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NOVEL REACTIONS OF 1,1,4,4-TETRAARYL-1,2,3-BUTATRIENES WITH ELEMENTAL SULFUR AND SELENIUM

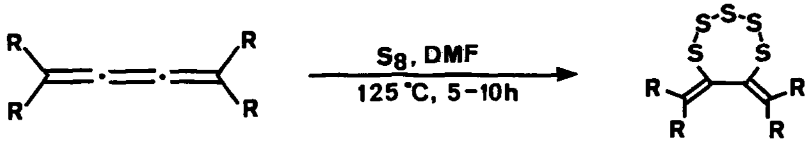
Norihiro Tokitoh, Hiroshi Hayakawa, Midori Goto†, and Wataru Ando*

Department of Chemistry, University of Tsukuba,
1-1-1, Tennohdai, Tsukuba, Ibaraki 305, Japan

†National Chemical Laboratory for Industry,
1-1, Higashi, Tsukuba, Ibaraki 305, Japan

Summary: Sulfurization and selenation reactions of 1,1,4,4-tetraaryl-1,2,3-butatrienes were examined to give novel 1,2,3,4,5-pentathiepane and 1,2,5-triselenepane ring systems. Further degradation of these new heterocycles using DBU/DMF was also described.

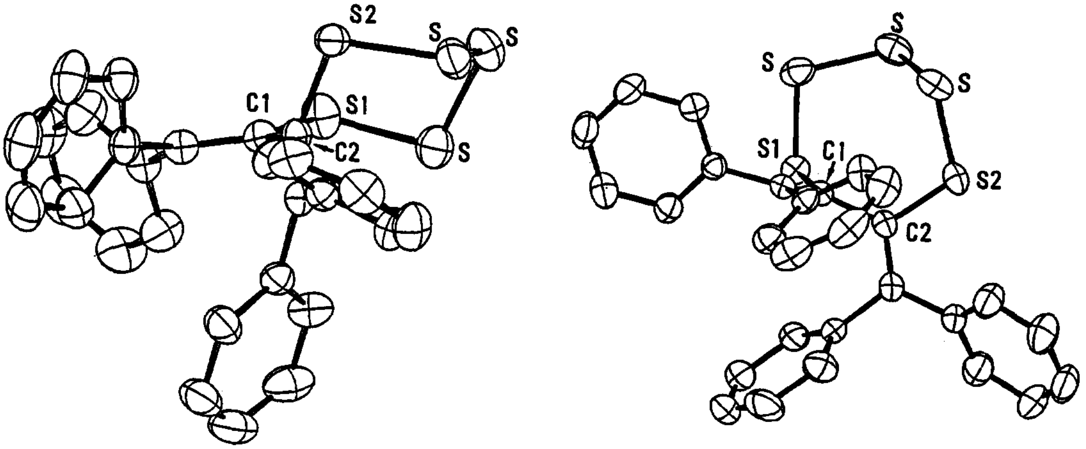
Although the synthesis of various types of 1,1,4,4-tetraaryl-1,2,3-butatrienes (**1**)1) and their fundamental reactions such as oxidation,2) hydrogenation,3) halogenation,4) metallation,5) and metal complexation6) have been extensively investigated, there have been no reports on the sulfurization of this unique cummulative system which is expected to provide a new synthetic route for the heteroatom-containing conjugated π-system. In this paper, we wish to report their direct reactions with elemental sulfur and selenium leading to a novel formation of new cyclic polysulfides and polyselenides.



1	**2**
a ; R=p-Tolyl	65 %
b ; Phenyl	87
c ; p-Chlorophenyl	56

Sulfurization of **1a-c**(1 mmol)1b) was readily performed by heating with excess of elemental sulfur(320 mg, 1.25 mmol) in 20 ml of N,N-dimethylformamide(DMF) at 125°C for several hours to give the corresponding 1,2,3,4,5-pentathiepane derivatives **2a-c**7) as yellow crystals in moderate to good yields, respectively. In contrast to the wide chemistry of 1,2,3,4,5-pentathiepins,8) only a few examples of 1,2,3,4,5-pentathiepane have been reported so far as we know.9) The structure of this new type of heterocycles(**2a-c**) was confirmed by ^{1}H-NMR, ^{13}C-NMR, UV, mass spectra, elemental analysis, and finally determined by X-ray crystal structure analysis in the case of **2b** as shown in Fig 1.10)

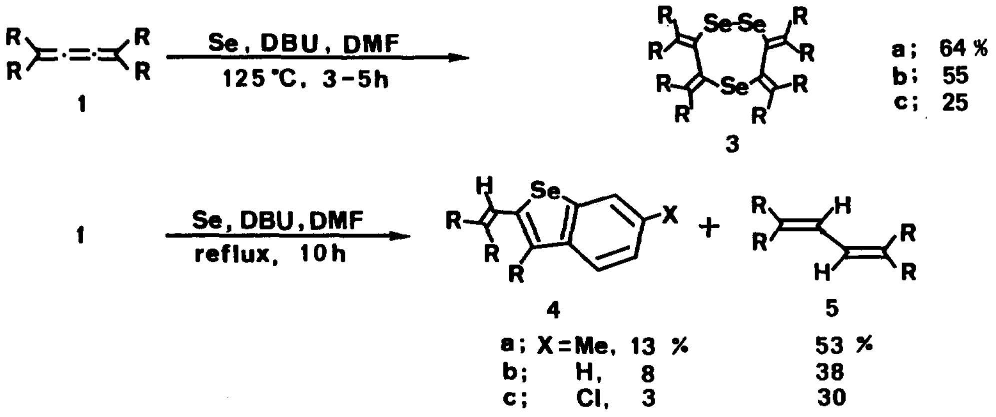
The bond lengths of C1-C2, C1-S1, and C2-S2 were 1.476, 1.790, and 1.792 Å respectively, which were longer than that of the aromatic and heteroaromatic fused pentathiepins.[8c] The bond angles of S1-C1-C2(115.4°) and S2-C2-C1(119.6°) were narrower about 10° than that of fused pentatiepins.



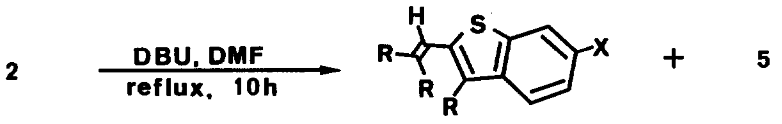
a) side view b) top view

Fig. 1 ORTEP drawing of **2b**.

Meanwhile, **1a-c** were inert to elemental selenium even in refluxing DMF for several days; however, in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene)[8d] elemental selenium dissolved in DMF at 125°C and smoothly reacted with **1a-c** to afford the 1,2,5-triselenepane derivatives (**3a-c**)[11] as a main product. When this reaction was carried out at reflux temperature, further deselenative reaction occurred to give the benzoselenophene derivatives (**4a-c**)[12] and the 1,1,4,4-tetraaryl-1,3-butadienes (**5a-c**)[13] which were independently obtained by the reactions of isolated 1,2,5-triselenepanes (**3a-c**) with DBU in refluxing DMF.



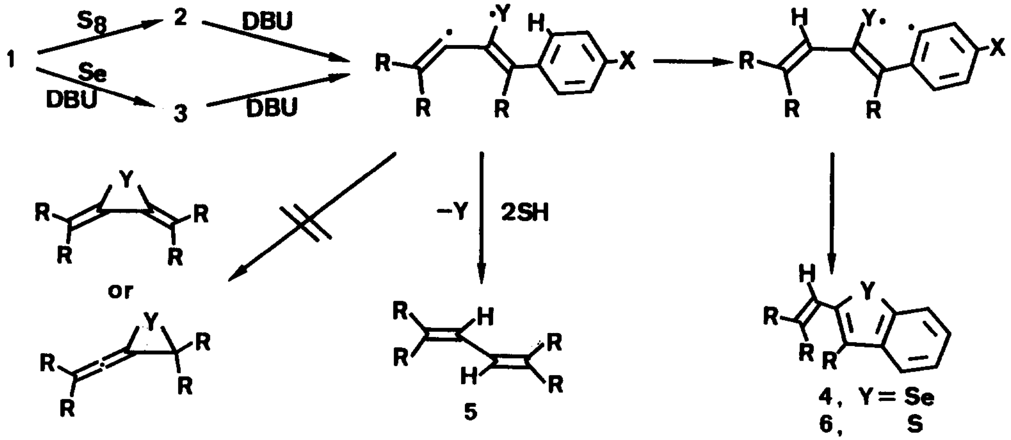
Under similar reaction conditions the pentathiepanes (**2a-c**) were also desulfurized into the corresponding benzothiophenes (**6a-c**)[14] and 1,3-butadienes (**5a-c**) respectively. The benzothiophene (**6b**) was alternatively obtained without any formation of the 1,3-butadiene (**5b**) from the flow pyrolysis of the benzene solution of **2b** at 450 °C (ca. 10%).



6

	6	5
a;	33%	40 %
b;	12	52
c;	2	32

The facile formation of the cyclic polysulfides (**2**) or cyclic polyselenides (**3**) and their subsequent degradation into benzothiophenes (**6**) or benzoselenophenes (**4**) along with the thoroughly degraded 1,3-butadienes (**5**) were successfully interpreted with an intermediacy of the radical species, though the clear role of DBU cannot be ascertained at this time and some another activated form of the polysulfides or polysenides with DBU might be involved in the early stage of these reactions. It seems that the 1,5-hydrogen shift followed by the intramolecular cyclization reaction into **4** or **6** and the extrusion of chalcogen atom resulting in a butadiene formation has the preference to the alternative formation of strained three-membered ring.[15] We thought that the ratio of the formation of 1,3-butadienes (**5**) to the cyclization products (**4** or **6**) is affected by the electronic character of the substituent on the aromatic ring which might be reflected to the relative stability and reactivity of the intermediary radical species.



In view of the ready formation of pentathiepanes (**2**) and triselenepanes (**3**) and their high reactivity leading to a novel formation of variety of substituted benzothiophenes, benzoselenophenes, and 1,3-butadienes, the above-mentioned sulfurization and selenation reactions of 1,2,3-butatrienes will provide a new field for organosulfur and organoselenium chemistry.

References and Notes

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7. **2a**: m.p. 197-9 °C, ^{1}H-NMR(CDCl$_3$, δ); 7.34-6,60(m,16H) 2.29(bs,12H), ^{13}C-NMR (CDCl$_3$, δ); 139.18(s) 138.01(s) 137.42(s x2) 129.70(d) 129.00(d) 128.47(d) 128.24(d) 21.24(q x2), UV(hexane); 246(log ε=3.30) and 370(2.90) nm, MS; m/z 572(M$^+$), E.A. Found: C, 66.98; H, 4.92; S, 27.29%, Calcd for $C_{32}H_{28}S_5$: C, 67.09; H, 4.92; S, 27.98%.
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10. Crystal data of **2b**: MW = 516.74, triclinic; space group $P\bar{1}$; Z = 2; a = 9.645(2), b = 10.389(1), c = 13.376(1) Å; α = 87.10(1), β = 76.97(4), γ = 76.44(3)° ; V = 1269.4(0.3) Å^3; D_c = 1.35 g cm^{-3}, R = 0.044 and Rw = 0.043 with w = $1/(A|F_o|^2 + B|F_o| + C)$; A = 0.00155, B = -0.05212, C = 0.8485. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.
11. **3a**: m.p. 245-7 °C; ^{1}H-NMR(CDCl$_3$, δ); 7.30-6.39(m,32H) 2.33(s,6H) 2.29(s.6H) 2.26(s,6H) 2.16(s,6H), ^{13}C-NMR(CDCl$_3$, δ); 143.11(s) 142.50(s) 140.16(s) 139.99(s) 138.99(s) 138.90(s) 137.26(s) 137.17(s) 136.87(s) 136.13(s) 135.70(s) 129.80(d) 129.72(d) 129.59(d) 129.28(d) 128.68(d) 128.37(d) 128.29(s) 127.98(d) 127.72(d) 21.32(q) 21.24(q) 21.15(q) 21.06(q), E.A., Found: C, 73.22; H, 5.50%, Calcd for $C_{64}H_{56}Se_3$: C, 72.68; H, 5.25 %.
12. **4b**: m.p. 184-6 °C, ^{1}H-NMR(CDCl$_3$, δ); 7.64-7.05(m,24H), ^{13}C-NMR(CDCl$_3$, δ); 142.24(s) 141.89(s) 141.65(s) 141.30(s) 139.43(s) 138.57(s) 136.86(s x2) 131.16(d) 130.66(d) 129.21(d) 128.59(d) 128.51(d) 128.28(d) 127.65(d) 127.50(d) 127.03(d) 125.04(d x2) 124.73(d) 123.34(d) 122.86(d), MS; m/z 436(M$^+$), E.A., Found: C, 77.36; H, 4.53%, Calcd for $C_{28}H_{24}Se$: C, 77.23; H, 4.26%.
13. **5a**: m.p. 255-6 °C, ^{1}H-NMR(CDCl$_3$, δ); 7.28-6.99(m,16H) 6.73(s,2H) 2.39(s,6H) 2.30(s,6H), ^{13}C-NMR(CDCl$_3$, δ); 143.33(s) 140.17(s) 137.21(s) 137.01(s x2) 130.66(d) 128.86(d) 128.78(d) 127,73(d) 125.51(d) 21.33(q) 21.09(q), MS; m/z 414(M$^+$), E.A. Found: C, 92.53; H, 7.26%, Calcd for $C_{32}H_{30}$: C, 92.71; H, 7.29%: a) D.Elmaleh, S. Patai, and Z. Rappoprt, *J. Chem. Soc.*, *(c)*, 3100(1971), b) B. Sket and M. Zupan, *Synth. Commun.*, *6*, 309(1976), c), W. Tadros, *J. Chem. Soc.*, 2966(1954).
14. **6a**: m.p. 217-9 °C, ^{1}H-NMR(CDCl$_3$, δ); 7.44-6.95(m,16H) 2.46(s,3H) 2.42(s,3H) 2.35(s,3H) 2.28(s,3H), ^{13}C-NMR(CDCl$_3$, δ); 141.75(s) 140.06(s) 139.76(s) 137.95(s) 137.54(s) 137.25(s) 136.84(s) 136.25(s) 136.14(s) 134.62(s) 130.81(d) 130.52(d) 129.53(d) 129.17(d) 128.82(d) 127.19(d) 125.66(d) 122.45(d) 122.45(d) 121.69(d) 120.05(d) 21.47(q) 21.30(q x2) 21.06(q), UV(hexane); 236(log ε=4.41), 248(4.38) and 350(4.49) nm, MS; m/z 444(M$^+$), E.A., Found: C, 86.45; H, 6.36%, Calcd for $C_{32}H_{28}S$: C, 86.44; H, 6.34%.
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