

A Convenient Method for the Generation of *o*-Quinodimethanes by Proton-Induced 1,4-Elimination of *o*-(1-Hydroxyalkyl)benzyltributylstannanes

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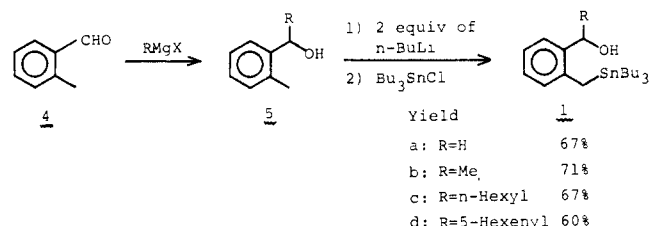
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There has been great interest in the synthesis of polycyclic compounds using *o*-quinodimethane intermediates, and various methods for the generation of *o*-quinodimethane intermediates such as metal¹ or anion² induced or thermal or photochemical elimination³ reactions of the corresponding precursors have been reported. By using these methodologies⁴ or thermolysis reactions of benzocyclobutene derivatives,⁵ numerous syntheses of steroidal frameworks have been developed.

We wish to report a convenient and new type of method for the generation of *o*-quinodimethane intermediates **2** by proton induced 1,4-elimination⁶ of *o*-(1-hydroxyalkyl)benzyltributylstannanes **1** followed by their cycloadditions with dienophiles.

First, we found that one-step synthesis of the precursor of *o*-quinodimethane, *o*-(hydroxymethyl)benzyltributylstannane **1a**,⁷



was successfully accomplished via stannylation of the dianion of *o*-methylbenzyl alcohol.⁸ Furthermore, the precursors of *o*-quinodimethanes which have alkyl substituents at the α position could be easily prepared by extremely short steps. Thus, *o*-(1-hydroxyalkyl)benzyltributylstannanes **1b–d** were obtained by

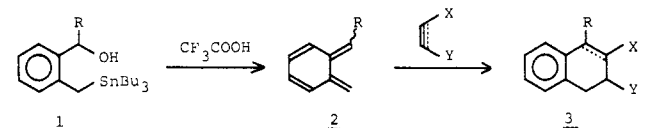
Table I. Cycloadditions of *o*-Quinodimethanes with Dienophiles^a

1	dienophile (molar equiv)	product	yield ^b (%)
	(3)		96 ^c
	<i>cis</i> -MeO ₂ CCH=CHCO ₂ Me (3)		85 ^c
	<i>trans</i> -NCCH=CHCN (2)		94 ^d
	CH ₂ =CHCOOMe (3)		72 ^e
	(3)		91 ^{f,g}
	MeO ₂ C≡CCO ₂ Me (1.5)		81 ^h

^a The reaction was carried out with 2 equiv of CF₃COOH in CH₂Cl₂ at room temperature for 1 h. ^b Yields are based on **1** used. ^c Reference 11. ^d Reference 12. ^e Reference 1f. ^f A *cis* and *trans* mixture. ^g Reference 13. ^h Reference 14.

alkylation of *o*-tolualdehyde **4** with Grignard reagent followed by similar stannylation of the resulting alcohols **5**.

The stannanes **1** were distillable compounds and stable in air. The generation of *o*-quinodimethane intermediates followed by their intermolecular cycloaddition with electron deficient olefins or acetylenes could be readily performed under mild conditions.



A typical procedure is as follows. To a solution of *o*-(hydroxymethyl)benzyltributylstannane **1a** (500 mg, 1.22 mmol) and maleic anhydride (358 mg, 3.65 mmol) in dichloromethane (1.0 mL) was added trifluoroacetic acid (0.19 mL, 2.43 mmol) at room temperature, and the mixture was stirred at the temperature for 1 h. After removal of the solvent, excess trifluoroacetic acid, and maleic anhydride under reduced pressure, *n*-hexane (5 mL) was added to the mixture, and the resulting mixture was filtered. Washing the remaining solid with *n*-hexane (20 mL) gave 235 mg (96% yield) of 1,2,3,4-tetrahydronaphthalene-2,3-dicarboxylic anhydride **3-i**.¹¹

Some examples of cycloadditions of *o*-quinodimethanes with dienophiles are summarized in Table I. The generality of this reaction is indicated by the finding that both nonsubstituted and α -substituted *o*-quinodimethanes are generated to produce cycloadducts in excellent yields.

Finally, we focussed on the application of the present method for intermolecular reactions to intramolecular cycloadditions of *o*-quinodimethanes leading to polycycles. When a solution of trifluoroacetic acid (0.1 mL, 1.2 mmol) in toluene (30 mL) was added dropwise over 5 h to a refluxing solution of *o*-(1-hydroxyhept-6-enyl)benzyltributylstannane (**1d**)⁹ (500 mg, 1.01 mmol) in toluene (50 mL), octahydrophenanthrene (**6**)¹⁰ which has *trans* stereochemistry was produced in 75% yield.

(9) **1d**: IR (neat) 3350, 1600, 1440, 1040 cm⁻¹; ¹H NMR (CCl₄) δ 0.5–2.4 (m, 36 H), 2.3 (s, 2 H), 4.5–6.3 (m, 4 H), 6.8–7.5 (m, 4 H).

(10) **6**: ¹³C NMR (CDCl₃) δ 26.3, 26.9, 29.8, 30.6, 30.9, 34.3, 49.6, 43.7, 125.1, 125.2, 125.3, 128.7, 136.7, 140.2. The *trans* stereochemistry of **6** was confirmed by comparison of its ¹³C NMR spectrum with that reported.^{2c}

(11) Müller, P.; Rey, M. *Helv. Chim. Acta* **1982**, 65, 1157.

(1) (a) Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1957**, 79, 1701. (b) Cava, M. P.; Deana, A. A.; Muth, K. *Ibid.* **1959**, 81, 6458. (c) Alder, K.; Fremery, M. *Tetrahedron* **1961**, 14, 190. (d) Sisido, K.; Kusano, N.; Noyori, R.; Nozaki, Y.; Simosaka, M.; Nozaki, H. *J. Polymer Sci., Part A* **1963**, 1, 2101. (e) Nozaki, H.; Noyori, R. *Tetrahedron* **1966**, 22, 2163. (f) Ito, Y.; Yonezawa, K.; Saegusa, T. *J. Org. Chem.* **1974**, 39, 2769. (g) Han, B. H.; Boudjouk, P. *Ibid.* **1982**, 47, 751. (h) Chew, S.; Ferrier, R. J. *J. Chem. Soc., Chem. Commun.* **1984**, 911.

(2) (a) Kerdesky, F. A. J.; Ardecky, R. J.; Lakshmikantham, M. V.; Cava, M. P. *J. Am. Chem. Soc.* **1981**, 103, 1992. (b) McOmie, F. W.; Perry, D. H. *Synthesis* **1973**, 416. (c) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, 102, 863. (d) Ito, Y.; Nakatsuka, M.; Saegusa, T. *Ibid.* **1982**, 104, 7609. (e) Trahanovsky, W. S.; Macias, J. R. *Ibid.* **1986**, 108, 6820.

(3) (a) Errede, L. A. *J. Am. Chem. Soc.* **1961**, 83, 949. (b) Cava, M. P.; Deana, A. A. *Ibid.* **1959**, 81, 4266. (c) Cava, M. P.; Mitchell, M. J.; Deana, A. A. *J. Org. Chem.* **1960**, 25, 1481. (d) Sisido, K.; Noyori, R.; Nozaki, H. *J. Am. Chem. Soc.* **1962**, 84, 3562. (e) Quinkert, G.; Opitz, K.; Wiersdorff, W.-W.; Weinlich, J. *Tetrahedron Lett.* **1963**, 1863. (f) Flynn, C. R.; Michl, J. *J. Am. Chem. Soc.* **1974**, 96, 3280.

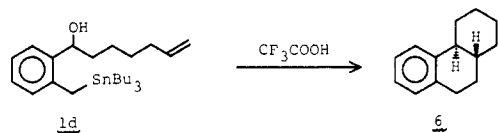
(4) (a) Oppolzer, W.; Roberts, D. A.; Bird, T. G. C. *Helv. Chim. Acta* **1979**, 62, 2017. (b) Nicolaou, K. C.; Barnette, W. E.; Ma, P. *J. Org. Chem.* **1980**, 45, 1463. (c) Djuric, S.; Sarkar, T.; Magnus, P. *J. Am. Chem. Soc.* **1980**, 102, 6885. (d) Ito, Y.; Nakatsuka, M.; Saegusa, T. *Ibid.* **1981**, 103, 476. (e) Ito, Y.; Miyata, S.; Nakatsuka, M.; Saegusa, T. *Ibid.* **1981**, 103, 5250.

(5) (a) Oppolzer, W.; Bättig, K.; Petrzilka, M. *Helv. Chim. Acta* **1978**, 61, 1945. (b) Kametani, T.; Nemoto, H.; Ishikawa, H.; Shiroyama, K.; Matsumoto, H.; Fukumoto, K. *J. Am. Chem. Soc.* **1977**, 99, 3461. (c) Grieco, P. A.; Takigawa, T.; Schlinger, W. J. *J. Org. Chem.* **1980**, 45, 2247. (d) Funk, R. L.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1980**, 102, 5245 and 5253. (e) Oppolzer, W. *Synthesis* **1978**, 793. (f) Kametani, T. *Pure Appl. Chem.* **1979**, 51, 747. (g) Funk, R. L.; Vollhardt, K. P. C. *Chem. Soc. Rev.* **1980**, 9, 41.

(6) It is known that proton-induced β -elimination of β -hydroxystannane proceeds to give an alkene: Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1982**, 21, 410.

(7) **1a**: IR (neat) 3340, 1605, 1460, 760 cm⁻¹; ¹H NMR (CCl₄) δ 0.5–2.0 (m, 28 H), 2.3 (s, 2 H), 4.5 (d, 2 H, *J* = 6 Hz), 6.8–7.3 (m, 4 H).

(8) Alkylation of dianion of *o*-methylbenzyl alcohol has been reported: Braun, M.; Ringer, E. *Tetrahedron Lett.* **1983**, 24, 1233.



Efforts to further expand the scope and utility of this methodology to polycyclic systems are under active investigation in our laboratory.

Supplementary Material Available: ^1H NMR data for the stannanes **1** and cycloadducts **3** (1 page). Ordering information is given on any current masthead page.

(12) The trans stereochemistry of **3-iii** was confirmed by comparison of the corresponding hydrolysis compound's mp (229–230 °C) with that reported: Haworth, R. D.; Slinger, F. H. *J. Chem. Soc.* **1940**, 1321.

(13) **3-v**: ^1H NMR (CDCl_3) δ 1.7 (d, 3 H, $J = 7$ Hz), 2.8–3.8 (m, 5 H), 7.1–7.4 (m, 4 H).

(14) **3-vi**: ^1H NMR (CDCl_3) δ 0.7–2.0 (m, 13 H), 3.6–4.0 (m, 3 H), 3.8 (s, 3 H), 3.83 (s, 3 H), 7.2 (s, 4 H).

Fingerprints of the C–N Bond Formation between Ethylenediamine and an Aldose on Cobalt(III) Complexes. Isotopic Multiplets in the ^{13}C NMR Spectra of Cobalt(III) Complexes with Partially Deuteriated Coordinated Amino Groups

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Interligand reactions on transition-metal complexes accompanied by the formation of new C–N bond(s)^{3,4} have been of great

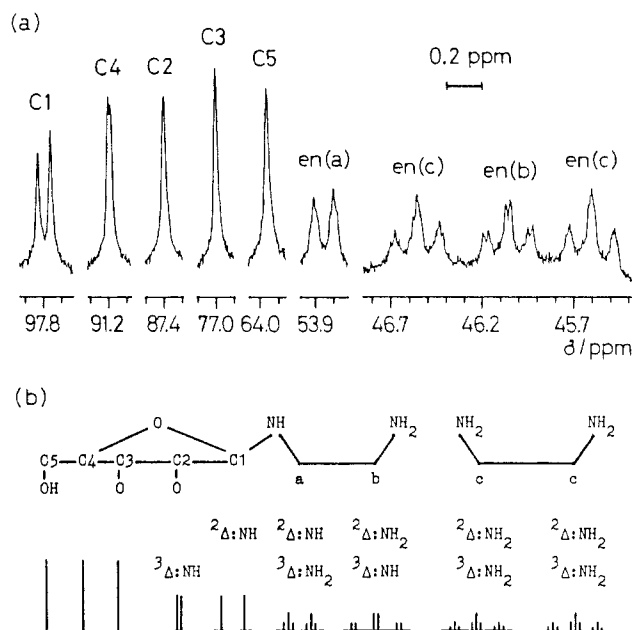


Figure 1. (a) Isotopic multiplets in the low power broad band proton decoupled 100 MHz ^{13}C NMR spectrum of $[\text{Co}(\text{D-Rib-en})(\text{en})]^+$ (**1**) in a neutral ca. 1:1 H_2O – D_2O mixture. (b) Possible two- and three-bond isotope effects and expected isotopic multiplet patterns of **1**.

interest in macrocyclic chemistry and coordination chemistry. In these investigations, it is desirable to identify the C–N bond formation unambiguously and easily. We wish to present here a simple method for identification of the C–N bond formation in diamagnetic complexes.

We have already reported the synthesis and characterization of Co(III) complexes containing an *N*-glycoside derived from ethylenediamine (en) and an aldose.⁴ In the report, the formation of a new C–N bond has been presumed according to the chemical shifts of the ^{13}C signals from the en units in their routine ^{13}C NMR spectra. One of the signals assigned to the en carbons, which presumably corresponds to the carbon atom adjacent to the glycosidic nitrogen, appears at 7–8 ppm downfield from the other three.

Deuterium isotope effects on ^{13}C NMR chemical shifts are very helpful in spectral assignments and molecular structure determination.^{5–14} Partial deuteration of exchangeable protons in amines,^{5–7} amides,⁸ alcohols,^{9,10} carbohydrates,^{11,12} and nucleosides,⁷ etc. leads to isotopic multiplets in ^{13}C NMR spectra observed under slow exchange conditions. In the spectra of the cobalt(III)–amine complexes, indeed, isotopic multiplets corresponding to isotopomers of coordinated amino groups could be observed even in neutral H_2O – D_2O mixtures.⁶ We applied this technique to the cobalt-

(1) The University of Tokyo.

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(3) (a) Curtis, N. F. *Coord. Chem. Rev.* **1968**, *3*, 3–47. Busch, D. H.; Farmery, K.; Goedken, V. L.; Katovic, V.; Melynyk, A. C.; Sperati, C. R.; Tokei, N. *Adv. Chem. Ser.* **1971**, no. 100, 44–78. Christensen, J. J.; Eatough, D. J.; Izatt, R. M. *Chem. Rev.* **1974**, *74*, 351–384. (b) Gainsford, A. R.; Pizer, A. R.; Sargeson, A. M.; Whimp, P. O. *J. Am. Chem. Soc.* **1981**, *103*, 792–805. Lawson, P. J.; McCarthy, M. G.; Sargeson, A. M. *Ibid.* **1982**, *104*, 6710–6716. Dixon, N. E.; Sargeson, A. M. *Ibid.* **1982**, *104*, 6716–6725. (c) Sargeson, A. M. *Chem. Br.* **1979**, *15*, 23–27. Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M. *Inorg. Synth.* **1980**, *20*, 85–86. Gahan, L. R.; Hambley, T. W.; Sargeson, A. M.; Snow, M. R. *Inorg. Chem.* **1982**, *21*, 2699–2706. Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Herlt, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. J. *Am. Chem. Soc.* **1982**, *104*, 6016–6025. Boucher, H. A.; Lawrence, G. A.; Lay, P. A.; Sargeson, A. M.; Bond, A. M.; Sangster, D. F.; Sullivan, J. C. *J. Am. Chem. Soc.* **1983**, *105*, 4652–4661. Harrowfield, J. M.; Herlt, A. J.; Lay, P. A.; Sargeson, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 5503–5505. Geue, R. J.; Hambley, T. W.; Harrowfield, J. M.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5478–5488. Geue, R. J.; McCarthy, M. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 8282–8291. Comba, P.; Creaser, I. I.; Gahan, L. R.; Harrowfield, J. M.; Lawrence, G. A.; Martin, L. L.; Mau, A. W. H.; Sargeson, A. M.; Sasse, W. H. F.; Snow, M. R. *Inorg. Chem.* **1986**, *25*, 384–389. (d) Yashiro, M.; Shimada, A.; Usui, T.; Yano, S.; Kobayashi, K.; Sakurai, T.; Yoshikawa, S. *J. Am. Chem. Soc.* **1985**, *107*, 4351–4353. (e) Takizawa, S.; Sugita, H.; Yano, S.; Yoshikawa, S. *J. Am. Chem. Soc.* **1980**, *102*, 7969–7971. Tsubomura, T.; Yano, S.; Toriumi, K.; Ito, K.; Yoshikawa, S. *Polyhedron* **1983**, *2*, 123–124. Shioi, H.; Yano, S.; Toriumi, K.; Ito, T.; Yoshikawa, S. *J. Chem. Soc., Chem. Commun.* **1983**, 201–202. Tsubomura, T.; Yano, S.; Toriumi, K.; Ito, T.; Ito, H.; Yoshikawa, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1833–1838. Yano, S.; Sakai, Y.; Toriumi, K.; Ito, T.; Ito, H.; Yoshikawa, S. *Inorg. Chem.* **1985**, *24*, 498–504. Tsubomura, T.; Yano, S.; Toriumi, K.; Yoshikawa, S. *Inorg. Chem.* **1985**, *24*, 3218–3223. Tanase, T.; Kurihara, K.; Yano, S.; Kobayashi, K.; Sakurai, T.; Yoshikawa, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1562–1563.

(4) Ishida, K.; Yano, S.; Yoshikawa, S. *Inorg. Chem.* **1986**, *25*, 3552–3554.

(5) Reuben, J. *J. Am. Chem. Soc.* **1985**, *107*, 1433–1435.

(6) Yashiro, M.; Yano, S.; Yoshikawa, S. *J. Am. Chem. Soc.* **1986**, *108*, 1096–1097.

(7) Reuben, J. *J. Am. Chem. Soc.* **1986**, *108*, 1082–1083; **1987**, *109*, 316–321.

(8) (a) Feeney, J.; Partington, P.; Roberts, G. C. K. *J. Magn. Reson.* **1974**, *13*, 268–274. (b) Newmark, R. A.; Hill, J. R. *Ibid.* **1976**, *21*, 1–7. (c) Hawkes, G. E.; Randall, E. W.; Hull, W. E.; Gattegno, D.; Conti, F. *Biochemistry* **1978**, *17*, 3986–3992.

(9) Reuben, J. *J. Am. Chem. Soc.* **1985**, *107*, 1756–1759.

(10) Newmark, R. A.; Hill, J. R. *Org. Magn. Reson.* **1980**, *13*, 40–44.

(11) Christofides, J. C.; Davies, D. B. *J. Am. Chem. Soc.* **1983**, *105*, 5099–5105. (b) Reuben, J. *Ibid.* **1984**, *106*, 6180–6186.

(12) (a) Gagnaire, D.; Vincendon, M. *J. Chem. Soc., Chem. Commun.* **1977**, 509–510. (b) Bock, K.; Lemieux, R. U. *Carbohydr. Res.* **1982**, *100*, 63–74. (c) Christofides, J. C.; Davies, D. B. *J. Chem. Soc., Chem. Commun.* **1982**, 560–562; **1983**, 324–326. Christofides, J. C.; Davies, A. B. *J. Chem. Soc., Perkin Trans. 2* **1984**, 481–488. (d) Reuben, J. *J. Am. Chem. Soc.* **1983**, *105*, 3711–3713; **1984**, *106*, 2461–2462; **1985**, *107*, 1747–1755; **1985**, *107*, 5867–5870.

(13) Reuben, J. *J. Am. Chem. Soc.* **1986**, *108*, 1735–1738.

(14) Majerski, Z.; Zuanic, M.; Metelko, B. *J. Am. Chem. Soc.* **1985**, *107*, 1721–1726, and references cited therein.