Tetrahedron Letters, Vol. 34, No. 1, pp. 115-118, 1993
Printed in Great Britain

0040-4039/93 $5.00 + .00
Pergamon Press Ltd

A Convenient Synthesis of 1,2-Dithietes and α-Dithiocarbonyl Compounds by Sulfuration of Acetylenic Compounds

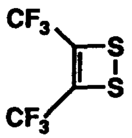
Juzo Nakayama,* Keun Soo Choi, Isao Akiyama, and Masamatsu Hoshino
Department of Chemistry, Faculty of Science, Saitama University,
Urawa, Saitama 338, Japan

Key Words: Sulfuration, Steric Protection, 1,2-Dithietes, α–Dithiocarbonyl Compounds, Elemental Sulfur

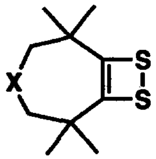
Abstract: Di-*tert*-butyl-, di-1-adamantyl-, 1-(1-adamantyl)-2-*tert*-butyl-, and 1-(1-adamantyl)-2-phenylacetylenes react with elemental sulfur to afford the corresponding 1,2-dithietes in 46-65% yields, while 1-*N,N*-diethylamino-2-phenylthio-, 1-*N,N*-diethylamino-2-phenylseleno-, and bis(*N,N*-diethylamino)acetylenes react with sulfur to give the corresponding α-dithiocarbonyl compounds in 18-74% yields.

In connection with our continuing interest in reactions of elemental sulfur with acetylenic compounds,[1] we report here a convenient synthesis of 1,2-dithietes and α-dithiocarbonyl compounds by sulfuration of some acetylenic compounds. 1,2-Dithietes are structurally interesting compounds which possess one carbon-carbon double bond and one disulfide linkage in their strained four-membered ring. Most of them are highly reactive and elude isolation at room temperature. Their facile tautomerization to reactive α-dithiones must be, at least in part, responsible for their instability.[2] Thus, the first isolable dithiete **1**, whose tautomeric α-dithione form is electronically disfavored by strongly electron-withdrawing trifluoromethyl groups, was obtained by sulfuration of highly reactive bis(trifluoromethyl)-acetylene under flow system.[3] Another factor of stabilizing dithietes is steric protection. Thus, dithietes **2** are prepared by sulfuration of 3,3,7,7-tetramethyl-5-thiacycloheptyne and its sulfone derivative whose triple bond are highly activated by angle strain.[4] Photochemical extrusion of ethylene from a 1,4-benzodithiane derivative also affords a sterically buttressed stable benzodithiete **3**.[5] The isolable stable dithiete **4** is also prepared in 45% yield by thionation of 2,2,5,5-tetramethylhexan-4-one-3-thione whose synthesis is tedious in low overall yield.[6]

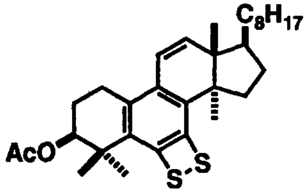
Our method is simple and practical. Preparation of **4** is typical. Heating of a mixture of elemental sulfur (2.56 g, 10 mmol as S_8) and di-*tert*-butylacetylene[7] (2.76 g, 20 mmol) in benzene (100 mL) at 190 °C for 15 h in a stainless steel autoclave affords **4** (2.34 g, 58%), bp 80-82 °C/1.4 mmHg.[6]



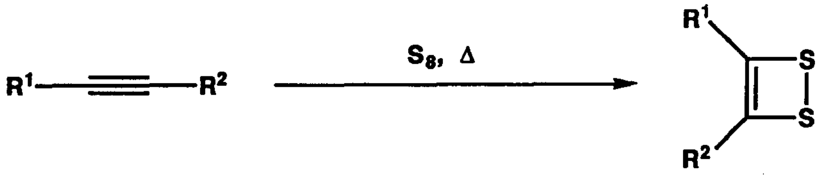
1



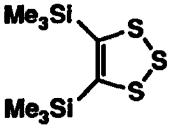
2: X=S, SO_2



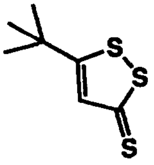
3



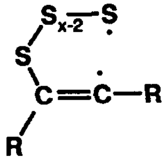
4: $R^1 = R^2 =$ *t*-butyl	58%
5: $R^1 = R^2 =$ 1-adamantyl	65%
6: $R^1 =$ *t*-butyl, $R^2 =$ phenyl	56%
7: $R^1 =$ 1-adamantyl, $R^2 =$ phenyl	46%



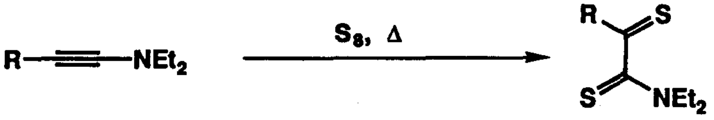
8



9



10



11: R =SPh	74%
12: R = SePh	12%
13: R = NEt_2	69%

Sulfuration of di-1-adamantylacetylene[7] smoothly proceeds in refluxing *o*-dichlorobenzene to give the dithiete **5**[8] as highly stable crystalline compound, mp 197-198 °C, in 65% yield. Similarly, sulfuration of 1-*tert*-butyl-2-phenylacetylene and 1-(1-adamantyl)-2-phenylacetylene[7] in refluxing *o*-dichlorobenzene gives dithietes **6**[8] and **7**[8] in 56% and 46% yields, respectively. The formation of highly strained dithietes from these unactivated acetylenes is quite unexpected. High stability of the dithietes **4-7** must be mostly ascribed to the transition state leading to dithiones which is disfavored by steric repulsion between bulky substituents. It is rather surprising that even **6** and **7** are thermally stable and exist in dithiete form, contrary to the expectation that the corresponding α-dithione forms, in which conjugation between thiocarbonyl and phenyl groups is possible, would be thermodynamically favorable.[9] Sulfuration of bis(trimethylsilyl)acetylene afforded the trithiole **8** though in low yield (5%); no dithiete was formed. Low material balance is due to the carbon-silicon bond cleavage by sulfur. Sulfuration of 4,4-dimethyl-2-pentyne did not give the expected dithiete, but afforded the known 1,2-dithiole-3-thione **9**[10] in 20% yield. Sulfuration of bis(pentafluorophenyl)acetylene produced tetrakis(pentafluorophenyl)thiophene in good yield as previously reported.[11,12] All of the dithietes **4-7** thus synthesized have characteristic weak absorptions at 330-350 nm in their UV-Vis spectra.[3,6]

The mechanism of the dithiete formation must involve the initial addition of thermally produced diradical sulfur $\cdot S_x \cdot$ to the triple bond to produce a diradical intermediate **9**, which then cyclizes to the dithiete with elimination of S_{x-2}.[3] Tautomerization of the dithiete to the corresponding α-dithione, its cycloaddition with the starting acetylene, and the extrusion of sulfur atom from the resulting 1,4-dithiin[13] should give rise to the thiophene as observed in the case of bis(pentafluorophenyl)acetylene and some diarylacetylenes.[14]

1-*N*,*N*-Diethylamino-2-phenylthioacetylene[15] smoothly reacts with sulfur in refluxing chlorobenzene for 1.5 h to give the resonance-stabilized α-dithione **11**[8] in 74% yield. Similarly, 1-*N*,*N*-diethylamino-2-phenylselenoacetylene[17] reacts with sulfur in refluxing toluene to give a new class of the dithione **12**[8] (12%) along with diphenyl diselenide (80%). Bis(*N*,*N*-diethylamino)acetylene[17] was also sulfurated in chlorobenzene at 75 °C to give the dithione **13** in 69% yield. In these cases, the initial products, dithietes, are assumed to tautomerize to more stable resonance-stabilized α-dithiones, althouth the initial step of the dithiete formation may involve electrophilic attack by cyclic octasulfur on the acetylenes rather than by biradical sulfur. The present reaction provides a new interesting synthesis of resonance-stabilized α-dithiocarbonyl compounds which are otherwise difficult to prepare.[18]

Acknowledgment. This work was suppoted by a Grant-in-Aid for Scientific Research from the Ministry of Education of Japan.

References and Notes

1. Nakayama, J.; Akimoto, K.; Hoshino, M. *Reviews on Heteroatom Chemistry* **1990**, *3*, 146.
2. Küsters, W.; de Mayo, P. *J. Am. Chem. Soc.* **1973**, *95*, 1973; **1974**, *96*, 3502.
3. (a) Krespan, C. G.; McKusick, B. C.; Cairns, T. L. *J. Am. Chem. Soc.* **1960**, *82*, 1515. (b) Krespan, C. G. *ibid.* **1961**, *83*, 3434.
4. Krebs, A.; Colberg, H.; Höpfner, U.; Kimling, H.; Odenthal, J. *Heterocycles* **1979**, *12*, 1153. See also: Schütz, K. Thesis, University of Hamburg, 1983.
5. Boar, R. B.; Hawkins, D. W.; McGhie, J. F.; Misra, S. C.; Barton, D. H. R.; Ladd, M. F. C.; Povey, D. C. *J. Chem. Soc., Chem. Commun.* **1975**, 756.
6. (a) Köpke, B.; Voss, J. *J. Chem. Research (S)* **1982**, 314. (b) Jacobson, N.; de Mayo, P.; Weedon, A. C. *Nouv. J. Chim.* **1978**, *2*, 331. Direct thionation of 2,2,5,5-tetramethylhexane-3,4-dione with Lawesson's reagent or phosphorus pentasulfide fails to give 4.[6a]
7. These acetylenes are easily obtainable in one pot from commercially available bis(trimethylsilyl)acetylene or 1-phenyl-2-trimethylsilylacetylene; Capozzi, G.; Romeo, G.; Marcuzzi, F. *J. Chem. Soc., Chem. Commun.* **1982**, 659.
8. **5**: mp 197-198 °C; pale yellow leaflets; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.38 (12H, m), 1.53 (12H, d), 1.71 (6H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.60 (d), 36.45 (t), 38.92 (s), 41.63 (t), 141.93 (s, sp^2 carbon); mass spectrum *m/e* 358 (M^+), 294, 179, 135 (base peak); IR (KBr) 1555, 1453, 1354, 1313, 1100, 984, 935, 794 cm^{-1}; UV/Vis λ_{max} (hexane) (ε) 229 (5600), 278 (491), 349 nm (265). **6**: pale yellow liquid; ^{1}HNMR ($CDCl_3$, 60 MHz) δ 1.67 (9H, s), 7.28 (5H, s); ^{13}C NMR ($CDCl_3$, 22.5 MHz) δ 29.85, 37.39, 128.14, 128.49, 128.92, 129.61, 137.07 (sp^2 carbon); mass spectrum *m/e* 222 (M^+), 207, 158, 144; UV/Vis λ_{max} (hexane) (ε) 233 (4494), 303 (2536), 349 nm (265). **7**: mp 81-82 °C; yellow crystals; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.65 (6H, m), 1.71 (6H, d), 1.94 (3H, s), 7.28-7.39 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 28.23 (d), 36.36 (t), 39.42 (s), 41.67 (t), 127.62 (s), 127.91 (d), 127.99 (d), 128.97 (d), 137.12 (s, dithiete ring), 144.28 (s, dithiete ring); mass spectrum *m/e* 300 (M^+), 236, 135 (base peak); UV/Vis λ_{max} (hexane) (ε) 233 (5360), 305 (3130), 345 nm (171). **8**: red oil; bp 90-92 °C/1.2 mmHg (bulb-to-bulb distillation); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.34 (s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 1.64, 145.08; mass spectrum *m/e* 266 (M^+), 202 (M^+-2S), 187, 155, 97, 73 (base peak). **11**: mp 47-49 °C; reddish orange crystals; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.08 (3H, t), 1.29 (3H, t), 3.65 (2H, q), 3.87 (2H, q), 7.45 (5H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.71 (q), 13.19 (q), 44.86 (t), 47.71 (t), 129.37 (s), 129.61 (d), 130.89 (d), 135.17 (d), 195.44 (s, C=S), 226.34 (s, C=S) (two ethyls are nonequivalent because of restricted rotation); mass spectrum *m/e* 269 (M^+), 254, 208, 88 (base peak); UV/Vis λ_{max} (hexane) (ε) 217 (10050), 271 (10560), 318 (6350), 349 (4590), 396 (2520), 495 nm (280). **12**: mp 72-73 °C; dark red plates; ^{1}H NMR ($CDCl_3$, 100 MHz) δ 0.98 (3H, t), 1.25 (3H, t), 3.60 (2H, q), 3.79 (2H, q), 7.46 (3H, m), 7.63 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.56, 12.93, 44.69, 47.33, 129.05, 129.61, 130.22, 136.40, 197.08 (C=S), 229.44 (C=S) (two ethyls are nonequivalent because of restricted rotation); mass spectrum *m/e* 319, 317, 315 (M^+), 205, 160 (base peak), 128, 116. All new compounds gave satisfactory elemental analyses results and/or high-resolution mass spectral data.
9. ^{1}H and ^{13}C NMR and UV/Vis spectra did not give any supporting evidence for the presence of the dithione form.
10. Christie, R. M.; Ingram, A. S.; Reid, D. H.; Webster, R. G. *J. Chem. Soc., Perkin 1*, **1974**, 722.
11. Birchall, J. M.; Bowden, F. L.; Haszeldine, R. N.; Lever, A. B. P. *J. Chem. Soc. (A)* **1967**, 747.
12. Sulfuration of a simple acetylene such as 3-hexyne affords a complex mixture in which no dithiete was detected.
13. (a) Grigg, R.; Hayes, R.; Jackson, J. L. *J. Chem. Soc., Chem. Commun.* **1969**, 1167. (b) Nakayama, J.; Shimomura, M.; Iwamoto, M.; Hoshino, M. *Heterocycles*, **1985**, *23*, 1907.
14. (a) Schmidt, U.; Kabitzke, K.; Markau, K.; Müller, A. *Liebigs Ann. Chem.* **1964**, *672*, 78. (b) Sawada, K.; Ishii, A.; Nakayama, J.; Hoshino, M. The 6th International Conference on the Chemistry of Selenium and Tellurium, 1991, Osaka, Abstract No. PP 14.
15. Nakai, T.; Tanaka, K.; Seto, H.; Ishikawa, N. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 3069.
16. Piettre, S.; Janousek, Z.; Viehe, H. G. *Synthesis*, **1982**, 1082.
17. Delavarenne, S. Y.; Viehe, H. G. *Chem. Ber.* **1970**, *103*, 1209.
18. (a) For preparation of dithionooxalate and tetrathionooxalate esters, see: Hartke, K.; Hoppe, H. *Chem. Ber.* **1974**, *107*, 3121; Kiessel, T.; Matusch, R.; Hartke, K. *Z. Chem.* **1976**, *16*, 318. (b) For methyl dithionooxalmorpholide, see: Wawzonek, S.; Heilmann, S. M. *J. Org. Chem.* **1974**, *39*, 511. (c) For dithionooxalamides, see: Milligan, B.; Swan, J. M. *J. Chem. Soc.* **1961**, 1194; Dutron-Woitrin, F.; Merenyi, R.; Viehe, H. G. *Synthesis*, **1985**, 77.

(Received in Japan 17 September 1992)