SULFURIZATION OF 1,4,7,10-TETRAARYLCYCLODODECA-1,2,3,7,8,9-HEXAENES

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Summary; Thermal reactions of 1,4,7,10-tetraarylcyclododeca-1,2,3,7,8,9-hexaenes 1a and 1b with elemental sulfur were examined, and found to give novel transannular bridged pentasulfides 2a and 2b, while cyclopentenethiones 3a and 3b were obtained by the sulfurization of 1a and 1b in the presence of 1,8-diazabicyclo-[5.4.0]undec-7-ene.

Apart from the industrial process of rubber vulcanization,³ one can see a number of sulfurization reactions of some reactive olefins using a variety of allotropes of sulfur resulting in facile formation of interesting cyclic polysulfides.⁴ We have also described thermal sulfurization of 1,2,3-butatrienes with elemental sulfur, and found that 1,1,4,4-tetraaryl-substituted ones gave 6,7-bis(alkylidene)-1,2,3,4,5-pentathiepans selectively ⁵ while 1,1-di-*t*-butyl-4,4-diphenyl-1,2,3-butatriene afforded an interesting bicyclic polysulfide, 1,2-dithiolo-1,2-dithiole derivative.⁶



Here, we have extended the study on sulfurization of cummulenic carbon-carbon double bond to cyclic biscummulenes leading to a novel transannular bridging reaction. When 1,4,7,10-tetraphenylcyclododeca-1,2,3,7,8,9-hexaene⁷ (1a; Ar = Ph, 460 mg, 1 mmol) was treated with an excess amount of sulfur (320 mg, 10 mmol as S₈) in 20 ml of DMF at 120 - 130 °C for 10 h, a new type of cyclic polysulfide 2a (150 mg, 24%) was obtained in a pale yellow crystalline form after the separation of excess sulfur followed by exhaustive chromatographic purification (HPLC and TLC). Sulfurization of cyclododecahexaene 1b⁸ (Ar = p-tolyl) also readily underwent to give a similar bridged cyclopolysulfide 2b in 24% yield.



The structures of these newly obtained cyclic polysulfides 2a and 2b were satisfactorily confirmed by ¹H-NMR, ¹³C-NMR, and mass spectroscopic data together with elemental analysis.⁹ Final molecular structure of 2a was determined by X-ray crystallographic analysis as shown in Figure 1(a),¹⁰ in which the cyclooctatriene ring was fixed in a *quasi*-boat form.

On the other hand, the sulfurization of hexaenes 1a and 1b in the presence of an equimolar amount of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in DMF at 120 °C resulted in the formation of quite different products, *i.e.* cyclopentenethione derivatives 3a and 3b in 22 and 27% yields, respectively.¹¹



The characteristic electronic spectra and low field ¹³C-NMR signals of 3a [$\lambda_{max} = 599$ nm, $\delta = 248.05$ ppm] and 3b [$\lambda_{max} = 579$ nm, $\delta = 248.65$ ppm] are considered to be associated with their conjugated thiocarbonyl unit. The final structure of 3b was also determined by X-ray crystallographic analysis as shown in Figure 1(b).¹⁰



Figure 1. Molecular structure of sulfurization products of cyclododecahexaenes 1; (a) ORTEP drawing of pentasulfide 2a and (b) ORTEP drawing of cyclopentenethione 3b

The formation mechanism of 2 from 1 can be rationalized by the initial attack of the activated sulfur radical to the cummulenic sp carbon of 1 followed by transannular bridging of the resulting radical reaction centers to another cummulenic unit as illustrated in Scheme I. Subsequent dehydorgenation by the excess sulfur radicals might result in the final armatization step leading to the new benzene ring formation. Meanwhile, the cyclopentenethione formation from 1 by S_g/DBU seems to include some ionic sulfur species as shown below. It is also worthy of note that the treatment of once isolated pentasulfide 2b with DBU under similar reaction conditions did



not afford any thiocarbonyl compound but an unusual fused dithiolane 4b¹² was isolated in 62% yield.

In addition, the pyrolysis of the newly obtained bridged pntasulfide 2a at 450 °C under N₂ flow was found to give a novel 1,4,5,8-tetraphenylbiphenylene 5a in 31% yield.¹⁴



Since there have been no reports on the functionalization of the hexaene 1a except for its complexation with metal carbonyls,¹⁴ the novel sulfurization reaction of 1a and 1b thus described is of great interest from a viewpoint of showing a new reactivity and potential synthetic utility of this unique cyclic biscummulene skeleton.

References and Notes

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- 8. 1b was prepared as yellow crystals (mp. 240-242 °C) from 4'-methylacetophenone by an analogous method for 1a.
- 9. 2a; pale yellow crystals, mp. 240-242 °C; ¹H-NMR(CDCl₃) δ 2.67(dd, J = 16 Hz, 2H), 3.16(dd, J = 16 Hz, 2H), 7.21-7.63(m, 22H); ¹³C-NMR(CDCl₃) δ 33.89(t), 127.73(d), 127.89(d), 128.14(d), 128.44(d), 128.59(d), 128.81(d), 130.59(d), 133.45(s), 136.05(s), 138.67(s), 141.07(s), 141.08(s), 141.20(s); MS, m/z 618(M⁺, 48%), 554(26), 522(100), 490(87), 458(22); E. A., found C; 69.67, H; 4.22, S; 25.56%, calcd for C₃₆H₂₆S₅, C; 69.86, H; 4.23, S; 25.90%. 2b; pale yellow crystals, mp. 255-257 °C; ¹H-NMR(CDCl₃) δ 2.36(s, 6H), 2.40(s, 6H), 2.62(dd, J = 15 Hz, 2H), 3.12(dd, J = 15 Hz, 2H), 7.09-7.53(m, 18H); ¹³C-NMR(CDCl₃) δ 21.28(q), 21.36(q), 33.90(t), 128.27(d), 128.71(d), 128.82(d), 129.24(d), 130.49(d), 133.14(s), 136.02(s), 137.33(s), 137.60(s), 138.24(s), 138.27(s), 138.39(s), 140.92(s); MS, m/z 674(M⁺, 12%), 610(4), 578(56), 546(100), 514(8); E. A., found C; 70.39, H; 5.06, S; 23.42%, calcd for C₄₀H₃₄S₅, C; 70.22, H; 5.05, S; 23.74%.
- 10.Crystal and experimental data for 2a; C₃₆H₂₆S₅, MW 618.9, triclinic, space group PI, a = 9.551(4), b = 111.678(5), c = 15.630(5) Å, β = 77.62(3) *, V = 1557(1) Å³, Dc = 1.32 g/cm³, μ(Mo-Kα) 5.97 cm⁻¹, z = 2, R = 0.057 (R_w = 0.059). 3b; C₄₀H₃₄S, MW 546.78, triclinic, space group PI, a = 10.013(1), b = 16.696 (1), c = 9.300(1) Å, β = 98.94(1) *, V = 1513.2 Å³, Dc = 1.20 g/cm³, μ(Mo-Kα) = 1.30 cm⁻¹, z = 2, R = 0.054 (R_w = 0.057). Data collection was performed by CAD4 (Enraf-Nonius) diffractometer with graphite-monochromated Mo-Kα radiation. The structure was solved by MULTAN 78 using 3912 reflections for 2a and 1971 reflections for 3b, and the program system SDP-package and UNICS III was used for calculation. As for 2a, 21 H atoms were found in D-fourier method and 5 H atoms were located by calculation. Refinement: full matrix least squares (Anisotropic thermal parameters for the non-hydrogen atoms, isotropic ones for the hydrogen atoms). Atomic co-ordiantes, bond lengths and angles, and thermal parameters for 2a and 3b have been deposited at Cambridge X-ray Crystallographic Data Centre.
- 11. 3a; green oil; ¹H-NMR(CDCl₃) δ 2.28(m, 1H), 2.61(m, 2H), 3.36(m, 1H), 6.82-7.79(m, 22H); ¹³C-NMR (CDCl₃) δ 37.05(t), 40.18(t), 86.53(s), 126.33(d), 126.78(d), 127.04(d), 127.07(d), 127.12(d), 127.35(d), 128.11(d), 128.13(d), 128.15(d), 128.23(d), 128.64(d), 128.87(d), 132.32(d), 134.52(s), 134.61(s), 137.07(s), 137.54(s), 139.60(s), 140.06(s), 140.35(s), 140.61(s), 141.51(s), 147.24(s), 248.05(s);MS, m/z 490(M⁺, 100%); HRMS, m/z 490.1755 calcd for C₃₆H₂₆S 490.1755; UV(CH₂Cl₂) λ_{max} 599(ε =44), 399 (2700) nm. 3b; blue crystals, mp. 254-256 °C; ¹H-NMR(CDCl₃) δ 2.17(s,3H), 2.20(s, 3H), 2.26(m, 1H), 2.34(s, 3H), 2.39(s, 3H), 2.57(m, 2H), 3.33(m, 1H), 6.31-7.66(m, 18H); ¹³C-NMR(CDCl₃) δ = 20.86(q), 21.03(q), 21.07(q), 21.36(q), 36.93(t), 40.03(t), 86.07(s), 126.19(d), 126.25(d), 127.52(d), 128.12(d), 128.65(d), 128.77(d), 128.83(d), 128.97(d), 129.30(d), 132.23(d), 134.22(s), 134.28(s), 134.96(s), 136.16(s), 136.65(s), 136.75(s), 137.03(s), 137.08(s), 137.23(s), 138.58(s), 139.66(s), 140.12(s), 140.43(s), 147.33(s), 248.65(s); MS, m/z 546(M⁺, 100%); HRMS, m/z 546,2360 calcd for C₄₀H₃₄S 546.2380; UV(CH₂Cl₂) λ_{max} 579(ε =51), 389(730) nm.
- 12. The formation mechanism of 4b has not been certainly elucidated. The structure of 4b was determined by the X-ray crystallographic analysis, the details of which have also been deposited at Cambridge X-ray Crystallographic Data Centre, along with satisfactory spectroscopic data.
- 5a; colorless crystals, mp.>300 °C; ¹H-NMR(CDCl₃) δ 6.86-7.10(m, 24H); ¹³C-NMR(CDCl₃) δ 126.92(d), 127.43(d), 127.45(d), 129.82(d), 131.35(s), 137.73(s), 148.09(s); MS, m/z 456(M⁺, 100%); HRMS, m/z 456.1867 calcd for C₃₆H₂₄ 456.1877.
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