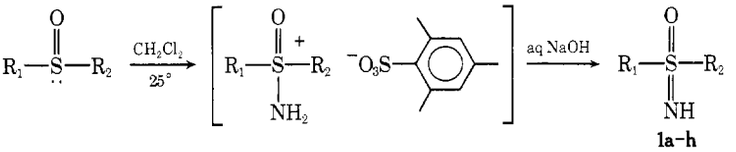
Table I
Reactions of Sulfoxides with MSH



1a-h

		Sulfoxide				Sulfoximine				
R_1	R_2	$[\alpha]^{25}D$, deg (c, acetone)	Absolute config	Optical purity, %	Registry no.	$[\alpha]^{25}D$, deg (c, acetone)	Absolute config	Optical purity, %	Reaction yield, %	Registry no.
CH_3	*p*-Tolyl	+145.0 (1.00)	*R*	99	1519-39-7	−31.9 (3.00)	*R*	98.5	80	20414-85-1
C_2H_5	*p*-Tolyl	+188.0 (1.10)	*R*	100	1519-40-0	−22.9 (1.00)	*R*	99[c]	70	51774-51-7
$CH(CH_3)_2$	*p*-Tolyl	+191.1 (1.255)	*R*	100[a]	1517-74-4	−17.1 (1.005)	*R*	99[c]	79	51774-52-8
$(CH_2)_3CH_3$	*p*-Tolyl	+193.8 (1.430)	*R*	100[b]	20288-49-7	−17.2 (1.530)	*R*	99[c]	77	51774-53-9
$C_6H_5CH_2$	*p*-Tolyl	+234 (1.00)	*R*	93	4820-07-9	+4.7 (1.26)	*R*	92[c]	60	51774-54-0
C_6H_5	*p*-Tolyl	+21.0 (1.090)	*R*	99.5	16491-20-6	+5.0 (1.075)	*R*	99[c]	19	51774-55-1
C_6H_5	CH_3	−137.0 (1.20)	*S*	94	18453-46-8	+34.1 (2.00)	*S*	93.5	70	33903-50-3
CH_3	$(CH_2)_3CH_3$	−110.3 (1.985)	*R*	92	51795-48-3	−5.00 (1.209)	*R*	91.5[c]	78	51774-56-2

[a] Highest rotation previously reported: +176.5° (ref 9). [b] Highest rotation previously reported: +187.0° (ref 9). [c] Assumed based on 99.5% retention of optical purity.

g) with a 40% excess of *O*-mesitylsulfonylhydroxylamine in methylene chloride (25 ml) at room temperature. After 2 hr the reaction mixture was poured into cold aqueous 10% NaOH (25 ml) solution, stirred for 10 min, and extracted with methylene chloride. The extracts were then washed with two 25-ml portions of 10% HCl solution and 5 ml of H_2O. If desired, unreacted sulfoxide (partially racemized) can be recovered by drying ($MgSO_4$) and concentrating the methylene chloride layer. Pure sulfoximine can be isolated as a colorless liquid or white solid by neutralizing the acidic aqueous layer with solid Na_2CO_3, extracting with methylene chloride, drying ($MgSO_4$), and concentrating. The solids were recrystallized from hexane.

Spectral data (ir and nmr) were consistent with the assigned structures. The most characteristic spectral feature indicative of the sulfoximine is noted in the infrared, where bands for the N-H (3270 cm^{-1}) and N=S=O (1110 and 1218 cm^{-1}) stretching are observed.

Registry No.—MSH, 36016-40-7.

References and Notes

(1) Part XLIX in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support of the National Science Foundation (GP 19623).
(2) C. R. Johnson, *Accounts Chem. Res.*, **6**, 481 (1973).
(3) (a) R. Fusco and F. Tericoni, *Chim. Ind. (Milan)*, **47**, 61 (1965); *Chem. Abstr.*, **62**, 10357*h* (1965); (b) C. R. Johnson and C. W. Schroeck, *J. Amer. Chem. Soc.*, **90**, 7418 (1973); (c) F. G Yamayishi, D. R. Rayner, E. T. Zuricker, and D. J. Cran, *ibid.*, **95**, 1916 (1973).
(4) H. Kwart and A. A. Kahn, *J. Amer. Chem. Soc.*, **89**, 1950 (1967).
(5) J. R. Whitehead and H. R. Bently, *J. Chem. Soc.*, 1572 (1952).
(6) Y. Tamura, K. Sumoto, J. Minamikawa, and M. Ikeda, *Tetrahedron Lett.*, 4137 (1972).
(7) D. R. Rayner, D. M. von Schriltz, J. Day, and D. J. Cram, *J. Amer. Chem. Soc.*, **90**, 2721 (1968); D. J. Cram, J. Day, D. R. Rayner, P. M. von Schriltz, and D. J. Duchamp, *ibid.*, **92**, 7369 (1970).
(8) C. W. Schroeck and C. R. Johnson, *J. Amer. Chem. Soc.*, **93**, 5306 (1971).
(9) K. Mislow, M. M. Green, P. Laur, J. T. Melillo, T. Simmons, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **187**, 1958 (1965).
(10) J. Jacobus and K. Mislow, *J. Amer. Chem. Soc.*, **89**, 5228 (1967).
(11) T. R. Williams, A. Nudelman, R. E. Booms, and D. J. Cram, *J. Amer. Chem. Soc.*, **94**, 4684 (1972).
(12) K. K. Anderson, *Tetrahedron Lett.*, 93 (1962).
(13) J. P. Lockard, C. W. Schroeck, and C. R. Johnson, *Synthesis*, 485 (1973). In footnote 11 of this paper a rotation of *n*-butyl methyl sulfoxide was reported as +071.7°. This is a typographical error. The $[\alpha]D$ observed for this sample was +51.7.°
(14) Y. Tamura, J. Minamikawa, K. Sumoto, S. Fujii, and M. Ikeda, *J. Org. Chem.*, **38**, 1239 (1973).
(15) MSH prepared by the exact procedure from ref 14 has exploded on several occasions in our laboratory. Our modified procedure results in small MSH crystals. To date we have not encountered difficulties in handling or storing (several months at 0°) MSH prepared by this modified method. R. Y. Ning, *Chem. Eng. News*, 36 (December 17, 1973), has recently issued a note of caution concerning MSH.

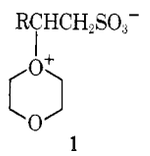
Sulfonation of 1-Butenes with Sulfur Trioxide

M. D. Robbins* and C. D. Broaddus

The Procter & Gamble Company, Miami Valley Laboratories, Cincinnati, Ohio 45239

Received April 13, 1974

The sulfonation of α-olefins can provide a variety of products ranging from sultones to alkanesulfonic acids[1] depending largely upon the sulfonating agent chosen. The reagents used most commonly are the sulfur trioxide–dioxane complex introduced by Suter[2] in 1938 and the sulfur trioxide–pyridine complex of Terent'ev,[1,3] although very nearly the entire range of ethers and amines have been investigated. These complexes have sufficient activity to react with most organic substrates but reduce substantially the charring of products observed historically with sulfur trioxide. Unfortunately, yields are often quite low and serious side reactions from stabilization of intermediates by the complexing agent are encountered. For example, it has been suggested[4] that dioxonium ions such as **1** are responsible for the formation of β-substituted al-



1

kanesulfonic acids in reactions of sulfur trioxide–dioxane with olefins. Attempts have been made to mitigate such complications by introducing sulfur trioxide as a gas, liquid, or solid[5] to long-chain 1-olefins with no real success. We have found, however, that liquid sulfur trioxide introduced to a dilute solution of an olefin at −78° has none of the problems discussed and report here details of the synthesis of several 1,3-sultones in high yields. We also present evidence for the general mechanism of sulfonation of 1-olefins.

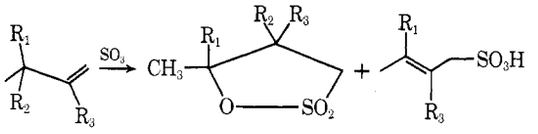
The addition of 1 equiv of liquid sulfur trioxide to 1-butenes in dichloromethane at −78° resulted in the formation of 1,3-propanesultones in at least 75% yield (Table I, examples 1, 3, 4, 5, and 6). Minor side products were 2-butene-1-sulfonic acids in 10–15% yield. An exception to

Table I
Yields of Sultones and 2-Butenesulfonic Acids from 1-Butenes and Sulfur Trioxide

	Olefin[a]	Rel yield, %: 1,3-Sultone	2-Butene-1-sulfonic acid[b]	Absolute yield, %
1	1-Butene[c] $R_1 = R_2 = R_3 = H$	87	13	90
2	2-Methyl-1-butene[d] $R_1 = R_2 = H$; $R_3 = CH_3$		100	90
3	3-Methyl-1-butene[d] $R_1 = CH_3$; $R_2 = R_3 = H$	89	11	73
4	2,3-Dimethyl-1-butene[d] $R_1 = R_3 = CH_3$; $R_2 = H$	90	10	80
5	3,3-Dimethyl-1-butene[d] $R_1 = R_2 = CH_3$; $R_3 = H$	100		83
6	2,3,3-Trimethyl-1-butene[d] $R_1 = R_2 = R_3 = CH_3$	100		98

[a] Concentration of the olefin was 0.1 *M* in dichloromethane at −78°. [b] Cis–trans isomerization of the double bond is not known. [c] Analytical data is by gc. [d] Analytical data is by nmr.

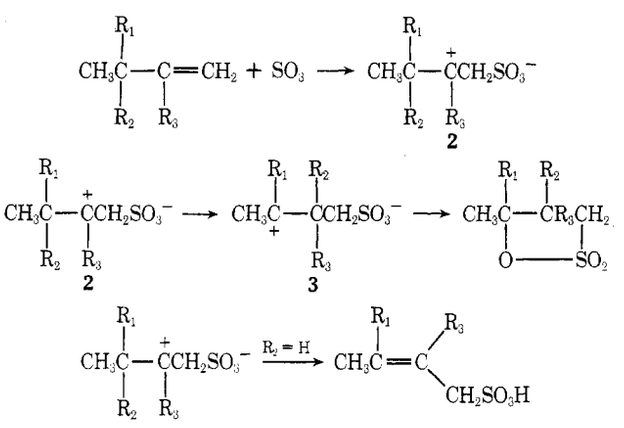
predominant sultone formation was 2-methyl-1-butene, where 2-methyl-2-butene-1-sulfonic acid is the sole product (Table I, example 2). Careful tlc and gc examination



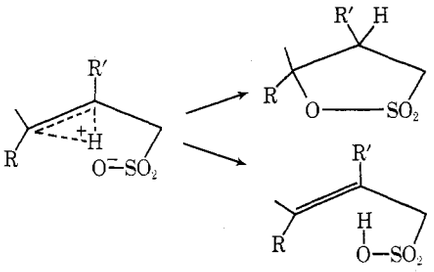
of the reaction mixtures showed only traces of unidentified hydrocarbons. The sultones were isolated either by distillation or crystallization, procedures simplified greatly by lack of the usual acid-catalyzed decomposition. The 2-butene-1-sulfonic acids can be separated by preparative tlc but are not stable for more than several hours. The methyl esters are quite stable and can be isolated directly by distillation. Nmr analysis of the reaction mixtures and the isolated acids and esters shows that only the 2-alkene isomers are present. Brouwer and van Doorn[6] have found that 6–7% 1-butene-1-sulfonic acid can be observed in 2-butene-1-sulfonic acid; so we assume that no more than that can be present in our reactions.

These data support electrophilic addition of sulfur trioxide to double bonds and the intermediacy of carbonium ions (see Scheme I). The hydride and methide migration pattern is typical of cationic species involved in electrophilic addition of olefins.[7] As implied by Bordwell[4] and other early workers,[1] it is clear now that the controlling factor in sultone *vs.* sulfonic acid formation is the relative stability of the carbonium ions formed at the β and γ carbons, *i.e.*, of **2** *vs.* **3**. For example, 2-methyl-1-butene (**2**, $R_1 = R_2 = H$; $R_3 = CH_3$) yields only elimination products whereas 3-methyl-1-butene (**2**, $R_1 = CH_3$; $R_2 = R_3 = H$) exhibits almost complete 1,2-hydride migration and 1,3-sultone formation. The former involves tertiary–secondary carbonium ions (no hydrogen rearrangement) and the latter secondary–tertiary. Furthermore, unpublished work on 1-pentenes indicates that high yields of 1,4-sultones may be obtained if the carbonium ion on the δ carbon is more stable than that on the γ.

Scheme I



The factor(s) responsible for exclusive formation of 2-butene-1-sulfonic acids are not so obvious and may involve a facile intramolecular transfer of a γ proton to the sulfonate moiety in **2**. Sulfonic acids are found only where the starting olefin had a γ hydrogen (*cf.* 2,3-dimethyl-1-butene and 3,3-dimethyl-1-butene) and no 1-butene-1-sulfonic acids were observed (loss of an α hydrogen). Rearranged carbonium ions apparently do not give rise to elimination, as both 2,3-dimethyl- and 3,3-dimethyl-1-butene ultimately yield the same carbonium ion after hydride or methide migration (Scheme I), but only 2,3-dimethyl-1-butene yields any trace of a butenesulfonic acid. Indeed, the fact that no elimination is observed into a methyl branch (*e.g.*, 2-methyl-1-butene) may suggest that the relative position of the proton and the sulfonate group in the transition state leading to elimination is not too dissimilar from that leading to sultone formation.



One major difference in this study from other sulfonation studies is the absence of β-substituted products. This may be due to the lack of formation of intermediates such as **1** or to a lack of β-sultones, as have occasionally been suggested[4] in connection with **1**. We presently have no evidence requiring the intermediacy of β-sultones. Low-temperature nmr of 3-methyl-1-butene and sulfur trioxide reaction mixtures shows immediate formation of 3,3-dimethyl-1,3-propanesultone and discounts the presence of a stable, observable intermediate. Work is currently in progress to determine the cyclic *vs.* noncyclic nature of the initial addition of sulfur trioxide to the double bond in an attempt to resolve this conflict.

Experimental Section

Materials and Methods. Pmr spectra were determined on a Varian T-60 or HA-100 spectrometer. Infrared spectra were obtained from a Perkin-Elmer Model 257. Melting points and boiling points are uncorrected. Gc measurements were made on an Aerograph Model 202 gas chromatograph using a 20 ft × 0.25 in. 10% Silicone SE-30 on Chromosorb P column.

Dichloromethane and sulfur trioxide were used as obtained from commercial sources. All olefins were obtained from Chemical Samples Co. except 1-butene (J. T. Baker Specialty Gas, 99.0%) and used without further purification after confirmation of purity by gc and nmr analyses.

General Procedure for the Sulfonation of Olefins. The same general method was used for all the olefins. To a quantity of 0.02 mol of the olefin dissolved in 200 ml of dichloromethane at −78° was added slowly from a syringe 1 equiv of liquid sulfur trioxide. The mixture was then allowed to come slowly to room temperature and the solvent was removed on a rotary evaporator at *ca.* 20°. Infrared analysis at this point showed the presence of the hy-

dronium ion [3000 (br, s), 1700 (br, s), and 900 cm^{-1} (br, s)] for all examples except 3,3-dimethyl- and 2,3,3-trimethyl-1-butene. The sultones were isolated by distillation (1-butene) or by crystallization from ethanol. The 2-butene-1-sulfonic acids were isolated by preparative tlc on silica gel using 50:50 chloroform–pentane. Quantitative nmr analyses were prepared by addition of the internal standard, diphenyl ether, after the reaction mixture had warmed to room temperature followed by the usual work-up. Comparison of the integral at δ 7.1 (m, Ph_2O) to the one at δ 6.0–5.0 (olefinic hydrogens of 2-butenesulfonic acids) and 2.2 (1,3-propanesultone β hydrogens) provided relative and absolute yields for entries 2–6 in Table I. Analysis for the products from 1-butene was by gc using diphenyl ether as internal standard.

The esters of 2-butene-1-sulfonic acids were prepared by addition of ethereal diazomethane to the reaction mixture at room temperature until a pale yellow color persisted and no further evolution of bubbles was noted. The esters were then separated by tlc (50:50 chloroform–pentane), by gc collection, or by distillation. Analytical data were difficult to obtain owing to decomposition during isolation and insufficient amounts of pure samples were obtained to include sulfur analysis. Where combustion analysis was outside accepted limits, assignments were confirmed by high-resolution mass spectra.

1-Butene. The reaction product was a dark oil from which could be distilled 1,3-butanesultone: bp 125° (0.1 mm) [lit.[8] bp 150° (12 mm)]; nmr[9] ($CDCl_3$, TMS) δ 5.0 (m, 1 H, CH_3CHO–), 3.3 (m, 2 H, $>CH_2CH_2SO_2$–), 2.2 (m, 2 H, $>CHCH_2CH_2SO_2$–), and 1.4 (d, J = 6 Hz, 3 H, $CH_3CH<$); ir 1350 (s), 1160 (s), 1030 (m), 920 (m), and 830 cm^{-1} (s). From a typical reaction mixture treated with ethereal diazomethane, a fraction was isolated and shown to be methyl 2-butene-1-sulfonate: bp 70–80° (0.1 mm); nmr[6] ($CDCl_3$, TMS) δ 5.8 (m, 2 H, $CH_3CH=CH$–), 3.9 (m, 5 H, $CH_2SO_3CH_3$), and 1.9 (m, 3 H, $CH_3CH=$); ir 1660 (vw, 1380 (s), 820 (m), and 770 cm^{-1} (m); mass spectrum M^+ m/e 150.0353 (calcd for $C_5H_{10}SO_3$, 150.0351).

Anal. Calcd for $C_5H_{10}SO_3$: C, 39.99; H, 6.91. Found: C, 40.44; H, 6.86.

2-Methyl-1-butene. Upon removal of the solvent from the reaction mixture, a brown, unstable oil was obtained, partially purified by tlc: nmr ($CDCl_3$, TMS) δ 5.5 (m, 1 H), 3.8 (m, 2 H), and 1.5 (m, 6 H); ir 3000, 1700, and 900 cm^{-1}, all very broad. Addition of ethereal diazomethane to the reaction mixture and subsequent distillation gave methyl 2-methyl-2-butene-1-sulfonate: bp 75–80° (0.4 mm); nmr ($CDCl_3$, TMS) δ 5.7 (m, 1 H, $CH_3CH=C<$), 3.8 (m, 5 H, $-CH_2SO_3CH_3$), and 1.8 (m, 6 H, $CH_3CH=CCH_3$); ir 1650 (vw), 1360 (s), 1160 (s), 1000 (s), 830 (m), and 770 cm^{-1} (m). Gc analysis of the methyl ester on SE-30 or Carbowax 20 M showed only one peak.

Anal. Calcd for $C_6H_{12}SO_3$: C, 43.89; H, 7.34. Found: C, 44.23; H, 7.48.

3-Methyl-1-butene. Recrystallization of the reaction mixture after evaporation of the solvent gave colorless needles of 3,3-dimethyl-1,3-propanesultone, mp 72–73° (lit.[10] mp 71.5–78°). Addition of ethereal diazomethane and separation by preparative tlc afforded a small amount of methyl 3-methyl-2-butene-1-sulfonate; nmr ($CDCl_3$, TMS) δ 5.3 (m, 1 H, $>C=H$–), 3.8 (m, 5 H, $-CH_2SO_3CH_3$), and 1.8 [m, 6 H, $(CH_3)_2C=CH$–]; ir 1650 (vw), 1360 (s), 1000 (s), 830 (m), and 770 cm^{-1} (m); mass spectrum M^+ m/e 164.050 (calcd for $C_6H_{12}SO_3$, 164.048).

Anal. Calcd for $C_6H_{12}SO_3$: C, 43.89; H, 7.34. Found: C, 44.58; H, 7.25.

2,3-Dimethyl-1-butene. Crystallization of the reaction mixture from ethanol gave colorless crystals of 2,3,3-trimethyl-1,3-propanesultone, mp 59–62° (lit.[4c] mp 61–63°). Formation of the methyl ester with diazomethane and collection from the gc gave methyl 2,3-dimethyl-2-butene-1-sulfonate: nmr ($CDCl_3$, TMS) δ 3.8 (s, 5 H, $-CH_2SO_3CH_3$) and 1.8 [m, 9 H, $(CH_3)_2C=C(CH_3)$–]; ir 1660 (vw), 1360 (s), 1160 (s), 1000 (s), and 830 cm^{-1} (m).

Anal. Calcd for $C_7H_{14}SO_3$: C, 47.17; H, 7.92. Found: C, 47.55; H, 8.00.

3,3-Dimethyl-1-butene. Crystallization from ethanol gave 2,3,3-trimethyl-1,3-propanesultone: mp 58–59°; ir 1340 (s), 1170 (s), 1050 (m), and 850 cm^{-1} (s). The ir of the reaction solution (CH_2Cl_2) and of the reaction mixture after evaporation of the solvent were identical with that of the sultone ($CHCl_3$ or CH_2Cl_2). The reaction mixture did not react with ethereal diazomethane. Tlc separation afforded only the sultone and trace amounts of a hydrocarbon.

2,3,3-Trimethyl-1-butene. Removal of solvent immediately gave a solid, 2,2,3,3-tetramethyl-1,3-propanesultone, recrystallized from ethanol, mp 142–143° (lit.[3] mp 145–146°). There was no evidence for sulfonic acids in the ir of the crude material.

Registry No.—Sulfur trioxide, 7446-11-9; 1-butene, 106-98-9; 1,3-butanesultone, 3289-23-4; methyl 2-butene-1-sulfonate, 51774-45-9; 2-methyl-1-butene, 563-46-2; 2-methyl-1,3-butanesultone, 51774-46-0; methyl 2-methyl-2-butene-1-sulfonate, 51774-47-1; 3-methyl-1-butene, 563-45-1; 3,3-dimethyl-1,3-propanesultone, 19028-67-2; methyl 3-methyl-2-butene-1-sulfonate, 51774-48-2; 2,3-dimethyl-1-butene, 563-78-0; 2,3,3-trimethyl-1,3-propanesultone, 51774-49-3; methyl 2,3-dimethyl-2-butene-1-sulfonate, 51801-40-2; 3,3-dimethyl-1-butene, 558-37-2; 2,3,3-trimethyl-1-butene, 594-56-9; 2,2,3,3-tetramethyl-1,3-propanesultone, 51774-50-6.

References and Notes

(1) E. E. Gilbert, *Chem. Rev.*, **62**, 549 (1962).
(2) C. M. Suter, P. B. Evans, and J. M. Kiefer, *J. Amer. Chem. Soc.*, **60**, 538 (1938).
(3) A. P. Terent'ev, V. M. Potapov, and V. M. Dem'yanovich, *Zh. Obshch. Khim.*, **29**, 949 (1959); *Chem. Abstr.*, **54**, 1334 (1960).
(4) (a) F. G. Bordwell and C. E. Osborne, *J. Amer. Chem. Soc.*, **81**, 1995 (1959); (b) F. G. Bordwell and M. L. Peterson, *ibid.*, **81**, 2000 (1959); (c) F. G. Bordwell, R. D. Chapman, and C. E. Osborne, *ibid.*, **81**, 2002 (1959).
(5) F. Püschel and C. Kaiser, *Chem. Ber.* **98**, 735 (1965), and references cited therein.
(6) D. M. Brouwer and J. A. van Doorn, *Recl. Trav. Chim. Pays-Bas*, **88**, 1041 (1969).
(7) P. B. D. de la Mare and R. Bolton, "Electrophilic Additions to Unsaturated Systems," American Elsevier, New York, N. Y., 1966.
(8) J. H. Helberger, J. R. Heyden, and H. Winter, *Justus Liebigs Ann. Chem.*, **586**, 147 (1954).
(9) Nmr spectra of the sultones are all consistent with published values. For example, see R. W. Ohline, A. L. Allred, and F. G. Bordwell, *J. Amer. Chem. Soc.*, **86**, 4641 (1964).
(10) T. Nilsson, Ph.D. Dissertation, University of Lund, Sweden, 1946.

Reaction of 2-Chloromethylpyridine with Sodium Acetylide[1]

Albert E. Zune,[2] Ulrich Hollstein,* and William M. Litchman

Department of Chemistry, University of New Mexico, Albuquerque, New Mexico 87131

Received November 9, 1973

Several alkenyl- and alkynylpyridines with chain end unsaturation are known; among them are 2-vinylpyridine, 2-allylpyridine,[3] (2-pyridyl)-4-butene-1, and (2-pyridyl)-4-butyne-1. Troyanowsky[5] discussed these products, and, in attempts to synthesize other members in this series, notably 2-propargylpyridine, studied the reaction of propargylmagnesium bromide with 2-bromopyridine, and 2-pyridylmagnesium bromide with propargyl bromide.[4] Reportedly, no new product was obtained from the first of these reactions, whereas the second one yielded 3-(α-pyridyl)hexyn-5-one-2. During studies of the preparation of propargylpyridine, coupling reactions between 2-chloromethylpyridine and sodium acetylide were investigated in this laboratory. Reaction between equivalent amounts of these two reagents in liquid ammonia resulted in the formation of two new compounds.

A white solid was isolated by filtration during the work-up. Extensive use of chromatographic techniques yielded only one other new product in the reaction mixture, and helped purify it as a yellow thick oil. Other products, such as the intermediates proposed in this paper, may have been present in trace amounts, but none of them could be isolated by column or thin layer chromatography. The yellow oil was analyzed by ir, uv, pmr, and cmr, and identified as 1′-ethynyl-1′,1′-di-α-picolyl-α-picoline (**5**). Absorbtions at 3300 and 2200 cm^{-1} in the ir spectrum indicate the presence of a terminal acetylenic moiety; uv absorption was consistent with the presence of three pyridine rings in the molecule; the pmr features an acetylenic