solid. On recrystallization of the tricyclic adduct from ethanol, the methoxy group on C_3 was replaced by ethoxy. The X-ray structure and spectral data were obtained from this adduct **3g**: mp 102–106 °C; IR ($CHCl_3$) 2940, 2860, 2810, 1585, 1525, 1450, 1350, 1120 (br), 1085 (br), 1020, 990, 970, 900 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (dd, 1 H, Ar *H*), 7.50–7.45 (m, 2 H, Ar *H*), 7.40–7.25 (m, 5 H, Ar *H*), 4.43 (m, 1 H, J = 2.5, 2.9 Hz, C_4-H), 4.27–4.21 (m, 1 H, J = 2.5, 4.9, 9.9 Hz, C_9-H), 3.85 (m, 1 H, C_6-H), 3.65 (d, 1 H, J = 2.9 Hz, C_3-H), 3.65–3.54 (m, 1 H, $^1/_2$ OCH_2CH_3), 3.52–3.40 (m, 1 H, $^1/_2$ OCH_2CH_3), 2.93 (ddd, 1 H, J = 3.4, 9.9, 13.9 Hz, $^1/_2$ C_{10}-H_2), 2.31 (s, 3 H, N-CH_3), 1.32 (m, 1 H, $^1/_2$ C_{10}-H_2), 1.26 (t, 3 H, OCH_2CH_3). NMR analysis indicates that the material contains 10% of the epimer at C_3: ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.4, 142.8, 135.1, 131.7, 130.7, 129.1, 129.0, 128.8, 127.2, 126.9, 122.9, 94.9, 62.9, 59.0, 43.4, 39.3, 35.5, 15.5; high-resolution mass spectrum (CI) calcd for $C_{20}H_{22}N_2O_3S$ + H^+ 371.1429, found 371.1491. Anal. Calcd for $C_{20}H_{22}N_2O_3S$: C, 64.85; H, 5.99; N, 7.56; S, 8.64. Found: C, 64.75; H, 5.93; N, 7.52; S, 8.45.

Crystal data: $C_{20}H_{22}N_2O_3S$, M = 370.47, monoclinic, a = 7.920 (5) Å, b = 16.151 (14) Å, c = 20.688 (15) Å, β = 134.62 (3)°, U = 1883 (2) Å^3, Z = 4, D_c = 1.307 g/cm^3, $F(000)$ = 784. Mo Kα radiation (λ = 0.71069 Å), μ = 0.2 cm^{-1}. Space group $P2_1/c$ (C_2^5h) from systematic absences: $0k0$ when $k \neq 2n$ and $h0l$ when $l \neq 2n$. The structure was solved by direct methods and refined by full-matrix least-squares iterations using 1333 data with $I \geq 2\sigma(I)$ to R = 0.072, R_w = 0.082.

Acknowledgment. We are indebted to the National Cancer Institute for Grant CA 39351, to the American Cancer Society for Grant CH 272 and to CUNY for PSC research awards, which supported this work. NMR instruments used were obtained through Grants NSF-PCM 111745 and NIH RR 03214. Crystallographic computations were aided by NSF Instrument Grant CHE-8700787.

Registry No. **1a**, 33107-14-1; **1b**, 1723-72-4; **2a**, 627-50-9; **2b**, 1822-73-7; **2c**, 22103-05-5; **3b**, 118629-88-2; **3a** (C3 = OEt), 118629-89-3; **3a** (C3 = OMe), 118629-90-6; **4a**, 66-77-3; **4b**, 63409-02-9; **4c**, 35689-27-1; **4d**, 118629-77-9; **5a**, 118629-78-0; **5b**, 118629-79-1; **5c**, 118629-80-4; **5d**, 118629-81-5; **5e**, 118629-82-6; **5f**, 118629-83-7; **6b**, 118629-84-8; **6c**, 118629-85-9; **7b**, 118629-86-0; **7c**, 118629-87-1; 5-methoxyisoquinoline, 90806-58-9; 5-hydroxyisoquinoline, 2439-04-5; 1-chloro-2,4-dinitrobenzene, 97-00-7; 2-methyl-5-nitroisoquinolinium iodide, 42792-95-0; Amberlite-IRA-400-OH^-, 9002-24-8.

Supplementary Material Available: Crystallographic details for the adduct **3g** including atomic coordinates, anisotropic thermal parameters for the non-hydrogen atoms, bond lengths, bond angles, and torsion angles and experimental data for 5-methoxyisoquinoline and compound **1b** (12 pages). Ordering information is given on any current masthead page.

Reaction of [Hydroxy(tosyloxy)iodo]benzene and [Hydroxy(mesyloxy)iodo]benzene with Trimethylsilyl Enol Ethers. A New General Method for α-Sulfonyloxylation of Carbonyl Compounds

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Reaction of [hydroxy(tosyloxy)iodo]benzene (**1**) with trimethylsilyl enol ethers of aromatic ketones **4a–d**, alicyclic ketone **7**, aliphatic ketone **10**, and esters **13a–c** in dichloromethane at room temperature gives good yields of α-(tosyloxy)carbonyl compounds **5a–d**, **8**, **11**, and **14a–c**, respectively. The trimethylsilyl enol ether of ε-caprolactone **16** yields α-(tosyloxy)-ε-caprolactone **17** upon treatment with **1** in hexane at room temperature. Similarly, the trimethylsilyl derivatives **4a–c** and **13a–c** yield α-(mesyloxy)carbonyl compounds **18a–c** and **19a–c** upon treatment with [hydroxy(mesyloxy)iodo]benzene (**2**) in dichloromethane at room temperature. A possible pathway for these processes is discussed.

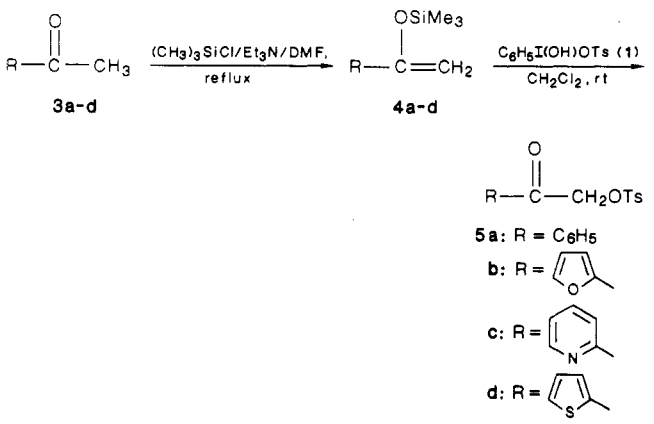
The preparation and reactions of α-(haloalkyl)carbonyl compounds have been widely studied,[1-3] and the scope and limitations of their reactions have been defined.[2] The chemistry of the related [1-(sulfonyloxy)alkyl]carbonyl compounds has received relatively little attention.[4-13] The superior nucleofugacity of sulfonyloxy group relative to halogen has been noted,[12] and α-sulfonyloxy ketones have been used in generation and study of α-keto carbocations[4-7,14] and in the functionalization of ketones.

The most common method for the synthesis of α-sulfonyloxy ketones obviously involves condensation of α-hydroxyalkyl ketones with a sulfonyl chloride, but the synthesis of α-hydroxyalkyl ketones often involves multiple steps.[6,7] There are other methods also for the synthesis of α-sulfonyloxy ketones, but they involve indirect ap-

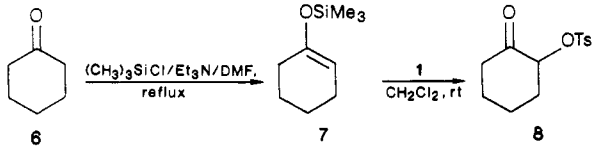
(1) Rappe, C. *The Chemistry of Carbon–Halogen Bond*; Patai, S., Ed.; Interscience: London, 1973; Part 2, pp 1071–1105.
(2) March, J. A. *Advanced Organic Chemistry*, 2nd ed.; McGraw-Hill: New York, 1977; pp 991–995.
(3) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: New York, 1972.
(4) Creary, X. *J. Am. Chem. Soc.* **1984**, *106*, 5568.
(5) Creary, X.; Geiger, C. C. *J. Am. Chem. Soc.* **1983**, *105*, 7123.
(6) Creary, X.; Geiger, C. C. *J. Am. Chem. Soc.* **1982**, *104*, 4151.
(7) Creary, X.; Rollin, A. J. *J. Org. Chem.* **1977**, *42*, 4226, 4231.
(8) Simons, S. S., Jr.; Pons, M.; Johnson, D. F. *J. Org. Chem.* **1980**, *45*, 3084 and references therein.
(9) Conia, J. M.; Salaun, J. R. *Acc. Chem. Res.* **1972**, *5*, 33.
(10) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487 and references therein.
(11) Hoffman, R. V. *Synthesis* **1985**, 760.
(12) Hoffman, R. V.; Jankowski, B. C.; Carr, C. S. *J. Org. Chem.* **1986**, *51*, 130.
(13) Newman, M. S.; Beal, P. F. *J. Am. Chem. Soc.* **1950**, *72*, 5161.
(14) Creary, X. *Acc. Chem. Res.* **1985**, *18*, 3.

0022-3263/89/1954-1101$01.50/0

Scheme I



Scheme II



proaches.[15,16] A recent paper[10] describes the preparation of α-(tosyloxy)alkyl ketones by the reaction of ketones with [hydroxy(tosyloxy)iodo]benzene (**1**).[17,18] The work we present here is complementary to this method with the advantages that the present reaction is regiospecific based on the structure of the trimethylsilyl ether (**10**), and it is general for any carbonyl compound for which the trimethylsilyl ether can be obtained. Another recent paper[12] reports that some α-[(arenesulfonyl)oxy]alkyl ketones can be prepared in good yields by the reaction of arenesulfonyl peroxide with enol acetates.

Recently, we described a facile route for the synthesis of α-methoxy ketones using hypervalent iodine oxidation of trimethylsilyl enol ethers.[19] We now report a general approach to α-sulfonyloxy ketones, esters, and a lactone by the reaction of [hydroxy(tosyloxy)indo]benzene (**1**) and [hydroxy(mesyloxy)iodo]benzene (**2**)[20] with the trimethylsilyl enol ethers of the corresponding carbonyl compounds.

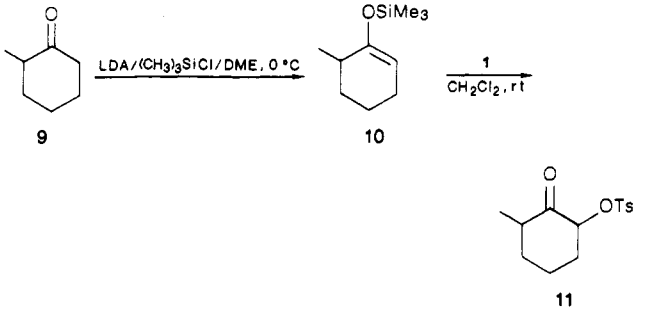
Results

Treatment of ketones **3a–d** and **6** (0.1 mol) with trimethylsilyl chloride (0.12 mol) and triethylamine (0.13 mol) in *N,N*-dimethylformamide (200 mL) at reflux temperature overnight afforded trimethylsilyl enol ethers **4a–d** and **7**, respectively,[21] and the reaction of ketone **9**, esters **12a–c**, and ϵ-caprolactone (**15**) (0.1 mol) with lithium diisopropylamide (0.1 mol) and trimethylsilyl chloride (0.12 mol) yielded trimethylsilyl enol ethers **10**,[22] **13a–c**,[23] and **16**,[24] respectively, in quantitative yield. When the trimethylsilyl enol ethers **4a–d** (12 mmol) were treated with [hydroxy(tosyloxy)iodo]benzene (**1**) (10 mmol) at room temperature for 2 h, α-tosyloxy ketones **5a–d** were obtained as is shown in Scheme I.

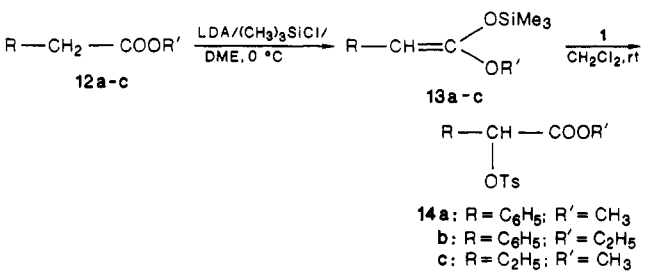
Similarly, the reaction of **1** with **7** afforded **8** (Scheme II).

The regioselectivity of the α-tosyloxylation was demonstrated by the reaction of regiospecifically prepared trimethylsilyl enol ether **10**[22] (12 mmol) with **1** (10 mmol)

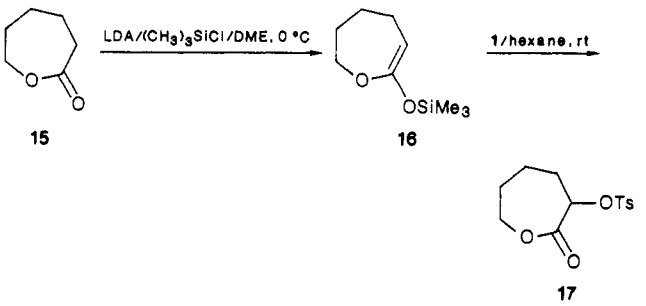
Scheme III



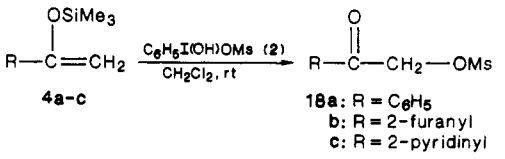
Scheme IV



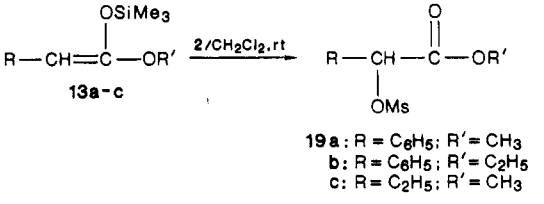
Scheme V



Scheme VI

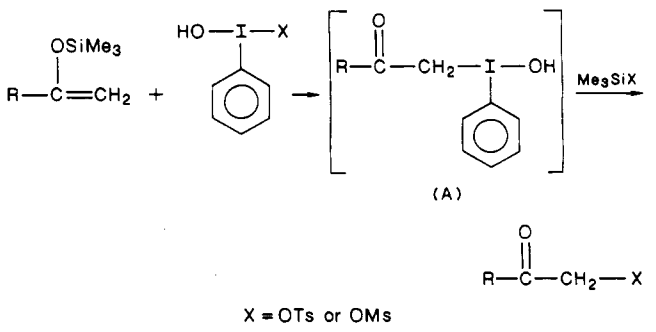


Scheme VII



(15) Tipson, R. S. *J. Org. Chem.* **1944**, *9*, 235.
(16) Crossland, R. K.; Servis, K. L. *J. Org. Chem.* **1970**, *35*, 3195.
(17) Neiland, O.; Karele, B. *J. Org. Chem. USSR (Engl. Trans.)* **1980**, *6*, 889.
(18) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1977**, *42*, 1476.
(19) Moriarty, R. M.; Prakash, O.; Duncan, M. P.; Vaid, R. K. *J. Org. Chem.* **1987**, *52*, 150.
(20) Zefirov, N. S.; Zhdankin, V. V.; Dankov, Y. V.; Kozmin, A. S.; Chizov, O. S. *Zh. Org. Khim.* **1985**, *21*, 2461.
(21) House, H. O.; Czuba, L. J.; Gall, M.; Olmstead, D. *J. Org. Chem.* **1969**, *34*, 2324.
(22) Fleming, I.; Paterson, I. *Synthesis* **1979**, 736.
(23) Ainsworth, C.; Chen, F.; Kuo, Y. *J. Organomet. Chem.* **1972**, *46*, 59.
(24) Paterson, I.; Fleming, I. *Tetrahedron Lett.* **1979**, 993.

Scheme VIII



in dichloromethane (50 mL) at room temperature to afford **11** (Scheme III).

The reaction was further extended to α-tosyloxylation of esters **12a–c** and a lactone **15**. Thus, when trimethylsilyl enol ethers of esters **13a–c** were treated with **1**, α-tosyloxy esters **14a–c** were obtained (Scheme IV), and trimethylsilyl enol ether of ε-caprolactone (**16**) on treatment with **1** afforded 2-(tosyloxy)-ε-caprolactone (**17**) (Scheme V).

The α-mesyloxylation reaction was performed in the same way for ketones and esters. Thus, when trimethylsilyl enol ethers **4a–c** and **13a–c** were treated with [hydroxy(mesyloxy)iodo]benzene (**2**), the α-mesyloxy ketones **18a–c** (Scheme VI) and α-mesyloxy esters **19a–c** (Scheme VII) were obtained, respectively.

Our method for the preparation of α-(sulfonyloxy)-carbonyl compounds offers several advantages over existing methods. In the first place the reaction is mild and general and gives uniformly high yields. In the second place, there is no need to prepare the α-hydroxyalkyl ketone precursors. Trimethylsilyl enol ethers are widely available and can be produced regiospecifically.[25] Furthermore, it is noteworthy that the N atoms in compounds **5c** and **18c** and the S atom in **5d** are not oxidized under the reaction conditions.

The structures of known compounds in literature are based upon comparison with the reported data. New compounds were characterized by microanalyses and spectral data (MS, IR, and ^1H and ^{13}C NMR).

Discussion

The α-sulfonyloxylation of carbonyl compounds may occur by the reaction of trimethylsilyl enol ethers and **1** or **2** to give the intermediate A. Subsequent nucleophilic attack by tosylate or mesylate ion with reductive elimination of iodobenzene then yields the product (Scheme VIII).

In effect, the polarity at the α-position with respect to silyl enol ether is reversed. The ease and moderate generality of this high-yield synthesis provides a convenient access to α-tosyloxylation or α-mesyloxylation of ketones, esters, and lactone, which are important synthetic intermediates.

Experimental Section

Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. The IR spectra were obtained with a Unicam SP 1000 IR spectrophotometer, and peak positions are expressed in cm^{-1}. ^1H NMR spectra were recorded in $CDCl_3$ at 60 MHz with a Varian EM-360 or 400 MHz with a WP-Bruker spectrometer, and ^{13}C NMR spectra were recorded at 400 MHz (WP-Bruker). Tetramethylsilane was used as an internal standard, and the chemical shifts were expressed in δ ppm values. Mass spectra were scanned with Hewlett-Packard GC/MS 5985 spectrometer at 70 eV. All ketones, iodobenzene diacetate, trimethylsilyl chloride, esters, lactone, and triethylamine were obtained from Aldrich.

Trimethylsilyl enol ethers of ketones[21] were synthesized by using the method of House et al. and were purified by Distillation before use. The trimethylsilyl enol ether of esters[23] were synthesized using the method of Ainsworth et al., the trimethylsilyl enol ether of 2-methylcyclohexanone[22] was synthesized using the method of Fleming, and the trimethylsilyl enol ether of ε-caprolactone[24] was synthesized using the method of Paterson.

General Procedure for the Preparation of α-Tosyloxy Ketones (5a–d, 8). [Hydroxy(tosyloxy)iodo]benzene (**1**) (3.92 g, 10 mmol) was added to the trimethylsilyl enol ether of ketone (**4a–d, 7**)[21] (15 mmol) in dry dichloromethane (50 mL). The reaction mixture was stirred at room temperature for 2 h and washed with aqueous sodium bicarbonate solution (3 × 50 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo to yield the crude product, which contained iodobenzene as a major impurity. Addition of hexane generally removed iodobenzene, and the crystalline solid separated out of the solution. Pure product was obtained by recrystallization from ether.

α-(Tosyloxy)acetophenone (5a): yield 2.67 g (92%); mp 89–91 °C (lit.[10] mp 91–92 °C); IR (KBr) 1715 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 2.48 (s, 3 H, $OSO_2C_6H_4CH_3$), 5.20 (s, 2 H, CH_2), 7.30–8.13 (m, 5 H, *aromatic*).

(Tosyloxy)methyl 2-furanyl ketone (5b): yield 2.46 g (88%); mp 65–67 °C; IR (KBr) 1710 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 2.48 (s, 3 H, $OSO_2C_6H_4CH_3$), 5.16 (s, 2 H, CH_2), 6.50–8.14 (m, 7 H, *aromatic*); ^{13}C NMR ($CDCl_3$) δ 179.3 (s), 149.8 (s), 147.4 (s), 145.5 (s), 130.0 (s), 132.6 (s), 128.2 (s), 119.4 (s), 113.0 (s), 69.2 (s), 22.0 (s). Anal. Calcd for $C_{13}H_{12}O_5S$: C, 55.71; H, 4.29. Found: C, 55.81; H, 4.07.

(Tosyloxy)methyl 2-pyridinyl ketone (5c): yield 2.27 g (78%); mp 65–68 °C; IR (KBr) 1740 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 2.46 (s, 3 H, $OSO_2C_6H_4CH_3$), 5.66 (s, 2 H, CH_2), 7.20–8.84 (m, 8 H, *aromatic*); ^{13}C NMR ($CDCl_3$) δ 191.2 (s), 151.0 (s), 149.1 (s), 145.1 (s), 137.2 (s), 132.9 (s), 129.7 (s), 129.6 (s), 128.3 (s), 121.9 (s), 70.9 (s), 21.7 (s); MS *m/e* (relative intensity) 155 (5), 136 (100), 120 (1), 106 (24), 78 (42). Anal. Calcd for $C_{14}H_{13}NO_4S$: C, 57.73; H, 4.47. Found: C, 58.06; H, 4.50.

(Tosyloxy)methyl 2-thienyl ketone (5d): yield 2.84 g (90%); mp 94–96 °C (lit.[10] mp 93–95 °C); IR (KBr) 1710 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 2.47 (s, 3 H, $OSO_2C_6H_4CH_3$), 5.14 (s, 2 H, CH_2), 7.22–8.28 (m, 7 H, *aromatic*); MS *m/e* (relative intensity) 296 (1), 155 (3), 141 (11), 111 (100), 91 (14).

α-(Tosyloxy)cyclohexanone (8): yield 2.21 g (85%); mp 76–78 °C (lit.[10] mp 74–76 °C); IR (KBr) 1744 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 1.30–2.70 (m, 11 H, cyclohexyl and $OSO_2C_6H_4CH_3$), 4.8 (1, 1 H, cyclohexyl), 7.10–8.02 (dd, 4 H, *aromatic*).

Preparation of 2-Methyl-6-(tosyloxy)cyclohexanone (11). [Hydroxy(tosyloxy)iodo]benzene (**1**) (3.92 g, 10 mmol) was added to 3-methyl-2-[(trimethylsilyl)oxy]cyclohexene (**10**)[22] (2.21 g, 12 mmol) in dry dichloromethane (50 mL). The mixture was stirred at room temperature for 2 h. After this period, the mixture was washed with aqueous sodium bicarbonate solution (3 × 50 mL). The organic phase was dried over magnesium sulfate and concentrated in vacuo to yield crude product, which contained iodobenzene and starting ketone as impurities. Addition of hexane followed by decantation of the hexane phase removed iodobenzene and ketone. Pure product was obtained by crystallization from ether: yield 2.25 g (80%); mp 112–114 °C; IR (KBr) 1745 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 0.98 (d, 3 H, CH_3), 1.30–2.72 (m, 9 H, cyclohexyl and $OSO_2C_6H_4CH_3$), 4.84–5.32 (m, 1 H, cyclohexyl), 7.18–8.10 (dd, 4 H, *aromatic*); MS *m/e* (relative intensity) 282 (11), 155, (27), 127 (24), 99 (19), 91 (87), 81 (100), 65 (44), 55 (25). Anal. Calcd for $C_{14}H_{18}O_4S$: C, 59.57; H, 6.38. Found: C, 59.37; H, 6.43.

General Procedure for the Preparation of α-Tosyloxy Esters (14a–c). [Hydroxy(tosyloxy)iodo]benzene (**1**) (3.92 g, 10 mmol) was added to the trimethylsilyl enol ether of the ester[23] (15 mmol) in dry dichloromethane (50 mL). The mixture was stirred at room temperature for 2 h. After this period, the mixture was washed with aqueous sodium bicarbonate solution (3 × 50 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo to yield the crude product, which contained iodobenzene

(25) Larock, R. C.; Oertle, K.; Beatty, K. M. *J. Am. Chem. Soc.* **1980**, *102*, 1966.

and starting ester as major impurities. Final purification was done by column chromatography with silica gel (hexane/dichloromethane, 3:1).

Methyl 2-phenyl-2-(tosyloxy)acetate (14a): yield 2.08 g (81%); mp 89–91 °C; IR (KBr) 1757 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 2.50 (s, 3 H, $OSO_2C_6H_4CH_3$), 3.60 (s, 3 H, OCH_3), 5.70 (s, 1 H, CH), 7.20–7.90 (m, 9 H, *aromatic*); ^{13}C NMR ($CDCl_3$) δ 169.9 (s), 145.1 (s), 133.3 (s), 132.8 (s), 129.7 (s), 129.6 (s), 128.8 (s), 128.4 (s), 127.5 (s), 78.8 (s), 52.9 (s), 21.6 (s); MS *m/e* (relative intensity) 261 (33), 155 (96), 91 (100), 77 (32), 65 (39). Anal. Calcd for $C_{16}H_{16}O_5S$: C, 60.00; H, 5.00. Found: C, 60.41; H, 5.09.

Ethyl 2-phenyl-2-(tosyloxy)acetate (14b): yield 2.0 g (60%); mp 45–47 °C; IR (KBr) 1757 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 1.10 (t, 3 H, CH_2CH_3), 2.50 (s, 3 H, $OSO_2C_6H_4CH_3$), 4.20 (q, 2 H, CH_2CH_3), 5.80 (s, 1 H, CH), 7.10–7.80 (m, 9 H, *aromatic*); ^{13}C NMR ($CDCl_3$) δ 167.3 (s), 145.1 (s), 133.4 (s), 132.9 (s), 129.8 (s), 129.7 (s), 128.8 (s), 128.1 (s), 127.5 (s), 78.9 (s), 62.1 (s), 21.6 (s), 13.9 (s); MS *m/e* (relative intensity) 261 (27), 155 (100), 149 (13), 90 (9), 77 (20). Anal. Calcd for $C_{17}H_{18}O_5S$: C, 61.08; H, 5.39. Found: C, 61.52; H, 5.53.

Methyl 2-(tosyloxy)butyrate (14c): yield 1.77 g (65%); colorless liquid; IR (neat) 1760 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 0.92 (t, 3 H, CH_2CH_3), 1.50–2.23 (m, 2 H, CH_2CH_3), 2.50 (s, 3 H, $OSO_2C_6H_4CH_3$), 3.72 (s, 3 H, OCH_3), 4.88 (t, 1 H, CH), 7.22–8.18 (dd, 4 H, *aromatic*); ^{13}C NMR ($CDCl_3$) δ 169.13 (s), 145.1 (s), 133.3 (s), 129.8 (s), 128.1 (s), 78.7 (s), 52.4 (s), 25.6 (s), 21.6 (s), 9.0 (s); MS *m/e* (relative intensity) 272 (14), 213 (52), 155 (95), 91 (100), 89 (29), 65 (63).

Preparation of α-(Tosyloxy)-ϵ-caprolactone (17). To a solution of **(16)**[24] (2.79 g, 15 mmol) in hexane (30 mL), **1** (3.92 g, 10 mmol) was added at room temperature and stirred for 8 h. During this period the color of the reaction mixture turned yellow. After this, the solvent was removed under reduced pressure, and the residue was dissolved in dichloromethane. The dichloromethane layer was then washed with saturated sodium bicarbonate solution (3 × 50 mL) and dried ($MgSO_4$). Evaporation of solvent and the chromatographic purification of the residual oil over silica gel using dichloromethane afforded the 2-(tosyloxy)-ϵ-caprolactone (17): 2.01 g (69%); mp 77–79 °C; IR (KBr) 1770 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 1.60–2.26 (m, 6 H, CH_2), 2.42 (s, 2 H, $OSO_2C_6H_4CH_3$), 4.10–4.66 (m, 2 H, CH_2), 5.00–5.38 (m, 1 H, CH), 7.26–8.02 (m, 4 H, *aromatic*); ^{13}C NMR ($CDCl_3$) δ 169.2 (s), 145.4 (s), 132.9 (s), 130.0 (s), 128.1 (s), 77.08 (s, 69.01 (s), 30.3 (s), 28.3 (s), 24.2 (s), 21.7 (s). Anal. Calcd for $C_{13}H_{16}O_5S$: C, 54.93; H, 5.63. Found: C, 54.92; H, 5.67.

General Procedure for the Preparation of α-Mesyloxy Ketones (18a–c). [Hydroxy(mesyloxy)iodo]benzene (**2**) (3.16 g, 10 mmol) was added to the trimethylsilyl enol ether of ketone (12 mmol) in dry dichloromethane (50 mL). The reaction mixture was stirred at room temperature for 2 h. After this period, the mixture was washed with saturated aqueous sodium bicarbonate solution (3 × 50 mL). The organic layer was separated and dried ($MgSO_4$). Evaporation of the solvent in vacuo yielded the crude product, which contained iodobenzene as a major impurity. Addition of hexane generally removed iodobenzene, and the crystalline solid separated out of the solution. Pure product was obtained by recrystallization from ether.

α-(Mesyloxy)acetophenone (18a): yield 1.9 g (89%); mp 80–82 °C (lit.[26] mp 76–77 °C); IR (KBr) 1720 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 3.30 (s, 3 H, OSO_2CH_3), 5.58 (s, 3 H, CH_2), 7.30–8.13 (m, 5 H, *aromatic*).

(Mesyloxy)methyl 2-furanyl ketone (18b): yield 2.01 g (90%); mp 89–90 °C; IR (KBr) 1700 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 3.30 (s, 3 H, OSO_2CH_3), 5.43 (s, 2 H, CH_2), 6.67–7.82 (m, 3 H, *aromatic*); ^{13}C NMR ($CDCl_3$) δ 180.4 (s), 149.9 (s), 147.41 (s), 118.7 (s), 112.9 (s), 69.5 (s), 39.1 (s); MS *m/e* (relative intensity) 149 (100), 121 (8), 95 (3), 70 (14), 69 (25), 55 (18). Anal. Calcd for $C_{17}H_8O_5S$: C, 41.18; H, 3.92. Found: C, 41.58; H, 3.96.

(Mesyloxy)methyl 2-pyridinyl ketone (18c): yield 1.91 g (89%); mp 76–78 °C; IR (KBr) 1730 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 3.36 (s, 4 H, OSO_2CH_3), 5.93 (s, 2 H, CH_2), 7.12–8.96 (m, 4 H, *aromatic*); ^{13}C NMR ($CDCl_3$) δ 192.4 (s), 151.0 (s), 149.2 (s), 137.2 (s), 128.4 (s), 121.9 (s), 71.5 (s), 39.0 (s); MS *m/e* (relative intensity) 120 (2), 106 (34), 79 (25), 78 (100). Anal. Calcd for $C_8H_9NO_4S$: C, 44.65; H, 4.19. Found: C, 44.69; H, 4.22.

General Procedure for the Preparation of α-Mesyloxy Esters (19a–c). [Hydroxy(mesyloxy)iodo]benzene (**2**) (3.16 g, 10 mmol) was added to the trimethylsilyl enol ether of ester[23] (15 mmol) in dry dichloromethane (50 mL). The mixture was stirred at room temperature for 2 h. After this period, the mixture was washed with aqueous sodium bicarbonate solution (3 × 50 mL). The organic phase was dried ($MgSO_4$) and concentrated in vacuo to yield the crude product, which contained iodobenzene and starting ester as major impurities. Final purification was done by column chromatography on silica gel (hexane/dichloromethane, 1:1).

Methyl 2-phenyl-2-(mesyloxy)acetate (19a): yield 1.58 g (65%); mp 91–92 °C; IR (KBr) 1760 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 3.10 (s, 3 H, OSO_2CH_3), 3.80 (s, 3 H, OCH_3), 6.00 (s, H, CH), 7.40–7.80 (m, 5 H, *aromatic*); ^{13}C NMR ($CDCl_3$) δ 168.2 (s), 132.2 (s), 130.0 (s), 129.0 (s), 127.7 (s), 78.9 (s), 53.0 (s), 39.45 (s); MS *m/e* (relative intensity) 185 (53), 165 (15), 149 (15), 107 (100), 90 (12), 79 (65), 51 (17). Anal. Calcd for $C_{10}H_{12}O_5S$: C, 49.18; H, 4.92. Found: C, 49.57; H, 4.87.

Ethyl 2-phenyl-2-(mesyloxy)acetate (19b): yield 2.19 g (85%); mp 61–63 °C; IR (KBr) 1753 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 1.20 (t, 3 H, CH_2CH_3), 3.00 (s, 3 H, OSO_2CH_3), 4.20 (q, 2 H, CH_2), 6.0 (s, 1 H, CH), 7.00–7.60 (m, 5 H, *aromatic*); ^{13}C NMR ($CDCl_3$) δ 167.7 (s), 132.9 (s), 129.9 (s), 129.0 (s), 128.0 (s), 79.1 (s), 62.3 (s), 39.4 (s), 13.9 (s); MS *m/e* (relative intensity) 185 (30), 90 (10), 77 (62), 71 (12).

Methyl 2-(mesyloxy)butyrate (19c): yield 1.27 g (65%); colorless liquid; IR (neat) 1761 cm^{-1} (carbonyl); ^1H NMR ($CDCl_3$) δ 1.03 (t, 3 H, CH_2CH_3), 1.70–2.40 (m, 2 H, CH_2CH_3), 3.20 (s, 3 H, OSO_2CH_3), 3.86 (s, 3 H, OCH_3), 5.06 (t, 1 H, CH); ^{13}C NMR ($CDCl_3$) δ 169.4 (s), 78 (s), 52.6 (s), 38.9 (s), 25.5 (s), 9.1 (s); MS *m/e* (relative intensity) 167 (9), 149 (100), 137 (17), 59 (11). Anal. Calcd for $C_6H_{12}O_5S$: C, 36.73; H, 6.12. Found: C, 36.81; H, 6.28.

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(26) Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1988**, *53*, 210.