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.

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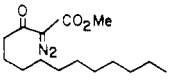
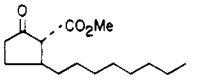
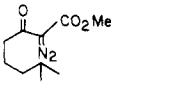
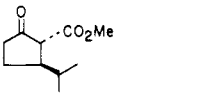
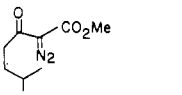
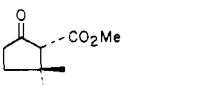
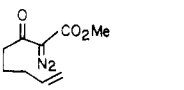
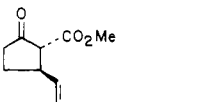
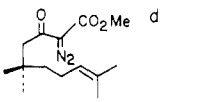
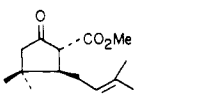
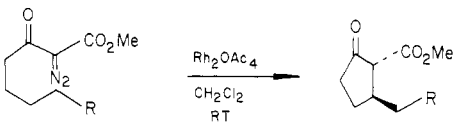
The development of new methods for carbocyclic ring formation is fundamental to the development of synthetic organic chemistry. We report a simple method for the preparation of 2-carbalkoxy cyclopentanones, versatile intermediates for the elaboration of highly functionalized cyclopentane derivatives.

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.
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carried out are summarized in Table I.

It should be noted that under these reaction conditions allylic C–H insertion, to produce **9**, competes effectively with the usually efficient[7a] intramolecular cyclopropanation.[8] Methylene C–H insertion is substantially more rapid than methyl C–H insertion,[9] allowing clean formation of **10**. While it might be extrapolated that methine should be more efficient than methylene insertion, ring-size effects predominate, so that **7** is formed from **2**.

The functionalized cyclopentanes produced by this cyclization should be versatile intermediates for elaboration to complex natural products. Keto ester **10**, for example, prepared by Tsuji,[10] has been converted by him to methyl dihydrojasmonate[10] and 18-hydroxyestrone.[11]

Experimental Section

General Methods. ^{1}H NMR spectra were determined on a JEOLCO MH-100 spectrometer as solutions in $CDCl_3$. Chemical shifts are reported in parts per million downfield from the internal reference tetramethylsilane. Couplings (J) are in hertz. The infrared spectra (IR) were recorded on a Perkin-Elmer 257 spectrometer as solutions in CCl_4 and are reported in reciprocal centimeters. Mass spectra were determined at 70 eV on an LKB 9000 gas chromatograph–mass spectrometer interfaced with a PDP-12 computer system and are reported as mass per unit charge, with intensities as a percentage of the peak of greatest ion current having $m/z \geq 100$ in parentheses. High-resolution mass spectroscopy was carried out on a VG 7070f double-focusing mass spectrometer. Organic chemicals were purchased from Aldrich Chemical Co. Organometallics were purchased from Alfa Inorganics and were titrated prior to use. Solvent mixtures (e.g., 5% ethyl acetate/hexane) are volume/volume mixtures. The R_f values indicated refer to thin-layer chromatography on Analtech 2.5 × 10 cm, 250-μm analytical plates coated with silica gel GF. Column chromatography was carried out by using TLC-mesh silica gel, following the procedure we have described.[12]

Preparation of 6.[13] Diazo ester **1** (1.55 g, 5.50 mmol), prepared by alkylation of the dianion of methyl acetoacetate[4] followed by diazo transfer,[5,6] was diluted with 30 mL of CH_2Cl_2 (dried by filtration through K_2CO_3) under N_2. Rhodium(II) acetate[7] (0.040 g) was added, and the mixture stirred at room temperature for 30 min. Vigorous gas evolution was observed, and the solution turned a bright emerald green. The reaction mixture was diluted with 4% aqueous HCl and extracted with CH_2Cl_2. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The residue was chromatographed on 50 g of silica gel with 4% EtOAc/petroleum ether. The first 950 mL was discarded. The next 350 mL was concentrated in vacuo to give **6** as a colorless oil: 0.948 g (68%); TLC (10% EtOAc/hexane) R_f 0.40; ^{1}H NMR 0.90 (t, J = 7, 3 H), 1.2–1.8 (m, 16 H), 2.20 (m, 1 H), 2.40 (t, J = 7, 2 H), 2.90 (d, J = 11, 1 H), 3.80 (s, 3 H); IR 2920, 2850, 1750, 1725, 1430, 1115; MS, 254 (4.6), 233 (15), 199 (33), 184 (27), 141 (100), 109 (56); exact mass calcd for $C_{15}H_{26}O_3$ 254.1882, obsd 254.1863.

7: TLC (10% EtOAc/hexane) R_f 0.27; ^{1}H NMR 0.94 (d, J = 8, 3 H), (0.98, d, J = 8, 3 H); 1.44 – 1.90, (m, 2 H); 2.04 – 2.26, (m, 1 H); 2.28 – 2.58, (m, 2 H); 2.96, (d, J = 11, 1 H); 3.80, (s, 3 H). IR: 2955, 1750, 1725, 1430, 1245, 1110, 970. MS, 184 (12), 152 (34), 141 (93), 109 (100); exact mass calcd for $C_{10}H_{16}O_3$ 184.1100, obsd 184.1085.

8: TLC (10% EtOAc/hexane) R_f 0.29; ^{1}H NMR 1.12 (s, 3 H), 1.24 (s, 3 H), 1.70–2.25 (m, 2 H), 2.35–2.60 (m, 2 H), 2.97 (s, 1 H), 3.80 (s, 3 H); IR 2940, 1715, 1645, 1605, 1430, 1315, 1200, 1030; MS, 170 (15), 155 (17), 138 (41), 123 (100), 115 (36); exact mass calcd for $C_9H_{14}O_3$ 170.0943, obsd 170.0942.

9: TLC (10% EtOAc/hexane) R_f 0.23; ^{1}H NMR 1.68 (m, 1 H), 2.1–2.6 (m, 3 H), 3.10 (d, J = 11, 1 H), 3.24 (m, 1 H), 3.78 (s, 3 H), 5.12 (d, J = 10, 1 H), 5.20 (d, J = 16, 1 H), 5.91 (ddd, J = 16, 10, 7, 1 H); IR 2950, 1755, 1725, 1650, 1430, 1265, 985, 910; MS, 168 (36), 136 (54), 112 (78), 108 (79), 81 (100); exact mass calcd for $C_9H_{12}O_3$ 168.0786, obsd 168.0769.

10: TLC (10% EtOAc/hexane) R_f 0.35; ^{1}H NMR 0.99 (s, 3 H), 1.28 (s, 3 H), 1.69 (s, 3 H), 1.72 (s, 3 H), 1.9–2.7 (m, 5 H), 3.05 (d, J = 11, 1 H), 3.78 (s, 3 H), 5.14 (m, 1 H); IR 1720, 1430, 1365, 1345, 1330, 1295, 1210, 1140, 1020; MS, 238 (6.2), 207 (4.9), 206 (4.6), 191 (3.8), 179 (9.1), 137 (16), 123 (100). Exact mass calcd for $C_{14}H_{22}O_3$ 238.1569 obsd 238.1580.

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Registry No. **1**, 83221-08-3; **2**, 83221-09-4; **3**, 83221-10-7; **4**, 83221-11-8; **5**, 83221-12-9; (±)-**6**, 83221-13-0; (±)-**7**, 83221-14-1; (±)-**8**, 83221-15-2; (±)-**9**, 83221-16-3; (±)-**10**, 83221-17-4; rhodium(II) acetate, 15956-28-2.

(7) (a) For use of Rh_2OAc_4 to catalyze intramolecular cyclopropanations, see Anciaux, A. J.; Hubert, A. J.; Noels, A. F.; Petinot, N.; Teyssie, P. *J. Org. Chem.* **1980**, *45*, 695. (b) For studies of other carbenoid reactions mediated by rhodium catalysts, see: Doyle, M. P.; Tamblyn, W. H.; Bagheri, V. *Ibid.* **1981**, *46*, 5094. (c) For an earlier study of copper-catalyzed C–H insertion to form cyclopentanes, see: Kuwajima, I.; Higuchi, Y.; Iwasawa, H.; Sato, T. *Chem. Lett.* **1976**, 1271.

(8) The cyclopropane is also formed in the cyclization of **4**, in about 10% yield. We have not investigated the other products of these cyclizations.

(9) For a study of intermolecular C–H insertion using rhodium catalysts, see: Demonceau, A.; Noels, A. F.; Hubert, A. J.; Teyssie, P. *J. Chem. Soc., Chem. Commun.* **1981**, 688.

(10) Tsuji, J.; Kobayashi, Y.; Kataoka, H.; Takahashi, T. *Tetrahedron Lett.* **1980**, *21*, 1475.

(11) Tsuji, J.; Okumoto, H.; Kobayashi, Y.; Takahashi, T. *Tetrahedron Lett.* **1981**, *22*, 1357.

(12) Taber, D. F. *J. Org. Chem.* **1982**, *47*, 1351.

(13) Cyclizations of **2–5** were carried out in the same way.

Acyl–Oxygen Cleavage in the Alkaline Hydrolysis of Activated Vinyl Esters

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The only observed route known for the basic hydrolysis of vinyl esters[2,3] is the $B_{Ac}2$ mechanism, which involves acyl–oxygen fission.[4] Nucleophilic catalysis in such hydrolysis also involves initial nucleophilic attack on the acyl group.[5] An earlier determination of the site of bond cleavage in the hydrolysis of vinyl acetate with $H_2{}^{18}O$ suggested simultaneous cleavage of the vinyl–oxygen and acyl–oxygen bonds,[6] but later work which used a similar technique showed that acyl–oxygen cleavage is the only route involved.[7]

In view of the facile nucleophilic substitution of electrophilic olefins substituted by a leaving group on the β

(1) On sabbatical leave from the Department of Chemistry, University of Vermont, Burlington, Vermont.

(2) For a review, see Rekasheva, A. F. *Usp. Khim.* **1968**, *37*, 2272–2299.

(3) For a recent review, see Euranto, E. K. *Pure Appl. Chem.* **1977**, *49*, 1009–1020.

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(6) Kiprianova, L. A.; Rekasheva, A. F. *Dokl. Akad. Nauk SSSR* **1962**, *144*, 386–389. *Ibid.* **1963**, *153*, 642–645.

(7) Euranto, E. K.; Alhoniemi, A. *Acta Chem. Scand.* **1972**, *26*, 855–856.

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