185 (14), 172 (24), 157 (100), 156 (13), 155 (66), 139 (85), 135 (53), 134 (38), 133 (25), 123 (12), 121 (11), 107 (12), 105 (76), 104 (12), 93 (27), 92 (48), 91 (61), 77 (30). Anal. Calcd for $C_{14}H_{12}N_4SO_3$: C, 53.14; H, 3.83; N, 17.72. Found: C; 53.11, H, 3.72; N, 17.86. Compound **9** dissolved in 10% NaOH or $NaHCO_3$ but could be recovered on neutralization only from the latter.

3-[*N*,*N*-Bis(*p*-tolylsulfonyl)amino]-1,2,3-benzotriazin-4-(3*H*)-one (12). A solution of 0.86 g (5.3 mmol) of the aminotriazinone **11**[7] and 2.03 g (10.6 mmol) of *p*-toluenesulfonyl chloride in 10 mL of pyridine was stirred for 3 h at 25 °C and added to 100 mL of H_2O, and the resulting 2.66 g (107%) of crude **12** (mp 218–221 °C dec) was collected. Recrystallization from toluene gave 1.70 g (68%) of an analytical sample: mp 236–237 °C dec; IR 3040 (w), 1715, 1580, 1380 (Ts_2N),[9] 1280, 1160, 1065, 975, 865, 635 cm^{-1}; ^1H NMR δ 2.48 (s, 6), 7.51 (d, 4, J = 8.3), 7.84 (d, 4, J = 8.4), 8.07 (t, 1, J = 8.6), 8.25 (t, 1, J = 8.2), 8.36 (d, 2, J= 8.4); ^{13}C NMR δ 21.4, 120.2, 125.9, 128.9, 129.4, 129.9, 134.2, 134.6, 137.1, 141.9, 146.5, 152.9; MS, m/e 470 (0.01), 315 (1), 155 (16), 140 (12), 139 (98), 105 (12), 104 (100), 92 (11), 91 (72), 77 (12), 76 (78), 65 (34), 50 (25); DCI/MS,[19] m/e 471 (17, MH^+), 351 (7), 275 (10), 259 (9), 157 (18), 155 (71), 140 (10), 139 (100), 133 (13), 93 (10). Anal. Calcd for $C_{21}H_{18}N_4S_2O_5$: C, 53.61; H, 3.86; N, 11.91. Found: C, 53.78; H, 3.91; N, 11.83.

Cleavage of 12 to 9. To a stirred suspension of 700 mg (1.49 mmol) of the disulfonimide **12** in 100 mL of dry benzene and 50 mL of dry methanol at 40 °C under nitrogen was added over a 1-h period from an addition funnel 50 mL of a dry methanol solution of sodium methoxide prepared from 34.2 mg (1.49 g-atom) of sodium. The resulting yellow solution was stirred for another 20 min, the solvent was removed on a Rotovap, and the residue was partially dissolved in 100 mL of water and stirred for 30 min. The remaining solid was removed by filtration, the cooled (0 °C) filtrate was acidified with 20% H_2SO_4, and the precipitate of the monotosyl derivative **9** was collected (290 mg, 62%) and recrystallized from benzene to give material whose mp (194–195 °C dec) and ^1H and ^{13}C NMR spectra were identical with the sample of **9** prepared as described above.

Photolysis of 3-Lithio[(*p*-tolylsulfonyl)amino]-1,2,3-benzotriazin-4(3*H*)-one (1a).[3] To a vigorously stirred suspension of 2.0 g (5.7 mmol) of the monotosylated aminotriazinone **9** in 250 mL of dry methanol under a nitrogen atmosphere was added 38 mg (5.7 mmol) of lithium hydride, and the resulting yellow solution [λ_{max} 320, log ϵ 4.48 (lit.[1,3] λ_{max} 320)] was irradiated with a 550-W[20] Hanovia high-pressure mercury vapor lamp[21] for 2 h with a Pyrex filter and a nitrogen sweep in an apparatus similar to that described in ref 3. Evaporation of the solvent on a Rotovap with no particular precautions to retain volatile products left a residue, which on TLC (10% ethanol in benzene) showed three spots with R_f 0.00, 0.23, and 0.56 (lit.[3] R_f 0.00, 0.26, and 0.55). Trituration of the residue with benzene, filtration, and then addition of hexane to the filtrate separated a total of 600 mg (59%) of the product with the lowest R_f, lithium *p*-toluenesulfinate (**2**): ^1H NMR δ 2.29 (s, 3), 7.15 (d, 2, J = 7.9), 7.43 (d, 2, J = 7.9); ^{13}C NMR δ 20.8, 124.4, 128.1, 136.9, 156.1.

Upon cooling of the above filtrate to 0 °C, 80 mg (4%) of the product with R_f 0.23 crystallized and was collected by filtration: mp 162–163 °C dec (lit.[3] mp 179–180 °C dec); IR 3270, 3210, 1660, 1600, 1570, 1490, 1430, 1325, 1250, 1150, 1080, 800, 740, 705 cm^{-1} [lit.[3] IR ($CHCl_3$) 3318, 1692, 1338, 1260, 1080 cm^{-1}]; ^1H NMR δ ($CDCl_3$), 2.42 (s, 3), 3.82 (s, 3), 6.44 (br s, 1), 6.78 (t, 1, J = 7.4), 7.32 (m, 4), 7.78 (d, 2, J = 8.4), 7.85 (d, 1 J = 7.8), 8.97 (br s, 1) [lit.[3] ^1H NMR ($CDCl_3$, 60 MHz), δ 2.42 (s, 3), 3.83 (s, 3), 6.12–7.00 (br, 2), 7.14–8.08 (m, 8)]; ^{13}C NMR ($CDCl_3$) δ 21.7, 51.9, 111.3, 113.8, 118.6, 128.2, 129.8, 130.9, 134.3, 134.6, 144.6, 150.2, 168.5; MS, m/e 320 (2), 166 (13), 165 (100), 135 (5), 134 (13), 133 (92), 105 (82), 104 (10), 92 (13), 91 (30), 78 (14), 77 (58), 76 (16), 65 (17), 51 (16) (lit.[3] MS, m/e 320).

The filtrate from this second filtration contained the component with R_f 0.56, which was identified as methyl benzoate (**4a**) by comparison of its GC retention time (2.36 min at 150 °C) and MS with those of an authentic sample: MS, m/e 137 (13), 136 (66), 135 (10), 106 (12), 105 (100), 92 (12), 91 (14), 78 (11), 77 (73), 76 (16), 74 (20), 51 (69), 50 (44). The yield of **4a** was calculated to be 15% by comparing the NMR integration of the methyl protons (3.70 ppm) with those of a known added quantity of *p*-nitrotoluene (2.15 ppm).

***o*-Methoxybenzoic Acid Tosylhydrazide (3a).** A solution of *p*-toluenesulfonyl chloride (860 mg, 4.5 mmol) in 5 mL of pyridine was slowly added to a stirred pyridine solution (10 mL) of 750 mg (4.5 mmol) of the known hydrazide **13**, mp 180–181 °C (lit.[22] mp 180–181 °C) prepared from methyl *o*-methoxybenzoate. The mixture was allowed to react at room temperature for 4 h and poured in 50 mL of water, and the precipitate was collected and recrystallized from 95% ethanol to give 820 mg (57%) of the product **3a**: mp 143–143.5 °C; IR 3330, 3120, 1645, 1600, 1480, 1410, 1340, 1300, 1230, 1160, 1110, 1010 cm^{-1}; ^1H NMR δ 2.37 (s, 3), 4.01 (s, 3), 7.00 (m, 2), 7.22 (d, 2, J = 9.0), 7.47 (t, 1 J = 7.4), 7.79 (m, 4), 9.61 (br s, 1); ^{13}C NMR δ 21.6, 56.2, 111.3, 118.1, 121.2, 128.3, 129.3, 131.9, 133.3, 133.8, 144.4, 157.2, 163.6; MS, m/e 320 (2), 136 (18), 135 (100), 105 (2), 92 (20), 91 (16), 78 (14), 77 (41), 76 (4), 65 (13), 51 (7). Anal. Calcd for $C_{15}H_{16}N_2O_4S$: C: 56.24; H, 5.03. Found: C, 56.25; H, 5.09.

1-(*o*-Carbomethoxyphenyl)-2-tosylhydrazine (15). To a solution of 2.00 g (13 mmol) of methyl anthranilate in 21 mL of concentrated HCl at 0 °C was added a cold solution of 970 mg (14.1 mmol) of $NaNO_2$ in 12 mL of water. The resulting solution of the diazonium salt at 0 °C was added in one portion to a solution of $SnCl_2 \cdot 2H_2O$ (10.00 g, 44.3 mmol) in 20 mL of concentrated HCl, and the resulting mixture was stirred at room temperature for 15 min. The white precipitate was collected and washed with cold concentrated HCl to give 5.3 g (69%) of the tin salt **14**: mp 163–165 °C dec; ^1H NMR δ 3.83 (s, 3), 6.84 (t, 1, J = 7.3), 7.22 (d, 1, J = 8.5), 7.54 (t, 1, J = 7.8), 7.85 (d, 1, J = 7.0), 8.68 (br s, 1), the NH_3^+ peak is probably part of the concentration dependent, broad, residual water peak between 3.6–4.2; ^{13}C NMR δ 51.9, 110.7, 112.8, 117.7, 130.8, 134.5, 149.9, 167.3; MS, m/e 166 (15), 134 (52), 105 (80), 78 (15), 77 (100), 52 (12), 51 (23), 50 (11), plus four tin isotope clusters whose most intense peaks are 260 (0.9) ($SnCl_4$), 225 (9) ($SnCl_3$), 155 (3) (SnCl), and 120 (4) (Sn).

A solution of 900 mg of *p*-toluenesulfonyl chloride in 10 mL of pyridine was added to a stirred solution of 1.00 g of the tin salt **14** in 10 mL of pyridine, and the mixture was allowed to stir at room temperature for 16 h. The precipitate that formed after the reaction was added to 80 mL of water was collected and recrystallized from benzene to give 400 mg (74%) of **15** whose melting point and spectral properties were identical with those of the photoproduct with R_f 0.23. Anal. Calcd for $C_{15}H_{16}N_2O_4S$: C, 56.24; H, 5.03. Found: C, 56.17; H, 4.98.

Acknowledgment. The hospitality of the Department of Chemistry of the University of British Columbia and especially Professor James P. Kutney during the preparation of this manuscript is gratefully acknowledged.

(20) This coincides with ref 3 rather than with the 450-W lamp reported in ref 1.

(21) We thank Professor David E. Minter for the use of this equipment.

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Direct α-Mesyloxylation of Ketones and β-Dicarbonyl Compounds with [Hydroxy(mesyloxy)iodo]benzene

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In view of the current interest in α-keto mesylates (**1**, R′ = Me) as progenitors of α-keto carbocations[1] and in the potential utility of α-(sulfonyloxy) ketones in organic

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Table I. Conditions and Yields for the α-Mesyloxylation of Ketones and β-Dicarbonyl Compounds with HMIB[a]

reactant (mmol)	CH_3CN, mL	time, temp	product (% yield)[b]
CH_3COCH_3 (81.6)[c]	25	12 min, reflux	CH_3COCH_2OMs (76)
$CH_3CH_2COCH_2CH_3$ (47.2)[d]	30	12 min, reflux	$CH_3CH_2COCH(OMs)CH_3$ (87)
$PhCOCH_3$ (11.6)	30	18.5 h, reflux	$PhCOCH_2OMs$ (62.5)
cyclopropyl methyl ketone (15.5)	30	35 min, reflux	cyclopropyl (mesyloxy)methyl ketone (91)
methyl 2-thienyl ketone (12.4)	45[e]	18 days, rt	(mesyloxy)methyl 2-thienyl ketone (72)[f]
cyclohexanone (38.6)[g]	29[e]	70 min, rt	2-(mesyloxy)cyclohexanone (49)
$CH_2(COCH_3)_2$ (12.1)	30	15 min, rt	$MsOCH(COCH_3)_2$ (60)
$CH_2(COPh)_2$ (12.0)	40	15 min, reflux	$MsOCH(COPh)_2$ (96)
5,5-dimethylcyclohexane-1,3-dione (10.2)	25	20 min, reflux	5,5-dimethyl-2-(mesyloxy)cyclohexane-1,3-dione (81)
$CH_3COCH_2CO_2Et$ (11.5)	33	8 min, reflux	$CH_3COCH(OMs)CO_2Et$ (81)
$PhCOCH_2CO_2Et$ (12.4)	30	15 min, reflux	$PhCOCH(OMs)CO_2Et$ (98.5)
$CH_2(CO_2Et)_2$ (10.4)	30	142 min, reflux	$MsOCH(CO_2Et)_2$ (64.5)

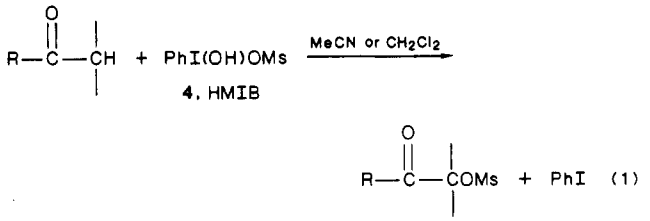
[a] 10 mmol of HMIB. [b] Based on initially isolated product from ether or chromatographic workup without further purification and HMIB as the limiting reagent. [c] 6 mL. [d] 5 mL. [e] CH_2Cl_2. [f] Based on 5.41 mmol of HMIB (4.59 mmol was recovered). [g] 4 mL.

synthesis,[1-5] *general* methods of preparation not requiring the prior availability of α-hydroxy ketones are desirable.

1 2 3

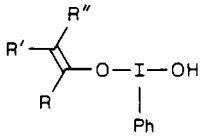
Two such schemes for the synthesis of α-keto arenesulfonates (**1**, R′ = Ar) have recently been described, one involving the *direct* functionalization of ketones and β-dicarbonyl compounds with [hydroxy(tosyloxy)iodo]benzene (**2**, HTIB)[6] and another involving the functionalization of enol acetates, enamines, and silyl enol ethers with arenesulfonyl peroxides (**3**), a regiospecific reaction from the standpoint of the ketonic product.[7-9] To our knowledge, the latter method has not yet been applied to the synthesis of α-keto mesylates. A recent report that [hydroxy(mesyloxy)iodo]benzene (**4**, HMIB) reacts with acetone to give α-(mesyloxy)acetone[10] prompts us to report our general study of the functionalization of ketones and β-dicarbonyl compounds with HMIB.

When various ketones, β-diketones, β-keto esters, and malonic ester were allowed to react with HMIB, usually in acetonitrile, the corresponding α-mesylates were isolated in yields ranging from 49% to 98% (eq 1, Table I). HMIB



is not very soluble in either acetonitrile or dichloromethane at room temperature but dissolves in acetonitrile at the boiling point to give deep yellow solutions. It was convenient, therefore, to conduct the α-mesyloxylation of ketones with HMIB in acetonitrile at reflux, the color of the reaction mixtures often fading significantly as the iodine reagent was consumed. Reactions were also conducted in dichloromethane or acetonitrile at room temperature (Table I, entries 5–7) and were monitored by noting the gradual disappearance of crystalline **4**. The workup procedure was dictated by the physical state of the α-mesylates at room temperature. Concentration of the reaction mixtures typically gave oils containing the byproduct iodobenzene.[11] Solid mesylates were obtained by treatment of the oils with ether (to dissolve PhI) and isolation of the ether-insoluble mesylate by filtration. Liquid mesylates were separated by chromatography of the crude oils on silica gel, first with hexanes (to remove PhI) and then with dichloromethane. All mesylates were characterized by elemental and spectral analysis.

That the α-mesyloxylation of cyclopropyl methyl ketone with HMIB is regiospecific is not surprising since such reactions probably proceed either by electrophilic attack of the hydroxyphenyliodonium ion, $(PhIOH)^+$, on the enol tautomer(s) of the ketone[6] or via enolic intermediates such as **5**. In any case, regiospecificity is not a general phenomenon. Thus, when 2-butanone was treated with HMIB in acetonitrile, a 1:1.26 mixture (by NMR analysis) of 1-(mesyloxy)- and 3-(mesyloxy)-2-butanones was obtained (eq 2).



5

$$CH_3C(O)CH_2CH_3 \xrightarrow[MeCN,\ \Delta]{PhI(OH)OMs} MsOCH_2C(O)CH_2CH_3 + CH_3C(O)CH(OMs)CH_3 \quad (2)$$

Experimental Section

General Procedures. ^1H NMR spectra were recorded on a Varian Model EM-360 spectrometer; chemical shifts are expressed relative to internal tetramethylsilane. In descriptions of spectra, any resonances due to minor impurities are not given. Infrared spectra were recorded on a Perkin-Elmer Model 597 spectrophotometer. Melting points are uncorrected. Elemental compositions were determined by Galbraith Laboratories, Knoxville, TN.

Detailed procedures for the α-mesyloxylation of 3-pentanone, cyclohexanone, and acetylacetone with HMIB are given below and serve as examples. Characterization data are given for all α-mesylates. Since the α-mesyloxylation of each substrate was conducted at least twice, the characterization data (melting points,

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(11) The oils were sometimes taken up in CH_2Cl_2 and washed with water prior to ether treatment or chromatography. The crude concentrate from dibenzoylmethane was a solid/liquid mixture.

analyses, spectra) were often collected on mesylate preparations other than those referred to in Table I or below. The "times" given for those reactions conducted in acetonitrile under reflux are measured from the moment of addition of the carbonyl compound to the hot HMIB solution until heating was discontinued; the temperature may have dropped a bit below the reflux temperature during the additions. Solvent volumes do not account for the small quantity of solvent that may have been used for rinsing purposes.

[Hydroxy(mesyloxy)iodo]benzene (4) previously reported by the groups of Zefirov[10] and Stang[12] was prepared from (diacetoxyiodo)benzene, $PhI(OAc)_2$, and methanesulfonic acid in acetonitrile. In one particular prep, 51.38 g (ca. 0.16 mol) of the diacetate gave 43.86 g (87%) of HMIB *after* its recrystallization from MeCN; mp 123–126 °C [lit.[10,12] mp 119–120 °C, 120–122 °C].

2-(Mesyloxy)-3-pentanone. To a solution of HMIB (3.16 g, 10.0 mmol) in MeCN (25 mL), stirred and heated under reflux, was added a solution of 3-pentanone (5 mL) in MeCN (5 mL). After 12 min at reflux, the reaction mixture was concentrated to an oil. A solution of the oil in CH_2Cl_2 (50 mL) was washed with H_2O (2 × 25 mL), dried ($MgSO_4$), and concentrated. Flash column chromatography of the residual oil on silica gel (37 g) first with hexanes (160 mL, to remove PhI) and then with CH_2Cl_2 (300 mL) gave 2-(mesyloxy)-3-pentanone as a bright yellow oil: yield 1.57 g (87%); ^1H NMR ($CDCl_3$) δ 1.07 (t, 3 H), 1.53 (d, 3 H), 2.62 (q, 2 H), 3.16 (s, 3 H), 5.07 (q, 1 H); IR (neat) ca. 1725 cm^{-1} (C=O). Anal. Calcd for $C_6H_{12}O_4S$: C, 39.99; H, 6.71. Found: C, 40.22; H, 6.93.

α-(Mesyloxy)cyclohexanone. To a stirred mixture of HMIB (3.16 g, 10.0 mmol) and CH_2Cl_2 (25 mL) at room temperature was added a solution of cyclohexanone (4 mL) in CH_2Cl_2 (4 mL). After 70 min, the reaction mixture, consisting of a solution phase and a floating globule of oil, was diluted with CH_2Cl_2 (15 mL), washed with H_2O (2 × 25 mL), dried ($MgSO_4$), and concentrated. Treatment of the residual oil with Et_2O (5 mL, 1 h, dry ice/acetone bath) gave α-(mesyloxy)cyclohexanone as a white powder: yield 0.949 g (49%); mp ~55 °C. Recrystallization of the crude product (0.821 g) from Et_2O (15 mL) returned 0.662 g, mp 58–59 °C.

In a similar experiment [HMIB (3.18 g, 10.0 mmol), cyclohexanone (1.03 g, 10.0 mmol), 21 h], α-(mesyloxy)cyclohexanone was isolated in 58% yield, mp 59–59.5 °C. ^1H NMR ($CDCl_3$) δ 1.13–2.77 (br m, 8 H), 3.15 (s, 3 H), 4.77–5.27 (m, 1 H); IR (Nujol) ca. 1728 cm^{-1} (C=O). Anal. Calcd for $C_7H_{12}O_4S$: C, 43.74; H, 6.29. Found: C, 43.75; H, 6.43.

3-(Mesyloxy)-2,4-pentanedione. To a stirred mixture of HMIB (3.16 g, 10.0 mmol) and MeCN (25 mL) at room temperature was added a solution of 2,4-pentanedione (1.21 g, 12.1 mmol) in MeCN (5 mL). After 15 min, the clear, colorless solution that resulted was concentrated to a light yellow oil. Flash column chromatography of the oil on silica gel first with hexanes (125 mL, to remove PhI) and then with CH_2Cl_2 (265 mL) gave 3-(mesyloxy)-2,4-pentanedione as a nearly colorless oil: yield 1.17 g (60%); ^1H NMR ($CDCl_3$) δ 2.37 (s, 6 H), 3.28 (s, 3 H), 5.55 (s, 1 H). Anal. Calcd for $C_6H_{10}O_5S$: C, 37.11; H, 5.19. Found: C, 36.85; H, 5.47.

α-Mesyloxylation of 2-Butanone. To a solution of HMIB (3.16 g, 10.0 mmol) in MeCN (25 mL), stirred and heated under reflux, was added 8 mL of 2-butanone. After 27 min at reflux, the reaction mixture was concentrated to an oil. A solution of the oil in CH_2Cl_2 (50 mL) was washed with H_2O (40 mL, an emulsion resulted) and saturated NaCl (aqueous), dried ($MgSO_4$), and concentrated. An ^1H NMR spectrum ($CDCl_3$) of the residual oil was recorded and reveals a fairly clean mixture of iodobenzene and (mesyloxy)butanones. The relative areas of the methyl triplet at δ 1.1 for 1-(mesyloxy)-2-butanone and the methyl doublet at δ 1.6 for 3-(mesyloxy)-2-butanone are consistent with a 1:1.26 mole ratio of these compounds.

α-(Mesyloxy)acetone: chromatographic workup; light-yellow oil (1.16 g); ^1H NMR ($CDCl_3$) δ 2.20 (s, 3 H), 3.16 (s, 3 H), 4.78 (s, 2 H); IR (neat) ca. 1738 cm^{-1} (C=O). Anal. Calcd for $C_4H_8O_4S$: C, 31.57; H, 5.30. Found: C, 31.68; H, 5.31.

α-(Mesyloxy)acetophenone: ether workup; light-brown solid (1.34 g); mp (Et_2O) 76–77 °C; ^1H NMR ($CDCl_3$) δ 3.20 (s, 3 H), 5.42 (s, 2 H), 7.08–8.12 (m, 5 H); IR (Nujol) ca. 1705 cm^{-1} (C=O). Anal. Calcd for $C_9H_{10}O_4S$: C, 50.46; H, 4.70. Found: C, 50.13; H, 4.47.

Cyclopropyl (mesyloxy)methyl ketone: ether workup; pale greenish-yellow powder (1.615 g); mp (Et_2O) 45–46 °C; ^1H NMR ($CDCl_3$) δ 0.87–1.37 (m, 4 H), 1.70–2.33 (m, 1 H), 3.19 (s, 3 H), 4.97 (s, 2 H); IR (Nujol) ca. 1710 cm^{-1} (C=O). Anal. Calcd for $C_6H_{10}O_4S$: C, 40.44; H, 5.66. Found: C, 40.51; H, 5.77.

(Mesyloxy)methyl 2-thienyl ketone: HMIB (1.45 g, 4.59 mmol) recovered; ether workup; white solid (0.86 g); mp (1:1, v/v Et_2O–CH_2Cl_2) 87–88 °C; ^1H NMR (CD_3COCD_3) δ 3.27 (s, 3 H), 5.55 (s, 2 H), 7.28 (symmetrical three-line m, 1 H), 8.05 (symmetrical two-line m, 2 H); IR (Nujol) ca. 1670 cm^{-1} (C=O). Anal. Calcd for $C_7H_8O_4S_2$: C, 38.17; H, 3.66. Found: C, 37.80; H, 3.55.

Dibenzoyl(mesyloxy)methane: ether workup; powder (3.06 g); mp (MeOH, crystalline rosettes) 153–154 °C; ^1H NMR (CD_3SOCD_3) δ 3.44 (s, 3 H), 7.20–7.83 (m, 7 H), 7.83–8.27 (m, 4 H); IR (Nujol) ca. 1688 cm^{-1} (C=O). Anal. Calcd for $C_{16}H_{14}O_5S$: C, 60.37; H, 4.43. Found: C, 60.17; H, 4.53.

2-(Mesyloxy)-5,5-dimethylcyclohexane-1,3-dione: ether workup; white solid (1.89 g); mp (CH_2Cl_2) 147–148 °C; ^1H NMR (CD_3COCD_3) δ 1.14 (s, 6 H), 2.46 (s, 4 H), 3.32 (s, 3 H), 6.56 (s, 1 H); IR (Nujol) broad adsorption, ca. 1540–1600 cm^{-1}. Anal. Calcd for $C_9H_{14}O_5S$: C, 46.14; H, 6.02. Found: C, 46.05; H, 5.91.

Ethyl (mesyloxy)acetoacetate: chromatographic workup; nearly colorless oil (1.81 g); ^1H NMR ($CDCl_3$) δ 1.28 (t, 3 H), 2.33 (s, 3 H), 3.20 (s, 3 H), 4.27 (q, 2 H), 5.38 (s, 1 H), 2.12 (d, impurity, ca. 0.4 H); IR (neat) ca. 1638, 1659 (sh) cm^{-1} (C=O). Anal. Calcd for $C_7H_{12}O_6S$: C, 37.49; H, 5.39. Found: C, 37.62; H, 5.48.

Ethyl (mesyloxy)benzoylacetate: chromatographic workup; light-yellow oil (2.82 g); ^1H NMR ($CDCl_3$) δ 1.16 (t, 3 H), 3.23 (s, 3 H), 4.24 (q, 2 H), 6.23 (s, 1 H), 7.23–8.23 (m, 5 H); IR (neat) ca. 1690 cm^{-1} (ketone C=O), ca. 1749 cm^{-1} (ester C=O). Anal. Calcd for $C_{12}H_{14}O_6S$: C, 50.34; H, 4.93. Found: C, 49.94; H, 5.09.

Diethyl (mesyloxy)malonate: chromatographic workup; bright-yellow oil (1.64 g); ^1H NMR ($CDCl_3$) δ 1.32 (t, 6 H), 3.24 (s, 3 H), 4.31 (q, 4 H), 5.43 (s, 1 H); IR (neat) ca. 1748 cm^{-1} (C=O). Anal. Calcd for $C_8H_{14}O_7S$: C, 37.79; H, 5.55. Found: C, 37.86; H, 5.57.

Registry No. 4, 105551-42-6; H_3CCOCH_3, 67-64-1; H_3CCOCH_2OMs, 23479-35-8; EtCOEt, 96-22-0; $EtCOCH(OMs)CH_3$, 111772-76-0; $PhCOCH_3$, 98-86-2; $PhCOCH_2OMs$, 20187-61-5; $CH_2(COCH_3)_2$, 123-54-6; $MsOCH(COCH_3)_2$, 111793-44-3; $CH_2(COPh)_2$, 120-46-7; $MsOCH(COPh)_2$, 111772-79-3; $H_3CCOCH_2CO_2Et$, 141-97-9; $H_3CCOCH(OMs)CO_2Et$, 111772-81-7; $PhCOCH_2CO_2Et$, 94-02-0; $PhCOCH(OMs)CO_2Et$, 111772-82-8; $CH_2(CO_2Et)_2$, 105-53-3; $MsOCH(CO_2Et)_2$, 88973-33-5; $PhI(OAc)_2$, 3240-34-4; H_3CSO_3H, 75-75-2; H_3CCOEt, 78-92-2; $MsOCH_2COEt$, 102096-20-8; $H_3CCOCH(OMs)CH_3$, 77611-73-5; cyclopropyl methyl ketone, 765-43-5; cyclopropyl (mesyloxy)methyl ketone, 111772-77-1; methyl 2-thienyl ketone, 88-15-3; (mesyloxy)methyl 2-thienyl ketone, 111772-78-2; cyclohexanone, 108-94-1; 2-(mesyloxy)cyclohexanone, 20187-64-8; 5,5-dimethylcyclohexane-1,3-dione, 126-81-8; 5,5-dimethyl-2-(mesyloxy)cyclohexane-1,3-dione, 111772-80-6.

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Studies on Polycyclic Azaarenes. 2.[1] Synthesis of *trans*-3,4-Dihydroxy-3,4-dihydrobenz[*c*]acridine and *trans*-8,9-Dihydroxy-8,9-dihydrobenz[*c*]acridine

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The benz[*c*]acridine derivatives are found to be carcinogenic in nature.[2] In analogy with corresponding

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