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Rapid Elimination Reactions of Vinyl Ethers and Sulfides with Potassium 3-Aminopropylamide. Vinyl Sulfides as Acetylene Equivalents[1]

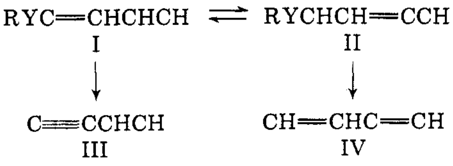
Summary: Potassium 3-aminopropylamide reacts rapidly with vinyl sulfides and vinyl ethers at room temperature to produce elimination products; vinyl sulfides yield alkynes with a high degree of selectivity, while vinyl ethers yield dienes or mixtures of dienes and alkynes. The reaction allows a mild, efficient transformation of vinyl sulfides into terminal acetylenes.

Sir: Potassium 3-aminopropylamide (KAPA) has been shown to be exceptionally active in base-catalyzed prototropic reactions[2] and in the elimination of vinyl and aryl halides.[3a] Reaction of vinyl compounds with hyperbases capable of catalyzing rapid prototropic isomerization raises the possibility of competing vinyl–alkyl interconversion, giving rise to dienes, rather than alkynes, from elimination (Scheme I);[3b] in general, simple alkynes and noncumulated dienes are not interconverted by hyperbases.

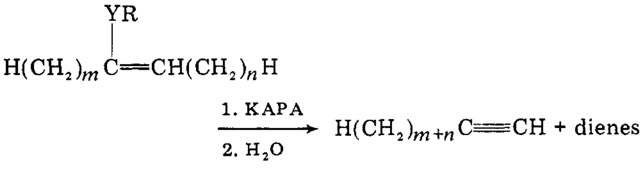
Base-catalyzed equilibrations of olefins, ethers, and sulfides containing a nonconjugated double bond have been studied;[4] examination of the data and conditions indicate the ease of I ⇌ II to be $Y = CH_2 \ll Y = O < Y = S$. In general, elimination has not been reported to accompany these equilibrations; however, few cases have been examined in which eliminations to noncumulated dienes and to alkynes (or allenes) are simultaneously possible, reactions largely being limited to allylic or propenyl systems. In fact, O'Connor and Lyness[4a] have reported slow formation of conjugated dienes during equilibration of 1-alken-1-yl sulfides with KO-*t*-Bu/Me_2SO.[5] A priori, elimination (1,2 or 1,4) of allylic structures to the more stable[6] conjugated dienes should be more facile than elimination of vinyl structures to alkynes, if base and leaving group are the same.

We find that KAPA reacts readily with both vinyl ethers and vinyl sulfides at room temperature to produce elimination products in good yield. In contrast to results obtained with KO-*t*-Bu/Me_2SO,[4a,5] eliminations with KAPA produce considerable proportions of alkynes, with vinyl sulfides yielding alkynes with high selectivity. Under the conditions of elimination, allenes and internal acetylenes are isomerized by KAPA in seconds to the anions of 1-alkynes;[2a] thus only 1-alkynes and noncumulated dienes were found as products after hydrolysis. These results are summarized in Scheme II.

Scheme I



Scheme II

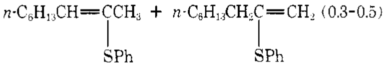
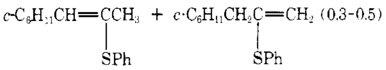
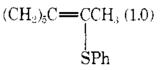
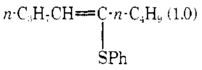
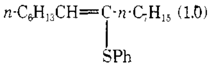
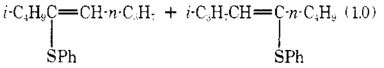
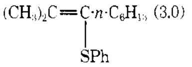


$$H(CH_2)_m\overset{YR}{\overset{|}{C}}{=}CH(CH_2)_nH \xrightarrow[2.\ H_2O]{1.\ KAPA} H(CH_2)_{m+n}C{\equiv}CH + \text{dienes}$$

			1-alkyne/diene
$n \geqslant 1, m = 0$	$Y = O$	$R = CH_3$	1:50
$n \geqslant 1, m = 0$	$Y = S$	$R = C_6H_5$	100:1
$n = 0, m > 1$ $n \geqslant 1, m = 1$	$Y = O$	$R = CH_3$	3:2
$n = 0, m > 1$ $n \geqslant 1, m = 1$	$Y = S$	$R = C_6H_5$	50:1
$n, m > 1$	$Y = O$	$R = CH_3$	1:2
$n, m > 1$	$Y = S$	$R = C_6H_5, CH_3$	15:1

GLC analysis of samples withdrawn and quenched revealed a constant "pattern" of the diene product mixtures which was

Table I. Reaction of Phenyl Vinyl Sulfides with KAPA[a]

substrate (time, h)[b]	product[c]	yield,[d] %
 $n\text{-}C_6H_{13}CH{=}\underset{SPh}{\underset{\vert}{C}}CH_3 + n\text{-}C_6H_{13}CH_2\underset{SPh}{\underset{\vert}{C}}{=}CH_2$ (0.3–0.5)	1-nonyne	86
 $c\text{-}C_6H_{11}CH{=}\underset{SPh}{\underset{\vert}{C}}CH_3 + c\text{-}C_6H_{11}CH_2\underset{SPh}{\underset{\vert}{C}}{=}CH_2$ (0.3–0.5)	3-cyclohexyl-1-propyne	83
 $(CH_2)_5C{=}\underset{SPh}{\underset{\vert}{C}}CH_3$ (1.0)	cyclohexyl acetylene	59[e]
 $n\text{-}C_3H_7CH{=}\underset{SPh}{\underset{\vert}{C}}\text{-}n\text{-}C_4H_9$ (1.0)	1-nonyne	83[f]
 $n\text{-}C_6H_{13}CH{=}\underset{SPh}{\underset{\vert}{C}}\text{-}n\text{-}C_7H_{15}$ (1.0)	1-pentadecyne	82
 $i\text{-}C_4H_9\underset{SPh}{\underset{\vert}{C}}{=}CH\text{-}n\text{-}C_3H_7 + i\text{-}C_3H_7CH{=}\underset{SPh}{\underset{\vert}{C}}\text{-}n\text{-}C_4H_9$ (1.0)	8-methyl-1-nonyne	80[f]
 $(CH_3)_2C{=}\underset{SPh}{\underset{\vert}{C}}\text{-}n\text{-}C_6H_{13}$ (3.0)	8-methyl-1-nonyne	62

[a] 2.5 mmol of substrate added to 7.5 mL of ~1.3 M KAPA in APA solution, 25 °C. [b] Prepared by heating an equimolar mixture of ketone and thiophenol with a trace of sulfuric or toluenesulfonic acids in benzene with azeotropic removal of water to Linde 4A molecular sieves in a Soxhlet extractor. [c] Product identification by comparison with authentic samples. [d] Reaction mixtures were subjected to normal extractive workup with pentane as the organic phase, dried over $MgSO_4$, treated with nonane or decane as internal standard, and analyzed by GLC (Carbowax 20M or polymethylphenylsilicone). [e] Plus ~15% ethylbenzene. This aromatization is under further study. [f] Average of three runs. Variations were ~±5%.

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nearly identical with that obtained by treatment of α,ω-dienes[7a,b] with KAPA.

The procedure is extremely simple. KAPA[2b] is prepared in a 50-mL centrifuge tube (oven dried and cooled under Ar or N_2, equipped with a TFE-covered magnetic stirring bar, closed with a rubber injection septum) from 10.0 mmol of oil-free KH and 7.5 mL of anhydrous 3-aminopropylamine (30–60 min, H_2 *evolved*). With stirring and water bath cooling, neat vinyl sulfide is injected.[7c] After 0.3–3.0 h the tube is cooled in an ice bath; the reaction mixture is quenched by addition of 10 mL of ice water over 10–20 s and worked up conventionally using pentane or ether. Examples are summarized in Table I.

This procedure was also employed in the product studies of eliminations of vinyl ethers and vinyl sulfides summarized in Scheme II.

The formation of alkynes, particularly with such a high degree of selectivity from vinyl sulfides, by KAPA is quite surprising in light of the complete absence of alkyne production with KO-*t*-Bu/Me_2SO. It is unclear why the change in base should result in such a pronounced change in the course of the reaction;[7d] these effects are under current investigation.

Aside from mechanistic considerations, however, the rapid eliminations of vinyl sulfides by KAPA allow the C═CSR unit to be considered a convenient acetylene equivalent. This unit is formed by a variety of structural elaboration reactions involving C–C bond formation,[8,9] by reactions of mercaptans with carbonyl compounds,[10] and by thermolysis[11] of α-thiomethyl alkylmethyl sulfoxides which have been employed as carbonyl anion synthons.[12]

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(5) (a) Preliminary results indicate no detectable alkyne formation (<0.5%) during elimination of terminal and internal vinyl sulfides and ethers with KO-*t*-Bu/Me_2SO at 65 °C;[5b] (b) C. A. Brown and A. Yamaichi, research in progress.

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(7) (a) Extensive investigation of substrate composition during the reaction has not yet been undertaken; however, preliminary results suggest that positional equilibrium (e.g., Δ^1/Δ^2 in 2-methoxy-1- and -2-alkenes) is maintained with vinyl ethers but *not* with vinyl sulfides. (b) Under the conditions of the elimination simple olefins undergo equilibration in seconds with KAPA; vinyl ethers and sulfides would be expected to react substantially faster. (c) Solutions of the substrate in 3-aminopropyl amine or its methylated derivatives may be added. Use of aliphatic or aromatic hydrocarbons as cosolvents resulted in lower yields. Alkyl ethers are attacked by KAPA. (d) Similar questions are raised by the differences between the reaction of vinyl ethers and that of vinyl sulfides with KAPA (but not with KO-*t*-Bu/Me_2SO); this is especially pronounced with 1-alken-1-yl substrates. It is conceivable that an α elimination, or elimination of a sulfur-stabilized metalated intermediate, may be involved. See W. H. Saunders, Jr., and A. F. Cockerill, "Mechanisms of Elimination Reactions," Wiley, New York, N.Y., 1973, pp 510–523.

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