4,5-disubstituted furan *o*-aminonitrile (**6**). This latter product was not isolated but, under the conditions employed, rapidly reacts with the vinyl ketone in a Diels–Alder manner (**7**) as previously demonstrated.[1] Treatment of the Diels–Alder adduct (**7**) with acid gave in modest yield the anthranilonitrile derivative (**8**), which was characterized by elemental analysis and NMR spectroscopy. Compound **8a** was also characterized by ^{13}C NMR and mass spectroscopy.

Interestingly, when **1** was treated with methyl acrylate or acrylonitrile, the only products (**3a,b**) obtained under these coonditions were those expected to arise via the Diels–Alder adduct. No evidence for the prior reaction of the methyl acrylate or acrylonitrile in a Michael addition was detected. Since vinyl ketones are known[6] to be better Michael acceptors than acrylates or acrylonitriles, this appears to account for the formation of **3** and **8**.

Furan *o*-aminonitriles can be used to synthesize highly substituted anthranilate derivatives,[1] and **1**, in particular, may be used to prepare anthranilate derivatives (**8**) not readily accessible from previously available furan *o*-aminonitriles.[2,7] Anthranilates are valuable intermediates,[1] and the ability to introduce additional functionality at positions 3 and 5 extends the potential synthetic value gained by the use of furan *o*-aminonitriles as precursors.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 467 grating spectrophotometer. The ^1H NMR spectra were obtained on a 60-MHz Hitachi Perkin-Elmer R20A high-resolution spectrometer using Me_4Si as an internal standard. ^{13}C NMR spectra (Me_4Si) were recorded on a JEOL PTS-100. Mass spectra were determined on a Finnigan 4000 GC–MS Quadrupole mass spectrometer or on a DuPont 21-490 low-resolution mass spectrometer. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, GA.

3-Acetyl-6-methyl-5-(3-oxobutyl)anthranilonitrile (8a). To a 250-mL round-bottomed flask equipped with a magnetic stirrer, reflux condenser, and a heating mantle was added 3.2 g (30 mmol) of 2-amino-3-cyano-4-methylfuran (**1**),[2] 7 mL of methyl vinyl ketone, and 100 mL of acetone. The reaction mixture was refluxed for 24 h, cooled, and concentrated in vacuo. The yellow-orange gum was dissolved in 50 mL of acetic acid and chilled in an ice–water bath. To the cold solution was added 30 mL of concentrated H_2SO_4. The mixture was stirred at room temperature for 1 h and then poured onto ice. A yellow solid was collected and recrystallized from methanol to yield 2.1 g (29%): mp 158–160 °C; IR (KBr) 3440, 3320, 2200, 1710, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.7 (s, 1 H), 6.9 (br, 2 H, exchangeable by D_2O), 2.8 (t, 4 H), 2.6 (s, 3 H), 2.5 (s, 3 H), 2.2 (s, 3 H); ^{13}C NMR ($CDCl_3$) 206.53 (s), 198.85 (s), 149.78 (s), 146.30, (s), 136.85 (d), 125.82 (s), 115.88 (s), 115.46 (s), 97.78 (s), 42.79 (t), 29.50 (q), 27.67 (q), 25.48 (t), 17.88 (q) ppm; mass spectrum, *m/e* 244.1 (M^+), calcd 244.299.

Anal. Calcd for $C_{14}H_{16}N_2O_2$: C, 68.83; H, 6.60; N, 11.47. Found: C, 68.83; H, 6.67; N, 11.42.

3-Benzoyl-6-methyl-5-(3-oxo-3-phenylpropyl)-anthranilonitrile (8b). The title compound was prepared as above from **1** and phenyl vinyl ketone.[8] The gum was purified on a silica gel column using methylene chloride as eluent. Concentration of the solvent gave a yellow solid, which was recrystallized from aqueous methanol to give **8b** (18%) as yellow crystals: mp 120–121 °C; IR (KBr) 3400, 3300, 2200, 1690, 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25–8.0 (m, 11 H), 6.8 (s, 2 H), 2.9–3.1 (2 t, 4 H), 2.55 (s, 3 H).

Anal. Calcd for $C_{24}H_{20}N_2O_2$: C, 78.24; H, 5.47; N, 7.60. Found: C, 78.29; H, 5.48; N, 7.56.

Methyl 3-Cyano-4-methylanthranilate (3a). The title compound was prepared as above from **1** and methyl acrylate. The off-white solid was recrystallized from benzene–hexane solution (26%): mp 106–108 °C; IR (KBr) 3420, 3310, 2950, 2200, 1695, 1600 cm^{-1}; ^1H NMR ($CDCl_3$–Me_2SO-d_6) δ 7.9 (d, 1 H, J = 8.5 Hz), 6.5 (d, 1 H, J = 8.5 Hz), 3.85 (s, 3 H), 2.45 (s, 3 H).

Anal. Calcd for $C_{10}H_{10}N_2O_2$: C, 63.15; H, 5.30; N, 14.73. Found: C, 63.15; H, 5.32; N, 14.72.

3-Cyano-4-methylanthranilonitrile (3b). The title compound was prepared as above from **1** and acrylonitrile. The solid was recrystallized from aqueous methanol to yield **3b** (35%): mp 158–159.5 °C; IR (KBr) 3500, 3390, 2220, 2210, 1640 cm^{-1}; ^1H NMR ($CDCl_3$–Me_2SO-d_6) δ 7.5 (d, 1 H, J = 8.0 Hz), 6.45 (d, 1 H, J = 8.0 Hz), 2.5 (s, 3 H).

Anal. Calcd for $C_9H_7N_3$: C, 68.78; H, 4.49; N, 26.73. Found: C, 68.55; H, 4.55; N, 26.63.

2-(Bromoacetamido)-3-cyano-4,5-dimethylfuran (9). To a solution of 4,5-dimethyl-2-amino-3-cyanofuran[2] (27.2 g, 0.2 mol) in 30 mL of acetonitrile and 50 mL of tetrahydrofuran was added dropwise 20.2 g (0.1 mol) of bromoacetyl bromide while maintaining the temperature below 5 °C during the addition. The mixture was stirred continuously for 2 h at this temperature. Upon completion of the reaction, the hydrogen bromide salt of the starting material was removed by filtration (ca. 52% yield). The acetonitrile and tetrahydrofuran were removed in vacuo to yield an orange solid. The product was recrystallized from ethyl acetate–ligroin (58% yield): mp 142–143 °C; IR (KBr) 3175, 3125, 3050, 2250, 1715, 1630, 1550 cm^{-1}; NMR (Me_2SO-d_6) δ 2.0 (s, 2 H), 2.2 (s, 3 H), 4.0 (s, 2 H), 11.40 (s, 1 H, exchangeable with D_2O).

Anal. Calcd for $C_9H_9N_2O_2Br$: C, 42.02; H, 3.50; N, 10.89. Found: C, 42.26; H, 3.66; N, 11.09.

***N,N'*-Bis(3-cyano-4,5-dimethyl-2-furyl)-2,5-diketopiperazine (10).** A solution of **9** (5.0 g, 17.0 mmol) in 500 mL of water was refluxed and stirred for 2 h. Upon cooling a white product was collected, washed with water, and recrystallized from dimethylformamide and water to give a 90% yield of **10**: mp 226–227 °C; IR (KBr) 2975, 2925, 2240, 1700, 1650, 1600 cm^{-1}; NMR (Me_2SO-d_6) δ 2.0 (s, 6 H), 2.35 (s, 6 H), 4.80 (s, 4 H); mass spectrum, *m/e* 352 (M^+), calcd 352.36.

Anal. Calcd for $C_{18}H_{16}N_4O_4$: C, 61.36; H, 4.55; N, 15.91. Found: C, 61.30; H, 4.62; N, 15.73.

Acknowledgment. This research was supported in part by the National Institute of Neurological and Communicative Disorders and Stroke Grant 5R01NS16988. We are grateful to Courtney Pape, Department of Chemistry, University of Georgia, for the ^{13}C NMR and mass spectra.

Registry No. **1**, 5117-87-3; **2a**, 96-33-3; **2b**, 107-13-1; **3a**, 81446-91-5; **3b**, 81446-92-6; **4a**, 78-94-4; **4b**, 768-03-6; **8a**, 81446-93-7; **8b**, 81446-94-8; **9**, 81446-95-9; **10**, 81446-96-0; 4,5-dimethyl-2-amino-3-cyanofuran, 5117-88-4; 4,5-dimethyl-2-amino-3-cyanofuran hydrobromide, 81446-97-1; bromoacetyl bromide, 598-21-0.

(7) Taylor, E. C.; McKillop, A. "The Chemistry of Cyclic Enaminonitriles and *o*-Aminonitriles"; Interscience: New York, 1970.

(8) (a) Gras, J.-L. *Tetrahedron Lett.* **1978**, 2955. (b) The original procedure employed trioxymethylene (*s*-trioxane) as a reagent in the synthesis of vinyl ketones. In our hands, use of this reagent gave low yields (ca. 40%) of the vinyl ketone. However, substitution of paraformaldehyde instead of trioxymethylene lead to 85–90% yield of the phenyl vinyl ketone.

Studies in the Elimination of Substituted Vinyl Halides to Acetylenes

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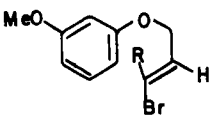
The elimination of the elements HX from a vinyl halide is one of the most important and general methods for preparing the carbon–carbon triple bond and has been reviewed several times.[1] In general, one finds that al-

0022-3263/82/1947-2484$01.25/0

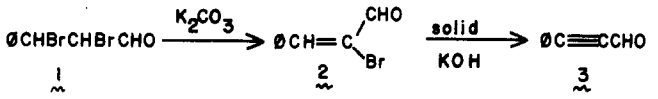
Table I



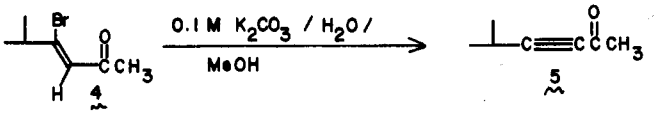
entry	R	base	reflux time, days	% yield acetylene	% yield starting mat
A	CH_2OH	K_2CO_3/MEK	1	100	0
B	CH_2OH	DBU/PhH	1	100	0
C	CH_2OAc[a]	K_2CO_3/MEK	4	100	0
D	CH_2OAc[a]	DBU/PhH	2.5	96	0
E	CH_2OCH_3[b]	K_2CO_3/MEK	7	96	0
F	CH_2OCH_3[b]	DBU/PhH	5	96	0
G	CH_2OSi-t-$Bu(CH_3)_2$[c]	K_2CO_3/MEK	9	51	31
H	CH_2OSi-t-$Bu(CH_3)_2$[c]	DBU/PhH	9	79	9
I	CH_2OTHP[d]	K_2CO_3/MEK	9	27	67
J	CH_2OTHP[d]	DBU/PhH	9	72	15
K	H[e]	K_2CO_3/MEK	9	0	100
L	H[e]	DBU/PhH	2	54	40[f]
M	H[g]	DBU/PhH	9	0	100
N	CH_3[h]	K_2CO_3/MEK	7	49	37
O	CH_3[h]	DBU/PhH	7	63	17

[a] Prepared from 6 and acetic anhydride/sodium acetate (100%). [b] Prepared from 6 and silver oxide/methyl iodide (93%). [c] Prepared from 6 and t-$BuSiMe_2Cl$/imidazole (100%). [d] Prepared from 6 and dihydropyran/H^+ (98%). [e] Approximately a 3:2 mixture of Z/E isomers. [f] Only the E isomer was recovered. [g] Pure E isomer. [h] Prepared from 6 by (1) p-TsCl/NaOH/acetone and then (2) $LiAlH_4$/ether (75%).

Scheme I



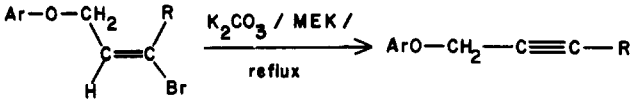
Scheme II



though the vinyl halides are usually readily accessible by a variety of methods, the subsequent dehydrohalogenation reactions can often only be accomplished with very strong bases. Alkoxides, solid alkali, and alkali metal amides are most commonly used for this conversion.[1a,b] The yields of these eliminations vary from 10% to 90%.[1] Weaker bases such as potassium carbonate will effect elimination of a vicinal dihaloalkane (1) to the vinyl halide (2)[2] but will not cause further elimination to the acetylene (3) to occur (Scheme I) unless the hydrogen to be abstracted is strongly activated[3] (e.g., 4 → 5 in Scheme II). Even the amidine bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and 1,5-diazabicyclo[5.3.0]non-5-ene (DBN) are not usually basic enough to cause the elimination of an unactivated vinyl halide.[4] The use of very strong bases and/or vigorous reaction conditions could pose problems in reactions in which the substrates or products are sensitive to one or both of these factors.

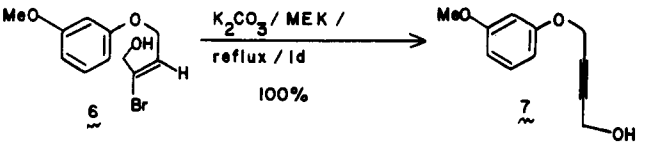
We report the elimination of a specific type of vinyl halide under mild conditions (K_2CO_3, methyl ethyl ketone, reflux) that gives the corresponding acetylenes in very high yields. The general pathway is outlined in Scheme III.

Scheme III



The first example of this remarkably facile and somewhat surprising reaction was observed on the alcohol 6[5] as shown in Scheme IV. When a mixture of 6, K_2CO_3, and methyl ethyl ketone was heated for 1 day, a quantitative yield of the acetylenic alcohol 7 was obtained. As a means of investigating the mechanism and scope of this reaction, we examined the reactivity of a series of derivatives of 6 toward elimination with both K_2CO_3/methyl ethyl ketone and DBU/benzene. The results of this study are shown in Table I.

Scheme IV



The structure of the acetylenic products was proven by preparing an authentic sample of 7 from 1-chloro-4-hydroxy-2-butyne[6] and m-methoxyphenol and converting this compound into several of the other acetylenes recorded in Table I[7] that were produced by the elimination reaction.

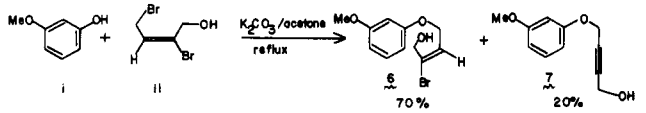
(1) (a) Kobrich, G.; Buck, P. In Viehe, H. G. "Chemistry of Acetylenes"; Marcel Dekker: New York, 1969; p 99. (b) Demlow, E. V.; Lisse, M. *Liebigs Ann. Chem.* **1980**, 1 and references cited therein. (c) Jacobs, T. L. *Org. React.* **1949**, *5*, 1. (d) Franke, G.; Ziengenbein, W.; Meister, H. *Angew. Chem.* **1960**, *72*, 391. (e) Kobrich, G. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 49.

(2) Allen, C. F. H.; Edens, C. O. "Organic Syntheses"; Wiley: New York, 1955; Collect Vol. III p 731.

(3) Eaton, P. E.; Stubbs, C. D. *J. Am. Chem. Soc.* **1967**, *89*, 5722.

(4) Eiter, K.; Oediger, H. *Justus Liebigs Ann. Chem.* **1965**, *682*, 62.

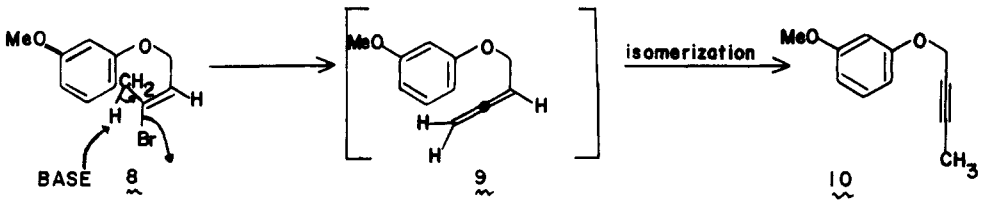
(5) Alcohol 6 was obtained by the O-alkylation of m-methoxyphenol: (i) with the allylic bromide; (ii) as shown below. Bromide ii was prepared from butyne-1,4-diol according to: Johnson, A. W. *J. Chem. Soc.* **1946**, 1014.



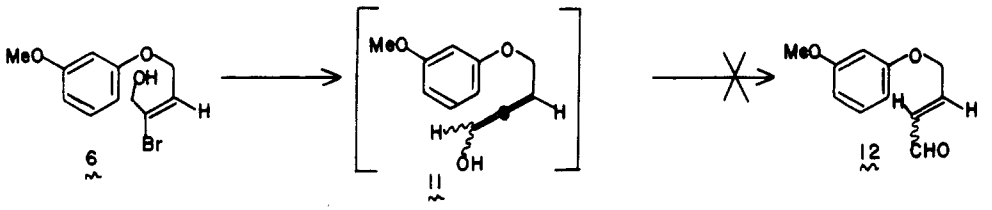
(6) Bailey, W. J.; Fujiwara, E. *J. Am. Chem. Soc.* **1955**, *77*, 165.

(7) All mixtures were easily separated by preparative TLC for convenience. All new compounds gave satisfactory NMR, IR, and analytical data. Details will appear in a full paper on this subject.

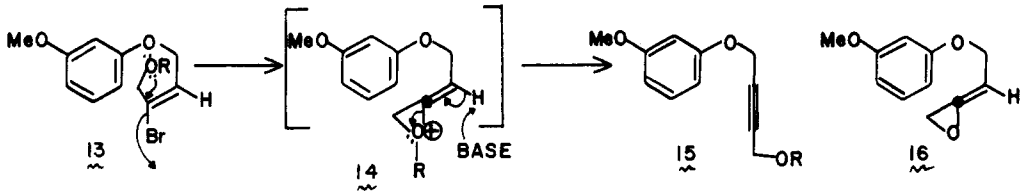
Scheme V



Scheme VI



Scheme VII



On the basis of these results, several mechanisms could be postulated. The most simple explanation would involve a simple direct removal of the vinyl proton and subsequent elimination of X^-. To test this mechanism, we prepared the unsubstituted vinyl halides (R = H)[8] and subjected them to the reaction conditions (entry K, Table I). No elimination product was observed in this reaction, although the use of the stronger base, DBU, did cause elimination of the *Z* isomer only (entries L and M, Table I). Thus, the presence of a substitutent on the halide-substituted carbon may be necessary for elimination to occur under mild conditions.

An alternative mechanistic argument is shown in Scheme V. It is possible that proton abstraction occurs at the allylic position of halide **8** (entries N and O, Table I), and elimination follows to give the allene **9**. Subsequently, base-catalyzed prototropic rearrangement[10] of **9** to the acetylene **10** could take place. In evaluation of this possibility, several factors should be considered: (i) the base-catalyzed allene–propargylic rearrangement equilibrium generally lies on the side of the allenic component; (ii) no allene was ever isolated from any of the reactions listed in Table I; (iii) in the case of the methylol compound **6**, elimination in this manner (Scheme VI) would occur through the intermediacy of enol–allene **11**. This pathway should lead to at least some of the α,β-unsaturated aldehyde **12**. None of this product was ever detected.

The third possibility (Scheme VII) involves anchimeric assistance by the allylic oxygen functionality in **13**. This would give a very reactive allene oxide intermediate **14**. Proton abstraction and ring opening would afford the acetylene **15**. This mechanism is supported by the fact that as the nature of the R group in **13** changes from hydrogen to ester or ether, the rate of the elimination process decreases rather markedly. This possibly reflects the fact that either **13** or **14** (R = H) is capable of deprotonation to give a neutral species allene oxide **16**. On the other hand, the O-substituted derivatives must go through the higher energy charged species **14** (R = Ac, CH_3, Si-*t*-Bu$(CH_3)_2$, THP). In addition, one notices that the rate of elimination decreases as the bulk of the R group in **14** increases (see Table I). This is the expected result if the oxygen is participating in the reaction. Obviously, this is the favored of the viable mechanistic alternatives.

In conclusion, the elimination of a series of vinyl halides to acetylenes has been shown to take place under the influence of much milder bases than has heretofore been reported. The experiments done (Table I) indicate that direct elimination is not a favored pathway under these conditions. However, the examples studied will not clearly distinguish whether the allene (Scheme V) or the allene oxide (Scheme VII) mechanism is operative in these cases. It is also possible that the mechanistic pathway followed is dependent on the particular vinyl halide substrate involved. We are currently engaged in studies that will further define the mechanism and scope of this reaction.

Experimental Section

Proton spectra were recorded on either a Varian EM360 or Varian XL-100 spectrometer with Me_4Si as an internal standard. Infrared spectra were recorded on a Perkin-Elmer Model 281 spectrophotometer. Silica gel for column chromatography was Baker reagent grade (60–200 mesh). Preparative thin-layer chromatography (PLC) was performed on Analtech glass-supported silica gel GF (2000 μm).

Preparation of 2-Bromo-4-[(3-methoxyphenyl)oxy]-but-2-en-1-ol (6). A solution containing (*E*)-2,4-dibromobut-2-en-1-ol (2.41 g, 10.5 mmol) and *m*-methoxyphenol (1.24 g, 10 mmol) in 25 mL of acetone was treated with anhydrous K_2CO_3 (2.76 g, 20 mmol) and the resulting suspension heated to reflux for 12 h. The reaction mixture was cooled, filtered through Celite, and concentrated in vacuo. The oily yellow residue was dissolved in 30 mL of CH_2Cl_2, washed with 5% aqueous NaOH (2 × 10 mL) and saturated NaCl (5 mL), dried over $MgSO_4$, and concentrated to a dark oil which was chromatographed on silica gel. Elution with

(8) 1,3-Dibromoprop-1-ene was prepared as a mixture of *E* and *Z* stereoisomers. Cf.: Parfenov, E. A.; Yurkevich, A. M. *Zh. Org. Khim.* **1971**, *7*, 2568. See also: Hatch, L. F.; Harwell, K. E. *J. Am. Chem. Soc.* **1953**, *75*, 6002.

(9) Rutledge, T. F. In "Acetylenes and Allenes"; Reinhold: New York, 1969; p1.

(10) Woitz, J. H. In Viehe, H. G. "Chemistry of Acetylenes"; Marcel Dekker: New York, 1969; p 365.

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.

Acknowledgment. This research was supported in part by Biomedical Research Support Grant No. RR-07042 to the University of Maryland from the Division of Research, Resources, National Institutes of Health, Public Health Service.

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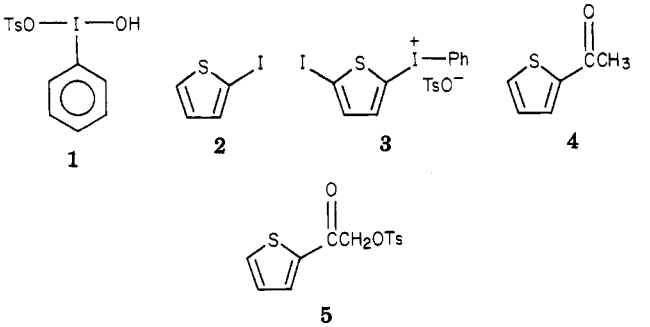
We have found [hydroxy(tosyloxy)iodo]benzene (**1**)[1,2] to be an effective reagent for the mild, one-step conversion of ketones to the corresponding α-tosyloxy ketones. Pursuant to an observation that 2-iodothiophene (**2**) reacts



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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