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HIGHLY SELECTIVE INTRODUCTION OF CONJUGATED DIENES TO GOOD DIENOPHILES, α,β-UNSATURATED CARBONYL COMPOUNDS AND p- QUINONES, WITHOUT FORMATION OF DIELS-ALDER ADDUCT

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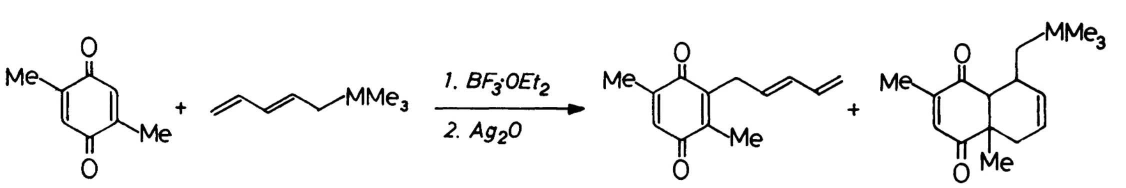
The reaction of 2,4-pentadienyltrimethylstannane with α,β-unsaturated carbonyl compounds and p-quinones in the presence of Lewis acid affords the corresponding pentadienylated products in fair to good yield without formation of any Diels-Alder adduct.

Introduction of conjugated dienes to organic molecules is very important for their versatile utility in organic synthesis.[1)] However, α,β-unsaturated carbonyl compounds, especially quinones, are excellent dienophiles, to which selective dienylation is generally difficult because of preferable formation of Diels-Alder adducts.[2)] In the course of total synthesis of naturally occurring quinones, e.g. anthracyclinones[3)] and mitomycins,[4)] increasing demand for direct 2,4-pentadienylation to the above good dienophiles made us develop a new methodology, which overcomes the expected difficulty and is of wide applicability to organic synthesis. We report here a successful 2,4-pentadienylation of quinones and α,β-unsaturated carbonyl compounds with 2,4-pentadienyltrimethylstannane in excellent selectivity.

In our previous papers,[5)] quinones were suitably allylated with allyltrialkylstannanes. This methodology was extended to the present reaction. Typical example of 2,4-pentadienylation of p-quinones was performed as follows. To a CH_2Cl_2 solution of 2,5-dimethylbenzoquinone (1.0 mmol), $BF_3 \cdot OEt_2$ (2.0 mmol) was added at -78 °C followed by the addition of 2,4-pentadienyltrimethylstannane[6)] ($\underline{1}$)(1.2 mmol) to afford the corresponding dienylated hydroquinone, which was oxidized with Ag_2O to give 2,5-dimethyl-3-(2',4'-pentadienyl)benzoquinone in an 86% isolated yield (Eq. 1a). Any Diels-Alder adduct was not detected in the reaction mixture by means of TLC and ^1H-NMR. Marked contrast was observed in the reactions used the corresponding silyl derivative ($\underline{2}$), which gave only an apparent Diels-Alder adduct under the simi-

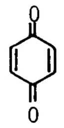
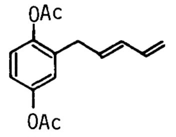
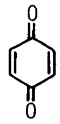
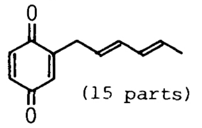
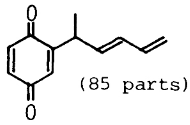
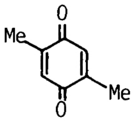
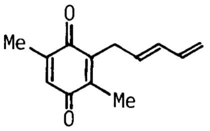
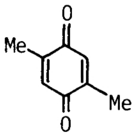
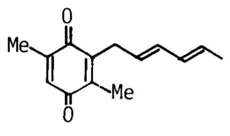
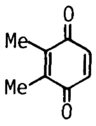
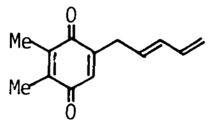
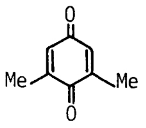
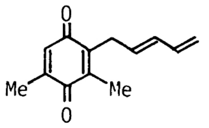
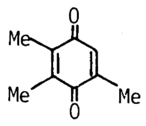
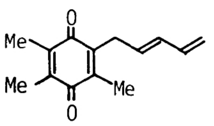
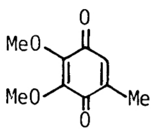
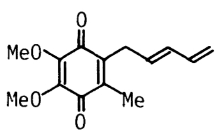
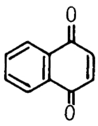
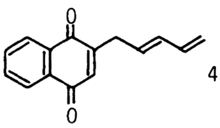
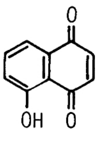
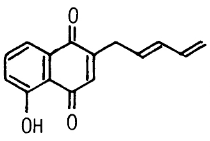


$\underline{1}$, M=Sn	86%	0%	(1a)
$\underline{2}$, M=Si	0%	91%	(1b)

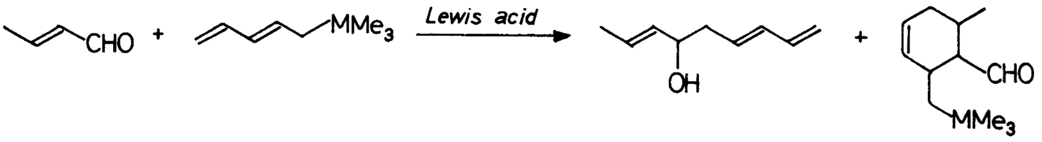
lar conditions (Eq. 1b). The remarkable difference may be attributed to the high ionizing ability of Me_3Sn group. The generality of the present reaction is obvious from Table 1.[7] In the reaction of 2,4-hexadienyltrimethylstannane (3),[8] $Me_3Sn\text{-}\overset{\alpha}{C}H_2CH=CHCH=\overset{\varepsilon}{C}HCH_3$, with quinones, regioselectivity concerning hexadienyl moiety depends on the substituents on p-quinones: in the case of p-benzoquinone, "ε adduct" was predominant product (Table 1, entry 2). On the other hand, when ortho position of p-benzoquinones was substituted, "α adduct" was exclusively obtained (Table 1, entry 4).[9]

The generality observed in the dienylation of quinones is also realized in the reaction of α,β-unsaturated carbonyl compounds. Crotonaldehyde was successfully converted to 1,3,7-nonatrien-6-ol in a 70% isolated yield ($1/BF_3OEt_2$/-78 °C /0.5 h) (Eq. 2a). When the silyl derivative 2 was utilized, only the cyclic adduct was reported to be obtained (Eq. 2b).[2a] Remarkable difference between the stannanes and the silanes was also observed. Other α,β- and α,β,γ,δ-unsaturated aldehydes react-

Table 1. 2,4-Penta- and Hexadienylation of p-Quinones with Stannyl Reagents[a)]

Entry	Quinone	Stannane	Product[b)]	Isolated yield / %
1		1		67(94)[c,d)]
2		3	 (15 parts)  (85 parts)	56[e)]
3		1		82(86)[c,e)]
4		3		52[e)]
5		1		76[e)]
6		1		38[e)]
7		1		75[e)]
8		1		61[e)]
9		1		43(58)[c,e)]
10		1		23(39)[c,e)]

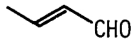
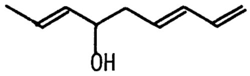
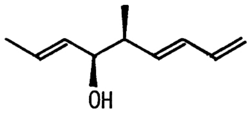
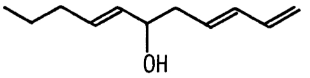
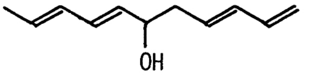
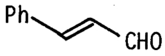
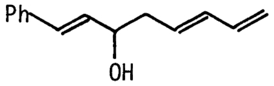
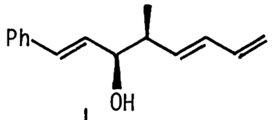
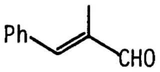
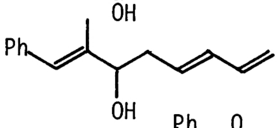
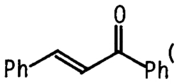
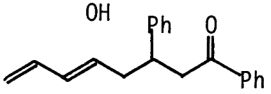
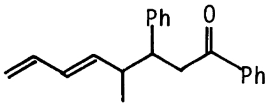
[a)] All reactions were performed as follows; to 10 ml of anhydrous CH_2Cl_2 solution of p-quinone (1.0 mmol), $BF_3\cdot OEt_2$ (2.0 mmol) was added at -78 °C. After successive addition of the organostannane (1.2 mmol), the reaction mixture was stirred for 1 h. [b)] Satisfactory IR, NMR, and mass spectral data were obtained. [c)] Yield in parentheses was determined by ^{1}H-NMR. [d)] Product was isolated after esterification with acetic anhydride-pyridine for the sake of the instability of the corresponding hydroquinone. [e)] Product was isolated after mild oxidation with silver oxide.



1, M=Sn 70% 0% (2a)

2, M=Si 0% 40% (2b)[2a)]

Table 2. 2,4-Penta- and Hexadienylation of α,β-Unsaturated Carbonyl Compounds with Stannyl Reagents

Entry	Substrate	Stannanes	Conditions[a)]	Products[b)]	Isolated yield / %
1	 (I)	1	A		70
2	I	3	A		51[c)]
3		1	B		50
4		1	B		36
5	 (II)	1	C		73
6	II	3	C		32[d)]
7		1	C		54
8	 (III)	1	D		70[f)]
9	III	3	D		58[e)]

[a)] Every dienylation was performed in 1.0 mmol scale according to the similar method shown in Table 1. Reaction conditions, A: BF_3OEt_2; -78 °C; 0.5 h. B: BF_3OEt_2; -78 °C–-50 °C; 0.5 h. C: BF_3OEt_2; -78 °C–-10 °C; 1 h. D: $AlCl_3$ (as 2 M ether solution); -78 °C–-10 °C; 1 h. [b)] Satisfactory IR, NMR, and mass spectral data were obtained. [d)] Erythro:threo=82:18. [e)] The starting ketone was recovered in 43% yield. [f)] Several ketones reacted similarly.

ed in the 1,2 fashion to afford the corresponding unsaturated alcohol in fair to good yield (Table 2). α,β-Unsaturated ketone afforded the corresponding 1,4 adducts in the reaction with 1 or 3. High erythro selectivity was attained in the reaction of 3 with aldehydes (Table 2, entries 2 and 6).[10)]

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References

1) For reviews of intramolecular [4+2] cycloaddition, see W.Oppolzer, Angew. Chem., Int. Ed. Engl., 16, 10 (1977), Heterocycles, 14, 1615 (1980); G.Brieger and J.N.Bennett, Chem. Rev., 80, 63 (1980).

2) Recently the reaction of 2 with α,β-unsaturated carbonyl compounds under the presence[2a)] or absence[2b)] of Lewis acid was reported to give preferentially Diels-Alder adducts, see a) D. Seyferth, J.Pornet, and R.M.Weinstein, Organometallics, 1, 1651 (1982); b) H.Hosomi, M.Saito, and H.Sakurai, Tetrahedron Lett., 21, 3783 (1980).

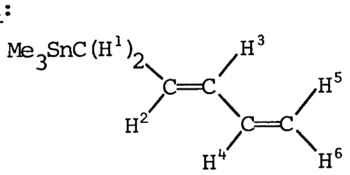
3) Y.Naruta, M.Kashiwagi, Y.Nishigaichi, H.Uno, and K.Maruyama, Chem. Lett., the following paper.

4) Y.Naruta, Y.Arita, N.Nagai, H.Uno, and K.Maruyama, Chem. Lett., 1982, 1859.

5) Y.Naruta, J. Am. Chem. Soc., 102, 3774 (1980); Y.Naruta, J. Org. Chem., 45, 4097 (1980); K.Maruyama, A.Takuwa, Y.Naruta, K.Satao, and O.Soga, Chem. Lett., 1981, 47; Y.Naruta, J. Chem. Soc., Chem. Commun., 1981, 1227.

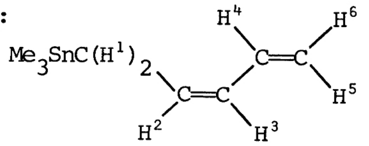
6) 2,4-Pentadienylstannane was prepared by the reaction of pentadienyl lithium with chlorotrimethylstannane and has a boiling point of 105 °C/1.6 kPa (Kugelrohr) and is the mixture of the stereoisomers (trans:cis=69:31), according to its 400 MHz ^{1}H-NMR spectrum in $CDCl_3$.

trans-1:



δ 0.11(9H, dd, $J_{^{119}Sn-H}$=53.4 Hz, $J_{^{117}Sn-H}$=51.0 Hz, $(CH_3)_3$-Sn), 1.81(1H, d, $J_{H^1-H^2}$=7.6 Hz, H^1), 4.79(1H, dd, $J_{H^4-H^6}$=10.1 Hz, $J_{H^5-H^6}$=1.8 Hz, H^6), 4.94(1H, dd, $J_{H^4-H^5}$=17.1 Hz, $J_{H^5-H^6}$=1.8 Hz, H^5), 5.84(1H, dt, $J_{H^2-H^3}$=15.0 Hz, $J_{H^1-H^2}$=7.6 Hz, H^2), 5.91(1H, dd, $J_{H^2-H^3}$=15.0 Hz, $J_{H^3-H^4}$=9.2 Hz, H^3), 6.28(1H, ddd, $J_{H^4-H^5}$=17.1 Hz, $J_{H^4-H^6}$=10.1 Hz, $J_{H^3-H^4}$=9.2 Hz, H^4).

cis-1:

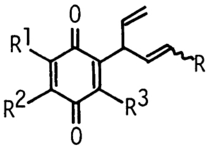


δ 0.12(9H, dd, $J_{^{119}Sn-H}$=53.4 Hz, $J_{^{117}Sn-H}$=50.9 Hz, $(CH_3)_3$-Sn), 1.92(1H, d, $J_{H^1-H^2}$=9.5 Hz, H^1), 4.96(1H, dd, $J_{H^4-H^6}$=10.4 Hz, $J_{H^5-H^6}$=2.4 Hz, H^6), 5.08(1H, dd, $J_{H^4-H^5}$=15.9 Hz, $J_{H^5-H^6}$=2.4 Hz, H^5), 5.64(1H, dt, $J_{H^2-H^3}$=10.7 Hz, $J_{H^1-H^2}$=9.5 Hz, H^2), 6.58(1H, ddd, $J_{H^4-H^5}$=15.9 Hz, $J_{H^3-H^4}$=11.0 Hz, $J_{H^4-H^6}$=10.4 Hz, H^4).

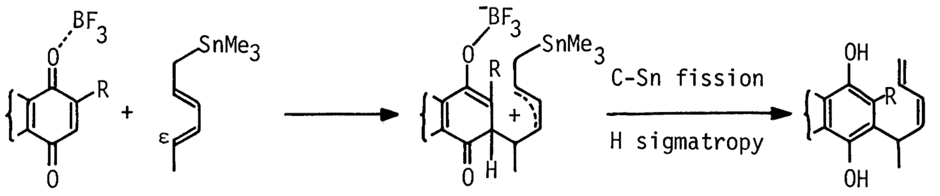
7) The possible γ adduct 4 was not obtained except in the entry 6 (19% isolated yield).

8) Stereoisomeric mixture was used.

9) If a polar, stepwise process shown in Eq. 3 were taking place in the reaction of quinone with 3, ε adducts would be exclusively obtained in every case.



4 R=H or Me



(3)

10) Similar excellent stereoselectivity was reported in the reaction of crotylstannane with aldehyde, see Y.Yamamoto, H.Yatagai, Y.Naruta, and K.Maruyama, J. Am. Chem. Soc., 102, 7107 (1980).

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