

FREE RADICAL CHAIN ELIMINATION REACTION ($E_{RC}1$). CONVERSION OF VICINAL
DINITRO COMPOUNDS OR β -NITRO SULFONES TO OLEFINS WITH TRIBUTYLTIN
HYDRIDE

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Vicinal dinitro compounds (1) or β -nitro sulfones (2) are converted to olefins in good yields on treatment with tributyltin hydride. This elimination proceeds by way of an electron transfer chain mechanism. The elimination from 1 is nonstereospecific and the elimination from 2 is stereospecific.

A conversion of vicinal dinitro compounds (1) or β -nitro sulfones (2) to olefins is a useful method for an olefin synthesis.¹⁻⁴ Sodium sulfide,^{1,2)} tin(II) chloride,³⁾ or calcium amalgam⁴⁾ has been used as a reducing agent for this transformation. However, they often suffer from low reactivity and selectivity. For example, tin(II) chloride cannot convert purely aliphatic vicinal dinitro compounds to olefins,³⁾ and sodium sulfide cannot apply to the synthesis of highly functionalized olefins owing to its strong nucleophilicity.⁴⁾ Then calcium amalgam has been devised as an improved reagent.⁴⁾ However, we feel that it still lacks reactivity and selectivity. Here we present a very effective and selective reagent for the conversion of 1 or 2 to olefins; 1 or 2 is readily converted to olefins with tributyltin hydride. Recently we have reported that tributyltin hydride is a highly selective reagent for replacing an aliphatic nitro group by hydrogen without affecting other functional groups such as keto, ester, cyano, chloro, or organic sulfur groups.⁵⁾ This functional selectivity is expected to be the case in the elimination from 1 or 2 with tributyltin hydride.

The procedure of the present olefin synthesis is quite simple. Simply heating 1 or 2 with tributyltin hydride (2.0 eq) in benzene at 80°C for 1-2 h gave olefins in good yields. The reaction was somewhat accelerated by the presence of a small amount of azobisisobutyronitrile (AIBN). Pure olefins were isolated by distillation after column chromatography by silica gel to remove tin components. The results are summarized in the table.

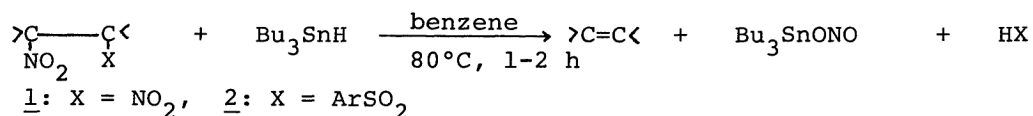
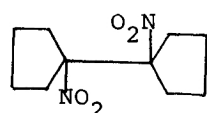
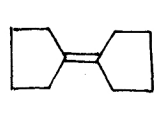
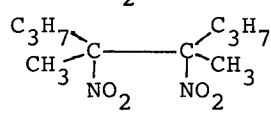
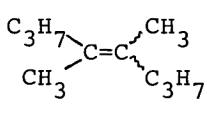
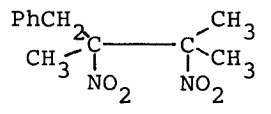
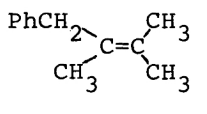
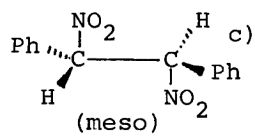
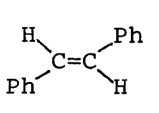
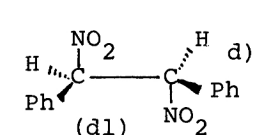
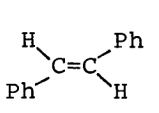
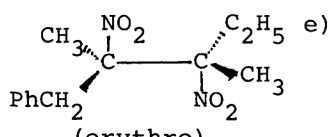
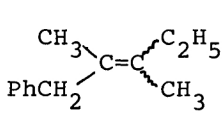
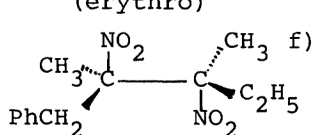
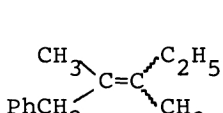
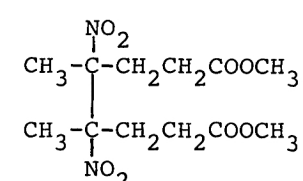
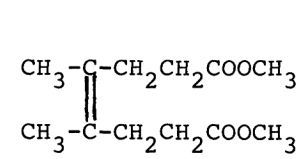
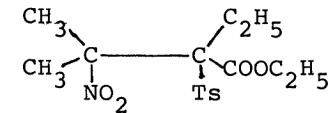
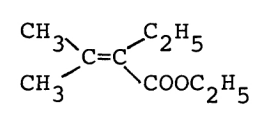
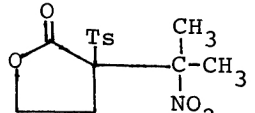
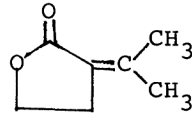
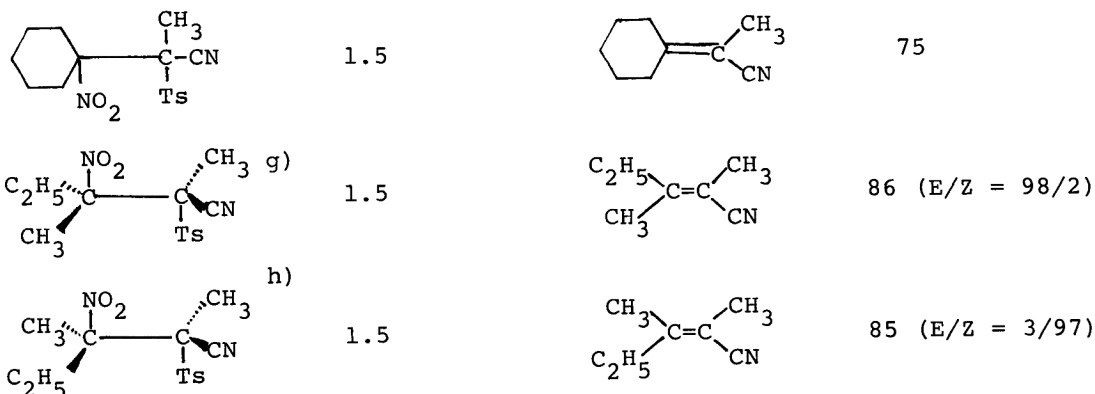


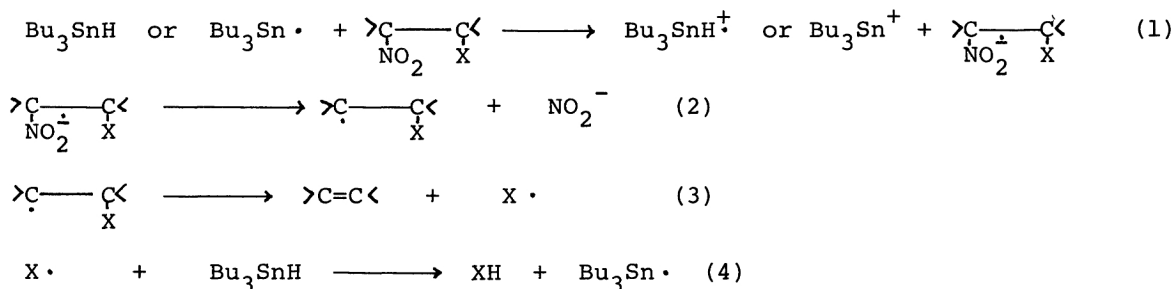
Table Conversion of Vicinal Dinitro Compounds (1) or β -Nitro Sulfones (2) into Olefins with Tributyltin Hydride^{a)}

<u>1</u> or <u>2</u>	Time, h	Product	Isol. Yield, %
	1.5		72
	1.5		78 (E,Z mixture) ^{b)}
	1.5		79
 (meso)	1.0		98 (E only)
 (dl)	1.0		98 (E only)
 (erythro)	2.5		75 (E/Z = 1.1)
 (threo)	2.5		75 (E/Z = 1.1)
	1.0		84 (E,Z mixture) ^{b)}
	1.5		81
	1.5		72



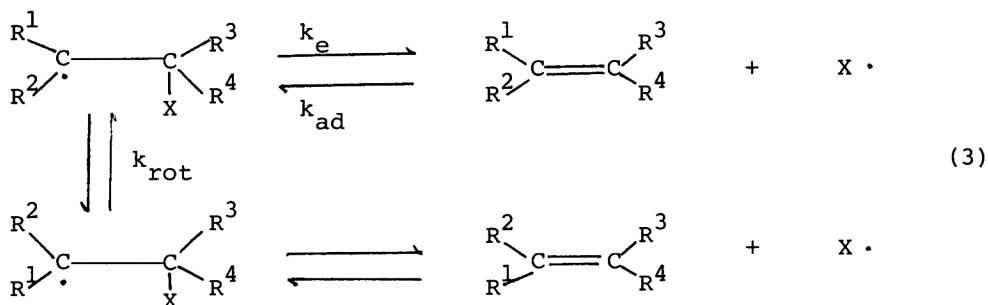
Ts = p-CH₃-C₆H₄SO₂ a) The reaction was carried out in the presence of AIBN (0.1 eq to 1 or 2). The reaction took place similarly in the absence of AIBN, but better results were obtained in the presence of AIBN. b) E/Z ratio was not determined. c) mp 230°C (ref. 3). d) mp 150°C (ref. 3). e) mp 133°C. f) mp 125°C. g) mp 129-130°C (ref. 2). h) mp 144°C (ref. 2).

Tributyltin hydride is evidently superior to other reagents to convert 1 or 2 to olefins in its effectiveness and selectivity. The observed selectivity seems to derive from the fact that the nitro group accept most readily one electron among all the common functional groups¹⁻⁴⁾ and tributyltin hydride or tributyltin radical is a good electron donor.^{5,6)} The mechanism of this elimination appears to be E_{RC}1 which is named for a radical anion-radical chain elimination process.⁷⁾ The fact that the elimination greatly retarded in the presence of a small amount of m-dinitrobenzene provides support for the proposed electron-transfer chain mechanism.



The most interesting feature of the present elimination reaction lies in the stereochemistry. In general a free radical elimination proceeds in a nonstereospecific way.⁸⁾ The elimination reaction from 1 or 2 with sodium sulfide is nonstereospecific⁹⁾ and that from 1 with tributyltin hydride is also nonstereospecific as shown here. However, the elimination reaction from 2 with tributyltin hydride is stereospecific.¹⁰⁾ The existence of free radical elimination presented in eq 3 is generally recognized, and it consists of an elimination-rotation-addition to give the product of the nonstereospecific elimination.⁸⁾

If the elimination of $X\cdot$ from a free radical intermediate is fast compared to rotation in the intermediate radicals and the addition of $X\cdot$ to olefins, the elimination of eq 3 becomes stereospecific. The elimination from 2 with tributyltin hydride may fit this condition to take place the stereospecific elimination. To our knowledge this is the first clean example of a stereospecific E_{RC}^1 .



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- 9) The reaction of 2^g or 2^h with sodium sulfide gave the same product, respectively, which consists of about equal mixture of E and Z olefin. (N. Ono, R. Tamura, and A. Kaji, to be published).
- 10) The structure of the diastereomer (1^c, 1^d, 1^e, 1^f, 2^g, 2^h) was determined on the basis of the literature and NMR data.^{3,11)} Although some uncertainty still remains on their structure, there is no doubt about the conclusion that the elimination reaction from 1 is nonstereospecific and that from 2 is stereospecific.
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