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.

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Reaction of 2-Chloromethylpyridine with Sodium Acetylide[1]

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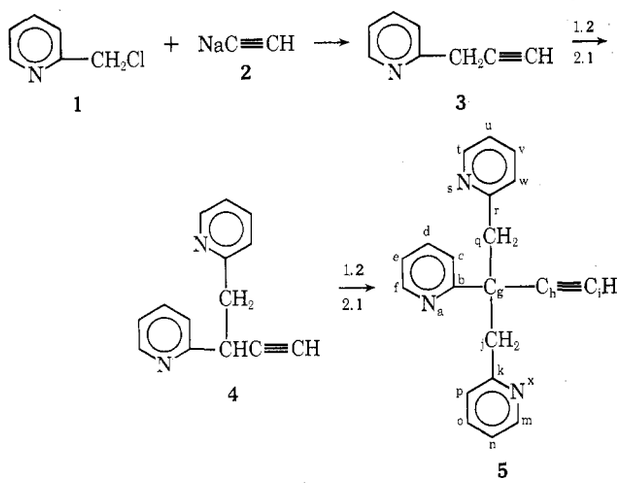
Several alkenyl- and alkynylpyridines with chain end unsaturation are known; among them are 2-vinylpyridine, 2-allylpyridine,[3] (2-pyridyl)-4-butene-1, and (2-pyridyl)-4-butyne-1. Troyanowsky[5] discussed these products, and, in attempts to synthesize other members in this series, notably 2-propargylpyridine, 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

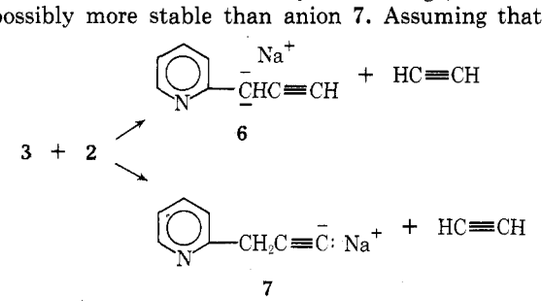
proton signal along with aromatic protons and an AB quartet centered at δ 3.65. This quartet was attributed to the signal of the protons of the methylene groups.

A model of **5** showed that a hydrogen atom of carbon atom j can form a hydrogen bond to nitrogen atom s. Similarly, a hydrogen atom of carbon q can form a hydrogen bond to nitrogen x. These two hydrogen bonds close two six-atom rings. Consequently, the two hydrogen atoms of each methylene group (j and q) become nonequivalent, and present different chemical shifts. In groups j and q the hydrogen involved in a hydrogen bond is more deshielded than one with a similar environment which is not hydrogen bonded. An AB quartet is therefore produced. Because of the thermal instability of **5**, elemental analytical results were poor and a mass spectrum, for which the sample had to be heated, indicated only fragments belonging to the pyridine moiety. Cmr, however, provided as expected signals for the 14 different types of carbons,[6] and those were unequivocally assigned.

It is proposed that **5** was formed by the following pathway. Because of resonance stabilization with the ring and

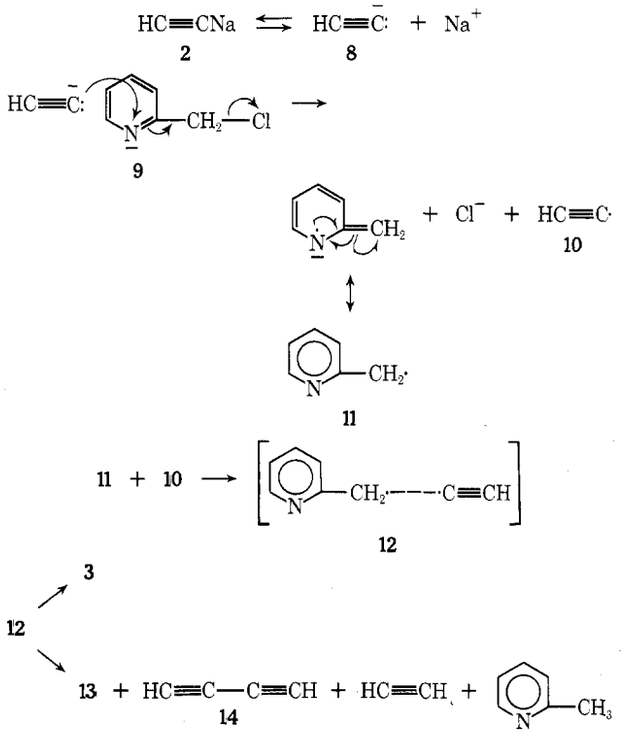


the inductive effect of the acetylenic linkage, the anion **6** is possibly more stable than anion **7**. Assuming that the



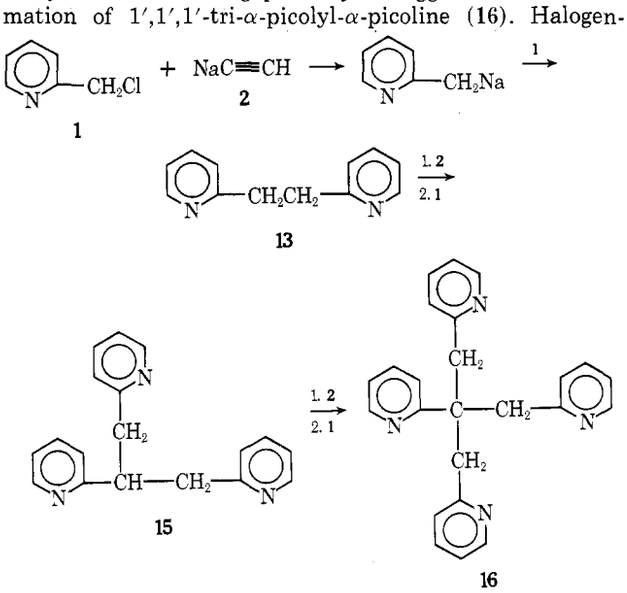
transition state for the reaction forming an anion of **3** partly resembles the products, one can expect the activation energy for the process leading to **6** to be lower than in the case of formation of **7**. Species **6** is thus formed faster than **7**, and, reacting immediately with **1**, forms **4**. The isolation of **5** as reaction product does not by itself necessarily imply that **6** is more stable than **7**. Indeed, a less stable anion will react faster. It can be argued that since **5** is obtained as product, **6** must be the faster reacting, and thus the least stable species. Metalation, however, has been shown to occur preferentially at the most acidic site in a molecule.[7] The site of metalation is clearly the methylene group. This indicates that in **3**, the methylenic protons are more acidic than the acetylenic one. Accordingly, we propose that **6** is, in fact, more stable than **7**. A similar discussion can be proposed about the reactions leading to **5**, **15**, and **16**.

Even though the reactions were run in an ionic solvent, a small proportion of intermediates **3** and **13** might have been formed by an alternative radical anion mechanism.

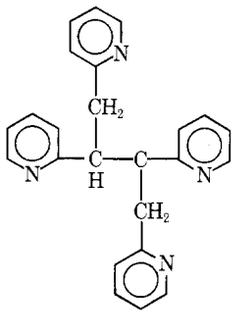


Caged radical pair **12** can yield **3** by coupling within the solvent cage or, when the cage breaks down, can go to **13** and **14**. *Via* proton abstraction from the solvent, acetylene and α-picoline can also be produced.

The solid product, isolated during the work-up of the same reaction, was analyzed by ir, pmr, and cmr. The infrared spectrum revealed the absence of acetylenic linkage, and this was confirmed by the absence of a pmr signal at δ 2.5. In the nmr, an AB quartet is found, similar to the one observed in the spectrum of **5**. The other signals belong to the aromatic region of the spectrum. These features suggest structure **16** for the analyzed solid. Hydrogen bonding can occur between three methylene hydrogens and three ring nitrogens in six different combinations. A dynamic equilibrium between those bonding combinations results in one AB quartet in the nmr. The proposed structure was confirmed by cmr[6] and elemental analysis. The following pathway is suggested for the formation of 1′,1′,1′-tri-α-picolyl-α-picoline (**16**). Halogen-



metal exchange yields 2-picolylsodium, which can couple with **1** to form **13**. A first metalation and coupling with **1** leads to **15**, where the methine group is a site of choice for further metalation, because of the inductive effect of the picolyl groups. Subsequent coupling forms **16**. The increased acidity at the methine group therefore overweighs steric hindrance, since no formation of **17** was observed.



17

The total yield of **5** and **16** is quantitative.

Experimental Section

Melting points were taken on a Kofler hot stage apparatus and are uncorrected. The ir spectra were recorded on a Perkin-Elmer 421 instrument, using KBr plates for the liquid sample and pressed KBr pellets for the solid. The nmr spectra were recorded on Varian A-60 and XL-100 spectrometers. The mass spectrum was obtained using a Du Pont 21-491 spectrometer. The uv spectra were recorded on a Cary 14 instrument.

Sodium Acetylide (2) and 2-Chloromethylpyridine (1). Ammonia was condensed into a three-neck flask fitted with a stopper, a potassium hydroxide drying tube, and a Dry Ice condenser. After 150 ml of liquid ammonia had been obtained, the condenser was disconnected from the gas cylinder and fitted with a potassium hydroxide drying tube. The contents of the flask were stirred magnetically. The stopper was replaced by a gas dispersing tube through which a stream of purified acetylene was passed. In the course of 15 min 2.3 g (0.1 mol) of sodium was added in small parts. The ammoniacal solution turned dark blue after each addition of sodium, but this color was soon discharged as a result of the reaction with acetylene. After completion of the sodium addition, the mixture was stirred for 5 min. The potassium hydroxide drying tube was replaced by a pressure-equalizing addition funnel containing 11.76 g (0.092 mol) of **1**. This reagent was added in the course of 5 min, causing the formation of a white precipitate. The mixture was stirred for 3 hr while the ammonia slowly evaporated. Water and ice were then cautiously added to the obtained dark, pasty residue. Suction filtration of the resulting mixture removed a white precipitate. This compound was recrystallized from di-*n*-butyl ether to yield 1.51 g (17.8%) of **16**, with a sharp melting point of 196°: ir 1590 (s), 1570 cm^{-1} (s); nmr ($CDCl_3$) δ 8.8–6.5 (m, 16 H, ring protons), 3.75 (d, 3 H, HCH···, J = 13 Hz), 3.45 (d, 3 H, HCH···, J = 13 Hz); cmr ($CDCl_3$) δ −34.07, −31.10, −21,14, −21.03, −8.03, −7.48, +2.65, +4.13, +6.21, +6.53, +77.95, +78.45 (shifts relative to benzene, used as an external reference).

Anal. Calcd for $C_{24}H_{22}N_4$: C, 78.66; H, 6.05; N, 15.29. Found: C, 79.03; H, 5.79; N, 15.16.

The filtrate was extracted with ether. After evaporation of the solvent, 8.0 g (86%) of a dark liquid was obtained, placed on an alumina column, and eluted with ether. A yellow liquid was collected, which decomposed when submitted to heat, thus rendering distillation or analysis by mass spectrometry impossible. A sample was analyzed by proton and ^{13}C nmr, and was identified as **5**: nmr (chloroform-*d*) δ 8.8–6.7 (m, 12 H, ring protons), 3.82 (d, 2 H, HCH···, J = 13 Hz), 3.5 (d, 2 H, HCH···, J = 13 Hz), 2.55 (s, 1 H, C=CH); cmr (chloroform-*d*) δ −32.70, −30.07, −21.22, −20.92, −8.26, −7.62, +2.90, +4.87, +5.94, +6.32, +42.12, +50.76, +78.35, +78.74 (shifts relative to benzene, used as an external reference).

Anal. Calcd for $C_{20}H_{17}N_3 \cdot 1.3H_2O$: C, 74.4; H, 6.1; N, 13.0. Found: C, 74.65; H, 5.91; N, 11.73.

Registry No.—**1**, 4377-33-7; **2**, 1066-26-8; **5**, 51510-19-1; **16**, 51510-20-4.

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A Hammett Relationship Study for the Thermal Decomposition of Sterically Hindered Hydrogen Phthalate Esters in Solution

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The presently accepted mechanism for the thermal decomposition of acetate, xanthate, and related esters involves a concerted six-membered cyclic transition state. An exception to this generalization is the pyrolysis of tertiary hydrogen phthalate esters, which decompose at relatively low temperatures (less than 150°) to yield exclusively olefinic products and phthalic acid.[2]

It has been found that considerable trans-elimination products are obtained from tertiary hydrogen phthalate decompositions.[2,3] To account for these products, it was suggested that carbonium ion character was apparent in the transition state. Further evidence of carbonium ion participation was obtained by partial decomposition of ^{18}O-enriched carbonyl oxygen labeled *trans*-1,2-dimethylcyclohexyl hydrogen phthalate ester which resulted in the enrichment of ^{18}O in the alkyl portion of the undecomposed ester.[4] A kinetic study of the decomposition of *cis*- and *trans*-1,2-dimethylcyclohexyl and *cis*- and *trans*-2-methyl-1-phenylcyclohexyl hydrogen phthalate esters[5] indicated that ion-pair formation was involved in the rate-determining step of the reaction.

More recently we reported that the thermal decomposition of 1,1-diphenylpropyl hydrogen phthalate ester followed first-order kinetics in DMSO solution.[6] The positive entropy of activation (7.3 eu) obtained precluded a cyclic transition state for this decomposition and gave support to the previously postulated mechanism involving heterolytic cleavage. Although homolytic decomposition of these esters has not been observed, this mode of decomposition could not be entirely ruled out. We wish to report in this paper a Hammett relationship study of the effect of substituents on the decomposition on a series of 1-aryl-1-phenylpropyl hydrogen phthalate esters which supports the concept of carbonium ion formation rather than radical pair formation in the rate-determining step.

Results and Discussion

The para 1-aryl-1-phenylpropyl alcohols were prepared by the Grignard method using the appropriate arylmagnesium halides and ketones (Table I). The hydrogen phthalate esters were prepared from the sodium salt of these alcohols and phthalic anhydride (Table I). A preparative-scale decomposition of the hydrogen phthalate esters in DMSO solution gave near-quantitative yields (>95%) of the corresponding olefin II and phthalic acid III. Kinetic decomposition studies of these esters were car-