Pergamon

Tetrahedron Letters, Vol. 38, No. 49, pp. 8529-8532, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10079-X

Preparation and Thermal Reaction of 1,3-Bis(alkylthio)allenes

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Abstract: Reactions of Ph_2C_3 dianion with alkyl thiocyanates or ethylene 1,2-dithiocyanate give 1,3-bis(alkylthio)allenes or tetrathiacyclic bisallene, respectively. Thermal reactions of 1,3-bis(benzylthio)allene and tetrathiacyclic bisallene afford 2,3,5-triphenylthiophene and 1,2-bismethylidene cyclobutane derivatives, respectively. © 1997 Elsevier Science Ltd.

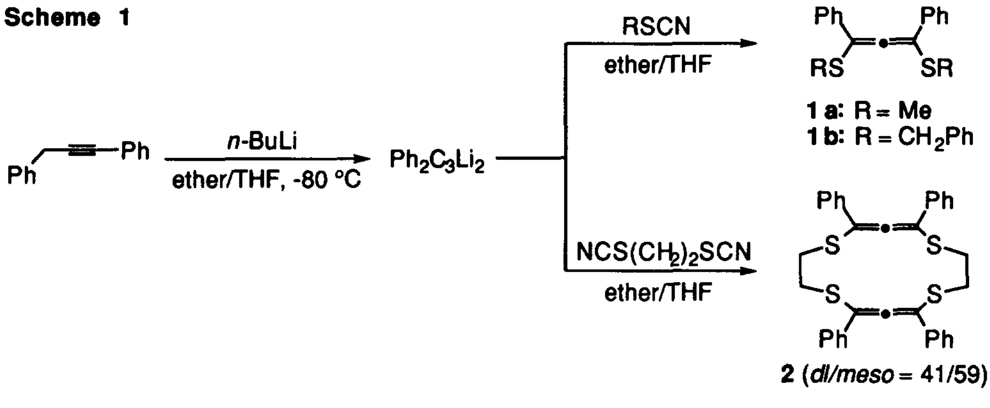
The chemistry of allenes has been extensively studied and many reviews on their preparation and reactivities have been published.[1,2] Substituted allenes by heteroatoms such as silicon, phosphorus and sulfur have also received attention.[1] Among the sulfur-substituted allenes, mono-,[3,4] 1,1-bis-,[5] tris-[6] and tetrakis[6]-(alkylthio)allenes had been synthesized in the 1960's. However, few reactions of the alkylthioallenes have been reported. We succeeded in preparing 1,3-bis(alkylthio)allenes and tetrathiacyclic bisallene by reactions of Ph_2C_3 dianion with the corresponding alkyl thiocyanates and found that the thermal reactions of the 1,3-bis(benzylthio)allene and the tetrathiacyclic bisallene gave 2,3,5-triphenylthiophene and 1,2-bismethylidene cyclobutane derivatives, respectively.

When a THF solution of two equiv. amount of methyl thiocyanate was added dropwise to Ph_2C_3 dianion, prepared from 1,3-diphenylpropyne and *n*-butyllithium in ether/THF solution, at -80 °C and allowed to warm to room temperature, 1,3-bis(methylthio)-1,3-diphenylpropadiene (**1a**)[7] was obtained in 62% yield after purification by column chromatography on silica-gel, then gel-permeation chromatography (Scheme 1). Similar reaction of the dianion with benzyl thiocyanate also gave 1,3-bis(benzylthio)-1,3-diphenylpropadiene (**1b**)[8] in 88% yield. 3,3-Bis(alkylthio)propyne, the formation of which is possible by the reactions with the dianion, was not detected in either reaction. Reaction of the dianion with ethylene 1,2-dithiocyanate formed tetrathiacyclic bisallene **2**[9] in 21% yield (*dl*/*meso* = 41/59), though the reaction with methylene dithiocyanate did not give the corresponding cyclic bisallene.

The stereochemistry of one isomer of the cyclic bisallenes, *meso*-**2**, was determined by the X-ray crystallographic analysis (Figure 1).[10] The bond lengths are almost normal, and the bond angle C(1)-C(2)-C(3*) and torsion angle S(1)-C(1)-C(3*)-S(2*) are 176 and 94°, respectively, indicating strain-free geometry.

Thermal reactivity of allenes which possess alkylthio substituents has been scarcely examined. 1,3-Bis(methylthio)allene **1a** and 1,3-bis(benzylthio)allene **1b** are stable at room temperature, whereas tetrakis(methylthio)allene is known to undergo dimerization to give a cyclic dimer on standing at room

Scheme 1



temperature.[6] When a *p*-xylene solution of **1a** was refluxed for 3 days, 68% of **1a** was consumed to give 2,4-diphenyl thiophene (**3**),[11] 1,3-dihydro-2-benzothiepin **4**[12] and bis(methylthiobenzylidene) cyclobutane **5**[13] in 30%, 18% and 8% yields, respectively (Scheme 2). A stereoisomer of **5** was also formed in this reaction in 8% yield, which has C_2 or C_s symmetry based on ^{1}H- and ^{13}C-NMR spectra, though the stereochemistry could not be clarified. 1,3-Bis(benzylthio)allene **1b** underwent thermal reaction more easily to give 2,3,5-triphenyl thiophene (**6**),[14] thiete **7**[15] and α,β-unsaturated ketone **8**[16] in 63%, 5% and 11% yields, respectively, under refluxing in *p*-xylene for 1 hour. It is clear that the thermal reaction of 1,3-bis(alkylthio)allenes is affected by the substituents on the sulfur atoms. Thermal reaction of cyclic bisallene *dl*-**2** caused intramolecular cyclization reaction, in preference to the other reactions found in the case of compound **1**, to give tricyclic compound **9**[17] in quantitative yield. The isomer *meso*-**2** also gave an identical compound under similar conditions, quantitatively.

Bismethylidene cyclobutane **5** and the stereoisomer, and tricyclic compound **9** are considered to be formed *via* 2,2'-bisallyl biradicals[18] **10** and **11**, respectively. Biradical intermediate **11** is formed from both the *dl*- and *meso*-isomers **2**, thus the tricyclic compound **9** is obtained as a sole product from both the isomers. Thiete **7** and ketone **8**, obtained from **1b**, are probably formed by the cyclization and hydrolysis of thioketone **12**, respectively, which is formed by homolytic cleavage of the C-S bond in **1b**. Details of the mechanism for formation of thiophenes **3** and **6**, and

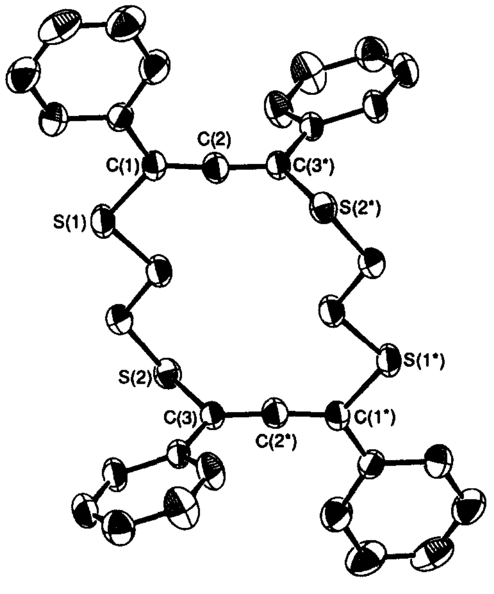
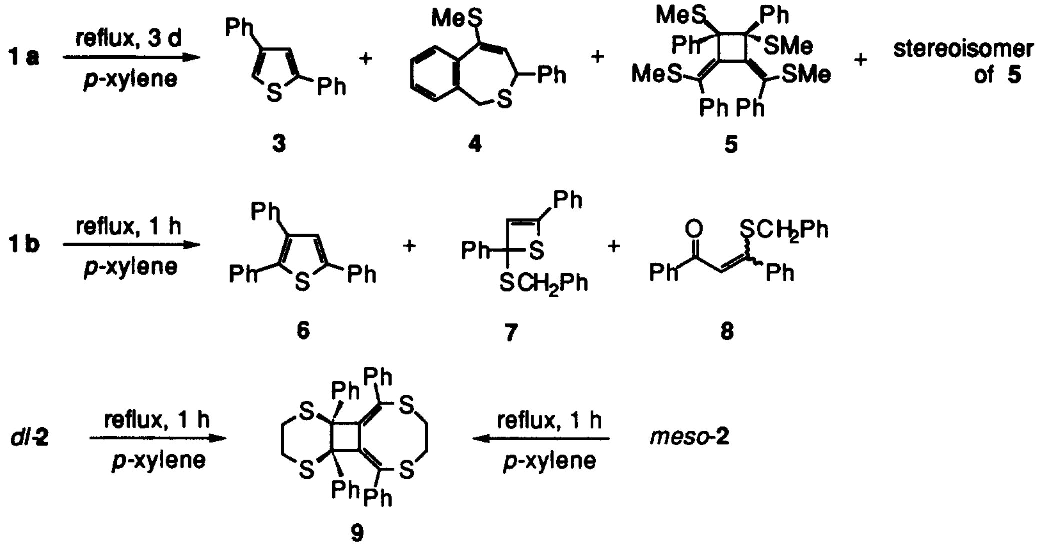
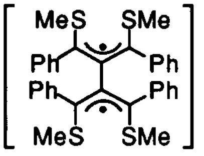


Fig. 1 Molecular structure of *meso*-**2** with 50% thermal ellipsoids. Selected bond distances (Å) and angles (°): S(1)-C(1) 1.7753(7), C(1)-C(2) 1.3095(8), C(2)-C(3*) 1.3162 (8), S(2*)-C(3*) 1.7873(7), S(1)-C(1)-C(2) 122.26(6), C(1)-C(2)-C(3*) 175.73(9), S(2*)-C(3*)-C(2) 117.85(6).

Scheme 2





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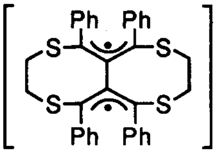

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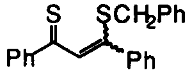

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benzothiepin **4** are now under investigation.

The present study was financially supported in part by a Grant-in-Aid for General Scientific Research from the Ministry of Education, Science, and Culture, Japan.

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7. **1a:** Yellow liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 6H), 7.26-7.59 (m, 10H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 15.55, 116.86, 126.35, 128.38, 128.53, 135.00, 194.68. MS (m/z) 284 (M^+), 237, 222, 191. Anal. calc. for $C_{17}H_{16}S_2$: C 71.78, H 5.67. Found: C 71.92, H 5.42.
8. **1b:** Pale yellow liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.65 (d, 2H, J = 13.2 Hz), 3.74 (d, 2H, J = 13.2 Hz), 7.13-7.47 (m, 20H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 36.89, 113.70, 126.54, 127.08, 128.29, 128.38, 128.53, 128.97, 134.62, 137.07, 197.31. MS (m/z) 345 (M^+-CH_2Ph), 313, 255, 222, 190, 123, 91. Anal. calc. for $C_{29}H_{24}S_2$: C 79.77, H 5.54. Found: C 79.94, H 5.40.
9. ***dl*-2:** Mp 144.0-145.0 °C (colourless powder from dichloromethane-hexane). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.07 (s, 8H), 7.27 (tt, 4H, J = 1.5 and 7.3 Hz), 7.32 (ddd, 8H, J = 1.5, 7.3, and 7.3 Hz), 7.53 (dd, 8H, J = 1.5 and 7.3 Hz). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 31.38, 112.39, 126.67, 128.53, 128.62, 134.19, 197.68. MS (m/z) 564 (M^+), 536, 508, 476, 472, 444, 412, 387, 282. Anal. calc. for $C_{34}H_{28}S_4$: C 72.34, H 4.96. Found: C 72.59, H 5.00. ***meso*-2:** Mp 162.0-163.0 °C (colourless needles from dichloromethane-hexane). ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.09-3.23 (m, 8H), 7.25-7.54 (m, 20H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 31.66, 110.26, 126.90, 128.51, 128.67, 133.98, 200.49. MS (m/z) 564 (M^+), 536, 508, 476, 472, 444, 412, 387, 282. Anal. calc. for $C_{34}H_{28}S_4$: C 72.34, H 4.96. Found: C 72.39, H 5.05.
10. *Crystal structure analysis* for *meso*-**2** (colourless prism from dichloromethane/hexane): formula $C_{34}H_{28}S_4$, M_r = 564.84, crystal dimensions 0.30 X 0.30 X 0.20 mm, a = 5.733(1), b = 11.069(3), c = 12.306(3) Å, α = 113.05(2), β = 91.25(2), γ = 99.24(2)°, V = 706.2(3) Å^3, ρ_{calct} = 1.328 gcm^{-3}, Z = 1, triclinic, space group $P\bar{1}$ (No. 2), Mac Science MXC 18 diffractometer, λ = 0.71073 Å, T = 298 K, 3512 measured reflections, 2575 independent, R = 0.037, Rw = 0.039.
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12. **4:** Brown liquid. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.32 (d, 1H, J = 12.2 Hz), 4.06 (d, 1H, J = 12.2 Hz), 4.42 (d, 1H, J = 7.8 Hz), 5.90 (d, 1H, J = 7.8 Hz), 7.21-7.49 (m, 9H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ 15.83, 33.78, 46.12, 122.02, 127.74, 127.82, 128.38, 128.58, 128.75, 128.97, 129.28, 137.42, 137.84, 138.11, 139.03. MS (m/z) 284 (M^+), 269, 252, 237, 203, 191, 135, 91, 77. HRMS calc. for $C_{17}H_{16}S_2$: 284.0693; found: 284.0713.
13. **5:** Mp 196.0-197.0 °C (decomp.) (yellow needles from dichloromethane-hexane). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 1.19 (s, 6H), 1.58 (s, 6H), 7.01-7.78 (m, 20H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 15.03, 15.92, 72.17, 127.40, 127.66, 127.83, 128.30, 128.58, 129.50, 134.29, 136.92, 137.33, 139.06. MS (m/z) 568 (M^+), 553, 521, 506, 491, 474, 459, 444, 427, 412, 380, 237. HRMS calc. for $C_{34}H_{32}S_4$: 568.1387; found: 568.1419. Stereochemistry of **5** was determined by the X-ray analysis (R = 0.052, Rw = 0.053).
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15. **7:** Yellow liquid. ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.60 (d, 1H, J = 13.1 Hz), 3.83 (d, 1H, J = 13.1 Hz), 6.18 (s, 1H), 6.92-7.58 (m, 15H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 46.71, 75.83, 123.87, 126.71, 127.09, 127.38, 127.74, 127.84, 128.59, 128.68, 129.18, 130.56, 133.29, 136.18, 142.33, 144. 07. MS (m/z) 346 (M^+), 313, 256, 224, 192, 91, 77. HRMS calc. for $C_{22}H_{18}S_2$: 346.0850; found: 346.0816.
16. **8:** Mp 122.0-123.0 °C (yellow needles from dichloromethane-hexane). ^{1}H-NMR (500 MHz, $CDCl_3$) δ 3.66 (s, 2H), 7.04 (s, 1H), 7.01-7.96 (m, 15H). ^{13}C-NMR (125 MHz, $CDCl_3$) δ 37.68, 119.87, 127.05, 128.07, 128.11, 128.30, 128.47, 128.54, 128.85, 128.98, 132.24, 136.66, 138.40, 138.97, 162.87, 188.35. MS (m/z) 239 (M^+-CH_2Ph), 105, 91, 77. Anal. calc. for $C_{22}H_{18}OS$: C 80.00, H 5.45. Found: C 79.65, H 5.46.
17. **9:** Mp 234.0-235.0 °C (decomp.) (yellow prisms from dichloromethane-hexane). ^{1}H-NMR (500 MHz, C_6D_6, 60 °C) δ 2.54-2.57 (m, 4H), 2.80-2.85 (m, 2H), 3.41 (br s, 2H), 6.73-7.80 (m, 20H). ^{13}C-NMR (125 MHz, C_6D_6, 60 °C) δ 28.20, 29.26, 66.10, 127.00, 127.05, 127.60, 128.42, 128.74, 129.64 (duplicate), 130.61, 138.89, 139.67. MS (m/z) 564 (M^+), 536, 508, 476, 472, 444, 412, 387, 366, 334, 302, 221, 189, 145, 121, 77. Anal. calc. for $C_{34}H_{28}S_4$: C 72.23, H 4.96. Found: C 72.56, H 5.15. Stereochemistry of **9** was determined by the X-ray analysis (R = 0.057, Rw = 0.063).
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(*Received in Japan* 23 *June* 1997; *revised* 21 *August* 1997; *accepted* 28 *August* 1997)