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2-Thiabicyclo[3.2.0]hepta-3,6-Dienes. 3. Desulfuration and Sulfuration of 2-Thiabicyclo[3.2.0]hepta-3,6-Dienes and X-Ray Crystal Structure of 3a,6,7,8,9,9a-Hexahydro-3a,5-Dimethylthieno[3,2-B][2]benzothiophene-2,3-Dicarbonitrile

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irradiation did not appear to affect this ratio substantially, but considerable darkening of the solution was observed.

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2-Thiabicyclo[3.2.0]hepta-3,6-dienes. 3. Desulfuration and Sulfuration of 2-Thiabicyclo[3.2.0]hepta-3,6-dienes and X-ray Crystal Structure of 3a,6,7,8,9,9a-Hexahydro-3a,5-dimethylthieno[3,2-*b*][2]benzothiophene-2,3-dicarbonitrile

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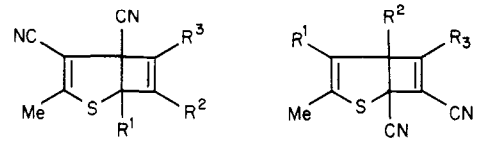
The 2-thiabicyclo[3.2.0]hepta-3,6-dienes 1–7 extrude sulfur in solution at 285 °C to give the 1,2-benzenedicarbonitriles 8–12 in yields of 42–56%. 5-(1,1-Dimethylethyl)-3,6-dimethyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-1,7-dicarbonitrile (6) reacts at 140 °C to give a mixture of the Cope-rearranged isomer 13, the 1,2-benzenedicarbonitrile 11, and possibly a 3a,6a-dihydrothieno[3,2-*b*]thiophene (14). Reaction of 2a,5,6,7,8,8a-hexahydro-2a,4-dimethylbenzo[*c*]cyclobuta[*b*]thiophene-1,2-dicarbonitrile (15) at 140 °C gives a mixture of desulfurated (16) and *sulfurated* (17) products in yields of 88% and 70%, respectively. Single-crystal X-ray analysis proved the 3a,6,7,8,9,9a-hexahydrothieno[3,2-*b*][2]benzothiophene structure (17). The possible mechanism of the insertion of sulfur in the carbon–carbon single bond of 15 is discussed.

The two preceding papers in this series[1,2] describe the preparation[1] of 2-thiabicyclo[3.2.0]hepta-3,6-diene-6,7-dicarbonitriles and their thermal (120–140 °C)[2] and photochemical[2] isomerization to the analogous 4,5- (1–3) and 1,7-dicarbonitriles (4–7), respectively. Since the two modes of isomerization did not lead to the desired thiepins,[1,2] it was decided to investigate the effect of higher temperatures on the 4,5- and 1,7-dicarbonitriles as a possible route to thiepins.

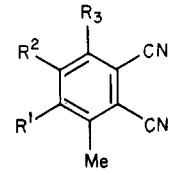
Further, it was considered that the 1,2-dicarbonitrile (15),[1] which cannot undergo photochemical isomerization by the described[2] mechanism and which is unlikely, because of the bridging, to undergo the Cope rearrangement[2] (thermal isomerization at moderate temperature), would undergo facile C-2a,C-8a cleavage on heating and result in thiepin formation.

Two factors make it difficult to predict the temperatures required for ring opening of the cis-fused cyclobutene ring in 1–7 and 15. Comparison with the reactivity of other cis-fused cyclobutenes indicates that both increased strain and participation of the π electrons of the vinyl group will lower the activation energy.[3,4] Frey et al.[5] found that the isomerization of bicyclo[3.2.0]hept-6-ene to cyclohepta-1,3-diene has an activation energy of 190.4 kJ mol^{-1} compared with a value of 143.9 kJ mol^{-1} for cis-3,4-dimethylcyclobutene.[3] However, the activation energy of the isomerization of bicyclo[3.2.0]hepta-3,6-diene to cycloheptatriene has an activation energy of only 165.3 kJ mol^{-1}.[6] An allylic stabilization of an intermediate biradical or of a biradicaloid transition state in the symmetry-forbidden disrotatory ring opening has been postulated to account for this difference.[6] To our knowledge, there is no information available as to how a sulfur or a thiovinyl substituent at the 3-position of cyclobutenes effects the rate of isomerization. Another unpredictable factor is the influence of cyano groups in compounds 1–7 and 15 be-

Chart I



1, $R^1 = R^2 = R^3 = Me$
2, $R^1 = Me$; $R^2 = CMe_3$; $R^3 = H$
3, $R^1 = Me$; $R^2 = H$; $R^3 = CMe_3$
4, $R^1 = R^2 = R^3 = Me$
5, $R^1 = CMe_3$; $R^2 = H$; $R^3 = Me$
6, $R^1 = H$; $R^2 = CMe_3$; $R^3 = Me$
7, $R^1 = H$; $R^2 = Me$; $R^3 = CMe_3$



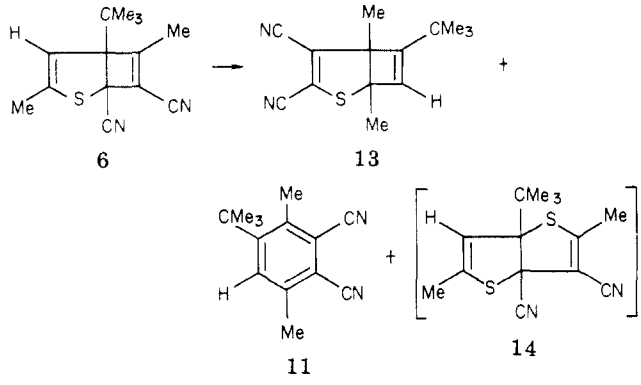
8, $R^1 = R^2 = R^3 = Me$
9, $R^1 = Me$; $R^2 = CMe_3$; $R^3 = H$
10, $R^1 = Me$; $R^2 = H$; $R^3 = CMe_3$
11, $R^1 = CMe_3$; $R^2 = H$; $R^3 = Me$
12, $R^1 = H$; $R^2 = Me$; $R^3 = CMe_3$

† Department of Organic Chemistry.
‡ Department of Chemical Physics.

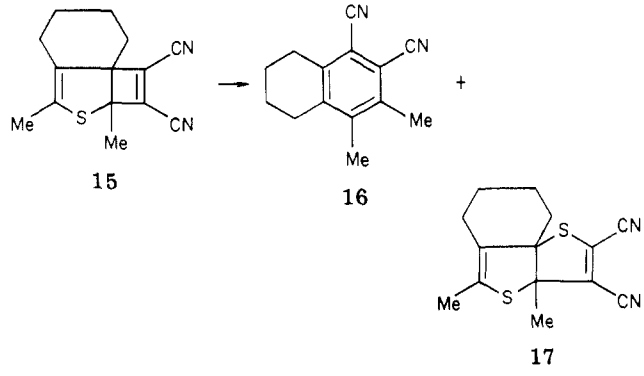
(1) Part 1: Hall, R. H.; den Hertog, H. J., Jr.; Reinhoudt, D. N. *J. Org. Chem.*, accompanying paper in this issue.
(2) Part 2: Hall, R. H.; den Hertog, H. J., Jr.; Reinhoudt, D. N. *J. Org. Chem.*, accompanying paper in this issue.
(3) Frey, H. M.; Walsh, R. *Chem. Rev.* **1969**, *69*, 103.
(4) Curry, M. J.; Stevens, I. D. R. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1391.

0022-3263/82/1947-0977$01.25/0

Scheme I



Scheme II



cause of their ability to stabilize radicals.[7,8]

Results

The pyrolyses of the 2-thiabicyclo[3.2.0]hepta-3,6-dienedicarbonitriles 1–7[2] (Chart I) at 285 °C for 15 min gave in each case single crystalline products (42–56% yield) which were shown by elemental analysis and mass spectrometry to result from the loss of a sulfur atom from the parent compounds. The products of the pyrolysis of 1 and 4 and of 5 and 6 were readily identified as 2,3,4,5-tetramethyl-1,2-benzenedicarbonitrile (8) and 4-(1,1-dimethylethyl)-3,6-dimethyl-1,2-benzenedicarbonitrile (11), respectively. Compounds 8 and 11 have been prepared earlier by the [4 + 2] cycloaddition of 2-butynedinitrile to 2,3,4,5-tetramethylthiophene and to 3-(1,1-dimethylethyl)-2,5-dimethylthiophene, respectively, with subsequent loss of sulfur from the resulting 1:1 adducts.[10] The same compounds were also isolated, in low yield, in the Lewis acid catalyzed reactions of the acetylene with the thiophenes.[1] Compound 8 has also been prepared by the Rosenmund–von Braun reaction from the corresponding dihalide.[11,12]

Pyrolysis of 2, 3, and 7 gives three other isomeric (1,1-dimethylethyl)dimethylbenzenedicarbonitriles. That they are all 1,2-benzenedicarbonitriles has not been *chemically* proved, but the formation of the 1,2-benzenedicarbonitriles 8 and 11 from their analogous precursors strongly supports the structures. Further, comparison of the UV spectra of the desulfurated products 8–12 with those of 1,2-, 1,3-, and 1,4-benzenedicarbonitrile[13–15] supports the formation of the 1,2-benzenedicarbonitrile compounds. Finally, their mode of preparation and the structural properties of the precursors lead us to believe that, in both the desulfurated products and their precursors,[1,2] the two carbonitrile groups are always adjacent. The analytical and spectral data (see Table I) give the structures of the 1,2-benzenedicarbonitrile compounds 8–12 as shown. In all cases pyrolysis at 285 °C leads formally to loss of sulfur with fission of the C-1,C-5 bond and no other skeletal change.

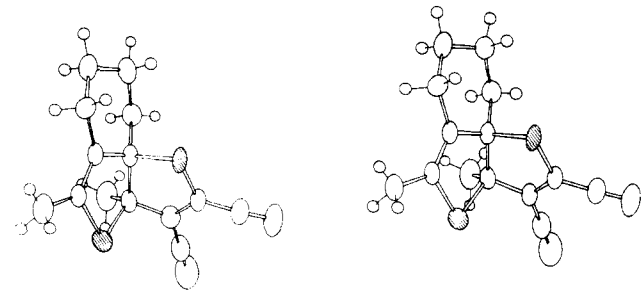


Figure 1. Stereoscopic view of the crystal structure of 17.

When the temperature is reduced to 140 °C, compounds 1–5 and 7 are relatively stable, being recovered in greater than 80% yield after 6 h. However, when 6 is heated at 140 °C, the corresponding Cope product[2] (13) was obtained: the usual spectral and analytical techniques clearly showed that 13 was as shown in Scheme I. In addition, two other products were obtained, the *1,2-benzenedicarbonitrile* 11 and a further compound which could not be obtained in the pure state but which is probably 14. Mass spectrometry showed that the compound contained two sulfur atoms ($C_{14}H_{16}N_2S_2$). Its ^1H NMR spectrum clearly showed allylic coupling between the proton at C-6 and the methyl group at C-5, and comparison of this spectrum with that of 17 (vide supra) strongly supports the assignment.

Thermal isomerization of 15 at 140 °C leads to the formation of two products: the *desulfurated derivative* 16 (Scheme II), which was readily identified by the usual analytical and spectral techniques, and a second yellow crystalline product. Elemental analysis and mass spectrometry showed that this compound contained two sulfur atoms ($C_{14}H_{14}N_2S_2$). Its ^1H and ^{13}C NMR spectra showed that the basic tricyclic structure had been retained: there was evidence of allylic coupling in the ^1H NMR spectrum, and its ^{13}C NMR spectrum indicated that four C_{sp^2} and two bridgehead C_{sp^3} carbon atoms were present. An X-ray single-crystal analysis showed that the compound was 17.

A stereoscopic figure of a molecule of 17 as found in the crystal structure is given in Figure 1.

Discussion

Our results reveal that the 2-thiabicyclo[3.2.0]hepta-3,6-dienes 1–5 and 7 are relatively heat stable, extruding sulfur only at high temperature. This is very different from the reported reactions of 5-(1-pyrrolidinyl)- and 5-benzoyl-2-thiabicyclo[3.2.0]hepta-3,6-dienes[9,16] which ex-

(5) Branton, G. R.; Frey, H. M.; Montague, D. C.; Stevens, I.D. R. *Trans. Faraday Soc.* **1966**, *62*, 659.
(6) Willcott, M. R.; Goerland, E. *Tetrahedron Lett.* **1966**, 6341.
(7) Belluš, D.; Rist, G. *Helv. Chim. Acta* **1974**, *57*, 194.
(8) Although a successfull thiepin synthesis requires that isomerizations take place under very mild conditions,[9] it is not known how the various substituents, particularly at C-2 and C-7, will influence the stability.
(9) Reinhoudt, D. N.; Geevers, J.; Trompenaars, W. P.; Harkema, S.; van Hummel, G. J. *J. Org. Chem.* **1981**, *46*, 424.
(10) (a) Helder, R.; Wynberg, H. *Tetrahedron Lett.* **1972**, 605. (b) Helder, R. Hesis, Groningen University 1974.
(11) Kovshev, E. I.; Solov'eva, L. I.; Mikhalenko, S. A.; Luk'yanets, E. A. *Zh. Vses. Khim. O-va.* **1976**, *21*, 465; *Chem. Abstr.* **1976**, *85*, 123531.
(12) Suzuki, H.; Hanafusa, T. *Synthesis* **1974**, 53.
(13) The Sadtler Standard Spectra, No. 2385, Sadtler Research Laboratories, Inc., Philadelphia, PA, 1967.
(14) Reference 13, No. 8891.
(15) Reference 13, No. 23086.
(16) Arnold, D. R.; Hadjiantoniou, C. P. *Can. J. Chem.* **1978**, *56*, 1970.

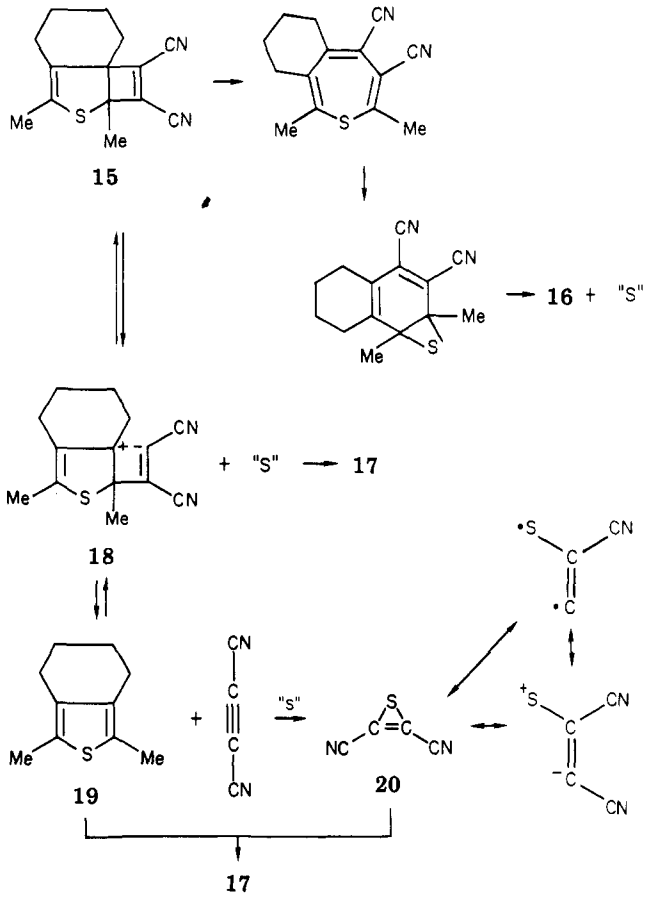
trude sulfur rapidly at room temperature. In the case of 5-(1-pyrrolidinyl)-2-thiabicyclo[3.2.0]hepta-3,6-dienes we have shown, by ^1H NMR spectroscopy, that the elimination of sulfur takes place via a thiepin that is formed by ring opening of the cis-fused cyclobutene ring.[9] The rapid isomerization is facilitated by the presence of the amino group at the bridgehead C-5 atom.[9,17] The reported[16] similar influence of a 5-benzoyl substituent is difficult to explain.[2] The desulfuration reactions of **1–5** and **7** at 275 °C are fast and not very selective, with yields of isolated 1,2-benzenedicarbonitriles **8–12** varying between 42% and 56%. Consequently, we have not been able to study the kinetics of the desulfuration reactions. The rate-determining step must be the isomerization of **1–5** and **7** to the corresponding thiepins. Therefore, we are tempted to conclude that the rate of ring opening of the cis-fused cyclobutene rings in **1–5** and **7** does not differ substantially from that found for the rate of the isomerization of bicyclo[3.2.0]heptadiene to cycloheptatriene and that presence of the sulfur atom in **1–5** and **7** has little effect on the rate of the cyclobutene isomerization.

The two other 2-thiabicyclo[3.2.0]hepta-3,6-dienes (**6** and **15**) desulfurate much faster (at 110–140 °C). The increased reactivity of **6** compared with that of isomer **7** is probably due to the presence of the bulky 1,1-dimethylethyl group at the bridgehead position.[18] Both desulfuration to give **11**, presumably via isomerization of **6** to a thiepin, and Cope rearrangement to **13** will result in the relief of steric strain. The same reasoning can be applied to the strained tricyclic **15**. It cannot be shown from our results if **4**, **5**, and **7** undergo the Cope rearrangement prior to desulfuration since the 1,2-benzenedicarbonitriles **8**, **11**, and **12**, respectively, would result in either case. However, if the Cope rearrangement does take place, it only occurs at a very much higher temperature than that required for 2-thiabicyclo[3.2.0]hepta-3,6-diene-6,7-dicarbonitriles which rearrange at 110–140 °C. This result supports our postulate that a fast antarafacial–antarafacial Cope rearrangement requires an electron-deficient C-6,C-7 double bond.[2] An exception, in this respect, is the facile rearrangement of **6** to **13**. However, this rearrangement again results in the relief of steric strain by migration of the 1,1-dimethylethyl group from the bridgehead C-5 to the C-6 position.

The most interesting result of the thermolysis reaction of these 2-thiabicyclo[3.2.0]hepta-3,6-dienes is the simultaneous desulfuration and sulfuration of **15** and possibly **6**. When **15** is heated at 140 °C the "disproportionation" products **16** (M − S) and **17** (M + S) in yields of 88% and 70%, respectively, are formed. Again the greater reactivity of **15** compared with that of **1–5** and **7** can be attributed to the steric strain in the tricyclic system. Presumably, there is formation of a thiepin which is not stable at 140 °C and extrudes sulfur.[9,19] The extruded sulfur reacts with **15** in what to our knowledge is an unprecedented sulfuration reaction which involves the insertion of sulfur into a carbon–carbon single bond. A possible explanation is that the extruded sulfur is in a highly reactive monomeric form[20] (see Scheme III).

There are at least two possibilities (Scheme III) for further reaction: (i) reaction of sulfur with a 1,4-dipole

Scheme III



(**18**) which is present in equilibrium with **15** and (ii) addition of sulfur to 2-butynedinitrile which results from [2 + 2] cycloreversion of **15** and then subsequent 1,3-dipolar addition of the 2,3-dicyanothiirene (or its 1,3-dipolar or 1,3-diradical form) with the second component of the [2 + 2] cycloreversion, 4,5,6,7-tetrahydro-1,3-dimethylbenzo[*c*]thiophene (**19**).

Equilibration of **15** and a 1,4-dipole is not unlikely in view of the expected weakness of the C–C bond and the stabilization of the charges by the cyano and alkyl groups, respectively. Further, we have recently found that dimethyl 4,4-dimethyl-5-(1-pyrrolidinyl)-2-thiabicyclo-[3.2.0]hept-6-ene-6,7-dicarboxylate rearranges in methanol to a pyrrolizine derivative also via a similar 1,4-dipole.[21] 2,3-Substituted thiirenes have been proposed[22] as intermediates in the formation of thiophenes from diamine disulfides and acetylenes.

The reason why only **6** and **15** produce both the desulfurated and sulfurated products whereas other 2-thiabicyclo[3.2.0]hepta-3,6-dienes only give desulfurated aromatics must be due to the weaker "C-5,C-6" bond in **6** and **15**, which results in a lowering of the activation energy of the [2 + 2] cycloreversion or generation of the 1,4-dipolar intermediate.

Further work on the trapping of sulfur in these thermolysis reactions is in progress.

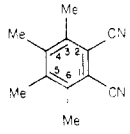
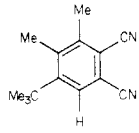
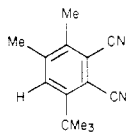
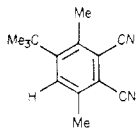
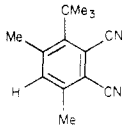
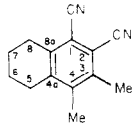
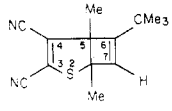
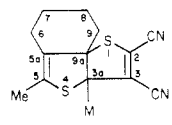
Experimental Section

See part 1 of this series[1] for general experimental information.

3,4,5,6-Tetramethyl-1,2-benzenedicarbonitrile (8). 1,3,6,7-Tetramethyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-4,5-di-

(17) Criegee, R.; Seebach, D.; Winter, R. E.; Börretzen, B.; Brune, H.-A. *Chem. Ber.* **1965**, *98*, 2339.
(18) 1,3-Dimethyl-5-(1,1-dimethylethyl)-2-thiabicyclo[3.2.0]hepta-3,6-diene-6,7-dicarbonitrile undergoes a rapid Cope rearrangement.[2]
(19) (a) Hoffman, J. M., Jr.; Schlessinger, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 5263. (b) Nishino, K.; Yano, S.; Kohashi, Y.; Yamamoto, K.; Murata, I. *Ibid.* **1979**, *101*, 5059.
(20) Chivers, T.; Drummond, I. *Chem. Soc. Rev.* **1973**, 223.
(21) Visser, G. W.; Trompenaars, W. P.; Verboom, W.; Reinhoudt, D. N. to be submitted for publication.
(22) Benitez, F. M.; Grunwell, J. R. *Tetrahedron Lett.* **1977**, 3413.

Table I. Melting Points and Mass, IR, UV, and ^1H and ^{13}C NMR Spectroscopic Data of

compd[a]	no.	mp, °C (hexane)	mass spectral data, *m/e* (relative intensity), fragment	IR,[d] cm^{-1} (assignment)	UV (EtOH), nm (ϵ)	H^g
	8	229-230	184 (51), M^+; 169 (100), $M^+ - Me$	2220 (C≡N), 1565 (C=C)	253 (9270), 298 (2720), 308 (3370)	
	9	139-140	212 (26), M^+; 197 (100), $M^+ - Me$; 169 (89), $M^+ - C_3H_5$	2240 (C≡N), 1590, 1555 (C≡C)	253 (9580), 291 (2510), 301 (3030)	7.68 (6)
	10	114-115	212 (15), M^+; 197 (100), $M^+ - Me$; 169 (22), $M^+ - C_3H_5$	2230 (C≡N), 1595, 1555 1545 (C=C)	248 (9000), 253 (8340), 296 (2800), 306 (3200)	7.48 (5)
	11	145-146[b]	212 (23), M^+; 197 (93), $M^+ - Me$; 169 (100), $M^+ - C_3H_5$	2230 (C≡N), 1595 (C=C)	246 (8730), 298 (2950), 308 (3390)	7.57 (5)
	12	105-106	212 (18), M^+; 197 (100), $M^+ - Me$; 169 (20), $M^+ - C_3H_5$	2230 (C≡N), 1590, 1560 (C=C)	253 (9450), 298 (2740), 306 (3290)	7.28 (5)
	16	195-196	210 (43), M^+; 195 (100), $M^+ - Me$	2225 (C≡N), 1555 (C=C)	253 (9660), 298 (2630), 308 (3150)	
	13	84-85[c]	244 (15), M^+; 229 (17), $M^+ - Me$; 162 (100), $M^+ - (HC{\equiv}CCMe_3)$; 147 (39), $M^+ - (HC{\equiv}CCMe_3) - Me$	2230, 2205 (C≡N), 1615, 1545 (C=C)	320 (6410)	5.93 (7)
	17	103-104	274 (88), M^+; 259 (25), $M^+ - Me$; 241 (25), $M^+ - HS$; 215 (100), $M^+ - C_2H_3S$; 204 (58), $M^+ - C_2NS$; 165 (67), $M^+ - C_4HN_2S$	2240, 2215 (C≡N), 1645, 1555 (C=C)	258 (5490), 285 (4120), 330 (5790), 396 (560)[e]	

[a] C, H, N, and S elemental analyses were done for all entries and agreed to ±0.2% of the theoretical values. [b] Lit. mp 144-144.5 °C.[10] [c] In pentane. [d] In a KBr disk. [e] Charge-transfer band. [f] Chemical shifts are given in parts per million relative to Me_4Si (δ 0). [g] Singlet unless otherwise stated. [h] Homoallylic $J_{CH_{3,6}}$ = 1.2 Hz. [i] Multiplet. [j] Triplet on partial

carbonitrile[2] (1, 1 mmol) was heated for 15 min at 275 °C in 20 mL of refluxing tetraethylene glycol dimethyl ether (275 °C), and the solution was then added to 150 mL of ice–water. The mixture was extracted with chloroform (3 × 50 mL), the combined extracts were dried over $MgSO_4$, and the solvent was removed. Thick-layer plate chromatography (hexane/ethyl acetate, 17:3) gave a solid which on recrystallization (hexane) gave **8** as colorless crystals: 52%; mp 229–230 °C (lit.[11] mp 230–231 °C).

Similar treatment of 3,4,5,6-tetramethyl-2-thiabicyclo[3.2.0]-hepta-3,6-diene-1,7-dicarbonitrile[2] (**4**) gave **8** in 47% yield.

5-(1,1-Dimethylethyl)-3,4-dimethyl-1,2-benzenedicarbonitrile (9). Similar treatment of 7-(1,1-dimethylethyl)-1,3-dimethyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarbonitrile[2] (**2**) gave **9** as colorless crystals: 56%; mp 139–140 °C.

6-(1,1-Dimethylethyl)-3,4-dimethyl-1,2-benzenedicarbonitrile (10). Similar treatment of 6-(1,1-dimethylethyl)-1,3-dimethyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-4,5-dicarbonitrile[2] (**3**) gave **10** as colorless crystals: 49%; mp 114–115 °C.

4-(1,1-Dimethylethyl)-3,6-dimethyl-1,2-benzenedicarbonitrile (11). Similar treatment of 4- and 5-(1,1-dimethylethyl)-3,6-dimethyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-1,7-dicarbonitrile (**5** and **6**, respectively) gave **11** as colorless crystals: 42% and 47%, respectively: mp 145–146 °C(lit.[10] mp 144–144.5 %C).

3-(1,1-Dimethylethyl)-4,6-dimethyl-1,2-benzenedicarbonitrile (12). Similar treatment of 6-(1,1-dimethylethyl)-3,5-dimethyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-1,7-dicarbonitrile[2] (**7**) gave **12** as colorless crystals: 44% mp 105–106 °C.

Thermal Reaction of 5-(1,1-Dimethylethyl)-3,6-dimethyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-1,7-dicarbonitrile (6) at 140 °C. Compound **6** (1.5 mmol) was heated in 25 mL of refluxing xylene (140 °C) for 7 h.[23] Removal of the solvent and repeated coevaporation with toluene and then hexane gave an oil which on examination by ^1H NMR spectroscopy was shown to contain **11** (1 H, s, δ 7.57), starting material (**6**; 1 H, s, δ 5.41),[2] and two other compounds (1 H, s, δ 5.93; 1 H, m, δ 5.28) in a ratio

(23) The same result was obtained when **6** was heated in toluene at 110 °C for 36 h.

Desulfuration and Sulfuration Products of 2-Thiabicyclo[3.2.0]hepta-3,6-dienes

^{1}H NMR ($CDCl_3$), δ^f (assignment)		^{13}C NMR ($CDCl_3$), δ^f (assignment)				
Me[g]	CH_2 and CMe_3	C_{sp^2}[g]	CN[g]	C_{sp^3}[g]	CH_2[j] and CMe_3[g]	Me[k]
2.53 (3, 6), 2.33 (4, 5)		141.6 (3, 6), 139.3 (4, 5), 113.2 (1, 2)	115.9 (1, 2)			19.2, 17.0 (3-6)
2.54, 2.51 (3, 4)	1.45[g] (5)	154.7 (5), 143.6, 142.6 (3, 4), 129.1[l] (6), 113.5, 112.8 (1, 2)	116.3, 115.4 (1, 2)		36.4, 30.7[k] (5)	19.6 (3, 4)
2.50 (3), 2.38 (4)	1.51[g] (6)	152.6 (6), 142.7, 139.4 (3, 4), 131.6[l] (5), 118.8 (2), 111.5 (1)	117.1, 115.7 (1, 2)		35.5, 30.0[k] (6)	20.9, 17.8 (3, 4)
2.77 (3), 2.56 (6)	1.44[g] (4)	154.1 (4), 140.6, 139.7 (3, 6), 132.0[l] (5), 118.2 (2), 113.9 (1)	115.8, 115.2 (1, 2)		36.6, 30.5[k] (4)	20.8, 20.6 (3, 6)
2.63 (4), 2.51 (6)	1.65[g] (3)	[m]				
2.52 (3), 2.26 (4)	2.97[i] (8), 2.73[i] (5), 1.85[i] (6, 7)	142.0, 141.7 (3, 4a), 140.0 (4, 8a), 138.5, 113.3, 113.2 (1, 2)	115.9, 113.3 (1, 2)		28.8, 28.0, 22.3 (5-8), 21.5	18.8, 15.9 (3, 4)
1.48 (1, 5)	1.16[g] (6)	164.5 (6), 130.3[l] (7), 125.9 (4), 121.2 (3)	113.9, 111.0 (3, 4)	67.9 (5), 64.2 (1)	34.1, 29.0[k] (6)	21.6, 17.5 (1, 5)
1.88[h] (5), 1.68 (3a)	2.75-1.0[i] (6-9)	130.0 (5a), 127.1 (5), 126.5, 123.4 (2, 3)	112.3, 108.1 (2, 3)	87.1 (9a), 70.1 (3a)	34.3 (9), 26.1, 25.4 (6-8), 23.8	21.0 (3a), 13.5 (5)

C-H decoupling. [k] Quartet on partial C-H decoupling. [l] Doublet on partial C-H decoupling. [m] Insufficient material to record a ^{13}C NMR spectrum.

of approximately 1:1:1:0.2. Thick-layer plate chromatography (multiple elution; hexane/ethyl acetate, 17:3) gave 6-(1,1-dimethylethyl)-1,5-dimethyl-2-thiabicyclo[3.2.0]hepta-3,6-diene-3,4-dicarbonitrile (**13**) as colorless crystals [21%; mp 84–85 °C; NMR δ 5.93 (1 H, s)] and a mixture of three compounds.

Multiple elution of this mixture with the same solvent mixture gave the starting material (**6**) in 24% yield and a mixture of **11** and an unknown compound (1 H, m, δ 5.28). Fractional crystallization partially removed **11** (25%) from the mixture, but all further attempts to remove the final traces of **11** from the mixture (16 mg) were unsuccessful. However, NMR and mass spectrometry indicated that the compound was 6a-(1,1-dimethylethyl)-3a,6a-dihydro-2,5-dimethylthieno[3,2-*b*]thiophene-3,3a-dicarbonitrile (**14**): mass M^+ found at m/e 276.076, calcd for $C_{14}H_{16}N_2S_2$ m/e 276.076; ^{1}H NMR δ 5.28 (1 H, m, H-6), 2.27 [3 H, s, Me(2)], 2.04 [3 H, d, $J_{CH_3,6}$ = 1.0 Hz, Me(5)], 1.26 [9 H, s, CMe_3(6a)].

Thermal Reaction of 2a,5,6,7,8,8a-Hexahydro-2a,4-dimethylbenzo[*c*]cyclobuta[*b*]thiophene-1,2-dicarbonitrile[1] (15) at 140 °C. Compound **15** (1 mmol) was heated in 25 mL of dry, refluxing xylene for 4 h. Removal of the solvent and repeated coevaporation with toluene and then hexane gave an oil. Thick-layer plate chromatography (multiple elution; hexane/ethyl acetate, 17:3) gave an oil which slowly solidified. Recrystallization (hexane) gave 3a,6,7,8,9,9a-hexahydro-3a,5-dimethylthieno[3,2-*b*][2]benzothiophene-2,3-dicarbonitrile (**17**) as yellow crystals: 70%; mp 103–104 °C. Also obtained was a solid which on recrystallization (hexane) gave 5,6,7,8-tetrahydro-3,4-dimethyl-1,2-napthalenedicarbonitrile (**16**) as colorless crystals: 88%; mp 195–196 °C.

Thermal Reaction of 1–5 and 7 at 140 °C. Compounds **1–5** and **7** were recovered in greater than 80% yield after being heated in refluxing xylene for 6 h.

Crystallographic Data and X-ray Structure Analysis of 17. Crystals of **17** belong to the triclinic space group $P\bar{1}$. The cell constants are as follows: a = 8.743 (3) Å, b = 11.369 (4) Å, c = 7.714 (3) Å, α = 94.29 (5)°, β = 104.70 (5)°, γ = 108.90 (5)°, Z = 2. X-ray intensities were measured with a Philips PW1100 single-crystal diffractometer by using graphite monochromated Mo Kα radiation (θ–2θ scan mode; θ_{max} = 25 °). The structure solution and refinement was based on 1945 reflections with an

intensity greater than the standard deviation estimated from counting statistics. The structure was solved by direct methods (MULTAN 78)[24] and refined by least-squares methods (ORFLS).[25] Hydrogen atoms were located from a difference Fourier synthesis. Parameters refined in the last cycles were positional parameters for all atoms, isotropic thermal parameters for the hydrogen atoms, and anisotropic thermal parameters for the other atoms. The resulting R factor was 3.5%. The drawing of the structure was made with the ORTEP program.[26]

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Registry No. 1, 37639-57-9; 2, 80242-89-3; 3, 80242-90-6; 4, 80242-91-7; 5, 80242-94-0; 6, 80242-92-8; 7, 80242-93-9; 8, 37639-56-8; 9, 80242-95-1; 10, 80242-96-2; 11, 36715-94-3; 12, 80242-97-3; 13, 80242-98-4; 14, 80242-99-5; 15, 80243-00-1; 16, 80243-01-2; 17, 80243-02-3.

Supplementary Material Available: X-ray structure, fractional atomic coordinates, mean square amplitudes of thermal vibration, bond distances, and bond angles of 17 (18 pages). Ordering information is given on any current masthead page.

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Kinetic Evidence for the Intermediacy of 1-Azirines in the Gas-Phase Thermal Isomerization of 3*H*-Isoxazoles to α-Carbonylacetonitrile Derivatives

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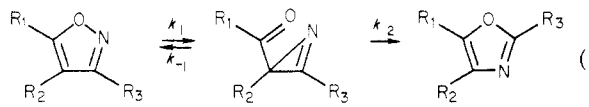
Thermal isomerization of 5-methylisoxazole and 5-amino-4-methylisoxazole to acetylacetonitrile and 2-cyanopropionamide, respectively, was studied in a flow system. The activation parameters are reported. According to the experimental results, a concerted 1,3 sigmatropic shift to 1-azirines is proposed as the rate-limiting step in these reactions. A general reaction mechanism for the isomerization of isoxazoles into 1-azirines, oxazoles, and α-carbonylacetonitrile derivatives is discussed.

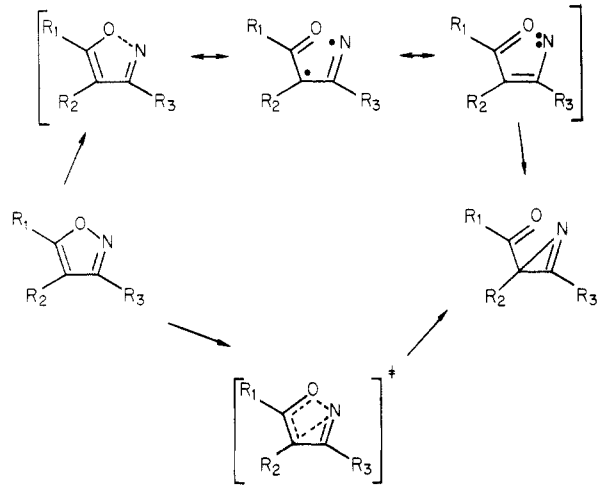
We have recently reported[2a,b] that in the gas-phase thermal isomerization of isoxazole derivatives to 1-azirines and oxazoles, the rate-limiting step is the formation of 1-azirines and its activation energy depends largely on substitution at position 5 of the isoxazole derivative (eq 1).



(1)

Moreover, we found that this effect can be rationalized through the incidence of the substituents on the HOMO of the migrating framework (MF) for the 1,3 sigmatropic shift. The E_a of the isomerization depends on the energy of the HOMO of the MF as predicted with the donor–acceptor model suggested by Epiotis.[3] The kinetic results lead us to suggest two alternative reaction pathways (eq 2).

On the basis of low A factors obtained, we proposed that the rate-determining step can hardly be attributed to a simple ring opening and then, in the stepwise mechanism, the transition state of the rate-limiting step must be attributed to the vinyl nitrene closure. On the other hand,



(2)

the concerted pathway is supported by both the activation parameters and the theoretical analysis, since whichever the reaction mode is (supra with inversion or supra with retention), the thermal 1,3 sigmatropic shift shows a net pericyclic bonding along the reaction coordinate.[3]

Continuing with our studies on the thermal behavior of isoxazoles in the gas phase, we studied the thermal reaction of 5-methylisoxazole **I** and 5-amino-4-methylisoxazole **2** to evaluate the influence of groups attached to position 3 of the isoxazole ring, by measuring the incidence of change of amino and methyl groups by hydrogen. The product analysis in both cases showed quantitative isomerization to the α-carbonylacetonitrile derivatives. Here

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