Hard Acid and Soft Nucleophile Systems. Part 14.[1a]
On the Reactivity of *a*–Nitroketones and Nitroolefins
Toward a Aluminum Chloride and Ethanethiol System

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Eiichi Fujita*, and Manabu Node**

Reductive displacement of nitro group into hydrogen took place in *a*–nitroketones **1a** and **5** by a treatment with aluminum chloride and ethanethiol, whereas carbon–carbon bond cleavage occurred in *a*–nitroketones **1b, 1c** and nitroolefins. A possible mechanism is proposed.

KEY WORDS: *a*–Nitroketone / Nitroolefin / Hard Acid / Soft Nucleophile / Reductive Displacement of Nitro Group / Dithioacetal / Sulfide/ Orthothioester

INTRODUCTION

We have reported bond–cleavage reactions of activated carbon–carbon double bonds with a hard acid and soft nucleophile system.[1b] Aluminum halides or boron trifluoride etherate are hard acids and ethanethiol is a soft nucleophile of choice, respectively. Reactions proceed *via* a conjugate addition of ethanethiol followed by an $S_N 1$ –type carbon–carbon bond cleavage as shown in Scheme I. Extension of the reaction to a carbon–carbon single bond cleavage of *a*–nitro ketones is possible, if the similar mechanism is operative. This paper describes the results of bond cleavage reacitions of *a*–nitro ketones and nitroolefins.[2]

Shceme I
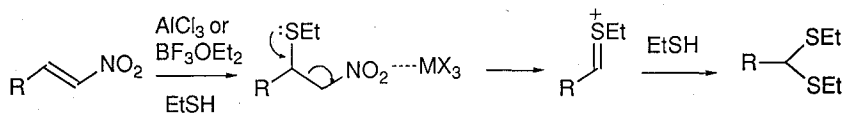
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RESULTS AND DISCUSSION

Reductive Displacement of Nitro Group into Hydrogen.

α–Nitro ketones **1** were prepared by a potassium fluoride–induced condensation[3] of nirtoalkanes with heptaldehyde followed by Jone's oxidation of the resulting nirto alcohols. Treatment of **1b** with aluminum chloride and ethanethiol afforded orthothioester **2** (59 % yield) and ketenethioacetal **3** (12 % yield) *via* the expected carbon–carbon bond cleavage.[4] Similarly, **1c** furnished **2** and **3** in 40 % and 23 % yield, respectively, under the similar reaction conditions.[5] On the other hand, **1a** gave **2** and **3** in ~0 % and 9 % yield, respectively. Instead, an unexpected product **4** was obtained in 63 % yield which resulted from reductive displacement of nitro group into hydrogen. Since a transformation of nitro group into hydrogen has been recognized to be important in synthetic organic chemistry,[6] generality of the reductive displacement of the nitro group in primary α–nitro ketones were examined. As seen in Table I, aliphatic as well as aromatic α–nitroketones **5** furnished dithioacetals **6** as the major product by the treatment with aluminum chloride and ethanethiol.

Mechanism for Reductive Displacement of the Nitro Group into Hydrogen.

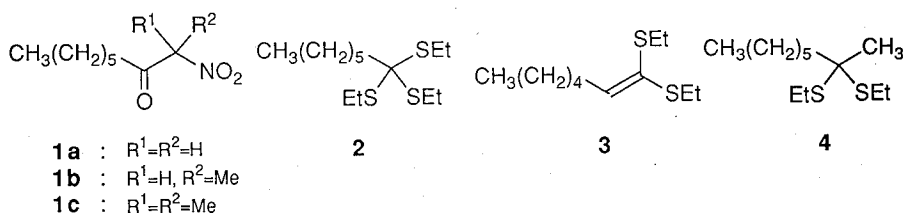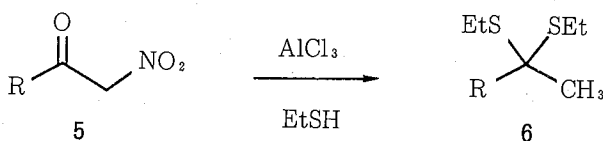Reported methods for reductive displacement of nitro group into hydrogen in-

$$\text{1a} : \text{R}^1=\text{R}^2=\text{H}$$
$$\text{1b} : \text{R}^1=\text{H, R}^2=\text{Me}$$
$$\text{1c} : \text{R}^1=\text{R}^2=\text{Me}$$

Table I Reductive Displacement of Nitro Group into Hydrogen.

substrate	R	mol eq of AlCl₃	temp	reaction time (h)	product	yield (%)
5a	Ph	3.0	rt	3.5	6a	78
5b	p-Me-Ph	3.0	rt	8	6b	60
5c	2-Naph	3.0	rt	20	6c	66
5d	PhCH₂	3.0+2.0[a]	0°-rt	8	6d	60
1a	CH₃(CH₂)₅	3.0+2.0[a]	0°-rt	8	4	57[b]

a) Additional two mol eq of AlCl₃ was added after 5h. b) Ketene thiocaetal **3** was also obtained in 9% yield.

Scheme II
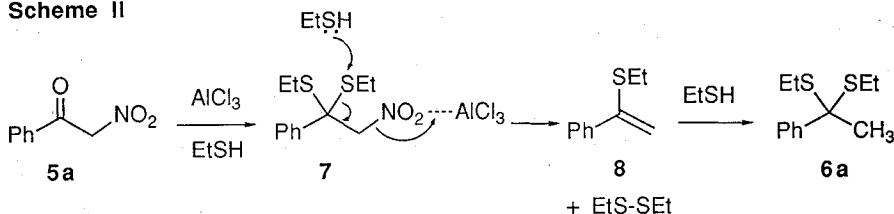
clude a use of sodium methyl sulfide,[7] a dihydronicotinamide derivative,[8] or tributyltin hydride.[9] Reduction of nitro group with these reagents are known to proceed through a one–electron transfer process. As the result, the reactivity for the transformation is in the order of *tert–>sec–>pri–* nitroalkanes due to the stability of the intermediary alkyl radicals. In contrast, the present reductive displacement of the nitro group seems to be specific to primary α–nitroketones. These observations indicate that the present reaction proceed *via* an ionic pathway rather than the one–electron transfer process. We propose a possible mechanism as shown in Scheme II. This mechanism is supported by the observation that dithoacetal **7** as well as vinyl sulfide **8** prepared by definite routes afforded **6a** in 41 % and 98 % yield, respectively, *under the same reaction conditions as those employed for* **5a**. If ethanethiol functions as a reducing agent, formation of **6a** should accompany with generation of diethyl disulfide. In the reaction of **5a** with aluminum chloride and ethanethiol, **6a** was obtained in 78 % yield together with diethyl disulfide in 80 % yield,[10a] which is consistent with the proposed mechanism. Diethyl disulfide, however, might be formed simply by a reaction of ethanethiol with aluminum chloride. To investigate the point, acetophenone was treated with aluminum chloride and ethanethiol. Dithioacethalization of acetophenone took place in 68 % yield, whereas any trace of diethyl disulfide was not observed in the reaction mixture. Treatment of **5a** with zinc chloride and ethanethiol gave **7** in 73 % yield without generation of the reduced product **6a**, where diethyl disulfide was again not detected in the reaction mixture. These findings clearly show that ethanethiol acts as a reducing agent in the transformation of **7** to **8**.[10b]

Difference in the Reactivity of Nitro Compounds.

The observed reactivity of three different–types of nitro compounds are summarized in Scheme III; i) carbon–carbon double bond cleavage in nitroolefins[1b], ii) reductive displacement of nitro group into hydrogen in unsubstituted α–nitroketones, iii) carbon–carbon single bond cleavage in subsitituted α–nitroketones. Different reactivity between i) and ii) could be attributed to a porarizability of the C–S bonds as well as a leaving ability of the nitro group. Dithioacetal **B** must adopt a conformation as shown in figure I according to the Deslongchamps' model[11], in which one of the lone pair orbitals on each sulfur atom is
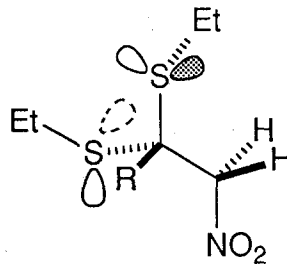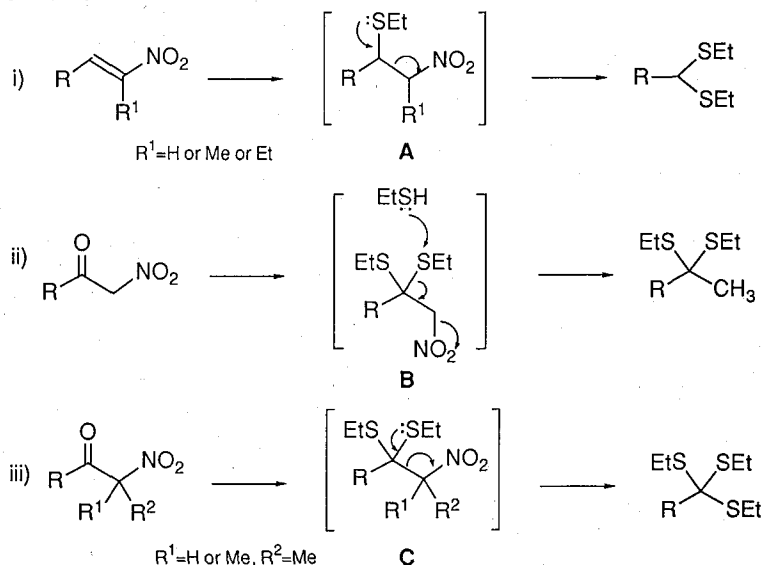

Fig. I

Scheme III

oriented antiperiplanar to another C–S bond. In other words, none– bonding electron of sulfur overlaps effectively with σ^* of the C–S bond. Thus, the C–S bond of **B** has larger polarizability than that of sulfides **A**, so that the former C–S bond cleaves easier.[12] The difference in the leaving ability between each nitro group in **A** and **B** may be another factor for the different reactivity. The orbital interation between high–lying σ^* of the C–NO$_2$ bond and σ of the C–S bond is expected to be better in **B** than that in **A** because the energy level of σ of the C–S bond is higher in **B** than in **A** due to the orbital interaction between σ^* of the C–S bond and none–bonding electron of the sulfur. As the result, the nitro group in **B** must have a higher leaving ability than that in **A**. The larger polarizability of the C–S bond as well as the better leaving ability of the nitro group in **B** would facilitate the cleavage of both the C–S and the C–NO$_2$ bonds as shown in **B**. On the other hand, none–bonding electron on sulfur interacts only with σ^* of C–C(NO$_2$) bond in **A**, which makes the C–C bond fission easier. The C–C bond fission, however, predominates over C–S bond fission, when mono– or disubstituted α–nitroketone, **1b** or **1c**, was employed as shown in **C**. The difference between **B** and **C** may be understood in terms of a steric acceleration caused by the substituents R^1 and R^2, where the unimolecular reaction (S_N1–type C–C bond fission) may reasonably take precedence over the bimolecular reaction (as in **B**). Another possible rationale involves unpreference of the conformation of the C–NO$_2$ bond antiperiplanar to the C–S bond in **C** due to a steric interaction between ethyl group on sulfur and R^1 or R^2.

Synthetic Utility.

Synthetic methodology utilizing nitro compounds is proud of its mildness of reaction conditions for the C–C bond formation. For examples, α–nitroketone **5a** could be prepared by a condensation reaction of benzoic acid and nitromethane in the

K. Fuji, T. Kawabata, M. Ueda, M. Fujimoto, E. Fujita and M. Node

presence of triethylamine and diethyl phosphorocyanidate[13]. Similarly, a mild base such as potassium fluoride is effective enough for a preparation of **1**. These process, when combined with the present denitration illustrated in the reactions of **1a** and **5** into **4** and **6**, respectively, provide a new method for methyl ketone synthesis from carboxilic acids or aldehydes utilizing a masked methyl anion. Since commonly used methyl anions such as methyl Grignard reagent and methyl lithium have much stronger basicity than that of triethylamine or potassium fluoride, the present transformation may be advantageous when the substrates are labile under strongly basic conditions. Another characteristic of the present process relies on chemoselectivity of the condensation reaction of nitromethane. Weak nucleophilicity of a anion of nitromethane made possible the selective C–C bond formation with heptaldehyde in the presence of a ketone **9** and a ester **10**.[14] When heptaldehyde was treated, in the presence of equal amounts of **9** and **10**, with nitromethane and potassium fluoride, **11** was obtained in 88 % yield with 96 % and 97 % recovery of **9** and **10**, respectively. Jone's oxidation of **11** afforded **1a** in 88 % yield which could be transformed to **4** as already described above. The overall scheme indicates that a methyl anion was introduced highly selectively into aldehyde in the presence of ketone and ester, which is hardly achieved by means of methyl Grignard reagent or methyl lithium.

$$CH_3(CH_2)_5\text{—}CO_2Me \qquad 10$$

9   **10**   **11**   **12**
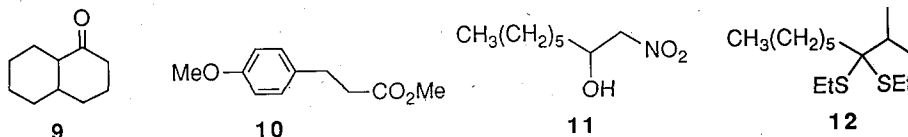
EXPERIMENTAL SECTION

General.

Melting points were measured using a Yanagimoto Micro Melting Point Apparatus and were uncorrected. ^{1}H NMR spectra (tetramethylsilane as an internal standard) were obtained with a Varian T–60 spectrometer or a JOEL JMN–FX 100 spectrometer, chemical shifts being given in ppm units. IR spectra were recorded with a JACSO A–202 diffracting grating infrared spectrometer. Exact mass spectra were recorded with a JEOL JMS–DX 300 mass spectrometer. TLC analyses were performed on commercial glass plates bearing a 0.25 –mm layer of Merck Kieselgel 60 F_{254}. Preparative TLC was performed with commercial glass plates precoated (0.5 mm) with Kieselgel 60 F_{254}. Column chromatography was carried out with silica gel (Wakogel C–200). Dichloromethane and ethanethiol were distilled from calcium hydride and calcium chloride, respectively. Aluminum chloride was purified by sublimation.

1–Nitro–2–octanone (1a). Prepared by a condensation reaction of heptaldehyde and nitromethane[3] followed by Jone's oxidation (62% yield from heptaldehyde): colorless plates (hexane); mp 49.5–50℃; ^{1}H–NMR (CDCl₃) δ 0.6–0.9 (m, 11 H), 2.55 (t, J= 7 Hz, 2 H), 5.24 (s, 2 H); IR (KBr) 2920, 1720, 1550, 1375 cm⁻¹. Anal.

Calcd for $C_8H_{15}NO_3$: C, 55.47; H, 8.74; N, 8.09. Found: C, 55.47; H, 8.80; N, 7.94.

2–Nitro–3–nonanone (1b). Prepared according to the procedure for **1a** using nitroethane instead of nitromethane (63 % yield from heptaldehyde): colorless plates (hexane); mp 26 – 27 ℃; ^1H–NMR (CDCl$_3$) δ 0.6 – 2.0 (m, 11 H), 1.68 (d, J = 7 Hz, 3 H), 2.55 (t, J = 7 Hz, 2 H), 5.19 (q, J = 7 Hz, 1 H); IR (CHCl$_3$) 2940, 1725, 1550, 1445 cm^{-1}; exact MS calcd for $C_9H_{17}NO_3$ (M$^+$) 187.1209, found *m/z* 187.1217. Anal. Calcd for $C_9H_{17}NO_3$: C, 57.73; H, 9.15; N, 7.48. Found: C, 57.81; H, 9.34; N, 7.81.

2–Methyl–2–nitro–3–nonanone (1c). Prepared according to the procedure for **1a** using 2–nitropropane instead of nitromethane(20% yield from heptaldehyde): colorless oil; ^1H–NMR (CDCl$_3$) δ 0.5 – 1.7 (m, 11 H), 1.72 (s, 6 H), 2.48 (br t, J = 6 Hz, 2 H); IR (CHCl$_3$) 2940, 1725, 1455, 1345 cm^{-1}. Anal. Calcd for $C_{10}H_{19}NO_3$: C, 59.67; H, 9.52; N, 6.96. Found: C, 60.02; H, 9.74; N, 7.18.

1,1–Tris(ethylthio)heptane（2）and 1,1–bis(ethylthio)–1–heptene（3）. To a solution of **1b** (56 mg, 0.3 mmol) in dichloromethane (1.0 mL) was added a solution of aluminum chloride (120 mg, 0.9 mmol) in ethanethiol (1.0 mL) at 0 ℃. After stirring for 2 h, the reaction mixture was warmed to room temperature and stirred for additional 5 h. The mixture was poured into dil HCl–ice and extracted with dichloromethane. The organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The residue was purified by preparative TLC (ethyl acetate : hexane = 1.5 : 98.5) to afford **2** (48 mg, 57% yield) and **3**（8 mg, 12% yield). **2** : colorless oil; ^1H–NMR (CDCl$_3$) δ 0.7 – 2.1 (m, 13 H), 1.23 (d, J = 7 Hz, 9 H), 2.69 (q, J = 7 Hz, 6 H); IR (CHCl$_3$) 2930, 1445, 1255 cm^{-1}; exact MS calcd for $C_{13}H_{28}S_3$ (M$^+$) 280.1353, found *m/z* 280.1329; **3** : colorless oil; ^1H–NMR (CDCl$_3$) δ 0.7 – 1.7 (m, 9 H), 1.21 (t, J = 7 Hz, 6 H), 2.1 – 2.5 (m, 2 H), 2.71 (q, J = 7 Hz, 2 H), 2.76 (q, J = 7 Hz, 2 H), 6.13 (t, J = 7 Hz, 1 H); IR (neat) 2930, 1670, 1445, 1370 cm^{-1}; exact MS calcd for $C_{11}H_{22}S_2$ (M$^+$) 218.1162, found *m/z* 218.1140. Anal. Calcd for $C_{11}H_{22}S_2$: C, 60.48; H, 10.15. Found: C, 60.37; H, 10.26.

2–Nitroacetophenone (5a). Prepared by a method of Shioiri[13] or a method of Field[15].

4′–Methyl–2–nitroacetophenone (5b). Prepared by a condensation reaction[15] of nitromethane with phenyl 4–methylbenzoate which was obtained from 4–methyl-benzoic acid and phenol by a method of Lowrance[16] (77% yield from phenyl 4–methylbenzoate): colorless needles (acetonitrile); mp 148 – 149° C; ^1H–NMR (CDCl$_3$) δ 2.45 (s, 3 H), 5.83 (s, 2 H), 7.29 (ABd, J = 8 Hz, 2 H), 7.75 (ABd, J = 8 Hz, 2 H); IR (KBr) 3090, 3030, 1700, 1615, 1565, 1335 cm^{-1}; Anal. Calcd for $C_9H_9NO_3$: C, 60.33; H, 5.06; N, 7.82. Found: C, 60.35; H, 5.03; N, 8.07.

2–Naphthyl nitromethyl ketone (5c). Prepared according to the procedure for **5b** using 2–naphthoic acid instead of 4–methylbenzoic acid (43% yield from phenyl 2–naphthoate). : pale yellow needles (methanol); mp 103 – 104° C; ^1H–NMR (CDCl$_3$) δ 5.93 (s, 2 H), 7.5 – 8.1 (m, 6 H), 8.23 (s, 1 H); IR (KBr) 1690, 1625, 1560, 1315 cm^{-1}; Anal. Calcd for $C_{12}H_9NO_3$; C, 66.97; H, 4.22; N, 6.51. Found: C, 67.05; H, 4.11; N, 6.55.

1–Nitro–3–phenyl–2–propanone (5d). Prepared according to the procedure for **1a** using phenyl acetaldehyde instead of heptaldehyde. Compound **5d** is known.[17]

General Procedure for Reductive Displacement of Nitro Group into Hydrogen. To a solution of **1 a** or **5** (0.5 mmol) in dichloromethane (1.0 mL) was added a solution of aluminum chloride (200 mg, 1.5 mmol) in ethanethiol (1.0 mL) at 0 °C. The reaction mixture was stirred under the conditions listed in Table I. The progress of the reaction was monitored by TLC. When it was slow, an additional amount (133 mg, 1.0 mmol) of aluminum chloride was added.* After the starting material was consumed, the reaction mixture was poured into ice–water and extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by preparative TLC. The products and the yields are given in the Table I. Physical Data of compounds **4**, **6 b**, **6 c**, and **6 d** are shown below. Compound **6 a** is known.[18]

* Use of 2.5 mmol of aluminum chloride at the beginning is to be avoided because the amount of Nef–type side reaction is increased.

2,2–Bis(ethylthio)octane (4): colorless oil; ^{1}H–NMR (CDCl$_3$) δ 0.7 – 2.0 (m, 13 H), 1.22 (t, J= 8 Hz, 6 H), 1.51 (s, 3 H), 2.60 (q, J= 8 Hz, 4 H); IR (neat) 2940, 1450, 1260 cm^{-1}; exact MS calcd for $C_{12}H_{26}S_2$ (M$^+$) 234.1477, found m/z 234.1484.

4–[1,1–Bis(ethylthio)ethyl]toluene (6b): colorless oil; ^{1}H–NMR (CDCl$_3$) δ 1.15 (t, J= 8 Hz, 6 H), 2.01 (s, 3 H), 2.33 (s, 3 H), 2.52 (q, J= 8 Hz, 4 H), 7.08 (AB d, J= 8 Hz, 2 H), 7.57 (AB d, J= 8 Hz, 2 H); IR (neat) 2980, 1510, 1445, 1370, 1260 cm^{-1}; exact MS calcd for $C_{13}H_{20}S_2$ (M$^+$) 240.1006, found m/z 240.0999. Anal. Calcd for $C_{13}H_{20}S_2$: C, 64.94; H, 8.39. Found: C, 65.26; H, 8.50.

2–[1,1–Bis(ethylthio)ethyl]naphthalene (6c): pale yellow oil; ^{1}H–NMR (CDCl$_3$) δ 1.15 (t, J= 8 Hz, 6 H), 2.12 (s, 3 H), 2.53 (q, J= 8 Hz, 4 H), 7.3 – 8.0 (m, 6 H), 8.00 (s, 1 H); IR (neat) 3070, 2980, 1595, 1445, 1265 cm^{-1}; exact MS calcd for $C_{16}H_{20}S_2$ (M$^+$) 276.1007, found m/z 276.1012. Anal. Calcd for $C_{16}H_{20}S_2$: C, 69.51; H, 7.29. Found: C, 69.08; H, 7.39.

2,2–Bis(ethylthio)propylbenzene (6d): colorless oil; ^{1}H–NMR (CDCl$_3$) δ 1.22 (t, J= 8 Hz, 6 H), 1.46 (s, 3 H), 2.63 (q, J= 8 Hz, 4 H), 3.07 (s, 2 H), 7.26 (s, 5 H); IR (neat) 2980, 1605, 1500, 1450, 1265 cm^{-1}; exact MS calcd for $C_{13}H_{20}S_2$ (M$^+$) 240.1006, found m/z 240.1010. Anal. Calcd for $C_{13}H_{20}S_2$: C, 64.94; H, 8.39. Found: C, 64.77; 8.60.

1, 1, –Bis(ethylthio)–2–nitroethylbenzene (7). To a solution of **5 a** (800 mg, 4.9 mmol) in dichloromethane (10 mL) was added ethanethiol (5.0 mL) followed by zinc chloride (3.3 g, 25 mmol) at 0 °C. After stirring for 2 h, the mixture was warmed to room temperature and stirred for additional 2 h. The reaction mixture was poured into dil HCl–ice and extracted with dichloromethane. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (ethyl acetate : hexane = 2.5 : 97.5) to afford **7** (960 mg, 73% yield): pale yellow oil; ^{1}H–NMR (100 MHz) (CDCl$_3$) δ 1.22 (t, J= 7.5 Hz, 6 H), 2.62 (q of ABq, $\Delta\nu_{AB}$= 6.9 Hz, J$_{AB}$= 11 Hz, J$_{AX}$= 7.5 Hz, 4H), 4.95 (s, 2 H), 7.2 – 7.8 (m, 5 H); IR (neat) 2985, 1555, 1440, 1370 cm^{-1}; exact MS calcd for $C_{12}H_{17}NO_2S_2$ (M$^+$) 271.0700, found m/z 271.0671.

1–(Ethylthio)ethenylbenzene (8). Prepared by pyrolysis of **6 a** (117 – 123°C / 19 mm Hg). Compound **8** is known[19].

Condensation of Heptaldehyde with Nitromethane in the Presence of 9 and 10.
To a solution of a mixture of equal amounts (0.35 mmol) of heptaldehyde, 9, and
10[14] in isopropanol (2.0 mL) was added nitromethane (57 μL, 1.1 mmol) followed by
potassium fluoride (20 mg, 0.34 mmol). After stirring at room temperature for 13 h,
the reaction mixture was poured into ice–water, neutralized with dil HCl, and
extracted with dichloromethane. The organic layer was washed with brine, dried
over Na$_2$SO$_4$, filtered, and concentrated in vacuo. The residue was purified by
preparative TLC (ethyl acetate : hexane = 15 : 85) to afford 11 (54 mg, 88% yield),
9 (50 mg, 96% recovery), and 10 (66 mg, 97% recovery). Structure of 11 was
deduced by its ^{1}H–NMR spectrum and confirmed by the transformation into 1 a. [1]H–
NMR (CDCl$_3$) δ 0.7 – 1.8 (m, 13 H), 2.92 (br s, 1 H), 4.1 – 4.6 (m, 3 H).

3,3–Bis(ethylthio)–2–methylnonane (12): colorless oil; ^{1}H–NMR (CDCl$_3$) δ 0.7 –
1.8 (m, 13 H), 1.05 (d, J = 7 Hz, 6 H), 1.22 (t, J = 7 Hz, 6 H), 1.95 (sept, J = 7 Hz,
1 H), 2.64 (q, J = 7 Hz, 4 H); IR (neat) 2930, 1455, 1380, 1260 cm^{-1}; exact MS calcd
for C$_{14}$H$_{30}$S$_2$ (M$^+$) 262.1789, found m/z 262.1774. Anal. Calcd for C$_{14}$H$_{30}$S$_2$: C, 64.05 ; H,
11.52. Found : C, 64.16 ; H, 11.29.

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