15% EtOAc/hexanes yielded vinyl bromide **6**: 1.91 g (70%); NMR ($CDCl_3$) δ 2.50 (br s, 1 H), 3.85 (s, 3 H), 4.23 (br s, 2 H), 4.66 (dt, 2 H, J = 1.0, 5.0 Hz), 6.29 (tt 1 H, J = 1.5, 5.0 Hz), 6.20–6.60 (m, 3 H), 7.12 (m, 1 H); IR ($CHCl_3$) 3600, 3400, 3020, 2960, 2830, 1600, 1590 cm^{-1}. Anal. Calcd for $C_{11}H_{13}BrO_3$: C, 48.37; H, 4.80. Found: C, 48.49; H, 4.83.

Preparation of 4-[(3-Methoxyphenyl)oxy]-but-2-yn-1-ol (7). Treatment of *m*-methoxyphenol (1.24 g, 10 mmol) with 1-chloro-4-hydroxy-2-butyne (1.10 g, 10 mmol) and anhydrous K_2CO_3 as described above for **6** yielded the acetylene **7**, 1.82 g (95%).

(*E*)- and (*Z*)-1-bromo-3-[(3-methoxyphenyl)oxy]propene was prepared as described for **6** by using 1,3-dibromoprop-2-ene[8] (6.30 g, 31.5 mmol) and *m*-methoxyphenol (3.72 g, 30 mmol). The crude product was chromatographed on silica gel (5% ether/pentane eluant) to yield a 3:2 mixture of *Z* and *E* isomers: 6.91 g (95%); NMR ($CDCl_3$) δ 3.78 (s, 3 H), 4.45 (m, 0.8 H, (*E*)-ArOCH_2), 4.70 (m, 1.2 H, (*Z*)-ArOCH_2), 6.35–6.65 (m, 5 H), 7.10–7.32 (m, 1 H; IR ($CHCl_3$) 2990, 2920, 2830, 1595 cm^{-1}.

General Procedure for Elimination with Potassium Carbonate. The vinyl bromide (0.5 mmol) in 5 mL of 2-butanone was treated with anhydrous K_2CO_3 (5.0 mmol) and the resulting suspension heated to reflux for 1–9 days. The reaction mixture was cooled, filtered through Celite, and concentrated under reduced pressure. The resulting oils were separated by preparative TLC (ether/hexanes eluant). The yields of acetylenes are summarized in Table I.

General Procedure for Elimination with DBU. The vinyl bromide (0.2 mmol) and DBU (0.4 mmol) in 4 mL of benzene were heated to reflux for 1–9 days. The reaction mixture was cooled, diluted with 10 mL of benzene, washed with 10% aqueous HCl (2 × 3 mL) followed by saturated NaCl (4 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The oily residues were separated by preparative TLC (ether/hexanes eluant). The yields of acetylenes are summarized in Table I.

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Registry No. (*E*)-**6**, 81446-98-2; (*E*)-**6** acetate, 81446-99-3; (*E*)-**6** methyl ether, 81447-00-9; (*E*)-**6** Si-*t*-Bu$(CH_3)_2$ ether, 81456-89-5; (*E*)-**6** THP ether, 81447-01-0; (*E*)-**6** dehydroxy, 81447-02-1; **7**, 81447-03-2; **10**, 50584-95-7; **15** (R = Ac), 81447-04-3; **15** (R = CH_3), 81447-05-4; **15** (R = Si-*t*-Bu$(CH_3)_2$), 81447-06-5; **15** (R = THP), 81447-07-6; *m*-methoxyphenyl 2-propynyl ether, 41580-72-7; (*E*)-2,4-dibromobut-2-en-1-ol, 81447-08-7; *m*-methoxyphenol, 150-19-6; 1-chloro-4-hydroxy-2-butyne, 13280-07-4; (*E*)-1-bromo-3-[(3-methoxyphenyl)oxy]propene, 81447-09-8; (*Z*)-1-bromo-3-[(3-methoxyphenyl)oxy]propene, 81447-10-1; (*E*)-1,3-dibromoprop-2-ene, 32121-07-6; (*Z*)-1,3-dibromoprop-2-ene, 32121-06-5.

One-Step α-Tosyloxylation of Ketones with [Hydroxy(tosyloxy)iodo]benzene

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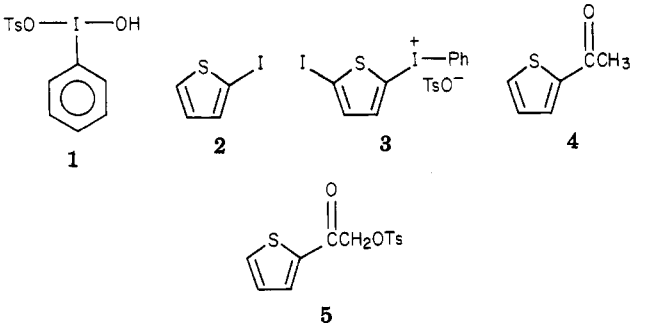
We have found [hydroxy(tosyloxy)iodo]benzene (**1**)[1,2] to be an effective reagent for the mild, one-step conversion of ketones to the corresponding α-tosyloxy ketones. Pursuant to an observation that 2-iodothiophene (**2**) reacts



with **1** to give phenyl-2-(5-iodothienyl)iodonium tosylate (**3**),[3] the action of **1** on 2-acetylthiophene (**4**) was investigated. However, an analogous iodonium salt was not obtained. When a solution of **4** (0.32g) in dichloromethane (10 mL) was mixed with **1** (1.00 g, solubility in CH_2Cl_2 ca. 5.3 mg mL^{-1} at 22 °C) and allowed to stand for several days at room temperature, 2-[(α-tosyloxy)acetyl]thiophene (**5**) was isolated in 79.5% yield following the workup. The α-tosyloxylation reaction under varying conditions exhibits some generality. For example, cyclopropyl methyl ketone (**6**, 2 mL) was added to a hot mixture of **1** (3.92 g) and acetonitrile (25 mL), and the reaction mixture was gently reluxed for about 20 min. Evaporation of the solvent left an oil which was taken up in dichloromethane, washed with water, dried, reconcentrated to an oil, and triturated with heptane to give 2.03 g (80%) of crude cyclopropyl (tosyloxy)methyl ketone (**7**) as a white solid. Other ketones which have been converted to their α-tosyloxy derivatives upon treatment with **1** include acetone, 3-pentanone, acetophenone, deoxybenzoin, and cyclohexanone, the product yields and reaction conditions being given in Table I.

[Hydroxy(tosyloxy)iodo]benzene (**1**) is largely insoluble in either dichloromethane or acetonitrile under ambient conditions, but it does dissolve in acetonitrile at its boiling point to give yellow solutions. It is, therefore, convenient to conduct the α-tosyloxylation of ketones with **1** in acetonitrile at the reflux temperature. Such conditions are, however, too severe for the conversion of cyclohexanone to α-(tosyloxy)cyclohexanone. This transformation was effected in dichloromethane at room temperature and could be monitored by the gradual disappearance of crystalline **1**. Thus far, we have been unable to obtain α-tosyloxy derivatives of either cyclopentanone or cycloheptanone.

The general reaction extends nicely to β-diketones. For example, acetylacetone (1.43 g), **1** (3.92 g), and acetonitrile (25 mL) were heated until the reaction mixture became homogeneous (ca. 10 min). The solvent was subsequently evaporated, and the crude solid which remained was triturated with ether and gave 1.96 g (73%) of 3-(tosyloxy)-2,4-pentanedione. Under similar conditions, dibenzoylmethane, dimedone, and ethyl benzoylacetate were converted to the corresponding tosyloxy derivatives (see Table I).

It seems plausible that the α-tosyloxylation of ketones by **1** is initiated by the electrophilic addition of $(PhIOH)^+OTS^-$ to the corresponding enol tautomers to give intermediate α-phenyliodonio ketones of general structure **8** (Scheme I). Nucleophilic displacement of iodobenzene from the α-carbon in **8** by the tosylate ion would eventuate in the observed products.

That the iodine–tosyloxy bond in **1** is at least partially ionic in the solid state has been established by single-

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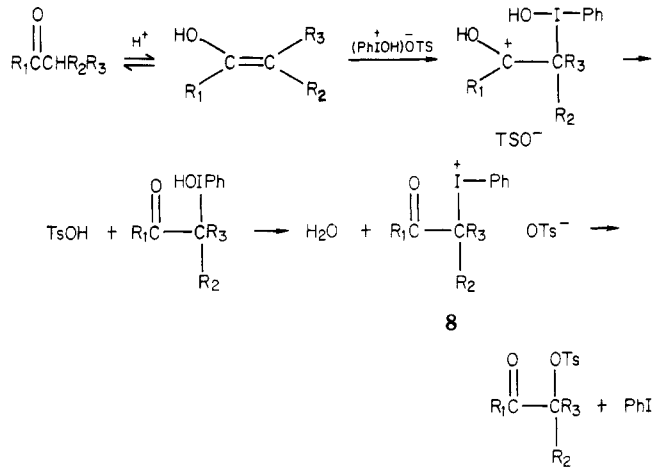
Table I. Reaction Conditions and Yields for the α-Tosyloxylation of Ketones with [Hydroxy(tosyloxy)iodo]benzene

ketone	product (mp, °C)[c]	solvent	time	temp, °C	% yield
4	5 (93-95)	CH_2Cl_2	several days	room	80[a]
CH_3COCH_3	CH_3COCH_2OTS (35)	CH_3CN	20 min	reflux	71[b]
$CH_3CH_2COCH_2CH_3$	$CH_3CH(OTS)COCH_2CH_3$	CH_3CN	10 min	reflux	94[b]
c-$C_3H_5COCH_3$	c-$C_3H_5COCH_2OTS$ (73-74)	CH_3CN	20 min	reflux	80[a]
$PhCOCH_3$	$PhCOCH_2OTS$ (91-92)	CH_3CN	45 min	reflux	73[b]
$PhCH_2COPh$	PhCH(OTS)COPh (105.5-106)	CH_2Cl_2	1 day	reflux	52[a]
cyclohexanone	2-(toxyloxy)cyclohexanone (74-76)	CH_2Cl_2	3 h	room	40[b]
$PhCOCH_2COPh$	PhCOCH(OTS)COPh (88-90)	CH_3CN	20 min	reflux	~100[a]
$CH_3COCH_2COCH_3$	$CH_3COCH(OTS)COCH_3$ (82-83)	CH_3CN	10 min	75	73[a]
$PhCOCH_2CO_2Et$	$PhCOCH(OTS)CO_2Et$ (oil)	CH_3CN	10 min	75	75[a]
9	11 (176-177 dec)	CH_3CN	20 min	reflux	86[b]

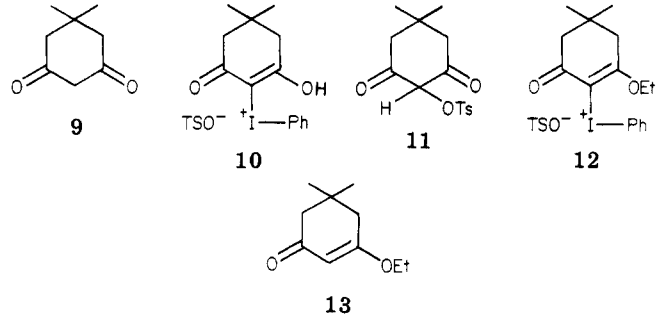
[a] Crude. [b] Pure. [c] Satisfactory analytical data (±0.4% for C and H) were obtained for all tosyloxy ketones listed.

Scheme I



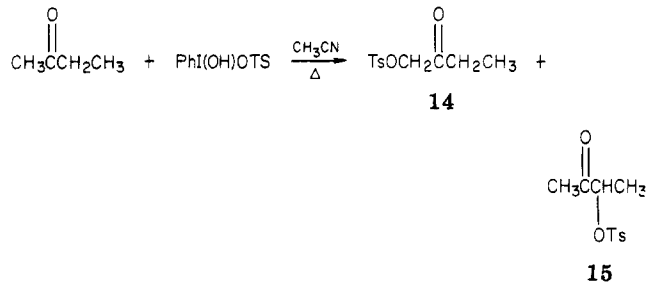
crystal X-ray analysis,[4] and some chemical demonstrations of the electrophilicity of 1 at the iodine atom have been reported.[1,3,5,6] [Hydroxy(tosyloxy)iodo]benzene is also a Brønsted acid and would be expected to catalyze the enolization of ketones.

In one case, an intermediate iodonium salt has been isolated. When dimedone (9) and 1 were mixed in aceto-



nitrile at *room temperature*, phenyl(2-dimedonyl)iodonium tosylate (10) was formed within ca. 5 min and was isolated in 89% yield. In hot acetonitrile (70–74 °C, 1 h), 10 was converted in 90% yield to 2-(tosyloxy)dimedone (11). The likelihood that 10 arises via electrophilic attack of 1 on the enol of 9 finds support in an earlier study of Neiland and Karele, who isolated the iodonium salt 12 from the reaction of 1 with 3-ethoxy-5,5-dimethylcyclohex-2-en-1-one (13) in chloroform.[1] Furthermore, other phenyl(2-dimedonyl)iodonium salts are known to undergo similar cleavage reactions.[7]

The regiochemistry of the α-tosyloxylation reaction was tested with 2-butanone as the substrate. After the ketone was treated with 1 in hot acetonitrile, the crude product, an oil, was subjected to ^1H NMR analysis and found to consist of 1-(tosyloxy)-2-butanone (14) and 3-(tosyloxy)-2-butanone (15) in a 1:1.57 ratio.



The reactions reported herein find precedent in the recent literature. Mizukami et al. have investigated the action of (diacetoxyiodo)benzene (16) on several acetophenones and β-diketones in acetic acid/acetic anhydride with sulfuric acid employed as a catalyst.[8] They obtained the corresponding α-acetoxy ketones in yields ranging from 22% to 66%. Three kinetic studies of the oxidation of ketones with (diacetoxyiodo)benzene under acid conditions have also been published.[9-11] The ketones examined include cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, acetone, acetone-d_6, 2-butanone, and various acetophenones, and in one study the effect of substituents in the (diacetoxyiodo)arene nucleus was assessed. More recently, Moriarty and co-workers have reported the α-hydroxylation of isophorone (at the unsaturated carbon atom), cyclohexanone, and various acetophenones with (diacetoxyiodo)benzene in basic methanol.[12]

α-(Tosyloxy)deoxybenzoin has previously been prepared in 19% yield by the base-catalyzed rearrangement of deoxybenzoin oxime tosylate[13] and, in 73% yield, by the action of silver tosylate on α-bromodeoxybenzoin in acetonitrile.[14] α-(Tosyloxy)acetophenone has been prepared

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in 70% yield by treatment of diazoacetophenone with toluenesulfonic acid in benzene.[15,16] The photochemistry of α-sulfonyloxy ketones (including some α-tosyloxy analogues) has also been investigated.[16-19] The ease and moderate generality of the synthesis reported herein provides convenient access to α-tosyloxy ketones and should facilitate further investigations of their chemistry.

Experimental Section

General Methods. The ^1H NMR spectra reported herein were recorded on a Varian EM-360 spectrometer, tetramethylsilane being employed as an internal standard. Melting points and boiling points are uncorrected. Elemental compositions were determined at Galbraith Laboratories in Knoxville, TN. The NMR and IR spectral data were sometimes collected on samples from experimental runs other than the ones given in this section.

Detailed procedures for the direct α-tosyloxylation of 3-pentanone and cyclohexanone follow and serve as examples. However, workups vary from ketone to ketone. For anyone wishing full preparative information on those experiments not included herein, see the paragraph at the end of the paper about supplementary material.

2-(Tosyloxy)-3-pentanone. To a hot mixture of 3.92 g (10.0 mmol) of 1 and 25 mL of CH_3CN was added 10 mL of 3-pentanone. After 10 min at reflux, the reaction solution was concentrated in vacuo (H_2O aspirator), and the residual material was dissolved in 30 mL of CH_2Cl_2. The CH_2Cl_2 solution was washed with H_2O (2 × 100 mL), dried, and concentrated (at 0.2 mmHg) to give 2.40 g (93.6%) of 2-(tosyloxy)-3-pentanone as an oil: ^1H NMR ($CDCl_3$) δ 0.98 (t, 3.0 H, $J \simeq 6.5$ Hz), 1.33 (d, 2.9 H, $J \simeq 6.5$ Hz), 2.44 and 2.58 (overlapping s and q, 4.7 H, $J \simeq 7$ Hz for q), 4.81 (q, 0.9 H, $J \simeq 7$ Hz), 7.57 (AA'BB' m, 4.0 H).

Anal. Calcd for $C_{12}H_{16}O_4S$: C, 56.23; H, 6.29. Found: C, 56.41; H, 6.49.

In another experiment, 2-(tosyloxy)-3-pentanone, obtained initially as an oil, gradually crystallized to a white, wet solid over a period of 5 days.

α-(Tosyloxy)cyclohexanone. To a solution of 1.2 mL of cyclohexanone in 30 mL of CH_2Cl_2 was added 3.93 g (10 mmol) of 1. After being stirred 3 h at room temperature, the reaction mixture was turbid and contained a floating light brown scum. It was then washed with H_2O (2 × 25 mL), dried over $MgSO_4$, and concentrated under aspirator vacuum to a clear yellow oil. The oil was taken up in 30 mL of warm diethyl ether and cooled for 19 h at −20 °C whereupon α-(tosyloxy)cyclohexanone crystallized from solution: yield 1.07 g (39.9%); mp 74–76 °C (unchanged after recrystallization from ether); ^1H NMR ($CDCl_3$) δ 1.30–2.70 (complex m overlapping with CH_3 singlet at 2.41, 11.2 H), 4.60–5.05 (complex m, 1.1 H); 7.51 (AA'BB' m, 4.0 H); IR (KBr) 1744 cm^{-1} (carbonyl).

Anal. Calcd for $C_{13}H_{16}O_4S$: C, 58.19; H, 6.01. Found: C, 58.18; H, 6.02.

Phenyl(2-dimedonyl)iodonium Tosylate. To a hot solution of 1.07 g (7.63 mmol) of dimedone in 25 mL of CH_3CN was added a hot solution of 3.0 g (7.65 mmol) of 1 in 50 mL of CH_3CN. The reaction mixture was cooled first to room temperature and then at −20 °C for 5 h with the concomitant crystallization of white solid phenyl(2-dimedonyl)iodonium tosylate which was washed with a few milliliters of acetone and dried: yield 1.52 g; mp 119.5–120.5 °C. The filtrate was subsequently concentrated, and the residual liquid/solid was triturated with a few milliliters of hexanes to give an additional 0.62 g of product: mp 119–120 °C; combined yield 2.14 g (54.5%); ^1H NMR ($CDCl_3$) δ 0.90 (s, 6.0 H); 2.28 (s, 2.7 H), 2.48 (s, 3.9 H), 7–8.1 (m with 8 apparent s at δ 6.92, 7.05, 7.13, 7.27, 7.38, 7.52, 7.72, and 7.85, 9.0 H); IR (KBr) 1660 cm^{-1} (carbonyl, not calibrated).

Anal. Calcd for $C_{21}H_{23}O_5IS$: C, 49.03; H, 4.51; I, 24.67. Found: C, 49.00; H, 4.67; I, 24.80.

Thermolysis of Phenyl(2-dimedonyl)iodonium Tosylate. A mixture of phenyl(2-dimedonyl)iodonium tosylate (3.63 g, 7.06 mmol) and 50 mL of CH_3CN was brought to gentle reflux (ca. 72 °C) for a period of 1 h. The reaction solution was subsequently cooled to about 0 °C, 50 mL of Et_2O was added, and the solution was concentrated to a total volume of 50 mL whereupon α-(tosyloxy)dimedone began to crystallize out. After further cooling for 10 min at −20 °C, the product was isolated and washed with several milliliters of Et_2O: yield, 1.35 g (62%); mp 159–164 °C. The filtrate, upon concentration and washing with several milliliters of Et_2O, gave an additional crop (0.63 g) of product, combined yield 1.98 g (90.4%).

Tosyloxylation of 2-Butanone. A mixture of 3.92 g (10.0 mmol) of [hydroxy(tosyloxy)iodo]benzene, 13.0 mL of 2-butanone, and 25 mL of CH_3CN was subjected to gentle reflux until a homogeneous solution resulted. The reaction mixture was then concentrated to an oil (4.07 g) shown by ^1H NMR analysis ($CDCl_3$) to consist of iodobenzene, 1-(tosyloxy)-2-butanone, and 3-(tosyloxy)-2-butanone. Integration of the methyl triplet at δ 1.0 for 1-(tosyloxy)-2-butanone and of the methyl doublet at δ 1.3 for 3-(tosyloxy)-2-butanone is consistent with a 1:1.57 mixture of these compounds.

Registry No. 1, 27126-76-7; 4, 88-15-3; 5, 81447-27-0; 6, 765-43-5; 7, 81447-28-1; 9, 126-81-8; 10, 81447-30-5; 11, 81447-31-6; 14, 80520-04-3; 15, 81447-32-7; 3-pentanone, 96-22-0; 2-(tosyloxy)-3-pentanone, 81447-33-8; α-(tosyloxy)cyclohexanone, 81447-34-9; cyclohexanone, 108-94-1; 2-butanone, 78-93-3; α-tosyloxyacetone, 1666-19-9; acetone, 67-64-1; α-tosyloxyacetophenone, 7257-94-5; acetophenone, 98-86-2; α-tosyloxydeoxybenzoin, 1678-43-9; deoxybenzoin, 451-40-1; 3-tosyloxy-2,4-pentanedione, 81447-35-0; 2,4-pentanedione, 123-54-6; tosyloxydibenzoylmethane, 81447-36-1; dibenzoylmethane, 120-46-7; ethyl tosyloxybenzoylacetate, 81447-37-2; ethyl benzoylacetate, 94-02-0.

Supplementary Material Available: Full experimental details on the α-tosyloxylations of 2-acetylthiophene, acetone, cyclopropyl methyl ketone, acetophenone, deoxybenzoin, 2,4-pentanedione, dibenzoylmethane, ethyl benzoylacetate, and dimedone with [hydroxy(tosyloxy)iodo]benzene (5 pages). Ordering information is given on any current masthead page.

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Decarbonylation of Aroyl Fluorides Using Wilkinson's Catalyst: A Reevaluation[1]

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Synthetic methods for incorporating fluorine into aromatic molecules are quite limited.[2] New potentially useful methods are thus needed and are continuously being explored.

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