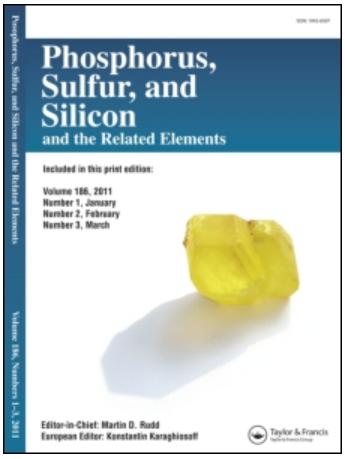

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REACTION OF POLYMERIZATION-RESISTANT 1,2-DITHIOLANES WITH LITHIATED PICOLINES: SIMPLE RING OPENING AND 1,3-DITHIANE FORMATION

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To cite this Article Tazaki, Masato , Okai, Shigeyuki , Hieda, Toshihiko , Nagahama, Shizuo and Takagi, Makoto(1996) 'REACTION OF POLYMERIZATION-RESISTANT 1,2-DITHIOLANES WITH LITHIATED PICOLINES: SIMPLE RING OPENING AND 1,3-DITHIANE FORMATION', Phosphorus, Sulfur, and Silicon and the Related Elements, 112: 1, 101 — 108
To link to this Article: DOI: 10.1080/10426509608046352
URL: http://dx.doi.org/10.1080/10426509608046352

Phosphorus, Sulfur, and Silicon, 1996, Vol. 112, pp. 101–108
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REACTION OF POLYMERIZATION-RESISTANT 1,2-DITHIOLANES WITH LITHIATED PICOLINES: SIMPLE RING OPENING AND 1,3-DITHIANE FORMATION

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(Received August 10, 1995; in final form October 12, 1995)

Reaction of polymerization resistant 1,2-dithiolanes **1** with excess pyridylmethyllithiums **3** in THF gave the corresponding ring-opened products **2** in good yields, but the by-products 2-pyridyl-1,3-dithianes **5** and 1,3-propanedithiols **6** could not be excluded. Addition of hexamethylphosphoric triamide (HMPT) to the reaction mixture resulted in the selective formation of **5**.

Key words: 1,2-Dithiolane, nucleophilic S—S bond cleavage, lithiated picolines, mono-S-picolyl-1,3-propanedithiols, ligands for transition metals, 1,3-dithianes.

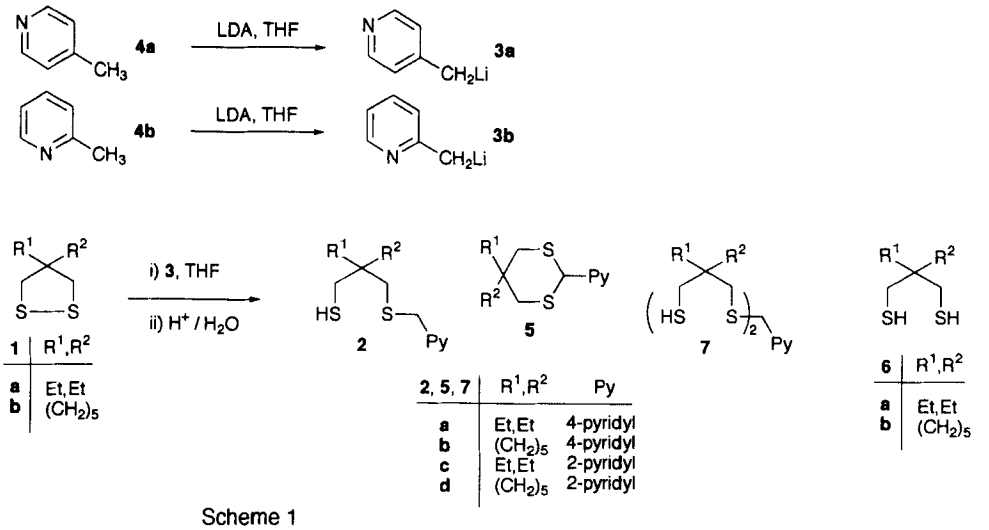
INTRODUCTION

The nucleophilic S—S bond cleavage of 1,2-dithiolanes **1** results in a quantitative ring-opening in many cases.[1] The products are the 1,3-propanedithiol derivatives, one SH group of which is selectively functionalized by the nucleophiles employed. One of the most important applications of these reactions would be the synthesis of asymmetric ligands for transition metals containing free SH and functionalized sulfide groups.[2]

Picolines **4** are known to be readily lithiated with lithium diisopropylamide (LDA) to give pyridylmethyllithiums **3**.[3] They were reacted with 1,2-dithiolanes **1** to develop a selective synthesis of pyridine-containing ligand for transition metals, but the reaction was not straightforward as reported here.

RESULTS AND DISCUSSION

We already found that the reaction of polymerization-resistant 1,2-dithiolane **1** with carbon nucleophiles, such as simple Grignard reagents and thienyllithiums, gives the



Scheme 1

ring opened products in a quantitative manner.[1] No unsubstituted 1,3-propanedithiols **6** nor disubstituted products 1,3-propane bis-(sulfide)s could be detected in the products. The reaction is straightforward and especially useful for the synthesis of asymmetrically substituted 1,3-propanedithiol derivatives.

We also found that sulfonium benzylides and acetylide anions cleave the S—S bond of the polymerization resistant 1,2-dithiolanes in a quantitative manner, but the ring-opening products isomerize readily to the cyclic products in excellent yields.[4] Thus the asymmetric 1,2-propanedithiol derivatives containing a free SH group are not obtained in these cases at all.[4]

The reaction of **1** with pyridylmethyllithium **3** in THF was the intermediate case: the reaction gave the corresponding ring opening product **2** but the by-products were always observed. Slight excess of 4-picolyllithium **3a** was prepared by mixing 4-picoline **4a** and BuLi at −78°C in THF and reacted with 4,4-diethyl-1,2-dithiolane **1a** at room temperature for 0.5 h (see Table I, entry 1). The mixture was acidified with aqueous acetic acid and extracted with dichloromethane. The organic layer was analyzed directly by glc and GC-MS, showing that the product contained the expected **2a** accompanied by the unexpected 2,2-diethyl-1,3-propanedithiol **6a** (not shown in the table) and the cyclic thioacetal **5a**. Disubstituted product 1,3-bis-(pyridylmethylthio)propanes were not found in the product. It is remarkable that the production of **5a** exceeded that of **2a** as shown in the entry 1.

The production of **5a,d** could be reduced to a few percent of **2a,d** when 2–3 equivalents of picolyllithium **3a,b** were employed as shown in the entries 2–4. This result suggested that two equivalents of lithium reagents **3** against 1,2-dithiolanes **1** are required for the reaction, i.e., one equivalent for the ring opening and the next for the proton abstraction from the ring opening product.

Based on these preliminary works, the ring opening of 1,2-dithiolanes **1a,b** was carried out using 3 equivalents of picolyllithiums **3a,b** in THF at 0°C to room temperature for 2–4 h. The products **2a,d** were purified by simple kugelrohr distillation, the results are shown in Table II. Reasonable purity of 95% was obtained for the preparation of 4-picolyl derivative **2a**, but only 84% purity was resulted for the 2-

TABLE I

Reaction of 1,2-dithiolane **1** with pyridylmethyllithium **3**[a]

entry	1	3	reagent[b] (additive)	ratio of products[c]	
				2	**5**
1	**1a**, 1.6	**3a**, 2.0	BuLi	**2a**, 46	**5a**, 54
2	**1a**, 1.5	**3a**, 3.0	LDA	**2a**, 96	**5a**, 4
3	**1a**, 1.0	**3a**, 3.0	LDA	**2a**, 98	**5a**, 2
4	**1b**, 1.0	**3b**, 3.0	LDA	**2d**, 98	**5d**, 2
5	**1a**, 1.6	**3a**, 2.0	LDA (HMPT)[d]	**2a**, 1	**5a**, 99
6	**1a**, 1.9	**3a**, 4.7	LDA (HMPT)[d]	**2a**, 14	**5a**, 96
7	**1b**, 1.0	**3b**, 2.5	LDA (HMPT)[d]	**2d**, 0	**5d**, 100

a) Reactions of **1** with **3** were performed in THF 5-10 ml at 0 °C to rt for 0.5-2 h.
b) Lithiations with BuLi and lithium diisopropylamide LDA were performed at -78 and 0 °C, respectively.
c) Estimated from direct glc of the reaction mixture acidified with aq. acetic acid or NH_4Cl.
d) Molar ratio of **3** and hexamethylphosphoric triamide HMPT was 1:1.

TABLE II

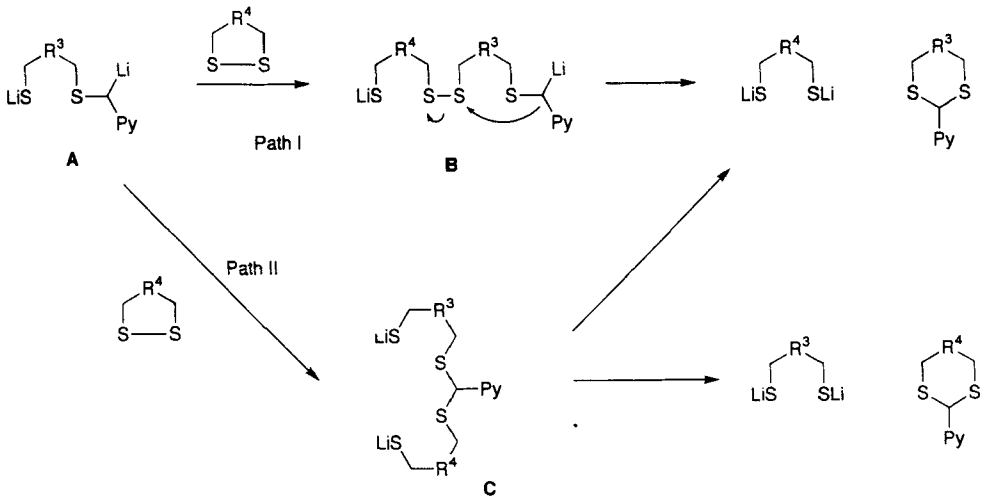
Syntheses of 3-pyridylmethylthiopropanethiol **2**[a]

entry	1	3	product	yield / %[b]	purity / %[c]
1	**1a**	**3a**	**2a**	84	95
2	**1b**	**3b**	**2d**	79	84

a) Reactions of **1** (1 mmol) with **3** (3 mmol) in THF 10 ml at room temp for 2 h.
b) Yields after kugelrohr distillation.
c) Estimated from glc of the distillate.

picolyl derivative **2d**. The structure of **2** was confirmed by the following evidence: ^{1}H NMR showed the presences of pyridine and 1,3-propanedithiols moieties in a 1:1 ratio, and the presence of CH_2SH group by the triplet at 1.1 ppm (SH) and the doublet at 2.5 ppm (CH_2) with a characteristic coupling constant ^3J = 8.8 Hz. ^{13}C NMR and DEPT (90 and 135° pulses) spectra were fully consistent with the proposed structure.

The discrepancy of the glc purities between the undistilled and distilled products, i.e., Entry 4 in Table I and Entry 2 in Table II suggested the presence of another by-product which does not appear in glc analysis and decomposes to the 1,3-dithiane **5d** during the distillation. Duplicated reaction was performed and the product before the distillation was analyzed by ^{1}H NMR. The results are summarized as follows: 1) only a trace amount of the 1,3-dithiane **5d** was detectable in the undistilled product, 2) major by-product (singlet at 4.99 ppm) was a thioacetal different from **5d** (singlet at 5.26 ppm), 3) the structure of the thioacetal was suggested as the 1:2 adduct **7d**



Scheme 2

of 2-methylpyridine **4b** and the 1,2-dithiolane **1b** produced via a further reaction of the ring opening product **2d** (doubly lithiated) and the 1,2-dithiolane **1b**. Similar 1:2 adduct **7a** (singlet at 4.77 ppm) was suggested in the undistilled product of **2a**, but its amount was negligible. These results show that the sulfenylation of excess 2-picolyllithium with the limited amount of 1,2-dithiolanes occurs in two steps. It is remarkable that the second sulfenylation of 2-picolyllithium can compete with the first sulfenylation under such conditions.

The results in Table I entries 5–7 show another aspect of the reaction involving picolyllithiums **3** and the 1,2-dithiolanes **1**, i.e., the production of **2** was suppressed in the presence of HMPT and the 1,3-dithiane formation became preferential. Subtle change in the lithium reagent by the coordination of HMPT to the lithium ion alters the product. The dithianes **5** were produced with 1,3-propanedithiols **6** in a molar ratio of 1:1 as confirmed by glc and ^{13}C NMR of the crude products. Therefore the reaction is described as in Equation 1. This kind of reaction is not recorded in the literature and may be characteristic to the strained 1,2-dithiolane ring.

The reaction in Equation 1 provides a facile synthesis of 2-(pyridyl)-1,3-dithiane useful for the masked pyridylcarbonyl anion equivalent in organic synthesis.[5] Thus 1,3-dithiane synthesis according to Equation 1 was attempted. Picolyllithium **3** (3.5 mmol) was prepared by lithiation with LDA in THF (10 ml) and reacted with 1,2-dithiolane **1** (2.0 mmol) in the presence of HMPT (3.5 mmol) at room temperature for 2–4 h. After being acidified with aqueous acetic acid, the mixture was extracted twice with hexane, and the organic layer was washed with water, dried, and concentrated. The 2-pyridyl-1,3-dithianes **5a–d** were obtained by a kugelrohr distillation or recrystallization in excellent yields and good purities as summarized in Table III.

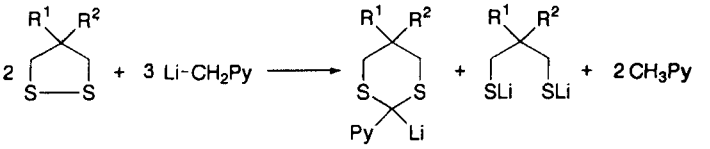
The structure of 1,3-dithiane was confirmed by the following evidence: ^1H NMR showed the presences of pyridine and parent dithiolane moieties in a 1:1 ratio. Two doublet at 2.6 and 2.8 ppm with characteristic bicinal coupling ^2J = 13.8 Hz clearly showed the cyclic structure. ^{13}C NMR and DEPT (90 and 135° pulses) spectra were fully consistent with the proposed structure: especially two substituents on C-5 became no longer equivalent.

TABLE III

Syntheses of 2-pyridyl-1,3-dithiane **5**[a]

entry	1	3	product	yield / %[b]	purity / %[c]
1	**1a**	**3a**	**5a**	92	93
2	**1b**	**3a**	**5b**	98	100
3	**1a**	**3b**	**5c**	85	100
4	**1b**	**3b**	**5d**	69	100

a) Reactions of **1** (2 mmol) with **3** (3.5 mmol) as described in eq. 1. Additive HMPT (3.5 mmol) in THF 10 ml at room temp for 4 h.
b) Yields after kugelrohr distillation or recrystalization.
c) Estimated by glc.



(1)

Two possible mechanisms for the formation of the 1,3-dithiane **5** are delineated in Scheme II ($R^3 = R^4$). In the path I, the ring-opened product A (doubly lithiated **2**) reacts further with the 1,2-dithiolane **1** at the thiolate site to produce the intermediate B which degrades into the 1,3-dithiane **5** and the 1,3-propanedithiol **6** via an intramolecular displacement. This mechanism appears likely since two S_N2 processes involved are common to the disulfide chemistry. In the other path II, the product A reacts at the carbanion site to produce the intermediate C (lithiated **7**) which decomposes into **5** and **6** as suggested above during the distillation of the ring-opened products **2**. The latter mechanism is unusual, since one of the two C—S bond in the thioacetal C must be cleaved.

Scheme II also shows the cross experiment ($R^3 \neq R^4$) that can discriminate the mechanisms described above. Thus, the ring opened product **2a** ($R^3 = CEt_2$) was lithiated with LDA (4.0 equivalents) in THF to produce the corresponding intermediate A and reacted with the 1,2-dithiolane **1b** ($R^4 = C(CH_2)_5$, 1.0 equivalent) in the presence of HMPT (4.0 equivalents). The product was an equimolar mixture of 1,3-dithianes **5a** and **5b** as analyzed by glc and ^1H NMR. The random formations of two possible 1,3-dithianes **5a,b** containing R^3 and R^4 clearly show that the unusual pathway II is operating, since the alternative pathway I would give only a 1,3-dithiane **5** containing R^3.

In conclusion, we found the reaction of polymerization resistant 1,2-dithiolane with picolyllithiums was not straightforward to give the ring opening products **2**, but was accompanied by a side reaction producing 2-pyridyl-1,3-dithiane **5** and 1,3-propanedithiols **6**. The ring opening becomes preferential, when large excess lithium reagent are employed, giving selectivity the asymmetric ligand **2** for transition met-

als. On the other hand, the 1,3-dithiane formation becomes preferential in the presence of HMPT giving masked carbonyl anion equivalent for organic synthesis.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL EX-90 instrument operating at 89.5 and 22.5 MHz, respectively. DEPT methods using 90 and 135 degree pulses were employed to determine the number of proton(s) attached to the carbon. MS spectra were taken at 70 eV on a JEOL AX500 equipment. IR spectra were obtained by using a JASCO FT/IR-7000 spectrometer on KBr pellets of liquid and solid samples.

Dithiolanes **1a,b** were prepared from the corresponding 1,3-propanediols according to the reported method.[6] THF solution of LDA was conveniently prepared by mixing BuLi and slight excess diisopropylamine at −78 to 0°C in THF. THF was refluxed and distilled from sodium benzophenone ketyl under argon just before use.

Reaction of 4,4-diethyl-1,2-dithiolane **1a** *with 4-pyridylmethyllithium* **3a**: 4-Methylpyridine **4a** (355 mg, 3.8 mmol) was added to a solution of LDA (3.0 mmol) in THF (5 ml) at −78°C under argon. Then, **1a** (158 mg, 1.0 mmol) was added to the solution at 0°C and the mixture was stirred for 2 h. The mixture was hydrolyzed with saturated NH_4Cl (0.5 ml) and water (10 ml), and extracted with dichloromethane (10 ml). The organic layer was concentrated under reduced pressure and distilled by kugelrohr.

4-(2-ethyl-2-mercaptomethylbutylthiomethyl)pyridine, **2a**. Yield 212 mg (84%), purity 95% (by glc containing 1,3-dithiane **5a** 1.6% and 1,2-dithiolane **1a** 2.9%), ot 82–153°C/0.5 mmHg. IR (KBr) ν 2968 (s), 2926 (m), 2568 (vw, S-H), 1601 (s), and 1415 cm^{-1} (m). ^{1}H NMR ($CDCl_3$) δ 0.712 (6H, t, J = 7.4 Hz, $2CH_3$), 1.102 (1H, t, J = 8.8 Hz, SH), 1.318 (4H, q, J = 7.4 Hz, $2CH_2$), 2.422 (2H, s, SCH_2), 2.466 (2H, d, J = 8.8 Hz, CH_2SH), 3.642 (2H, s, SCH_2), 7.268 (2H, dd, J = 4.4, 1.6 Hz), and 8.538 ppm (2H, dd, J = 4.4 and 1.6 Hz). ^{13}C NMR ($CDCl_3$) δ 7.54 ($2CH_3$), 26.40 ($2CH_2$), 30.50 (CH_2SH), 36.36 (CH_2), 37.84 (CH_2), 40.30 (C), 43.60 (CH_2S), 123.88 (2CH), 147.84 (C), and 149.80 ppm (2CH).

Reaction of 4,4-pentamethylene-1,2-dithiolane **1b** *with 2-pyridylmethyllithium* **3b**: 2-Picoline **4b** 376 mg (4.0 mmol) was mixed with LDA (3.0 mmol) in THF (10 ml) at −78°C to prepare the solution of **3b** (3.0 mmol). 4,4-Pentamethylene-1,2-dithiolane **1b** 187 mg (1.1 mmol) was added to the solution at 0°C and the mixture was stirred at room temperature for 4 h. After hydrolysis and extraction as described above for **2a**, the product **2b** was purified by kugelrohr distillation.

2-(1-mercaptomethylcyclohexylmethylthiomethyl)pyridine, **2d**, ot 87–171°C/0.5 mmHg. Yield 258 mg (95%), purity 80.2% by glc (containing 1,3-dithiane **5d** 14.8%). IR (KBr) ν 2928 (s CH), 1454 (m CH_2), and 748 cm^{-1} (m). ^{1}H NMR ($CDCl_3$) δ 1.118 (1H, t, J = 9.0 Hz, SH), 1.380 (10H, broad, s, $5CH_2$), 2.578 (2H, d, J = 9.0 Hz, CH_2SH), 2.660 (2H, s, CH_2S), 3.830 (2H, s, SCH_2Py), 7.06–7.82 (3H, m, Py), and 8.48–8.62 ppm (1H, m, Py). ^{13}C NMR ($CDCl_3$) δ 21.58 ($2CH_2$), 25.98 (CH_2), 32.48 (CH_2), 34.22 ($2CH_2$), 37.48 (C), 39.00 (CH_2), 39.26 (CH_2), 121.88 (CH) 123.06 (CH), 136.66 (CH), 149.18 (CH), and 158.76 ppm (C).

5,5-diethyl-2-(4-pyridyl)-1,3-dithiane **5a**: To a solution of LDA (BuLi 3.0 mmol plus HN-*i*-Pr_2 3.0 mmol) in THF (5 ml), 4-methylpyridine 0.35 ml (3.5 mmol) and HMPT 0.62 ml (3.5 mmol) were added under argon at room temperature and the mixture was stirred for 10 min. Then 4,4-diethyl-1,2-dithiolane **1a** 332.2 mg (2.0 mmol) was added and the mixture was stirred at room temperature for 2 h. After addition of acetic acid (2 ml) and water (20 ml), the mixture was extracted with hexane (20 ml). The organic layer was washed with water to remove the trace HMPT, dried and concentrated under reduced pressure. The residue was distilled by kugelrohr.

5a, yield 247.8 mg (92%), faint violet liquid, ot 48–160°C/0.6 mmHg, purity 93% by glc (containing **2a** 5.4%). IR (KBr) ν 2968 (s), 2942 (m), 1601 (m), 1412 (m), and 766 cm^{-1} (m). ^{1}H NMR ($CDCl_3$, 89.5 MHz) δ 0.802 (3H, t, J = 7.4 Hz, CH_3), 0.868 (3H, t, J = 7.0 Hz, CH_3), 1.398 (2H, q, J = 7.4 Hz, CH_2), 1.904 (2H, q, J = 7.6 Hz, CH_2), 2.630 (2H, d, J = 14.0 Hz, 2SCH), 2.822 (2H, d, J = 13.8 Hz, 2SCH), 4.988 (1H, s, CH), 7.442 (2H, dd, J = 4.6, 1.6 Hz), and 8.582 ppm (2H, dd, J = 4.6 and 1.6 Hz). ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 6.88 (CH_3), 7.26 (CH_3), 23.22 (CH_2), 30.02 (C), 30.74 (CH_2), 40.08 ($2CH_2S$), 49.76 (CH), 122.76 (2CH), 147.60 (C), and 150.06 ppm (2CH). MS m/Z (%) 253 (M^+, base), 206 (25), 189 (40), 136 (30), 124 (65).

3-(4-pyridyl)-2,4-dithiaspiro[5.5]undecane **5b**: 4-Methylpyridine 0.35 ml (3.5 mmol) was lithiated by adding to a solution of LDA (3.0 mmol) under argon at room temperature and then HMPT 0.62 ml (3.5

mmol) was added to the solution. 2,3-Dithiaspiro[4.5]decane **1b** 346.4 mg (2.0 mmol) was added to the solution by means of a gas tight syringe and the mixture was stirred at room temperature for 2 h. The mixture was diluted with water (20 ml), neutralized with acetic acid (pH 6), and extracted with hexane (20 ml). The precipitates produced during the extraction was collected with suction (**5b**, 122.7 mg). The remaining organic layer was concentrated and the crystalline residue was recrystallized from CH_2Cl_2-hexane to give **5b** 136.2 mg.

5b, total yield 259 mg (98%). Colorless crystal, mp 166.5–167.0°C. ^{1}H NMR ($CDCl_3$, 89.5 MHz) δ 1.46 (8H, broad s, CH_2 in cyclohexane), 1.90 (2H, broad m, CH_2 in cyclohexane), 2.790 (4H, broad s, $2CH_2S$), 5.002 (1H, s, SCHS), 7.438 (2H, d, J = 6.0 Hz), and 8.582 ppm (2H, d, J = 6.2 Hz). ^{13}C NMR ($CDCl_3$) δ 21.00 (CH_2), 21.28 (CH_2), 26.38 (CH_2), 27.56 (C), 31.42 (CH_2), 38.84 (CH_2), 41.36 ($2CH_2S$), 50.20 (CH), 122.80 (2CH), 147.60 (C), and 150.20 ppm (2CH).

5,5-diethyl-2-(2-pyridyl)-1,3-dithiane, **5c**: In a three necked flask, there were added successively dry THF (5 ml), diisopropylamine 0.45 ml (3.2 mmol), BuLi (1.5 M hexane solution) 2.0 ml (3.0 mmol), and 2-methylpyridine **4b** 0.35 ml (3.5 mmol) under argon at room temperature. To this 2-picolyllithium solution, HMPT 0.62 ml (3.5 ml) and 4,4-diethyl-1,2-dithiolane **1a** 324.1 mg (2.0 mmol) were added and the mixture was stirred for 4 h. After dilution with water (20 ml) and neutralization with acetic acid (pH 6), the mixture was extracted with hexane (20 ml). The organic layer was concentrated under reduced pressure and the residue redissolved in hexane (50 ml), washed with water, and concentrated with evaporator. The residue was distilled by kugelrohr to remove the 2,2-diethyl-1,3-propanedithiols **6a**. The residue was finally recrystallized from dichloromethane-hexane to give colorless crystal **5c** 214 mg (85%); mp 76.5–77.5°C. IR (KBr) ν 2966 (s, CH), 2900 (m), 1586 (s), 1470 (s), 1435 (s), and 750 cm^{-1} (s). ^{1}H NMR ($CDCl_3$, 89.5 MHz) δ 0.802 (3H, t, J = 7.0 Hz, CH_3), 0.874 (3H, t, J = 6.6 Hz, CH_3), 1.400 (2H, q, J = 7.0 Hz, CH_2), 1.946 (2H, q, J = 7.4 Hz, CH_2), 2.272 (2H, d, J = 13.8 Hz, 2SCH), 2.864 (2H, d, J = 14.0 Hz, 2SCH), 5.238 (1H, s, CH), 7.10–7.32 (1H, m), 7.42–7.80 (2H, m), and 8.578 ppm (1H, d, J = 5.0 Hz). ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 6.88 (CH_3), 7.26 (CH_3), 23.22 (CH_2), 30.02 (C), 30.74 (CH_2), 40.08 ($2CH_2S$), 49.76 (CH), 122.76 (2CH), 147.60 (C), and 150.06 ppm (2CH). MS m/Z (%) 253 (M^+, base), 206 (25), 189 (40), 136 (30), 124 (65).

3-(2-pyridyl)-2,4-dithiaspiro[5.5]undecane **5d**: An LDA (3.0 mmol) solution was prepared by mixing BuLi (3.0 mmol) and diisopropylamine (3.2 mmol) in dry THF (5 ml) under argon. To this solution, 2-methylpyridine 0.35 ml (3.5 mmol), HMPT 0.62 ml (3.5 mmol), and 2,3-dithiaspiro[4,5]decane **1b** 347.8 mg (2.0 mmol) were added successively under ice-water cooling, and the mixture was stirred over the ice-water bath for 4 h. The mixture was diluted with water (20 ml), neutralized with acetic acid (pH 6), and extracted with hexane (20 ml). The organic layer was once concentrated by an evaporator, redissolved in hexane (10 ml), washed with water (50 ml), and evaporated. The residue was crystallized upon addition of few drops of hexane.

5d, yield 170 mg (69%). Colorless crystal, mp 113.5–114°C. IR (KBr) ν 2928 (s), 2852 (m), 1584 (m), 1466 (m), 1433 (m), 750 (m), and 721 cm^{-1} (m). ^{1}H NMR ($CDCl_3$, 89.5 MHz) δ 1.456 (8H, broad s, CH_2 in cyclohexane), 1.942 (2H, broad m, CH_2 in cyclohexane), 2.841 (4H, broad s, $2CH_2S$), 5.262 (1H, s, SCHS), 7.12–7.27 (1H, m), 7.47–7.78 (2H, m) and 8.54–8.62 ppm (1H, m). ^{13}C NMR ($CDCl_3$) δ 21.02 (CH_2), 21.34 (CH_2), 26.44 (CH_2), 27.84 (C), 31.32 (CH_2), 39.08 (CH_2), 41.54 ($2CH_2S$), 53.60 (CH), 122.36 (CH), 122.96 (CH), 136.84 (CH), 149.46 (CH), and 157.84 ppm (C).

Random formation of **5a** *and* **5b** *from reaction of lithiated* **2a** *with* **1b**: Diisopropylamine 60 μl (0.45 mmol) and 1.42 M BuLi 280 μl (0.4 mmol) were mixed in THF (0.5 ml) at 0°C under argon to prepare an LDA solution. To this solution, HMPT 70 μl (0.4 mmol), the ring opened product **2a** 30 μl (0.1 mmol), and then the 1,2-dithiolane **1b** 17.6 μl (0.1 mmol) were added successively and the mixture was stirred at room temperature for 4 h. The mixture was neutralized with aqueous acetic acid to pH = 6 and extracted with dichloromethane. Glc analysis of the organic layer showed the presences of **5a**, **5b**, **6a**, **6b**, **1a**, and **1b** in a molar ratio of 1.00:1.05:1.04:0.93:0.74:0.77, respectively. No dithioacetals other than **5a** and **5b** were detectable from the 4.5–5.5 ppm region of the ^{1}H NMR.

ACKNOWLEDGEMENT

Authors wish to thank Mr. Tsutomu Nishimura for technical assistance.

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