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Attempted reduction of 1,2,3-thiadiazole-4-carboxylates with samarium/iodine in methanol. Unexpected ring enlargement to 1,2,5-trithiepan-4,6-dicarboxylates

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Received 1st June 2004, Accepted 4th August 2004
First published as an Advance Article on the web 6th September 2004

When stirred with powdered samarium and iodine in methanol at ice-cold temperature, ethyl 1,2,3-thiadiazole-4-carboxylate **5** underwent unusual reduction involving the dimeric ring enlargement with a sulfur addition, giving dimethyl 1,2,5-trithiepan-4,6-dicarboxylates **7a,b** as a *cis*/*trans*-isomeric mixture in acceptable yield. The 1,2,3-thiadiazole ring of **5** proved to resist reduction by ordinary reducing agents, where the only choice in most cases was either recovery of the unchanged substrate or decomposition to an intractable mixture of unidentified products and tar.

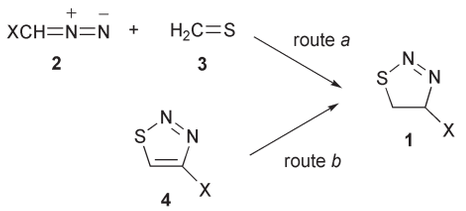
Introduction

Organic nitrogen in plants can be stoichiometrically recoverable as ammonia by the Kjeldahl method. However, Morikawa and coworkers have recently discovered that some plants, when exposed to a NO_2-contaminated atmosphere, begin to produce a noticeable amount of unidentified organic nitrogen compounds (hereafter abbreviated as UN) that respond negatively to the Kjeldahl nitrogen analysis.[1] As part of our program to identify UN, *Arabidopsis thaliana* was fumigated with diluted NO_2 and its leaves were freeze-dried, homogenized, and extracted. The organic extract was subjected to HPLC separation to obtain several UN-enriched fractions as a complex mixture of metabolites. After close examination of these fractions on the basis of ^{1}H, ^{13}C and ^{15}N NMR spectra (1D/2D NMR) as well as MS fragmentation patterns, a Δ^2-1,2,3-thiadiazoline derivative **1** has emerged as one of the possible UN candidates (Scheme 1). Since the compound proved not to be highly stable and gradually decomposed on standing, we thought it better to have some substituted Δ^2-1,2,3-thiadiazolines **1** in hand as the reference for grasping the chemical stability as well as spectroscopic characteristics of this type of less common heterocycle. Unfortunately, a literature search revealed that there was very little description of Δ^2-1,2,3-thiadiazolines. They were accessible, with difficulty, from less common precursors.[2]

Formally, the 1,3-dipolar cycloaddition of substituted diazomethane **2** to thioformaldehyde **3** would be a straightforward way to construct the Δ^2-1,2,3-thiadiazoline framework **1** (Scheme 1, route *a*).[2] However, this route does not work in our case, since thioaldehyde **3** is known to exist in a trimeric form as 1,3,5-trithiane. Therefore, we chose an alternative approach (route *b*), in which the selective reduction of a carbon–carbon double bond of the 1,2,3-thiadiazole ring has been investigated using a variety of reducing agents under a variety of conditions. In this paper, we describe the attempted reduction of ethyl 1,2,3-thiadiazole-4-carboxylate **5** and the unexpected results arising therefrom.

Results and discussion

We chose the ester **5** as substrate, since this compound was readily available by the condensation of ethyl pyruvate and ethyl carbazate followed by treatment of the resulting hydrazone with



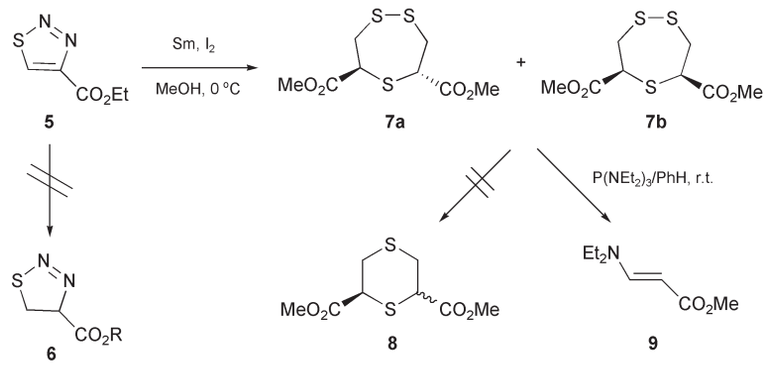
Scheme 1

thionyl chloride.[3] 1,2,3-Thiadiazole is an electron-deficient 6π aromatic system and the literature so far contains no report on the direct reduction of this ring system. We first attempted the hydrogenation of its carbon–carbon double bond using a variety of hydride and hydrogen transfer reagents in the presence or absence of an appropriate catalyst. 1,2,3-Thiadiazole **5** proved to be highly resistant to reduction and all attempts to convert it into Δ^2-1,2,3-thiadiazoline **6** (R = Et) failed (Scheme 2). Attempts using $NaBH_4$, $LiAlH_4$, BH_3·THF, DIBAL/$Co(acac)_2$,[4] $Et_3SiH/RhCl(PPh_3)_3$[5] and $Ph_2SiH_2/ZnCl_2/Pd(PPh_3)_4/PPh_3$[6] resulted in the recovery of unchanged substrate, while attempts using Et_3B/Ph_3SnH[7] and N_2H_4·$H_2O/CuSO_4/NaIO_4/AcOH$[8] led to a complex mixture of unidentified products. A combination of powdered metal and protic solvent led to extensive decomposition. Reagents employed included Mg/MeOH, Zn/AcOH, $Zn/NiCl_2$/EtOH[9] and Li/*tert*-BuOH. In contrast, attempted hydrogenation of **5** over transition metal catalyst resulted in the recovery of the substrate intact. Catalysts employed included Pd/C, PtO_2, Raney Ni, Ir black[10] and Rh/Al_2O_3.[11]

When the reduction of **5** was attempted using powdered samarium and iodine in methanol at ice-cold temperature,[12] the reaction proceeded cleanly and two isomeric sulfur-containing products were successfully isolated from the product mixture by chromatography on silica gel followed by HPLC purification. One was a stable crystalline solid of mp 60–62 °C and the other a pale yellow oil. Much to our surprise, however, neither one of these proved to be the expected reduction product (**6**, R = Et) but were the ring enlarged products, dimethyl *trans*- and *cis*-1,2,5-trithiepan-4,6-dicarboxylates **7a,b** (Scheme 2). The combined yield of these isomers was 29% based on sulfur atom.

These structures were determined as follows. From elementary analysis as well as EI and FAB mass spectra, compounds

DOI: 10.1039/b408195a



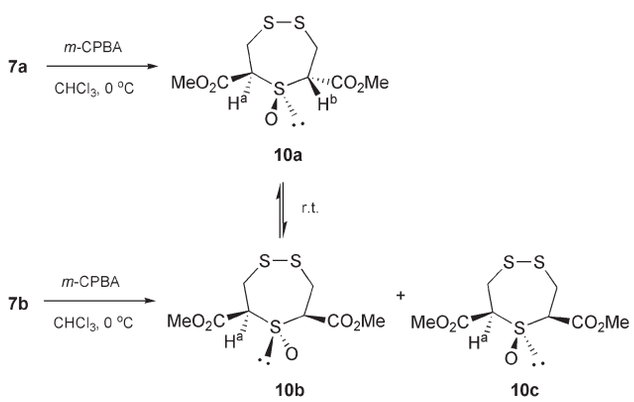
Scheme 2

7a and **7b** were found to share a molecular formula $C_8H_{12}O_4S_3$. The fragmentation pattern of their mass spectra was identical, suggesting that both were diastereotopic. The elemental composition meant that compound **5** suffered reductive dimerization involving the loss of two nitrogen molecules as well as the incorporation of one sulfur atom during the course of reaction. Strong infrared bands at 1728 and 1736 cm^{-1} were consistent with the presence of two types of ester groups. ^1H NMR spectra showed methyl ester signals at δ 3.72 for **7a** and 3.73 for **7b** instead of the expected ethyl ester signals, suggesting ester exchange during the reduction. The original aromatic proton signal at $\delta = 9.27$ disappeared, while pairs of methine (δ 5.23 for **7a** and 5.10 for **7b**) and methylene proton signals (δ 3.05, 2.88 for **7a** and 3.09, 2.99 for **7b**) appeared instead, revealing that the olefinic bond of **5** was saturated in the products. ^{13}C NMR spectra exhibited signals due to the ester carbonyl carbon at δ 170.7 for **7a** and 170.4 for **7b**, and signals due to the methyl carbon at δ 52.0 for **7a** and 52.1 for **7b**. Signals at $\delta = 59.7$ for **7a** and 60.7 for **7b** were characteristic of the methine carbon atom bonded to the sulfide and ester functions, while the ones at $\delta = 42.7$ for **7a** and 40.7 for **7b** were attributable to the methylene carbon bearing the disulfide group. On the basis of these data, two products were identified as **7a** and **7b**, to which the relative configurations (4*R**,6*S**) and *meso* were assigned, respectively. Due to the deshielding effect of two ester carbonyl functions located in a *trans* configuration, a considerable downfield shift was observed for the methine proton of **7a**, which appeared at δ 5.23 compared with δ 5.10 for **7b** in a *cis* configuration.

In order to obtain further evidence for structures **7a** and **7b**, we examined the desulfurization and oxidation of these products. First, the desulfurative ring contraction of 1,2,5-trithiepane **7a** to 1,4-dithiane **8** was attempted using $P(NEt_2)_3$ according to the reported procedure (Scheme 2).[13] However, the ring structure was destroyed with simultaneous loss of all sulfur atoms, leading to methyl (*E*)-3-(diethylamino)acrylate **9** as the sole product. Compound **9** was identified by comparison of ^1H NMR data with those of the authentic specimen.[14] On similar treatment, **7b** again produced **9** in comparable yield.

Next, the reaction of **7a** with equimolar *m*-chloroperoxybenzoic acid (*m*-CPBA) afforded sulfoxide **10a** as the single product in 63% isolated yield. Similar oxidation of **7b** gave **10b** and **10c** in 23 and 39% isolated yield, respectively (Scheme 3). When compound **10a** was dissolved in chloroform and stood at room temperature, it gradually underwent isomerization to form an equilibrium mixture of **10a** and **10b**. In contrast, **10c** proved to be indefinitely stable and showed no tendency toward isomerization under similar conditions.

These structures were determined as follows. The three sulfoxides **10a**–**c** shared a formula $C_8H_{12}O_5S_3$ in accord with the mono-oxide structure and showed characteristic IR bands at 1049, 1057 and 1053 cm^{-1}, respectively. ^{13}C NMR spectra showed peaks due to the methine carbon at δ 78.9 and 70.8 for **10a**, δ 70.8 and 70.6 for **10b**, and δ 80.5 for **10c**. The values were about 10–20 ppm downfield as compared with those of the parent compounds (δ 59.7 for **7a** and δ 60.7 for **7b**) in accord with preferential oxidation of the sulfur atom at the 5-position. Due to the anisotropic influence of the sulfur–oxygen bond, a considerable downfield shift was observed for H^b of **10a** and H^a of **10b** (δ 4.91 and 4.85, respectively) as compared with H^a of **10a** and **10c** (δ 4.55 and 4.53, respectively). Based on these observations, the relative configurations (*r*-4, *t*-5, *t*-6), (*r*-4, *t*-5, *c*-6) and (*r*-4, *c*-5, *c*-6) were assigned to **10a**–**c**, respectively (Scheme 3).



Scheme 3

From a synthetic point of view, a simple two-step construction of the 1,2,5-trithiepan framework from such cheap commercial products as ethyl pyruvate, ethyl carbazate and thionyl chloride is quite attractive. Recently, a biologically active 1,2,5-trithiepan derivative named lissoclinotoxin F was isolated from *Philippine didemnid ascidian*, which proved to possess strong cytotoxicity against the MDA-MB-468 human breast carcinoma cell line (Fig. 1).[15] Reported syntheses of 1,2,5-trithiepan derivatives involve oxidative ring closure of bis(ß-mercaptoethyl) sulfides,[16] reaction of thiirans with $BF_3{\cdot}OEt_2$[17] or dithiols,[18] sulfurization of olefins with H_2S–LiOH or H_2S–NEt_3,[19] 1,2,3,4-tetra- and 1,2,3,4,5-pentathiepans,[20] photolysis of 1,2,3-thiadiazole[21] and 1,2,3-trithiolane,[22] treatment of bis(ß-bromoalkyl) disulfides with Na_2S_2,[23] and alkaline decomposition of 1,2-dithiete.[24] In most cases, the substrates employed were less common and accessible *via* multi-step processes. Product yields ranged from a trace amount up to 90%.

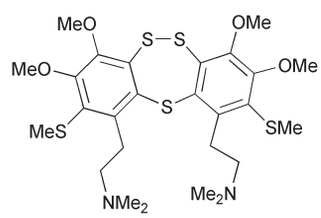


Fig. 1

A possible mechanism for the formation of 1,2,5-trithiepans **7a,b** from 1,2,3-thiadiazole **5** is depicted in Scheme 4. The initial step would involve reduction of the carbon–carbon double bond of **5** to form Δ^2-1,2,3-thiadiazoline **6**, which releases a nitrogen molecule to give a *S*,*C*-biradical **11**. The biradical trimerizes stepwise to form a *C*,*C*-biradical intermediate **13**, which would undergo intramolecular cyclization to afford **7a,b** under the expulsion of an acrylate molecule (Scheme 4, path *a*). A referee has suggested an alternative pathway (path *b*), in which the initial biradical **11** reacts with **6** *via* the S–S bond formation with concomitant loss of a nitrogen molecule to produce a symmetrical *C*,*C*-biradical **14**, which will then be intercepted by a second molecule of **6**, eventually leading to **7a,b** *via* the third biradical **13**.

In conclusion, we have found that ethyl 1,2,3-thiadiazole-4-carboxylate **5** resists reduction by ordinary reducing agents. Under forced conditions using powdered samarium and iodine in methanol, it underwent unusual ring enlargement, giving 1,2,5-trithiepane derivatives **7a,b** in acceptable yield. The cytotoxic nature of these and related products are now under study.

Experimental

General

Melting points were determined on a Yanaco MP-S3 hot-stage apparatus and are uncorrected. IR spectra were measured as films for oils and KBr disks for solids with a JASCO FT-5300 spectrophotometer. NMR spectra were measured in $CDCl_3$ on a JEOL ECA-300 (^{1}H-NMR: 300 MHz, ^{13}C-NMR: 75 MHz) spectrometer with tetramethylsilane as an internal standard. EI-MS spectra were taken on a Shimadzu GC-MS QP-5000 mass spectrometer at 70 eV using a direct inlet probe. FAB-MS spectra were recorded with a JEOL-HX110 spectrometer using 3-nitrobenzyl alcohol as a matrix. Merck precoated silica gel 60 F_{254} plates were used for TLC and Wakogel C-200 for column chromatography. HPLC analyses were performed on a Shimadzu CLASS-LC10 instrument using TOSOH TSK-GEL (Silica-60) columns at ambient temperature. Elemental analyses were performed at the Advanced Instrumentation Center, Ehime University.

Dimethyl 1,2,5-trithiepan-4,6-dicarboxylate (7a and 7b)

Powdered samarium (0.75 g, 5.0 mmol) was suspended in a solution of ethyl 1,2,3-thiadiazole-4-carboxylate **5** (0.36 g, 2.3 mmol) in methanol (8.6 mL) and iodine (0.58 g, 2.3 mmol) was slowly added at ice-cold temperature. After standing for 30 min at this temperature, the mixture was diluted with 1 M HCl (50 mL). The aqueous phase was extracted with ether (50 mL × 3). The combined organic extracts were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The oily residue was subjected to column chromatography on silica gel using benzene as the eluent to give **7a** and **7b** as an inseparable mixture (58 mg, 29% based on sulfur). Successful separation of **7a** and **7b** was performed by HPLC (flow rate, 4 mL min^{-1}) using hexane–ethyl acetate (3 : 1) as the solvent to obtain **7a** (retention time of 37.5 min, 19 mg, 9%) and **7b** (retention time of 39.5 min, 28 mg, 14%). **7a**: colorless needles with mp 60–62 °C. ^{1}H NMR: δ 5.23 (dd, J = 8.1, 6.7 Hz, 2H, 2 × CH), 3.72 (s, 6H, 2 × CH_3), 3.05 (dd, J = 17, 8.1 Hz, 2H, 2 × C*H*H), 2.88 (dd, J = 17, 6.5 Hz, 2H, 2 × CH*H*); ^{13}C NMR: δ 170.7 (2 × C=O), 59.7 (2 × CH), 52.0 (2 × CH_3), 42.7 (2 × CH_2); IR: 1728 (C=O) cm^{-1}; MS (EI): *m*/*z* 268 (M$^+$). $C_8H_{12}O_4S_3$ requires: C, 35.81; H, 4.51; S, 35.84; found: C, 35.86; H, 4.48; S, 35.90%. **7b**: pale yellow oil. ^{1}H NMR: δ 5.10 (t, J = 7.2 Hz, 2H, 2 × CH), 3.73 (s, 2 × CH_3), 3.09 (dd, J = 17, 7.5 Hz, 2H, 2 × C*H*H), 2.99 (dd, J = 17, 7.1 Hz, 2H, 2 × CH*H*); ^{13}C NMR: δ 170.4 (2 × C=O), 60.7 (2 × CH), 52.1 (2 × CH_3), 40.7 (2 × CH_2); IR: 1736 (C=O) cm^{-1}; MS (EI): *m*/*z* 268 (M$^+$). HRMS (FAB+) calc. for $C_8H_{12}O_4S_3$ 267.9898, found 267.9899.

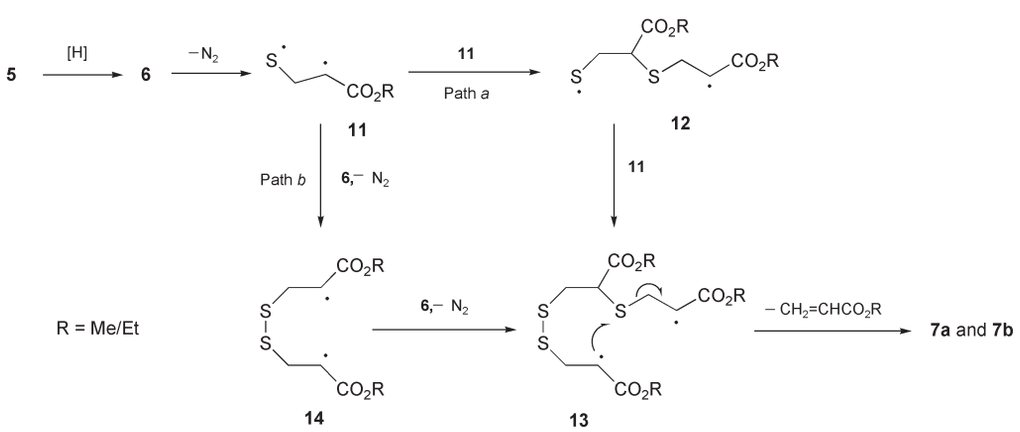
Methyl (*E*)-3-(diethylamino) propenoate (9)

To a stirred solution of **7a** (19 mg, 0.069 mmol) in dry benzene (1.5 mL) was added dropwise a solution of $P(NEt_2)_3$ (52 mg) in benzene (0.4 mL) at room temperature. After 40 min, excess reagent was destroyed by the addition of sulfur (50 mg) and the solvent was removed under reduced pressure. The residue was chromatographed on silica gel using hexane–ethyl acetate (10 : 1 v/v) to give **9** (13 mg, 31%).[14] Colourless oil. ^{1}H NMR: δ 7.44 (d, J = 13 Hz, 1H, NC*H*=CH), 4.57 (d, J = 13 Hz, 1H, CH=C*H*CO_2Me), 3.66 (s, 3H, CH_3), 3.19 (q, J = 7.2 Hz, 4H, 2 × C*H*$_2$CH$_3$), 1.16 (dd, J = 7.2 Hz, 6H, 2 × CH$_2$C*H*$_3$); MS (EI): *m*/*z* 157 (M$^+$).

Dimethyl 1,2,5-trithiepan-4,6-dicarboxylate-5-oxide (10a–c)

To a stirred solution of **7a** (30 mg, 0.11 mmol) in dry $CHCl_3$ (0.6 mL) was added dropwise a solution of *m*-CPBA (20 mg, 0.12 mmol) in $CHCl_3$ (1.8 mL) at 0 °C under argon. After stirring for 1 h, the mixture was concentrated under reduced pressure to leave a residue, which was chromatographed on silica gel using benzene–ethyl acetate (5 : 1 v/v) as the solvent to give **10a** (21 mg, 63%). Colourless solid with mp 90–91 °C. ^{1}H NMR: δ 4.91 (t, J = 7.0 Hz, 1H, CH), 4.55 (dd, J = 7.6, 6.2 Hz, 1H, CH), 3.78 (s, 3H, CH_3), 3.76 (s, 3H, CH_3), 3.28 (dd, J = 18, 7.1 Hz, 1H, C*H*H), 3.14 (d, J = 6.2 Hz, 1H, C*H*H), 3.13 (d, J = 7.9 Hz, 1H, CH*H*), 2.95 (dd, J = 18, 7.0 Hz, 1H, CH*H*); ^{13}C NMR: δ 170.6 (C=O), 169.5 (C=O), 78.9 (CH), 70.8 (CH), 52.6 (CH_3), 52.4 (CH_3), 34.3 (CH_2), 30.8 (CH_2). ^{13}C NMR spectrum was taken for an equilibrium mixture of **10a** and **10b**. IR: 1736 (C=O), 1049 (S=O) cm^{-1}; HRMS (FAB+) calc. for $C_8H_{13}O_5S_3$ (M$^+$ + H) 284.9925, found 284.9945.

Similar oxidation of compound **7b** (24 mg, 0.9 mmol) using *m*-CPBA (16 mg, 0.94 mmol) in $CHCl_3$ (2.0 mL) followed by chromatography on silica gel gave **10b** (6 mg, 23%) and **10c** (13 mg, 39%). **10b**: colourless solid with mp 40–41 °C. ^{1}H NMR: δ 4.85 (t, J = 7.0 Hz, 2H, 2 × CH), 3.76 (s, 6H, 2 × CH_3), 3.13



Scheme 4

(dd, J = 18, 7.4 Hz, 2H, 2 × C*H*H), 2.81 (dd, J = 18, 6.7 Hz, 2H, 2 × CH*H*); ^{13}C NMR: δ 170.4 (2 × C=O), 70.8 (CH), 70.6 (CH), 52.6 (CH_3), 52.5 (CH_3), 31.0 (2 × CH_2). ^{13}C NMR spectrum was taken for a mixture of **10a** and **10b**. IR: 1736 (C=O), 1057 (S=O) cm^{-1}; HRMS (FAB+): calc. for $C_8H_{13}O_5S_3$ (M^+ + H) 284.9925, found 284.9929. **10c**: colourless needles with mp 126–127 °C. ^{1}H NMR: δ 4.53 (dd, J = 7.2, 6.2 Hz, 2H, 2 × CH), 3.77 (s, 6H, 2 × CH_3), 3.13 (d, J = 6.2 Hz, 2H, 2 × C*H*H), 3.13 (d, J = 7.6 Hz, 2H, 2 × CH*H*); ^{13}C NMR: δ 169.4 (2 × C=O), 80.5 (2 × CH), 52.7 (CH_3), 52.5 (CH_3), 33.4 (2 × CH_2). IR: 1728 (C=O), 1053 (S=O) cm^{-1}; MS (FAB): *m*/*z* 285 (M^+ + H). $C_8H_{12}O_5S_3$ requires C, 33.79; H, 4.25; found: C, 33.77; H, 4.12%.

Acknowledgements

This research was supported by Japan Science and Technology Corporation (JST). We greatly acknowledge the support.

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