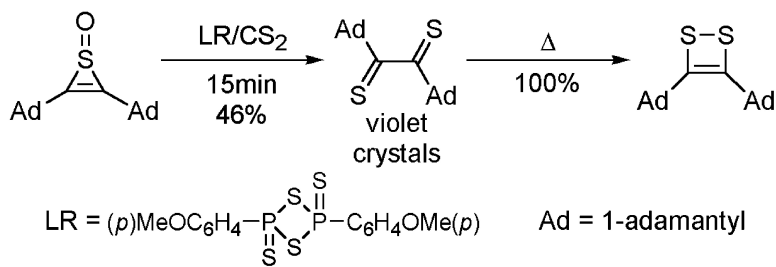


Synthesis and Characterization of Aliphatic λ -Dithiones, Di(1-adamantyl)- and Di-*tert*-butylethanedithiones

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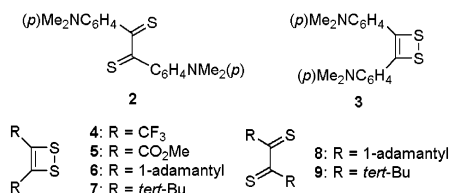
Synthesis and Characterization of Aliphatic α -Dithiones, Di(1-adamantyl)- and Di-*tert*-butylethanedithiones

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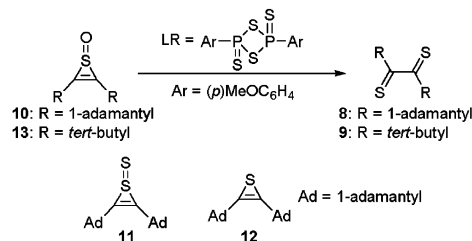
In 1973, Küsters and de Mayo succeeded in the first synthesis of a stable α -dithione, 4,4'-bis(*p*-dimethylamino)dithiobenzil (**1**).^{1,2} The dark red crystalline **1** has the *s-trans* structure **2** in the solid, but exists in solution as an equilibrium mixture of α -dithione **2** and its valence tautomer 1,2-dithiete **3**. The position of the dithione–dithiete equilibrium depends on the substituent attached to the sp^2 carbon atom.^{3,4} Thus, electron-donating substituents stabilize dithiones as is true for **1**, while electron-withdrawing substituents favor dithietes as is evidenced by successful preparation of dithietes **4**⁵ and **5**.⁶ On the other hand, several 1,2-dithietes, which are stabilized by bulky alkyl substituents, are also known.^{7,8} Typical examples are highly stable **6** and **7**, whose convenient synthesis was developed by us.⁷ Here, we report the synthesis, isolation, and characterization of the first aliphatic α -dithiones, di(1-adamantyl)-ethanedithione (**8**) and di-*tert*-butylethanedithione (**9**), the valence tautomers of **6** and **7**, respectively.²



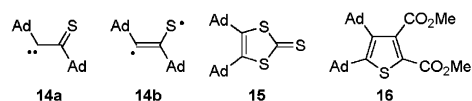
Recently, we developed a convenient synthesis of thiirene 1-oxide **10** and related derivatives.⁹ With the expectation of obtaining thiirene 1-sulfide **11** or its desulfurization product **12**, **10** was treated with Lawesson's Reagent (LR) in CH₂Cl₂ at room temperature.¹⁰ The reaction took place with quick development of violet coloration. The reaction mixture was treated after 15 min to provide thermally labile violet crystals of **8**¹¹ in 20% yield (65% yield based on the UV/vis spectral data). The ¹³C NMR spectrum of **8** showed the single C=S carbon peak at δ 269.7, while the UV/vis spectrum exhibited a weak absorption at 520 nm (ϵ 124) characteristic of the C=S group.¹¹ The FAB mass spectrum gave the molecular ion peak at m/z 358.^{11,12} DFT calculations (B3LYP/6-31G* level) predicted that the IR spectrum of **8**, based on the optimized geometry, would show the intense absorption at 1118 cm⁻¹ that originates from the asymmetrical vibration associated with the two C=S bonds, while the observed spectrum showed an intense absorption at 1149 cm⁻¹.^{13,14} Meanwhile, the same calculations predicted that the Raman spectrum would show an intense band at 1116 cm⁻¹ that originates from the symmetrical vibration of the two C=S bonds, while the observed spectrum showed an intense band at 1148 cm⁻¹.^{13,14}

Dithione **9** was also formed in about 20% yield by treatment of thiirene 1-oxide **13** with LR, although it was not isolated in pure form.¹⁵

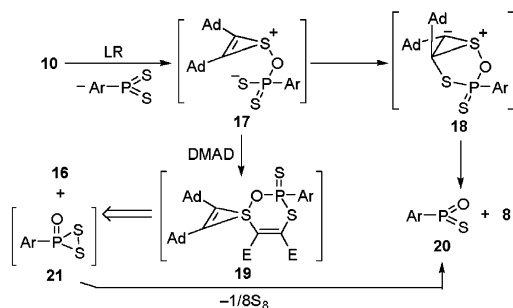
We thought initially that the unexpected formation of **8** would be explained by reaction of carbene **14a** (ring-opening product of **12**) or isomeric biradical **14b** with activated sulfur species generated



during the reaction. Reportedly **14a** (or **14b**) is trapped by cycloaddition with CS₂ to give dithiole-2-thione **15**.¹⁶ The reaction was therefore carried out in CS₂ as the solvent. Unexpectedly, however, the reaction gave **8** in a better yield (46% isolated yield), and not the expected **15**. On the other hand, the reaction in the presence of dimethyl acetylenedicarboxylate (DMAD), a trapping agent of α -keto carbenes,¹⁷ in CS₂ gave congested thiophene **16** in 51% yield. A separate experiment revealed that DMAD does not react with **8** to give **16**.



Thus, a tentative mechanism that involves the formation of sulfonium ion **17** and then sulfur ylide **18** is proposed. **18** would produce **8** with a highly twisted structure by extrusion of **20**, while reaction of **17** with DMAD would produce **19**, which finally leads to the formation of **16**.



The violet crystals of **8** turn faint-yellow at 151–153 °C and melt at 194–196 °C due to isomerization to dithiete **6**, mp 197–198 °C. It also isomerizes to **6** in solution quantitatively. The progress of the isomerization was thus monitored by ¹H NMR in dilute CDCl₃ solution (0.014 M) to determine the kinetic parameters. The reaction is first order in **8** and gave the rate constants of (6.13 ± 0.08) × 10⁻⁶, (2.33 ± 0.10) × 10⁻⁵, and (1.34 ± 0.03) × 10⁻⁴ s⁻¹ at 295, 308, and 328 K, respectively, thus providing kinetic parameters of $\Delta H^\ddagger = 17.6 \pm 0.2$ kcal mol⁻¹, $\Delta S^\ddagger = -23.0 \pm 0.7$ cal K⁻¹ mol⁻¹, and $\Delta G^\ddagger_{298} = 24.4 \pm 0.4$ kcal mol⁻¹. The ΔS^\ddagger value of the isomerization is comparable to that of the cyclization of **22**

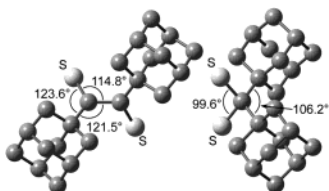
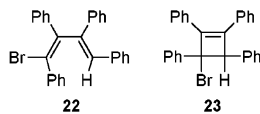


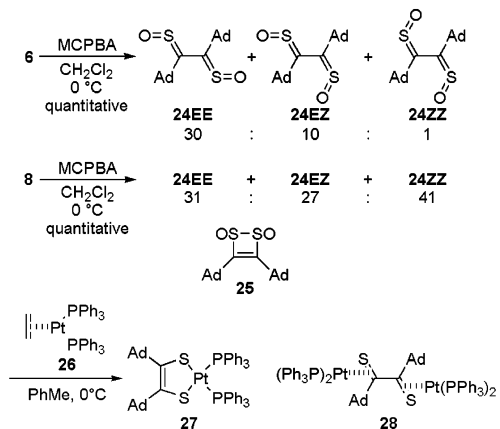
Figure 1. Optimized structure of **8**.

to **23**,¹⁸ $-15.6 \pm 1.7 \text{ cal K}^{-1} \text{ mol}^{-1}$, rather than that of **2** to **3**, $0.5 \pm 0.9 \text{ cal K}^{-1} \text{ mol}^{-1}$.^{1b,19}



Because, despite numerous attempts, we could not obtain good single crystals of **8** suitable for X-ray crystallographic analysis, the optimized structure was determined by DFT calculations (Figure 1). The two adamantyl groups are twisted with a large dihedral angle of 106.2° . Reportedly the two adamantyl groups in **6** are twisted only by about 6.0° in the crystalline state.^{20,21} Thus, the isomerization of **8** to **6** would require that the two adamantyl groups become nearly coplanar with *s-cis* conformation at the transition state against increasing steric repulsion; the *s-trans* coplanar conformation of **8** is less stable by $34.7 \text{ kcal mol}^{-1}$ than the optimized twisted conformation. This would be the very reason that **8** is isolated in pure form. The calculations also predicted that **8** is less stable than the optimized structure of **6** by $2.69 \text{ kcal mol}^{-1}$.²²

The oxidation of **6** with *m*-chloroperbenzoic acid (MCPBA, 3 equiv), where the final products are furnished by ring-opening of bis-sulfoxide intermediate **25**, produces a mixture of bis-sulfines, **24EE**, **24EZ**, and **24ZZ**, in a ratio of ca. 30:10:1.²³ On the other hand, the oxidation of **8** with MCPBA (3 equiv) in CH_2Cl_2 , which proceeds through stepwise oxidation of the $\text{C}=\text{S}$ groups, furnished **24EE**, **24EZ**, and **24ZZ** in 31%, 27%, and 41% yields (thus in the ratio 31:27:41), respectively.



Treatment of **8** with two molar amounts of ethylenebis-(triphenylphosphine)platinum(0) (**26**) gave a 1:1 dithiolene complex **27** in 45% yield; no expected bis-platinum complex **28** was formed. The same complex **27** was also produced in 48% yield by treatment of **6** with **26**.

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Supporting Information Available: Experimental procedures for the preparation and reactions of **8** and kinetic parameter determination of the isomerization of **8** to **6**. Calculated and observed IR and Raman spectra of **8** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (2) Note that **1** is thought to be a sort of analogue of dithiooxalamides, $\text{R}_2\text{NC}(\text{=S})\text{C}(\text{=S})\text{NR}_2$. Dithiooxalamides and related compounds, stabilized by push–pull effects, are known; see references cited in ref 7b.
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- (4) Both dithiones and dithietes are reactive transient intermediates unless stabilized either electronically or sterically. The dithione–dithiete equilibrium has been the object of a great number of theoretical and experimental studies. Particularly, numerous calculation studies have been reported on the parent compound.³
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- (11) **8**: Violet fine needles (from pentane); ^1H NMR (CDCl_3 , 400 MHz) δ 1.67–1.74 (12H, br m), 2.07–2.13 (18H, br m); ^{13}C NMR (CDCl_3 , 100.6 MHz) δ 28.77, 36.19, 43.78, 53.96, 269.70; IR (KBr) ν 2908, 2848, 1451, 1342, 1149, 1060, 1010, 965, 884, 881, 710, 655, 636, 573 cm^{-1} ; Raman ν 2914, 2891, 2849, 1433, 1351, 1313, 1265, 1252, 1206, 1180, 1148, 1098, 1058, 1008, 973, 933, 881, 823, 812, 766, 673, 646, 623 cm^{-1} ; UV/vis (CH_2Cl_2) λ_{max} (ϵ) 347 (3780) 520 (124) nm; HRMS (FAB) calcd for $\text{C}_{22}\text{H}_{30}\text{S}_2$ (M^+), 358.1789; found, 358.1780.
- (12) In the EI mode, the fragmentation pattern of **8** resembles that of **6** closely because of probable isomerization of **8** to **6** prior to the ionization.
- (13) (a) The calculations have been performed by using the Gaussian 98 (revision A.7) program on personal computers running RedHat Linux 7.2. (b) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (14) Vibration modes were visualized by GaussView 2.1 program. Gaussian, Inc.: Pittsburgh, PA, 2000.
- (15) **9**: ^1H NMR (CDCl_3 , 400 MHz) δ 1.46 (18H, s); ^{13}C NMR (CDCl_3 , 100.6 MHz) δ 30.1, 32.3, 270.8 (C=S); UV/vis (CH_2Cl_2) λ_{max} 518 nm.
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- (19) The small ΔS^\ddagger value in conversion of **2** to **3** would be attributed to the restricted rotation of the aryl group by conjugation with the $\text{C}=\text{S}$ group.^{1b} Such conjugation is not expected for the aliphatic dithione **8**, thus conversion of **8** to **6** giving a larger ΔS^\ddagger value than that of **2** to **3**.
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