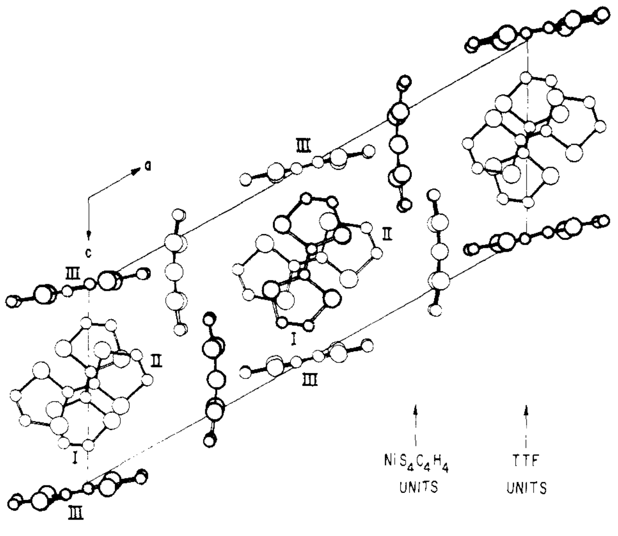

Figure 1. The unit cell of the (TTF)$_2$NiS$_4$C$_4$H$_4$ crystal structure viewed down [010]. The molecules whose centers are at $y = \frac{1}{2}$ are darkened; except for molecules labeled II, all other molecules have their centers at $y = 0$. The three types of TTF units discussed in the text are identified by Roman numerals.

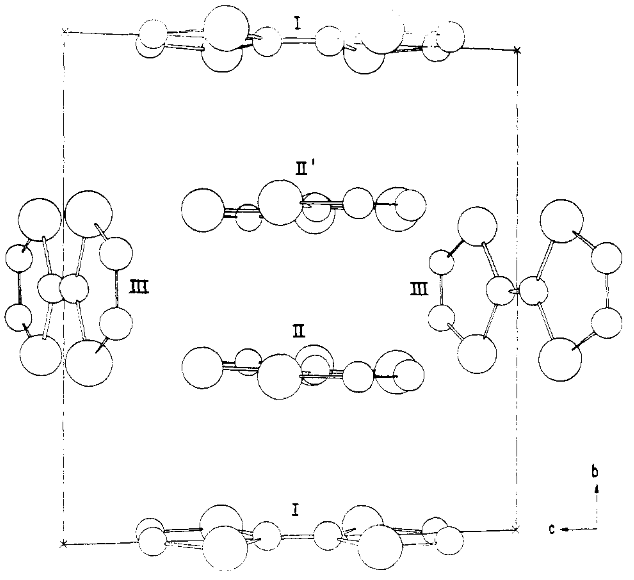

Figure 2. A view of the (TTF)$_2$NiS$_4$C$_4$H$_4$ structure normal to (100) showing the three types of TTF molecules (labeled I, II, and III).

principally in the replacement of a metal atom by a C=C unit.

The third type of TTF unit (type III) is centered at 0 ½ 0 and has its molecular plane oriented perpendicular to both the TTF units in the columnar stacks and the NiS$_4$C$_4$H$_4$ units. Two of the S atoms in this TTF unit make rather close contacts (3.5 Å) with S atoms of the type II TTF units on either side of the molecular plane effectively bridging the stacks of TTF molecules together along the [001] direction.

The two-dimensional character of the arrangement of TTF units is manifested in the observed variation of electrical conductivity with crystallographic direction. An appreciable electron delocalization along both [010] and [001] is indicated by such measurements.[1]

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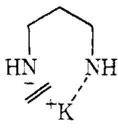
The Acetylene Zipper. An Exceptionally Facile "Contrathermodynamic" Multipositional Isomerization of Alkynes with Potassium 3-Aminopropylamide[1]

Sir:

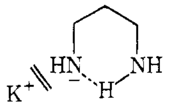
Potassium 3-aminopropylamide (KAPA), a readily prepared difunctional "superbase," exhibits exceptional activity in prototropic reactions. KAPA produces exceptionally rapid migrations of triple bonds from the interior to the terminus of the carbon chain *in seconds at 0°*.

Base-catalyzed isomerizations of 2-alkynes to 1-alkynes have been reported with very strong bases: sodium[2,3] (4.5 hr, 100°, accompanied by substantial polymerization), NaNH$_2$ in aromatic hydrocarbons[4] (1.5-2 hr, 160°), and, recently, KNH$_2$-NH$_3$-HMPA[5] (0.5-1 hr, room temperature). Migrations of two or more positions have been observed with NaNH$_2$ but required even more vigorous conditions with diminished returns. Weaker bases—even potassium *tert*-butoxide or methyl sulfinyl methide (dimsyl) in dimethyl sulfoxide—do not produce the Δ^2 to Δ^1 migration.[5-7] As the equilibrium in linear alkynes has been shown to favor heavily the internal isomers,[8,9] these internal-to-terminal migrations are "contrathermodynamic" overall, presumably reflecting formation of the stable acetylide ion assisted possibly by precipitation of the metal acetylide.

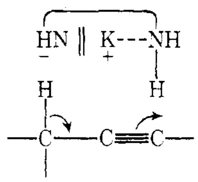
KAPA is rapidly formed by quantitative reaction of KH with excess 3-aminopropylamine (APA, trimethylenediamine). This alkylamide—in contrast to alkylamides of monofunctional amines—is quite soluble in excess amine (≥1.5 *M*), forming solutions which appear stable for at least 8 hr at room temperature. The high solubility may result from the higher solvating power of the diamine or "internal solvation" of the amide (I, II). Structures such as I and II are potentially favorable for concerted isomerizations (III).[10]



I



II



III

The KAPA-APA system proved exceptionally active both for isomerization of 2,4,4-trimethyl-1-pentene (10^4-10^5 times as reactive as KO-*t*-Bu-DMSO,[11a] based on k_ψ at 0.7 *M*) and for exchange of C-D in deuteriobenzene (10^3-10^4 times as reactive as lithium cyclohexylamide in cyclohexylamine,[11b] based on k_2).

This activity has proven exceptionally useful in "contrathermodynamic" migrations of triple bonds. In sharp contrast to the previously reported isomerizations, addition of an alkyne (IV) to KAPA (1.25 equiv, 1.0 *M* in APA) at 20° results in almost instantaneous precipitation of the potassium acetylide (V); hydrolysis yields the 1-alkyne (VI) in

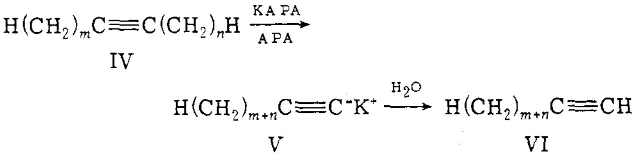
Table I. "Contrathermodynamic" Isomerization of Alkynes with KAPA[a]

Compound	Product[b]	Yield, %[c]
3-Hexyne	1-Hexyne	96
4-Octyne	1-Octyne	93
5-Decyne	1-Decyne	74
7-Tetradecyne	1-Tetradecyne	93 (89)
2-Methyl-4-nonyne	8-Methyl-1-nonyne	100
3-Methyl-4-nonyne	7-Methyl-1-nonyne	84
	3-Methyl-1-nonyne	0
2,2-Dimethyl-3-nonyne	8,8-Dimethyl-1-nonyne	94

[a] 20°, 1.2–1.5 equiv of KAPA (~1.0 *M* in APA), 2–10 min. There appears neither benefit nor detriment to the longer reaction times. [b] Purified by glpc and identified by comparison with authentic samples and/or from spectra. New compounds possessed consistent spectra and microanalyses. [c] After work-up and extraction, by glpc, ( ) = isolated yield.

essentially quantitative yield. Although multiposition migrations are reported to be generally unsatisfactory or very slow,[4,5] even 7-tetradecyne (IV, $m = n = 6$) was rapidly and quantitatively isomerized (Scheme I). These migrations are totally unprecedented regarding rate, mildness of conditions, and number of positions. Isomerization of 7-tetradecyne requires a *minimum* of 13 proton transfers and probably substantially more considering the presumably random nature of migration before the triple bond is "trapped" at the end.[12]

Scheme I



$$\underset{\text{IV}}{H(CH_2)_mC{\equiv}C(CH_2)_nH} \xrightarrow[\text{APA}]{\text{KAPA}} \underset{\text{V}}{H(CH_2)_{m+n}C{\equiv}C^-K^+} \xrightarrow{H_2O} \underset{\text{VI}}{H(CH_2)_{m+n}C{\equiv}CH}$$

Presence of a single chain branch blocks migration completely, consistent with the alkyne–allene migration mechanisms suggested in other base systems.[13] In no case were dienes observed in the products.[14]

The procedure is exceedingly simple. With cooling (15–20°) under argon or nitrogen, 7-tetradecyne (4.9 g, 25 mmol) was injected rapidly to a vigorously stirred solution of KAPA[15] (30 ml of 1.2 *M* in APA). The reaction mixture darkened and precipitation of potassium 1-tetradecynide was observed almost immediately. After 1–2 min the mixture was quenched by addition of 30 ml of water, extracted with pentane (backwash with 10% HCl), dried ($MgSO_4$), and evaporated under vacuum to yield 4.4 g, 89%, of 1-tetradecyne, ir 3310 (≡C—H) and 2120 cm^{-1} (terminal C≡C), one peak on glpc (DC 710), identical by coinjection with authentic material. Starting material was absent, and quantitative glpc with an internal standard confirmed the absence of nonvolatile products.

"Contrathermodynamic" isomerizations of various hydrocarbons with KAPA are summarized in Table I.

This remarkably facile migration—the "acetylene zipper"—represents a novel movement of functionality from the center to the terminus of a chain under exceptionally mild conditions.[16] We are currently exploring applications of this reaction to functional alkynes and synthesis.

Acknowledgment. Support from Research Corporation, the Cornell Chemistry Department, and Exxon Research and Engineering Co. are gratefully acknowledged.

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(11) These conditions appear more vigorous than necessary; 7-tetradecyne is completely converted to 1-tetradecyne in less than 60 sec at 0°.

(12) (a) Such a process ("random walk") requires that the mean time for passage of the triple bond (and the number of proton transfers) be proportional to the square of the number of positions involved.[13b] Preliminary competitive studies appear to provide experimental confirmation but are complicated by differing solubilities of alkynes (with substantially different chain lengths) in the amine. (b) We are indebted to Professor Michael Fisher of the Cornell University Chemistry and Physics Departments for helpful discussions relating to the "random walk" problem.

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Accuracy of Transition State Theory for the Threshold of Chemical Reactions with Activation Energy. Collinear and Three-Dimensional H + H_2

Sir:

One of the major failures of the classical trajectory description of chemical reactions is the inability to deal correctly with the threshold region of a reaction with an activation barrier, for here quantum effects (i.e., tunneling) become important. This is a serious shortcoming, too, since it is primarily this threshold region which determines the thermally averaged rate constant.[1]

For low energies, however, the fundamental assumption[2] of transition state theory—namely, that flux through a particular surface in configuration space which divides reactants from products can be identified as the reactive flux—becomes valid. As has been recently emphasized,[3,4] though, the additional assumption of separability of motion along a reaction coordinate, which is invoked in traditional transition state theory, is a poor approximation in the threshold region. The suggestion has been made,[3] therefore, that tran-