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Table 1. Polymerization of Propargyl Bromide and Propargyl Chloride by Transition Metal Catalysts[a]

Experiment number	Monomer	Catalyst System[b] (mole ratio)	Polymer Yield(%)[c]			$\overline{M}n$[d]
			Sol.[e]	Insol.	Total	
1	PB	WCl₆	10	20	30	8,700
2	PB	WCl₆-EtAlCl₂(1:4)	46	32	78	18,200
3	PC	WCl₆	11	29	40	9,400
4	PC	WCl₆-EtAlCl₂(1:4)	61	30	91	19,500
5	PC	MoCl₅-EtAlCl₂(1:4)	64	11	75	17,600
6[f]	PB	TiCl₄-EtAlCl₂(1:4)	52	0	52	10,100
7[f]	PC	TiCl₄-EtAlCl₂(1:4)	42	0	42	9,700

[a]Polymerization was carried out in chlorobenzene for 24 hrs. at 40 °C. Monomer to catalyst mole ratio(M/C) was 50. Initial monomer concentration([M],) of PB and PC were 1 and 1.5M, respectively. [b]Mixture of catalyst and cocatalyst was aged at 30 °C for 15 min. before use. [c]Methanol-insoluble polymer. [d]Determined by GPC in tetrahydrofuran using a calibration curve for polystyrene. [e]Soluble polymer in chloroform. [f]Polymerization solvent was benzene.

(PPC), a characteristic peak of the conjugated double bond, broad and weak $\pi \to \pi^*$ absorption, appeared at visible region(400-580 nm). The IR spectra of PPB and PPC showed an absorption at 1600m⁻¹ owing to the stretching frequency of conjugated double bond in the polymer backbone. From these spectral data, it was concluded that these polymers possess conjugated polyene structures.

More detailed study on the polymerization of the acetylene monomers by other transition metal catalysts and the physical properties of the resulting polymers are in progress.

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Micellar and Metal Ion Effects on the Reactions of 1,4-Dihydronicotinamide

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1,4-Dihydronicotinamides are widely investigated, mainly as model compounds of the coenzyme NADH.[1] While NADH and its model compounds can reduce various functionalities, they are known to be unstable in aqueous medium and undergo acid catalyzed hydration reaction.[2] Thus most NADH mimic reductions of organic substrates have been performed in non-aqueous media. For efficient NADH reductions in biological systems which is obviously aqueous, there must be some mechanisms which retard the hydration reaction and accelerate the reduction reactions. This can be achieved by the interactions of the coenzyme with the NADH-dependent enzymes and substrates. The catalysis of metal ions is necessary for reduction reactions in alcohol dehydrogenases that require NADH as a cofactor.[3] Similarly, it was found that the metal ions have large effects on NADH

mimic reductions in non-aqueous media.[1] The surfactant micelles are extensively utilized as enzyme mimetic systems.[4] It was reported that the micelles greatly affect the hydration reaction of NADH model compounds.[5] The reactions of NADH model compounds in surfactant micellar solutions containing metal ions would mimic the reactions in biological systems more closely. In this communication, we wish to report the micellar and metal ion effects on the reduction of 2,2,2-trifluoroacetophenone (TFA) by 1-benzyl-1,4-dihydronicotinamide (BNAH) and the hydration of BNAH.

1-Benzyl-1,4-dihydronicotinamide was prepared by reaction of 1-benzyl-3-carbamoylpyridinium salt by sodium dithionite.[6] Kinetic studies were performed in 0.01 M surfactant (CTAB or SDS) medium containing 2% 2-propanol of pH 7.0. 0.01 M cacodylate was used for pH 7.0 buffer solu-

Table 1. Pseudo first-order rate constant k_ψ^o for the hydration of BNAH and second order rate constant k_r for the reduction of TFA with BNAH in various conditions of pH 7.0 at 40°C

| Media	M^{2+}	$k_\psi^o \times 10^6$ sec^{-1}	$k_r \times 10^3$ M^{-1}sec^{-1}
2% 2-propanol	none	88	—^{a}
	1×10^{-4}M Mg^{2+}	89	—^{a}
	1×10^{-4}M Zn^{2+}	90	—^{a}
25% 2-propanol	none	12	0.66
0.01 M SDS	none	110	3.3
	1×10^{-4}M Mg^{2+}	60	5.0
	1×10^{-4}M Zn^{2+}	62	5.3
0.01 M CTAB^b	none	22	2.3

^{a}Because of limited solubility of TFA in aqueous solution in the absence of surfactant, we could not perform experiments at high concentrations of TFA to obtain k_r with reasonable accuracy. ^{b}No significant effects of metal ions were observed in CTAB solutions presumably due to electrostatic repulsion between the CTAB micelle and metal ion.

tions. The concentration of BNAH was 1.0×10^{-4} M, and for reduction reaction TFA was added in excess and its concentration was 0.5, 1.0, 1.5, 2.0 or 3.0 mM. The reaction temperature was maintained at 40 °C using a shaking bath and the reactions were followed by observing the decrease in absorbance of the solutions at the characteristic absorption peak of BNAH of 354 nm. In the study of the metal ion effects the concentration of the metal ion (Mg^{2+} from Mg(ClO$_4$)$_2$ or Zn^{2+} from ZnCl$_2$) was 1.0×10^{-4} M and the ionic strength of the medium was held constant at 0.1 M by addition of KCl.

In the presence of excess TFA, the disappearance of dihydronicotinamide followed first-order kinetics with respect to dihydronicotinamide.[7] The pseudo first-order rate constants, k_{obsd} are obtained from the plot of logarithm of absorbance of BNAH at 354 nm against time and follow the Equation (1).

$$k_{obsd} = k_\psi^o + k_r[\text{TFA}] \qquad (1)$$

The first term is due to hydration of BNAH and the second is due to the reduction of the ketone by BNAH. Thus the reactions of BNAH in aqueous media containing TFA are expressed in terms of two independent reactions:
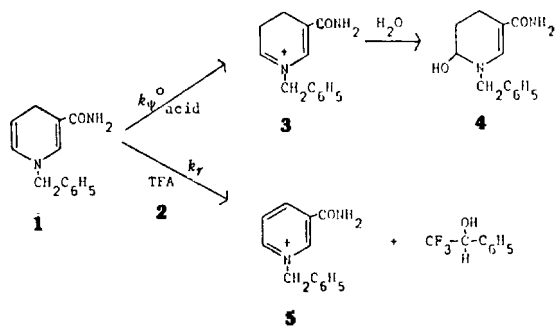
The pseudo first-order rate constants k_ψ^o for the hydration of BNAH and second order rate constants k_r for the reduction of TFA with BNAH were obtained from the plots of k_{obsd} against [TFA] (Equation 1) and are listed in Table 1.

Table 1 shows that the hydration reaction is retarded in cationic CTAB solution while it is accelerated in anionic SDS solution, compared to 2% 2-propanol solution. This agrees

well with the previous reports.[5] The retardation of the hydration rate in cationic CTAB micellar solution can be attributed to destabilization of a charged intermediate **3** (or the transition state to form the intermediate) and diminution of H$_3$O$^+$ ion which catalyzes the reaction, in the micellar surface where BNAH resides. The acceleration effect by an anionic SDS micelle can be accounted for by the opposite effects.

The hydration rate in 25% 2-propanol is found to be much less than those in 2% 2-propanol and in 0.01 M CTAB despite of the above-mentioned retardation effects of CTAB. This can be attributed, in part, to the lower content of water, which behaves as a general acid catalyst for the reaction,[5b] in the former system. The sensitivity of the hydration reaction to the solvent media, similar to that observed in the reduction reaction by dihydronicotinamide,[7b] through variation of activation parameters, would be another explanation for the observation.

Table 1 also shows that introduction of metal ions such as Mg^{2+} and Zn^{2+} into 0.01 M SDS solution causes considerable degrees of depression in hydration rates. This is noteworthy since the presence of these metal ions in 2% 2-propanol and in CTAB solutions didn't make any significant difference in hydration rates. The condensation of the metal ions on the Stern layer of the anionic SDS micelle might reduce the concentration of H$_3$O$^+$ in the region and thus retard the hydration reaction. However, this alone cannot explain the lower k_ψ^o in SDS solutions containing metal ions than that in 2% 2-propanol. The formation of metal ion-BNAH complex assisted by the anionic SDS micelle can also account for the effect of metal ions in SDS micellar solution (See below).

It is evident from Table 1 that the reduction of TFA by BNAH is also sensitive to the presence of micelles and metal ions. The reduction rate is greater in SDS than in CTAB. This result suggests that the positive charge is developed in the transition state of BNAH for reduction of TFA and is stabilized by an anionic micelle, SDS. The higher reduction rates of TFA by BNAH both in SDS and in CTAB than that in 25% 2-propanol indicate that the micelles, regardless of their charges, concentrate the substrate and BNAH and thereby increase the reaction rate.

Table 1 exhibits that the metal ions enhance the reduction rates in SDS in contrast to their retardation effects on hydration of BNAH. As explained before, metal ions are concentrated in the Stern layer of SDS micelles due to Coulombic attraction and TFA and BNAH bind micelle because of their hydrophobic character. The incorporation of the metal ion, TFA and BNAH molecules in SDS micelles makes the formation of TFA-metal, BNAH-metal and/or TFA-metal-BNAH complexes quite plausible and these interactions contribute to speed up the reduction of TFA by BNAH. The BNAH-metal ion complex which bears positive charge may resist the H$_3$O$^+$ catalyzed hydration reaction. It was reported that 1,4-dihydropyridines form complexes with Mg^{2+} or Zn^{2+} in organic media.[8] It was also suggested that reduction occurrs in a ternary complex in which 1,4-dihydropyridine, Mg^{2+} ion and carbonyl component are associated together.[8]

To our knowledge, this paper is the first description of the catalytic effect of metal ions for reduction by 1,4-dihydropyridines and their retardation effect for hydration of the same compounds in aqueous media. The mechanism which retards the hydration reaction while activating the reduction

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reaction as demonstrated in this paper might play an important role in the action of NADH in biological systems.

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Selective Oxidations of Steroids: The Oxidation of 6β-Acetoxy- and 6β-Benzoyloxy-3α,5α-cyclocholestane Using the Gif System

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Recently Barton and coworkers described a new system for the oxidation of saturated hydrocarbons. In its most developed form, it consists of an iron catalyst in pyridine-aqueous acetic acid, containing metallic zinc, stirred under oxygen or air at room temperature.[1] Use of iron powder in place of the iron complex and zinc is also known to be effective.[2] For convenience this is called the Gif system and it oxidizes saturated hydrocarbons selectively in secondary positions; primary and tertiary positions are much less prone to be attacked by the oxidizing agents.[3-5]

Several steroid derivatives were oxidized by Barton using the Gif system in an effort to find ways to synthesize useful steroidal compounds from readily available sterols. For example, in the oxidation of 3β,5α,6β-triacetoxycholestane (1)[6,7] the three major products were the 20-ketone (2) (12%), the 15-ketone (7%) and the 16-ketone (6%). Most of possible ring ketones were also found as minor products as well as the 24-ketone and the 26-aldehyde. Oxidation of 5α-cholestan-3-one (3)[8] again produced the 20-ketone (4) as the major product, followed by the ring oxidized products at the 6-, 7-, 15-, and 16-positions and the 24-ketone. A dramatic effect in the selectivity of oxidation was discovered with cholest-4-en-3-one (5), which gave rise to 15- and 16-ketones as the major ring oxidation products and none of 6- or 7-oxo products. The 20-ketone (6) (7.6%) was again found to be the major product together with a smaller quantity of the 24-ketone. Deactivation of ring A and ring B was apparent in this system. Similarly, oxidation of cholesta-1,4-dien-3-one (7) led to the formation of the 20-ketone (8) (9.4%) and 15- and 24-ketones as the major products. In all these cases 20-ketones
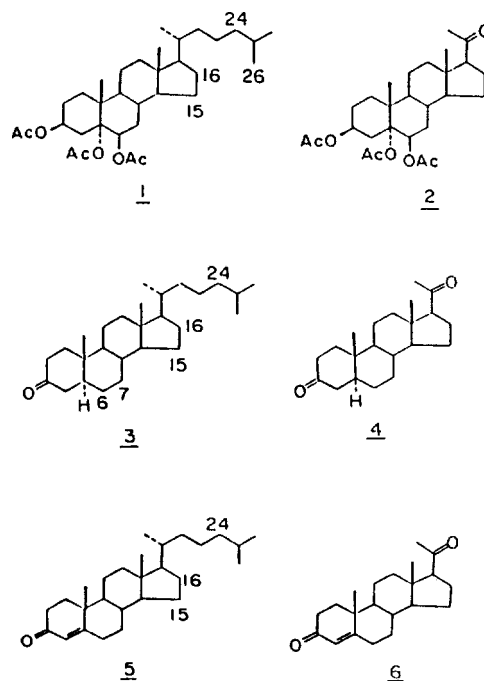
were the most abundant major products and the mechanism for the side chain degradation via 25-hydroxyl radical is well documented.[9]

Derivatives of 6β-hydroxy-3α,5α-cyclocholestane[10] are ideal candidates for selective oxidations due to their easy preparation and facile conversion back to cholesterol. Thus