Convenient and General Synthesis of 2-Alkoxy-3-arylcyclopropenones

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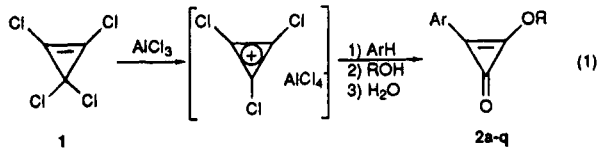
Introduction

Since the original preparation of diphenylcyclopropenone by Breslow[3] and Vol'pin[4] in 1959, the syntheses and reactions of a wide variety of cyclopropenones have been studied for many years.[5] Remarkably, however, there have been only a few references to the syntheses of alkoxy-substituted cyclopropenones, and these suffer from very poor yields and/or multistep procedures.[6-8] Although a fairly general approach to 3-aryl-2-hydroxycyclopropenones has been reported,[9] no further work toward O-substituted cyclopropenones, other than isolated references to the reactivity of 2-methoxy-3-phenylcyclopropenone (**2a**) and arylhydroxycyclopropenones has appeared.[10,11] We wish to report here a convenient and general synthesis of 2-alkoxy-3-arylcyclopropenones, which allows for the preparation of a variety of derivatives in a one-pot procedure.

The title compounds can be easily synthesized *via* the use of cyclopropenium ion chemistry (eq 1). Formation of the known trichlorocyclopropenium tetrachloroaluminate from tetrachlorocyclopropene (**1**)[12] followed by sequential treatment with an activated aromatic system, 3 equiv of an appropriate alcohol, and then careful aqueous hydrolysis provides 2-alkoxy-3-arylcyclopropenones in good yields **2a–q** (Table 1). Although the alcoholysis of isolated monoaryltrichlorocyclopropenones



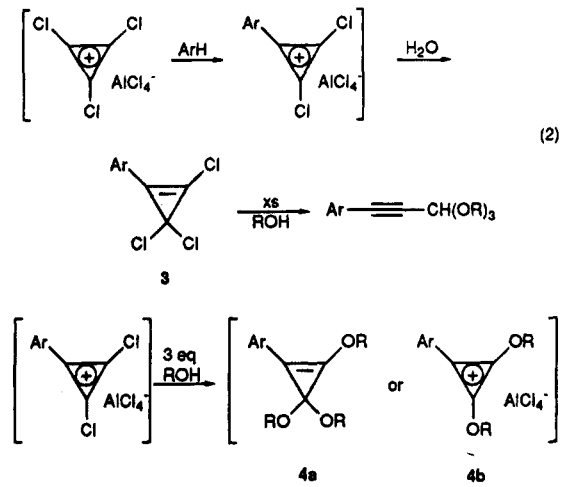
(1)

has been shown to generate arylpropiolate orthoesters,[13] careful addition of 3 equiv of the alcohol at low temperature to their cyclopropenium ion precursors apparently forms either the 3-aryl-1,1,2-trialkoxycyclopropenes **4a** or the 3-aryl-1,2-dialkoxycyclopropenium ion **4b**, both of which can be hydrolyzed to the title compounds (eqs 2, 3).[14]

Table 1. Data for 2-Alkoxy-3-arylcyclopropenones

compd	Ar	R	temp[a] (°C)	yield[b] (%)	mp (°C)
2a	Ph	Me	0	80	56–57[c]
2b	Ph	Et	0	88	oil
2c	Ph	*i*-Pr	0	78	oil
2d	mesityl	Me	−30	90	128.5–129
2e	mesityl	Et	−30	83	76–77
2f	mesityl	*i*-Pr	−30	71	68–69
2g	*p-tert*-butylphenyl	Me	0	88	79–81
2h	*p-tert*-butylphenyl	Et	0	97	oil
2i	*p-tert*-butylphenyl	*i*-Pr	0	99	oil
2j	2,5-dimethoxyphenyl	Me	−78	84	148–149
2k	2,5-dimethoxyphenyl	Et	−78	94	57–58[d]
2m	4-methoxyphenyl	Et	−78	67	oil[e]
2n	mesityl	CH_2CH_2OMe	−30	94	56–57
2o	2-methoxy-naphthalene	Me	−78	77	110–111[d]
2p	Ph	*n*-Bu	0	91	oil

[a] For addition of aromatic to $C_3Cl_3^+$. [b] Yields represent crude yields of products (90–95% pure by ^1H NMR) except for soil products that are isolated, recrystallized (petroleum ether) yield. [c] Literature mp[4] 54–57 °C. [d] Recrystallization from cyclohexane. [e] ~9:1 mixture of para:ortho isomers by ^1H NMR.



Although the mechanistic details of the processes depicted in eqs 2 and 3 are not fully understood, the remarkable difference in product distribution can be rationalized in several ways. During the formation of arylpropiolate orthoesters (eq 2), the 3-aryl-1,1,2-trichlo-

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(14) Although there is no direct experimental evidence for preferring one of these species over the other, either of them are logical intermediates given the stoichiometry of the reaction and the observed products.

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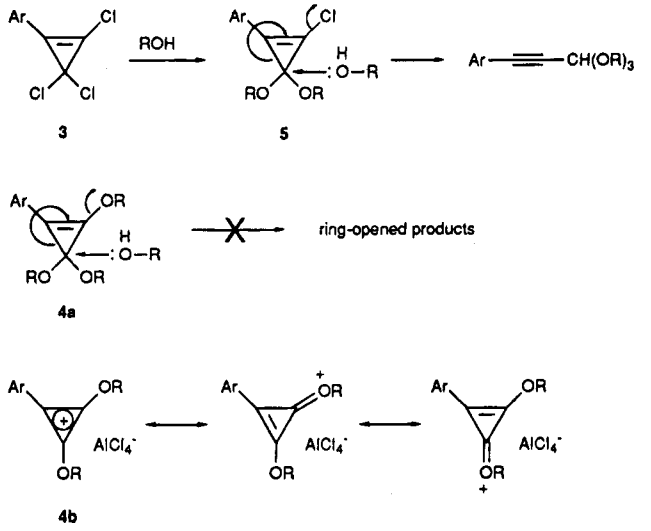
Scheme 1



rocyclopropene **3** is presumed to undergo an alcoholysis of both *gem*-dichlorides in the presence of an *excess* of alcohol to generate a 1,1-dialkoxy-3-arylcyclopropene **5** (Scheme 1), which subsequently undergoes ring opening with stepwise or concerted elimination of chloride to provide the orthoester. On the other hand, if addition of alcohol to the aryldichlorocyclopropenium ion first generates the intermediate **4a** ring opening should be disfavored because the 2-alkoxy is a poorer leaving group than the halogen, and the concentration of alcohol is low. This difference in propensity to eliminate may prevent the ring-opening process from competing effectively, and allow for subsequent hydrolysis of the cyclopropene intermediate to cyclopropenone products.[15] If an intermediate like **4b** is generated upon addition of an alcohol, it could be argued that the additional stabilization imparted by the corresponding oxonium ion resonance structures prevents the ring-opening pathway from competing effectively. In any event, good to excellent yields of the alkoxyarylcyclopropenones are obtained following the described experimental procedure.

As exemplified in Table 1, a wide variety of alkoxyarylcyclopropenones can be prepared in good-to-excellent yields. The synthesis of the known 2-methoxy-3-phenylcyclopropenone **2a** by this procedure further confirms the structure of these products.[6] Many of the alkoxyarylcyclopropenones tend to be hydrolytically unstable, and products obtained as oils are not amenable to further purification; however, spectroscopic analysis generally indicated the products to be >90% pure. See the supplementary material for some representative ^{1}H NMR spectra of crude reaction products. Analytical samples of solid products were obtained by quick recrystallization from petroleum ether or cyclohexane. The more sterically hindered derivatives such as **2d–f** and **2j** tend to be considerably more stable to hydrolysis, although all the materials were sufficiently stable under dry, cold storage. The alkoxyarylcyclopropenones are readily characterized by ^{1}H NMR, and, in particular, by their distinctive absorption bands in the IR (~1850, 1650 cm^{-1}). The IR spectra proved to be useful diagnostic tools to determine if ring-opened hydrolysis products are present, as these ring-opened adducts exhibit strong bands in the 1725 cm^{-1} region.

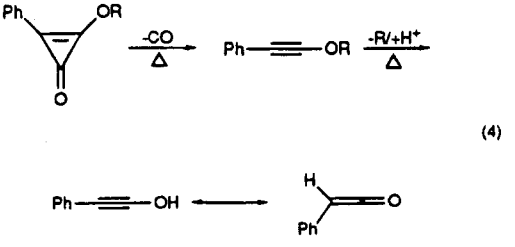
Table 2. 1-Alkoxy-2-arylacetylenes from Photolysis of 1-Alkoxy-2-arylcyclopropenones

compd	Ar	R	time (h)	yield[a] (%)
3a	Ph	Et	24	87
3b	4-methoxyphenyl	Et	25	69[b]
3c	4-*tert*-butylphenyl	Et	18	81
3d	mesityl	Et	20	78
3e	mesityl	*i*-Pr	22	78
3f	mesityl	Me	28	65

[a] Yields represent those for isolated pure materials. [b] Only *p*-methoxyisomer isolated from an initial 9:1 mixture of *p*:*o*-methoxy isomers.

An attempt to apply the general procedure to the preparation of 2-*tert*-butoxy-3-phenylcyclopropenone *via* the general method generated isobutylene and a mixture of unidentified materials, not surprising given the reaction environment. The use of hydrophobic alcohols of higher MW than butanol in the procedure also led to purification difficulties because the alkoxyarylcyclopropenones are thermally, hydrolytically, and chromatographically unstable. Products from the reaction with *n*-hexanol were isolated and identified spectroscopically, but could not be completely separated from the *n*-hexanol contaminant.

Attempts to analyze **2a–c** by GC-MS further demonstrated the thermal instability of these species. Injection of a solution of **2c** provided a material of *m*/*z* 118 as the only identifiable thermal product, consistent with either 1-hydroxy-2-phenylacetylene or phenylketene.[16] Compound **2b**, on the other hand, provided two thermal products, one with *m*/*z* 118 as seen with **2c**, and a second one with *m*/*z* of 146, consistent with the formation of 1-ethoxy-2-phenylacetylene. Subjecting **2a** to the same analysis gave a single product of *m*/*z* 132, consistent with 1-methoxy-2-phenylacetylene. These results are in accord with the known propensity of cyclopropenones to thermally decarbonylate to provide acetylenes,[5] as well as the relative tendencies of *i*-propyl, ethyl, and methyl to eliminate the corresponding alkene or alkylidene fragment under the ionizing conditions of the mass spectrometer (eq 4). Although no preparative attempts were made, the relative ease of cleanly generating these ketenes or acetylenes under thermal conditions suggests their potential use as reactive intermediates that could be trapped *in situ*.



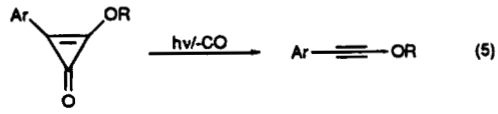
(4)

On the other hand, photolyses of these 2-alkoxy-3-arylcyclopropenones cleanly generated 1-alkoxy-2-arylacetylenes **3** in good yields (eq 5 and Table 2). Flash photolyses of methoxyphenylcyclopropenone and methoxymesitylcyclopropenone have been shown to generate methoxyphenylacetylene and methoxymesitylacetylene,

(15) A similar argument has been proposed for the hydrolysis of monoaryltrihalocyclopropenes: West, R.; Zecher, D. C.; Tobey, S. W. *J. Am. Chem. Soc.* **1969**, *92*, 168.

(16) For a discussion of the behavior of alkoxyacetylenes during mass spectral analysis, see: Tanaka, R.; Miller, S. I. *Tetrahedron Lett.* **1971**, 1753.

respectively, although these materials were not made on a preparative scale.[11] Starting with the appropriately substituted cyclopropenones, a variety of 1-alkoxy-2-



(5)

2 3

arylacetylenes **3** can be prepared, a representative sampling of which is shown in Table 2. Preparations of alkoxyarylacetylenes from halogenated styrenes are plagued by low yields and limited structural variations.[17,18] Alternative syntheses based on nucleophilic substitution of haloacetylenes are also subject to low yields, lack of generality, and the use of unstable haloacetylenes.[16,19] The photolytic decarbonylations can be carried out in CH_2Cl_2 (monitored easily by IR) and the product acetylenes isolated by simply evaporating the solvent. Because these alkoxyacetylenes are unstable and tend to polymerize under ambient conditions, they must be made fresh prior to their utilization for other purposes.[17]

In conclusion, a facile, one-pot synthesis of 2-alkoxy-3-arylcyclopropenones has been shown. The reaction is general and lends itself to the synthesis of a wide variety of substituted 2-alkoxy-3-arylcyclopropenones. These materials undergo photolytic decarbonylation to generate the corresponding 1-alkoxy-2-arylacetylenes in good to excellent yields on a preparative scale. Investigation of the reactivity of these and related species is currently ongoing in these laboratories.

Experimental Section

Spectral and analytical procedures have been outlined previously,[20] solvents were dried over activated 3 Å sieves and all other reagents were used as received from Kodak Laboratory & Research Products or Aldrich Chemical Co.

General Procedure for the Preparation of Alkoxyarylcyclopropenones 2. The synthesis of 2-ethoxy-3-phenylcyclopropenone (**2b**) is representative:

A mixture of tetrachlorocyclopropene (1.78 g, 10.0 mmol) and anhydrous aluminum chloride (1.47 g, 11.0 mmol) in 15 mL of dry dichloromethane was cooled to 0 °C and treated dropwise with a solution of benzene (0.78 g, 10.0 mmol) in 5 mL of dichloromethane. After the addition is complete, the mixture was heated to reflux for 10 min, cooled to −10 °C, and treated with ethanol (1.38 g, 30.0 mmol) dropwise. The mixture was stirred at room temperature for 1 h, cooled to 0 °C, and washed with three portions of ice−water.[21] The organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo* to provide 1.53 g (88%) of 2-ethoxy-3-phenylcyclopropenone (**2b**) as an oil: ^{1}H NMR ($CDCl_3$) δ 7.68−7.60 (m, 2 H), 7.55−7.48 (m, 3 H), 4.55 (q, J = 7.1 Hz, 2 H), 1.53 (t, J = 7.1 Hz, 3 H); IR (neat) 1855, 1650, 1327 cm^{-1}; HRFABMS for $C_{11}H_{11}O_2$ (M^+ + H) requires m/z 175.0759, found 175.0767.

For the synthesis of products that contain an aryl group that was added to the trichlorocyclopropenium ion at temperatures below 0 °C (**2d−f**, **j-m**, **o**, and **p**, see Table 1), the aromatic derivative was generally dissolved in CH_2Cl_2 and added via an addition funnel to minimize the amount of diarylcyclopropenium byproducts produced. Spectral properties for all other compounds follow:

2-Methoxy-3-phenylcyclopropenone (2a): mp 56−57 °C, lit. mp[6] 54-57 °C; ^{1}H NMR ($CDCl_3$) δ 7.65−7.60 (m, 2 H), 7.55−7.48 (m, 3 H), 4.30 (s, 3 H); IR (neat) 1856, 1661, 1342 cm^{-1}.

2-*i*-Propoxy-3-phenylcyclopropenone (2c): ^{1}H NMR ($CDCl_3$) δ 7.70−7.65 (m, 2 H), 7.50−7.40 (m, 3 H), 4.82 (septet, J = 6.3 Hz, 1 H), 1.51 (d, J = 6.3 Hz, 6 H); IR (neat) 1850, 1657, 1315 cm^{-1}; HRFABMS for $C_{12}H_{13}O_2$ (M^+ + H) requires m/z 189.0916, found 189.0920.

2-Methoxy-3-(2,4,6-trimethylphenyl)cyclopropenone (2d): ^{1}H NMR ($CDCl_3$) δ 6.89 (s, 2 H), 4.29 (s, 3 H), 2.54 (s, 6 H), 2.30 (s, 3 H); IR (KBr) 1851, 1650, 1329 cm^{-1}; FABMS m/z 203 (M^+ + H). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 77.16; H, 6.95.

2-Ethoxy-3-(2,4,6-trimethylphenyl)cyclopropenone (2e): ^{1}H NMR ($CDCl_3$) δ 6.89 (s, 2 H), 4.55 (q, J = 7.1 Hz, 2 H), 2.55 (s, 6 H), 2.30 (s, 3 H), 1.53 (t, J = 7.1 Hz, 3 H); IR (KBr) 1846, 1641, 1317 cm^{-1}; FABMS m/z 217 (M^+ + H). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 78.01; H, 7.27.

2-*i*-Propoxy-3-(2,4,6-trimethylphenyl)cyclopropenone (2f): ^{1}H NMR ($CDCl_3$) δ 6.89 (s, 2 H), 4.83 (septet, J = 6.3 Hz, 1 H), 2.55 (s, 6 H), 2.30 (s, 3 H), 1.51 (d, J = 6.3 Hz, 6 H); IR (KBr) 1843, 1635, 1312 cm^{-1}; FABMS m/z 231 (M^+ + H). Anal. Calcd for $C_{15}H_{18}O_2$: C, 78.23; H, 7.88. Found: C, 77.78; H, 7.88.

2-Methoxy-3-(4-*tert*-butylphenyl)cyclopropenone (2g): ^{1}H NMR ($CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 2 H), 7.47 (d, J = 8.2 Hz, 2 H), 4.30 (s, 3 H), 1.33 (s, 9 H); IR (neat) 1859, 1657, 1336 cm^{-1}; HRFABMS for $C_{14}H_{17}O_2$ (M^+ + H) requires m/z 217.1229, found 217.1226.

2-Ethoxy-3-(4-*tert*-butylphenyl)cyclopropenone (2h): ^{1}H NMR ($CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2 H), 7.46 (d, J = 8.3 Hz, 2 H), 4.54 (q, J = 7.1 Hz, 2 H), 1.53 (t, J = 7.1 Hz, 3 H), 1.33 (s, 9 H); IR (neat) 1859, 1651, 1325 cm^{-1}; HRFABMS for $C_{15}H_{19}O_2$ (M^+ + H) requires m/z 231.1385, found 231.1386.

2-*i*-Propoxy-3-(4-*tert*-butylphenyl)cyclopropenone (2i): ^{1}H NMR ($CDCl_3$) δ 7.61 (d, J = 8.3 Hz, 2 H), 7.46 (d, J = 8.3 Hz, 2 H), 4.81 (septet, J = 6.3 Hz, 1 H), 1.50 (d, J = 6.3 Hz, 6 H), 1.33 (s, 9 H); IR (neat) 1856, 1656, 1319 cm^{-1}; HRFABMS for $C_{16}H_{21}O_2$ (M^+ + H) requires m/z 245.1541, found 245.1542.

2-Methoxy-3-(2,5-dimethoxyphenyl)cyclopropenone (2j): ^{1}H NMR ($CDCl_3$) δ 7.18 (d, J = 3.0 Hz, 1 H), 6.99 (dd, J = 9.0, 3.0 Hz, 1 H), 6.88 (d, J = 9.0 Hz, 1 H), 4.28 (s, 3 H), 3.88 (s, 3 H), 3.79 (s, 3 H); IR (neat) 1858, 1649, 1489, 1213 cm^{-1}; HRFABMS for $C_{12}H_{13}O_4$ (M^+ + H) requires m/z 221.0814, found 221.0811.

2-Ethoxy-3-(2,5-dimethoxyphenyl)cyclopropenone (2k): ^{1}H NMR ($CDCl_3$) δ 7.18 (d, J = 3.1 Hz, 1 H), 6.97 (dd, J = 9.0, 3.1 Hz, 1 H), 6.88 (d, J = 9.0 Hz, 1 H), 4.54 (q, J = 7.1 Hz, 2 H), 3.89 (s, 3 H), 3.79 (s, 3 H), 1.52 (t, J = 7.1 Hz, 3 H); IR (KBr) 1860, 1650 cm^{-1}; FABMS m/z 235 (M^+ + H); Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 6.02. Found: C, 66.26; H, 6.01.

2-Ethoxy-3-(4-methoxyphenyl)cyclopropenone (2m): ^{1}H NMR ($CDCl_3$) δ 7.60 (d, J = 8.6 Hz, 2 H), 6.92 (d, J = 8.6 Hz, 2 H), 4.49 (q, J = 7.1 Hz, 2 H), 3.83 (s, 3 H), 1.49 (t, J = 7.1 Hz, 3 H; IR (neat) 1857, 1644, 1256 cm^{-1}; HRFABMS for $C_{12}H_{13}O_3$ (M^+ + H) requires m/z 205.0865, found 205.0898.

2-(2-Methoxyethoxy)-3-(2,4,6-trimethylphenyl)cyclopropenone (2n): ^{1}H NMR ($CDCl_3$) δ 6.89 (s, 2 H), 4.65−4.55 (m, 2 H), 3.85−3.75 (m, 2 H), 3.43 (s, 3 H), 2.56 (s, 6 H), 2.30 (s, 3 H; IR (KBr) 1864, 1841, 1637, 1611, 1311 cm^{-1}; HRFABMS for $C_{15}H_{19}O_3$ (M^+ + H) requires m/z 247.1334, found 247.1343.

2-Methoxy-3-(2-methoxynaphthyl)cyclopropenone (2o): ^{1}H NMR ($CDCl_3$) δ 8.59 (d, J = 8.6 Hz, 1 H), 7.97 (d, J = 9.0 Hz, 1 H), 7.79 (d, J = 8.2 Hz, 1 H), 7.67 (t, J = 7.8 Hz, 1 H), 7.42 (t, J = 7.8 Hz, 1 H), 7.27 (d, J = 8.6 Hz, 1 H), 4.35 (s, 3 H), 4.06 (s, 3 H); IR (neat) 1855, 1655 cm^{-1}; HRFABMS for $C_{15}H_{13}O_3$ (M^+ + H) requires m/z 241.0865, found 241.0865.

2-*n*-Butoxy-3-phenylcyclopropenone (2p): ^{1}H NMR ($CDCl_3$) δ 7.70−7.62 (m, 2 H), 7.50−7.40 (m, 3 H), 4.50 (t, J = 6.6 Hz, 2 H), 1.90−1.80 (m, 2 H), 1.55−1.43 (m, 2 H), 0.99 (t, J = 7.4 Hz, 3 H); IR (neat) 1854, 1657, 1332 cm^{-1}; HRFABMS for $C_{13}H_{15}O_2$ (M^+ + H) requires m/z 203.1072, found 203.1088.

General Procedure for the Preparation of 1-Alkoxy-2-arylacetylenes. The synthesis of 1-ethoxy-2-phenylacetylene (**3a**) is representative:

(17) Jacobs, T. L.; Scott, W. R., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 5497.
(18) Viehe, H. G. *Angew. Chem. Int. Ed. Engl.* **1963**, *2*, 477.
(19) Verboom, W.; Westmijze, H.; Bos, H. J. T.; Vermeer, P. *Tetrahedron Lett.* **1978**, 1441.
(20) Weidner, C. H.; Michaels, F. M.; Beltman, D. J.; Montgomery, C. J.; Wadsworth, D. H.; Briggs, B. T.; Picone, M. L. *J. Org. Chem.* **1991**, *56*, 5594.
(21) The aqueous hydrolysis must be done quickly with ice−water to avoid the formation of undesired ring-opened products.

A solution of 2-ethoxy-3-phenylcyclopropenone (**2b**) (0.72 g, 4.1 mmol) in CH_2Cl_2 (60 mL) was thoroughly flushed with Ar and irradiated through Pyrex with a 200 W Xe–Hg lamp for 24 h. The mixture was concentrated *in vacuo* and purified by column chromatography (SiO_2; pentane/CH_2Cl_2 9:1 v/v) to provide 0.52 g (87%) of acetylene **3a** as an oil, identical in all respects to the known literature compound:[16] ^{1}H NMR ($CDCl_3$) δ 7.40–7.20 (m, 5 H), 4.22 (q, J = 7.1 Hz, 2 H), 1.45 (t, J = 7.1 Hz, 3 H); IR (neat) 2983, 2259, 1321, 1063 cm^{-1}.

Spectral data for the other acetylenic ethers in Table 2 follows:

1-Ethoxy-2-(4-methoxyphenyl)acetylene (3b): ^{1}H NMR ($CDCl_3$) δ 7.27 (d, J = 8.7 Hz, 2 H), 6.80 (d, J = 8.7 Hz, 2 H), 4.19 (q, J = 7.1 Hz, 2 H), 3.79 (s, 3 H), 1.44 (t, J = 7.1 Hz, 3 H); IR (neat) 2955, 2243, 1040 cm^{-1}.

1-Ethoxy-2-(4-*tert*-butylphenyl)acetylene (3c): ^{1}H NMR ($CDCl_3$) δ 7.28 (s, 4 H), 4.21 (q, J = 7.0 Hz, 2 H), 1.33 (t, J = 7.0 Hz, 3 H), 1.30 (s, 9 H); IR (neat) 2960, 2248, 1108 cm^{-1}.

1-Ethoxy-2-(2,4,6-trimethylphenyl)acetylene (3d): ^{1}H NMR ($CDCl_3$) δ 6.80 (s, 2 H), 4.19 (q, J = 7.1 Hz, 2 H), 2.31, (s, 6 H), 2.21 (s, 3 H), 1.43 (t, J = 7.1 Hz, 3 H); IR (neat) 2980, 2875, 2244, 1035 cm^{-1}.

1-*i*-Propoxy-2-(2,4,6-Trimethylphenyl)acetylene (3e): ^{1}H NMR ($CDCl_3$) δ 6.82 (s, 2 H), 4.41 (septet, J = 6.3 Hz, 1 H), 2.34 (s, 6 H), 2.24 (s, 3 H), 1.44 (d, J = 6.3 Hz, 6 H); IR (neat) 2980, 2240, 1035 cm^{-1}.

1-Methoxy-2-(2,4,6-Trimethylphenyl)acetylene (3f): ^{1}H NMR ($CDCl_3$) δ 6.83 (s, 2 H), 4.00 (s, 3 H), 2.34 (s, 6 H), 2.24 (s, 3 H); IR (neat) 2935, 2250, 1040 cm^{-1}.

Supplementary Material Available: ^{1}H NMR spectra for compounds **2c–2h**, **n–p**, **3b,** and **3c** (11 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.