is formed by elimination, and rearranges to **3** in a fast step:

$$\underset{\mathbf{2}}{F_5Sb + ClCH_2CH_2CH_2CO^+} + B \rightarrow \underset{\mathbf{4}}{H_2C{=}CHCH_2CO^+}$$

$$\mathbf{4} \xrightarrow{+D^+;\ -H^+} \underset{\mathbf{3\text{-}4d}}{DCH_2CH{=}CHCO^+}$$

Under the same conditions, no deuterium incorporation was observed in a sample of **3** prepared from crotonyl chloride.

A clue as to the nature of the base B was offered by a careful kinetic study of the conversion. Thus, the reaction in fluoroantimonic acid followed clean first-order kinetics ($k_1 = 8.96 \times 10^{-4}$ s^{-1} at 50 °C,[17] $\Delta H^{\ddagger} = 15.4$, $\Delta S^{\ddagger} = -24.9$[18]). The reaction in the fluorosulfuric acid based composites, however, showed an induction period, after which the reaction exhibited second-order kinetics overall, first-order in **2** and first-order in the reaction product **3** ($k_2 = 1.23 \times 10^{-4}$ L mol^{-1} s^{-1} at 50 °C,[17] $\Delta H^{\ddagger} = 16.0$, $\Delta S^{\ddagger} = -27.1$, and $k_2 = 1.94 \times 10^{-4}$ at 50 °C, $\Delta H^{\ddagger} = 16.6$, $\Delta S^{\ddagger} = -25.2$, for the 1:1 and 4:1 acid, respectively).

When **2** and **3** were prepared in the same solution from the corresponding acid chlorides at low temperature, and conversion of **2** was followed, no induction period was observed. It appears, therefore, that **3** is assisting the proton loss from **2**.

(17) Calculated from data at other temperatures.
(18) $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values are in kcal/mol and cal/mol deg, respectively (1 cal = 4.184 J).

Deamination of *n*-Octylamine in Aqueous Solution: The Substitution/Elimination Ratio Is Not Altered by a Change of 10^8 in Hydroxide Ion Concentration

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Received August 31, 1989

Summary: Two different pathways for breakdown of the *n*-octyldiazonium ion appear to account for the several products obtained from the reactions of *n*-octylamine with both aqueous nitrous acid at low pH and with nitroprusside ion under alkaline conditions.

Sir: Deaminations of primary aliphatic amines by nitrous acid are known to yield a variety of products reflecting solvolysis, elimination, and rearrangement of the intervening carbonium ions. The idea that such reactions involve unusually reactive or "hot" carbonium ions came about as a result of observations that the products in such cases usually differed from those obtained from solvolyses of corresponding alkyl halides, tosylates, etc., that are thought to involve the same carbonium ion intermediates.[1-5] As compared to the latter, deaminations of amines tend to give a greater proportion of elimination and rearranged products. The amount of rearrangement and elimination is greatest in polar, protic solvents due, presumably, to the greater stabilization of those intermediates by those solvents.

In 1971, Maltz and co-workers[6] described the use of sodium nitroprusside to bring about the deamination of primary aliphatic amines. Unlike the reaction with nitrous acid, that with sodium nitroprusside proceeds most readily under alkaline conditions. This study was conducted to determine the extent to which solvent composition, particularly pH, might be used to influence the nature of the products obtained upon the deamination of an amine. The absence of a single predictable product in good yield has limited the use of nitrous acid as a means to effect the deamination of amines for most synthetic and analytical purposes.

A relatively large number of products can be identified following the reaction of *n*-octylamine with either nitrous acid or sodium nitroprusside. Yields of the six major products of its reaction with nitrous acid varied with pH as shown in Figure 1. The reaction was most rapid at approximately pH 3.5-4, and the main product under those conditions was 1-octyl nitrite. The formation of both 1- and 2-octyl nitrites at low pH in the presence of excess nitrite appears to reflect the initial formation of 1- and 2-octanol and their subsequent equilibrium as follows:[7]

$$ROH + NO_2^- + H^+ \rightleftharpoons RONO + H_2O \qquad (1)$$

although direct formation of small amounts of these compounds according to eq 2 cannot be precluded. In the

$$RN{=}N^+ + NO_2^- \rightarrow RONO + N_2 \qquad (2)$$

presence of chloride ion, for example, an analogous reaction as follows:

$$RN{=}N^+ + Cl^- \rightarrow RCl + N_2 \qquad (3)$$

gives rise to significant amounts of 1- and 2-chlorooctane, with the former becoming the principal product (i.e. ~53% of the total) in 5 M sodium chloride (Table I).

In contrast to the reaction with nitrous acid, that with sodium nitroprusside proceeds optimally under alkaline conditions. Thus, as shown in Table I, yields were greatest at high pH, in accord with a kinetic dependence on the unprotonated amine.[8] Under such conditions, no alkyl nitrites and, in the absence of added chloride ion, no alkyl chlorides were observed. Aldehydic products, as detected following reactions under similar conditions by Maltz et

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Table I. Product Compositions/Yields for the Deamination of *n*-Octylamine from pH 2 to 10[a]

	% yield					
	pH[f]				solvent	
product	2	4	8	10	HOAc[g]	5 M NaCl[i]
1-octanol[b]	18.4	24.2	23.1	38.1	(46)[h]	27.0 (53.2)[j]
2-octanol[b]	4.8	6.2	6.7	11.7	(18.5)[h]	3.9 (~5)[j]
1-octene	5.1	5.8	5.7	8.5	19.5	10.8
2-octene[c]	1.5	2.3	2.1	3.5	9.8	2.2
	product ratios					
prim/sec RX[d]	3.8	3.9	3.4	3.3	2.5	~9
substit/elimin[e]	3.5	3.8	3.8	4.2	2.2	~7

[a] Reactions of 100 mM *n*-octylamine at pH 2 and 4 with 500 mM sodium nitrite at 22 °C for 30 min and at pH 8 and 10 with 500 mM sodium nitroprusside at 22 °C for 24 h. Products were identified by GC–MS and quantitatively determined by GLPC (6 ft × $^1/_8$ in. i.d. column of 3% OV-17 on 100–200 mesh Gas-Chrom Q), those amounting to less than 1% of the total are not included. [b] The sum of the alcohol and the corresponding nitrite ester. [c] trans/cis ratio ~4:1. [d] Includes all primary and secondary substitution products, alcohols, nitrite esters, acetates, and chlorides. [e] Ratios of the major (shown) products. [f] The initial pH values in 0.2 M sodium succinate buffer at pH 2 and 4 and in 0.2 M triethanolamine buffer at pH 8 and 10. [g] From ref 11. [h] Octyl acetates. [i] Conducted at pH 3.5 in 0.2 M sodium succinate, 5 M NaCl buffer as described in footnote *a*. [j] Yields of 1- and 2-chlorooctane.

al.[6] were also not observed. The major products were, however, the same and, as shown in Table I, identical with those produced upon reaction with nitrous acid at much lower pH.[9]

Although yields of each product varied with pH and other reaction conditions (i.e. temperature, reaction time, reactant concentrations), relative amounts of the major products were essentially identical for the two reagents from pH 2 to 10 (Table I). The principal product in all cases, 1-octanol, varied, for example, over a very narrow range from ~60 to 64% of the total product. Proportions of the other major products, 2-octanol, 1- and 2-octene, varied by similarly small amounts.

On the basis of these results it is clear that the reactions of nitrous acid and sodium nitroprusside with octylamine proceed through one or more identical intermediates, presumably an alkyldiazonium ion and, perhaps, the corresponding alkyl carbonium ion, and that neither hydroxide nor hydrogen ions are involved in the product-forming steps.[10] Dissociation of the pentacyanoferrate moiety is very advanced, and its presence has no influence on the formation of products.

Although both reactions appear to proceed via the same cationic intermediates, it is at first difficult to imagine how three different and, presumably, competing reaction pathways (i.e. substitution, elimination, and rearrangement), from which the four major products arise, might proceed to exactly the same extent over a range of 10^8 in solvent basicity. As similar amounts of substitution, elimination, and rearrangement have also been observed upon deamination of comparable primary aliphatic amines in other polar solvents, for example, glacial acetic acid,[11] 50% aqueous acetic acid,[12] and aqueous 5 M NaCl (Table I), a single mechanism or explanation probably applies in all such cases.

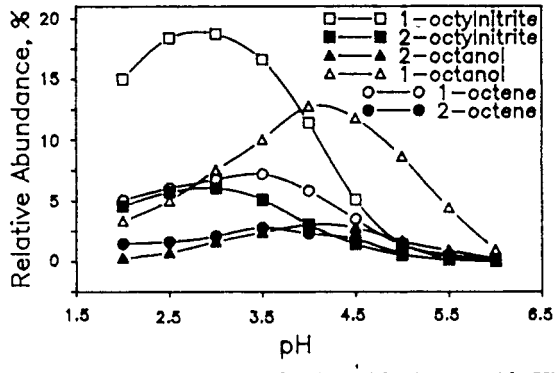
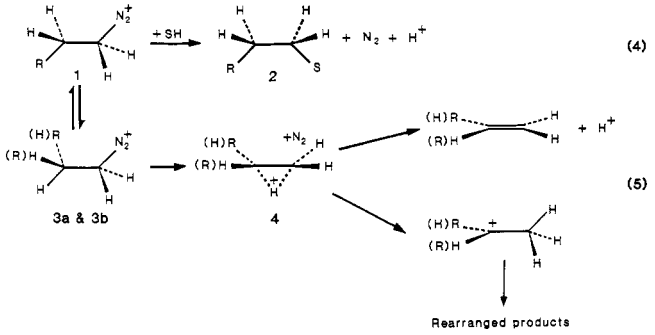


Figure 1. The reaction of *n*-octylamine with nitrous acid. Yields of the major products obtained from pH 2 to 6, under the conditions described in Table I, are shown.

To account for such results, it appears necessary to assume two different pathways. In accord with Streitwieser[1,13] and others,[5,11] we assume the two pathways begin with the alkyl diazonium ion but, as shown in eq 4 and 5,



in two major nonequivalent conformations. The most abundant form, 1, is thus assumed to largely undergo substitution, as shown in eq 4, without, or with little, intervention of a free carbonium ion. The comparable conversion of (+)-*n*-butylamine-*1-d* to *n*-butyl-*1-d* acetate in glacial acetic acid is, for example, also highly concerted as indicated by a high degree of net inversion.[13] The less abundant conformational forms, **3a** and **3b**, with β-hydrogens aligned anti to the departing nitrogen moiety, on the other hand, should be much more predisposed to elimination and rearrangement, as illustrated in eq 5, and,

(9) Small amounts of di-*n*-octyl ether and di-*n*-octylamine were also usually detectable by GC–mass spectrometry in reactions with sodium nitroprusside. After long reaction times, very small amounts of tri-*n*-octylamine and nitrosodi-*n*-octylamine were also sometimes detectable by the same means. A few other very, very minor products were also detected on some occasions. None was in significant amount as compared to the amounts of the major products presented in Table I.

(10) It is also possible that hydroxide and/or hydrogen ions might affect each pathway to exactly the same extent. We think this is unlikely, however, as even very small differences in sensitivity to hydroxide and/or hydrogen ions should have some effect on product composition when their concentrations are varied 10^8-fold.

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presumably, account for most of the observed olefinic and rearranged products. According to this hypothesis the substitution products derive largely from conformer **1**, whereas the elimination and rearrangement products are derived primarily from conformers **3a** and **3b**, perhaps via a common hydrogen-bridged intermediate, **4**.

As the relative abundance of the major conformational forms largely determines the extent to which these different reactions take place and neither hydrogen nor hydroxide ion are directly involved, there is no significant change in product composition with a change of 10^8 in hydrogen ion concentration.

Acknowledgment. We would like to acknowledge the assistance of David Chang and Kathleen Ault of the Ohio State University Chemical Instrument Center for their assistance with GC-MS analyses of the reaction products and E. J. Behrman for his helpful suggestions concerning this manuscript.

Stereoselective Aldol Coupling of Cobalt-Complexed Alkynyl Aldehydes

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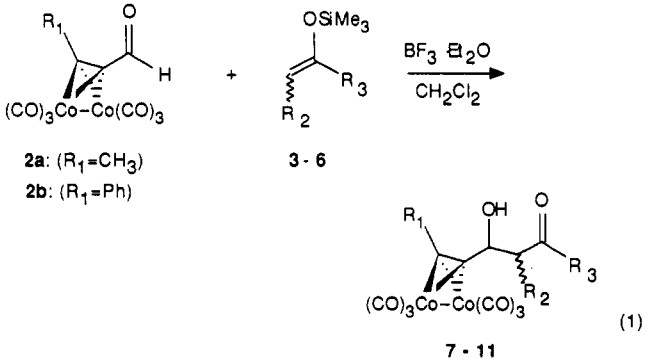
Received June 13, 1989

Summary: Although alkynyl aldehydes undergo crossed aldol condensation with trimethylsilyl enol ethers with little stereoselectivity, their dicobalt hexacarbonyl derivatives react with moderate to excellent syn diastereoselectivity. The selectivity is significantly dependent on the structure of the enol derivative and on temperature but relatively insensitive to the Lewis acid and the complex structure. The stereochemical assignment has been confirmed in one case by an X-ray crystal structure determination.

Sir: Despite intense interest in stereoselective C-C bond construction via aldol-type condensation reactions,[1] surprisingly little is known of the prospects for aldol coupling of alkynyl aldehydes.[2,3] The resulting acetylenic aldols are not only of interest in their own right, e.g. their presence in the remarkable macrocyclic antitumor antibiotics esperamycin and related compounds,[4] but also because the synthetic versatility of the C-C triple bond promises to make such compounds useful synthetic intermediates. Studies, primarily in this laboratory, have demonstrated the broad synthetic utility of [(propargylium)$Co_2(CO)_6$]BF_4 complexes (**1**) as propargyl cation synthons,[5] and, recently, results from Schreiber's group[6,7] and our own[8-10] have begun to realize the potential of these complexes in stereocontrolled C-C bond formation. In this report we present our initial findings on the contrasting Lewis acid promoted reactions of alkynyl aldehydes and their cobalt-complexed counterparts **2** with silylenol ethers. The latter reactions have been found to proceed with moderate to excellent syn stereoselectivity. Subsequent demetalation of these products provides a convenient stereocontrolled route to β-hydroxy-γ-acetylenic ketones.

The requisite alkynyl aldehyde complexes **2** are conveniently prepared in nearly quantitative yield from the reaction of dicobalt octacarbonyl with the alkynyl aldehyde (hexane, 20 °C, 3 h) or by facile acidic hydrolysis of the corresponding acetal complexes (THF/dilute HCl, 20 °C, 1 h).[11] Treatment of an equimolar mixture of **2a** or **2b** and silylenol ethers **3-5** in CH_2Cl_2 with 1-3 equiv of BF_3·Et_2O results in rapid production (15 min) of the corresponding aldol product complexes **7-10**, isolated in good yield following addition of Et_3N and aqueous workup (eq 1, Table I). The major product in each case at -78



2a: (R_1=CH_3) **2b**: (R_1=Ph) **3-6** **7-11** (1)

°C was assigned a syn stereochemistry on the basis of its ^1H NMR characteristics[12] and, for verification, by X-ray diffraction of the predominant isomer of **8** (ref 13, Figure 1). Efficient coupling of complex **2b** with silyl ketene acetal **6** (E/Z = 6:1) proceeded under identical conditions to afford ester derivative **11**; however, the major product in this case is assigned an anti stereochemistry.[14]

Several additional important features of the reactions of the complexed acetylenic aldehydes should be noted from the table: (1) both *E*- and *Z*-enol derivatives give syn product preferentially; (2) the degree of selectivity, how-

(1) Reviews: (a) Heathcock, C. H. In *Asymmetric Synthesis*; Academic Press: New York, 1984; Vol. 3, p 111. (b) Evans, D. A.; Nelson, J. V.; Taber, T. R. *Top. Stereochem.* **1982**, *13*, 1.

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(11) Representative procedures and spectroscopic data for all new compounds are provided in the supplementary material.

(12) The C*H*OH resonances for the syn isomers uniformly appear at lower field than those of the anti isomers ($\Delta\delta$ ca. 0.5 ppm); the former were also characterized by a smaller vicinal coupling constant (2-5 Hz vs 6-7 Hz for the anti); see ref 1a (pp 115-118) for supporting discussion.

(13) X-ray crystal data for *syn*-**8** is available in the supplementary materials.

(14) The C*H*OH resonance for the major isomer of **11** was at higher field than for the minor isomer (5.45 vs 5.64 ppm) and exhibited a larger vicinal coupling (6.7 vs 4.2 Hz) as well, consistent with an anti arrangement.

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