which would enable us to introduce an appropriate isotope at specific positions.

The key step in our four-step synthesis from pyridine-3-aldehyde (**1**) is the 1,4 addition of the anion of α-morpholino-α-(3-pyridyl)acetonitrile (**2**), an acyl-carbanion equivalent,[4] to acrylonitrile, affording γ-cyano-γ-morpholino-γ-(3-pyridyl)butyronitrile (**4**). The scope of this novel addition is being investigated. Compound **2** was obtained by the addition of aqueous potassium cyanide to the iminium salt formed by heating pyridine-3-aldehyde with morpholine perchlorate in morpholine.[5] Hydrolysis of **4** with aqueous acetic acid[6] yielded 3-cyano-1-(3-pyridyl)propan-1-one (**3**). Hydrogenation of this β-ketonitrile in ethanolic ammonia in the presence of Raney nickel at 3-atm pressure for 24 hr yielded a mixture of myosmine (30%) and nornicotine (60%), separated by preparative thin layer chromatography. The overall yield of the combined alkaloids from pyridine-3-aldehyde was 67%.

Experimental Section

Melting points are corrected. Microanalyses were carried out by Clark Microanalytical Laboratories, Urbana, Ill. Mass spectra were determined on an Hitachi Perkin-Elmer RMU-6D mass spectrometer.

α-Morpholino-α-(3-pyridyl)acetonitrile (2).—Pyridine-3-aldehyde (Aldrich Chemical Co.) (6.95 g) was added to a solution of morpholine perchlorate (13.3 g) in morpholine (64 ml) and the mixture was heated at 80° for 1 hr. Potassium cyanide (4.5 g), dissolved in a minimum amount of water, was added and the mixture was heated at 100° for an additional hour. The cooled reaction mixture was added to aqueous potassium carbonate (10%) and extracted with $CHCl_3$ (4 × 50 ml). The combined extract was washed with aqueous $NaHSO_3$ and then dried ($MgSO_4$). Evaporation yielded **2** as a colorless oil (12.4 g, 92%) which crystallized on standing. Crystallization from cyclohexane afforded **2** as colorless plates, mp 53–54.5°, mass spectrum *m/e* 203 (parent peak).

Anal. Calcd for $C_{11}H_{13}N_3O$: C, 65.01; H, 6.45; N, 20.67. Found: C, 65.62; H, 6.20; N, 20.33.

γ-Cyano-γ-morpholino-γ-(3-pyridyl)butyronitrile (4).—Acrylonitrile (0.61 g) dissolved in *tert*-butyl alcohol (30 ml) was added slowly (during 30 min) to a stirred solution of **2** (1.89 g) in *tert*-butyl alcohol (100 ml) which contained 11 drops of a methanolic solution of KOH (30%), the reaction being carried out at room temperature under N_2. After stirring for an additional 5 min the reaction mixture was diluted with an equal volume of water and extracted with $CHCl_3$ (4 × 50 ml). The residue obtained on evaporation of the dried ($MgSO_4$) extract was crystallized from a mixture of $CHCl_3$ and Et_2O, affording **4** as colorless prisms (2.14 g, 90%), mp 120–121°, mass spectrum *m/e* 256 (parent peak), 202 (M − CH_2CH_2CN).

Anal. Calcd for $C_{14}H_{16}N_4O$: C, 65.61; H, 6.29; N, 21.86. Found: C, 65.21; H, 6.46; N, 21.70.

3-Cyano-1-(3-pyridyl)propan-1-one (3).—Compound **4** (1.70 g) was dissolved in a mixture of acetic acid (10 ml), water (5 ml), and tetrahydrofuran (1.5 ml) and warmed at 53° for 24 hr. The reaction mixture was made basic with solid K_2CO_3 and extracted with $CHCl_3$. The residue obtained on evaporation of the dried ($MgSO_4$) extract was crystallized from Et_2O, affording the β-ketonitrile **3** as colorless plates (0.96 g, 90%), mp 66–67°.

Anal. Calcd for $C_9H_8N_2O$: C, 67.49; H, 5.03; N, 17.49. Found: C, 67.80; H, 5.13; N, 17.53.

Myosmine (5) and Nornicotine (6).—The β-ketonitrile **3** (2.31 g), dissolved in ethanol (200 ml) which had previously been saturated with ammonia, was hydrogenated at room temperature in the presence of Raney nickel (one spoonfull) at 3-atm pressure for 24 hr. The filtered mixture was acidified with HCl and evaporated to dryness *in vacuo*. The residue was made basic with aqueous K_2CO_3 and extracted with CH_2Cl_2. The liquid obtained on evaporation of the dried ($MgSO_4$) extract was subjected to preparative tlc on silica gel PF-254 (Merck), developing with the mixture of $CHCl_3$, ethanol, and concentrated NH_3 (85:14:1). The higher zone (R_f 0.63) on extraction with $CHCl_3$ afforded myosmine (0.64 g, 30%), identical (nmr, ir, tlc) with an authentic specimen. It afforded a dipicrate, mp 183–185° (lit.[3a] mp 184–185°). The lower zone (R_f 0.20) yielded *dl*-nornicotine (1.29 g, 60%), identical with an authentic specimen.

By reducing the duration of the hydrogenation the yield of myosmine was increased at the expense of the nornicotine.

Registry No.—**2**, 36740-09-7; **3**, 36740-10-0; **4**, 36740-11-1; **5**, 532-12-7; **6**, 5746-86-1.

(4) (a) G. Stork and L. Maldonado, *J. Amer. Chem. Soc.*, **93**, 5286 (1971), describe the use of protected aldehyde cyanohydrins for the synthesis of ketones; (b) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **8**, 639 (1969), has reviewed other acyl carbanion equivalents.

(5) D. J. Bennett, G. W. Kirby, and V. A. Moss, *J. Chem. Soc. C*, 2049 (1970), prepared α-aryl-α-morpholinoacetonitriles by this method, and utilized them for the synthesis of [*formyl*-^2H]-labeled aldehydes by quenching the carbanions, generated from these nitriles with base, with deuterium oxide, followed by acid hydrolysis.

(6) Hydrolysis of **4** with hydrochloric acid resulted in the formation of 4-(3-pyridyl)-4-oxobutanoic acid.

An Improved Synthesis of Arylacetylenes

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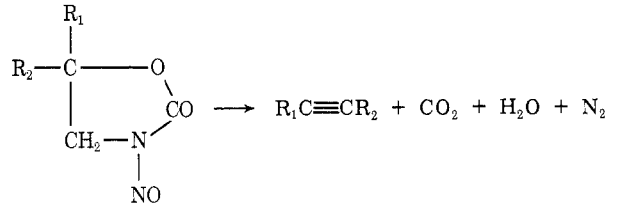
Studies of the alkaline decomposition of the readily prepared[1] 5,5-disubstituted 3-nitroso-2-oxazolidones (**1**)



$R_1 = C_6H_5$; $R_2 = H$
$R_1 = C_6H_5$; $R_2 = CH_3$
$R_1 = R_2 = C_6H_5$
$R_1 = C_6H_5CH_2$; $R_2 = CH_3$

have provided preparative pathways to rather elusive organic structures, *i.e.*, vinyl ethers,[2] vinylsilanes,[3] and vinyl halides.[3] Newman[1] has previously reported obtaining mixtures of acetylenes and carbonyl compounds in a ratio of about 2:1 from the methanolic KOH decompositions of **1a–c**. We wish to report that butylamine in ether quantitatively converts **1a**, **1b**, or **1c** to phenylacetylene, 1-phenylpropyne, and diphenylacetylene, respectively. When an aryl ring is not present in the 5 position of the nitroso oxazolidone, as in **1d**, little acetylenic product is obtained (less than 4%), and a mixture of carbonyl compounds is produced.[4] That this reaction provides an excellent general preparative route to arylacetylenes is illustrated in the following papers.[5,6]

(1) M. S. Newman and A. Kutner, *J. Amer. Chem. Soc.*, **73**, 4199 (1951).

(2) M. S. Newman and A. O. M. Okorodudu, *J. Org. Chem.*, **34**, 1220 (1969).

(3) M. S. Newman and C. D. Beard, *J. Amer. Chem. Soc.*, **91**, 5678 (1969).

(4) Newman[1] has observed the same results with various 5,5-dialkyl-substituted nitroso oxazolidones.

(5) M. S. Newman and L. F. Lee, *J. Org. Chem.*, **37**, 4468 (1972).

(6) T. B. Patrick, J. M. Disher, and W. J. Probst, *ibid.*, **37**, 4467 (1972).

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.

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Synthesis and Metalation of 2-Ethynylthiophene

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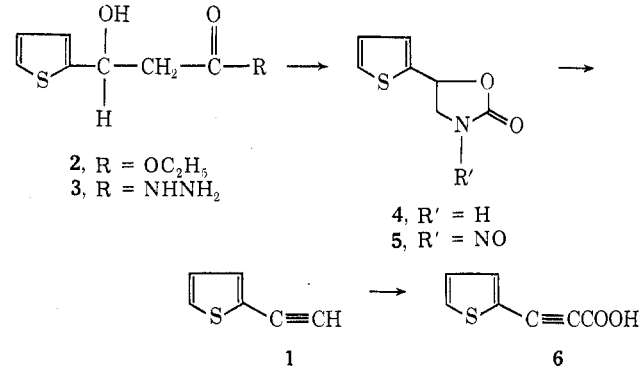
Initiation of a study designed to develop new and improved syntheses of naturally occurring acetylenes[1] required us to prepare 2-ethynylthiophene (**1**). After many attempts to prepare **1** by dehydrohalogenation of α,α-dichloro-2-ethylthiophene using described literature procedures[2] were found 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°.

(1) F. Bohlmann, "Chemistry of Acetylenes," H. G. Viehe, Ed., Marcel Dekker, New York, N. Y., 1969, p 977.

(2) (a) A. Vaitiekunas and F. F. Nord, *J. Org. Chem.*, **19**, 902 (1954); (b) A. J. Osbar, A. Vaitiekunas, and F. F. Nord, *J. Amer. Chem. Soc.*, **77**, 1911 (1955).

(3) (a) M. S. Newman and A. Kutner, *J. Amer. Chem. Soc.*, **73**, 4199 (1951). (b) See accompanying papers by M. S. Newman and L. F. Lee, *J. Org. Chem.*, **37**, 4468 (1972), and H. P. Hogan and J. Seehafer, *ibid.*, **37**, 4466 (1972).

(4) (a) D. W. H. MacDowell, R. A. Jourdenais, R. Naylor, and G. E. Paulovicks, *J. Org. Chem.*, **36**, 2683 (1971), and references cited therein; (b) D. W. H. MacDowell and A. T. Jefferies, *ibid.*, **35**, 871 (1970), and references cited therein; (c) P. L. Kelly, S. F. Thames, and J. E. McCleskey, *J. Heterocycl. Chem.*, **9**, 141 (1972).

(5) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, p 3.

(6) A. Streitwieser, Jr., and D. M. E. Reuben, *J. Amer. Chem. Soc.*, **93**, 1794 (1971).

(7) A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *ibid.*, **91**, 529 (1969).

(8) R. Schuetz and W. Houff, *ibid.*, **77**, 1836 (1955).