CHEMISTRY LETTERS, pp. 1603-1606, 1992.

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

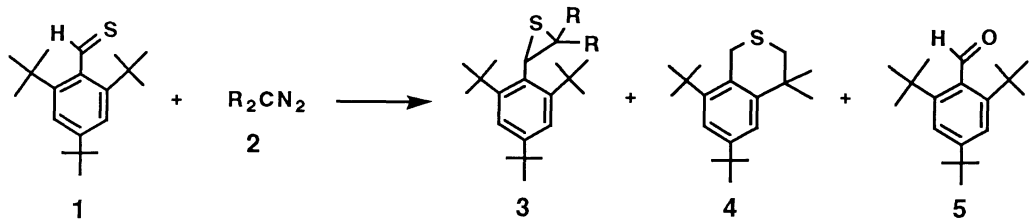
Takayuki KAWASHIMA, Soichiro WATANABE, and Renji OKAZAKI*
Department of Chemistry, Faculty of Science, The Univsersity of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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**.



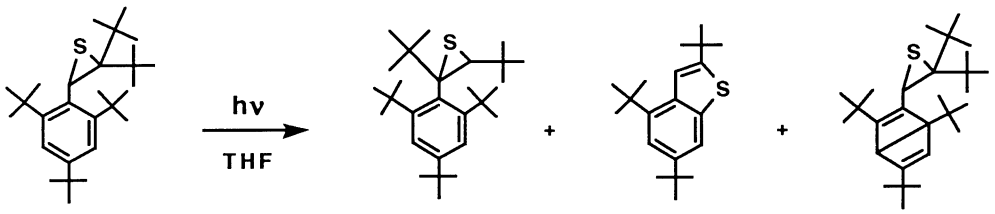
a: R= t-Bu; b: RR= -$CMe_2(CH_2)_3CMe_2$- ; c: R=Ph

†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.

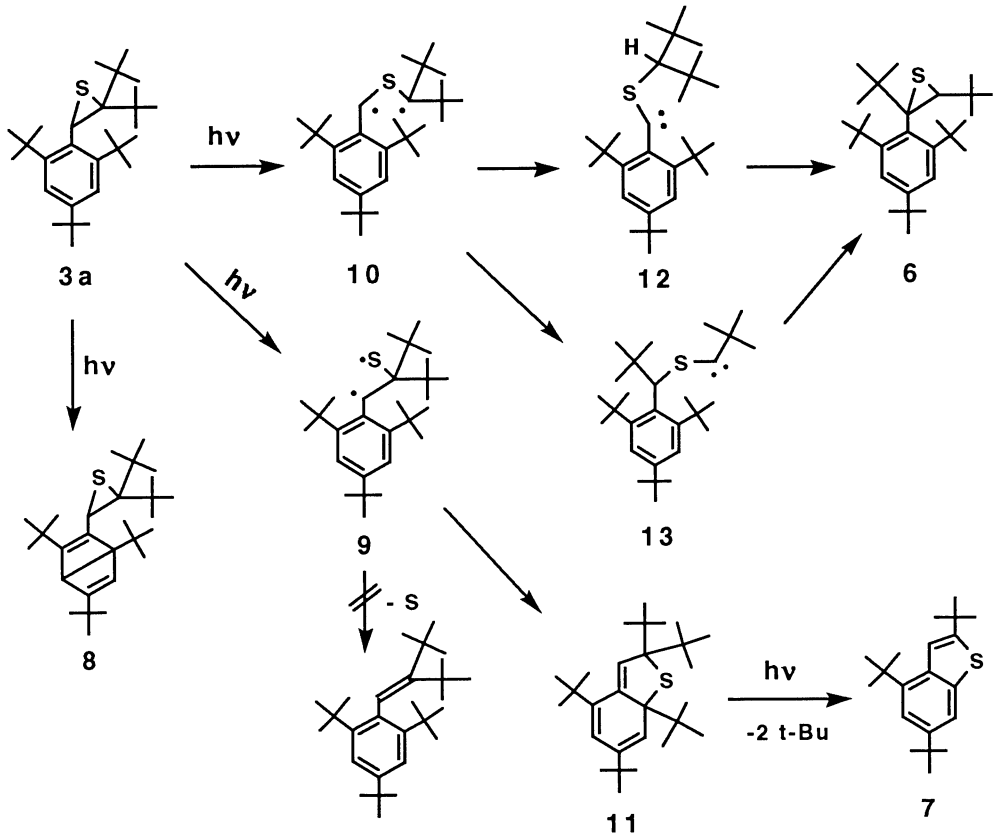


3a **6** **7** **8**

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.

References

1) A. Greenbery and J. F. Liebmann, "Strained Organic Molecules," Academic Press, New York (1978); T. T. Tidwell, *Tetrahedron*, **34**, 1855 (1978); H. Sakurai, K. Ebata, C. Kabuto, and A. Sekiguchi, *J. Am. Chem. Soc.*, **112**, 1799 (1990) and references cited therein.

2) For some recent reviews, see G. Raabe and J. Michl, "Multiple Bonds to Silicon," in "The Chemistry of Organic Silicon Compounds," ed by S. Patai and Z. Rappoport, John Wiley and Sons, Inc., New York (1989), p. 1015; A. H. Cowley, *Polyhedron*, **3**, 389 (1984); R. Okazaki, *Yuki Gosei Kagaku Kyokai Shi*, **46**, 1149 (1988).

3) R. Okazaki, A. Ishii, N. Fukuda, H. Oyama, and N. Inamoto, *J. Chem. Soc., Chem. Comunn.*, **1982**, 1187; R. Okazaki, A. Ishii, and N. Inamoto, *J. Am. Chem. Soc.*, **109**, 279 (1987); R. Okazaki, N. Kumon, and N. Inamoto, *ibid.*, **111**, 5949 (1989); M. A. Cremonini, L. Lunazzi, G. Placucci, N. Kumon, A. Ishii, T. Kawashima, and R. Okazaki, *J. Chem. Soc., Perkin Trans. 2*, **1991**, 1045.

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<u>H</u>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 (2xC($\underline{C}H_3)_3$, 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 (2xC($CH_3)_3$, 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).

5) R. Okazaki, A. Ishii, N. Fukuda, H. Oyama, and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, **1982**, 1187; R. Okazaki, N. Fukuda, H. Oyama, and N. Inamoto, *Chem. Lett.*, **1984**, 101.

6) A. G. Hortmann and A. Bhattacharjya, *J. Am. Chem. Soc.*, **98**, 7081 (1976) and references cited therein.

7) B. F. Bonini, G. Maccagnani, G. Mazzanti, and P. Piccinelli, *Tetrahedron Lett.*, **1979**, 3987.

8) J. A. Moore and T. Isaacs, *Tetrahedron Lett.*, **1973**, 5033; R. C. Petterson, A. L. Herbert, C. W. Griffin, I. Sarkar, O. P. Strausz, and J. Font, *J. Heterocycl. Chem.*, **10**, 879 (1973).

9) A similar cyclization reaction onto the *ortho*-position was reported in the following papers: Y. Inagaki, R. Okazaki, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **52**, 1998 (1979); Y. Inagaki, R. Okazaki, N. Inamoto, K. Yamada, and H. Kawazura, *ibid.*, **52**, 2008 (1979); M. Takahashi, R. Okazaki, N. Inamoto, T. Sugawara, and H. Iwamura, *J. Am. Chem. Soc.*, **114**, 1830 (1992).

10) Thermal formation of benzothiophene was reported in the following paper: D. Seyferth, W. Tronich, R. S. Marmor, and W. S. Smith, *J. Org. Chem.*, **37**, 1537 (1972).

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.

12) M. Jones, Jr., *Chem. Rev.*, **72**, 181 (1972); R. Okazaki, A. Ishii, N. Fukuda, H. Oyama, and N. Inamoto, *Tetrahedron Lett.*, **25**, 849 (1984).

(Received May 29, 1992)