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Rate Constants for the β-Elimination of Tosyl Radical from a Variety of Substituted Carbon-Centered Radicals

Vitaliy I. Timokhin,[†,‡] Stéphane Gastaldi,[†] Michèle P. Bertrand,*[,†] and Chryssostomos Chatgilialoglu[§]

Laboratoire de Chimie Moléculaire Organique, UMR 6517, Boite 562, Faculté des Sciences St Jérôme, Université d'Aix-Marseille III, Av. Escadrille Normandie-Niemen, 13397 Marseille Cedex 20, France, and ISOF, Consiglio Nazionale delle Ricerche, Via P. Gobetti 101, 40129 Bologna, Italy

michele.bertrand@univ.u-3mrs.fr

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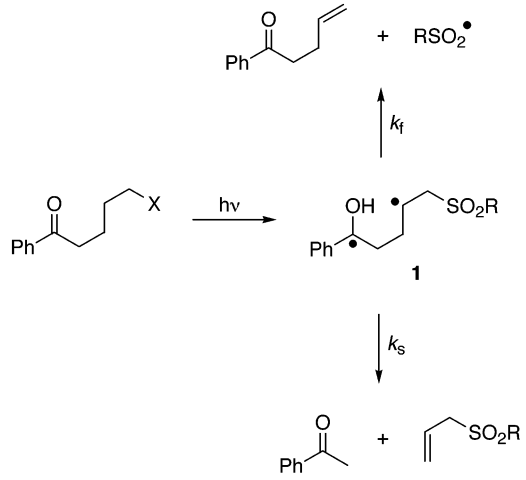
The rate constants for the β-elimination of tosyl radical (Ts•) from a series of carbon-centered radicals have been determined by using the radical clock methodology. Depending on the substituents R in Ts-CH_2-CH(•)R radicals, the rate constants at 293 K vary by more than 2 orders of magnitude in the range of 10^3-10^6 s^{-1}. The lowest values were found for the 2-naphthyl and carbamoyl substituents, whereas the benzyl substituent is located at the other extremity. The effect of the substituent upon the stabilization of the starting radical exerts a predominant influence in this reaction in decreasing the rate of fragmentation.

Introduction

Owing to the reversible character of their addition to double bonds, sulfonyl radicals (RSO_2•) are versatile intermediates that can be used either as entering or as leaving groups, or both sequentially in complex cascade processes.[1] These radicals play a major role in the technologically important free-radical copolymerization of olefins with SO_2 and offer routes to a great variety of sulfones.[1] Over the past decade, the number of publications exploiting the synthetic potential of these short-lived species has increased considerably. During the course of our studies on tosyl radical mediated cyclizations of 1,6-dienes, we frequently came to the conclusion that the rates of β-elimination of sulfonyl radicals might have as much influence as the rates of the addition of the tosyl radical to olefins on the course of these reactions.[2]

However, despite their practical importance, there is a lack of kinetic data for the β-elimination of sulfonyl radicals from carbon-centered radicals. The rationalization of their chemistry is based on the isolated report of 1978 by Wagner and co-workers,[3] who have measured rate constants for the β-cleavage of photogenerated diradical **1** (Scheme 1). In particular, estimated k_f values of 7.8×10^5 s^{-1} for $BuSO_2$• and 1.1×10^7 s^{-1} for $PhSO_2$• based on $k_s = 1 \times 10^7$ s^{-1} were reported. The k_f value for $PhSO_2$• was 15 times faster than that for $BuSO_2$•, which at that time even sounded reasonable from the thermochemistry of sulfonyl radicals. Indeed, it was reported

SCHEME 1



[†] Université d'Aix-Marseille III.

[§] Consiglio Nazionale delle Ricerche.

[‡] Present address: Department of Chemistry, University of Wisconsin-Madison, 1101 University Ave., Madison, WI 53706.

(1) (a) Bertrand, M. P.; Ferreri, C. In *Radical in Organic Synthesis*; Renaud, P., Sibi, M., Eds.; Wiley-VCH: Weinheim, 2001; Vol. 2, pp 485−503. (b) Chatgilialoglu, C.; Bertrand, M. P.; Ferreri, C. In *S-Centered Radicals*; Alfassi, Z. B., Ed.; Wiley: Chichester, 1999; pp 312−354. (c) Crich, D. In *Organosulfur Chemistry*; Page, P., Ed.; Academic Press: London, 1995; Vol. 1, pp 49−88. (d) Bertrand, M. P. *Org. Prep. Proc. Int.* **1994**, *26*, 257−290. (e) Chatgilialoglu, C.; Guerra, M. In *Supplement S: The Chemistry of Sulphur-Containing Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, 1993; pp 363−394. (f) Chatgilialoglu, C. In *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; Wiley: Chichester, 1988; pp 1089−1113.

(2) (a) De Riggi, I.; Gastaldi, S.; Surzur, J.-M.; Bertrand, M. P.; Virgili, A. *J. Org. Chem.* **1992**, *57*, 6118−6125. (b) De Riggi, I.; Nouguier, R.; Surzur, J.-M.; Bertrand, M. P.; Jaime, C.; Virgili, A. *Bull. Soc. Chim. Fr.* **1993**, *130*, 229−235. (c) Bertrand, M. P.; De Riggi, I.; Lesueur, C.; Gastaldi, S.; Nouguier, R.; Jaime, C.; Virgili, A. *J. Org. Chem.* **1995**, *60*, 6040−6045. (d) Bertrand, M. P.; Gastaldi, S.; Nouguier, R. *Tetrahedron Lett.* **1996**, *37*, 1229−1232. (e) Lesueur, C.; Nouguier, R.; Bertrand, M. P.; Hoffmann, P.; De Mesmaeker, A. *Tetrahedron* **1994**, *50*, 5369−5380. (f) Bertrand, M. P.; Lesueur, C.; Nouguier, R. *Carbohydrate Lett.* **1995**, *1*, 393−398. For closely related studies, see: (g) Wang, C.; Russell, G. A. *J. Org. Chem.* **1999**, *64*, 2346−2352.

(3) Wagner, P. J.; Sedon, J. H.; Lindstrom, M. J. *J. Am. Chem. Soc.* **1978**, *100*, 2579−2580.

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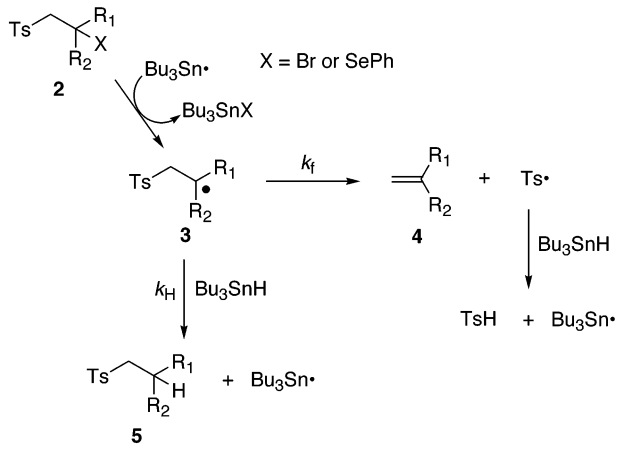
SCHEME 2



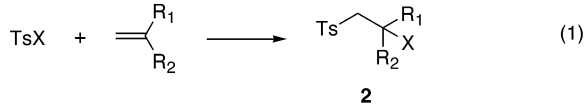
that bond dissociation energies of $PhSO_2-Me$ were 14 kcal/mol lower than in $MeSO_2-Me$, implying a strong delocalization of the unpaired electron into the phenyl group.[4]

Later EPR[1f,5] and optical absorption[6] spectra of sulfonyl radicals indicated they are σ-type species with similar spin density of the unpaired electron on the SO_2 moiety. Theoretical calculation supports these findings and shows that the spin distribution for the unpaired electron in $MeSO_2^{\bullet}$ is 42% on sulfur and 44% on the oxygens, whereas for $PhSO_2^{\bullet}$ there is very little difference, with the corresponding figures being 43% and 39%.[6] Moreover, the $DH_{298}(RSO_2-Cl)$ were measured for R = Me or Ph by photoacoustic calorimetry and were found to be equal (70.5 kcal/mol) and it was also suggested that $DH_{298}(RSO_2-R')$ are independent of R for a given R′.[7] These findings are in contrast with the different k_f value for $PhSO_2^{\bullet}$ and $BuSO_2^{\bullet}$ in Scheme 1.

In the present study, we have made use of the radical clock methodology[8,9] to determine rate constants for the β-elimination of $p\text{-}CH_3C_6H_4SO_2^{\bullet}$ radical (Ts•) from a series of carbon-centered radicals **3** bearing different types of substituents in the α position (Scheme 2).

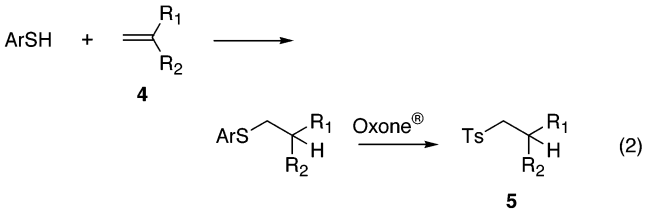
Results

Starting Materials and Reaction References. The choice of bromides and/or phenylselenides as the precursors of radicals **3** (Scheme 2) for the present study was guided by literature reports on the reactivity of TsBr and TsSePh toward alkenes and on the stability of their adducts.[1,2] Bromides were chosen when possible, although the selenide precursors are much more stable than the analogous bromides. The starting compounds **2** were synthesized by the standard reactions (eq 1) following literature procedure.[2a,10]



where Ts = *p*-Me-C_6H_4-SO_2 and X = Br or SePh

On the other hand the products **5** derived from the reaction of radical **3** (Scheme 2) were prepared as authentic samples by reaction of an appropriate olefin with the *p*-toluenethiol followed by oxidation with oxone (eq 2) and compared with the reaction products.[11,12]



Kinetics. According to the radical clock methodology,[8,9] the relative rate constant k_H/k_f can be obtained by the chain reaction of bromide or selenide **2** with Bu_3SnH, provided that conditions can be found under which the radicals **3** are partitioned between the two reaction channels, i.e., hydrogen transfer from Bu_3SnH and β-fragmentation (Scheme 2).

In addition, the trapping of tosyl radicals by Bu_3SnH must be efficient to ensure the irreversibility of the fragmentation process.[13] This scenario can be achieved under pseudo-first-order conditions at an appropriate temperature depending on the starting material. Under these conditions eq 3 holds:

$$\frac{[\mathbf{5}]}{[\mathbf{4}]} = \frac{k^{H}}{k_f}[Bu_3SnH]_0 \qquad (3)$$

A series of experiments was conducted in which the bromides and/or selenides **2** were treated with a large excess of tin hydride in known concentrations at various temperatures, i.e., $[Bu_3SnH]_0 \cong 10 \times [\mathbf{2}]$. The concentrations of **5** and **4** were determined by ^1H NMR analysis, using pentamethylbenzene as an internal standard. The [**5**]/[**4**]ratio varied in the expected manner with the change in the Bu_3SnH concentration at each temperature. The plots of [**5**]/[**4**] vs $[Bu_3SnH]_0$ provided values of k_H/k_f, and the results obtained for radicals **3** are sum-

(4) Benson, S. W. *Chem. Rev.* **1978**, *78*, 23−35. Also, see: Herron, J. T. In *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappoport, Z., Stirling, C. J. M., Eds.; Wiley: Chichester, 1988; pp 95−106.

(5) Chatgilialoglu, C.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1979**, 770−775. Chatgilialoglu, C.; Gilbert, B. C.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1429−1436.

(6) Chatgilialoglu, C.; Griller, D.; Guerra, M. *J. Phys. Chem.* **1987**, *91*, 3747−3750.

(7) (a) Chatgilialoglu, C.; Griller, D.; Kanabus-Kaminska, J. M.; Lossing, F. P. *J. Chem. Soc., Perkin Trans. 2* **1994**, 357−360. (b) See, also: Laarhoven, L. J. J.; Mulder, P.; Wayner, D. D. M. *Acc. Chem. Res.* **1999**, *32*, 342−349.

(8) Griller, D.; Ingold, K. U. *Acc. Chem. Res.* **1980**, *13*, 317−323.

(9) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151−1176. Newcomb, M. In *Radicals in Organic Synthesis*; Renaud, P., Sibi, M., Eds; Wiley-VCH: Weinheim, 2001; Vol. 1, pp 317−335.

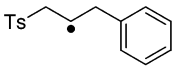
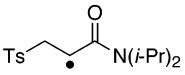
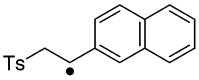
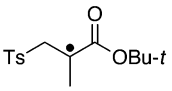
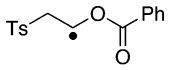
(10) Gancarz, R. A.; Kice, J. L. *J. Org. Chem.* **1981**, *46*, 4899−4906.

(11) Hauser, F. M.; Ellenberg, S. R.; Glusker, J. P.; Smart, C. J.; Carrell, H. L. *J. Org. Chem.* **1986**, *51*, 50−57.

(12) Trost, B. M.; Curran, D. *Tetrahedron Lett.* **1981**, *22*, 1287−1290.

(13) The rate constants for hydrogen abstraction by $RSO_2^{\bullet}$ radicals (R = Me, *n*-Pr, and *n*-Bu) from cyclohexane were estimated to be ca. 2×10^2 M^{-1} s^{-1} at 393 K.[14] The bond dissociation energies of *c*-$C_6H_{11}-H$ and Bu_3Sn-H are 95.5[15] and 78 kcal/mol,[7b] respectively. One would expect the reaction of tosyl radical with Bu_3SnH to be much faster because it is 17 kcal/mol more exothermic, and polar effects are more favorable. Therefore, it is reasonable to assume that the β-elimination of radical **3** is irreversible under the above-mentioned experimental conditions.

TABLE 1. Relative Rate Constants for β-elimination of Tosyl Radical (k_f) vs Hydrogen Abstraction from Bu_3SnH (k_H) for Radicals 3a−e

Radical (R•)	precursor (RX)	*T*, K	k_H/k_f,[a] M^{-1}	k_H,[b] M^{-1} s^{-1}	k_f, s^{-1}
 **3a**	RBr (**2a**)	293	1.0 ± 0.1	1.9×10^6	1.5×10^6
	RSePh (**2a'**)	293	1.6 ± 0.2		
 **3b**	RSePh (**2b**)	293	325 ± 47	3.0×10^6	9.5×10^3 [c]
		353	19.8 ± 1.5		
		373	10.6 ± 0.5		
		393	7.5 ± 1.1		
		410	3.2 ± 0.8		
 **3c**	RBr (**2c**)	403	0.26 ± 0.01	4.2×10^5	1.6×10^6
		293			4.5×10^3 [d]
 **3d**	RSePh (**2d**)	293	159 ± 39	3.2×10^6	2.0×10^4
 **3e**	RBr (**2e**)	293	4.4 ± 0.4	1.2×10^6	2.7×10^5

[a] Errors correspond to one standard deviation of at least three independent measurements. [b] Taken from ref 21; see text for details. [c] Calculated from the Arrhenius expression in eq 4. [d] Calculated by taking the rate constant at 403 K and assuming $\log(A/s^{-1}) = 13$; see text.

marized in Table 1. The values of the intercepts obtained from the plots are very small, near zero, as is expected from eq 3.

The k_H/k_f ratios for radical **3b** were also obtained at different temperatures. Linear regression analysis of a plot of $\log(k_H/k_f)$ vs $1/T$ yields the relative Arrhenius parameters given in eq 4, where $\theta = 2.3RT$ kcal/mol and the errors correspond to one standard deviation.

$$\log \frac{k_H}{k_f}(M^{-1}) = -(4.3 \pm 0.3) + \frac{9.1 \pm 0.5}{\theta} \qquad (4)$$

It is gratyfing to see that the k_H/k_f value for radical **3a** is independent of whether the starting material is bromide (**2a**) or selenide (**2a′**) and that the formation of the undesired PhSeH byproduct is unimportant.[16,17] A possible source of experimental errors resides in the partial consumption of the olefin via hydrostannation.[18] Hydrostannation would lead to overestimating the k_H/k_f ratio, and as a consequence the rate constant for the fragmentation reaction would be underestimated. Although the experiments were conducted in the presence of a large excess of reducing agent compared to selenide or bromide, we took care to use as low as possible an absolute concentration of Bu_3SnH, short reaction course, and rate of conversion superior to 40%. Usually preparative hydrostannylations are conducted at high tin hydride concentrations and long runs because the addition of tin radical is reversible and high concentrations of tin hydride favors the trapping of the adduct.[19] However, blank experiments were carried out in the case of olefin $CH_2{=}CHC(O)N(i\text{-}Pr)_2$ (**4b**) that derived from the fragmentation of radical **3b**. This olefin was selected because

(14) Horowitz, A.; Rajenbach, I. A. *J. Am. Chem. Soc.* **1975**, *97*, 10−13.

(15) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(16) These results indicate that under our conditions the formation of PhSeH as byproduct is unimportant.[17] Indeed, the involvement of PhSeH, which reacts with alkyl radicals approximately 3 orders of magnitude faster than does Bu_3SnH, would lead to an overestimated k_H/k_f ratio.

(17) Simakov, P. A.; Martinez, F. N.; Horner, J. H.; Newcomb, M. *J. Org. Chem.* **1998**, *63*, 1226−1232. Crich, D.; Jiao, X.-Y.; Yao, Q.; Harwood, J. S. *J. Org. Chem.* **1996**, *61*, 2368−2373.

(18) For the discussion of a similar situation, see: Halgren, T. A.; Roberts, J. D.; Horner, J. H.; Martiner, F. N.; Tronche, C.; Newcomb, M. *J. Am. Chem. Soc.* **2000**, *122*, 2988−2994.

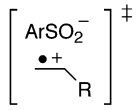
(19) Davies, A. G. In *Organotin Chemistry*; VCH: Weinheim, 1997 and references therein.

the rate constant for the addition of $Bu_3Sn^•$ radical is ca. 10^8 M^{-1} s^{-1} at 25 °C[20] and the reverse fragmentation is expected to be relatively slow, i.e, ideal situation for hydrostannylation. When **4b** was treated at 100 °C for 1 h in a 0.129 M solution of Bu_3SnH in toluene ($[Bu_3SnH]_0$/[**4b**] = 173), 17% of the olefin was consumed. The same experiment conducted at 80 °C on a 0.074 M solution of Bu_3SnH in benzene ($[Bu_3SnH]_0$/[**4b**] = 70) led to 11% consumption of **4b**. These experiments lead to the conclusion that the partial consumption of **4b** via hydrostannation did not interfere substantially in the determination of the k_H/k_f value. Therefore, potential loss of **4** through hydrostannation might induce a small error in the determination of the k_H/k_f value.

Discussion

Table 1 also shows the k_H values for the reaction of a specific alkyl radical with Bu_3SnH.[21] It can be seen that these values are very similar and in the range of $1-3 \times 10^6$ M^{-1} s^{-1} at 293 K with the exception of benzyl-type radical, which is 2 orders of magnitude slower. Indeed, the k_H values for the reaction of $PhCH_2^•$ with Bu_3SnH are 3.0×10^4 at 293 K and 4.2×10^5 M^{-1} s^{-1} at 403 K. Then k_f values at 293 K (403 K for radical **3c**) can be calculated and are reported in the last column of Table 1. The temperature dependence of k_f values for radical **3b** can also be calculated from eq 4 because the Arrhenius parameters for the reaction of α-amide secondary alkyl radicals with Bu_3SnH are reported by Newcomb and co-workers to be $\log(A/M^{-1}\ s^{-1}) = 7.6$ and $E_a = 1.5 \pm 0.4$ kcal/mol.[22] The combination of these data yields the temperature dependence: $\log(k_f/s^{-1}) = (11.9 \pm 0.6) - (10.6 \pm 0.9)/\theta$, where $\theta = 2.3\ RT$ kcal/mol. However, this expression should be treated with caution since Newcomb and co-workers[22] also suggested caution for the Arrhenius parameters of the reference reaction. They noted that the log A is smaller than that found for the tin hydride trapping of secondary alkyl radicals (log $A = 8.7$).[23] If this last value is used with eq 4 then a $\log(A/s^{-1}) = 13$ is obtained for the β-elimination. However, there is no doubt about the accuracy of k_H values at 293 K and, consequently, of k_f in this temperature.[24]

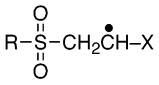
The k_f values in Table 1 are strongly affected by the nature of the substituent. For the fragmentation of radical **3c** a $k_f = 4.5 \times 10^3$ s^{-1} at 293 K can be calculated by taking the rate constant value at 403 K and assuming a $\log(A/s^{-1}) = 13$. The β-elimination of tosyl radical from radical **3b**, **3c**, and **3d** is ca. 2 orders of magnitude slower than from radical **3a**. This suggests that the carbonyl groups, like the aromatic, substantially increase the activation energy due to resonance stabilization of the starting radical.[25] No correlation can be established between the values determined for k_f and the IE of the resulting olefin. The polar effect seems to play a minor role in the β-elimination of the reputed electrophilic tosyl radical. It is worth noting that the β-elimination of tosyl radical from **3e** is ca. 5 times slower than from **3a**.



6

If polar contributions of the type **6** play an important role in the transition state, one would expect any substituent stabilizing the development of a positive charge on the carbon atom (like the benzoyloxyl group in **3e**) to accelerate the β-fragmentation, and carbonyl groups would slow it down even more efficiently than the aromatic substituent does. The resonance stabilization of the starting radical exerts a major influence on the rate of β-fragmentation of tosyl radical.[26] The extent of contribution of polar effects and steric effects is difficult to evaluate.

The k_f value for radical **3a** is 1.5×10^6 s^{-1} as an average of the two sets of experiments (RBr and RSePh). This value is two times higher and seven times smaller than the k_f value reported by Wagner et al.[3] for diradical **1**, RSO_2 being a $BuSO_2$ and $PhSO_2$ group, respectively (Scheme 1). On the basis of the structural characteristics[5,6] and thermochemical data[7] of sulfonyl radical (see introduction for more details), the rate constant for the β-elimination of $RSO_2^•$ from the carbon-centered radical **7** should be independent of the nature of R, being aryl or alkyl, for a given substituent X. Therefore, we suggest that the k_f values in Table 1 can be safely extended to the β-elimination of alkanesulfonyl radicals.



7

Conclusion

Radical clock methodology has been used to provide the first set of β-elimination rate constants for tosyl radical. In particular, bromides and/or selenides of type **2** react with Bu_3SnH in the radical chain reaction shown in Scheme 2 and afford a mixture of desired products (**4** and **5**). By the choice of starting radicals **3**, we were able to evaluate the influence of the nature of the substituent on the β-elimination. The values are in the range of 10^3-10^6 s^{-1} at room temperature. Radicals **3** having substit-

(20) Ingold, K. U.; Lusztyk, J.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 343−348.

(21) Chatgilialoglu, C.; Newcomb, M. *Adv. Organomet. Chem.* **1999**, *44*, 67−112.

(22) Musa, O. M.; Choi, S.-Y.; Horner, J. H.; Newcomb, M. *J. Org. Chem.* **1998**, *63*, 786−793.

(23) Chatgilialoglu, C.; Ingold, K. U.; Scaiano, J. C. *J. Am. Chem. Soc.* **1981**, *103*, 7739−7742.

(24) The k_f values reported in Table 1 are associated with relatively large errors (up to 30%) because the k_H/k_f were calculated on the basis of the ^1H NMR integration and the k_H contain ca. 10% uncertainties. When possible, it is better to use the relative rate constants for planning synthesis.

(25) It is worth mentioning that the rate constants for the analogous β-elimination of $PhS^•$ are in the range of 10^5-10^8 s^{-1} depending on the stabilizing effect of the α-substituent in the carbon-centered radical; see: Ito, O. In *S-Centered Radicals*; Alfassi, Z. B., Ed.; Wiley: Chichester, 1999; pp 193−224. Chatgilialoglu, C.; Altieri, A.; Fischer, H. *J. Am. Chem. Soc.* **2002**, *124*, 12816−12823.

(26) According to Timberlake (see: Timberlake, J. W. In *Substituent Effects in Radical Chemistry*; Viehe, H. G., Janousek, Z., Merényi, R., Eds; NATO ASI Series; Reidel: Dordrecht, 1986; Vol. 189, pp 271−281) the stabilization of radicals $(Me)_2C^•$-X varies slightly in the series $C(=O)NH_2 < C(=O)OMe <$ Ph (the rate constants for the decomposition of the corresponding azoalcanes (free from polar effects) differ by 1 order of magnitude from one to the next). The 2-naphthyl group is likely to stabilize the carbon-centered radical more or less as efficiently as a phenyl group. Of course, some polar contribution is not completely excluded in the case of carbonyl substituents.

uents such as 2-naphthyl or carbamoyl exhibit the lowest tendency to eliminate the tosyl radical as a result of resonance stabilization.

Experimental Section

General. NMR spectra of $CDCl_3$ solutions were recorded at 300 MHz (^1H) and 75 MHz (^{13}C); *J* values are given in Hz. Column chromatographies were performed on silica gel 60. Initiators azobisisobutyronitrile, benzoyl and *tert*-butyl peroxides were commercially available and used without additional purification. Pentamethylbenzene was used as internal standard for ^1H NMR analysis of the crude product after reaction. Tributyltin hydride was distilled and stored under argon. Alkenes **4a**, **4c**, **4d**, and **4e** were commercially available and used without additional purification. Amide **4b** was prepared from the appropriate acyl chloride[2g] and the corresponding amine according to a standard procedure. TsBr and TsSePh were prepared according to known procedures[10,27] and were dried under vacuum before use. Starting compounds **2** (bromides and phenylselenides) were synthesized by standard methods [2a,10] and were purified by column chromatography on silica gel. Spectral data for new compounds are listed below.

General Procedure for Preparation of Bromo- or Phenylselanylalkyl Sulfones (2). All reactions were carried out under argon atmosphere. A solution of alkene **4** (1 mmol), TsSePh (or TsBr) (1.3 mmol), and AIBN (0.13 mmol) in degassed benzene (2 mL) was refluxed for 3−5 h (TLC monitoring) (every 90 min additional portions of AIBN (5%) were added). The solvent was evaporated, and the crude product was purified by flash chromatography on silica gel (EtOAc/pentane).

1-Phenyl-2-bromo-3-(toluene-4-sulfonyl)-propane (**2a**) was prepared from **4a** (99 mg, 0.838 mmol) and TsBr. Column chromatography (EtOAc/pentane, 0:100 to 10:90) gave **2a** (266 mg, 0.754 mmol, 90%). ^1H NMR: δ 2.44 (s, 3H), 3.17 (dd, 1H, J = 14.5, 8.3), 3.49 (dd, 1H, J = 14.5, 5.1), 3.60−3.70 (AB part of an ABX spectra, 2H, J_{AB} = 13.8), 4.45−4.55 (m, 1H), 7.18−7.37 (m, 7H), 7.79 (d, 2H, J = 8.3). ^{13}C NMR: δ 22.1, 44.6, 45.2, 63.3, 127.7, 128.5, 129.0, 129.9, 130.5, 136.7, 137.1, 145.7.

1-Phenyl-2-phenylselanyl-3-(toluene-4-sulfonyl)-propane (**2a′**) was prepared from **4a** (119 mg, 1.003 mmol) and TsSePh. Column chromatography (EtOAc/pentane, 0:100 to 10:90) gave **2a′** (373 mg, 0.869 mmol, 87%). ^1H NMR: δ 2.41 (s, 3H), 3.05 (dd, 1H, J = 14.4, 8.3), 3.35 (dd, 1H, J = 14.4, 3.4), 3.42−3.51 (m, 2H), 3.61−3.72 (m, 1H), 7.12−7.33 (m, 12H), 7.62 (d, 2H, J = 8.3). ^{13}C NMR: δ 22.1, 38.5, 40.2, 60.7, 127.4, 128.3, 128.5, 128.9, 129.7, 129.9, 130.4, 135.1, 136.5, 138.3, 145.2.

***N,N*-Diisopropyl-2-phenylselanyl-3-(toluene-4-sulfonyl)-propionamide** (**2b**) was prepared from **4b** (100 mg, 0.64 mmol) and TsSePh. Column chromatography (EtOAc/pentane, 1:99 to 25:75) gave **2b** (230 mg, 0.49 mmol, 77%). ^1H NMR: δ 1.14 (d, 3H, J = 6.8), 1.22−1.29 (m, 9H), 2.39 (s, 3H), 3.34 (sept, 1H, J = 6.8), 3.45 (d, 1H, J = 12.7), 4.12 (sept, 1H, J = 6.6), 4.29−4.50 (m, 2H), 7.20−7.38 (m, 5H), 7.48−7.52 (m, 2H), 7.70 (d, 2H, J = 8.2). ^{13}C NMR: δ 20.0, 20.3, 20.9, 21.6, 33.5, 46.2, 49.4, 59.3, 126.3, 128.0, 129.1, 129.4, 129.7, 135.5, 135.6, 136.4, 144.6, 166.4.

1-[1-Bromo-2-(toluene-4-sulfonyl)-ethyl]-naphthalene (**2c**) was prepared from **4c** (111 mg, 0.721 mmol) and TsBr. Column chromatography (EtOAc/pentane, 0:100 to 20:80) gave **2c** (169 mg, 0.435 mmol, 60%). ^1H NMR: δ 2.13 (s, 3H), 4.11 (dd, 1H, J = 14.6, 5.0), 4.24 (dd, 1H, J = 14.6, 9.9), 5.53 (dd, 1H, J = 9.9, 5.0), 6.85 (d, 2H, J = 8.1), 7.26 (dd, 1H, J = 8.2, 2.0), 7.37 (d, 2H, J = 8.3), 7.44−7.50 (m, 2H), 7.58−7.61 (m, 2H), 7.67−7.73 (m, 2H). ^{13}C NMR: δ 21.7, 44.8, 64.2, 124.8, 127.0, 127.4, 127.44, 127.9, 128.3, 128.5, 129.3, 129.8, 133.1, 133.7, 135.8, 136.1, 145.1.

2-Methyl-2-phenylselanyl-3-(toluene-4-sulfonyl)-propionic acid *tert*-butyl ester (**2d**) was prepared from **4d** (116 mg, 0.816 mmol) and TsSePh. Column chromatography (EtOAc/pentane, 0:100 to 10:90) gave **2d** (88 mg, 0.194 mmol, 48%). ^1H NMR: δ 1.39 (s, 9H), 1.67 (s, 3H), 2.34 (s, 3H), 3.48 (d, 1H, J = 13.8), 3.88 (d, 1H, J = 13.8), 7.19−7.25 (m, 4H), 7.29−7.36 (m, 1H), 7.46−7.49 (m, 2H), 7.66 (d, 2H, J = 8.3). ^{13}C NMR: δ 22.0, 22.3, 28.1, 45.6, 65.3, 82.4, 126.7, 128.1, 129.5, 130.3, 130.4, 138.6, 138.8, 145.0, 170.8.

Benzoic acid 1-bromo-2-(toluene-4-sulfonyl)-ethyl ester (**2e**) was prepared from **4e** (105 mg, 0.709 mmol) and TsBr. Column chromatography (EtOAc/pentane, 5:95 to 15:85) gave **2e** (210 mg, 0.547 mmol, 77%). ^1H NMR: δ 2.24 (s, 3H), 3.95 (dd, 1H, J = 14.8, 1.5), 4.30 (dd, 1H, J = 14.8, 10.4), 7.11−7.18 (m, 3H), 7.35−7.43 (m, 2H), 7.56−7.61 (m, 1H), 7.67−7.72 (m, 4H). ^{13}C NMR: δ 21.9, 64.2, 67.0, 128.5, 128.8, 130.5, 130.6, 134.5, 136.3, 145.8, 163.3.

General Procedure for Preparation of Reduction Products (5), as Authentic Samples. A solution of alkene **4** (1 mmol), TolSH (1.3 mmol) and AIBN (0.2 mmol) in degassed benzene (2 mL) was refluxed for 3−5 h (TLC monitoring) (every 90 min additional portions of AIBN (5%) were added). The solvent was evaporated, the crude product was dissolved in ethanol (10 mL) and cooled at 0°C, and then a solution of Oxone (3.5 equiv) in water (9 mL) was added. After stirring for 4 h, the mixture was diluted with water and extracted three times with Et_2O. The combined organic phases were dried over sodium sulfate, concentrated, and purified by flash chromatography (EtOAc/pentane).

1-Phenyl-3-(toluene-4-sulfonyl)-propane (**5a**)**.** Following the general procedure, the title compound was prepared in 9% yield. Column chromatography (EtOAc/pentane, 0:100 to 10:90).^1H NMR: δ 1.98−2.08 (m, 2H), 2.45 (s, 3H), 2.69 (t, 2H, J = 7.5), 3.03−3.08 (m, 2H), 7.09−7.11 (m, 2H), 7.17−7.29 (m, 3H), 7.34 (d, 2H, J = 7.9), 7.76 (d, 2H, J = 8.3). ^{13}C NMR: δ 22.0, 24.7, 34.5, 55.9, 126.8, 128.5, 128.8, 129.0, 130.3, 136.5, 140.3, 145.0.

***N,N*-Diisopropyl-3-(toluene-4-sulfonyl)-propionamide** (**5b**)**.** Following the general procedure, the title compound was prepared in 59% yield. Column chromatography (EtOAc/pentane, 0:100 to 30:70).^1H NMR: δ 1.19 (d, 6H, J = 6.8), 1.30 (d, 6H, J = 6.8), 2.45 (s, 3H), 2.77−2.85 (m, 2H), 3.40−3.48 (m, 3H), 3.94 (sept, 1H, J = 6.8), 7.36 (d, 2H, J = 8.3), 7.80 (d, 2H, J = 8.3). ^{13}C NMR: δ 20.5, 20.8, 21.6, 27.6, 45.9, 48.4, 52.2, 127.9, 129.9, 136.3, 144.8, 167.1.

1-[2-(Toluene-4-sulfonyl)-ethyl]-naphthalene (**5c**)**.** Following the general procedure, the title compound was prepared in 65% yield. Column chromatography (EtOAc/pentane, 0:100 to 15:85).^1H NMR: δ 2.41 (s, 3H), 3.16−3.21 (m, 2H), 3.40−3.45 (m, 2H), 7.18−7.25 (m, 1H), 7.32 (d, 2H, J = 7.9), 7.39−7.46 (m, 2H), 7.52 (s, 1H), 7.70−7.78 (m, 3H), 7.81 (d, 2H, J = 8.1). ^{13}C NMR: δ 22.0, 29.5, 57.9, 126.2, 126.7, 126.9, 127.2, 127.9, 128.0, 128.5, 128.9, 130.4, 132.7, 133.9, 135.3, 136.4, 145.2.

2-Methyl-3-(toluene-4-sulfonyl)-propionic Acid *tert*-Butyl Ester (**5d**)**.** Following the general procedure, the title compound was prepared in 64% yield. Column chromatography (EtOAc/pentane, 0:100 to 10:90).^1H NMR: δ 1.27 (d, 2H, J = 7.2), 1.40 (s, 9H), 2.44 (s, 3H), 2.82−2.93 (m, 1H), 3.00 (dd, 1H, J = 14.3, 5.4), 3.65 (dd, 1H, J = 14.2, 7.2), 7.36 (d, 2H, J = 7.9), 7.79 (d, 2H, J = 8.3).^{13}C NMR: δ 18.4, 22.0, 28.2, 36.0, 59.1, 81.7, 128.5, 130.3, 136.8, 145.2, 173.1.

Benzoic acid 2-(toluene-4-sulfonyl)-ethyl ester (**5e**) was prepared as described in the literature.[28] ^1H NMR: δ 2.35 (s, 3H), 3.59 (t, 2H, J = 5.9), 4.65 (t, 2H, J = 5.9), 7.26−7.29 (m, 2H), 7.33−7.38 (m, 2H), 7.45−7.64 (m, 1H), 7.70−7.73 (m, 2H), 7.81 (d, 2H, J = 8.1). ^{13}C NMR: δ 22.0, 55.7, 58.8, 128.5, 128.6, 128.9, 129.4, 130.0, 130.4, 130.6, 133.7, 134.1, 136.9, 145.3, 166.2.

(27) Truce, W. E.; Heuring, D. L.; Wolf, G. C. *J. Org. Chem.* **1974**, *39*, 238−244.

(28) Miller, A. W.; Stirling, C. J. M. *J. Chem. Soc. C* **1962**, 2612−2617.

Kinetic Experiments. Benzene, toluene, or *o*-xylene containing a small amount of pentamethylbenzene as an internal standard was used as solvent. The solution containing the radical precursor **2** (0.001−0.01M) and the initiator was flushed with a stream of argon. The flask was placed in a bath maintained at a constant temperature. After thermal equilibration, ca. 10 equiv of Bu_3SnH was injected with a syringe through a rubber septum, and the reaction was initiated thermally or irradiated with a water-cooled 150-W high-pressure mercury lamp at a distance of ca. 0.1 m for a period of 5−60 min. The crude mixture was analyzed by ^1H NMR. The products were identified by comparison of their ^1H NMR spectra with authentic samples.

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Supporting Information Available: ^1H, ^{13}C, and DEPT HMR spectra and kinetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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