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Substituted *o*-[(Trimethylsilyl)methyl]benzyl *p*-Tolyl Sulfones: Practical Reagents for Preparing Cycloadducts of *o*-Quinodimethanes

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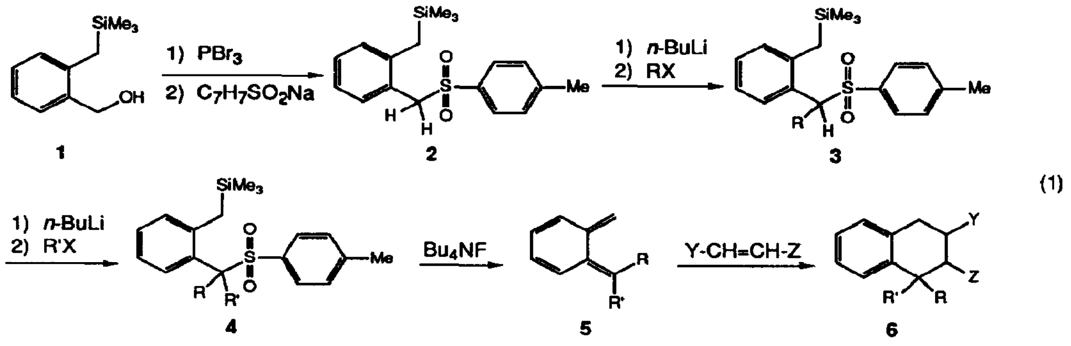
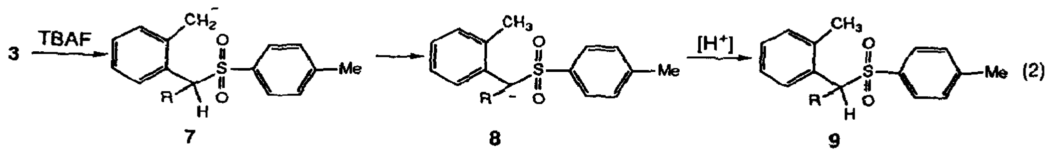
Abstract: Effective methods for synthesis and 1,4-elimination of silyl sulfones to *o*-quinodimethanes have been developed.

It is now reported that α,α-disubstituted silyl sulfones 4 (Eq 1), readily prepared from *o*-[(trimethylsilyl)methyl]benzyl alcohol[1a,b] (1) as illustrated, are eliminated by tetra-*n*-butylammonium fluoride (TBAF) or cesium fluoride in acetonitrile at 20-25°C[1c] to give *o*-quinodimethanes 5[2a-c] that are trapped effectively by dienophiles to yield tetrahydronaphthalenes 6. The chemistry, synthetic utility, and mechanistic aspects of the new methodology are now described.

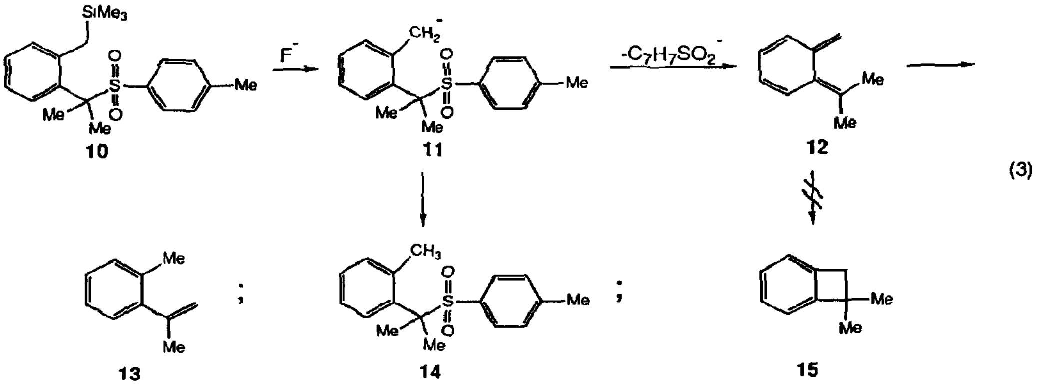


(1)

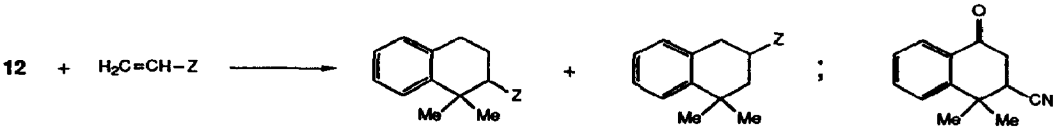
o-[(Trimethylsilyl)methyl]benzyl *p*-tolyl sulfone (2) is converted (Eq 1) in 69-81% yields to monoalkyl sulfones 3 (R = methyl, allyl, and benzyl) by reactions with *n*-butyllithium in tetrahydrofuran or ethyl ether at -78°C and then methyl iodide, allyl bromide, and benzyl bromide, respectively. The secondary halide, 2-bromopropane, suffers extensive elimination. By multiple additions of *n*-butyllithium and 2-bromopropane to 2 in tetrahydrofuran containing hexamethylphosphoramide at 0°C, 2-propyl sulfone 3 (R = 2-propyl) is obtained satisfactorily (66%). None of the monoalkyl sulfones (3) prepared however are eliminated by TBAF or cesium fluoride. Sulfones 9 (Eq 2) are produced instead in >61-70% yields by stepwise removal of the trimethylsilyl groups from 3 by fluoride ion, transfer of hydrogens *alpha* to the sulfone groups in 7, and protonations of 8 on neutralization.



Dialkylated sulfones **4** are obtained from **2** (Eq 1) by successive additions of *n*-butyllithium, a halide, *n*-butyllithium, and a halide. Such derivatives prepared from **2** in 57-82% yields are α,α-dimethyl sulfones **10** and **4** (R = ethyl, R' = methyl; R and R' = ethyl; R = allyl, R = methyl; R and R' = allyl; and R = methyl, R' = 2-propyl). Much of the elimination chemistry of **4** is revealed upon addition of TBAF (2 equiv) to α,α-dimethyl sulfone **10** (Eq 3) in acetonitrile at 20-25°C to give 2-(2-methylphenyl)propene (**13**) and its oligomers along with 2-(2-methylphenyl)-2-propyl *p*-tolyl sulfone (**14**). *o*-Quinodimethane **12** is not isolated because of 1,5-sigmatropic rearrangement of hydrogen from its (Z)-methyl group to give 13.[2d] (1,1-Dimethylcyclobuta)benzene (**15**), the ring-closure isomer of **12**, is not found. The desilylated product, sulfone **14** (Eq 3), arises by protonation of **11** and implies that elimination of **10** to **12** by fluoride ion is not concerted. The latter conclusion is consistent with the prior observations that monoalkylated silyl sulfones **3** are desilylated by fluoride ion (Eq 2).



Dimethylquinodimethane **12** is trapped efficiently, however, when generated in the presence of electron-deficient olefins. Thus **10** (1 equiv), TBAF (2 equiv), and acrylonitrile (**16a**, 40 equiv) in acetonitrile at 20-25°C (Eq 4) yield 2-cyano-1,1-dimethyltetralin (**17a**, 78%)[2e] regiospecifically along with **13** (17%) and **14**. 3-Cyano-1,1-dimethyltetralin (**18a**) was not detected. The structure of **17a** is established from its ^1H and ^{13}C NMR, NOE, and oxidation with chromium trioxide to 3-cyano-4,4-dimethyl-1-tetralone (**19**). The regiochemistry in cycloaddition of **12** and **16a** to give **17a** rather than **18a** is in agreement with a low activation energy mechanism in which **12** reacts either as a diradical[2b] or a dipolar enophile. The behavior of methyl acrylate (**16b**) is similar (Eq 4) to that of **16a** since 2-carbomethoxy (**17b**, 90%)- rather than 3-carbomethoxy-1,1-dimethyltetralin (**18b**, ~10%) is formed.[2e] The electron deficient olefin, ethyl vinyl ether, cycloadds poorly to **12**.



(4)

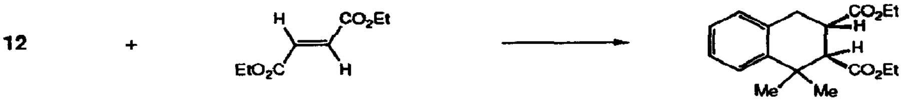
16a, Z = CN
16b, Z = CO_2Me

17a, Z = CN
17b, Z = CO_2Me

18a, Z = CN
18b, Z = CO_2Me

19

Addition of TBAF or cesium fluoride to **10** in diethyl fumarate (**20**, 2 equiv) or diethyl maleate (2 equiv) under various conditions at 0°C is noteworthy in that diethyl *trans*-1,2,3,4-tetrahydro-1,1-dimethyl-2,3-naphthalene dicarboxylate (**21**) is obtained with no *cis*-isomer in 32-59% yields along with **13** and its derivatives, and **14** (10%). In all experiments the diethyl maleate is extensively isomerized by fluoride ion to **20**.[3a] The stereochemistry of **21** is assigned by ^1H NMR and NOE methods. *Trans*-dicarboxylate **21** is apparently formed exclusively because (1) cycloaddition of **12** and **20** is stereospecific (Eq 5), (2) capture of **12** by **20** is much faster than by diethyl maleate[3b-c], and (3) fluoride ion isomerizes diethyl maleate to **20** more rapidly than it eliminates **10** to **12** (Eq 3).



(5)

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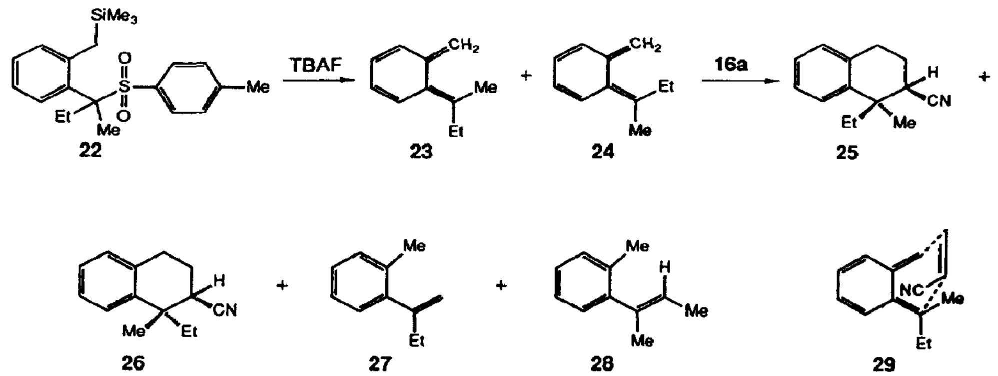
Reaction of α-ethyl-α-methyl sulfone **22**, TBAF, and **16a** (Eq 6, 40 equiv) reveals that (1) (Z)-1-ethyl-1,2,3,4-tetrahydro-1-methyl-2-naphthonitrile (**25**, 28%) is formed in preference to its (E)-isomer (**26**, 14%),[4a] (2) more 2-(2-methylphenyl)-1-butene (**27**, 24%) is produced than (E)-2-(2-methylphenyl)-2-butene (**28**, 5%),[4b] and (3) desilylation gives 2-(2-methylphenyl)-2-butyl *p*-tolyl sulfone (10%). Thus, (1) (E)-α-ethyl-α-methylquinodimethane (**23**), the lesser-strained isomer, is generated more extensively than is (Z)-**24**, (2) the regioselectivities in cycloadditions of **23** and **24** with **16a** are similar to that for **12** and **16a** and for reactions of unsymmetrical dienes with dienophiles,[4c] (3) formation of **25** rather than **26** implies that the most favored transition state, **29**, exhibits Alder-Stein *endo*-interaction along with diradical or dipolar character[4c-g], and (4) **27** is formed from **23** and **28** comes from **24** by 1,5-hydrogen migration processes. Further, **22**, fluoride ion, and dimethyl fumarate yield the diastereomeric pairs of **30** and **31** in 58:42 ratio along with **27** and **28**.[4a] The results are of further interest in that **30**, although presumably more stable than **31**, may become the major cycloadduct because *endo*-interaction may be more extensive in diradical or dipolar transition states related to **32** than **33**.[4c-g] The stereochemistries of cycloadditions of **5**, elimination of α,α-dielectronegatively-substituted analogs of **4**, and generation of hetero- and polynuclear *o*-and *p*-quinodimethanes are now being studied in detail.



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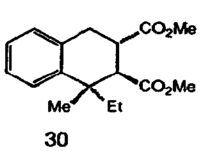

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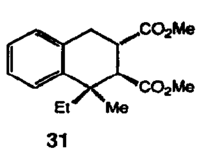

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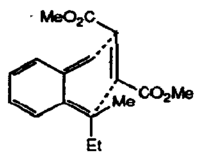

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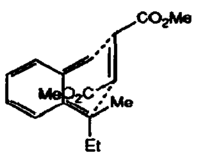

33

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References and Footnotes

1. (a) Dai-Ho, G.; Mariano, P. S. *J. Org. Chem.* **1982**, *47*, 2688. (b) Lan, A. J. Y.; Heuckeroth, R. O.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 2738. (c) For previous development of silyl sulfone elimination methodologies, see Kocienski, P. J. *J. Org. Chem.* **1980**, *45*, 2037; Eisch, J. J.; Behrooz, M.; Dua, S. K. *J. Organomet. Chem.* **1985**, *285*, 121; Hsiao, C-N.; Shechter, H. *J. Org. Chem.* **1988**, *53*, 2688; and citations therein.

2. *o*-Quinodimethanes are described and reviewed by (a) Charlton, J. L.; Alauddin, M. M. *Tetrahedron*, 1987, *43*, 2873; (b) Trahanovsky, W. S.; Macias, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 6820; (c) Ito, Y. "Current Trends in Organic Synthesis", Pergamon Press, 1983, 169. 1,5-H rearrangements of *o*-quinodimethanes are reported by (d) deFonseka, K. K.; McCullough, J. J.; Yarwood, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 3271 and references therein. (e) Regioselective cycloadditions of acrylonitrile and methyl acrylate to *o*-quinodimethanes are described, along with prior references, by Ito, Y.; Nakatsuda, M.; Saegusa, T. *J. Am. Chem. Soc.* **1982**, *104*, 7609.

3. (a) Dimethyl maleate in acetonitrile at 20-25°C is rapidly isomerized by TBAF to **20** in the absence of **10**. See also Ito, Y.; Nakajo, E.; Saegusa, T. *Synth. Commun.* **1986**, *16*, 1073. (b) 1,4-Cycloadditions of 1,3-dienes are reported to occur much faster with **20** than with dimethyl maleate.[3c] (c) Miki, T.; Matsuo, T. *Chem. Pharm. Bull.* **1971**, *19*, 858.

4. (a) Assignments of **25**, **26**, **30**, and **31** are based on NMR and NOE data. (b) In the absence of **16a**, isomers **27** and **28** are produced in 93:7 ratio and in 48% yield. (c) Martin, J. G.; Hill, R. K. *Chem. Rev.* **1961**, *61*, 537; (d) Alder, K.; Stein, G. *Angew. Chem.* **1937**, *50*, 510; (e) Woodward, R. B.; Baer, H. *J. Am. Chem. Soc.* **1944**, *66*, 645; (f) Sauer, J.; Sustmann, R. *Angew Chem.* **1980**, *92*, 773; (g) Van Mele, B.; Huybrechts, G. *Int. J. Chem. Kinet.* **1989**, *21*, 967.

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