CHEMISTRY LETTERS, pp. 1603-1606, 1992.

Synthesis and Unusual Photochemical Reaction of Highly Congested 2,4,6-Tri-t-butylstyrene Episulfides†

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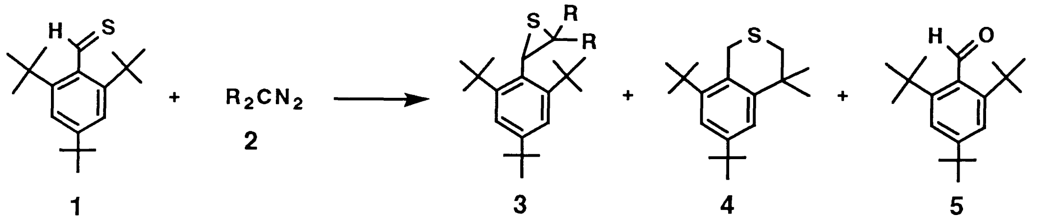
Title compounds were synthesized by the reaction of 2,4,6-tri-*t*-butylthiobenzaldehyde with some diazomethanes. The photolysis of the most sterically congested episulfide obtained from *t*-Bu_2CN_2 gave an unusual product resulting from 1,2-migration of *t*-butyl group instead of the corresponding styrene, a normal photo-product, the corresponding styrene, together with Dewar benzene and benzothiophene derivatives.

Recently, much attention has been paid to sterically congested molecules because of their unique and interesting properties$^{1)}$ as well as their utility for kinetic stabilization of highly reactive molecules such as multiple-bond compounds of heavier typical elements.$^{2)}$ In the course of our studies on sterically congested molecules having 2,4,6-tri-t-butylphenyl group,$^{3)}$ we became interested in the synthesis and reaction of highly congested episulfides. We have found that the reaction of 2,4,6-tri-*t*-butylthiobenzaldehyde **1** with various diazomethanes **2** affords the corresponding styrene episulfides **3** and that the most crowded one **3a** undergoes unusual 1,2-migration of a substituent on a thiirane ring and conversion into a benzothiophene derivative in the photolysis.

The reaction of **1** with diazomethanes **2** in the presence of catalytic amounts of Cu_2Cl_2 gave the corresponding styrene episulfides **3**, along with benzothiane **4** and 2,4,6-tri-*t*-butylbenzaldehyde (**5**).$^{4)}$ The results are summarized in Table 1. Benzothiane **4** and benzaldehyde **5** are considered to be formed by intramolecular cyclization of the anion radical of **1** generated by a single electron transfer from **2** and by oxidation of **1** during work-up, respectively.$^{5)}$

Desulfurization of styrene episulfide **3c** with a tertiary phosphine such as triphenylphosphine proceeded smoothly to afford the corresponding styrenes, but **3a** could not be desulfurized even by the treatment with a strong desulfurization reagent like hexamethylphosphorous triamide$^{6)}$ or alkyllithiums$^{7)}$ under drastic conditions, suggesting the extreme steric congestion of **3a**.



a: R= t-Bu; b: RR= $-CMe_2(CH_2)_3CMe_2-$; c: R=Ph

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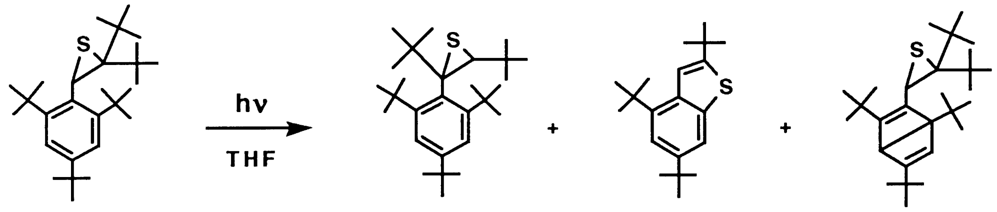
† Dedicated to Professor Emeritus Osamu Simamura of The University of Tokyo on the occasion of his 80th birthday.

Table 1. Reaction of **1** with Diazomethanes **2**$^{a)}$

Diazomethanes 2	Equiv.$^{c)}$	Time	Yields$^{b)}$/% **1**	**3**	**4**	**5**
2a	1.4	5.5 h	27	47	-	10
2b	1.3	2 d	15	36	-	14
2c	1.7	4.5 h	-	78	-	12
	5.3$^{d)}$	6 d	-	20	55	13

a) Reactions were carried out THF in the presence of catalytic amounts of Cu_2Cl_2 in THF at room temperature. b) Isolated yields based on **1**. c) Molar equivalents. d) Refluxed without Cu_2Cl_2.

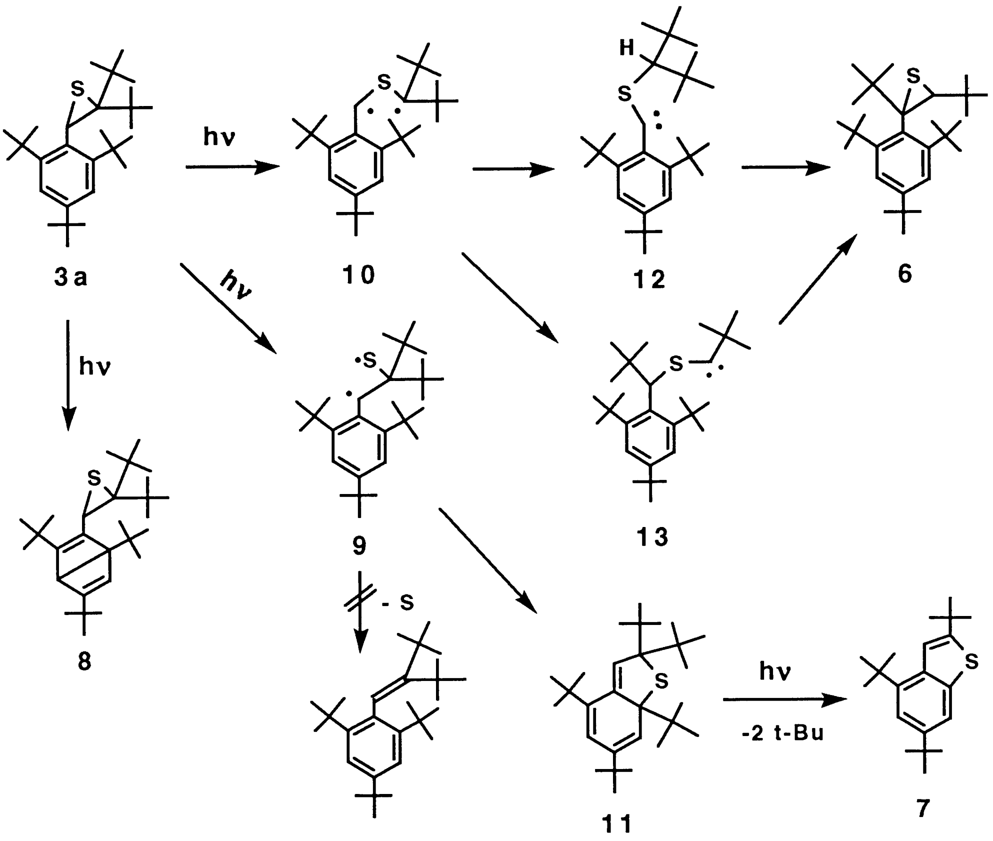


3a **6** **7** **8**

When styrene episulfide **3a** (65 mg, 0.15 mmol) was photolyzed with a 400 W medium pressure mercury lamp in THF (5 ml) at room temperature for 8 h, an isomeric episulfide **6** resulting from 1,2-migration of *t*-butyl group, benzothiophene **7**, and Dewar benzene **8** were obtained in the yields of 39, 25, and 8%, respectively, together with 15% recovery of **3a**.4) The plausible formation mechanism of these products is shown in Scheme 1.

It is very interesting that the unusual photo-product **6** could be obtained as a major product instead of the corresponding styrene, a product expected from the normal photolytic behavior for episulfides.8) This result strongly suggests that bond cleavage occurs competitively at both the C-S and C-C bonds of the thiirane ring leading to **9** and **10**. The thiyl radical **9** formed *via* the C-S bond cleavage can not undergo desulfurization to afford the styrene, but instead cyclization at the *ortho*-position of the benzene ring occurs to give **7**, probably *via* dihydrobenzothiophene intermediate **11**,9) offering the first example for formation of a benzothiophene derivative from a styrene episulfide under irradiation.10)

On the other hand, carbon centered diradical **10** formed *via* the C-C bond cleavage may abstract a hydrogen attached to its radical center to give carbene **12**, which undergoes insertion to C-*t*-Bu bond to afford **6**.11) This is the first example, to our knowledge, for photochemical 1,2-migration of a substituent on the thiirane ring. The formation of Dewar benzene **8** can be explained in terms of intramolecular [2+2]photocycloaddition; similar Dewar benzene formation has some precedents for highly congested benzene derivatives having very bulky substituents.12)



Scheme 1.

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4) Physical and spectral data of **3a**, **6**, **7**, and **8** are shown as typical examples. **3a**: Mp 104-106 °C. Anal. Found: C, 80.59; H, 11.68; S, 7.79%. Calcd for $C_{28}H_{48}S$: C; 80.70; H, 11.61; S, 7.69%. ^1H NMR ($CDCl_3$): δ=0.56 (9H, s, $C(C\underline{H}_3)_3$), 1.23 (9H, s, $C(C\underline{H}_3)_3$), 1.30 (9H, s, $C(C\underline{H}_3)_3$), 1.42 (9H, s, $C(C\underline{H}_3)_3$), 1.50 (9H, s, $C(C\underline{H}_3)_3$), 4.64 (1H, s, $C\underline{H}S$), 6.99 (1H, d, *J*=2.7 Hz, m-H), and 7.08 (1H,

d, J=2.7 Hz, m'-H). ^{13}C NMR ($CDCl_3$): δ=31.37(q), 31.56(q), 33.62(q), 34.09 (2x$C(\underline{C}H_3)_3$, q), 34.06 (s), 38.96 (s), 39.30 (2C, s), 40.22 (s), 52.14 (d), 66.38 (s), 119.26(d), 123.05 (d), 132.87 (s), 146.52 (s), 150.41 (s), and 154. 55 (s); **6**: colorless viscous oil. HRMS (70 eV): m/z Found: 416.3495. Calcd for $C_{28}H_{48}S$: 416.3477. ^{1}H NMR ($CDCl_3$): δ= 0.76 (9H, br s, $C(C\underline{H}_3)_3$), 1.26 (9H, s, $C(C\underline{H}_3)_3$), 1.34 (9H, s, $C(C\underline{H}_3)_3$), 1.38 (9H, s, $C(C\underline{H}_3)_3$), 1.56 (9H, s, $C(C\underline{H}_3)_3$), 4.53 (1H, s, $SC\underline{H}$), 7.14 (1H, d, J=2.2 Hz, m-H), and 7.25 (1H, d, J=2.2 Hz, m'-H). ^{13}C NMR ($CDCl_3$) (340 K): δ=31.24 (q), 32.12 (q), 33.74 (s), 34.58 (q), 34.96 (2x$C(CH_3)_3$, q), 38.77 (s), 39.69 (s), 39.76 (s), 40.08 (s), 54.27 (d), 67.92 (s), 124.66 (d), 125.85 (d), 139.14 (s), 142.93 (s), 146.28 (s), and 152.15 (s); **7**: mp 140.8-141.3 °C. Anal. Found: C, 79.26; H, 10.01; S, 10.74%. Calcd for $C_{20}H_{30}S$: C, 79.41; H, 10.00; S, 10.60%. ^{1}H NMR ($CDCl_3$): δ=1.36 (9H, s, $C(C\underline{H}_3)_3$), 1.44 (9H, s, $C(C\underline{H}_3)_3$), 1.51 (9H, s, $C(C\underline{H}_3)_3$), 7.32 (1H, s, 3-H), 7.32 (1H, d, J=1.4 Hz, 5-H or 7-H), 7.63 and (1H, d, J=1.4 Hz, 5-H or 7-H). ^{13}C NMR ($CDCl_3$): δ=30.92 (q), 31.57 (q), 32.24 (q), 34.81 (s), 34.95 (s), 36.13 (s), 116.26 (d), 118.10 (d), 118.93 (d), 134.76 (s), 140.48 (s), 144.19 (s), 146.19 (s), and 155.41 (s). UV (hexane): 206 nm (ε 20200), 229 (30200), 263 (11800), 269 (12200), 289 (2760), and 300 (2050). UV data suggest that **7** has a benzothiophene skeleton, not benzoisothiophene: A. J. Kiss and B. R. Muth, *Acta Chim. Acad. Sci. Hung.*, **11**, 365 (1957); **8**: colorless viscous oil. HRMS (70 eV): m/z Found: 416.3494. Calcd for $C_{28}H_{48}S$: 416.3477. ^{1}H NMR ($CDCl_3$): δ=0.97 (9H, s, $C(C\underline{H}_3)_3$), 1.08 (9H, s, $C(C\underline{H}_3)_3$), 1.19 (9H, s, $C(C\underline{H}_3)_3$), 1.20 (9H, s, $C(C\underline{H}_3)_3$), 1.33 (9H, s, $C(C\underline{H}_3)_3$), 3.35 (1H, d, J=1.4 Hz, $C\underline{H}$), 3.48 (1H, s, $SC\underline{H}$), and 6.09 (1H, d, J=1.4 Hz, $C{=}C\underline{H}$). ^{13}C NMR ($CDCl_3$): δ=28.44 (q), 28.86 (q), 29.68 (q), 31.54 (q), 33.05 (s), 33.11 (s), 33.25 (q), 34.45 (s), 38.54 (s), 39.61 (s), 45.61 (d), 49.67 (d), 63.16 (s), 68.14 (s), 131.01 (d), 143.16 (s), 158.52 (s), and 165.27 (s).

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11) An alternative formation mechanism of **6** involving a proton abstraction or a hidride shift *via* the corresponding thiocarbonyl ylide can be ruled out, because **6** could not be obtained in the reaction of **1** with **2a**. A mechanism *via* carbene **13** is unlikely, because any insertion product to the C-Me bond of the α-position was not obtained.

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(Received May 29, 1992)