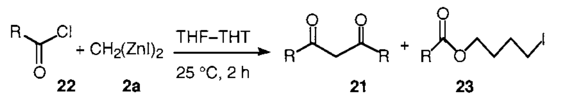


Scheme 11.



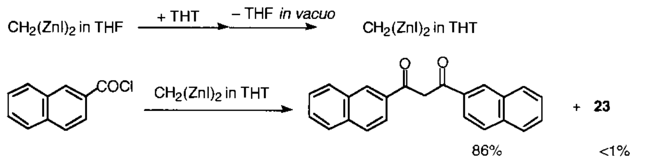
PR3	21	23
PPh3	58%	22%
P(2-fur)3	50	1
P(C6H4-OMe-p)3	79	5
Ph2P(CH2)4PPh2	21	64

Scheme 12.



22	21	23
Phenyl	98%	<1%
2-Furan	96	<1
2-Thiophene	82	<1
2-Naphtyl	71	23
(E)-2-phenylethenyl	58	34

Scheme 13.



Scheme 14.

30 min at 20°C. A solution of allyl bromide (0.15 g, 1.2 mmol) in THF (1 ml) was added at 20°C. The resulting mixture was stirred for 2 h. The mixture was poured into 1 M HCl (20 ml) and extracted with ether. The combined organic layers were washed with brine and dried over Na_2SO_4. Purification with a short silica-gel column chromatography gave 1-phenyl-1,6-heptadiene in 87% yield.

5.2. Preparation of a 1,3-diketone

As we have found that **2a** reacted with various electrophiles under Pd catalysis, reaction of **2a** with two acyl groups was examined [22]. Reaction of benzoyl cyanide (**17**, 2.0 mmol) with **2a** (1.0 mmol) afforded 1,3-diphenyl-1,3-propanedione (**21**) in 44% yield. The yield of the diketone **21** was improved to 90% by the reaction of **17** with **2a** in a molar ratio of 1:1. Deprotonation of an active methylene of 1,3-diketone by **2a** forms **20** and requires excess amount of a dizinc species (Scheme 10).

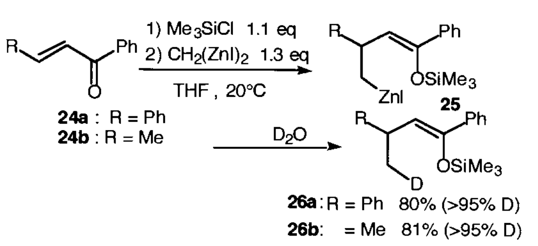
Reaction of **2a** with benzoyl chloride (**22**) gave 4-iodobutyl benzoate (**23**) as a major product; a zinc salt-catalyzed reaction of acyl chlorides **22** with THF proceeded mainly (Scheme 11) [23]. Coupling reaction under Pd catalysis proceeded smoothly, yielding symmetrical 1,3-diketone. Ligand tuning was necessary to obtain satisfactory results, although PPh_3 gave the expected 1,3-diketone **21** in good yield. As can be seen from the results shown in Scheme 12, $P(C_6H_4\text{-}p\text{-OMe})_3$ gave the best result. A bidentate ligand afforded an unsatisfactory result.

In another way, an addition of an appropriate solvent activates **2a** and makes possible a nucleophilic attack to the carbonyl group of acyl chloride. Among the examined solvents, THT showed reasonable activation and characteristic function for the stabilization of **2a** [9]. The ^{1}H-NMR spectra of **2a** in THF–THT implies an effective coordination of THT to the dizinc compound. A methylene proton signal of **2a** in THF appears at − 1.12 ppm (20°C) which shifted to − 0.90 ppm upon addition of THT. A THT solution of **2a** also gave a signal at − 0.90 ppm (20°C). It shows that THT coordinates **2a** more effectively than THF. As we described above, EXAFS study also showed the control of Schlenk equilibrium by THT. The relation between the reactivity and the structure has not been clarified yet. The results of 1,3-diketone synthesis from acyl chloride and **2a** in THT–THF are summarized in Scheme 13.

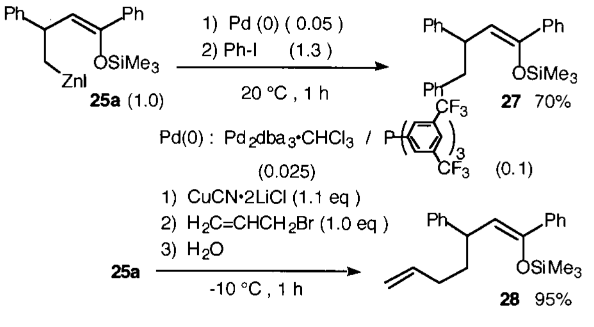
In Scheme 13, the reaction of 2-naphtoyl chloride and (*E*)-2-phenylethenoyl chloride afforded the 1,3-diketones **21** with accompanying **23** that is formed from THF and acyl chloride. This problem was overcome by removing THF from the reagent as described in the following experimental section (Scheme 14).

*5.2.1. Preparation of a 1,3-diketone from **2a** in THT [9]*

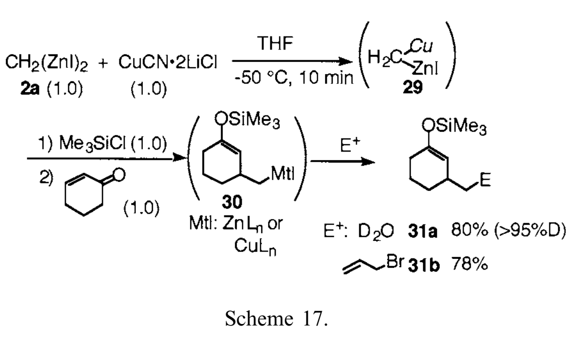
To a THF solution of **2a** (0.4 M, 2.0 mmol), THT (7.5 ml) was added and stirred for 5 min. The mixture was concentrated in vacuo at 0°C until half of the volume of the mixture was obtained. A selective evaporation of THF from the mixture, owing to the difference in boiling points, gave a THT solution of **2a** that was free from THF. 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 a solid which would not dissolve in THF and THT. A direct concentration from **2a** in THF caused a structural change. To the thus-obtained THT solution of **2a**, a solution of 2-naphthoyl chloride (2.0 mmol) in THT (1 ml) was added at 25°C, and the resulting mixture was stirred for 30 min. An aqueous work-up gave 1,3-diketone in 86% yield. The THF derived product **23** was not detected.



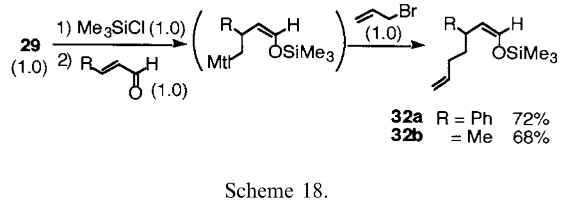
Scheme 15.



Scheme 16.



Scheme 17.



Scheme 18.

5.3. 1,4-Addition of bis(iodozincio)methane to α,β-unsaturated ketones

As another application of the sequential reaction, we examined a reaction of a *gem*-dizinc compound with an α,β-unsaturated carbonyl compound to perform 1,4-addition. This reaction will afford the zinc enolate of β-zinciomethylketone.

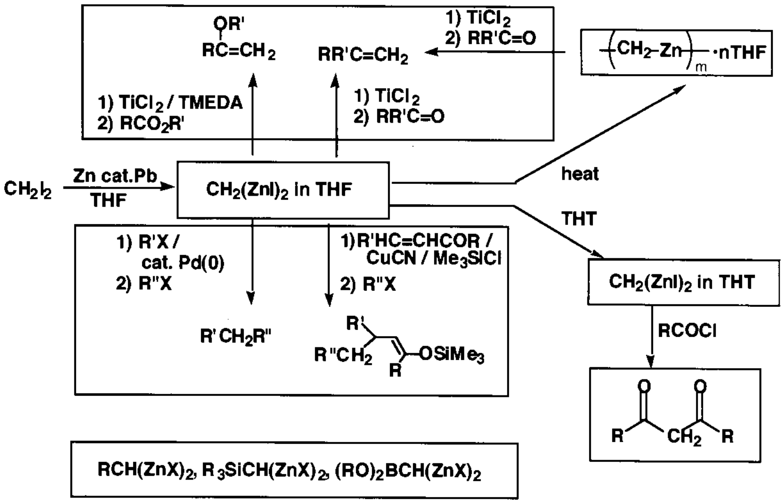
A reaction of bis(iodozincio)methane (**2a**) with α,β-unsaturated ketone **24** was examined [24]. The zinc enolate being formed in situ was trapped with an equimolar amount of chlorotrimethylsilane. The procedure afforded a silyl enolate of organozinc compound **25**. Treatment of **25** with D_2O gave the corresponding silyl enolate **26** (Scheme 15).

The organozinc moiety in **25** could be reacted with an organic halide as shown in Scheme 16. The zinc species **25a** was treated with iodobenzene in the presence of a catalytic amount of $Pd_2dba_3 \cdot CHCl_3/[3,5\text{-}(CF_3)_2C_6H_3]_3P$. The reaction gave **27** in 70% yield. The copper salt-mediated reaction of **25a** with allyl bromide gave the coupling product **28** in 95% yield (Scheme 16). It is well-known that the silyl enolate reacts with various electrophiles, so the procedure makes the four-components coupling possible.

Treatment of 2-cyclohexen-1-one with bis(iodozincio)methane and chlorotrimethylsilane resulted in the recovery of enone. In this case, we tried to prepare an organocopper species from the *gem*-dizinc compound and copper salt to perform 1,4-addition. To the species **29** prepared from **2a** and CuCN·2LiCl, chlorotrimethylsilane and 2-cyclohexen-1-one were added sequentially. After the reaction was completed, D_2O was added to quench the C–Zn bond. The silyl enolate **31a** was obtained in 80% yield via **30** (Scheme 17). The intermediary organozinc **30** reacted also with organic halides. The copper salt which already existed in the reaction mixture, mediated reaction of **30** with allyl halide to give **31b** as a product in 78% yield.

The function of copper salt was obvious in the reaction of an α,β-unsaturated aldehyde. As shown in Scheme 18, the species **29** was treated with chlorotrimethylsilane and aldehyde, followed by an addition

Scheme 19.



Scheme 20.

of allyl bromide to afford the silyl enolate **32** having *Z*-configuration. The reaction without copper salt also proceeded to give diene **33** via methylenation as shown in Scheme 19.

5.3.1. *Copper salt-mediated 1,4-addition of* ***2a*** *[24]*

To a solution of bis(iodozincio)methane (**2a**) in THF (0.4 M, 2.0 mmol) was added dropwise a solution of CuCN (2.0 mmol) and LiCl (4.0 mmmol) in THF (5.0 ml) at − 50°C over 15 min. The mixture was stirred for 5 min at the same temperature. To the mixture, cinnamyl aldehyde (2.0 mmol) and chlorotrimethylsilane (2.0 mmol) were added at − 50°C. The resulting mixture was allowed to warm up to 0°C and allyl bromide (2.0 mmol) in THF (3.0 ml) was added at 0°C. The mixture was stirred for 1 h at 20°C. The resulting mixture was poured into ice-cooled saturated NH_4Cl(aq.), and extracted with ether. The organic layers were washed with saturated $Na_2S_2O_3$ and brine. The ethereal solution was dried over $MgSO_4$. A short silica-gel column chromatography gave **33** in 72% yield.

6. Conclusion

Bis(iodozincio)methane showed utility in the area of methylenation of carbonyl compounds and as a molecular hinge of two electrophiles. The transformations are summarized in Scheme 20. Our preliminary work for the structural study requires further elaboration, which is underway.

The use of 1,1-bis(iodozincio)ethane is also attractive. We have already reported some part of the work. The use of 1,1-bis(iodozincio)ethane gave rise to a problem of stereoselectivity, as the symmetrical structure of the *gem*-dimetal species would afford a stereogenic center via desymmetrization. This will offer a possibility for a new type of stereocontrolled transformation.[3] The heteroatom-substituted dizinc reagent (i.e. silyl-, boryl-, and germyl-substituted ones) also offered a novel route to the corresponding alkenyl and allyl derivatives via olefinations and sequential coupling reactions [8b,c,d].

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