Supporting information for

Laser Flash Photolysis Studies of Alkoxyl Radical Kinetics Using 4-Nitrobenzenesulfenate Esters as Radical Precursors

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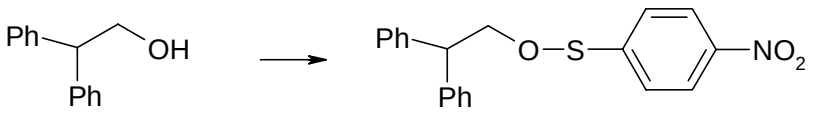

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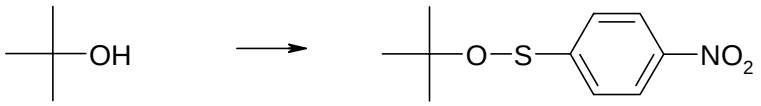
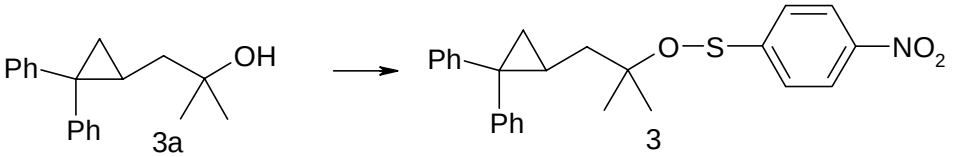
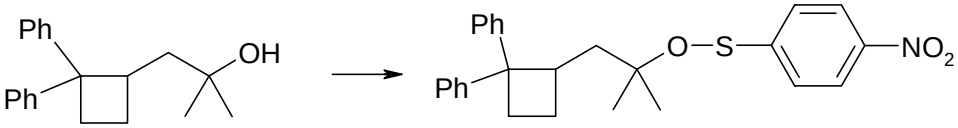


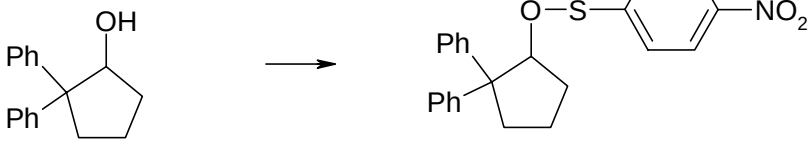
2a 2



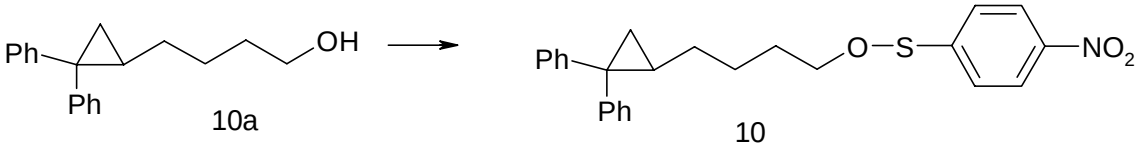
3a 3



4a 4



9a 9



10a 10

General. ^{1}H NMR spectra were recorded at 300 or 400 MHz. ^{13}C NMR spectra were recorded at 75 or 100 MHz. $CDCl_3$ was used as the solvent and tetramethylsilane was used as the internal standard. High resolution mass spectra were obtained by the central instrumentation facility of the Wayne State University Chemistry Department.

General Method for Preparations of Alkyl 4-Nitrobenzenesulfenates (1-4, 9, 10). To a stirred solution of the alcohol (1 eq) and distilled triethylamine (2.5 eq) in 10 mL of anhydrous CH_2Cl_2 under a nitrogen atmosphere at –78 ^{o}C, a solution of 4-nitrobenzenesulfenyl chloride (1.1 eq) in 10 mL of CH_2Cl_2 was added dropwise over 10 min under subdued light. After 20 min, the dry-ice/acetone bath was removed, and the mixture was stirred for 30 min at room temperature. The reaction mixture was diluted with 20 mL of water, washed with 5% HCl (10 mL) and saturated aqueous NaCl (10 mL), and dried over $MgSO_4$. The solvent was removed *in vacuo* at room temperature. Column chromatography on silica gel (hexanes/CH_2Cl_2 1/1, v:v) gave the desired 4-nitrobenzene sulfenate esters as reddish oils or solids. The products were judged to be greater than 95% pure based on proton and carbon-13 NMR spectra.

2,2-Diphenylethyl 4-nitrobenzenesulfenate (1). This was prepared by the general procedure using 2,2-diphenylethanol (**1a**) (0.50 g, 2.5 mmol), 4-nitrobenzene sulfenyl chloride (0.52 g, 2.7 mmol), and Et_3N (0.58 g, 5.8 mmol). The product was isolated as a yellow oil in 72% yield (0.62 g, 1.8 mmol). ^{1}H NMR: δ 4.44 (s, 3 H), 6.93 (d, J = 9.3 Hz, 2 H), 7.26-7.39 (m, 10 H), 8.07 (d, J = 9.3 Hz, 2 H). ^{13}C NMR: δ 51.5 (CH), 82.0 (CH_2), 120.0 (CH), 124.1 (CH), 127.0 (CH), 128.2 (CH), 128.6 (CH), 140.6 (C), 145.1 (C), 150.9 (C).

2-Methyl-2-propyl 4-nitrobenzenesulfenate (2). This was prepared by the general procedure using 2-methyl-2-propanol (**2a**) (0.20 g, 2.7 mmol), 4-nitrobenzene sulfenyl chloride (0.56 g, 3.0 mmol), and Et_3N (0.82 g, 8.1 mmol). The product was isolated as a pale yellow solid (0.46 g, 2.0 mmol, 74% yield), mp 58-60 °C. ^{1}H NMR: δ 1.36 (s, 9 H), 7.28 (d, *J* = 8.8 Hz, 2 H), 8.16 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR: δ 27.6 (CH_3), 84.6 (C), 119.9 (CH), 123.9 (CH), 144.8(C), 154.3 (C).

1-(2,2-Diphenylcyclopropyl)-2-methyl-2-propanol (3a). To an excess CH_3MgBr (2.5 eq, 7.5 mmol, 2.5 mL of 3M solution in ethyl ether) at 0 ^{o}C under nitrogen was added dropwise (2,2-diphenylcyclopropyl)acetyl chloride, which was freshly prepared from the reaction of (2,2-diphenylcyclopropyl)acetic acid (0.76 g, 3.0 mmol) and excess oxalyl chloride (2.5 eq, 654 μL, 7.5 mmol) in the presence of catalytic DMF. The reaction mixture was stirred for 15 hr at room temperature and then diluted with cold saturated NH_4Cl. The organic phase was washed with brine (2 x 10 mL) and was dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel (hexanes/EtOAc 7/3) to yield **3a** 73% (0.59 g, 2.2 mmol, 73%). ^{1}H NMR: δ 0.68 (dd, *J* = 13.8, 10.6 Hz, 1 H), 1.25 (s, 3 H), 1.27 (s, 3 H), 1.32 (m, 1 H), 1.37 (m, 1 H), 1.74 (m, 1 H), 1.89 (dd, *J* = 13.6, 3.2 Hz, 1 H), 7.11-7.33 (m, 10 H). ^{13}C NMR: δ 21.9 (CH_2), 22.0 (CH), 29.1 (CH_3), 29.9 (CH_3), 33.2 (C), 44.9 (CH_2), 71.7 (C), 125.7 (CH), 126.3 (CH), 127.6 (CH), 128.1 (CH), 128.2 (CH), 130.4 (CH), 141.5 (C), 147.2 (C). MS (EI): *m*/*e* (intensity) 266 (2), 248 (32), 205 (100), 192 (41), 183 (42), 165 (37). HRMS: Calc for $C_{19}H_{20}$ (M-H_2O), 248.1565; found, 248.1562.

1-(2,2-Diphenylcyclopropyl)-2-methyl-2-propyl 4-nitrobenzenesulfenate (3). This was prepared from alcohol.(**3a**) by the general procedure (0.27 g, 1.0 mmol), 4-nitro benzenesulfenyl chloride (1.1 eq, 0.208 g, 1.1 mmol) and Et_3N (2.3 eq, 0.232 g, 2.3 mmol) in 76% yield (0.32 g, 0.76 mmol). ^{1}H NMR: δ 0.81 (dd, *J* = 14.6, 10.6 Hz, 1 H), 1.32 (s, 3 H,), 1.36 (m, 1 H), 1.39 (s, 3 H), 1.42 (m, 1 H), 1.73 (m, 1 H), 2.12 (dd, *J* = 14.4, 3.2 Hz, 1 H), 7.14-7.32 (m. 12 H), 8.13 (d, *J* = 7.2 Hz, 2 H). ^{13}C NMR: δ 21.7 (CH), 22.0 (CH_2), 25.3 (CH_3), 25.7 (CH_3), 33.6 (C), 42.3 (CH_2), 87.2 (C), 120.2 (CH), 123.9 (CH), 125.8 (CH), 126.4 (CH), 127.5 (CH), 128.20 (CH), 128.23 (CH), 130.3 (CH), 141.2 (C), 144.7 (C), 146.8 (C), 153.9 (C).

1-(2,2-Diphenylcyclobutyl)-2-methyl-2-propanol (4a). This was prepared from methyl (2,2-diphenylcyclobutyl)acetate[1] (0.37 g, 1.31 mmol) by the procedure similar to that given above for alcohol **3a**. The product was isolated in 95% yield (0.35 g, 1.25 mmol). ^{1}H NMR: δ 0.90 (dd, *J* = 14.8, 11.8 Hz, 1 H), 1.18 (s, 3 H), 1.21 (s, 3 H), 1.40 (bs, 1 H), 1.56 (dd, *J* = 14.0 Hz, 2.0 Hz, 1 H), 2.02 (pentet, *J* = 10.8 Hz, 1 H), 2.26 (m,1 H), 2.45 (td, *J* = 10.4 Hz, 8.9, 1 H), 2.97 (m, 1 H), 3.35 (q, *J* = 9.6 Hz, 1 H), 7.15-7.33 (m, 10 H). ^{13}C NMR: δ 27.1 (CH_2), 29.5 (CH_3), 30.1 (CH_3), 33.1 (CH_2), 40.2 (CH), 47.4 (CH_2), 53.9 (C), 71.5 (C), 125.5 (CH), 125.7 (CH), 126.3 (CH), 127.8 (CH), 128.1 (CH), 128.2 (CH), 144.1 (C), 151.7 (C). MS (EI): *m/e* (intensity) 262 (0.5), 206 (20), 180 (100), 165 (22). HRMS: Calc for $C_{20}H_{22}$ (M-H_2O), 262.1721; found, 262.1724

1-(2,2-Diphenylcyclobutyl)-2-methyl-2-propyl 4-nitrobenzenesulfenate (4). This was prepared by the general procedure using alcohol **4a** (0.35 g, 1.25 mmol), 4-

nitrobenzenesulfenyl chloride (237 mg, 1.25 mmol), and Et_3N (290 mg, 2.9 mmol). The product was isolated as a yellow oil in 78% yield (0.42 g, 0.97 mmol). ^{1}H NMR: δ 1.03 (dd, *J* = 14.0, 11.6 Hz, 1 H), 1.24 (s, 3 H), 1.32 (s, 3 H), 1.76 (dd, *J* = 14.0, 2.0 Hz, 1 H), 2.03 (pentet, *J* = 10.0 Hz, 1 H), 2.27 (m, 1 H), 2.45 (td, *J* = 11.4, 8.8 Hz, 1 H), 2.97 (t, *J* = 10.0 Hz, 1 H), 3.32 (q, *J* = 10.0 Hz, 1 H), 7.11-7.26 (m, 10 H), 7.31 (t, *J* = 7.6 Hz, 2 H), 8.13 (d, *J* = 8.8 Hz, 2 H). ^{13}C NMR: δ 25.5 (CH_3), 26.1 (CH_3), 27.0 (CH_2), 33.0 (CH_2), 39.9 (CH), 44.6 (CH_2), 53.9 (C), 87.0 (C), 120.1 (CH), 123.9 (CH), 125.6 (CH), 125.8 (CH), 126.2 (CH), 127.8 (CH), 128.0 (CH), 128.3 (CH), 143.6 (C), 144.7 (C), 151.4 (C), 153.9 (C).

2,2-Diphenylcyclopentyl 4-nitrobenzenesulfenate (9). This was prepared by the general procedure from **9a**[1,2] (300 mg, 1.27 mmol), 4-nitrobenzenesulfenyl chloride (265 mg, 1.4 mmol) and Et_3N (295 mg, 2.92 mmol). The product was isolated as a yellow orange oil in 73% yield (0.36 g, 0.93 mmol). ^{1}H NMR: δ 1.50 (m, 1 H), 1.89 (m, 1 H), 2.11 (m, 1 H), 2.21 (m, 1 H), 2.39 (dd, *J* = 12.0, 7.2 Hz, 1 H), 2.81 (dt, *J* = 12.4, 9.6 Hz, 1 H), 4.75 (dd, *J* = 4.8, 1.6 Hz, 1 H), 6.77 (d, *J* = 9.2 Hz, 2 H), 7.18-7.35 (m, 10 H), 8.01 (d, *J* = 9.2, 2 H). ^{13}C NMR: δ 19.9, 30.8, 34.5, 60.5, 95.1, 120.5, 123.9, 126.3, 126.4, 126.7, 127.9, 128.4, 128.9, 141.1, 143.7, 145.5, 151.6.

4-(2,2-Diphenylcyclopropyl)-1-butanol (10a). To a solution of 6,6-diphenyl-5-hexene-1-ol (1.2 g, 4.8 mmol) and Et_2Zn (24 mL, 1M in hexanes) in anhydrous dichloromethane (40 mL) at 0 ^{o}C under nitrogen was added diiodomethane (12.8 g, 48 mmol) over 30 min. The reaction mixture was stirred for 15 h at room temperature, and then poured into saturated NH_4Cl (30 mL). The organic layer was washed with brine (20

mL) and dried over $MgSO_4$. Treatment of crude product mixture with m-CPBA and column chromatography on silica gel (hexanes/EtOAc, 7/3) gave **10a** in 60% yield (0.77 g, 2.9 mmol). ^{1}H NMR: δ 0.82 (m, 1 H), 1.22 (m, 3 H), 1.43-1.55 (m, 5 H), 1.63 (m, 1 H), 3.57 (t, *J* = 5.6 Hz, 2 H), 7.11-7.33 (m, 10 H). ^{13}C NMR: δ 20.6 (CH_2), 25.4 (CH_2), 26.3 (CH), 30.5 (CH_2), 32.5 (CH_2), 35.2 (C), 62.8 (CH_2), 126.2 (CH), 126.5 (CH), 127.7 (CH), 128.1 (CH), 130.5 (CH), 141.8 (C), 147.4 (C). MS (EI): *m/e* (intensity) 266 (37, 248 (16), 205 (53), 193 (100), 180 (81), 167 (86), 115 (78). HRMS: Calcd for $C_{19}H_{22}O$, 266.1671; found, 266.1671.

4-(2,2-Diphenylcyclopropyl)butyl 4-nitrobenzenesulfenate (10). This was prepared by the general procedure using alcohol **10a** (160 mg, 0.6 mmol), 4-nitrobenzenesulfenyl chloride (125 mg, 0.66 mmol) and Et_3N (140 mg, 1.38 mmol). The product was isolated as a yellow oil in 63% yield (170 mg, 0.40 mmol). ^{1}H NMR: δ 0.81 (m, 1 H), 1.27 (m, 2 H), 1.46-1.64 (m, 4 H), 1.72 (m, 2 H), 3.84 (t, *J* = 7.2 Hz, 2 H), 7.12-7.35 (m, 12 H), 8.21 (d, *J* = 8.8 Hz, 2 H). ^{13}C NMR: δ 20.7 (CH_2), 25.5 (CH_2), 26.2 (CH), 30.1 (CH_2), 30.5 (CH_2), 35.1 (C), 79.5 (CH_2), 119.8 (CH), 124.3 (CH), 125.6 (CH), 126.3 (CH), 127.6 (CH), 128.2 (CH), 130.5 (CH), 141.6 (C), 144.7 (C), 147.2 (C), 151.7 (C).

References

(a) Choi, S.-Y.; Horner, J. H.; Newcomb, M. *J. Org. Chem.* **2000**, *64*, 4447-4449.

(b) Potin, D.; Dumas, F.; d'Angelo, J. *J. Am. Chem. Soc*. **1990**. *112*, 3483-3486

Table S1: Kinetic Data for the β-Scission of 3•.[a]

Temperature °C	$k_{frag} \times 10^7$
-30.6	0.216
-30.6	0.219
-20.3	0.346
-20.0	0.358
-9.5	0.605
-9.5	0.596
0	0.955
0	0.982
9.7	1.46
9.7	1.53
18.4	2.23
18.4	2.22
30.7	3.65
30.7	3.70
42.6	5.23
42.6	5.48
52.5	7.53
52.5	6.97

(a) Typical errors in kinetic measurements were ± 5%
(b) Sample temperature was measured by a 0.2 mm diameter thermocouple inserted directly into the sample flow cell. Typical temperature fluctuations were ± 0.2 °C.

Table S2: Kinetic Data for the Competing β-Scission and 1,5-Hydrogen Atom Abstraction of 4•.[a]

Temperature °C	$k_{obs} \times 10^7$	k_{abs}/k_{frag} [b]	$k_{abs} \times 10^7$	$k_{frag} \times 10^7$
-22.7	0.445	0.92/0.08	0.41	0.036
-11.8	0.664	0.87/0.13	0.58	0.086
-11.8	0.626		0.54	0.081
-1.6	0.846	0.83/0.17	0.70	0.14
-1.6	0.879		0.73	0.15
11.1	1.12	0.79/0.21	0.88	0.24
11.1	1.11		0.88	0.23
20.1	1.53	0.73/0.27	1.1	0.41
20.1	1.48		1.1	0.40
31.1	2.49	0.66/0.34	1.6	0.84
31.1	2.43		1.6	0.83
40.4	3.18	0.64/0.36	2.0	1.1
40.4	2.84		1.8	1.0
51.0	4.02	0.60/0.40	2.4	1.6
51.0	3.97		2.4	1.6

(a) See notes to table S1

(b) Relative fractions of abstraction vs fragmentation for radical **4•** determined from the relative signal intensity of the fragmentation product of **4•** to the fragmentation product of **9•**.

Table S3: Kinetic Data for the 1,5-Hydrogen Abstraction of 10•.[a]

Temperature °C	$k_{obs} \times 10^7$
-19.5	0.884
-19.5	0.909
-10.6	1.23
-10.6	1.16
-0.6	1.62
-0.6	1.82
2.4	1.63
2.4	1.63
11.6	2.16
11.6	2.14
20.3	2.83
20.3	2.65
30.7	3.36
30.7	3.53
40.3	4.08
40.3	4.26
49.3	4.98
49.3	4.85

(a) See notes to table S1.