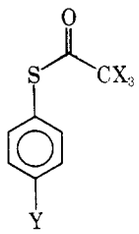
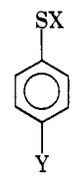
be independent of ring size. The observed difference in the relative abundances of the M − 42 ions may reflect the fact that in the transition state for the six-centered mechanism the 5–6 ring junction for **1** is less stable than the 6–6 ring junction for **2**.

Phenyl thiolacetate (**3**) and the 4-methoxy, 4-dimethylamino, 4-chloro, and 4-methyl analogues all lost ketene from the parent ion to form M − 42 ions. Phenyl thiolacetate-d_3 (**4**) and 4-toluene thiolacetate-d_3 (**5**) lose ketene-d_2 from the parent ions to form ions at *m/e* 111 and 125, respectively. As discussed below, these spectra show that deuterium has been transferred from the acetyl group to the benzene ring carbons either by the six-centered mechanism directly or by the thiol intermediate formed by the four-centered mechanism.





3, X = Y = H
4, X = D; Y = H
5, X = D; Y = CH_3
9, X = H; Y = CH_3

6, X = Y = H
7, X = D; Y = H
8, X = H; Y = CH_3

Thiophenol **6** and **3** form the same ions below *m/e* 110, although ions derived directly from *m/e* 110 are more intense for **6** than for **3**.

The cyclopentadiene radical cation appears at *m/e* 66 in the spectra of **6** and **3** and at *m/e* 67 in the spectra of the thiophenol-*s*-d_1 (**7**) and **4**. 4-Toluene thiol (**8**) and 4-toluene thiolacetate (**9**) form analogous, but less intense, ions at *m/e* 80, while **5** forms the deuterated ion at *m/e* 81. These ions arise from loss of CS from the 2,4-cyclohexadienethione radical cations which would be formed in the six-centered fragmentation of the aryl thiolacetates.

The phenyl cation is partially deuterated in the spectra of **7** and **4** and appears at *m/e* 77 and 78. The analogous ion at *m/e* 91 is the most intense ion in the spectrum of **8** and is very intense for **9**. **5** shows large peaks at *m/e* 91 and 92.

Deuterated and nondeuterated thiophene radical cations appear at *m/e* 85/84 in a ratio of 2:1 for both **7** and **4**. This scrambling of deuterium in **7** from sulfur onto the benzene ring before the loss of acetylene[5] and also before other fragmentations[6,7] represents complete randomization and is evidence for the interconversion of the thiophenol and 2,4-cyclohexadiene thione ions. Therefore, interpretation of the loss of ketene for the aryl thiolacetates in terms of whether a four- or six-centered mechanism is operative is precluded.

Photolysis of **3** produces **6**, which was thought to arise from the secondary photolysis of diphenyl disulfide.[8,9] However, **6** could be formed either by abstraction of a hydrogen atom from the acetyl group by the thiyl radical produced from photocleavage of the *S*-acyl bond or by transfer of a hydrogen atom from the acetyl group to the ortho carbon atom prior to photocleavage of the *S*-acyl bond.

In order to test these possibilities of hydrogen-atom transfer from the acetyl group, **4** and **5** were irradiated in cyclohexane for 3 h at 254 nm. Products were isolated by gas chromatography of the photolysis mixture after removal of solvent. The photolysis of **4** produced deuterium-free diphenyl disulfide and deuterium-free **6**. The deuterium label of **7** is not lost under the gas chromatographic isolation procedure employed. Likewise, **5** photolyzed to deuterium-free 4,4′-ditolyl disulfide. Thus, **6** is not formed by hydrogen-atom transfer from the acetyl group.

In summary, the ICR evidence for the transfer of the β-hydrogen atom of alkyl vinyl sulfides, the lack of M − 42 ions in the spectra of saturated alkyl thiolacetates, and the difference in intensity of M − 42 ions for **1** and **2** indicate that hydrogen-atom transfer from the acetyl group to the sulfur fragment occurs by a six-centered mechanism for alkenyl thiolacetates. However, the interconversion between cyclohexadienethione and thiophenol radical cations precludes distinguishing between four- and six-centered mechanism for arene thiolacetates. The analogy between the photochemistry and mass spectra of arene thiolacetates is limited to simple cleavage of the *S*-acyl bond and does not extend to the transfer of hydrogen from the acetyl group to the sulfur entity.

Experimental Section

Mass spectra were obtained on a Hitachi-Perkin Elmer RMU-6 spectrometer at 70 eV. Gas chromatography was performed on a Hewlett-Packard Model 700 gas chromatograph equipped with a thermal conductivity detector and a 20 ft × 1/8 in. OV-225 column. Thiol esters were prepared according to literature procedures as listed: methyl thiolacetate,[10] ethyl thiolacetate,[11] propyl thiolacetate,[11] isobutyl thiolacetate,[11] vinyl thiolacetate,[12] isobutenyl thiolacetate,[12] β-*tert*-butyl vinyl thiolacetate,[13] cyclopentenyl thiolacetate[16] (**1**), cyclohexenyl thiolacetate[16] (**2**), phenyl thiolacetate[17] (**3**), 4-methoxyphenyl thiolacetate,[17] 4-dimethylaminophenyl thiolacetate,[18] 4-chlorophenyl thiolacetate,[17] 4-toluene thiolacetate[17] (**9**). Structure assignments were confirmed by NMR and IR spectra. Phenyl thiolacetate-d_3 (**4**) and 4-toluene thiolacetate-d_3 (**5**) were prepared from the thiol and acetic-d_3 acid using dicyclohexylcarbodiimide.[11] Photochemistry of the deuterated esters was conducted exactly as previously reported.[2]

Supplementary Material Available: A table of mass spectra data for compounds which are not reported in the literature (1 page). Ordering information is given on any current masthead page.

Registry No.—$CH_3CH_2SCOCH_3$, 625-60-5; $(CH_3)_2CHCH_2SCHOCH_3$, 2432-37-3; 4-Cl-$C_6H_4SCOCH_3$, 21021-60-3; 4-$CH_3OC_6H_4SCOCH_3$, 60787-31-7; $C_6H_5SCOCD_3$, 60860-51-7; 4-$CH_3C_6H_4SCOCD_3$, 60860-52-8.

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Synthesis of Aryl Alkynes. 1. 2-Ethyl-4-methoxyphenylacetylene

Deanna J. Nelson* and Ellen A. Uschak[1]

Organic Chemistry Laboratory, Indiana University of Pennsylvania, Indiana, Pennsylvania 15701

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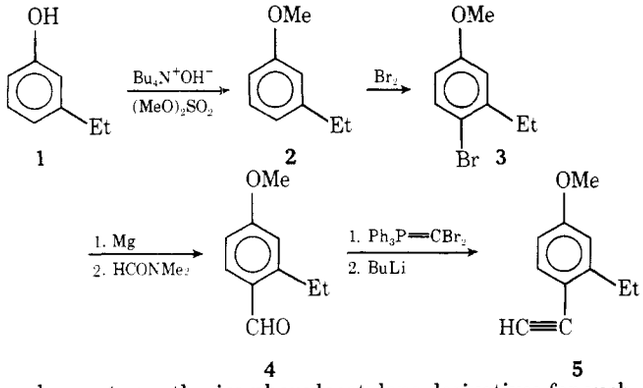
While many aryl alkenes and alkanes have been synthesized for study as potential synthetic estrogens,[2] no systematic

Scheme I



endeavor to synthesize phenylacetylene derivatives for such application has been documented. The synthesis of 2-ethyl-4-methoxyphenylacetylene (**5**) is reported. It is a precursor for a series of alkynes to be synthesized for study of structure–estrogenic activity relationships in such compounds.

Synthetic Approach

Scheme I summarizes the synthesis of the title compound **5**. Two convenient starting materials, 3-ethylphenol (**1**) and 3-methoxyacetophenone, are readily available. Phase-transfer-catalyzed methylation of **1** provided quantitatively 3-methoxyethylbenzene (**2**). Similar high yields of **2** are obtained by Clemmenson reduction of the acetophenone. Attempts to obtain **2** from 3-methoxybenzaldehyde via Wittig reaction with triphenylmethylenephosphorane and subsequent hydrogenation of 3-methoxystyrene are unsatisfactory.

Two methods for carbonylation were studied. Bromination of **2** yielded exclusively 4-bromo-3-ethylanisole (**3**), underscoring the applicability of partial rate factors to this electrophilic aromatic substitution.[3] (The position of bromination was confirmed by conversion to the known 2-ethyl-4-methoxybenzoic acid.[4]) Grignard reaction with *N,N*-dimethylformamide yields 2-ethyl-4-methoxybenzaldehyde (**4**). Friedel–Crafts reaction (Cl_2CHOCH_3 and $TiCl_4$)[5] of **2** is unsatisfactory, as an isomeric mixture of aldehydes results.

Ethinylation, the final conversion, was first attempted using the method of Oliver and Walton.[6] In this procedure an arylcopper reagent couples with iodoethinyl(trimethyl)silane to give an arylethinyl(trimethyl)silane, which may be quantitatively desilylated by treatment with alkali. In our hands this conversion failed, and 3-ethyl-4-iodoanisole was isolated. Steric factors often hinder organocopper reactions,[7] and in this case the *o*-ethyl group probably facilitated exchange over ethinylation. Ethinylation was achieved using the two-step method of Corey and Fuchs (Wittig reaction followed by alkyllithium-promoted rearrangement).[8]

Experimental Section

All reagents were suitably purified before use. Anhydrous $MgSO_4$ served as the drying agent. Boiling points are uncorrected. Infrared spectra of thin films were recorded on the Beckman IR-10 and calibrated using the 6.24-μm band of polystyrene. NMR spectra of dilute solutions in Silanor-C were recorded on the Varian T60 spectrometer. Standard spectral notations apply. X-ray data were obtained using the Picker x-ray fluorescence spectrometer.

3-Ethylanisole (2). To a slurry of NaOH (20 g, 0.5 mol) and tetrabutylammonium hydroxide (10 mol %) in 100 mL of H_2O was added dropwise a solution of 3-ethylphenol (**1**, Aldrich Chemical Co., 30.5 g, 0.25 mol) in 50 mL of H_2O. To the resulting solution was added dropwise 30 mL of dimethyl sulfate (0.3 mol). Rapid, exothermic reaction ensued. After stirring 2 h, separation of the organic layer, extraction of the aqueous layer with CH_2Cl_2, drying and concentration, distillation afforded 31.2 g (95%) of **2** as a colorless oil: bp 70–71 °C (9 Torr); lit.[9] bp 74 °C (10 Torr); IR (film) 1600, 1480, 1260, 1150, 1030, 865, 770, and 680 cm^{-1}; NMR ($CDCl_3$) δ 6.9 (m, 4, phenyl), 3.8 (s, 3, OCH_3), 2.55 (quartet, 2, J = 8 Hz, $-CH_2CH_3$), 1.2 (t, 3, J = 8 Hz, $-CH_2CH_3$).

2-Ethyl-4-methoxybromobenzene (3). A slurry of **2** (6.8 g, 0.05 mol) and 0.1 g of iron filings in 50 mL of CCl_4 was stirred and cooled in an ice–salt bath as a solution of bromine (2.9 mL, 0.055 mol) in 20 mL of CCl_4 was added dropwise over 3 h. After stirring 3 h, the mixture was poured into water and worked up. Drying and concentration gave 9.6 g (90%) of **3** as a colorless oil: bp 79–80 °C (0.5 Torr); IR (film) 1590, 1570, 1470, 1235, 1135, 1005, 860, 840, and 790 cm^{-1}; NMR ($CDCl_3$) δ 7.25 (doubled doublets, 1, J = 1 and 2 Hz, phenyl), 6.7 (m, 2, phenyl), 3.7 (s, 3, OCH_3), 2.75 (quartet, 2, J = 8 Hz, $-CH_2CH_3$), 1.2 (t, 3, J = 8 Hz, $-CH_2CH_3$); x-ray fluorescence K α-Br 29.96°, K β-Br 26.79°.

Anal. Calcd for $C_9H_{11}BrO$: C, 50.26; H, 5.16; Br, 37.15. Found: C, 50.49; H, 5.25; Br, 37.09.

2-Ethyl-4-methoxybenzaldehyde (4). To magnesium turnings (1.6 g, 0.065 g-atom) in 30 mL of anhydrous ether was added a solution of 4.3 g of ethyl bromide (0.04 mol) and 4.3 g of **3** (0.02 mol) in 50 mL of anhydrous ether. After refluxing for 1 h an ethereal solution of 4.3 mL (0.06 mol) of *N,N*-dimethylformamide was added with external cooling. After 1 h it was decomposed with aqueous NH_4Cl. After separation the aqueous layer was extracted twice with ether. Combined ethereal extracts were washed and dried. Concentration and distillation gave 3.1 g (94%) of colorless liquid: bp 107–108 °C (2.5 Torr); IR (film) 2720, 1690, 1610, 1240, 900, and 810 cm^{-1}; NMR ($CDCl_3$) δ 10.3 (s, –CHO), 7.7 (d, 1, J = 7 Hz, phenyl), 6.7 (m, 2, phenyl), 3.8 (s, 3, $-OCH_3$), 2.6 (quartet, 2, J = 8 Hz, $-CH_2CH_3$) and 1.1 (t, 3, J = 8 Hz, $-CH_2CH_3$).

Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.12; H, 7.39.

2-Ethyl-4-methoxyphenylacetylene (5). A mixture of Zn powder (2.62 g, 0.04 g atom), 10.5 g of triphenylphosphine (0.04 mol), 13.3 g of CBr_4 (0.04 mol), and 300 mL of CH_2Cl_2 was stirred under Ar for 24 h. After the dropwise addition of 3.3 g of **4** (0.02 mol) the mixture was stirred an additional 2 h. Addition of 1.2 L of pentane, filtration, and evaporation of solvents gave dibromo-2-(2′-ethyl-4′-methoxyphenyl)ethene. Insoluble material was reworked by additional cycles of CH_2Cl_2 extraction–pentane precipitation to maximize yield of dibromoolefin to 5.5 g (86%). This yellow liquid was used without further purification.

A solution of 5.5 g of dibromoolefin in 60 mL of THF was cooled to −78 °C (dry ice–acetone) and *n*-butyllithium (44 mL, 0.8934 M) was added dropwise. After 1 h at −78 °C, the reaction was warmed to room temperature and poured into 200 mL of water. The alkyne was extracted with pentane. Distillation afforded 2.5 g (80%) of clear colorless liquid: bp 112–113 °C (7.5 Torr); IR (film) 3300, 2100, 1605, 1490, 1235, 1030, and 640 cm^{-1}; NMR ($CDCl_3$) δ 6.8 (m, 3, phenyl), 3.7 (s, 3, OCH_3), 2.95 (s, 1, C≡CH), 2.7 (quartet, 2, J = 8 Hz, $-CH_2CH_3$), 1.2 (t, 3, J = 8 Hz, $-CH_2CH_3$).

Anal. Calcd for $C_{11}H_{12}O$: C, 82.46; H, 7.55. Found: C, 82.62; H, 7.64.

Registry No.—**1**, 620-17-7; **2**, 10568-38-4; **3**, 34881-44-2; **4**, 6161-69-9; **5**, 62929-98-0; dibromo-2-(2′-ethyl-4′-methoxyphenyl)ethene, 62929-99-1.

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Synthesis of Olefins via Reduction–Decyanation of β,γ-Unsaturated Nitriles

James A. Marshall* and Richard Bierenbaum

Department of Chemistry, Northwestern University, Evanston, Illinois 60201

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As part of a program aimed at developing methodology for the synthesis of natural products, we are examining dual uses of the cyano function as an activating and leaving group. We