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Metal-ion-catalyzed Fluxionality of Pentadienyltins and Its Application to the Diels-Alder Reaction

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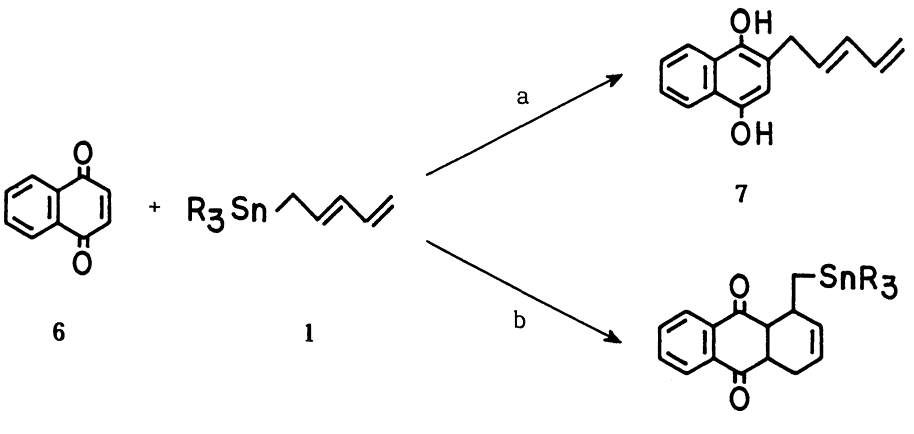
(Z)-Pentadienyltins (PDT) as well as (Z)-allylic tins are isomerized to (E)-isomers most effectively by alkaline earth metal ions. The resulted (E)-PDT is trapped by 1,4-naphthoquinone to give the Diels-Alder adducts efficiently behaving as a reactive equivalent of 1,3-pentadiene.

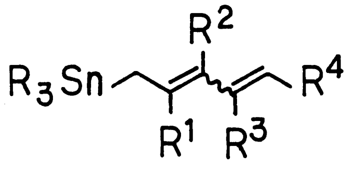
Pentadienyltin (PDT) is now recognized as a useful reagent for the nucleophilic introduction of a pentadienyl group.[1] One of the most distinctive features of it is to pentadienylate successfully even α,β-unsaturated carbonyl compounds, especially quinones (product **7** via path a in Scheme 1), in the presence of a suitable Lewis acid[2] without any formation of possible Diels-Alder adducts (**8** via path b). It can be also agreed that its usefulness is due to its thermal stability to isomerization.[3] Therefore, some of regiochemically pure PDTs have been employed to the regiodefined introduction of pentadienyl chains.[2b,c]



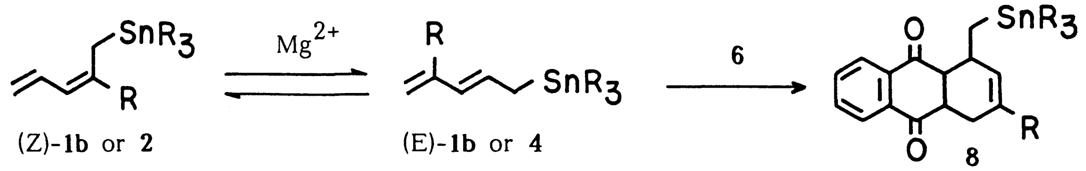
Scheme 1.

On the contrary, we report herein that the fluxionality (or isomerization) of PDTs was catalyzed by metal ions, and was effectively applied to the Diels-Alder reaction between PDTs and 1,4-naphthoquinone for the synthesis of *peri*-methylanthraquinones.[4]

In the course of our studies on the reaction of PDTs, we found that the addition of



PDT	R	R^1	R^2	R^3	R^4
1a	Me	H	H	H	H
1b	n-Bu	H	H	H	H
2	Me	Me	H	H	H
3	Me	H	Me	H	H
4	Me	H	H	Me	H
5	Me	H	H	H	Me



(1)

$Mg(ClO_4)_2$ to the reaction mixture of 1,4-naphthoquinone **6** and PDT (Z)-**1b**[5] in acetonitrile allowed the Diels-Alder reaction to proceed[6] (Eq. 1). More interestingly, under similar reaction conditions, (Z)-2-methyl-2,4-pentadienyltin **2** also gave a Diels-Alder adduct, which, however, was found to be derived from 4-methyl-2,4-pentadienyltin **4**. These results clearly indicated that the isomerization of PDTs was promoted by the magnesium ion. Indeed, when only (Z)-**1b** was exposed to the acetonitrile solution of $Mg(ClO_4)_2$, the recovered PDT was a mixture of (E)- and (Z)-**1b** [(E)-**1b** : (Z)-**1b** = 79 : 21]. It was confirmed that this isomeric composition was given by the equilibrated state, because (E)-**1b**[7] and $Mg(ClO_4)_2$ gave the same isomeric ratio. In a similar way, (Z)-**2** partially isomerized to (E)-**2** and (E)-**4** [(Z)-**2** : (E)-**2** : (E)-**4** = 42 : 21 : 37]; the last is much more reactive toward the Diels-Alder reaction.[6]

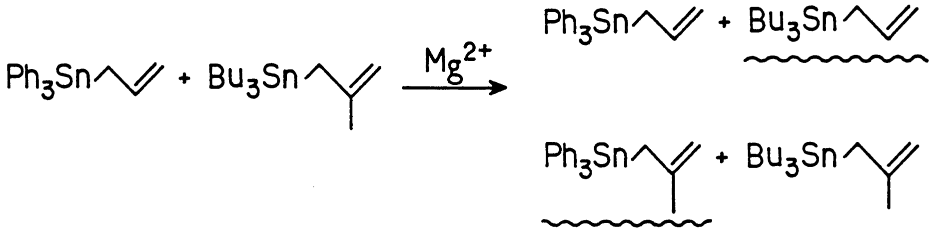
This fluxional isomerization was also effected by other alkaline earth metal perchlorates in acetonitrile, but inhibited in THF and ethanol[8] (Table 1). Thus, the isomerization appeared

Table 1. Metal-ion-catalyzed isomerization of (Z)-**1b**[a]

Metal perchlorate	Solvent	Isomeric ratio[b]	
		(E)-**1b**	(Z)-**1b**
$Mg(ClO_4)_2$	CH_3CN	79	21
	THF	5	95
	C_2H_5OH	6	94
$Ca(ClO_4)_2$	CH_3CN	79	21
$Sr(ClO_4)_2$	CH_3CN	80	20
$Ba(ClO_4)_2$	CH_3CN	81	19
$LiClO_4$	CH_3CN	48	52
$NaClO_4$	CH_3CN	10	90

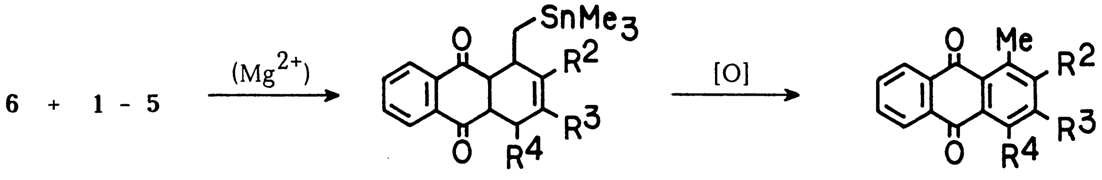
a) A mixture of the metal perchlorate (ca. 1 equiv.) and (Z)-**1b** (E/Z = 5/95) in the indicated solvent was stirred for 12 h at room temperature. b) Determined by ^1H NMR.

to be initiated by the metal ion—π-electron interaction, which was precluded by the coordination of the donating solvent to the metal ion. Lithium and sodium perchlorates were much less effective even in acetonitrile.



(2)

It should be noted that the isomerization includes the cleavage of the relatively labile Sn-C bond. The corresponding (Z)-trimethylpentadienylsilane was not isomerized under the same conditions. Moreover, when a mixture of allyltriphenyltin and tributyl(2-methylallyl)tin was treated with $Mg(ClO_4)_2$ in acetonitrile, the additional formation of the redistributed products, (2-methylallyl)triphenyltin and allyltributyltin (indicated by underlines in Eq. 2), was observed,[9] implying the intermolecular trialkylstannyl-transfer.



8

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Scheme 2.

a : $R^2=R^3=R^4=H$ b : $R^2=Me$, $R^3=R^4=H$
c : $R^3=Me$, $R^2=R^4=H$ d : $R^4=Me$, $R^2=R^3=H$

As shown in Scheme 2, the fluxional character of the PDT was applied to a part of the synthesis of peri-methylanthraquinones.[4)] PDT **2** played as **4**, whose facile preparation has not been known yet. Other 2-substituted PDTs (R^1= t-Bu, i-Pr, CH_2OMe in **2**)[5)] also underwent the isomerization and the Diels-Alder reaction with **6**. As for (E)-PDTs **1a**, **3**, and **5**, the Diels-Alder reaction proceeded smoothly[10)] in CH_2Cl_2 without any additives. It is a matter of course that the presence of the magnesium ion will make (Z)-PDTs available for the reaction.

The adducts, **8a-d**, were readily oxidized to the corresponding peri-methylanthraquinones, **9a-d**, under an oxygen atmosphere. Interestingly, the concomitant destannylation proceeded.[11)] The variously methylated anthraquinone were isolated in pure forms in good overall yields from **6** (64%, 66%, 50%, and 58% for **9a**, **b**, **c**, and **d**, respectively). Other adducts **8** (R^1= t-Bu, i-Pr, CH_2OMe) were also oxidized to **9** (55%, 46%, 32% yields from **6**, respectively).

In conclusion, it should be stressed that the isomerization can be underwent under nearly neutral conditions.[12)] Therefore, the Michael addition of the PDT to **6** was suppressed. Thus, it may be possible to apply this methodology to a more delicate substrate.

References

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5) (Z)-PDT (E/Z = 5/95) was prepared by the reaction of pentadienylpotassium and tributyltinchloride in THF in a similar manner for the preparation of **2**; see, Y. Naruta, Y. Nishigaichi, and K. Maruyama, J. Org. Chem., in press.

6) In the absence of the salt, the reaction did not proceed at all. In most cases, (Z)-1-substituted-butadienes such as (Z)-**1** and 1,1-disubstituted-butadienes such as (E)- and (Z)-**2** are not suitable for the Diels-Alder reaction, because they are apt to take the s-trans conformation; J. G. Martin and R. K. Hill, Chem. Rev., **61**, 537 (1961).

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8) Though 1-methylallyltin isomerizes readily to crotyltin in alcohol, it may follow a different mechanism. J. A. Verdone, J. A. Mangravite, N. M. Scarpa, and H. G. Kuivila, J. Am. Chem. Soc., **97**, 843 (1975).

9) Isomerization in the allylic tin system, from (Z)-tributyl-2-pentenyltin to the (E)-isomer, was also observed.

10) Though only the nucleophilic addition of PDTs has been emphasized so far, their reactivity toward the Diels-Alder reaction is extremely high. It was also found that PDT **1** reacted much faster with **6** than 1,3-pentadiene and trimethyl-2,4-pentadienylsilane.

11) The corresponding silylated adduct did not undergo oxidative desilylation. The silylated anthraquinone was obtained.

12) It has been reported that BF_3 promotes the 1,3-shift of a trialkylstannyl group in the allyltin systems. J. A. Marshall and W. Y. Gung, Tetrahedron Lett., **30**, 7349 (1989); P. Harston, J. L. Wardell, D. Marton, G. Tagliavini, and P. J. Smith, Inorg. Chim. Acta, **162**, 245 (1989); J. E. Denmark, T. Wilson, and T. M. Willson, J. Am. Chem. Soc., **110**, 984 (1988); see also Ref. 3b.

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