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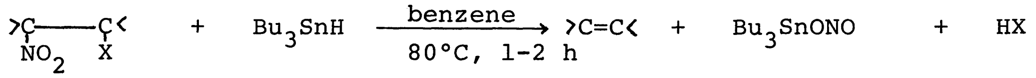
Vicinal dinitro compounds (1) or β-nitro sulfones (2) are converted to olefins in good yields on treatment with tributyltin hydride. This elimination proceeds by way of an electron transfer chain mechanism. The elimination from 1 is nonstereospecific and the elimination from 2 is stereospecific.

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 amalgam[4] 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 replaing 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 tribuyltin hydride.

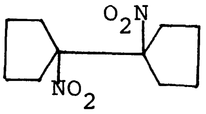
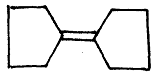
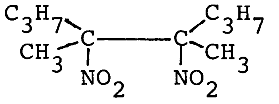
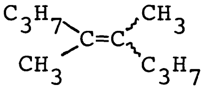
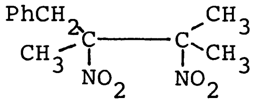
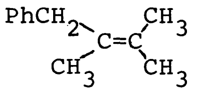
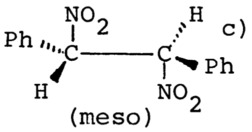
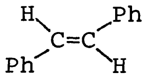
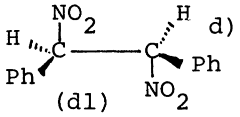
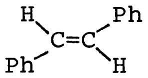
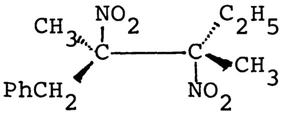
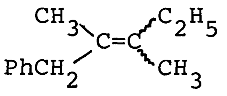
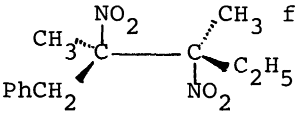
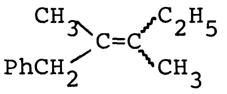
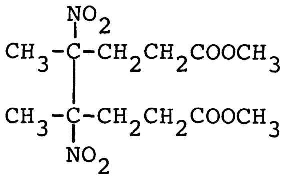
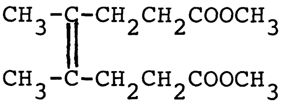
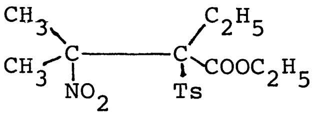
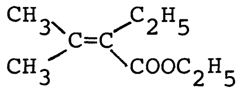
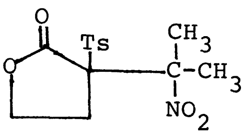
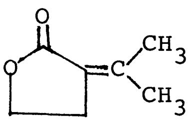
The procedure of the present olfin synthesis is quite simple. Simply heating 1 or 2 with tributyltin hydride (2.0 eq) in benzene at 80°C for 1-2 h gave olefins in good yields. The reaction was somewhat accelerated by the presence of a small amount of azobisisobutyronitrile (AIBN). Pure olefins were isolated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

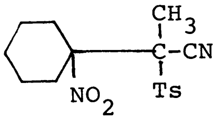
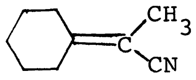
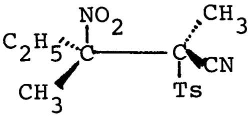
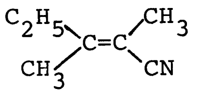
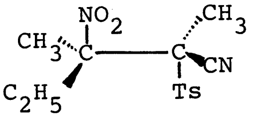
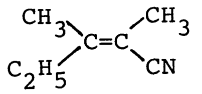


$$>\underset{NO_2}{C}-\underset{X}{C}< \; + \; Bu_3SnH \xrightarrow[80°C,\ 1\text{-}2\ h]{benzene} >C=C< \; + \; Bu_3SnONO \; + \; HX$$

1: X = NO_2, 2: X = $ArSO_2$

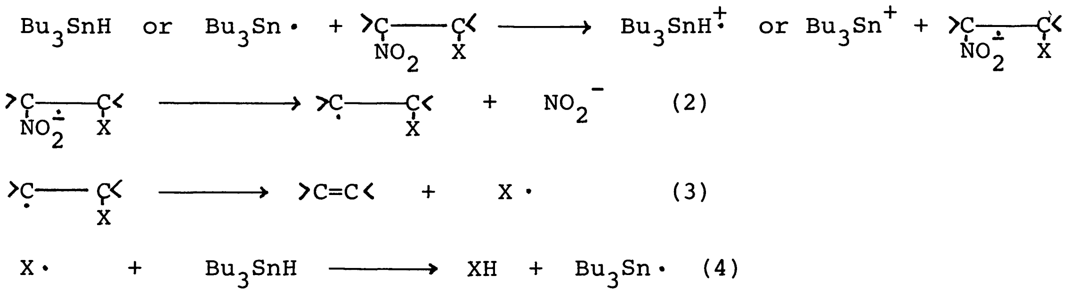
Table Conversion of Vicinal Dinitro Compounds (1) or β-Nitro Sulfones (2) into Olefins with Tributyltin Hydride a)

1 or 2	Time, h	Product	Isol. Yield, %
	1.5		72
	1.5		78 (E,Z mixture) b)
	1.5		79
 c) (meso)	1.0		98 (E only)
 d) (dl)	1.0		98 (E only)
 e) (erythro)	2.5		75 (E/Z = 1.1)
 f) (threo)	2.5		75 (E/Z = 1.1)
	1.0		84 (E,Z mixture) b)
	1.5		81
	1.5		72

	1.5		75
 g)	1.5		86 (E/Z = 98/2)
h) 	1.5		85 (E/Z = 3/97)

Ts = $p\text{-}CH_3\text{-}C_6H_4SO_2$ 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 groups[1-4] and tributyltin hydride or tributyltin radical is a good electron donnor.[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.



$$\mathrm{Bu_3SnH} \text{ or } \mathrm{Bu_3Sn\cdot} + \underset{NO_2}{>\!C}-\underset{X}{C\!<} \longrightarrow \mathrm{Bu_3SnH^{+\cdot}} \text{ or } \mathrm{Bu_3Sn^+} + \underset{NO_2^{\,\overset{-}{\cdot}}}{>\!C}-\underset{X}{C\!<} \qquad (1)$$

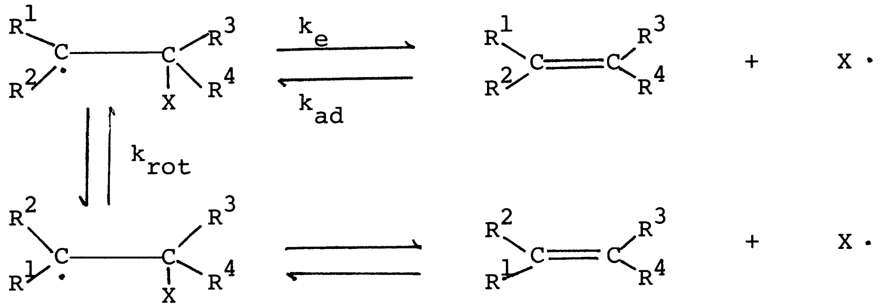
$$\underset{NO_2^{\,\overset{-}{\cdot}}}{>\!C}-\underset{X}{C\!<} \longrightarrow \underset{\cdot}{>\!C}-\underset{X}{C\!<} + NO_2^- \qquad (2)$$

$$\underset{\cdot}{>\!C}-\underset{X}{C\!<} \longrightarrow >\!C{=}C\!< + X\cdot \qquad (3)$$

$$X\cdot + \mathrm{Bu_3SnH} \longrightarrow XH + \mathrm{Bu_3Sn\cdot} \qquad (4)$$

The most interesting feature of the present elimination reaction lies in the stereochemistry. In general a free radical elimination proceeds in a nonsterospecific way.[8] The elimination reaction from 1 or 2 with sodium sulfide is nonstereospecific[9] and that from 1 with tributyltin hydride is also nonsterospecific as shown here. However, the elimination reaction from 2 with tributyltin hydride is sterospecific.[10] The exsistence 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· from a free radical intermediate is fast compared to rotation in the intermediate radicals and the addition of X· 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 $E_{RC}1$.



(3)

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8) J. E. McMurry and T. Hoz, J. Org. Chem., 40, 3797 (1975); P. J. Kocienski, B. Lythgoe, and S. Ruston, J. C. S. Perkin I, 1978, 829; T. E. Boothe, J. L. Greene, Jr., and P. B. Shevlin, J. Am. Chem. Soc., 98, 951 (1976); A. G. M. Barrett, D. H. R. Barton, and R. Bielski, J. C. S. Perkin I, 1979, 2378; ref. 3 and references therein.
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 diasteromer (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.
11) A. H. Pagano and H. Shechter, J. Org. Chem., 35, 295 (1970).

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