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SYNTHESES OF " THIIRANORADIALENES "

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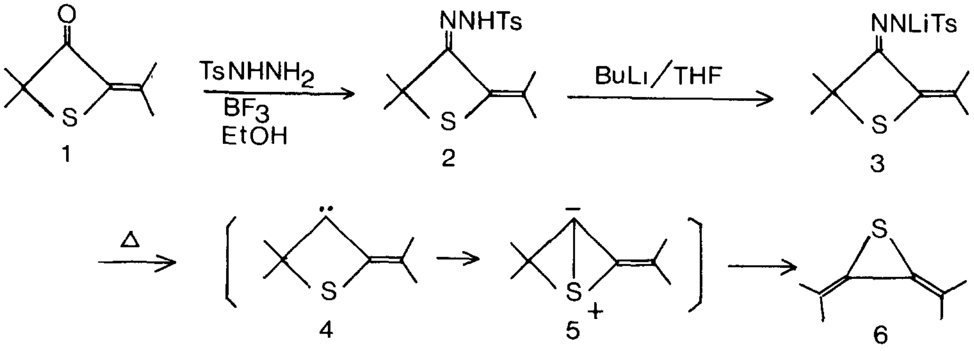
Summary: A stable tetramethylthiiranoradialene, 2,3-diisopropylidenethiirane 6, was prepared by pyrolysis of lithium salt of tosyl hydrazone of 2,2-dimethyl-4-isopropylidene-3-thietanone. The corrsponding sulfoxide 7 was also prepared by oxidation of 6.

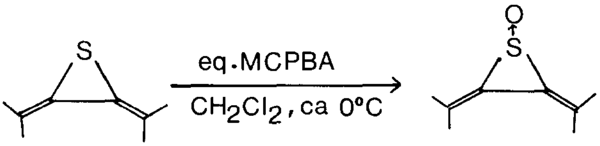
Special interest has long been focused on the syntheses of [3] ~ [6] radialenes.[1] Nature of these unique π-systems has been associated with the aromaticity as well as unusual reactivity. Although recently preparation of " furanoradialene " has been reported[2], no heteroradialene has been prepared for three-membered ring or any closely related derivatives. We present here first preparations of three-membered sulfur-radialene, " thiiranoradialene " 6, and its S-oxide 7, in connection with our carbene chemistry.[3]

2,2-Dimethyl-4-isopropylidene-3-thietanone 1, prepared by Kellogg et al.[4], was treated with excess tosyl hydrazine for a few minutes in the presence of catalytic amount of BF_3 etherate in EtOH at 50 ~ 70°C, yielding hydrazone 2.[5] The purified hydrazone 2 was treated with equimolar of BuLi at -70°C in THF under dry conditions. Removal of the solvent afforded lithium salt of the hydrazone 2 which then was subjected to the usual bulk vacuum pyrolysis at 130 ~ 160°C (at ca 10^{-4} torr). During the pyrolysis, nitrogen was



evolved and colorless crystalline solid was collected in liq. nitrogen trap. The solid purified by silica gel column chromatography (60 ~ 70% yield) showed m.p. of 42.5 ~ 43.5°C and is stable under the conditions. The spectral data of the solid: IR(cm^{-1}, $CDCl_3$), 2960_w, 2900_m, 2850_w, 1440_m, 1360_w, 1060_w; ^{1}H-NMR(δ, $CDCl_3$), 2.05(s, 6H), 1.97(s, 6H); ^{13}C-NMR(δ, $CDCl_3$), 115.5, 111.3, 23.0, 22.7; MS(70eV), m/e 140(M^+), and elemental analysis (found: C: 68.69; H: 8.66; S: 22.59, required for $C_8H_{12}S$) established unequivocally the structure of 6. The ring contraction of carbene (4) derived from the pyrolysis of lithium salt 3 may afford 6 in good yield via intermediary bicyclic sulfur ylide, 5.[2,6]

Oxidation of thiiranoradialene 6 with equimolar of MCPBA in CH_2Cl_2 at ca 0°C gave readily " thiiranoradialene S-oxide " 7 in quantitative yield. The sulfoxide 7 was colorless crystals having m.p. 58.0 ~ 58.5°C and more labile than sulfide 6, slowly decomposing to unidentified substances even at -20°C. The structure of 7 was confirmed by following spectral data: IR(cm^{-1}, $CDCl_3$) 1035(ν_{S-O}); ^{1}H-NMR(δ, $CDCl_3$), 2.22(s, 6H), 2.17(s, 6H); ^{13}C-NMR(δ, $CDCl_3$), 131.2, 125.2, 23.4, 23.0.



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