Photochemical Alkylation of Ketene Dithioacetal *S,S*-Dioxides. An Example of Captodative Olefin Functionalization

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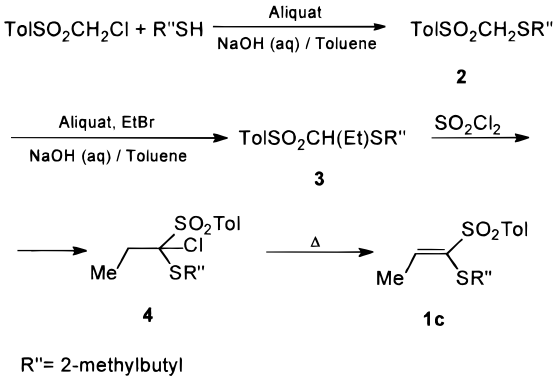
Radical alkylation of some ketene dithioacetal *S,S*-dioxides failed through the tin hydride promoted chain process but was successfully performed through stoichiometric photochemical initiation, either by electron transfer or hydrogen abstraction. In the first case, alkyl radicals were produced from tetralkylstannanes (*t*-Bu-, *i*-Pr-, *n*-Bu-SnR_3) via radical cation fragmentation, while in the second case these were produced from alkanes (cyclohexane, adamantane) by benzophenone triplet. When bulky radicals (*t*-Bu, adamantyl) were involved, the addition occurred with complete diastereoselectivity.

Captodative olefins have been shown to be convenient substrates for C−C bond formation via cycloaddition and addition reactions.[1] Ketene dithioacetal *S,S*-dioxides, as an example, are easily prepared;[2] *β*-alkylation of such derivatives may lead to highly substituted α-thiosulfones. These, in turn, are convenient synthetic intermediates in view of several possible elaborations, e.g., *C*-alkylation and -arylation,[3] substitution of an allyl for a sulfone group,[4] desulfurization,[5,6] pyrolysis to yield a carbonyl derivative,[7] Pummerer rearrangement.[8] Ketene dithioacetal *S,S*-dioxides have been shown to act as efficient acceptors of carbenes[9] as well as of 1-hydroxy- (or alkoxy-)alkyl radicals.[5,10] Furthermore, intramolecular radical addition of *β*-(*ω*-iodoalkyl) derivatives has been shown to occur under classic radical chain conditions yielding five-, six-, and also four-membered cyclic derivatives, a result rationalized on the basis of the peculiar stability of the adduct radical due to the captodative effect.[11] Somewhat surprisingly, no corresponding intermolecular radical alkylation has been reported except for the above-mentioned case of hydroxyalkyl radicals. It appeared worthwhile to test the generality of such a reaction since this would widen the scope of thiosulfones synthesis. We thus explored the radical alkylation of these substrates and found that, while standard tin hydride methods were ineffective, a satisfactory addition could be obtained by photochemical means. Bulky radicals could be added under this condition with excellent diastereoselectivity.

Scheme 1



Results

Attempted Tin Hydride Induced Alkylation. We focused our attention on three ketene dithioacetal *S,S*-dioxides, viz. 1-(methylthio)-1-[(4-methylphenyl)sulfonyl)]-ethene (**1a**) and (*E*)-1-(methylthio)-1-[(4-methylphenyl)-sulfonyl)]propene (**1b**) (both known as useful dienophiles in cycloaddition reaction)[9] as well as (*E*)-1-(2-methylbutylthio)-1-[(4-methylphenyl)sulfonyl)]propene (**1c**, see Scheme 1 for the synthesis). Alkene **1b** was treated with *t*-BuI in the presence of Bu_3SnH/AIBN under standard conditions[12] at 110 °C for 7 h. The alkene was not significantly consumed. Likewise, with $Bu_3SnCl/NaBH_4$ under UV irradiation, no reaction occurred (see Experi-

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Scheme 2

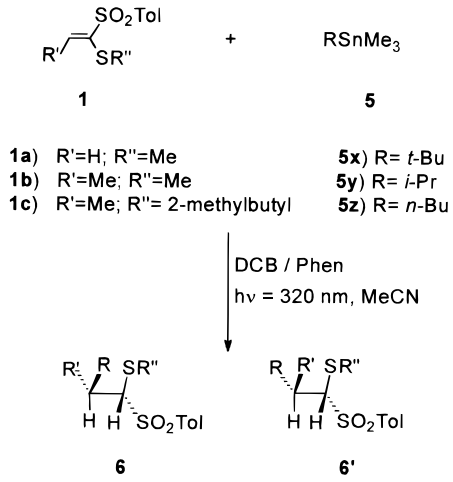

Table 1. Alkylation Yield by Irradiation of Alkenes 1 with Stannane 5 in the Presence of DCB/Phen

alkene	stannane	irradn time (h)	product (% yield)[a]	isomer distribution (% on the total adduct yield)
1a	**5x**	6	**6ax** (40), **7** (8)	
1b	**5x**	6	**6bx** (52)	**6** (100)
1b	**5y**	6	**6by** + **6′by** (60)	**6/6′** (69/ 31)
1b	**5z**	20	**6bz** + **6′bz** (59)	**6/6′** (50/50)
1c	**5x**	18	**6cx** (52)[b]	**6** (100)

[a] Isolated yields. [b] Mixture of diastereoisomers (in 1 to 1 ratio) due to the presence of a further stereogenic center with R″ group (= 2-methylbutyl).

mental Section), showing that the alkylation of ketene dithioacetal *S*,*S*-dioxides by using radical-chain methods in the intermolecular mode is ineffective. We thus turned to stoichiometric methods for producing the key alkyl radicals. These were obtained in two ways, through the recently developed photoinduced electron transfer (PET) method and by photochemical hydrogen transfer.

Alkylation via Photoinduced Electron Transfer. This is based upon the oxidation of a donor by an excited acceptor and the fragmentation of the resulting radical cation.[13] Tetraalkylstannanes were chosen as donors, and various acceptors were tested. These were 1,4-dicyanobenzene (DCB), 1,4-dicyanonaphthalene, 1,2,4,5-tetracyanobenzene, and tetramethyl pyromellitate. All of these acceptors worked to some extent, but the best results were obtained by using DCB as electron-acceptor and phenanthrene (Phen) as a secondary donor. This allowed us to carry out the reaction by using Pyrex-filtered light which is absorbed by Phen. The reactivity of alkene **1** was tested by employing three stannanes as a radical source: *t*-$BuSnMe_3$ (**5x**), *i*-$PrSnMe_3$ (**5y**), and Bu_4Sn (**5z**). Under these conditions, the alkylation was successful, and the results are shown in Scheme 2 and Table 1.

The isolated yields of the thiosulfones **6** were moderate (40−60%), in part due to the fact that precipitation of tin-containing byproducts during the irradiation made it difficult to carry out the reaction to completion. The reaction generally led cleanly to adducts **6**, as shown by GC and TLC, except in the case of **1a**, where disulfone **7** was formed as a side product. This resulted from the

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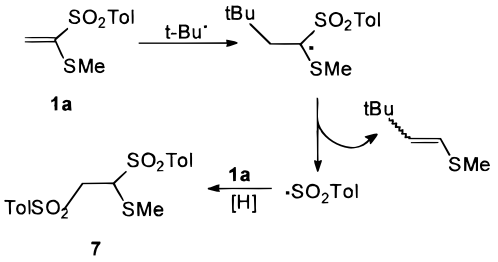
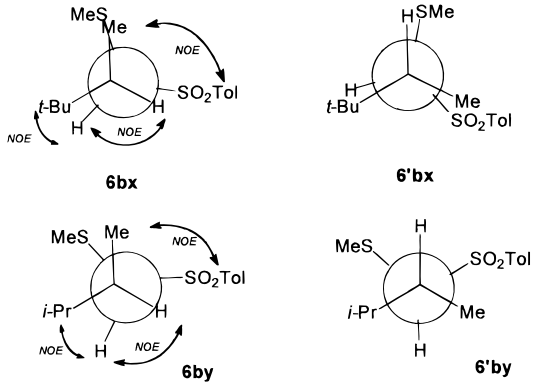
Scheme 3



Scheme 4



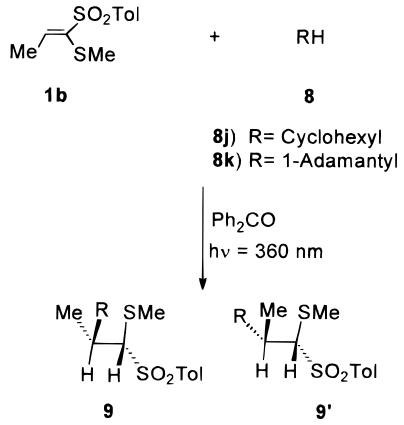
addition of the tosyl radical to the starting material (see Scheme 3 for a rationalization). This side path caused a decrease in the yield of **6ax** (40%, compare with 50% with **1b** as the substrate). Addition to alkene **1b** led to the formation of two diastereomers **6** and **6′** (two stereogenic centers were formed). The stereoselectivity of the reaction depended on the steric hindrance of the attacking alkyl radical. With a tertiary radical (*t*-Bu), a single diastereoisomer was isolated and identified as the *u* (1*R*,2*S*/1*S*,2*R*) diastereoisomer (**6bx**) with the NMR data. The presence of bulky substituents made the rotation around C_1-C_2 bond hindered, so that the most favored rotamer was observed. In the proton spectrum, a close to zero coupling constant between H-1 and H-2 was observed, resulting from a gauche arrangement with a dihedral angle ca. 90°. The most stable rotamer had the *t*-Bu group near to H-1 (Scheme 4 shows the Newman projections along C_1-C_2 bond). The spatial arrangement of substituents was derived from 1D-NOE difference and 2D-NOESY spectra (see Experimental Section). A computational study was carried out for the two *t*-Bu derivatives and confirmed that **6bx** was the low energy isomer. A conformational search showed that the two diastereoisomers (**6bx** and **6′bx**) exhibited four and six minima, respectively. The most stable conformer of **6bx** (Scheme 4) was 3.22 kcal/mol lower in energy than the most stable conformer of the other isomer (**6′bx**). The large computed difference ensured that isomer **6bx** was more stable than **6′bx** and confirmed the above NMR experimental evidence. The situation changed with secondary or primary radicals. Addition of an *i*-Pr radical gave both stereoisomers (**6by** and **6′by**) with a low selectivity (**6**/**6′** 2.2/1). As in the previous case, the rotation around C_1-C_2 bond was hindered for the major one (**6by**); the coupling constant between H-1 and H-2 (1.5 Hz) was consistent with a dihedral angle of ca. 60° (Scheme 4). The configuration of both diastereisomers was attributed on the basis of NMR data (see Experimental Section). With the *n*-butyl radical, no stereoselection was observed (**6bz**/**6′bz** 1/1). Introducing a bulky group R″ in the sulfide moiety caused

Table 2. Alkylation Yield by Irradiation of Alkenes 1 with Hydrocarbons in the Presence of Benzophenone

alkene	hydrocarbon	irradn time (h)	product (% yield)[a]	isomer distribution (% on the total adduct yield))
1b	**8j**	15	**9bj** + **9′bj** (89)	**9/9′** (82/18)
1b	**8k**	18	**9bk** (90)	**9** (100)

[a] Isolated yields.

Scheme 5



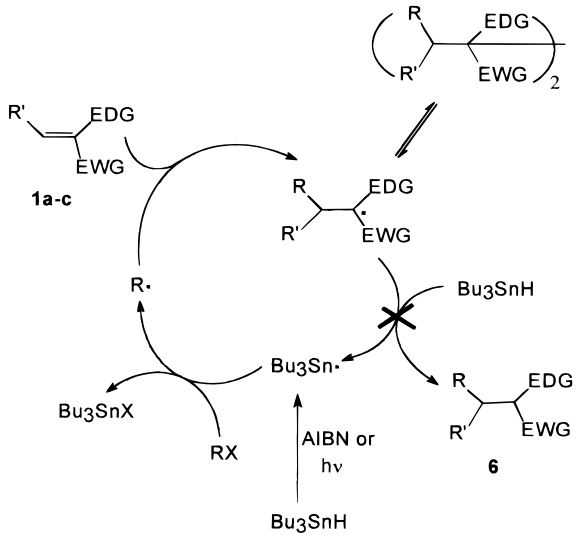
no change in the reaction course, and addition of the *tert*-butyl radical to **1c** (R″ = 2-methylbutyl) occurred with the same selectivity as in the case of **1b**.

The Hydrogen Transfer Pathway. Another stoichiometric method for generating a radical is photochemical hydrogen abstraction by means of an nπ* triplet, e.g., benzophenone.[14] Ogura reported the high yield functionalization of ketene thioacetal *S*,*S*-dioxides with various hydroxy (alkoxy)alkyl radicals generated from alcohols or ethers by irradiation with an equimolecular amount of benzophenone.[5,10] We explored whether the same scheme could be applied to hydrocarbons possessing no activated C−H bond. As it appears from Table 2 and Scheme 5 the result was positive. The reaction was first tested with the cyclohexyl radical. The alkylation in neat cyclohexane occurred with a surprisingly high yield (89%), and the stereoselectivity was larger than with the isopropyl radical (**9bj/9′bj** 4.5/1, compared to **6by/6′by** 2/1, see Tables 1 and 2). Furthermore the radical coupling product cyclohexyldiphenylmethanol was detected only in traces. The reaction with adamantane was also carried out. In this case the selectivity of the alkylation (at the bridged or bridgehead position) was a further interesting issue. The reaction was best carried out in benzene (1 M, in acetonitrile the yield was lower), and a single isomer, the 1-adamantyl derivative **9bk**, was isolated by column chromatography (90%). Most of the adamantyl radicals were trapped by the olefin, and only traces of side products (phenyladamantane, bisadamantane) were detected (see Experimental Section). Traces of 1-adamantanol and, to an even lesser extent, of 2-adamantanone were also detected and arose from the reaction of the radicals with residual oxygen.

Discussion

A large body of theoretical and experimental evidence supports the stabilization of a radical site by the copresence of an electron-donating and an electron-withdrawing group ("captodative effect" or "merostabilization").[1h,i] From the synthetic point of view, this has been exploited in the easy addition of various radicals to alkenes such as α-amino or α-thio nitriles or esters.[15a−d]

Scheme 6



The presently studied α-thiosulfones **1a**−**c** are known to pertain to this category. However, our attempt to alkylate these molecules through classical tin hydride methods, both thermal or photochemical, led to no result (in contrast vinyl sulfones undergo easy radical chain alkylation under these conditions).[15e] We feel that this can be rationalized by the peculiar captodative stabilization of the adduct radical.[11] It has previously been shown that captodative radicals are poor hydrogen abstractors and easily dimerize. In the present case, the stabilization of the adduct radical makes hydrogen abstraction from Bu_3SnH too slow and precludes propagation of the radical-chain process (Scheme 6).

Stoichiometric methods were successful, however. The first method we used is based on photoinduced electron transfer. When a light-absorbing acceptor A is excited (A*), it becomes a strong oxidant [E_{red} (A*) = E_{red} (A) + E_{exc} (A)]. This oxidizes a donor RD,where D is a donating moiety (eq 1), and the radical cation thus formed fragments to generate an alkyl radical (R•) (eq 2).[13]

$$A^* + RD \rightarrow A^{-\bullet} + RD^{+\bullet} \quad (1)$$

$$RD^{+\bullet} \rightarrow R\bullet + D^{+} \quad (2)$$

$$A^{-\bullet} + RD^{+\bullet} \rightarrow A + RD \quad (3)$$

This method produces radicals from unconventional donors [RD may be a tetraalkylstannane, a tetralkylsilane, a 2,2-dialkyl (or 2-alkyl-2-aryl)dioxolane] under mild conditions since the oxidant is the in situ generated A*, and the use of a strong inorganic oxidant normally employed in ET methods for radical reactions is avoided.

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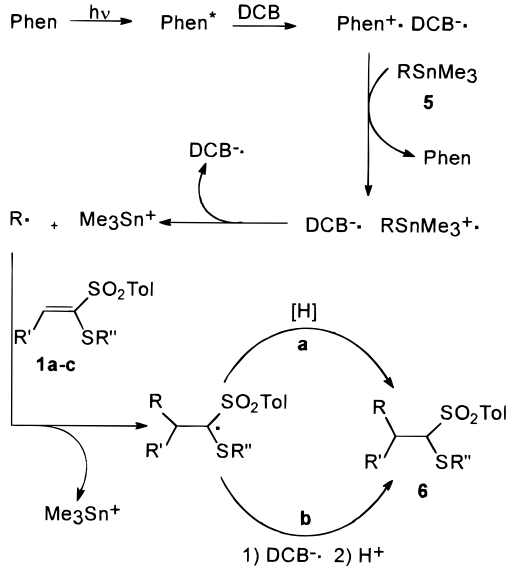
Scheme 7



Aromatic nitriles and esters are used as acceptors. Recently we described the synthetic application of this process for the addition of photogenerated radicals to electron-poor olefins.[16,17] When a synthesis of this type is planned, some requirements must be met: (1) E_{red} (A*) must be high enough to oxidize the donor; (2) E_{red} (A) must be low enough to allow the reduction of the adduct radical by $A^{-\bullet}$ (See Scheme 7); (3) back electron transfer (eq 3) must be controlled. Choosing the right donor−acceptor couple according to the olefin used as a trap (α,β-unsaturated ketones,[18] esters and nitriles[16,19]) determines the outcome. In the present case the best results were obtained by using the DCB/Phen pair.

The mechanism of the reaction is depicted in Scheme 7. When Phen is excited, it transfers an electron to the acceptor, and the radical cation thus formed oxidizes the stannane, finally yielding an alkyl radical after fragmentation.[20] The use of a secondary donor (Phen in this case) favors radical ion diffusion and thus offers an enhanced chance of radical cation fragmentation (eq 2) vs back electron transfer (eq 3); in turn, the radical adds to the captodative olefin. The process is terminated by reduction of the radical, either through hydrogen abstraction (from the solvent or the stannane; path a) or by electron transfer from the radical anion and proton addition[16] (path b). When the reaction was carried out in the presence of 0.1% D_2O, no deuteration was observed in the product by NMR spectroscopy (see Experimental Section). This is in contrast with what observed in the alkylation of α,β-unsaturated esters and nitriles by the same method[16] and is in accordance with the fact that captodative carbanions are difficult to obtain and are quite unstable. Indeed, such anions are known to be readily oxidized to captodative radicals.[1a] Thus, we infer that path a is preferred. Apparently, despite the markedly negative reduction potential of DCB (E_{red} $A/A^{-\bullet}$ = −1.6 V vs SCE), ET from the corresponding radical anion to the adduct radical is slow. It may be that the radical adduct accumulates as the dimer (see Scheme 6) and then is slowly reduced to the final products **6**.

The formation of product **7** from **1a** is likely to result from the liberation of tosyl radicals from the adduct radical, again an indication that pathways different from hydrogen abstraction are significant for such a species. There is previous evidence for the elimination of tosyl radicals from α-thiosulfones under radical conditions.[21]

The addition gives exclusively the *u* (1*R*,2*S*/1*S*,2*R*) diastereoisomer with tertiary radicals, although a 1 to 1 mixture is obtained with primary radicals. This supports that the selectivity depends on the energy difference between the isomers **6** and **6′** as determined by the repulsion between the entering radical and the *p*-tosyl group. Thus, despite the different mechanism in the PET pathway (the educt radical is generated through an *oxidative* step, and then a *reduction* step completes the sequence), the regio- and stereochemistry of the reaction (the latter one determined in the final hydrogen abstraction step) are the same as in the classical radical-chain alkylation.

The second method for the generation of radicals involves triplet benzophenone. Hydrogen abstraction from cyclohexane under these conditions in fluid media has been thoroughly studied,[22−24] but no intermolecular addition of cyclohexyl radical produced by this pathway has been hitherto reported. The addition occurs with some stereoselectivity (4.5 to 1) with cyclohexane and with complete selectivity when the adamantyl radical is involved. The bulkiness of the latter species is obviously responsible for this result (as in the *t*-Bu case). Noteworthy, no adduct containing the 2-adamantyl radical has been obtained, despite the fact that hydrogen abstraction from adamantane by benzophenone, as in general by nπ* ketone triplets, is known to be rather unselective.[25] It thus appears that the selectivity arises at the addition step.

Conclusions

Captodative olefins are known as radicophiles, due to the stabilization of the adduct radical. However, this very fact may undermine the success of an alkylation reaction when this depends, as it is the case in a chain process, on the rate of hydrogen abstraction by this radical (see

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(20) (a) ΔG_{ET} (S_1) for electron transfer from phenanthrene (E_{OX} = 1.50 V vs SCE)[20b] to DCB is negative (−7.6 kcal/mol).[20c] ΔG_{ET} (S_1)for the electron-transfer process between DCB and Bu_4Sn is −20 kcal/mol as calculated by means of the Weller equation (E_{OX} Bu_4Sn = 1.75 V vs SCE, converted from the IP value[20d] by means of the Miller equation).[20e] K_{SV} measured from fluorescence quenching is 80 M^{-1}.[19] Under the present conditions, however, the absorbing species is phenanthrene and oxidation of the stannane **5** is accomplished by $Phe^{+\bullet}$, a slightly endothermic process. Cosentisization by this method has been previously demonstrated to be particularly effective.[16,20c,f] (b) Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1963**, *85*, 2124. (c) Borg, R. M.; Arnold, D. R.; Cameron, T. S. *Can. J. Chem.* **1984**, *62*, 1785. (d) Wong, C. L.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5593 (e) Miller, L. L.; Nordblom, G. D.; Mayeda, E. A. *J. Org. Chem.* **1972**, *37*, 916. (f) Schaap, A. P.; Lopez, L.; Gagnon, S. D. *J. Am. Chem. Soc.* **1983**, *105*, 663.
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Scheme 6), hence, the failure of the tin hydride method with ketene dithioacetal *S,S*-dioxides. Stoichiometric methods are effective, however, and we reported here two photoinitiated methods for the radical alkylation of such alkenes. These procedures involve unusual radical precursors and are based on the activation of the C−Sn bond in tetraalkylstannanes via SET oxidation and, even more remarkably, of the C−H bond in alkanes by H abstraction. The reaction is carried out under mild conditions and, at least with bulky groups, occurs with a degree of selectivity (100% with tertiary radicals) not often documented with open-chain derivatives. This contrasts with the failure of the tributyltin hydride method and enlarges the scope of the synthesis of substituted α-thiosulfones, affording an alternative to direct alkylation of α-thiosulfones via the enolate,[2] which is complementary to that method when the required alkyl halide is not easily available.

Experimental Section

General. ^{1}H, ^{13}C, ^{13}C-DEPT and 2D-Correlated NMR spectra were recorded on a 300 MHz spectrometer in $CDCl_3$ solutions, and chemical shifts are reported in ppm downfield from TMS. 1-(Methylthio)-1-[(4-methylphenyl)sulfonyl)]ethene **1a**,[26] (*E*)-1-(methylthio)-1-[(4-methylphenyl)sulfonyl)]propene **1b**,[2] and stannanes **5x**[18] and **5y**[18] were prepared according to literature methods. Tetrabutylstannane, chloromethyl *p*-tolyl sulfone, 2-methylbutanthiol, and 1,4-dicyanobenzene were commercial samples and were used without purification. Acetonitrile was refluxed over CaH_2 and distilled just before use; benzene and toluene were distilled from sodium−benzophenone ketyl radical. The photochemical reactions were performed by using nitrogen-purged solution and a multilamp reactor fitted with six 15-W phosphor-coated lamps (maximum of emission, 320 or 360 nm) for the irradiation. The reaction course was followed by TLC (cyclohexane−ethyl acetate) and GC. Workup of the photolytes involved concentration in vacuo and chromatographic separation using Merck 60 silica gel. Calculations reported in this paper were performed with the Gaussian 94 suite program.[27] Computational study was carried out using semiempirical PM3 method.[28]

Synthesis of (*E*)-1-(2-Methylbutylthio)-1-[(4-methylphenyl)sulfonyl)]propene (1c). This compound was prepared according to Lissel's[29] and Ogura's[2] procedures as detailed in the following. To a biphasic mixture of chloromethyl *p*-tolyl sulfone (500 mg, 2.44 mmol) and methyltrioctylammonium chloride (Aliquat) (99 mg, 0.24 mmol) in toluene (6 mL) and a 17.6% aqueous NaOH solution (5 mL) was added 2-methylbutanthiol in toluene (2 mL). The resulting mixture was stirred at room temperature for 17 h. The toluene layer was separated, and the aqueous one was extracted with further toluene. The combined organic phase was dried over anhydrous Na_2SO_4 and evaporated. The residue was purified on a silica gel column (cyclohexane/ethyl acetate 98:2 as eluant) to give 359 mg of 2-(methylbutylthio)-methyl *p*-tolyl sulfone **(2)** (54% yield) as a colorless syrup.

2: ^{1}H NMR δ 0.85 (t, 3H, J = 7 Hz), 0.95 (d, 3H, J = 7 Hz), 1.1−1.3 (m, 1H), 1.3−1.5 (m, 1H), 1.5−1.65 (m, 1H), 2.45 (s, 3H), 2.6−2.75 (AB part of an ABX system, 2H), 3.9 (s, 2H), 7.35−7.85 (AA′BB′ system, 4H). IR, (neat) ν/cm^{-1} 1316, 1149. Anal. Calcd for $C_{13}H_{20}S_2O_2$: C, 57.32; H, 7.40. Found: C, 57.4; H, 7.3.

A biphasic mixture of **2** (1.1 g, 4.03 mmol) and Aliquat (1.63 g, 4.03 mmol) in toluene (20 mL) and 50% aqueous NaOH solution (23 mL) was stirred at room temperature for 1 h. Then freshly distilled ethyl bromide (600 μL, 8.07 mmol) in toluene (1 mL) was slowly dropped during 2 h, and the mixture was stirred overnight. The toluene phase was washed with water and separated, while the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was dried and evaporated under reduced pressure to give a syrup. Purification on a silica gel column (cyclohexane/ethyl acetate 96:4 as eluant) gave 1.02 g of 1-(2-methylbutylthio)-1-[(4-methylphenyl)sulfonyl)]propane **(3)** (84% yield) as a colorless syrup (mixture of diastereoisomers).

3: ^{1}H NMR δ 0.85 (t, 3H, J = 7 Hz), 0.95 (d, 3H, J = 7 Hz), 1,10 (t, 3H, J = 7 Hz), 1.1−1.6 (m, 4H), 2.15−2.35 (m, 1H), 2.45 (s, 3H), 2.4−2.8 (m, 2H), 3.65 (m, 1H), 7.35−7.85 (AA′BB′ system, 4H). IR, (neat) ν/cm^{-1} 1313, 1143. Anal. Calcd for $C_{15}H_{24}S_2O_2$: C, 59.96; H, 8.05. Found: C, 60.0; H, 8.0.

To a stirred solution of **3** (300 mg, 1.0 mmol) in CH_2Cl_2 (1.0 mL) under argon atmosphere, was added sulfuryl chloride (120 μL, 1.5 mmol) in CH_2Cl_2 (1.0 mL) dropwise at −15 °C, and the mixture was stirred at the same temperature for 30 min. The organic phase was then washed with water and separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried (anhydrous Na_2SO_4). After removal of the volatile compounds under reduced pressure, the residue was purified on a silica gel column (cyclohexane/ethyl acetate 97:3 as eluant) to give 315 mg of 1-chloro-1-(2-methylbutylthio)-1-[(4-methylphenyl)sulfonyl)]propane **(4)** (94% yield, mixture of diastereoisomers) as a colorless oil.

4: ^{1}H NMR δ 0.9 (t, 3H, J = 7 Hz), 1.0 (d, 3H, J = 7 Hz), 1,20 (t, 3H, J = 7 Hz), 1.15−1.35 (m, 1H), 1.35−1.55 (m, 1H), 1.55−1.7 (m, 1H), 2.1−2.3 (m, 2H), 2.45 (s, 3H), 2.85−3.1 (AB part of an ABX system, 2H), 7.35−7.85 (AA′BB′ system, 4H). IR, (neat) ν/cm^{-1} 1324, 1149. Anal. Calcd for $C_{15}H_{23}ClS_2O_2$: C, 53.79; H, 6.92. Found: C, 53.7; H, 6.9.

In a round-bottom flask fitted with a reflux condenser with a HCl trap on top was placed **4** (425 mg, 1.26 mmol) in toluene (40 mL). The solution was refluxed under nitrogen for 48 h while its color changed to brown. Water was added, and the toluene phase separated. The aqueous phase was extracted with CH_2Cl_2, and the combined organic phases were dried over Na_2SO_4. After solvent removal, the residue was purified on a silica gel column (cyclohexane/ethyl acetate 96:4 as eluant) obtaining 308 mg of 1-(2-methylbutylthio)-1-[(4-methylphenyl)-sulfonyl)]propene **(1c)** (*E* isomer) as a colorless oil (82% yield).

1c: ^{1}H NMR δ 0.85 (t, 3H, J = 7 Hz), 0.90 (d, 3H, J = 7 Hz), 1.1−1.55 (m, 3H), 2.05 (d, 3H, J = 7 Hz), 2.45 (s, 3H), 2.55−2.75 (AB part of an ABX system, 2H), 7.35−7.85 (AA′BB′ system, 4H), 7.60 (q, 1H, J = 7 Hz). IR, (neat) ν/cm^{-1} 1600, 1321, 1153. Anal. Calcd for $C_{15}H_{22}S_2O_2$: C, 60.37; H, 7.43. Found: C, 60.3; H, 7.4.

Attempted Alkylation of 1b by Using Bu_3SnH. Thermal Standard Procedure. To a stirred solution of **1b** (50 mg, 0.206 mmol), AIBN (2.4 mg, 0.015 mmol), and *tert*-butyl iodide (30 μL, 0.25 mmol) in dry toluene (7 mL) at reflux temperature under argon atmosphere was slowly added tributyltin hydride (67 μL, 0.25 mmol) in dry toluene (1.2 mL) via a dropping funnel in 3 h. Then another aliquot of AIBN was added (2.4 mg), and further tributyltin hydride (67 μL, 0.25 mmol) in dry toluene (1.2 mL) was added in 3,h. The reflux was continued for a further 1 h. The alkene was recovered almost quantitatively (consumption < 5%) at the end of the reaction.

Photochemical Standard Procedure. A solution of 145 mg (0.6 mmol, 0.12 M) of **1b**, 57 μL (0.48 mmol, 0.1 M) of *t*-BuI, and 27 mg (0.71 mmol, 0.14 M) of $NaBH_4$ in dry EtOH (5 mL) was purged under argon for 10 min, 26 μL (0.1 mmol, 0.02 M) of Bu_3SnCl were added, and the resulting mixture was irradiated at 320 nm for 45 min. A further aliquot of Bu_3SnCl

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(26 μL) was added, and irradiation was continued for 45 min. GC analysis showed only a small consumption of the substrate (<5%).

Alkylation of Alkenes 1 by Using Stannanes 5. General Procedure. The alkene (**1**) (0.1 M), a stannane (**5**) (0.05 M), Phen (0.05 M), and DCB (0.05 M) were dissolved in MeCN (35 mL), and the solution was divided into two portions that were irradiated (320 nm) in quartz tubes until the stannane was consumed. The solvent was then removed and the residue purified on a chromatographic column by using cyclohexanes−ethyl acetate mixtures as eluants.

Photochemical Reaction between 1a and 5x. A solution of **1a** (400 mg, 0.05 M), **5x** (390 mg, 0.05 M), Phen (315 mg, 0.05 M), and DCB (225 mg, 0.05 M) in MeCN (35 mL) was irradiated for 6 h. Workup gave 200 mg of 1-(methylthio)-1-[(4-methylphenyl)sulfonyl)]-3,3-dimethylbutane (**6ax**) (40%) as a white solid (mp 108−109 °C) and 49 mg of 1-(methylthio)-1,2-(bis-*p*-tolylsulfonyl)ethane (**7**) (8%) as a white solid (mp 155−157 °C dec).

6ax: ^{1}H NMR δ 0.95 (s, 9H), 1.4 (dd, 1H, J = 8 Hz and 14 Hz), 2.05 (dd, 1H, J = 2 Hz and 14 Hz), 2.25 (s, 3H), 2.45 (s, 3H), 3.6−3.7 (dd, 1H, J = 2 and 8 Hz), 7.35−7.85 (AA′BB′ system, 4H). IR, (KBr) ν/cm^{-1} 1300, 1140. Anal. Calcd for $C_{14}H_{22}S_2O_2$: C, 58.70; H, 7.74. Found: C, 58.6; H, 7.7.

7: ^{1}H NMR δ 2.15 (s, 3H), 2.49 (s, 3H), 2.5 (s, 3H), 3.4 (dd, 1H, J = 11 and 14 Hz), 3.9 (dd, 1H, J = 2 and 14 Hz), 4.2 (dd, 1H, J = 2 and 11 Hz), 7.37 and 7.85 (AA′BB′ system, 4H), 7.40 and 7.85 (AA′BB′ system, 4H). IR, (KBr) ν/cm^{-1} 1304, 1139. Anal. Calcd for $C_{17}H_{20}S_3O_4$: C, 53.10; H, 5.24. Found: C, 53.2; H, 5.3.

Photochemical Reaction between 1b and 5x. A solution of **1b** (425 mg, 0.05 M), **5x** (390 mg, 0.05 M), Phen (315 mg, 0.05 M), and DCB (225 mg, 0.05 M) in MeCN (35 mL) was irradiated for 6 h. Workup gave 274 mg of [1*R*,2*S*/1*S*,2*R*]-1-(methylthio)-1-[(4-methylphenyl)sulfonyl)]-2,3,3-trimethylbutane (**6bx**) (52% yield) as a colorless oil. The stereochemistry of this diastereoisomer was attributed on the basis of the following spectroscopic evidences. The coupling constant between H-1 and H-2 in the proton spectrum was close to zero (J < 1 Hz), and this was consistent with a dihedral angle ca. 90°. The relative configuration was derived from NOE experiments. Thus, the irradiation of H-1 caused enhancements for H-2 and *t*-Bu resonances in the corresponding 1D-NOE difference spectrum. A selective irradiation of *t*-Bu group was not possible owing to the small chemical shift difference between *t*-Bu and Me-2 signals. Thus, the spatial arrangement of the other substituents was derived from the NOESY experiment in C_6D_6 solution (a better chemical shifts separation was found). A NOE correlation between SMe and *t*-Bu groups was found as well as a correlation between Me-2 and the *ortho*-aromatic protons.

The same experiment was carried out in the presence of 0.1% D_2O, and the ^{1}H NMR spectrum **of 6bx** showed no significant deuteration on H-1.

6bx: ^{1}H NMR δ 0.8 (d, 3H, J = 7 Hz), 0.9 (s, 9H), 2.10 (s, 3H), 2.20 (dq, 1H, J = 0.7 and 7 Hz), 2.45 (s, 3H), 3.85 (d, 1H, J = 0.7 Hz), 7.35−7.85 (AA′BB′ system, 4H). ^{13}C NMR δ 10.7 (CH_3), 17.8 (CH_3), 21.5 (CH_3), 27.3 (3 CH_3), 33.9, 41.0 (CH), 74.7 (CH), 129.4 (CH), 128.8 (CH), 134.1, 144.6. IR, (neat) ν/cm^{-1} 1301, 1140. Anal. Calcd for $C_{15}H_{24}S_2O_2$: C, 59.96; H, 8.05. Found: C, 59.9; H, 8.0.

Photochemical Reaction between 1b and 5y. A solution of **1b** (425 mg, 0.05 M), **5y** (360 mg, 0.05 M), Phen (315 mg, 0.05 M), and DCB (225 mg, 0.05 M) in MeCN (35 mL) was irradiated for 6 h. Workup gave 300 mg of 1-(methylthio)-1-[(4-methylphenyl)sulfonyl)]-2,3-dimethylbutane as a diastereomeric mixture (**6by** + **6′by**) (60% yield, **6**/**6′** 69/31) as a colorless oil. In the proton spectrum, the resonances of each diastereoisomer were separated in C_6D_6 solution and were identified with COSY spectra. As in the case above, the major one (**6by**) showed a small coupling constant between H-1 and H-2 (1.5 Hz), thus a value which corresponded to a gauche arrangement with a torsion angle close to 60°. In the NOE difference experiment, the irradiation of H-1 caused enhancements for H-2 and H-3. The NOESY spectrum revealed a close neighboring between the *ortho*-hydrogens of the aromatic ring and H-2 as well as with Me-2. In the minor one (**6′by**), the coupling constant between H-1 and H-2 was 6 Hz; this value corresponded to an average coupling between different rotamers. In the NOE difference experiment, the irradiation of H-1 caused enhancement only of Me-2. Thus **6by** was the 1*R*,2*S*/1*S*,2*R* isomer and **6′by** the 1*R*,2*R*/1*S*,2*S* isomer.

6by: ^{1}H NMR (C_6D_6) δ 0.81 (d, 6H, J = 7 Hz), 1.1 (d, 3H, J = 7 Hz, Me-2), 1.75 (m, 1H, H-3), 1.9 (s, 3H, SMe), 1.95 (s, 3H, CH_3), 2.4 (m, 1H, H-2), 3.92 (d, 1H, J = 1.5 Hz, H-1), 6.8 (m, 2H), 8.0 (m, 2H). IR, (neat) ν/cm^{-1} 1311, 1143. ^{13}C NMR (C_6D_6) δ 12.6 (CH_3), 17.3 (CH_3), 19.4 (CH_3), 20.2 (CH_3), 20.8 (CH_3), 32.1 (CH), 38.8 (CH), 75.7 (CH), 129.1 (CH), 129.7 (CH), 135.7, 143.8. **6′by:** ^{1}H NMR (C_6D_6) δ 0.85 (d, 3H, J = 7 Hz), 0.9 (d, 3H, J = 7 Hz), 1.3 (d, 3H, J = 7 Hz, Me-2), 1.8 (s, 3H, SMe), 2.0 (s, 3H, CH_3), 2.25 (m, 1H, H-2), 2.5 (m, 1H, H-3), 3.6 (d, 1H, J = 6 Hz, H-1), 6.8 (m, 2H), 8.0 (m, 2H). ^{13}C NMR (C_6D_6) δ 12.8 (CH_3), 16.2 (CH_3), 16.8 (CH_3), 20.8 (CH_3), 21.8 (CH_3), 28.7 (CH), 39.4 (CH), 76.2 (CH), 128.9 (CH), 129.4 (CH), 136.9, 143.6. IR, (neat) ν/cm^{-1} 1301, 1140.

Photochemical Reaction between 1b and 5z. A solution of **1b** (425 mg, 0.05 M), **5z** (575 μL, 0.05 M), Phen (315 mg, 0.05 M), and DCB (225 mg, 0.05 M) in MeCN (35 mL) was irradiated for 20 h. After workup the two diastereoisomers of 1-(methylthio)-1-[(4-methylphenyl)sulfonyl)]-2-methylhexane were isolated (about 165 mg each) (**6bz** and **6′bz**) (59% yield, **6**/**6′** 50/50) both as colorless oils.

6bz: ^{1}H NMR δ 0.85 (t, 3H, J = 7 Hz), 0.9 (d, 3H, J = 7 Hz), 1.2 (m, 4H), 1.45 (m, 2H), 2.05 (s, 3H), 2.4 (dq, 1H, J = 1.5 and 7 Hz), 2.5 (s, 3H), 3.7 (d, 1H, J = 1.5 Hz), 7.35−7.85 (AA′BB′ system, 4H). ^{13}C NMR δ 13.9 (CH_3), 15.0 (CH_3),18.1 (CH_3), 21.5 (CH_3), 22.3 (CH_3), 29.0 (CH_2), 32.6 (CH_2), 35.2 (CH_2), 77.6 (CH), 129.4 (CH), 129.5 (CH), 135.0, 144.6. IR, (neat) ν/cm^{-1} 1313, 1145. Anal. Calcd for $C_{15}H_{24}S_2O_2$: C, 59.96; H, 8.05. Found: C, 60.0; H, 7.9.

6′bz: ^{1}H NMR δ 0.85 (t, 3H, J = 7 Hz), 1.1 (d, 3H, J = 7 Hz), 1.2 (m, 4H), 1.45 (m, 2H), 2.05 (s, 3H), 2.4 (dq, 1H, J = 2 and 7 Hz), 2.5 (s, 3H), 3.6 (d, 1H, J = 2 Hz), 7.35−7.85 (AA′BB′ system, 4H). ^{13}C NMR δ 13.8 (CH_3), 18.3 (CH_3), 18.6 (CH_3), 21.5 (CH_3), 22.5 (CH_3), 29.6 (CH_2), 30.4 (CH_2), 33.4 (CH_2), 79.4 (CH), 129.4 (CH), 129.4 (CH), 135.0, 144.6. IR, (neat) ν/cm^{-1} 1313, 1145. Anal. Calcd for $C_{15}H_{24}S_2O_2$: C, 59.96; H, 8.05. Found: C, 59.9; H, 8.1.

Photochemical Reaction between 1c and 5x. A solution of **1c** (1.05 g, 0.1 M), **5x** (390 mg, 0.05 M), Phen (315 mg, 0.05 M), and DCB (225 mg, 0.05 M) in MeCN (35 mL) was irradiated for 18 h. Workup gave 325 mg of 1-(2-methylbutylthio)-1-[(4-methylphenyl)sulfonyl)]-2,3,3-trimethylbutane (**6cx**) (52%, mixture of two diastereoisomer, ratio 1:1) as a white solid (mp 48−50 °C). Diastereoisomerism arose from the presence of a chiral center in the sulfide moiety (1*R*2*S*2′*R*/1*S*2*R*2′*S* and 1*S*2*R*2′*R*/1*R*2*S*2′*S* isomers). These were indistinguishable by ^{1}H NMR, while most signals were split in ^{13}C NMR (as indicated in parentheses).

6cx ^{1}H NMR δ 0.75−1 (m, 18H), 1.0−1.5 (m, 3H), 2.15−2.25 (m, 1H), 2.35−2.65 (m, 2H), 2.45 (s, 3H), 3.9 (bs, 1H), 7.35−7.85 (AA′BB′ system, 4H). ^{13}C NMR δ 11.1 (10.8) (CH_3), 18.7 (18.9) (CH_3), 21.5 (21.5) (CH_3), 27.4 (27.4) (CH_3), 28.7 (28.5), 34.0 (34.0) (CH_2), 34.5 (34.4) (CH_2), 41.0 (40.9) (CH), 41.9 (42.1) (CH) 73.1 (73.2) (CH), 129.3 (129.3) (CH), 129.9 (129.9) (CH), 134.2 (134.2), 144.5 (144.5).

Alkylation of Alkene 1b by Using Alkanes. Photochemical reaction of 1b in Cyclohexane (8j) in the Presence of Benzophenone. A solution of **1b** (127 mg, 0.015 M) and benzophenone (96 mg, 0.015M) in cyclohexane (35 mL) was irradiated for 15 h (λ = 360 nm). After the usual workup, the residue was purified on a silica gel column (cyclohexane/ethyl acetate 95:5 as eluant) to give 153 mg of 2-cyclohexyl-1-(methylthio)-1-[(4-methylphenyl)sulfonyl)]propane as a diastereomeric mixture **9bj** + **9′bj** (89% yield, **9**/**9′** 82/18) as a colorless oil.

9bj: ^{1}H NMR (from the mixture) δ 0.9 (d, 3H), 0.75−1.8 (m, 11H), 2.05 (s, 3H), 2.15 (dqui, 1H, J = 2 and 7 Hz), 2.45 (s, 3H), 3.85 (d, 1H, J = 2 Hz), 7.35−7.85 (AA′BB′ system, 4H). IR, (neat) ν/cm^{-1} 1312, 1143.

9′bj: ^{1}H NMR (from the mixture) δ 0.9 (d, 3H), 0.75−1.8 (m, 12H), 1.95 (s, 3H), 2.45 (s, 3H), 3.65 (d, 1H, J = 6 Hz), 7.35−7.85 (AA′BB′ system, 4H). IR, (neat) ν/cm^{-1} 1312, 1143.

Photochemical Reaction of 1b with Adamantane (8k) in the Presence of Benzophenone. A solution of **1b** (850 mg, 0.1 M), adamantane (4.77 g, 1.0 M), and benzophenone (638 mg, 0.1 M) in benzene (35 mL) was irradiated for 18 h (λ = 360 nm). After the usual workup, the residue was purified on a silica gel column (cyclohexane/ethyl acetate 96:4 as eluant) to give 1.18 g of 2-(1′-adamantyl)-1-(methylthio)-1-[(4-methylphenyl)sulfonyl)]propane (90% yield) as a white solid (mp 109−110 °C, from methanol). Traces of 1-adamantanol, 2-adamantanone, 1-phenyladamantane,[30] and bisadamantane[31] were detected by GC and identified through their MS spectra and by comparison with authentic samples (commercial samples, Aldrich, for the first two).

9bk: ^{1}H NMR δ 0.8 (d, 3H, J = 7 Hz), 1.4−1.9 (m, 12H), 1.95 (bs, 3H), 2.0 (q, 1H, J = 7 Hz), 2.10 (s, 3H), 2.45 (s, 3H), 3.90 (bs, 1H), 7.35−7.85 (AA′BB′ system, 4H). ^{13}C NMR δ 9.2 (CH_3), 17.5 (CH_3), 21.5 (CH_3), 28.2 (CH), 35.4, 36.7 (CH_2), 39.3 (CH_2), 41.6 (CH), 73.3 (CH), 129.2 (CH), 129.7 (CH), 134.0, 144.5. IR, (KBr) ν/cm^{-1} 1309, 1143. Anal. Calcd for $C_{21}H_{30}S_2O_2$: C, 66.62; H, 7.99. Found: C, 66.7; H, 7.9.

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