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# A NOVEL FORMATION AND PHOTOCHEMICAL REACTION OF 3,3-DI-t-BUTYL-3',3'-DIPHENYL[1,2]DITHIOLO[5,4-d][1,2]DITHIOLE

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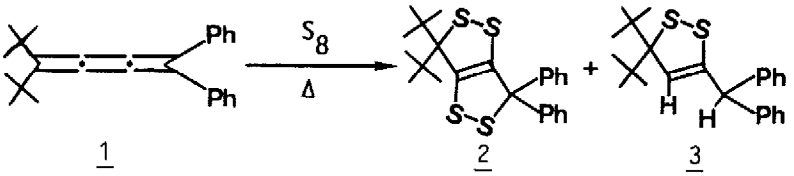
**Summary**: Sulfurization of 1,1-di-t-butyl-3,3-diphenyl-1,2,3-butatriene **1** with elemental sulfur afforded a novel fused 1,2-dithiole **2**, the photolysis of which resulted in a facile formation of isomerized 1,3-dithiole **4** and alkylidenethietanethione **5**.

The 1,2-dithiole system and related compounds possessing two adjacent sulfur atom in a five-membered ring are of great interest from both structural and biological aspects.[1a-n] 1,6,6a$\lambda^4$-Trithiapentalene, one of the interesting tetravalent sulfur compounds, is easily obtained by the reaction of 1,2-dithiole-3-thiones with sulfur and alkyne,[1m] while lipoic acid is known as a growth factor and an essential component of enzyme systems involved in oxidative decarboxylation of pyruvic and related acids.[1n] Furthermore, many 1,2-dithioles and 1,2-dithiolylium ions, especially highly conjugated derivatives, undergo charge transfer with electron acceptors or donors respectively to form derivatives with ranges of conductivity.[1l]

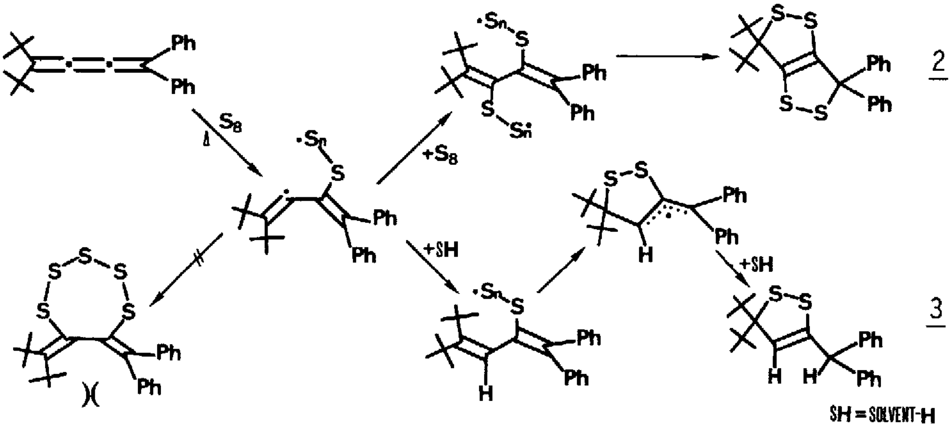
However, few examples are known for simple and stable 1,2-dithiole ring systems without exocyclic conjugated double bond.[2] 1,2-Dithiolo-1,2-dithiole ring system, which is a uniquely fused case of 1,2-dithiole derivative, has never been reported so far as we know. Here, we present a novel formation of the new type of fused 1,2-dithiole **2** by the sulfurization of 1,1-di-t-butyl-3,3-diphenyl-1,2,3-butatriene **1**[3] with elemental sulfur and also delineate the characteristic photochemical reaction of **2**.

Heating of the butatriene (**1**; 1.58 g, 5.0 mmol) in an excess amount of molten sulfur (1.60 g, 6.3 mmol as $S_8$) at 130 °C for 19 h afforded 3,3-di-t-butyl-3',3'-diphenyl[1,2]dithiolo[5,4-d][1,2]dithiole (**2**; 1.10 g, 48%)[4] as an orange yellow crystalline product (mp. 144-145 °C). The structure of **2** was confirmed by the molecular symmetricity reflected in its $^1$H- and $^{13}$C-NMR spectra and the two distinguishable absorption maxima in the electronic spectra which are assigned to the transitions of each 1,2-dithiole ring systems. Molecular composition of **2** was satisfactorily determined by MS spectra and elemental analysis. Although the sulfurization of **1** with $S_8$ also proceeded at similar reaction temperature in some organic solvents such as diphenyl ether or N,N-dimethylformamide(DMF), the yield of 2 was found to be somewhat diminished. In the case of DMF another 1,2-dithiole derivative 3,[5] which might be a hydrogen abstraction product of the intermediary radical species from the solvent, was obtained as a major product(52%) along with 19% of 2.

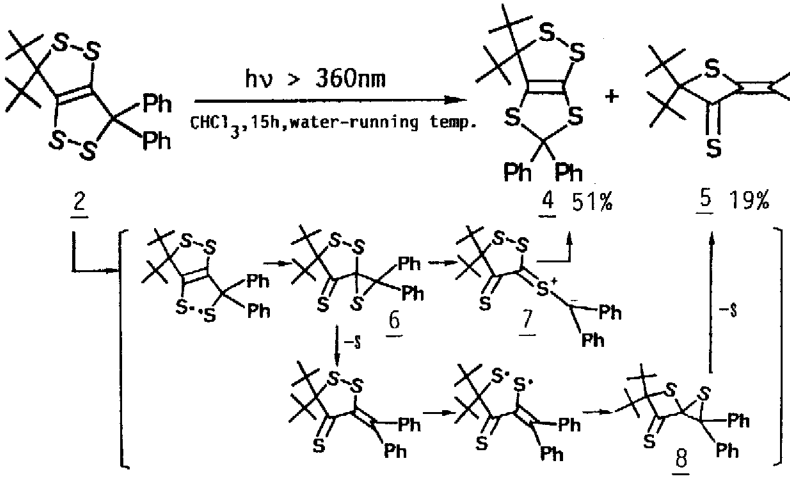


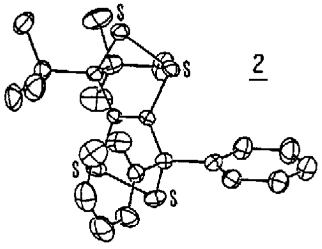
| Entry | Solvent | Conditions | 2 | 3 |
|---|---|---|---|---|
| 1 | DMF | 135°C,18h | 19% | 52% |
| 2 | Ph$_2$O | 135 ,20 | 35 | — |
| 3 | none | 120 ,19 | 48 | — |

The unusual formation of 2 and 3 and the absence of any other sulfurization products in the reaction of 1 with elemental sulfur, which is in striking contrast to our recent report on the direct sulfurization of 1,1,4,4-tetraaryl-1,2,3-butatrienes leading to a novel formation of 6,7-bisalkylidene-1,2,3,4,5-pentathiepanes,[6] is attributable to the large repulsive steric hindrance between the bulky t-butyl group and phenyl group to construct the cyclopolysulfide skeleton.

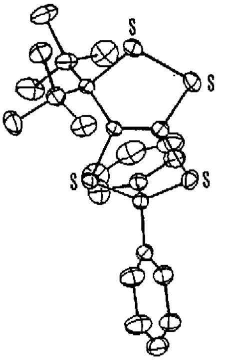


Of particular note among the reactions of the newly obtained fused 1,2-dithiole 2 is the photochemical transformation into 1,3-dithiole 4[7] and thietanethione 5.[8] When the chloroform solution of 2 was irradiated by high pressure mercury lamp through a phenanthlene filter solution (hν λ>360 nm) for 15 h, 4 and 5 were isolated as stable products in 51 and 19% yields, respectively. 2 was also photolyzed with light of λ= 254 nm to give 4(54%) and 5(11%). Since it is hard to discriminate between 4 and 2 spectroscopically, they were subjected to X-ray crystallographical analysis[9] to reveal their final molecular structure as shown below.





2



4

The mechanism of this unique ring transformation is tentatively rationalized by assuming 1,2-dithione S-ylide **7** derived from initially formed spirothiirane intermediate **6**. Formation of **5** is also interpreted with the sequential desulfurization and S-S bond cleavage of the common intermediate **6** followed by redesulfurization of the resulting spirothietanethione **8**. When the photolysis of **2** was performed with light of λ= 254 nm in 3-methylpentane glass matrix at 77 K and monitored by electronic spectroscopy, an absorption maximum at 468 nm was observed and it has disappeared with annealing the matrix sample. The mutability of this new absorption and its disagreement with the absorption maximum of **5** implies an intermediacy of some unstable thiocarbonyl species such as **6** and/or **7**. Another 1,2-dithiole ring of **2**, i.e. t-butyl substituted one, is reluctant to isomerize into 1,3-dithiole system. No photolyzed product but a quantitative recovery of substrate was obtained by the exhaustive irradiation of **4** with light of λ= 254 or λ>300 nm. Since **4** has an adequate chromophore for the photochemical S-S bond cleavage, the above recovery of **4** is probably due to the rapid recombination of once generated diradical intermediate.

In view of the characteristic structure and the promising reactivities of the newly obtained fused 1,2-dithioles, the sulfurization of 1,2,3-butatrienes thus described would provide a new field for organosulfur chemistry.

## References and Notes

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3. **1**; white crystals, mp. 88-90 °C; $^{1}$H-NMR(CDCl$_3$) δ 1.33(s,18H), 7.26-7.55(m,10H); $^{13}$C-NMR(CDCl$_3$) δ 32.18(q), 39.26(s), 117.42(s), 127.13(d), 128.12(d), 128.82(d), 139.41(s), 143.10(s), 152.40(s), 160.92(s); IR(KBr), 1995 cm$^{-1}$; MS, m/z 316(M$^{+}$); E. A., Found C; 91.08, H; 8.91%, Calcd for $C_{24}H_{28}$, C; 90.87, H; 8.98%.
4. **2**; mp. 144-145 °C; $^{1}$H-NMR(CDCl$_3$) δ 1.39(s,18H), 7.30-7.70(m,10H); $^{13}$C-NMR(CDCl$_3$) δ 30.85(q), 45.66(s), 73.23(s), 89.95(s), 127.90(d), 128.24(d), 129.54(d), 130.00(s), 139.64(s), 142.98(s); MS, m/z 444(M$^{+}$); E. A., Found C; 64.81, H; 6.34, S; 28.83%, Calcd for $C_{24}H_{28}S_4$, C; 64.67, H; 6.46, S; 28.25%; UV(hexane) $\lambda_{max}$ 305(ε3200), 375(ε2740).
5. **3**; pale yellow crystals, mp. 128-129 °C; $^{1}$H-NMR(CDCl$_3$) δ 1.15(s,18H), 5.13(brs,1H), 5.22(brs,1H), 7.26(s, 10H); $^{13}$C-NMR(CDCl$_3$) δ 30.03(q), 44.36(s), 53.51(d), 92.96(s), 126.26(d), 126.95(d), 128.38(d), 128.86(d), 141.82(s), 143.73(s); MS, m/z 382(M$^{+}$); E. A., Found C; 75.33, H; 7.90, S; 16.70%, Calcd for $C_{24}H_{30}S_2$, C; 74.99, H; 7.92, S; 16.90%.
6. N. Tokitoh, H. Hayakawa, M. Goto, and W. Ando, Tetrahedron Lett., **29**, 1935 (1988).
7. **4**; yellow crystals, mp. 142-143 °C; $^{1}$H-NMR(CDCl$_3$) δ 1.18(s,18H), 7.17-7.25(m,10H); $^{13}$C-NMR(CDCl$_3$) δ 30.35(q), 45.29(s), 87.64(s), 91.48(s), 128.02(d), 128.06(d), 128.07(d), 128.66(s), 129.76(s), 145.75(s); MS, m/z 444(M$^{+}$,<1%), 387(M$^{+}$-57,100); E. A., Found C; 64.87, H, 6.38; S, 28.67%, Calcd for $C_{24}H_{28}S_4$, C; 64.82, H; 6.35, S; 28.84%, UV(hexane), $\lambda_{max}$ 300 nm (ε 3180).
8. **5**; reddish brown oil, $^{1}$H-NMR(CDCl$_3$) δ 1.33(s,18H), 7.12-7.47(m,10H); $^{13}$C-NMR(CDCl$_3$) δ 30.55(q), 41.04(s), 94.81(s), 128.07(d), 128.48(d), 128.68(d), 128.82(d), 129.24(d), 129.78(d), 134.51(s), 139.16(s), 140.12(s), 142.71(s), 237.85(s); MS, m/z 380(M$^{+}$, 47%), 323(100), 308(85); HRMS, m/z found 380.1626, calcd for $C_{24}H_{28}S_2$ 380.1631; UV (hexane), $\lambda_{max}$ 455 nm (ε 1930).
9. Crystal data,**2**; $C_{24}H_{28}S_4$, MW 444.75, monoclinic, space group $P2_1/c$, a=11.909(3), b=14.755(1), c=13.998(2) Å, β=111.27(3)° , V=2292.2(1) Å$^3$, $D_c$=1.28 g cm$^{-3}$, μ(Mo-K$_\alpha$)=3.0 cm$^{-1}$, z=4, R=0.049; **4**; $C_{24}H_{28}S_4$, MW 444.75, monoclinic, space group $P2_1/c$, a=9.179(1), b=17.027(2), c=14.967(2) Å, β=97.14(1)° , V=2321(1) Å$^3$, $D_c$=1.28 g cm$^{-3}$, μ(Mo-K$_\alpha$)=3.0 cm$^{-1}$, z=4, R=0.044. Data collection was performed by Rigaku four-circle diffractometer (AFC4) with graphite-monochromated Mo-K$_\alpha$radiation (μ=0.71069 Å). Their structures were solved by direct methods using MULTAN 78, and the program system UNICS III was used for calculations. Details of the X-ray crystallographical analysis of these novel 1,2-dithioles will be described elsewhere.

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