Experimental Section

The nitroso oxazolidones 1a–d were prepared by the method of Newman.[1] The structures of all intermediates in these syntheses were established by nmr, ir, and agreement of physical constants with published data.

5-Benzyl-5-methyl-2-oxazolidone was obtained in 53% yield: mp 103°; nmr ($CDCl_3$) τ 8.60 (s, 3, CH_3), 7.05 (s, 2, CH_2C_6H), 6.65 (2 d, AB pattern of C-4 hydrogens), 3.59 (s, 1, O=CNH), 2.70 (s, 5, C_6H_5).

Anal. Calcd for $C_{11}H_{13}NO_2$: C, 69.11; H, 6.81; O, 16.75; N, 7.33. Found: C, 69.15; H, 6.90; N, 7.20.

5-Benzyl-5-methyl-3-nitroso-2-oxazolidone was obtained in 80% yield: mp 80°; nmr τ 8.49 (s, 3, CH_3), 7.00 (s, 2, $CH_2C_6H_5$) 6.0–6.7 (2 d, 2, C-4 hydrogens, AB pattern), 2.72 (s, 5, C_6H_5).

Anal. Calcd for $C_{11}H_{12}O_3N_2$: C, 60.00; H, 5.45; O, 21.82; N, 12.73. Found: C, 59.91; H, 5.56; N, 12.51.

Decompositions.—To a stirred solution of 0.10 mol of the nitroso oxazolidone in 100 ml of dried ether at room temperature, 0.10 mol of butylamine was added in one portion. The evolved gases were passed through a $Ba(OH)_2$ solution trap and the nitrogen was measured by displacement of water. The theoretical nitrogen volume was obtained within 2 hr. The ether solution was washed with dilute HCl and then H_2O, dried (Na_2SO), and concentrated. Distillation gave a 99–100% yield of the arylacetylene. Vpc, ir, and nmr analyses failed to indicate any trace contaminates. The physical properties were in agreement with published data.

Registry No.—**1d,** 36783-10-5; 5-benzyl-5-methyl-2-oxazolidone, 36838-64-9; butylamine, 109-73-9.

Acknowledgment.—The authors are grateful to Professor James Wilt, Loyola University, Chicago, Ill., for providing the nmr facilities.

Synthesis and Metalation of 2-Ethynylthiophene

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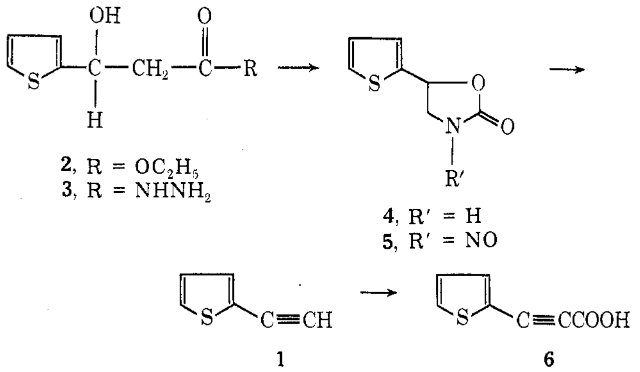
Initiation of a study designed to develop new and improved syntheses of naturally occurring acetylenes[1] required us to prepare 2-ethynylthiophene (**1**). After many attempts to prepare **1** by dehydrohalogenation of α,α-dichloro-2-ethylthiophene using described literature procedures[2] were found to give only small amounts of impure **1**, we pursued other means of preparing the title compound.

A successful route to **1** is shown in Scheme I. The conversion of **2** → **1** occurred in 57% overall yield. Best results were obtained when 5-(2-thienyl)-3-nitroso-2-oxazolidone (**5**) was used immediately following its preparation. Basic decomposition of 5-substituted 3-nitroso-2-oxazolidones to yield acetylenic compounds has been developed by Newman and coworkers,[3] and proves to be a very useful procedure for preparing various types of acetylenes.

SCHEME I



Metalation of thiophene derivatives having more than one acidic position has received increased attention for both synthetic and theoretical reasons.[4] Metalation of **1**, which has both an acidic acetylenic hydrogen and an acidic hydrogen on the thiophene 5 position, with *n*-butyllithium followed by carbonation and acidification of the reaction mixture gave a 73% yield of 2-thienylpropiolic acid. Spectral evidence for reaction at the thiophene 5 position was not found. Lithium 2-thienylacetylide seems to have more synthetic utility than sodium 2-thienylacetylide, since it is reported that the latter compound yields only small amounts of carbonation product.[2b]

Competitive metalation of equal molar amounts of **1** and phenylacetylene with insufficient amounts of *n*-butyllithium showed that the ratio of lithium 2-thienylacetylide to lithium phenylacetylide was 2.4:1, indicating that **1** is more acidic than phenylacetylene. The ratio was determined by nmr analysis of the carbonation products. The pK_a of **1** was thus determined to be 22.4[5] using a value of 23.2 for the pK_a of phenylacetylene.[6] The *J* (^{13}CH) values of 257 for **1** and 246 for phenylacetylene are in agreement with the greater acidity found for **1**.[7]

Experimental Section

3-Hydroxy-3-(2-thienyl)propionic Acid Hydrazide (**3**).—Anhydrous hydrazine (2.4 g, 0.09 mol) was added to a mixture of 15 g (0.08 mol) of ethyl 3-hydroxy-3-(2-thienyl)propionate[8] and 10 ml of methanol. After 1 hr, the entire contents had solidified. Recrystallization from methanol furnished pure **3** (13.0, g, 93%), mp 139–140°.

Anal. Calcd for $C_7H_{10}N_2O_2S$ (mol wt 186): C, 45.2; H, 5.4; N, 15.1. Found: C, 45.2; H, 5.5; N, 14.8.

5(2-Thienyl)-2-oxazolidone (**4**).—A solution of 10.0 g (0.05 mol) of **3** in 30 ml of 6 *N* hydrochloric acid was treated at −5° with a solution of 4.0 g of sodium nitrite in 10 ml of water during 30 min. The mixture was stirred for 30 min and gave a positive nitrous acid test. The cold solution was extracted with three 100-ml portions of 3:1 benzene–chloroform. The dried organic solution ($MgSO_4$) was heated at reflux until nitrogen evolution ceased (1.5 hr). Solvents were removed and the remaining brown oil was crystallized from hexane–ether to yield 6.4 g (71%) of pure **4**, mp 92–94°.

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The nmr spectrum ($CDCl_3$) showed absorptions at δ 3.6–4.1 (m, 2 H, CH_2), 5.8–6.1 (m, 6.7 (broad, NH), and 7.1–7.7 (m, 3 H, C_4H_3S–).

Anal. Calcd for $C_7H_7NO_2S$: C, 49.7; H, 4.1; N, 8.3. Found: C, 49.9; H, 4.3; N, 8.4.

5-(2-Thienyl)-3-nitroso-2-oxazolidone (5).—A mixture of 4.0 g (0.23 mol) of **4** in 40 ml of dry ether and 4.2 g of sodium bicarbonate was treated at −60° with 2.0 g of N_2O_4. The mixture was allowed to come to room temperature and then filtered. The solvent was removed on a rotary evaporator and the yellow solid thus obtained was converted immediately into 2-ethynylthiophene.

A small sample of **5** was dried *in vacuo* for 20 min and gave a melting range of 60–65° with gas evolution. An nmr spectrum ($CDCl_3$) showed absorptions at δ 4.0–4.8 (CH_2), 6.1–6.4 (CH), and 7.3–7.9 (C_4H_3S–).

2-Ethynylthiophene (1).—The product obtained from the previous reaction was dissolved in methanol (50 ml) and treated with sodium methoxide solution until gas evolution stopped. The mixture was poured into water, extracted with ether, and dried. The dried extracts from three runs were combined and distilled. The yield of **1** was 6.0 g (79%), bp 54–60° (20 mm), n^{24}D 1.5882 (lit.[2a] n^{20}D 1.5886).

The infrared spectrum showed strong absorption at 3300 cm^{-1} (C≡CH) and medium absorption at 2100 cm^{-1} (C≡C). The nmr spectrum (CCl_4) showed absorption at δ 3.18 (C≡CH) and 6.8–7.4 (C_4H_3S–).

2-Thienylpropiolic Acid (6).—To a solution of 0.50 g (4.6 mmol) of **1** in dry ether was added 1.2 ml (6.7 mmol) of freshly prepared ethereal *n*-butyllithium (1.6 *N*). After 3 hr, 3 g of Dry Ice was added to the mixture with stirring. Water (5 ml) was added to the mixture and the contents were extracted with ether. The water layer was acidified to give 0.5 g (72%) of **6** which had mp 130–133° dec after drying (lit.[2b] mp 130–133°). Unreacted **1** accounted for the balance of the material. The infrared spectrum (KBr) showed absorptions at 3000 (broad, acid), 2200 (C≡C), and 1675 cm^{-1} (C=O). The nmr spectrum (acetone-d_6) showed absorption at δ 7.4–7.6 (1 H), 7.8–8.2 2 H, (m, C_4H_3S–), and 9.9 (s, 1 H, COOH).

Competitive Metalation of 2-Ethylthiophene (1) and Phenylacetylene.—A freshly prepared ethereal solution of 1.6 *N* *n*-butyllithium (1.8 ml, 2.9 mequiv) was added under a dry nitrogen atmosphere to a solution of 0.32 g (3.0 mequiv) of **1** and 0.31 g (3.0 mequiv) of phenylacetylene in 10 ml of dry ether. After 3–4 hr, 1 g of powdered Dry Ice was added to the mixture. Water (5 ml) was added and the layers were separated. The acidified water layer was extracted with ether and worked up to give a mixture of **6** and phenylpropiolic acid, δ 7.6–8.0 (m, 5 H, C_6H_5–). A complete material balance was obtained.

Analysis of the mixture was accomplished by integration of the aromatic region of the nmr spectrum using the one-proton resonance of **6** at δ 7.4–7.6 as a standard. The ratio of **6** to phenylpropiolic acid was determined to be 2.4:1 from an average of six experiments.

Registry No.—**1**, 4298-52-6; **3**, 20795-13-5; **4**, 20805-23-6; **5**, 36740-08-6.

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The Synthesis of Arylacetylenes. 3,5-Di-*tert*-butylphenylacetylene[1]

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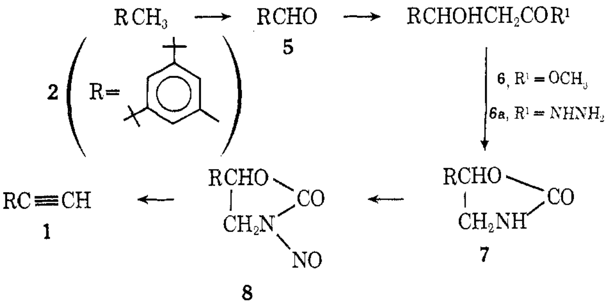
In connection with a research program designed to provide molecules of the rotaxane type[2] we required a quantity of 3,5-di-*tert*-butylphenylacetylene (**1**). As starting material 3,5-di-*tert*-butyltoluene (**2**) was readily available.[3] Our first route involved oxidation of **2** to 3,5-di-*tert*-butylbenzoic acid (**3**), which was converted into 3,5-di-*tert*-butylacetophenone (**4**). Hopefully reaction of **4** with phosphorus pentachloride followed by treatment of the dichloride (or chloro olefin) produced with strong base should yield **1**. Although **4** was readily prepared, all attempts to convert **4** in good yield to **1** were unsuccessful. A similar failure to convert 2-acetylthiophene to 2-thienylacetylene in good yield is reported.[4]

The successful route is illustrated in Scheme I. The good overall yield of 41% (all yields of pure material) from **2** to **1** indicates that this route deserves serious consideration for the synthesis of arylacetylenes.

SCHEME I



The conversion of **5** to **8** was accomplished essentially as described.[5] On treatment of **8** with butylamine[6] a 95% yield of **1** was obtained. This reagent proved superior to the aqueous alcoholic alkali previously used for the synthesis of phenylacetylene.[5,6a]

Experimental Section[7]

3,5-Di-*tert*-butylbenzaldehyde (5).—A solution of 228 g of **2**, 300 g of *N*-bromosuccinimide, and 1 g of benzoyl peroxide in 600 ml of CCl_4 was heated at reflux for 4 hr. After filtration the CCl_4 was removed on a rotary evaporator and the residue was added to a solution of 430 g of hexamethylenetetramine in 300 ml of water and 300 ml of ethanol. This solution was refluxed for 4 hr, 200 ml of concentrated HCl was added, and refluxing was continued for 30 min. The organic product was isolated as usual to yield a residue which was recrystallized from Skellysolve B [petroleum ether (bp 60–68°)] to yield 153 g (63% from **2**) of **5**,[8] mp 84–85°.

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[1] Research sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, U. S. Air Force, under Grant No. AFOSR-72-2237. The U. S. Government is authorized to reproduce and distribute reprints for Governmental purposes notwithstanding any copyright notation hereon.

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(4) See accompanying article by T. Patrick, J. M. Disher, and W. J. Probst, *J. Org. Chem.*, **37**, 4467 (1972).

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(6) Private communication from Father H. P. Hogan. See accompanying article by H. P. Hogan and J. Seehafer, *J. Org. Chem.*, **37**, 4466 (1972).

(6a) NOTE ADDED IN PROOF.—Recently, **5** has been converted into **1** by the method of E. J. Corey and P. L. Fuchs, *Tetrahedron Lett.*, 3769 (1972).

(7) All melting points are uncorrected. Analyses were performed by M-H-W Laboratory, Garden City, Mich. 48135. The phrase "worked up as usual" means that an ether–benzene solution of the products was washed with aqueous acid and/or alkali and saturated salt solution, and was filtered through anhydrous magnesium sulfate. The solvents were then removed on a rotary evaporator and the residue was treated as described. All experiments were repeated at least once. All new compounds gave ir, nmr, and mass spectra consistent with the assigned structures.

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