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The Reaction of Vicinal Dinitro Compounds with Tin(II) Chloride

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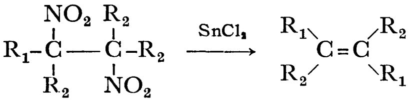
The reactions of vicinal dinitro compounds with tin(II) chloride have been studied. The reactions of α,β-diaryl vicinal dinitro compounds and tin(II) chloride in polar solvents gave the corresponding olefins in good yields. The aliphatic vicinal dinitro compounds did not react with tin(II) chloride under the same reaction conditions. A reaction mechanism of elimination involving a radical anion intermediate has been proposed.

The bimolecular removal of two atoms or groups from vicinal dihalides,[1,2] vicinal diols,[3] and vicinal dicarboxylates[4] have been investigated extensively, but there have been few papers on the bimolecular elimination reactions of vicinal dinitro compounds. Kornblum *et al.* reported the denitration of purely aliphatic vicinal dinitro compounds to alkenes with sodium sufide or sodium benzenethiolate.[5]

It has been reported that 1,2-diaryl-1,2-dinitroethanes (**1**) react with tin(II) compounds in ethanol to give 1,2-diarylethylenes (**2**)[6] and this paper will report the reaction in detail.



$$R_1\text{-}\overset{NO_2}{\underset{R_2}{C}}\text{—}\overset{R_2}{\underset{NO_2}{C}}\text{-}R_2 \xrightarrow{SnCl_2} \begin{matrix}R_1 & & R_2\\ & C{=}C & \\ R_2 & & R_1\end{matrix}$$

1 (a—g) **2 (a—g)**

a: R_1, R_2=fluorenyl
b: $R_1=C_6H_5$, $R_2=H$
c: R_1=*p*-$CH_3C_6H_5$, $R_2=H$
d: R_1=*o*-$CH_3C_6H_5$, $R_2=H$
e: R_1=*o*-ClC_6H_5, $R_2=H$
f: R_1=α-naphthyl, $R_2=H$
g: $R_1=C_6H_5$, $R_2=CH_3$

Scheme 1.

Results and Discussion

*Syntheses of **1**.* 1,2-Diaryl-1,2-dinitroethane (**1b**—**f**) has been prepared by the reaction of the sodium or potassium salt of α-arylnitromethane with potassium peroxodisulfate. Two isomeric structures are possible for the vicinal dinitro compounds. Figure 1 shows the NMR spectra of the configurationally known *dl*-1,2-dinitro-1,2-diphenylethane (*dl*-**1b**) and *meso*-**1b** pairs.[7] The methine proton of *meso*-**1b** at δ 3.74 is broad compared with that of *dl*-**1b**. These results indicate that the stereochemical assignment can possibly be made for the isomeric **1b**—**f** on the basis of the band width of the methine proton peaks.

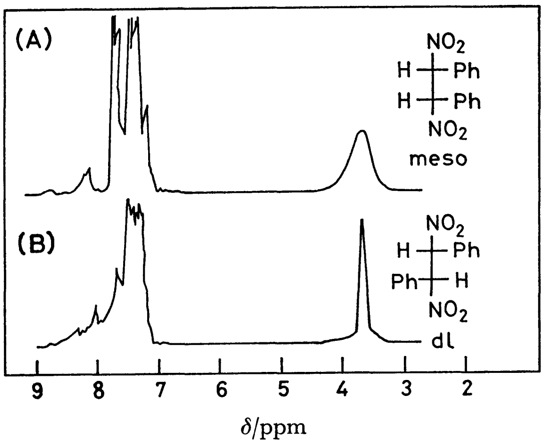
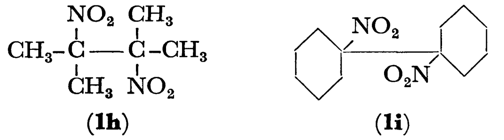


Fig. 1. NMR spectra of **1b** in $(CD_3)_2NCD$; (A): for *meso*-**1b**; (B): for *dl*-**1b**.

2,3-Dinitro-2,3-diphenylbutane (**1g**) was prepared as a mixture of the *dl* and *meso* forms by the reaction of the sodium salt of 1-nitro-1-phenylethane with silver nitrate. The ratio of the stereoisomers in this product has been determined by NMR in $CDCl_3$ which exhibited resonances at δ 2.30 and 2.22 due to two kinds of methyl groups. Other vicinal dinitro compounds (9,9′-dinitro-9,9′-bifluorenyl (**1a**), 2,3-dinitro-2,3-dimethylbutane (**1h**), and 1,1′-dinitrobicyclohexyl (**1i**)) have been prepared by the methods reported in the literature.[6,8]

The analytical data for **1a**—**i** are summarized in Table 1.

*Reaction of **1** with Tin(II) Chloride.* α,β-Diaryl vicinal dinitro compounds (**1a**—**f**) react readily with tin(II) chloride in boiling ethanol to give the corresponding 1,2-diarylethylenes (**2a**—**f**). The products thus obtained were identified with authentic samples by mixed melting point determination and a comparison of IR spectra. The β-elimination products, such as α-nitrostilbenes, were not obtained. Refluxing of the purely aliphatic vicinal dinitro compound, **1h** or **1i** with tin(II) chloride in ethanol gave the starting materials unchanged, even after 48 h. Thus, the presence of the aromatic ring attached to the carbon atom bearing the nitro group is essential for denitration.



$$CH_3\text{-}\overset{NO_2}{\underset{CH_3}{C}}\text{—}\overset{CH_3}{\underset{NO_2}{C}}\text{-}CH_3$$

(**1h**) (**1i**)

Scheme 2.

The results of this reaction are shown in Table 2.

The reaction of **1a** with tin(II) chloride has been conducted in various solvents. As shown in Table 3, the reaction is remarkably affected by the polarity of the solvent, and proceeds smoothly with a solvent more polar than ethyl acetate (ε=6.0). In dipolar aprotic solvents, the reaction proceeds more readily, and lower temperature being sufficient for reaction. A vigorous evolution of nitrogen oxide was observed during the reaction employing acetic acid or ethyl acetate as

TABLE 1. PHYSICAL PROPERTIES AND ANALYTICAL DATA OF VICINAL DINITRO COMPOUNDS (**1**)

Compd No.	Mp °C (Recryst solvent)	Formula	Found (Calcd), % C	H	N	IR spectrum, cm^{-1} in KBr NO_2	NMR spectrum, δ in DMF-d_7 CH	CH_3
1a	175 (Benzene)	$C_{26}H_{16}O_4N_2$	—			1550, 1340	—	—
meso-**1b**	230 (AcOH)	$C_{14}H_{12}O_4N_2$	61.83 (61.76)	4.41 (4.44)	10.18 (10.29)	1555, 1380	3.74(bs)	—
dl-**1b**	149—150 (EtOH)	$C_{14}H_{12}O_4N_2$	—			1550, 1360	3.73(s) 6.36(s)[a]	—
dl-**1c**	148 (EtOH)	$C_{16}H_{16}O_4N_2$	63.92 (63.99)	5.26 (5.37)	9.29 (9.33)	1550, 1370	6.36(s)[a]	2.27(d)[a]
dl-**1d**	157—158 (EtOH)	$C_{16}H_{16}O_4N_2$	63.90 (63.99)	5.44 (5.37)	9.24 (9.33)	1560, 1360	4.24(s)	2.31(q)
dl-**1e**	233—234 (AcOH)	$C_{14}H_{16}O_4Cl_2$	49.25 (49.29)	2.88 (2.95)	8.22 (8.21)	1560, 1300	3.46(s)	—
dl-**1f**	141—142 (AcOH)	$C_{22}H_{16}O_4N_2$	70.94 (70.96)	4.30 (4.33)	7.49 (7.52)	1518, 1310	6.89(s)	—
dl-**1g**	139—141 (MeOH-H_2O)	$C_{16}H_{16}O_4N_2$	63.82 (63.99)	5.33 (5.37)	9.32 (9.33)	1550, 1350	—	2.30(s)[a]
1g[b]	118—126 (MeOH-H_2O)	$C_{16}H_{16}O_4N_2$	63.79 (63.99)	5.35 (5.37)	9.34 (9.33)	1550, 1350	—	2.30(s) 2.22(s)[a]
1h	212—213 (EtOH)	$C_6H_{12}O_4N_2$	—			1560, 1360	—	1.75(s)[a]
1i	215—216 (Acetone)	$C_{12}H_{20}O_4N_2$	—			—	—	—

a) Measured in $CDCl_3$. b) The mixture of *dl*-**1g** (73%) and *meso*-**1g** (27%).

TABLE 2. REACTIONS OF VICINAL DINITRO COMPOUNDS (**1a**—**f**, **1h**, AND **1i**) WITH TIN(II) CHLORIDE IN ETHANOL[a]

No.	Vicinal dinitro compound	Product	Yield[b] %
1	**1a**	**2a**	94
2	*dl*-**1b**	**2b**[c]	92
3	*dl*-**1c**	**2c**[c]	89
4	*dl*-**1d**	**2d**[c]	83
5	*dl*-**1e**	**2e**[c]	88
6	*dl*-**1f**	**2f**[c]	85
7	**1h**	None	0
8	**1i**	None	0

a) In 15 ml solvent at reflux temp using 1.25 mmol of **1** and 5.0 mmol of tin(II) chloride. b) Isolated yield. c) *trans*-Isomer.

TABLE 3. REACTIONS OF **1a** WITH TIN(II) CHLORIDE IN VARIOUS SOLVENTS

Run	Solvent	Dielectric constant (ε)	Yield of **2a**[b] (%)
1	n-C_6H_{14}	1.9	0
2	PhH	2.3	2.1
3	EtOEt	4.2	2.0
4	$CHCl_3$	4.9	8.2
5	AcOEt	6.0	89.6
6	AcOH	6.2	90.3
7	THF	7.6	92.4
8	n-BuOH	17.1	94.6
9	Me_2CO	20.7	95.8
10	EtOH	23.8	98.1
11	MeOH	33.1	98.5
12	DMF	36.1	97.8
13	MeCN	37.8	98.0

a) In 10 ml solvent at the reflux temp of each solvent for 0.5 h using **1a** (0.625 mmol) and tin(II) chloride (2.50 mmol). b) Yield was determined spectrophotometrically at 453 nm.

solvent. The formation of nitrogen oxide in acidic medium indicates the formation of the nitrite ion during the reaction. In order to find the optimum reaction conditions, several runs were conducted with **1a** and *dl*-**1b** employing ethanol or DMF as the solvent. An solution of ethanol or DMF solution and **2a** had an intense absorption maximum at 453 nm (ε_{max} 2.4×10^4 in EtOH, ε_{max} 3.0×10^4 in DMF). A very small absorption and weak absorption were observed at this wavelength for a solution of tin(II) chloride and **1a** respectively. Therefore, the spectrophotometric determination of **2a** in the reaction mixture from **1a** and tin(II) chloride has been conducted at 453 nm. In the reaction with *dl*-**1b**, the yield of **2b** was determined by GLPC, the results of which are summarized in Tables 4 and 5. As can be seen from the Tables, the best result were obtained with a mole ratio of tin(II) chloride to **1** greater than 4 to 1 was used. Longer reaction time did not significantly increase the yield of elimination product, **2**. It has been reported that a solution of tin(II), except for tin(II) fluoride is oxidized on exposure to air.[9] Consequently an excess of tin(II) chloride has been used.

Stereochemistry of Elimination. Table 6 shows that the product of the reaction of **1b** was solely the *trans* isomer (*trans*-**2b**) regardless of the stereochemical nature of the starting material or the condition of the reaction. The isomerization of *cis*-**2b** to *trans*-**2b** was not observed under these reaction conditions. Similarly a series of *dl*-1,2-diaryl-1,2-dinitroethanes (*dl*-**1c**—**f**) were treated

Table 4. REACTIONS OF **1a** WITH TIN(II) CHLORIDE UNDER VARIOUS CONDITIONS

Run	SnCl$_2$/**1a**[a] (mol/mol)	Solvent (10 ml)	Yield of **2a**[b] (%)
1	0.87	EtOH[c]	18.2
2	0.95	EtOH[d]	19.6
3	1.54	EtOH[d]	48.9
4	1.90	EtOH[d]	50.4
5	3.80	EtOH[d]	97.1
6	4.12	EtOH[d]	100
7	2.00	DMF[e]	51.4
8	2.28	DMF[e]	46.7
9	4.80	DMF[e]	82.8
10	5.20	DMF[e]	98.2

a) **1a**=0.625 mmol. b) Yield was determined spectrophotometrically at 453 nm. c) At reflux temp for 3 h. d) At reflux temp for 0.5 h. e) At room temp for 2 h.

Table 5. REACTIONS OF *dl*-**1b** WITH TIN(II) CHLORIDE UNDER VARIOUS CONDITIONS

Run	SnCl$_2$/*dl*-**1b**[a] (mol/mol)	Solvent (10 ml)	Yield of **2b**[b] (%)
1	0.72	EtOH[c]	27.3
2	0.78	EtOH[d]	29.9
3	1.16	EtOH[c]	48.8
4	2.14	EtOH[c]	79.5
5	3.34	EtOH[c]	94.6
6	4.13	EtOH[c]	100
7	4.10	DMF[e]	78.9
8	4.55	DMF[e]	86.2

a) *dl*-**1b**=2.50 mmol. b) Yield was determined by GLPC. c) At reflux temp for 0.5 h. d) At reflux temp for 3 h. e) At room temp for 2 h.

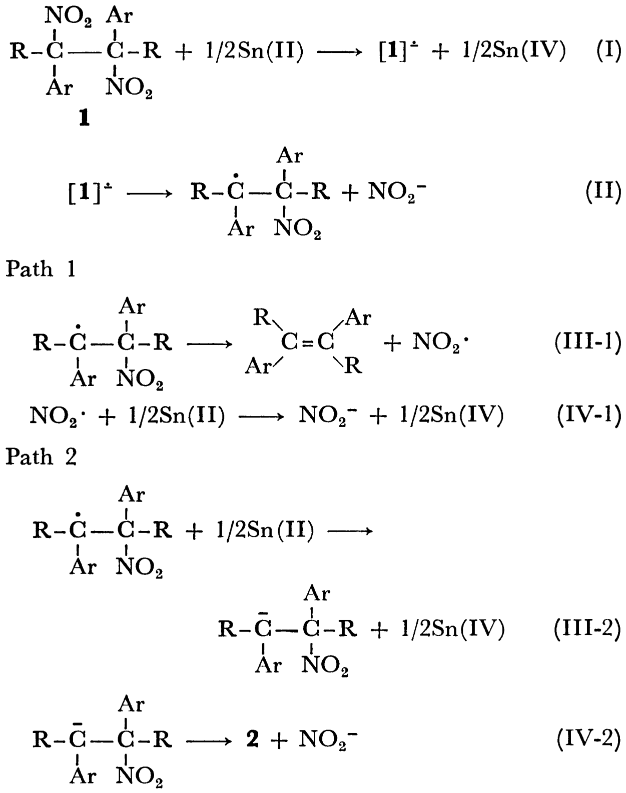
to give *trans*-1,2-diarylethylenes (*trans*-**2c**—**f**), some typical results of which are summarized in Table 2. In the reactions of **1g**, *dl*-**1g** gave a mixture of *cis* and *trans*-2,3-diphenyl-2-butene (*cis* and *trans*-**2g**) in a ratio of 54 to 46, and a mixture of *dl* and *meso*-**1g** in a ratio of 51 to 49, respectively (Table 6). These results suggest that present elimination reaction is not stereospecific.

Table 6. REACTIONS OF *dl*-**1b**, *meso*-**1b**, *dl*-**1g**, AND *meso*-**1g** WITH TIN(II) CHLORIDE

Run	Substrate[a]	Solvent (10 ml)	Reaction conditions		Yield of olefin	
			Time (h)	Temp (°C)	*cis* (%)	*trans* (%)
1	*dl*-**1b**	EtOH	0.5	reflux	0	97
2	*dl*-**1b**	DMF	2	r.t.	0	69
3	*dl*-**1b**	THF	2	50	0	88
4	*meso*-**1b**	EtOH	0.5	reflux	0	96
5	*meso*-**1b**	DMF	2	r.t.	0	70
6	*dl*-**1g**	EtOH	0.5	reflux	43.2	36.8[b]
7	*dl* and *meso*-**1g**[c]	EtOH	0.5	reflux	41.8	40.2[d]

a) SnCl$_2$/substrate=10 mmol/2.5 mmol. b) *cis*/*trans*=54/46. c) The ratio of *dl*-**1b** and *meso*-**1b** was 73:27. d) *cis*/*trans*=51/49.

Reaction Mechanism. Since no dehydronitration of **1b**—**f** was observed, there appears to be little, if any, formation of an ionic intermediate. On the basis of the stereochemical results, it appears probable that the elimination is not concerted and that a labile mononitro intermediate is involved. Furthermore, the stoichiometric results indicate that the reaction is markedly affected by the concentration of tin(II) chloride. Therefore the carbanion (E1cb), unimolecular (E1), and concerted bimolecular (E2) elimination mechanisms are not possible mechanisms in the elimination.[10] A possible mechanism is Scheme 3:



Scheme 3.

The favored coordination numbers for tin(II) are three[11,12] and for tin(IV) four to six,[13] and the tin(II) is coordinated to the oxygen of the nitro group. The first coordination process involving a neutral species should be aided by solvents of high polarity. Under such conditions electron transfer takes place from tin(II) to the nitro group of the vicinal dinitro compounds (Step I), and radical intermediates are formed (Step II). In the thermodynamically controlled conformation, they then react with a second molecule of tin(II) to give the final products (Steps III and IV). In Scheme 3, two mechanisms for the elimination of the second nitro group from the radical intermediate are presented. One is based on the reductive elimination of ·NO$_2$, and the other, on the intermediate formation of a carbanion that subsequently loses a nitrite ion. It appears probable that the elimination reaction in Step III proceeds *via* a carbanion mechanism rather than a radical mechanism when the second leaving group is a group such as an acetoxyl group that is not easily lost with its bonding

TABLE 7. THE INFLUENCE OF NITRO AROMATICS AND SULFUR ON THE REACTION OF **1a** WITH TIN(II) CHLORIDE

Run	Added inhibitor	mmol	Yield of **2a** (%)[b]
1	None	0	96.2
2	$PhNO_2$	0.125	97.0
3	*m*-DNB	0.063	94.5
4	*m*-DNB	0.250	95.1
5	*p*-DNB	0.125	96.7
6	Sulfur	1.25	97.6

a) In ethanol (30 ml) at reflux temp for 0.5 h using **1a** (1.25 mmol) and tin(II) chloride (5.00 mmol).
b) Yield was determined spectrophotometrically.

electron pair.[10] It should be noted here that the reaction of *threo*-1-acetoxy-2-nitro-1,2-diphenylethane with tin(II) chloride afforded no *trans*-**2b** under the same conditions.[14] Therefore, the elimination of the second nitro group proceeds *via* a radical mechanism (Steps III-1 and IV-1 in Scheme 3). Kwok and Miller[15] previously proposed a similar sequence for the reaction of stilbene dibromide with tin(II) chloride. Kornblum *et al.*[5] reported that similar reactions of purely aliphatic vicinal dinitro compounds with sodium sulfide are inhibited by the presence of dinitrobenzene (DNB) or sulfur. In the reactions here of **1a** with tin(II) chloride, however, the presence of DNB or sulfur had no influence on the product yield, as shown in Table 7. Norris and Girdler[16] reported that the reaction of the lithium salt of 2-nitropropane with *p*-nitrobenzylidene diacetate in DMSO was not catalyzed by light, nor was it inhibited by oxygen or *p*-DNB. Presumably the greater stability of the nitroaromatic radical stabilized by α-aromatic substituent allows sufficient time for successful competition between electron transfer and loss of the nitrite ion. Therefore, the difference in the reactivity of α,β-diaryl vicinal dinitro compounds (**1a**—**g**) and purely aliphatic vicinal dinitro compounds (**1h** and **1i**) with tin(II) chloride may be attributed to the stability of the intermediate radical.

Experimental

All melting points are uncorrected. The products were identified, unless otherwise mentioned, by mixed melting point determination and comparing the IR and NMR spectra data with those of authentic samples. The IR, UV, and NMR spectra were measured with a Hitachi Model IR-215 spectrometer, a Shimadzu Model UV-200 spectrometer, and a JNM-MH 100 spectrometer using tetramethylsilane as an internal standard. Gas-liquid partition chromatographic (GLPC) analysis was conducted on a Hitachi Model 063 gas chromatograph.

Materials. Anhydrous tin(II) chloride was prepared from commercial tin(II) chloride dihydrate according to the method of Stephen.[17] Phenylnitromethane, (*o*-chlorophenyl)nitromethane, 1-naphthylnitromethane, and *o*-tolylnitromethane were prepared from corresponding arylacetonitriles[18] with methyl nitrate according to the method of Black and Baker.[19] *p*-Tolylnitromethane was synthesized according to the method previously reported.[20] 1-Nitro-1-phenylethane was prepared from α-methylbenzyl bromide with sodium nitrite in DMSO.[21] 2-Nitropropane, nitrocyclohexane, and diphenylmethane were commercial materials and used without further purification. *cis*-Stilbene and *trans*-2,3-diphenyl-2-butene were prepared from the corresponding diols.[3] Organic solvents were purified by standard methods and the commercial inorganic materials were used without purification.

Preparations of Vicinal Dinitro Compounds (1). Vicinal dinitro compounds, **1b**—**f**, **1h**, and **1i** were prepared according to the method of Dornow *et al.*[8] Each product **1b**—**f** showed a sharp singlet at δ 4.2—3.5 (2H, methine protons) and assigned to the *dl* form. *meso*-1,2-Dinitro-1,2-diphenylethane (*meso*-**1b**) was prepared by the reaction of *trans*-**2b** and dinitrogen tetraoxide in benzene.[22]

The synthesis of **1a** has been described.[6] Compound **1g** was synthesized by the reaction of the sodium salt of 1-nitro-1-phenylethane with silver nitrate, and NMR revealed *dl*- and *meso*-**1g**. The isomer ratio was determined as 73:27 by integration of the NMR spectra on the assumptions that the methyl protons of *dl*-**1g**, being *cis* to the vicinal phenyl group, are shielded by the phenyl group and appear at higher field than that of the *meso* isomer. Pure *dl*-**1g** was separated by repeated fractional recrystallization from methanol-water, and the melting point and IR spectrum were identical with those published.[23] The physical properties and analytical data of **1** are summarized in Table 1.

Reactions of Vicinal Dinitro Compounds (1) with Tin(II) Chloride. General Procedure: The following example shows a typical run. A mixture of *meso*- or *dl*-**1b** (2.50 mmol) and tin(II) chloride (10 mmol) was refluxed in ethanol (10 ml) for 0.5 h. After the solvent had been removed *in vacuo*, the residue was triturated with cold 2 M sodium hydroxide (50 ml) and the resulting organic product extracted with benzene. The extract was washed with water, and dried over anhydrous sodium sulfate, and the solvent removed *in vacuo* to give a crude reaction product. The UV and NMR spectra of this product [UV(EtOH) λ_{max} 295, 308, 320 (shoulder) nm; NMR ($CDCl_3$) δ 7.1 (2H, s, -CH=CH-), 7.2—7.6 (10H, m, $2C_6H_5$)] were characteristic of *trans*-**2b** free of the *cis* isomer. Recrystallization from ethanol afforded colorless fine crystals of *trans*-**2b**, mp 122—123 °C (lit,[24] 123—124 °C). The products obtained by the same procedure were 9,9′-bifluorenylidene (**2a**): Mp 182—183 °C (lit,[25] 189—190 °C); *trans*-4,4′-dimethylstilbene (*trans*-**2c**): Mp 179—180 °C (lit,[26] 179—180 °C); *trans*-2,2′-dimethylstilbene (*trans*-**2d**): Mp 80—81 °C (lit,[26] 82.5—83.5 °C); *trans*-2,2′-dichlorostilbene (*trans*-**2e**): Mp 95—96 °C (lit,[27] 96—97.2 °C); *trans*-1,2-di-(1-naphthyl)ethene (*trans*-**2f**): Mp 160—161 °C (lit,[26] 158—159 °C). The 2,3-diphenyl-2-butene (**2g**) obtained was found to be a *ca.* 1:1 mixture of the *cis* and *trans* isomers from the NMR spectra. In the case of the reaction of **1h** and **1i** the starting material was recovered unchanged.

Reaction of dl-**1b** *with Tin(II) Chloride in Ethanol*: A mixture of *dl*-**1b** (2.50 mmol) and tin(II) chloride (1.80—10.3 mmol) was refluxed in ethanol (10 ml) for 0.5—3 h. The reaction product, after the usual work up procedure, was analyzed by GLPC with diphenylmethane as an internal standard using a Tenax GC column 2 m long (steel tube) at 245 °C (He as a carrier gas). Retension time: *dl*-**1b**, 7 min; diphenylmethane, 23 min; *trans*-**2b**, 56 min.

Reaction of dl-**1b** *with Tin(II) Chloride in DMF*: A DMF (10 ml) solution containing *dl*-**1b** (2.50 mmol) and tin(II) chloride (10.25 and 11.4 mmol) was stirred at room temperature for 2 h. The solution was poured into cold 2 M sodium hydroxide (100 ml). After the usual work up, the organic extract was submitted for GLPC analysis.

Isomerization of cis-*Stilbene (*cis-**2b**) *during the Reaction.* A mixture of *cis*-**2b** (2.50 mmol) and tin(II) chloride (10 mmol) in ethanol (10 ml) was refluxed for 0.5 h, and analysis of the product was conducted using GLPC and NMR. *cis*-Stilbene was unchanged under the reaction conditions.

The Influence of Dinitrobenzene or Sulfur on the Reaction of **1a** *with Tin(II) Chloride.* A mixture of **1a** (1.25 mmol) and tin(II) chloride (5.0 mmol) was refluxed in ethanol (30 ml) for 0.5 h in the presence of various amounts of an inhibitor. The yields of **2a** were determined spectrophotometrically employing ethanol as a solvent. The various additives did not affect the yield of **2a** (Table 7).

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