

FORMATION OF DITHIA[6]RADIALENES BY BORON TRIFLUORIDE-CATALYZED
REACTION OF " THIRANORADIALENE "

Wataru Ando*, Yukio Hanyu, Toshikazu Takata and Katsuhiko Ueno#

Department of Chemistry, The University of Tsukuba

Sakura, Ibaraki 305, Japan

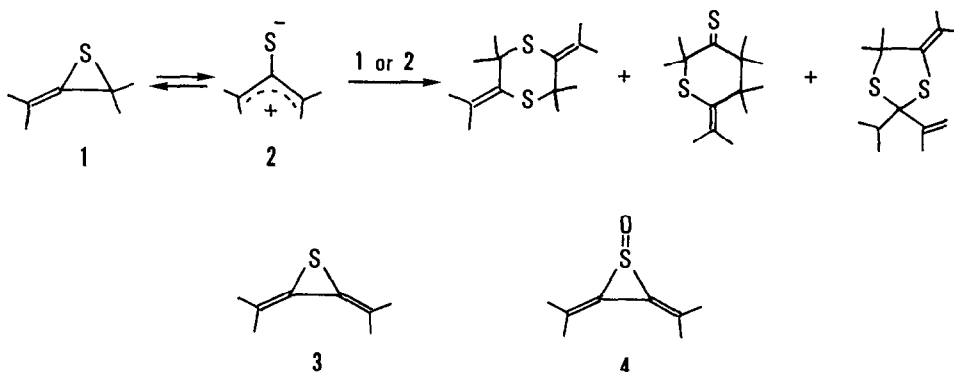
#Research Institute for Polymers and Textile

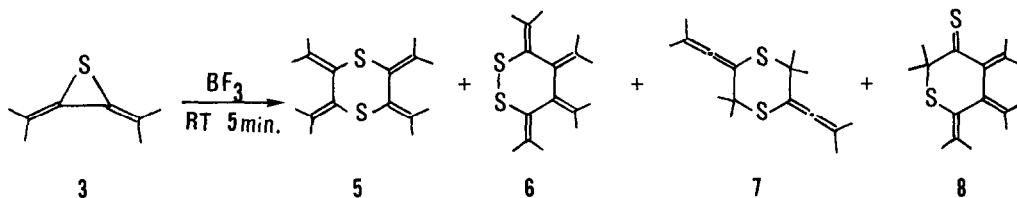
Yatabe, Ibaraki 305, Japan

Abstract: A boron trifluoride-catalyzed reaction of thirane 1 afforded dimerization products including two novel dithia[6]radialenes, whose structures were determined by spectroscopies and X-ray crystal analyses.

Allene episulfide 1 is a unique thirane having an exomethylene group and thereby is suggested to participate a tautomerism involving thioxyallyl ion 2¹. Thus, in the reaction with acid, we have observed an efficient ring opening of 1 to form a few dimerization products.

Meanwhile recently, the [n]radialenes have received considerable attention from not only synthetic but also theoretical aspects.² In the course of





studying our recent syntheses of hetero[3]radialenes such as thiranoradialene 3 and its S-oxide 4,³ we have performed acid-catalyzed reaction of 3 and found the formation of dithia[6]radialenes as novel products.

Treatment of 3³ (7 mmol) with boron trifluoride etherate (47%, 1.0 ml) in dichloromethane (15 ml) at 20°C caused a rapid disappearance of 3 and appearance of new spots with lower R_f values than that of 3 on TLC within five min. Successful isolation of the products was carried out by preparative high pressure liquid chromatography. Besides polymeric part, four components were separated respectively after twenty recyclings through a column (20 ϕ x 600mm x 2). The products were recrystallized from hexane and then subjected to the usual spectral analyses.⁴ Inspection of the spectral data⁴ revealed the product structures of 5 - 8. Both 5 and 6 have 1,4 and 1,2-dithia[6]radialene structures as first hetero[6]-radialenes. The 7 is 2,5-diallyl-1,4-dithiane while thioketone chromophore is suggested for 8 by its characteristic purple-red color.

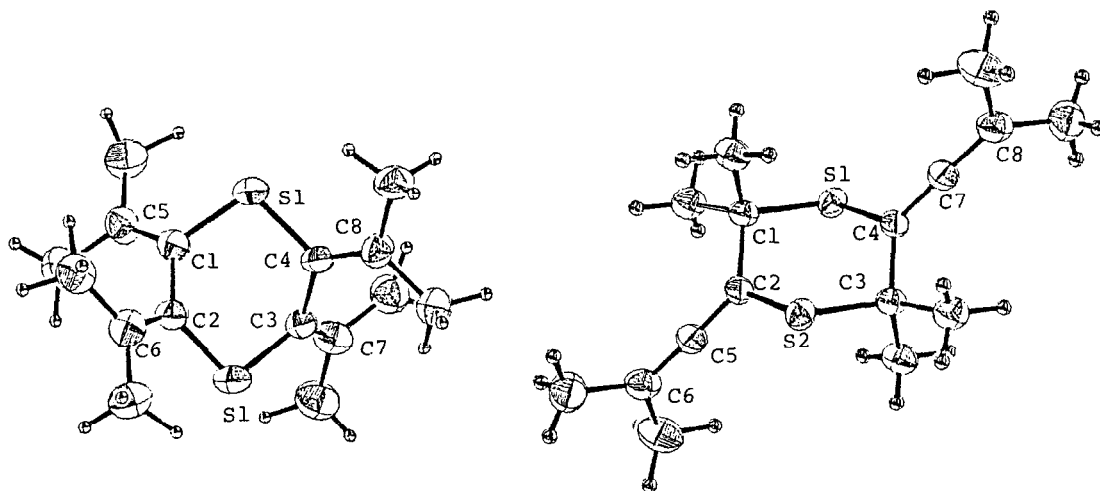
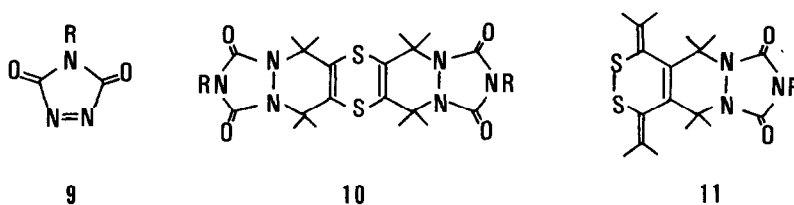


Figure 1. ORTEP drawings of the molecular structures of 5 and 7. Bond lengths (Å): 5: S₁-C₁ 1.78, C₁-C₂ 1.50, C₁-C₅ 1.33; 7: S₁-C₁ 1.84, C₁-C₂ 1.52, C₂-S₂ 1.79, C₂-C₅ 1.30, C₅-C₆ 1.30.

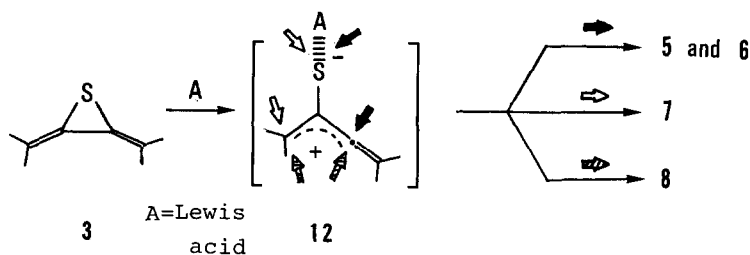
The total isolated yield was ca. 30% (i.e. 5% for 5, 3% for 6, 14% for 7 and 7% for 8), although it is not optimized. The yield, however, is rather high in comparison with dimerization yields of common thiiranes⁵. With catalytic amount of boron trifluoride, the reaction became slow and the yields of the products were low. Better result was obtained with excess boron trifluoride in nonpolar solvent such as dichloromethane or hexane.

X-Ray crystal analyses were done for suitable single crystals of both 5 and 7.⁶ The molecular structures are shown in Figure 1 which clearly convinces the proposed structures.

Although diene parts of 5 are not plane probably due to steric constraints of terminal methyl groups, 5 underwent double [2+4]cycloaddition with two equivalents of a strong dienophile 9 to give dithiine 10 (R=Ph) in quantitative yield. Similarly 1,2-dithia[6]radialene 6 afforded selectively the cycloaddition product 11 (R=Me) in quantitative yield.



Formation of the dithia[6]radialenes is explained by assuming a common opened intermediate (12) as shown in Scheme 1.



Scheme 1

Scheme 1. Courses for product formation. Arrows indicate sites of C-S and C-C bond formation.

REFERENCES AND FOOTNOTES

1. (a) W. Ando, Y. Hanyu, T. Furuhashi, T. Takata, J. Am. Chem. Soc., **105**, 6151, 1983. (b) E. Block, R. E. Penn, M. D. Ennis, T. A. Owens, S.-L. Yu, J. Am. Chem. Soc., **100**, 7436, 1978. (c) E. Longejan, Th. S. V. Buys, H. Steinberg, Th. J. De Boer, Recl. Trav. Chim. Pays-Bas, **97**, 214, 1978.
2. (a) G. Köbrich, H. Heinemann, W. Zundorf, Tetrahedron, **23**, 565, 1967. (b) L. G. Harruff, M. Brown, V. Boekelhide, J. Am. Chem. Soc., **100**, 2893, 1978. (c) A. J. Barkovich, E. S. Strauss, K. P. C. Vollhardt, J. Am. Chem. Soc., **99**, 8321, 1977. (d) T. Fukunaga, J. Am. Chem. Soc., **98**, 610, 1976.
3. W. Ando, Y. Hanyu, T. Takata, Tetrahedron Lett., **22**, 4815, 1981.
4. 5: mp. 99.5 - 100°C; ^1H NMR(δ , CDCl_3) 1.87(s, 12H), 1.70(s, 12H); ^{13}C NMR(δ , CDCl_3) 130.5, 125.5, 22.0, 21.0; MS m/e 280 [M^+ , 100%]; Elemental analysis, Calcd for $\text{C}_{16}\text{H}_{24}\text{S}_2$: C, 68.51; H, 8.62; Found: C, 68.61; H, 8.67; 6: mp. 97.5 - 99.5°C; ^1H NMR(δ , CDCl_3) 1.90(s, 6H), 1.80(s, 6H), 1.73(s, 6H), 1.66(s, 6H); ^{13}C NMR(δ , CDCl_3) 135.2, 133.7, 132.5, 125.3, 23.9, 22.1, 21.2, 21.0; MS m/e 280 [M^+ , 100%]; Elemental analysis, Calcd for $\text{C}_{16}\text{H}_{24}\text{S}_2$: C, 68.51; H, 8.62; Found: C, 68.46; H, 8.72; 7: mp. 155.5 - 156.0°C; ^1H NMR(δ , CDCl_3) 1.78(s, 12H), 1.53(s, 12H); ^{13}C NMR(δ , CDCl_3) 199.5, 101.8, 97.3, 46.3, 28.3, 20.6; MS m/e 280 [M^+ , 100%]; Elemental analysis, Calcd for $\text{C}_{16}\text{H}_{24}\text{S}_2$: C, 68.51; H, 8.62; Found: C, 68.52; H, 8.66; 8: purple red oil; ^1H NMR(δ , CDCl_3) 1.87(s, 3H), 1.82(s, 3H), 1.77(s, 3H), 1.72(s, 3H), 1.67(s, 6H), 1.58(s, 6H); MS m/e 280 [M^+ , 100%]
5. A. Noshay, C. C. Price, J. Polymer Sci., **54**, 533, 1961.
6. Intensity data were collected on a NICOLET P3/F four circle diffractometer with graphite monochromated $\text{Cu}/\text{K}\alpha$ radiation. 5: crystal data, space group = $\text{P}2/\text{c}$; $a = 14.406(3)$, $b = 12.206(3)$, $c = 10.219(3)\text{\AA}$; $\beta = 107.46(2)^\circ$; $Z = 4$; $D_x = 1.09\text{gcm}^{-3}$; A total of 2854 independent reflection measured within $2\theta < 150^\circ$, 1884 had intensities greater than $3\sigma|F_o|$ and used for structure analysis. The structure was solved by direct method and refined by full matrix least squares to a final R value of 0.068. 7: crystal data, space group = Pbca ; $a = 8.096(1)$, $b = 12.161(2)$, $c = 17.141(3)\text{\AA}$; $Z = 4$; $D_x = 1.10\text{gcm}^{-3}$; A total of 1601 independent reflection measured within $2\theta < 150^\circ$, 1489 had intensities greater than $3\sigma|F_o|$ and used for structure analysis. The structure was solved by direct method and refined by full matrix least squares to a final R value of 0.054.

(Received in Japan 16 March 1985)