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A Novel Method for the Generation of *o* - Quinodimethane by Selenium - Induced Fragmentation of *o* -Vinyl benzyltributylstannane

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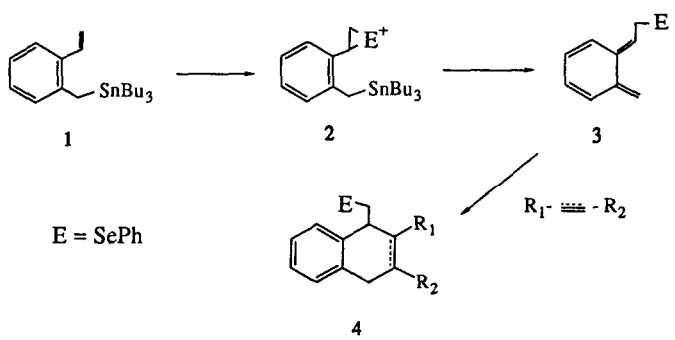
Abstract : *Treatment of o-vinyl benzyltributylstannane 1 with N-phenylselenophthalimide in the presence of $ZnBr_2$ at 0° can generate o-quinodimethane 3, which can then undergo Diels-Alder reactions.*

After the utility of *o* -quinodimethanes in organic synthesis based on Diels-Alder cycloaddition was recognized, a variety of methods for the generation of these reactive intermediates have been developed.[1] Included among them are the thermal ring opening of benzocyclobutenes[2], cheletropic extrusion of sulfur dioxide from a benzo[c]thiophene 2, 2-dioxide[3], photoenolization of *o* - alkylphenyl ketone[4], and various 1, 4-elimination of *o* -xylene derivatives.[5] In the latter approach, Sano and coworkers[5c] reported an efficient generation of *o* -quinodimethanes by proton induced 1, 4-elimination of *o* - (1-hydroxyalkyl) benzyltributyl-stannanes. This method represents the first example to utilize the potential of the carbon-tin σ bond as a latent nucleophile in this area. In this report, we wish to introduce a novel and mild method for the generation of *o* -quinodimethane **3** from o-vinyl benzyltributylstannane **1**[6] via eletrophile-mediated intenal cleavage reaction of the carbon-tin σ bond, as illustrated below.



In the event, the generation of *o*-quinodimethane **3** could be triggered by addition of N-phenylselenophthalimide(NPSP) to o-vinyl benzyltributylstannane **1** in the presence of a stoichiometric amount of zinc bromide. This reaction proceeds rapidly in methylene chloride at 0° C, presumably via the intermediacy of the initially formed selenium species **2** which undergoes electrophilic cleavage reaction by internal stannane leading to **3**. The formation of *o*-quinodimethane **3** in the present reaction was manifested in the successful intermolecular Diels-Alder trappings with typical dienophiles. The results are summarized in Table 1. As evidenced in Table 1, this procedure allows convenient access to the synthesis of aryl tetralins containing the synthetically useful phenylseleno group in good yields. Furthermore, the cycloaddition reactions of **3** with certain dienophiles proceed with a high degree of stereoselectivity. For example, cyclic dienophiles such as maleic anhydride, N-methylmaleimide, and naphthoquinone gave only 1, 2-cis adducts **5**, **6**, and **16** via endo addition (Entries 1, 2, and 8). No other isomers were detected in ^{1}H - and ^{13}C - NMR of the crude reaction mixture. The endo configuration of these adducts was deduced by measuring coupling constant ($J_{H_1-H_2}$) between the benzylic and ring junction protons.[7] The addition of **3** to methyl acrylate and acrylonitrile also took place both stero- and regioselectively to yield predominantly 1, 2 - cis, endo adduct **11** (8.7:1) and **13** (9.2:1), respectively(Entries 5 and 6). In contrast, analoguous reaction with dimethyl fumarate and dimethyl maleate proceeded with less pronounced endo vs exo selectivity (Entries 3 and 4). The reaction denoted in Entry 7 is also noteworthy in that acetylenic dienophiles often afford olefinic isomerized adducts.[5e] In our case, however, the reaction conditions are neutral and mild enough to yield exclusively 1, 4 - dihydronaphthalene **15**.

In summary, the ease of preparation combined with the mild conditions required to effect both generation of *o*-quinodimethane and the cycloaddition reactions makes this method the attractive and viable alternative to the existing methods. Further extensions of the present strategy utilizing other eletrophiles as initiators are currently in progress.

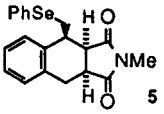
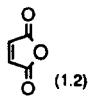
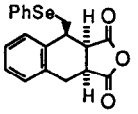
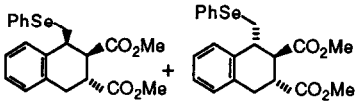
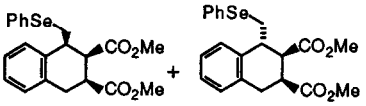
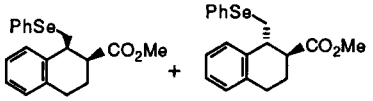
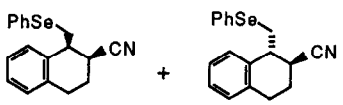
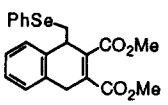
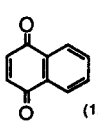
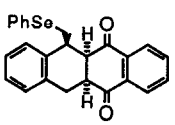
Typical Experimental Procedure : To a stirred solution of 1 (203 mg, 0.5 mmol) and N-methylmaleimide (67 mg, 0.6 mmol) in dry methylene chloride(1ml) under argon at 0° C was added N-phenylselenophthalimide (167 mg, 0.55 mmol) followed by zinc bromide (135mg, 0.6 mmol). After stirring at 0° C for 1.5h, the resulting pale yellow mixture was diluted with ethyl ether (15 ml) and filtered. The filtrate was washed with water, dried($MgSO_4$), and concentrated. The residue obtained was dissolved in acetonitrile(20 ml) and washed with hexane(15 ml, x5) to remove organotin products. The acetonitrile layer was concentrated under reduced pressure and the residue purified by flash chromatography on silica gel eluting with hexane / ethyl acetate (4 /1) to give **5** (180 mg, 94%) as a white solid .

Acknowledgment. I am grateful to Professor George A. Kraus at Iowa State Univ. for helpful discussions.

REFERENCES AND NOTES

1. For a review on this area, see : (a) Martin, N. ; Seoane, C. ; Hanack, M. *Org. Pre. Proc. Int*. **1991**, 23, 237-272. (b) Charlton, J. L. ; Alauddin, M. M. *Tetrahedron* , **1987**, *43*, 2873-2889. (c) Funk, R. L. ; Vollhardt, K. P. C. *Chem. Soc. Rev*. **1980**, *9*, 41-61. (d) Oppolzer, W. *Synthesis*, **1978**, 793-802. (e) Kametani, T. ; Nemoto, H. *Tetrahedron* , **1981**, 37, 3-16.

Table 1. Cycloadditions of *o*-Quinodimethane 3 with Dienophiles[a]

Entry	Dienophile (Molar equiv)	Product	Ratio[b]	Yield[c] (%)
1	 (1.2)	 5	> 9.9 : 0.1	94[d]
2	 (1.2)	 6	> 9.9 : 0.1	92[d,g]
3	trans $MeO_2CCH=CHCO_2Me$ (3)	 7 + 8	1.2 : 1	84
4	cis $MeO_2CCH=CHCO_2Me$ (3)	 9 + 10	2.5 : 1	42
5	$CH_2=CHCO_2Me$ (3)	 11 + 12	8.7 : 1	71[e]
6	$CH_2=CHCN$ (3)	 13 + 14	9.2 : 1	88[f]
7	$MeO_2CCH\equiv CHCO_2Me$ (1.5)	 15	–	52[d]
8	 (1.5)	 16	> 9.9 : 0.1	84[h]

[a]All reactions were carried out at 0°C in methylene chloride with NPSP(1.1 equiv) in the presence of $ZnBr_2$ (1.2 equiv). [b] Isomeric ratios (endo vs exo) were determined on the crude reaction mixture by 300MHz ^{1}H- NMR and /or HPLC. [c]Isolated yields are based on starting material 1. [d] Ref. 8. [e] Contaminated with another regioadduct (<5%). [f] Ref. 9. [g] Purified by recrystallization from hexane/ethyl acetate. [h] Purified by recrystallization from toluene.

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3. (a)Oppolzer, W. ; Battig, K.; Petrzilka, M. *Helv. Chim. Acta*, **1978**, *61*, 1945-1947. (b) Durst, T. ; Kozma, E. C. ; Charlton, J. L. *J. Org. Chem.* **1985**, *50*, 4829-4833.
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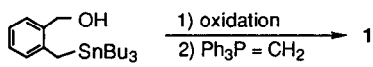
5. (a) Cava, M.P. ; Deana, A. A. ; Muth, K. *J. Am. Chem. Soc.* **1959**, *81*, 6458-6460. (b) Ito, Y. ; Amino, Y. ; Nakatsuka, M. ; Saegusa, T. *J. Am. Chem. Soc.* **1983**, *105*, 1586-1590. (c) Sano, H. ; Ohtsuka, H.; Migita, T. *J. Am. Chem. Soc.* **1988**, *110*, 2014-2015.
6. The requisite precursor **1** for the present study was easily prepared in 71% overall yield from the known stannane **17**[5c] by oxidation ($NCS\text{-}Me_2S/Et_3N$/toluene/ -30°C/3h) followed by Wittig reaction ($PPh_3CH_3^+Br^-$/n-BuLi/Et_2O/0°C). **1** : ^{1}H-NMR (80MHz, $CDCl_3$); δ 0.68 - 1.47 (m, 27H), 2.36 (s, 2H), 5.15 -5.68(m, 2H), 6.91 -7.32 (m, 5H).



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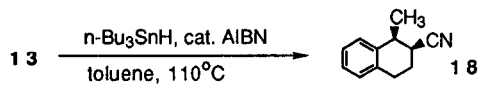
7. Adducts **5** and **6** exhibit a $J_{1,2}$ = 5.4 Hz and 5.3 Hz respectively in accord with data of Jefford and Houk[2] who finds $J_{1,2}$ = 5 - 6 Hz for analoguous endo adducts and $J_{1,2}$ = 2 - 3 Hz for the corresponding exo isomers.
8. **5** : mp ; 106.6 -107.4° C. ^{1}H-NMR(300MHz, $CDCl_3$) ; δ 2.65(s, 3H), 2.80(dd, 1H, J =14.7Hz, J = 7.2Hz), 3.02 -3.10 (m. 1H), 3.19(dd, 1H, J =14.7Hz, J =2.3 Hz), 3.34(ddd, 1H, J = 9.0Hz, J= 7.2Hz, J= 2.3 Hz), 3.73(dd, 1H, J=12.5Hz, J=6.2Hz), 3.79(dd, 1H, J=9.0Hz, J=5.3Hz), 3.83 (dd, 1H, J = 12.5Hz, J= 9.4 Hz), 7.17 -7.58(m, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) ; δ 24.46, 27.17, 29.70, 39.22, 40.65, 42.69, 123.57, 124.35, 127.18, 127.35, 127.38, 127.97, 129.25, 132.79, 134.26, 137.11, 177.45, 179.07. **6** : mp ; 121.7 -123° C. ^{1}H-NMR(300MHz, $CDCl_3$) ; δ 2.81 (dd, 1H, J = 15.0 Hz, J =7.1Hz), 2.90 -3.05 (m. 1H), 3.17(dd, 1H, J=15.0Hz, J =2.0 Hz), 3.59(ddd, 1H, J=10.1Hz, J=7.1Hz, J=2.0 Hz), 3.64 - 3.79 (m, 2H), 4.08 (dd, 1H, J = 10.1Hz, J= 5.4 Hz), 7.17 -7.58(m, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) ; δ 26.47, 29.72, 36.68, 41.31, 43.29, 124.46, 127.53, 127.98, 128.06, 128.23, 129.31, 129.40, 133.03, 133.97, 136.52, 171.10, 173.27. **15** : ^{1}H-NMR(300MHz, $CDCl_3$) ; δ 3.19(dd, 1H, J =12.3Hz, J= 6.6Hz), 3.40(dd, 1H, J =12.3Hz, J=4.5 Hz), 3.65(dd, 1H, J=21.3Hz, J=1.4 Hz), 3.76(s, 3H), 3.81(s, 3H), 3.86(dd, 1H, J = 21.3Hz, J=2.5 Hz), 4.20 -4.22(m, 1H), 7.15 -7.36(m, 9H). ^{13}C-NMR (75 MHz, $CDCl_3$) ; δ 32.09, 35.45, 42.06, 52.28, 52.33, 126.65, 126.81, 127.63, 127.74, 128.12, 128.83, 130.33, 132.61, 132.68, 135.47, 135.88, 136.59, 167.31, 168.08.
9. To assign the relative stereochemistry, adduct **13** was converted to **18** in 84% yield by reductive removal of the phenylseleno group as shown below. 1.2 - cis configuration of **18** was established by decoupling technique which revealed a sharp doublet ($J_{1,2}$ = 5.1Hz) at δ 3.17 ascribed to a benzylic hydrogen.



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