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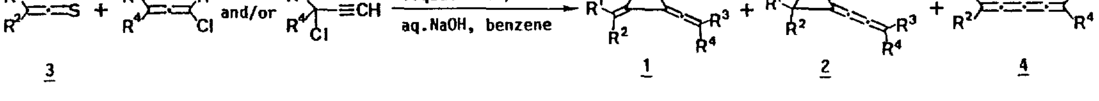
A FACILE SYNTHESIS AND NOVEL REACTIONS OF 1, 2, 3, 4 - PENTATETRAENE EPISULFIDES

Norihiro Tokitoh, Tomoko Suzuki, and Wataru Ando*
Department of Chemistry, University of Tsukuba,
1-1-1 Tennohdai, Tsukuba, Ibaraki 305, JAPAN

Summary: Various types of 1,2,3,4-pentatetraenes 4 and 1,2,3,4-pentatetraene episulfides (1 and 2) were synthesized readily and selectively by the alkenylidene carbene addition to thioketene. Thermal , photochemical , and acid-promoted reactions of 1 and 2 resulted in a formation of novel conjugated thiones 5 and 6.

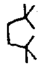
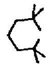
In contrast to the wide chemistry of allene episulfides,[1] which have attracted much attention from a viewpoint of characteristic tautomerizm via thioxyallyl intermediate, there have been few examples of their methylene homologues because of a scarcity of good synthetic methods.[2] In our continuous work on strained episulfides, we have recently reported some interesting isomerization of allene episulfide via thioxyallyl intermediate and also described the relative stability between the regioisomeric tautmers in the reactions of 1,2,3-butatriene episulfides.[3] However, we cannot neglect the sterically repulsive influence of the bulky substituents on these labile systems and their intrinsic reactivity has not been fully investigated.

We now delineate (i) a new and convenient method for the synthesis of novel 1,2,3,4-pentatetraene episulfides 1 and 2 by an alkenylidene carbene addition to thioketene, which can be useful in turn as a route to 1,2,3,4-pentatetraenens 4, (ii) an unusual sulfur transfer reaction by the thermolysis and photolysis of 1 and 2 leading to a novel formation of alkenylidenethietanethiones via thioxyallyl-type diradical intermediate, and (iii) a characteristic acid promoted rearrangement of 1 and 2 into stable cyclobutanethione skeleton.

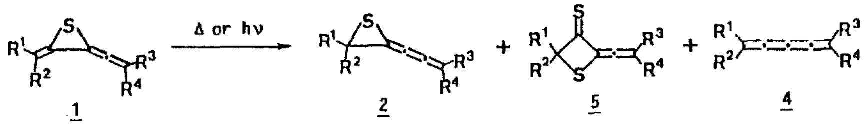


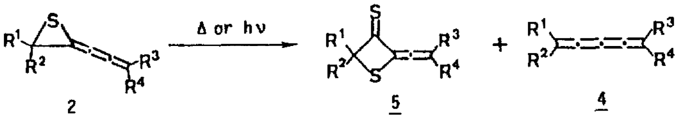
When thioketenes 3a-d (1.5 mmol) were treated with several kinds of haloallenes (0.5 mmol) under phase transfer reaction conditions (5 ml of 50% aq. NaOH + 2 ml of benzene) using methyltrioctylammonium chloride (aliquat 336) as a catalyst (ca. 10 mol%), the corresponding 1,2,3,4-pentatetraene 2-episulfides 1a-d were obtained in moderate yields based on the carbene sources along with a small amount of desulfurized 1,2,3,4-pentatetraenes 4a-d. **(Method A)** Using an excess ammount of carbene sources (3eq. to thioketene) resulted in an almost exclusive formation of 4a-d in good yields. **(Method B)** Products and yields of each reactions are listed in Table 1.[4] In the case of 3d, isomerized 1-episulfide 2d was formed together with 1d and 4d. Method B is of particular note as a useful synthetic method for a variety of substituted 1,2,3,4-pentatetraenes, which are difficult to construct by the common carbene coupling reactions.

Table 1. Alkenylidene Carbene Addition to Thioketenes

	Thioketenes(3)	Carbene Sources	Methods	Products and Yields (%)		
a	$R^1=R^2=t\text{-Bu}$	$R^3=R^4=t\text{-Bu}$	A	1a (53)		4a (17)
			B	(14)		(72)
b	$R^1=R^2=t\text{-Bu}$	$R^3,R^4=$ 	A	1b (33)		4b (21)
			B	(--)		(61)
c	$R^1=R^2=t\text{-Bu}$	$R^3=t\text{-Bu},\ R^4=Me$	A	1c (39)		4c (9)
			B	(--)		(82)
d	$R^1,R^2=$ 	$R^3=R^4=t\text{-Bu}$	A	1d (8)	2d (26)	4d (6)
			B	(--)	(--)	(58)

Tetraene episulfides 1 were isolated as stable crystalline products, however, they readily underwent a thermal C-S bond cleavage in refluxing benzene to give the corresponding 2-alkenylidenethietane-3-thiones 5 in addition to the isomerized 1-episulfides 2 and desulfurized tetraenes 4. Once isolated 1-episulfide 2a was also converted into 5a and 4a slowly in refluxing benzene.[5]





a : $R^1=R^2=R^3=R^4=t\text{-Bu}$

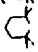
d : $R^1,R^2=$  $,R^3=R^4=t\text{-Bu}$

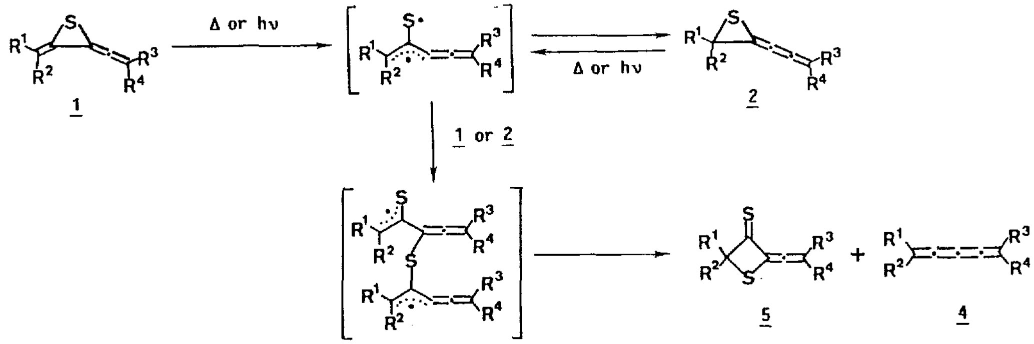
Table 2. Thermolysis and Photolysis of Tetraene Episulfides 1 and 2

Substrates	Reaction Conditions[a]	Products and Yields (%)		
		1-Episulfide(2)	Thietanethione(5)	Tetraene(4)
1a ($R^1=R^2=R^3=R^4=t\text{-Bu}$)	Δ / 4.5 h	2a (28)	5a (16)	4a (50)
1a	hν / 16 h	--	5a (6)	4a (54)
1d ($R^1,R^2=$  $,R^3=R^4=t\text{-Bu}$)	Δ / 10 h	2d (20)	5d (14)	4d (59)
2a ($R^1=R^2=R^3=R^4=t\text{-Bu}$)	hν / 26 h	--	5a (13)	4a (69)
2a	hν / 4 h	--	5a (20)	4a (62)
2d ($R^1,R^2=$  $,R^3=R^4=t\text{-Bu}$)	Δ / 48 h	--	5d (18)	4d (66)
2d	hν / 26 h	--	5d (9)	4d (56)

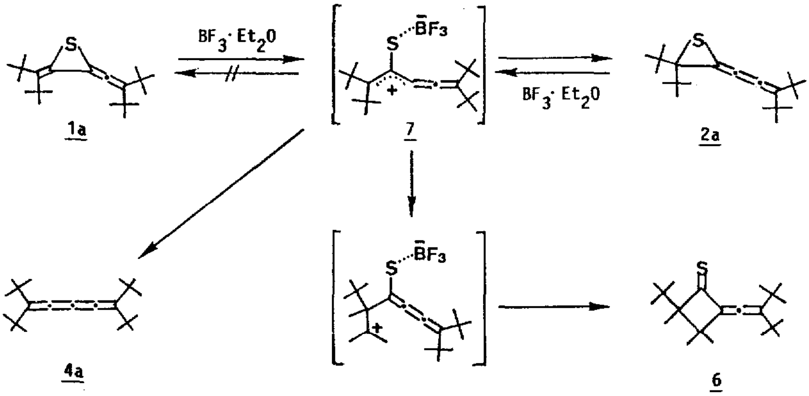
a) Δ : 80°C / benzene ; hν : λ > 300 nm / chloroform

Meanwhile, similar formation of thietanethiones 5 was attained by the irradiation of 1 and 2 with light of λ > 300 nm in chloroform at room temperature. The results obtained from the thermolysis and photolysis of 1a , 1d , 2a , and 2d are listed in Table 2.

The formation of 5 from 1 or 2 might be rationalized by the intermolecular sulfur transfer reaction mechanism with the intermediacy of thioxyallyl-type diradical species as shown in the following scheme, since no improvement of the yield of 5 was achieved by the addition of excess amount of elemental sulfur in both thermolysis and photolysis of 1a and 2a. However, one cannot abandon the possible effectiveness of once extruded nascent sulfur atom as a sulfur source. The lack of any dimerization products of thioxyallyl intermediates suggest the large steric repulsion of the bulky substituents in these systems, which allows only a sulfur transfer reaction.



On the other hand, treatment of 1a with an equimolar amount of $BF_3 \cdot Et_2O$ in dichloromethane resulted in a formation of 2-alkenylidenecyclobutanethione 6 (6%) as stable purple crystals together with the isomerized episulfide 2a (23%) and tetraene 4a (10%). Similarly, 1-episulfide 2a was converted into 6 (14%) and 4a (13%) by the action of $BF_3 \cdot Et_2O$.[6] The formation of 6 is consistently interpreted with the initial generation of the thioxyallyl cation intermediate 7 followed by the well-known methyl group rearrangement in the reacitons of di-t-butyl substituted allyl cation system.[7]



In view of a novel formation of various types of conjugated cyclic thiones, the reactions of 1,2,3,4-pentatetraene episulfides thus described will provide a new field for organosulfur chemistry.

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References and Notes

1. a) W. J. Middleton, *J. Org. Chem.*, **34**, 3201 (1969); b) A. G. Hortmann and A. Bhattacharijya, *J. Am. Chem. Soc.*, **98**, 7081 (1976); c) E. Block, R. E. Penn, M. D. Ennis, T. A. Owens, and S. -L. Yu, *ibid.*, **100**, 7436 (1978); d) E. Schaumann, *Tetrahedron*, **44**, 1827 (1988); e) W. Ando, Y. Hanyu, T. Furuhata, and T. Takata, *J. Am. Chem. Soc.*, **105**, 6151 (1983); f) W. Ando, T. Furuhata, Y. Hanyu, and T. Takata, *Tetrahedron Lett.*, **25**, 4011 (1984).
2. a) W. Ando, Y. Hanyu, and T. Takata, *Tetrahedron Lett.*, 22, 4815 (1981); b) W. Ando, Y. Hanyu, Y. Kumamoto, and T. Takata, *Tetrahedron*, **42**, 1989 (1986).
3. a) W. Ando, A. Itami, T. Furuhata, and N. Tokitoh, *Tetrahedron Lett.*, **28**, 1787 (1987); b) N. Tokitoh, N. Choi, and W. Ando, *Chem. Lett.*, **1987**, 2177; c) W. Ando, H. Hayakawa, and N. Tokitoh, *Tetrahedron Lett.*, **28**, 1803 (1987); d) N. Tokitoh, H. Hayakawa, and W. Ando, *ibid.*, **29**, 5161 (1988).
4. All the products described here gave satisfactory spectral data, and the data of **1a** and **4a** are shown as the representative as follows: **1a**; white crystals, mp. 106-107.5 °C; ^{1}H-NMR(CDCl$_3$) δ 1.40 (s, 9H), 1.27 (s, 9H), 1.24 (s, 18H); ^{13}C-NMR(CDCl$_3$) δ 31.42(q), 31.83(q), 32.35(q), 37.68(s), 38.49(s), 40.13 (s), 86.99(s), 110.63(s), 137.31(s), 138.42(s), 185.63(s); MS, m/z 320 (M$^+$); IR (KBr) 1975, 2050 cm^{-1}; UV(hexane) λ_{max} 231 (log ε = 4.67), 244 (sh, 4.46), 255 (sh, 4.26), 280 (3.78); E. A., Found C; 78.55, H; 11.61%, calcd for $C_{21}H_{36}S$ C; 78.68, H; 11.32%; **4a**; white crystals, mp. 97-98 °C; ^{1}H-NMR(CDCl$_3$) δ 1.25 (s, 36H); ^{13}C-NMR(CDCl$_3$) δ 32.06(q), 37.32(s), 123.62(s), 128.65(s), 171.24(s); MS, m/z 288(M$^+$), IR(KBr) 2060 cm^{-1}; UV(hexane) λ_{max} 232 (log ε = 4.98), 256 (4.46); E. A., Found C; 87.46, H; 12.75%, calcd for $C_{21}H_{36}$C; 87.42, H; 12.57%.
5. **5a**; dark red crystals, mp. 150-152 °C; ^{1}H-NMR(CDCl$_3$) δ 1.23 (s, 18H), 1.32 (s, 18H); ^{13}C-NMR (CDCl$_3$) δ 30.51(q), 31.84(q), 37.99(s), 41.14(s), 96.90(s), 117.55(s), 136.31(s), 198.90(s), 242.92(s); MS, m/z 352(M$^+$, 19%), 57(100); IR(CCl$_4$) 1280, 1720, 1900 cm^{-1}; UV(hexane) λ_{max} 283 (log ε = 3.62), 425 (3.66), 514 (1.35), 551 (1.26), 591 (1.11); HRMS, m/z 352.2262, calcd for $C_{21}H_{36}S_2$ 352.2259.
6. **6**; purple crystals, mp. 56-57 °C; ^{1}H-NMR(CDCl$_3$) δ 1.17 (s, 9H), 1.23 (s, 9H), 1.24 (s, 9H), 1.32 (s, 3H), 1.35 (s, 3H), 1.63 (s, 3H); ^{13}C-NMR(CDCl$_3$) δ 21.02(q), 27.00(q), 27.43(q), 32.18(q), 32.26(q), 36.93(s), 37.07(s), 37.20(s), 49.55(s), 72.46(s), 128.91(s), 131.67(s), 195.30(s), 255.58(s); MS, m/z 320 (M$^+$, 100); IR(CCl$_4$) 1270, 1900 cm^{-1}; E. A., Found C; 78.79, H; 11.38%, calcd for $C_{21}H_{36}S$ C; 78.68, H; 11.32%.
7. J. K. Crandall, W. W. Conover, J. B. Komin, and W. H. Machleder, *J. Org. Chem.*, **39**, 1723 (1974).

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