

Communications to the Editor

Electron Transfer from Trialkyltin Radicals to Nitrosugars: The Synthesis of C-Glycosides with Tertiary Anomeric Carbon Atoms

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Recently Tanner¹ and Ono² have observed that secondary and tertiary nitro compounds can be reductively denitrated by tributyltin hydride. They suggested that this chain reaction may involve a one-electron transfer from the tin radical to the nitro compound as a key step in the reaction, thereby resembling the denitration with (a) the sodium salt of methanthiol,³ (b) KOH in ethylene glycol,⁴ and (c) N-benzyl-1,4-dihydronicotinamide.⁵ Vasella⁶ has applied this tin hydride reduction to nitro sugars **1**, and **6** which gave C-glucosides in good yields. We have now proved that in this tin hydride reaction a nitro radical anion with a tributyltin cation as counterion is involved and that nitro compounds can be used as precursors for radical C-C bond-forming reactions.

By following the reaction of **1** with Bu₃SnH by ESR spectroscopy under photolytic⁷ or AIBN-initiated⁸ conditions a 1:1:1 triplet is observed with a coupling constant of 25.75 ± 0.05 G and a g value of 2.00543 (Figure 1). These data are typical for nitro group radical anions.⁹ Each hyperfine line of the triplet is surrounded by a doublet with an intensity of ca. 12% which arises from the nearly equivalent couplings of 3.0–3.4 G (depending on the solvent) of the tin isotopes ¹¹⁹Sn and ¹¹⁷Sn.¹⁰ Analogous results were obtained by irradiating a THF solution of hexamethylditin in presence of **1**.

The tin coupling shows that the organotin group is close to the nitro radical anion thus forming a radical ion pair **2** which is generated via electron transfer from the tributyltin radical to the nitro compound **1** (Scheme I). In the thermal reaction at 50–60 °C the steady-state concentration of the radical ion pair **2** was determined by ESR spectroscopy to be in the range 10⁻⁵–10⁻⁶. The first-order lifetime at 53 °C in benzene is 0.13 s.

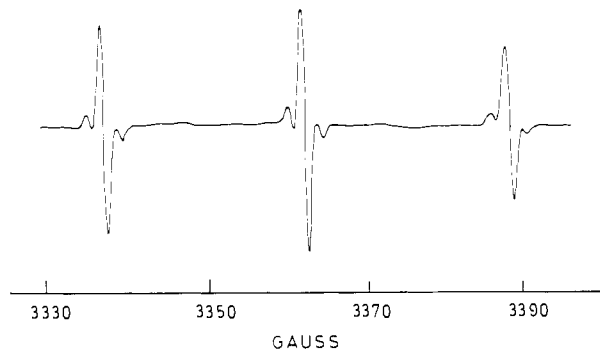
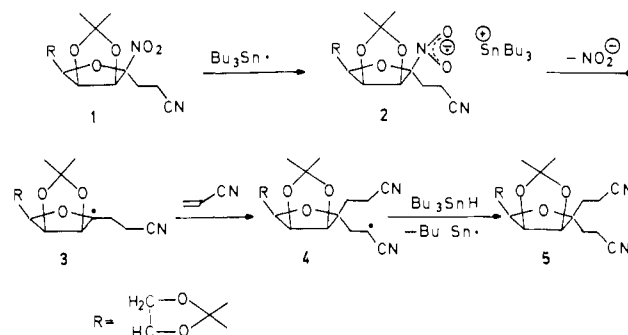


Figure 1. ESR spectrum of radical salt **2** generated by irradiation of nitro sugar **1** and Bu₃SnH in THF at 15 °C.

Scheme I



In the photolytic experiment, the ESR signal for **2** disappears immediately, if the light is switched off, but comes back upon further irradiation. This proves that **2** is a short-lived intermediate that decomposes readily, presumably by splitting off NO₂⁻ to give the neutral sugar radical **3**, which could not be observed by ESR under these conditions, although we were able to detect secondary sugar radicals generated from glycosyl bromides and glycosyl selenides.¹²

Acrylonitrile reacts with **3** from the exo side to give, via adduct radical **4**, product **5** in 55% overall yield.¹³ The stereochemistry of the attack has been proved by trapping adduct radical **4** with

(1) Tanner, D. D.; Blackburn, E. V.; Diaz, G. E. *J. Am. Chem. Soc.* **1981**, *103*, 1557.

(2) Ono, N.; Miyake, H.; Tamura, R.; Kaji, A. *Tetrahedron Lett.* **1981**, *22*, 1705. Ono, N.; Miyake, H.; Fujii, H.; Kaji, A. *Ibid.* **1983**, *24*, 3477.

(3) Kornblum, N.; Carlson, S. C.; Smith, R. *J. Am. Chem. Soc.* **1979**, *101*, 647.

(4) Krasuska, A. L.; Piotrowska, H.; Urbanski, T. *Tetrahedron Lett.* **1979**, *20*, 1243.

(5) Ono, N.; Tamura, R.; Kaji, A. *J. Am. Chem. Soc.* **1980**, *102*, 2851.

(6) Baumberger, F.; Vasella, A. *Helv. Chim. Acta* **1983**, *66*, 2210.

(7) Bu₃SnH (0.1 mL), solvent (benzene or THF) (0.4 mL), and **1** (ca. 50 mg) were irradiated at 15 °C in a quartz tube of 4-mm outer diameter using a 1-kW Hg-Xe high-pressure lamp (Hanovia 977-B), ESR spectrometer BRUKER ER 420. No ESR signal of the nitro radical anion could be observed upon irradiation or a benzene solution of **1** in the absence of Bu₃SnH.

(8) Bu₃SnH (0.1 mL), toluene (0.4 mL), **1** (ca. 0.1 g), and AIBN (ca. 20 mg) at 50–60 °C.

(9) Berndt, A. In "Landolt-Börnstein"; Fischer, H., Hellwege, K. H., Eds.; Springer: Berlin, 1980; New Series, Vol. II/9d1, p 376.

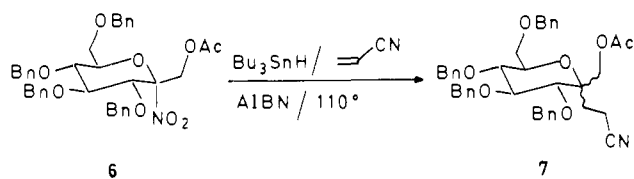
(10) Tin coupling have been observed in semiquinone and semidione radical anions,¹¹ however, to our knowledge, not for radical anions of nitro compounds. In separate ESR experiments it was demonstrated that under our conditions electron transfer takes place also in the case of simpler alkyl nitro compounds and Bu₃SnH.

(11) Lehnig, M., ref 9, p 5. Ulmschneider, K. B. and Stegmann, H. B., ref 9, p 112.

(12) Dupuis, J.; Giese, B.; Ruegge, D.; Fischer, H.; Korth, H.-G.; Sustmann, R. *Angew. Chem.* **1984**, *96*, 887; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 896.

(13) In a typical procedure 1 mmol of the nitro sugars **1** or **6** and 20 mmol of acrylonitrile were heated in 30 mL of refluxing toluene. Within 1 h 2 mmol of Bu₃SnH and 0.2 mmol of AIBN in 20 mL of toluene were dropped into the reaction mixture. Evaporation of the solvent and column chromatography (silica gel, ethyl ether) afforded products **5** and **7**. **5**: 300-MHz ¹H NMR (CDCl₃) δ 4.84 (dd, J = 4.0, 5.6 Hz, 1 H), 4.36 (d, J = 6.1 Hz, 1 H), 4.35 (ddd, J = 4.7, 6.3, 7.4 Hz, 1 H), 4.10 (dd, J 6.3, 8.8 Hz, 1 H), 4.00 (dd, J = 4.7, 8.8 Hz, 1 H), 3.72 (dd, J = 4.0, 7.4 Hz, 1 H), 2.50 (m, 2 H), 2.40 (t, J = 7.5 Hz, 2H), 2.40 (t, J = 7.5 Hz, 2 H), 2.02 (t, J = 7.5 Hz, 2 H), 1.82 (dt, J = 7.5, 15.0 Hz, 1 H), 1.74 (dt, J = 7.5, 15.0 Hz, 1 H), 1.50 (s, 3 H), 1.44 (s, 3 H), 1.37 (s, 3 H), 1.32 (s, 2 H). In reactions of radical **3** with acrylonitrile and Bu₃SnD the signal at δ 2.40 exhibits only half of the intensity, but the multiplet signal at δ 2.50 remains unchanged. Vasella⁶ has shown in reduction experiments of **3** with Bu₃SnH that the signal at δ ≈ 2.5 belongs to the isomer with an endo-CH₂CH₂CN group. From this we conclude that attack of acrylonitrile leads to radical **4** which is deuterated by Bu₃SnD at the exo substituent. Anal. Calcd for C₁₈H₂₆O₅N₂: C, 61.71%, H, 7.43%, N, 8.00%. Found: C, 61.52%; H, 7.50%; N, 8.12%. **7**: 300-MHz ¹H NMR (CDCl₃) δ 7.38–7.20 (m, 20 H), 4.96–4.82 (m, 4 H); 4.64–4.50 (m, 4 H), 4.20 (d, J = 11.7 Hz, 1 H), 3.92 (d, J = 11.7 Hz, 1 H), 3.85 (dd, J = 8.5, 9.5 Hz, 1 H), 3.73 (d, J = 9.5 Hz, 1 H), 3.68–3.55 (m, 4 H), 2.48–2.38 (m, 2 H), 2.36–2.10 (m, 2 H), 1.97 (s, 3 H). Anal. Calcd for C₄₀H₄₃O₇N: C, 73.92%, H, 6.67%; N, 2.15%. Found: C, 73.57%; H, 6.74%; N, 2.27%.

Scheme II



Bu_3SnD . In an analogous procedure the glucose derivative **6** gives the product of the C-C bond-forming reaction in 45% yield (Scheme II).^{13,14} Compounds **5** and **7** are C-glycosides with a tertiary carbon atom at C-1.¹⁵ This class of compounds can be, therefore, easily synthesized from the nitro sugars via a radical chain reaction.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support of this research and to Professor A. Vasella for helpful comments.

Registry No. 1, 85398-22-7; 2, 96481-44-6; 3, 96455-41-3; 4, 96455-42-4; 5, 96455-43-5; 6, 89023-65-4; 7, 96455-44-6; Bu_3SnH , 688-73-3; acrylonitrile, 107-13-1.

(14) The addition is stereoselective, but the NMR spectra do not show unambiguously whether the new C-C bond is axial or equatorial. From the reduction experiments of **6** with Bu_3SnH one expects the formation of an axial bond.⁶

(15) These are the C-glycosides of keto sugars: Tam, T. F.; Fraser-Reid, B. *J. Org. Chem.* **1980**, *45*, 1344.

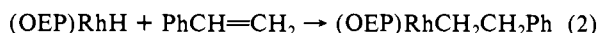
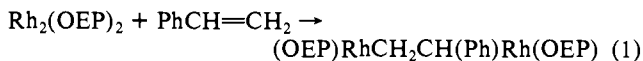
Insertion and Oxidative Addition Reactions of Rhodium Porphyrin Complexes. Novel Free Radical Chain Mechanisms

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We have found that styrene and certain other olefins (including propylene and substituted styrenes) undergo facile insertion reactions into the Rh-Rh and Rh-H bonds of $\text{Rh}_2(\text{OEP})_2$ and $(\text{OEP})\text{RhH}$, respectively, in accord with eq 1 and 2 (OEP = octaethylporphyrin).¹



The facile occurrence of reaction 2 was somewhat unexpected since it is not apparent that $(\text{OEP})\text{RhH}$ possesses an accessible vacant cis-coordination site that is generally considered to be necessary for olefin migratory insertion.⁴

(1) $\text{Rh}_2(\text{OEP})_2$ and $(\text{OEP})\text{RhH}$ have previously been prepared and characterized by Ogoshi² and by Wayland.³

(2) Ogoshi, H.; Setsume, J.; Yoshida, Z. *J. Am. Chem. Soc.* **1977**, *99*, 3869.

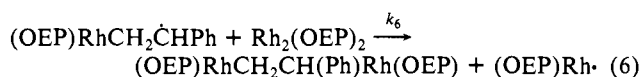
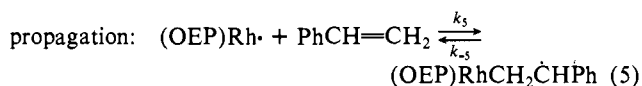
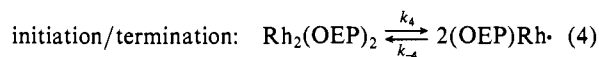
(3) (a) Wayland, B. B.; Woods, B. A. *J. Chem. Soc., Chem. Commun.* **1981**, 475. (b) Wayland, B. B.; Woods, B. A. *J. Chem. Soc.* **1981**, 700. (c) Wayland, B. B.; Woods, B. A.; Pierce, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 302. (d) Wayland, B. B.; Del Rossi, K. J. *J. Organomet. Chem.* **1984**, *276*, C27.

(4) (a) An alternative mechanism of olefin insertion that also does not require an accessible cis-coordination site involves a nonchain free radical sequence, initiated by H atom transfer from the metal hydride to the olefin, i.e., $\text{L}_n\text{M}-\text{H} + \text{PhCH}=\text{CH}_2 \rightarrow \text{L}_n\text{M}\cdot + \text{CH}_3\dot{\text{C}}\text{HPh} \rightarrow \text{L}_n\text{MCH}(\text{CH}_3)\text{Ph}$. While such a mechanism has previously been demonstrated for certain cobalt hydrides^{5b} it does not appear to contribute significantly to the reaction of $(\text{OEP})\text{RhH}$ with $\text{PhCH}=\text{CH}_2$ (eq 2) which yields exclusively the β - rather than α -phenylethyl adduct. (b) Halpern, J. *Pure Appl. Chem.* **1979**, *51*, 2171 and references therein.

In this paper we report results of our preliminary studies on the kinetics of reactions 1 and 2 which reveal that these reactions proceed through free radical chain mechanisms some features of which are without direct precedent in transition-metal chemistry.⁵ Such mechanisms also would appear to have relevance to the related insertion reactions of CO and acetylenes reported by Ogoshi² and Wayland,^{3b,c} as well as to certain oxidative addition reactions of $\text{Rh}_2(\text{OEP})_2$.

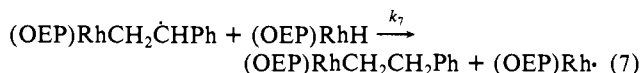
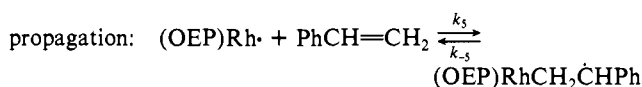
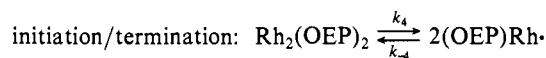
Reaction 1 proceeds readily in C_6D_6 at ambient temperatures and attains a measurable equilibrium defined by $K_1^{\text{eq}}(25^\circ\text{C}) = 8.5 \times 10^4 \text{ M}^{-1}$, $\Delta H_1^0 = -11.2 \pm 2.5 \text{ kcal/mol}$, and $\Delta S_1^0 = -15 \pm 8 \text{ cal/(mol K)}$.⁷ Kinetic measurements⁷ at 30°C yielded the rate law eq 3, which is interpreted in terms of the free radical chain mechanism of eq 4-6.

$$-d[\text{Rh}_2(\text{OEP})_2]/dt = k_3^{\text{obsd}}[\text{Rh}_2(\text{OEP})_2]^{3/2}[\text{PhCH}=\text{CH}_2] \quad (3)$$



Under the conditions where reactions 4 and 5 effectively attain equilibrium and reaction 6 is rate limiting, the rate law for this mechanism reduces to eq 3, with $k_3^{\text{obsd}} = (k_4/k_{-4})^{1/2}(k_5/k_{-5})k_6 = (1.35 \pm 0.1) \times 10^2 \text{ M}^{-3/2} \text{ s}^{-1}$ at 30°C .

Further evidence for this mechanism and, particularly, for the intermediacy of the $(\text{OEP})\text{RhCH}_2\dot{\text{C}}\text{HPh}$ radical was provided by trapping of the latter. Efficient trapping by $(\text{OEP})\text{RhH}$ was manifested in catalysis by $\text{Rh}_2(\text{OEP})_2$ of reaction 2 in accord with the mechanistic scheme of eq 4, 5, and 7.^{8,9}



Under the conditions of our kinetic measurements on reaction 2 (42°C ; initial concentrations, 5.8×10^{-4} to $1.9 \times 10^{-3} \text{ M}$ $(\text{OEP})\text{RhH}$, 3.8×10^{-4} to $2.4 \times 10^{-3} \text{ M}$ $\text{Rh}_2(\text{OEP})_2$, 0.036-0.36 M styrene),¹⁰ the equilibrium corresponding to eq 1 is rapidly

(5) Reference has previously been made to free radical like reactivity of $\text{Rh}(\text{OEP})$ and nonchain radical mechanisms have been suggested for some of its reactions.³ At the same time, free radical chain mechanisms related to those identified in the present study have been proposed for the addition of trialkyltin hydrides to olefins.⁶ However, certain features of the present mechanisms, notably the chain propagation sequences involving addition of metal free radicals to olefins and $\text{S}_{\text{H}}2$ displacement of metal radicals at metal-metal bonds (eq 5, 6) are, to our knowledge, without direct precedent in transition-metal chemistry.

(6) Kuivila, H. G. *Acc. Chem. Res.* **1968**, *1*, 299.

(7) The equilibrium measurements were made by ^1H NMR. The kinetic measurements encompassed the initial concentration ranges (2.9×10^{-5} to $4.7 \times 10^{-4} \text{ M}$ $\text{Rh}_2(\text{OEP})_2$ and 1.9×10^{-3} to $1.6 \times 10^{-1} \text{ M}$ styrene); the disappearance of $\text{Rh}_2(\text{OEP})_2$ was monitored spectrophotometrically at 600 nm and the products were identified by NMR. $[(\text{OEP})\text{RhCH}_2\text{CH}(\text{Ph})\text{Rh}(\text{OEP})]$: ^1H NMR (C_6D_6 , 12°C , 500 MHz) δ 9.183 (s, 4 H, meso H), 9.223 (s, 4 H, meso H), 3.94, 3.76 (overlapping m, 32 H, CH_2CH_3), 1.779 (overlapping t, 48 H, CH_2CH_3), -8.870, -9.855, -11.269 (m, 1 H, m, 1 H, m, 1 H, $\text{CHH}'\text{C}'\text{HPh}$), 0.5556 (d, 1 H, $J_{\text{HH}} = 7.5 \text{ Hz}$, ortho H); 0.788 (d, 1 H, $J_{\text{HH}} = 7.5 \text{ Hz}$, ortho H), 4.948 (dd, 1 H, meta H); 5.486 (dd, 1 H, meta' H), 6.232 (dd, 1 H, para H).

(8) A reaction paralleling eq 5 has been proposed by Ogoshi² as a step in a nonchain radical mechanism for the reaction of $\text{Rh}_2(\text{OEP})_2$ with $\text{CH}_2=\text{CHCH}_2\text{R}$ ($\text{R} = \text{Ph}$, CN, $n\text{-C}_3\text{H}_7$) to yield $(\text{OEP})\text{RhCH}_2\text{CH}=\text{CHR}$, i.e., $(\text{OEP})\text{Rh}\cdot + \text{CH}_2=\text{CHCH}_2\text{R} \rightarrow (\text{OEP})\text{RhCH}_2\dot{\text{C}}\text{HCH}_2\text{R} \xrightarrow{-\text{H}\cdot} \text{RhCH}_2\text{CH}=\text{CHR}$.