

(11), 95 (25), 77 (15); HMRS  $m/z$  calcd 230.1143, obsd 230.1128;  $^1\text{H}$  NMR  $\delta$  7.5–7.1 (m, 5H), 3.05 (s, 2H), 2.5–2.0 (m, 11H);  $^{13}\text{C}$  NMR  $\delta$  150.16, 128.30, 125.97, 124.71, 44.18 ( $\text{C}_{4,9}$ ), 41.70 ( $\text{C}_6$ ), 37.61 ( $\text{C}_{8,10}$ ), 35.37 ( $\text{C}_6$ ), 34.55 ( $\text{C}_{1,3}$ ), 28.14 ( $\text{C}_7$ ).

**5-Phenyl-2-thiaadamantane S-Oxides E- and Z-2.** Oxidation of 1 by any of the means detailed below gave liquid mixtures of *E* and *Z*-2 would could not be separated:  $^1\text{H}$  NMR  $\delta$  7.3–7.0 (m, 5H), 3.15 and 3.08 (2s, 2H,  $\text{H}_{1,3}$  (*Z* and *E*, respectively)), 2.88 and 2.76 (2d, 2H,  $\text{H}_{4,9\text{ax}}$  (*Z*)  $\text{H}_{8,10\text{ax}}$  (*E*), respectively,  $J = 13.5$  Hz), 2.25–1.60 (m, 9H); the assignments rest on a  $^1\text{H}$ – $^{13}\text{C}$  NMR correlation spectrum;  $^{13}\text{C}$  NMR  $\delta$  148.56, 147.54, 128.38, 128.28, 126.37, 126.21, 124.47, 49.37 ( $\text{C}_{1,3}$  (*Z*)), 48.65 ( $\text{C}_{1,3}$  (*E*)), 40.54 and 40.04 ( $\text{C}_6$  (*E*) and (*Z*)), 38.57 ( $\text{C}_{8,10}$  (*E*), calcd 38.18, slope 4.5), 33.58 and 33.30 ( $\text{C}_5$  (*E*) and (*Z*)), 31.83 ( $\text{C}_{8,10}$  (*Z*), calcd 32.84, slope 1.1), 31.39 ( $\text{C}_{4,9}$  (*Z*), calcd 31.16, slope 4.0), 25.78 and 25.61 ( $\text{C}_7$  (*E*) and (*Z*)), 24.94 ( $\text{C}_{4,9}$  (*E*), calcd 24.81, slope 1). The calculated values for  $\text{C}_{4,9}$  and  $\text{C}_{8,10}$  are based on those of thiaadamantane, 5-phenyl-2-thiaadamantane, and thiaadamantane S-oxide; the slopes are those of the responses to additions of  $\text{Eu}(\text{fod})_3$ , in arbitrary units.

**Oxidations of 1. With Oxone:** a solution of this reagent (0.10 g, 0.32 mM) in water (2.5 mL) was added to a solution of 1 in acetone (2 mL) and methanol (3 mL) at 0 °C in 10 min. After 30 min, 5 mL of aqueous  $\text{NaHSO}_3$  (10%) was added. After extraction with  $\text{CH}_2\text{Cl}_2$  and evaporation of the solvent, a colorless liquid residue consisting of *E*- and *Z*-2 was obtained in 98% yield which was analyzed by  $^1\text{H}$  NMR ( $\text{H}_{1,3}$  signals). **With  $\text{NaIO}_4$ :** a solution of this reagent (20 mg, 0.093 mM) in water (5 mL) was added at 0 °C to a solution of 1 in methanol (1 mL) and kept at that temperature for 7 h. The yield was 80% after workup as above. **With  $\text{N}_2\text{O}_4$ :** this reagent (liquified, 2 mL) was added to

1 (20 mg, 0.09 mM) dissolved in  $\text{CH}_2\text{Cl}_2$  (2 mL) at 0 °C. After 30 min, the solvent and the reagent were allowed to evaporate and the residue was analyzed as before. It was also verified that other mixtures reached the same composition upon treatment with this reagent. **With *m*-CPBA:** a mixture of *m*-CPBA (30 mg, 0.17 mM),  $\text{CH}_2\text{Cl}_2$  (7 mL), and 1 (20 mg, 0.09 mM) was allowed to react at 0 °C for 12 h. After the mixture was quenched with  $\text{NaHCO}_3$  and worked up, the product was analyzed as before. **With *tert*-butyl hypochlorite:** this reagent (1.2 equiv), dissolved in methanol (2 mL) and  $\text{CH}_2\text{Cl}_2$  (2 mL), was added to 1 (30 mg, 0.14 mM) in methanol (3 mL) at –78 °C. The dry ice–acetone bath was allowed to warm to –40 °C, whereupon anhydrous  $\text{Na}_2\text{CO}_3$  was added. When the mixture had reached rt, the solvent was removed and the residue worked up and analyzed in the usual way.

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**Supplementary Material Available:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the new compounds mentioned in this paper and plots of the effect of  $\text{Eu}(\text{fod})_3$  on the  $^{13}\text{C}$  NMR chemical shifts of the sulfoxides (27 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

## Additions and Corrections

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Rui Tamura,\* Masatoshi Kohno, Sei Utsunomiya, Kunihiro Yamawaki, Nagao Azuma, Akira Matsumoto, and Yasutaka Ishii. Synthesis of  $\text{PBG}_1$  Analogues by Radical Chain Substitution Reaction.

Page 3953, column 1, lines 16–19. Introduction should read Its intriguing photochemical behavior shows that the single electron transfer reaction from  $\text{R}\text{Nu}^{\cdot-}$  to  $\text{RX}$  should be the rate-determining step in the dark.<sup>3</sup>