2. $KMnO_4/t$-BuOH/H_2O. A mixture of 1.00 g (3.02 mmol) of **6b**, 200 mL of *tert*-butyl and 40 mL of water was heated to 75–80 °C, and potassium permanganate (6.19 g, 0.0392 mol) was then added. After 17 h, the solution was filtered while hot to remove MnO_2, and a 20% t-BuOH/H_2O mixture was used to wash the solid well. Enough aqueous $NaHSO_3$ was added to the filtrate to destroy any residual MnO_2. Solvents were evaporated until a minimum amount of water remained. When the aqueous solution was acidified with 2 N HCl, **7b** precipitated as a yellow solid, 0.61 g (70%).

4-(2-Methoxyphenyl)-3-methylpyridine (8b). In 36 mL of diphenyl ether, 7.28 g (0.0254 mol) of **7b** was heated at 220 °C until CO_2 evolution was complete. The dark-brown solution was taken up in diethyl ether and then extracted four times with 3 N HCl. The resulting aqueous solution was backwashed with diethyl ether and then brought to pH 9 with concentrated NH_4OH. The basic solution was extracted three times with CH_2Cl_2. The combined extracts were washed with water and brine and then dried over $MgSO_4$. Solvent was evaporated and the resulting crude oil was distilled by Kugelrohr [100–130 °C (0.2 mmHg)] to give 4.20 g (83%) of **8b** as a clear oil: MS, m/z 199 (M^+), 184, 168; ^1H NMR ($CDCl_3$, 100 MHz) δ 2.12 (3 H, s), 3.74 (3 H, s), 6.93–7.46 (5 H, m), 8.43 (1 H, d, J = 5 Hz), 8.46 (1 H, s); IR (thin film) 2970, 2840, 1600, 1480, 1270, 1240, 750 cm^{-1}.

Anal. Calcd for $C_{13}H_{13}NO$: M_r 199.100. Found: M_r 199.100.

Acknowledgment. We are grateful to the National Institute of Drug Abuse and the Oregon State University Honors Program for support. We also thank the N. L. Tartar Foundation for providing a fellowship (D.L.W.).

Registry No. 3a, 83463-00-7; **3c**, 3988-74-7; **3f**, 83463-01-8; **4a**, 1192-62-7; **4b**, 3194-15-8; **4e**, 4208-57-5; **5a**, 81115-35-7; **5b**, 83463-02-9; **5c**, 80927-46-4; **5d**, 83463-03-0; **5e**, 83463-04-1; **5f**, 83463-05-2; **5g**, 83463-06-3; **6a**, 81115-36-8; **6b**, 83463-07-4; **6c**, 5689-65-6; **6d**, 83463-08-5; **6e**, 83463-09-6; **6f**, 83463-10-9; **6g**, 83476-27-1; **7a**, 81115-37-9; **7b**, 83463-11-0; **7c**, 83463-12-1; **7d**, 83476-28-2; **7e**, 83463-13-2; **7f**, 83463-14-3; **8a**, 5958-00-9; **8b**, 83463-15-4; **8c**, 939-23-1; **8d**, 2052-92-8; **8e**, 83463-16-5; **8f**, 14924-93-7; **11b**, 10477-94-8; **12**, 83463-17-6; iii, 3557-70-8; hydroxylamine hydrochloride, 5470-11-1; 1,3-diphenyl-1-oxo-2-propene, 94-41-7; *p*-bromophenyl acetate, 99-90-1.

Supplementary Material Available: Full experimental data for the preparation of **8a,c–g**, **9**, **10**, **11a,b**, **12** (13 pages). Ordering information is given on any current masthead page.

Reduction of Sulfonyl Halides with Iodotrimethylsilane: New Observations[1]

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Sulfonyl chlorides are easily and efficiently prepared by the chlorosulfonation reaction of arenes and alkanes.[2] For this reason their conversion to other organic sulfur compounds, in which the sulfur atom has a lower oxidation state, is of great synthetic value. Since organic disulfides are valuable starting materials for the synthesis of a variety of sulfenyl[3] and sulfinyl[4] compounds, the reductive coupling of sulfonyl chlorides to the corresponding disulfides constitutes an important process.

Table I. Reduction of Sulfonyl Halides and Related Compounds with Iodotrimethylsilane (1)

entry	reduced compd	% yield of disulfide	
1	$PhSO_2Cl$	94	95[a]
2	p-$CH_3C_6H_4SO_2Cl$	95	80[a]
3	o-$CH_3C_6H_4SO_2Cl$	95[b]	94[a,b]
4	2,4,6-$Me_3C_6H_2SO_2Cl$	80[b]	77[a,b]
5	2,4,6-i-$Pr_3C_6H_2SO_2Cl$	85[b,c]	
6	$PhSO_2I$	97	
7	$PhSO_2F$	97	
8	$PhSO_2SPh$	97.5	
9	$PhSO_2SMe$	mixture of disulfides	
10	PhS(O)SPh	98	96[a]
11	p-$CH_3C_6H_4S(O)SC_6H_4$-p-CH_3		96[a]
12	$CH_3S(O)SPh$	mixture of disulfides	
13	$PhSOCH_3$	96	

[a] Me_3SiCl/NaI in CH_2Cl_2 or benzene. [b] Compounds not obtained in a pure form after short-column chromatography. [c] This disulfide appeared to decompose partially during storage; it was purified by preparative TLC with hexane as a developing solvent (mp 82–87 °C) and analyzed by MS: m/e 470 (M^+), 235 (i-$Pr_3C_6H_2S^+$), 193 (i-$Pr_3C_6H_2^+$). However, its elemental analysis was not fully correct.

A recent report of Olah et al.[5] on the synthesis of disulfides from sulfonyl halides using iodotrimethylsilane as a reducing agent prompted us to publish the results of our independent studies on the synthetic and mechanistic aspects of this reaction which in some important details are different from those described by the above-quoted authors.

Thus, we have found that the reaction between sulfonyl chlorides and iodotrimethylsilane (1) in methylene chloride solution proceeds smoothly at room temperature within minutes (in some cases, hours), giving the corresponding disulfides **2** in high yields together with iodine, chlorotrimethylsilane, and hexamethyldisiloxane.

$$2RSO_2Cl + 10Me_3SiI \rightarrow RSSR + 5I_2 + 2\,Me_3SiCl + 4Me_3SiOSiMe_3$$

The reduction of sulfonyl halides can also be carried out with chlorotrimethylsilane in an inert solvent (benzene, chloroform, methylene chloride) and a suspension of sodium iodide even in the absence of a phase-transfer catalyst. In this case, however, the reaction requires a much longer time and a higher temperature especially for sterically hindered compounds. The results obtained are summarized in Table I.

However, in contrast to the report of Olah et al.,[5] we were able to detect the reaction intermediates formed during the reduction. Moreover, by means of the preparative TLC we succeeded in isolating these intermediates, which appeared to be the corresponding thiosulfonates **9**. It was also found that they are transiently formed not only during the reaction of **1** with sulfonyl chlorides and iodides but also with sulfinyl chlorides and alkyl sulfinates and that they disappear when the reduction is completed. Furthermore, in an independent experiment it was demonstrated that thiolsulfonates **9** are easily reduced by **1** to disulfides **2** at room temperature. These observations clearly demonstrate that thiolsulfonates **9** lie on the re-

(1) Organosulfur Compounds, Part 28. Part 27: Drabowicz, J.; Mikolajczyk, M. *Synth. Commun.* **1981**, *11*, 1025.
(2) Suter, C. M., "The Organic Chemistry of Sulfur"; Intrascience Research Foundation: Santa Monica, CA, 1969.
(3) Kühle, E. "The Chemistry of the Sulfenic Acids"; Georg Thieme Verlag: Stuttgart, 1973.
(4) Douglas, I. B.; Norton, R. V. *J. Org. Chem.* **1968**, *33*, 2104. Douglas, I. B. *J. Org. Chem.* **1974**, *39*, 563.
(5) Olah, G. A.; Narang, S. C.; Field, L. D.; Salem, G. F. *J. Org. Chem.* **1980**, *45*, 4792.

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action path to the formation of the disulfides and strongly suggest that the formation of the S–S bond must take place at least partially at an earlier reduction stage and not only as a result of the sulfenyl iodide coupling reaction as claimed by Olah et al.[5] It seems reasonable to asssume that sulfinyl iodide **7** is responsible for the S–S bond formation, giving at first unstable α-disulfoxide **8**, which undergoes rearrangement to thiolsulfonate **9**.[6]

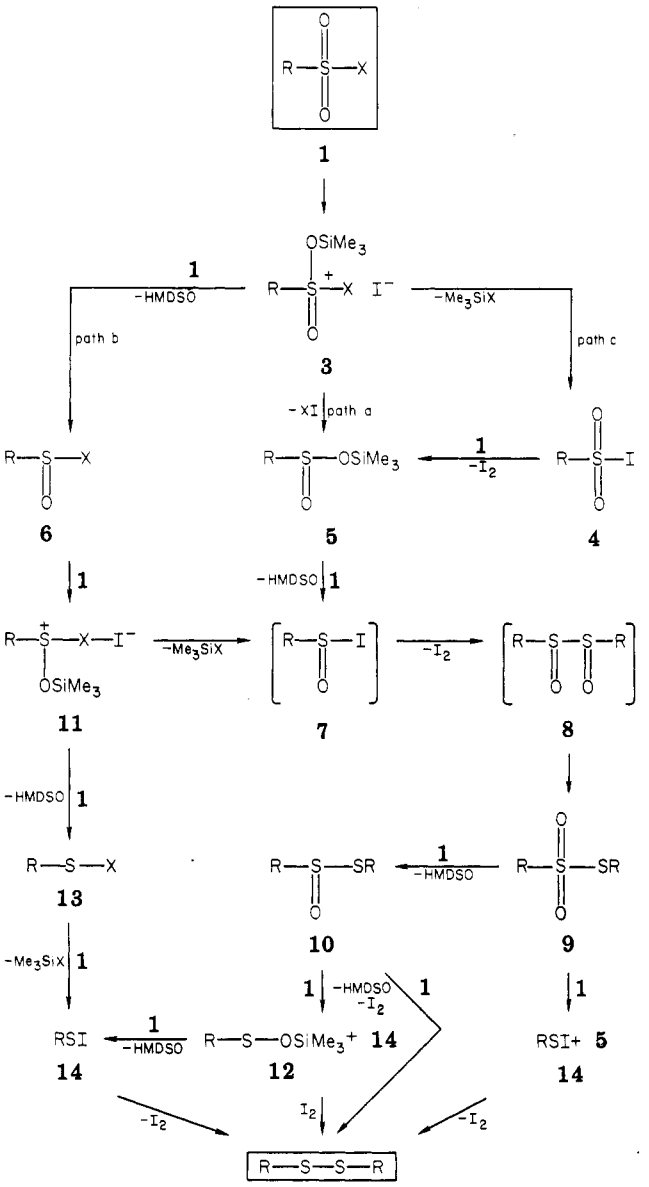
In regard to the reduction of thiolsulfonates by **1**, one should note that the reduction of thiolsulfonates having different substituents at the sulfonyl and sulfenyl sulfur atoms should afford unsymmetrical disulfides. We have found, however, that a mixture of unsymmetrical and both possible symmetrical disulfides was always produced in such a reaction. This may be caused either by the disproportionation of the unsymmetrical disulfide formed upon reduction or rather by cleavage of thiolsulfonate **9** by **1**, leading to trimethylsilyl sulfinate **5** and sulfenyl iodide **14**. Unsymmetrically substituted thiosulfinates **10** behave similarly.

Another interesting feature of the reaction under consideration is that when an insufficient amount of **1** is used or when the reaction is stopped before completion, in addition to disulfide **2** and thiolsulfonate **9**, unreacted sulfonyl chloride is also always present. On the contrary, sulfonyl iodide **4**, when reacted with **1** under the same reaction conditions, is consumed immediately, while thiolsulfonate **9** still can be observed. On the other hand, benzenesulfonyl fluoride is reduced by **1**[7] much more slowly than the corresponding chloride and no thiolsulfonate **9** is observed.

In view of the experimental observations presented above the mechanistic interpretation of the reduction of sulfonyl halides to disulfides by **1** suggested by Olah et al. seems to be oversimplified. We propose, therefore, a more complex mechanistic picture for the reaction under consideration shown in Scheme I. It should be noted that all isolated and hypothetical intermediary compounds were also proved to undergo reduction to disulfides under the conditions described above (see Table I).

The reaction of sulfonyl halides with iodotrimethylsilane **1** is most likely initiated by the formation of the sulfoxonium salt **3**, which can further react three different ways. The attack of the iodide anion on the halogen atom in **3** (path a) may lead to silyl sulfinate **5**, which, in turn, on treatment with **1** splits off hexamethyldisiloxane (HMDSO) and gives sulfinyl iodide **7**. As mentioned above, **7** couples to α-disulfoxide **8**, which rearranges to the stable and isolable thiolsulfonate **9**. Its further reduction to disulfide by **1** occurs via thiosulfinate **10** and/or sulfenyl iodide **14** as shown in Scheme I. The salt **3** can also react with the second molecule of **1** (path b) to give sulfinyl halide **6**, which may be transformed into **7** via **11** or converted into **14** upon reacting with **1**. Finally, the attack of iodide anion on the positively charged sulfur atom in **3** followed by elimination of chlorotrimethylsilane (path c) may result in the formation of sulfonyl iodide undergoing the reduction according to path a.

Scheme I



The relative contribution of each direction is, in our opinion, strongly dependent on the nature of X in **3**. When X = I, the attack of the iodide anion on the iodine atom should be fast, and reaction leading to **5** (path a) should predominate. Additionally, the low electronegativity of iodine facilitates the formation of the salt **3** (X = I), which, in sum, results in an immediate disappearance of sulfonyl iodide. When X = Cl, the attack of iodide anion on the chlorine atom in **3** (X = Cl) takes place more slowly. Therefore, it seems reasonable to assume that in this case the reduction may follow also path b or c. At last, when X = F, the formation of the salt **3** (X = F) is much more difficult due to the high electronegativity of fluorine. This may be responsible for a significantly lower reduction rate as compared with sulfonyl chloride and iodide. Since the attack of iodide anion on the fluorine atom in **3** (X = F; path a) as well as the fluorine–iodine exchange (path c) due to the higher sulfur–fluorine bond energy in comparison with other sulfur–halogen bonds[8] is less probable,

(6) For the discussion on the rearrangement of α-disulfoxides to thiolsulfonates, see: Chan, M. M.; Kice, J. L. *J. Am. Chem. Soc.* **1976**, *98*, 7711. Oae, S.; Kim, Y. H.; Takata, T.; Fukushima, D. *Tetrahedron Lett.* **1977**, 1195.

(7) Benzenesulfonyl fluoride was found in our hands to undergo the reduction with **1** under the conditions described in the experimental section in contrast to the statement of Olah et al.[5] In control experiments carried out with a double excess of iodotrimethylsilane we found that benzenesulfonyl chloride was fully converted into the corresponding disulfide after 1 h, whereas in the reduction of benzenesulfonyl fluoride the beginning of the reduction was observed (TLC) only after ca. 20 h and the reaction was completed after ca. 50 h. When this reaction was performed as described by Olah et al.[5] in an inert atmosphere, the same relation was observed.

(8) Sokolskii, G. A. *Zh. Obshch, Khim.* **1966**, *36*, 860; *J. Gen. Chem. USSR* **1966**, *36*, 875.

it is believed that the fluorine–iodine exchange takes place only as a result of the reaction between sulfenyl fluoride **13** (X = F) and **1** and, therefore, no formation of thiosulfonate **9** can be observed.

Experimental Section

General Procedures. TLC was performed on the Kieselgel $60F_{254}$ plates produced by Merck. Mass spectra were recorded with a GCMS-LKB-900S instrument. Melting points are uncorrected. All sulfonyl chlorides were commercially available compounds. Iodotrimethylsilane was synthesized from HMDSO and I_2 in the presence of Al.[9] Benzenesulfonyl iodide and fluoride were prepared by the standard procedures.[2]

Reduction of Benzenesulfonyl Chloride with Iodotrimethylsilane (1). To a solution of benzenesulfonyl chloride (0.69 g, 0.0039 mol) in CH_2Cl_2 (10–15 mL) was added iodotrimethylsilane (4.3 g, 0.0215 mol, ~10% excess) and the mixture was left at room temperature. The progress of the reaction was monitored by TLC ($CHCl_3/CCl_4$, 1:1), and following spots were observed: $PhSO_2SPh$, R_f 0.29; $PhSO_2Cl$, R_f 0.5; and Ph_2S_2, R_f 0.66. When the reduction was completed, the reaction solution was poured into a solution of sodium bicarbonate and iodine was reduced by the solution of sodium thiosulfate. The aqueous layer was extracted with methylene chloride. The combined organic layers were dried over $MgSO_4$ and evaporated to give the crude product, which was purified by short-column chromatography on silica gel with CCl_4 or hexane as eluents. Evaporation of the solvent gave diphenyl disulfide (0.4 g, 93.9%), mp 58–60 °C (lit.[10] mp 61–62 °C).

For isolation of the intermediary compound the reaction was stopped before completion or carried out with an insufficient amount of Me_3SiI. The reaction mixture obtained after the usual workup with $NaHCO_3$ and $Na_2S_2O_3$ was separated by means of preparative TLC ($CHCl_3/CCl_4$, 1:1). The product having R_f 0.29 was isolated. Its structure as phenyl benzenethiosulfonate was established by MS: m/e 250 (M^+), 218 ($PhSSPh^+$). This compound was independently reduced by Me_3SiI to give diphenyl disulfide (Table I, entry 8).

Acknowledgment. We thank Ms. Janina Kmiec for her helpful experimental assistance.

Registry No. **1**, 16029-98-4; $PhSO_2Cl$, 98-09-9; *p*-$CH_3C_6H_4SO_2Cl$, 98-59-9; *o*-$CH_3C_6H_4SO_2Cl$, 133-59-5; 2,4,6-$Me_3C_6H_2SO_2Cl$, 773-64-8; 2,4,6-*i*-$Pr_3c_6H_2SO_2Cl$, 6553-96-4; $PhSO_2I$, 1950-77-2; $PhSO_2F$, 368-43-4; $PhSO_2SPh$, 1212-08-4; $PhSO_2SMe$, 1125-25-3; PhS(O)SPh, 1208-20-4; *p*-$CH_3C_6H_4S(O)SC_6H_4$-*p*-CH_3, 6481-73-8; $CH_3S(O)SPh$, 40249-95-4; $PhSOCH_3$, 28715-70-0; PhSSPh, 882-33-7; *p*-$CH_3C_6H_4SSC_6H_4$-*p*-CH_3, 103-19-5; *o*-$CH_3C_6H_4SSC_6H_4$-*o*-CH_3, 4032-80-8; 2,4,6-$Me_3C_6H_2SSC_6H_2$-2,4,6-Me_3, 1483-92-7; 2,4,6-*i*-$Pr_3C_6H_2SSC_6H_2$-2,4,6-*i*-Pr_3, 20875-34-7; PhSSMe, 14173-25-2.

(9) Jung, M. E.; Lyster, M. *J. Am. Chem. Soc.* **1977**, *99*, 968.
(10) Reid, E. E. "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Co.: New York, 1960; Vol. 3.

General Route to Highly Functionalized Cyclopentane Derivatives by Intramolecular C–H Insertion

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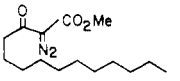
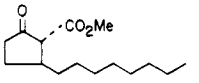
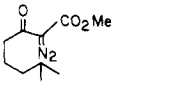
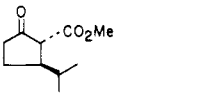
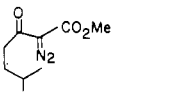
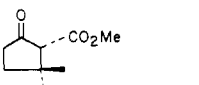
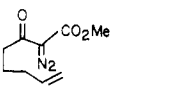
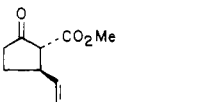
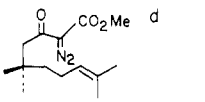
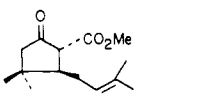
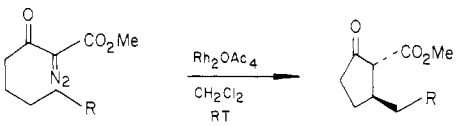
The development of new methods for carbocyclic ring formation is fundamental to the development of synthetic organic chemistry. We report a simple method for the preparation of 2-carbalkoxy cyclopentanones, versatile intermediates for the elaboration of highly functionalized cyclopentane derivatives.

Table I

starting diazo ester [a]	product [b]	yield, [c] %
 1	 6	68
 2	 7	55
 3	 8	64
 4	 9	48
 [d] 5	 10	77

[a] See the Experimental Section for details of ester preparation and cyclization. [b] All products are racemic. [c] Yields are for pure chromatographed material. [d] Reference 3.



There are a variety of examples in the literature of intramolecular C–H insertion by diazo ketones.[2] In many of these cases, the diazo moiety was constrained to be quite close to the C–H bond into which insertion took place. We have found that C–H insertion can be an efficient process even in an acyclic, freely rotating system.

We chose to investigate the cyclization of α-diazo β-keto esters because they are readily prepared, by the method of Weiler[3,4] followed by diazo transfer,[5,6] and because the resultant β-keto esters would be versatile intermediates for further elaboration. The cyclizations that have been

(1) Correspondence should be addressed to this author at the Department of Chemistry, University of Delaware, Newark, DE 19711.
(2) (a) For a recent review of intramolecular reactions of diazocarbonyl compounds, see: Burke, S. D.; Grieco, P. A. *Org. React.* **1979**, *26*, 361. (b) For an early study of intramolecular C–H insertion, see: Ledon, H.; Linstrumelle, G.; Julia, S. *Bull. Soc. Chem. Fr.* **1973**, 2071. (c) For a detailed analysis of metal-catalyzed carbenoid reactions, see: Wulfman, D. S.; Poling, B. "Reactive Intermediates"; Abramovitch, R. A., Ed.; Plenum: New York, 1980; Vol. 1.
(3) The keto ester corresponding to **5** was prepared from citral. Addition of methyl lithium followed by PCC oxidation gave the enone. Exposure to Me_2CuLi led to the saturated methyl ketone, which was carbomethoxylated by treatment with NaH and dimethyl carbonate in THF at reflux. We thank Mr. Samir A. Saleh for carrying out this preparation.
(4) Huckin, S. N.; Weiler, L. *J. Am. Chem. Soc.* **1974**, *96*, 1082.
(5) Regitz, M.; Hocker, J.; Liedhegener, A. "Organic Synthesis"; Wiley; New York, 1973; Collect. Vol. V, p 197.
(6) Taber, D. F.; Saleh, S. A.; Korsmeyer, R. W. *J. Org. Chem.* **1980**, *45*, 4699.

0022-3263/82/1947-4808$01.25/0