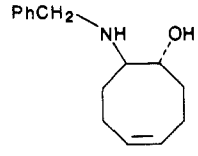
ketone **6** (45% yield). Alkylation of **6** with 1.05 equiv of allyl bromide via the boron enolate[10] (1.0 equiv of potassium hydride, 1.05 equiv of triethylborane) in THF at 0–25 °C for 3 h afforded, after chromatography on silica (CH_2Cl_2), the desired α-allyl ketone **7** (75% yield).[11]



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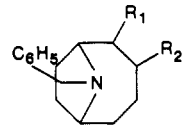

5: R_1 = α-OH, R_2 = H
6: R_1 = O, R_2 = H
7: R_1 = O, R_2 = $CH_2CH{=}CH_2$
8: R_1 = CN, R_2 = $CH_2CH{=}CH_2$
9: R_1 = CHO, R_2 = $CH_2CH{=}CH_2$
10: R_1 = CHO, R_2 = CH_2CHO

Conversion of **7** to the nitrile **8** was accomplished with 2 equiv of tosylmethyl isocyanide[12] and 5 equiv of potassium *tert*-butoxide in dimethoxyethane at 45 °C for 6 h (74% yield). DIBAL reduction (1.2 equiv) in benzene at 25 °C for 5 h converted the nitrile to the aldehyde **9** (75% yield).[13] Protection of the amino functionality as the TFA salt and oxidative cleavage of the allyl group with ozone at −78 °C in CH_2Cl_2, followed by treatment with excess dimethyl sulfide and warming to room temperature, afforded the 1,5-dialdehyde **10** (75% yield). Treatment of **10** with 3 equiv of hydroxylamine hydrochloride in glacial acetic acid[15] at 100 °C for 20 min produced the desired fused pyridine **11** in 55% yield after chromatography on silica (CH_2Cl_2/MeOH 9/1). Debenzylation of **11** with $Pd(OH)_2$ on carbon[16] in EtOH and 1 equiv of HCl proceeded cleanly in the desired fashion to afford the target compound **2** (80% yield after chromatography on silica with CH_2Cl_2/MeOH/TEA 90/9.85/0.15).[17]

Pyridohomotropane was tested both in vivo and in vitro in order to determine its activity relative to nornicotine. The results (see Table I) show that the new derivative possesses 3 times the toxicological activity (intravenous mouse injection) and 16 times the receptor binding (rat brain membranes[18]) of nornicotine. Pyridohomotropane is thus the first nicotinoid to combine high activity with conformational rigidity and provides a further refinement in our understanding of the chemical and spatial requirements of the nicotinic acetylcholine receptor.

Acknowledgment. We acknowledge Drs. Michael Broadhurst, Charles Chavdarian, Karl Fisher, and William Haag and Prof. Henry Rapoport for useful discussions. We also thank William Callahan and Rose Chan for technical assistance.

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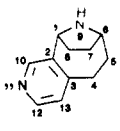

^{13}C NMR (100 MHz; $CDCl_3$, 77.0 ppm) δ 149.2 (C_2, 148.5 (C_{12}), 148.1 (C_{10}), 142.6 (C_3), 125.5 (C_{13}), 60.5 (C_1), 58.2 (C_6), 33.5 (C_5), 31.7 (C_4), 31.4 (C_8), 29.8 (C_7); ^1H NMR (400 MHz; $CDCl_3$, 7.24 ppm) δ 8.3 (d, H_{12}), 8.2 (s, H_{10}), 7.0 (d, H_{13}), 4.4 (dd, H_1), 3.8 (dddd, H_6), 3.1 (ddd, $H_{4\alpha}$), 2.7 (ddd, $H_{4\beta}$), 2.4 (dddd, $H_{8\beta}$), 2.1 (dddd, $H_{7\beta}$), 1.8 (dddd, $H_{5\alpha}$), 1.8 (dddd, $H_{7\alpha}$), 1.8 (dddd, $H_{8\alpha}$), 1.6 (dddd, $H_{5\beta}$); measured coupling constants (Hz) J_{12-13} = 4.9; $J_{1-8\alpha}$ = 2.3; $J_{1-8\beta}$ = 9.8; $J_{8\beta-8\alpha}$ = 13.3; $J_{8\beta-7\alpha}$ = 2.8; $J_{8\beta-7\beta}$ = 13.2; $J_{8\alpha-7\beta}$ = 2.0; $J_{7\beta-7\alpha}$ = 18; $J_{7\beta-6}$ = 6.7; $J_{6-5\beta}$ = 2.9; $J_{5\beta-5\alpha}$ = 13.6; $J_{5\beta-4\alpha}$ = 13.7; $J_{5\beta-4\beta}$ = 3.5; $J_{5\alpha-4\beta}$ = 3.8; $J_{5\alpha-4\alpha}$ = 3.5; $J_{4\beta-4\alpha}$ = 15.7. HRMS: *m/e* calculated for $C_{11}H_{14}N_2$ (M^+) 174.1157, found 174.1136.
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Topological Control of Reactivity by Interfacial Orientation: Excimer Fluorescence and Photodimerization of 4-Stilbazolium Cations in Aerosol OT Reversed Micelles[1]

K. Takagi,[2] B. R. Suddaby, S. L. Vadas, C. A. Backer, and D. G. Whitten*

Department of Chemistry, University of Rochester Rochester, New York 14627
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Photocycloaddition and cyclodimerization reactions have been the subject of extensive study. Although widely used, their employment in solution frequently is limited by a lack of stereochemical or regiochemical selectivity or control. In contrast, many photodimerization reactions occur in crystals; these are frequently selective with often only a single product resulting.[3-9] Several studies have shown correlation between monomer packing in the crystal and photodimer structure;[3-5,11] while such topological control appears general for solids,[3-7] it is often difficult to predict or control the packing of different substances so as to generally utilize this property.[8-11] The ability of microheterogeneous media such as micelles, vesicles, films, or microemulsions to provide an environment of variable order and properties intermediate between solid and solution suggests an opportunity to control or at least obtain some selectivity in these photoreactions. Indeed, several investigations in micellar media have shown both high yields of photodimers and some selectivity in product distribution;[12-20] for a number of reactions including photodimerizations many of the

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Table I. Photoproducts from Irradiation of 4-Stilbazolium (**1b**) in Reversed Micelles and Homogeneous Solution[a]

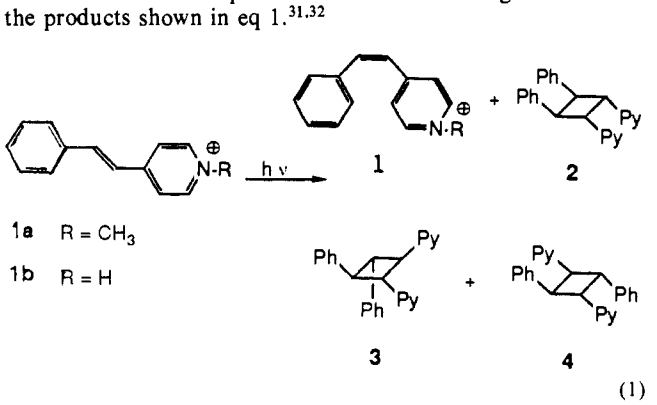
					products[b]				
$[HStb^+]_0$	$[AOT^-]_0$	ω	solvent	% conv.	*cis*-**1**	**2**	**3**	**4**	**2/4**
0.028	0		1 M $HCl_{(aq)}$	78	13	0	5	60	0
0.0024	0.0065	78	*n*-hexane	84	77	6		17	0.4
0.0013	0.0079	64	*n*-hexane	86	49	29	7	15	2.0
0.0010	0.0020	20	*n*-hexane	88	27	60	8	6	10
0.0024	0.0048	11	*n*-hexane	93	9	72	9	11	6.4

[a] Solutions degassed by bubbling with nitrogen, irradiated with a 150-W halogen lamp through Pyrex. [b] Products analyzed by NMR after neutralization and extraction with CH_2Cl_2.

effects observed in micelles and related media are attributable to interfacial solubilization and cannot be correlated directly with order or compared to a corresponding homogeneous solvent.[19-22] Since micelles are probably among the least "organized" of microheterogeneous assemblies,[23-27] much more precise control might be anticipated for other media.

In the present paper we report a study of photodimerization and "excimer" fluorescence from *trans*-4-stibazolium cations in reversed micelles formed from hexane- or heptane-aerosol OT (sodium bis(2-ethylhexyl) sulfosuccinate, AOT)-water. The significant result of this study is the finding that efficient and selective formation of the syn head-to-head photodimer **2** is correlated with a ground-state association that can be controlled by the stilbazolium/surfactant and surfactant/water ratios. These results indicate that for small water pools the charged interface of a reversed micelle presents an organized surface that can lead to a topological control not readily attainable in other fluid media.

trans-4-Stilbazole[29] was converted to the N-methyl (**1a**) and protonated (**1b**) stilbazolium salts by treatment with CH_3I or HCl, respectively. The corresponding salts of AOT were isolated by mixing equimolar amounts of stilbazolium salt and AOT and then using standard extraction and drying procedures. Reversed micelles were prepared by bath sonicating mixtures of stilbazolium bis(2-ethylhexyl) sulfosuccinate, AOT, heptane or hexane, and water for 20 min. The photolysis products from **1b** were extracted with CH_2Cl_2 and separated by column chromatography over silica gel. Identification of dimers **2-4** was by NMR and comparison with authentic samples produced according to literature methods.[8,30] The product distribution on partially converted samples of **1b** was quantitatively analyzed by using 400-MHz NMR for the H_α of the pyridine rings; the chemical shifts of these protons are distinct and well separated for both the starting material and the products shown in eq 1.[31,32]



(1)

Homogeneous solutions of *trans*-**1a** or *trans*-**1b** in water or organic solvents show only "monomer" absorption (330 nm) and fluorescence (370 nm) at concentrations of 0.005 M or lower; for these solutions direct irradiation results only in trans → cis photoisomerization. In aqueous HCl (0.1-1.0 M) solutions having concentrations of 0.01 M or higher, *trans*-**1b** exhibits a red-shifted "excimer" fluorescence (520 nm) with a slight broadening of the absorption spectrum. Concurrent with the appearance of excimer fluorescence is the onset of photodimerization (Table I) to produce chiefly the head-tail (tct) photodimer **4**[8,30] and a decrease in $\phi_{t\rightarrow c}$.

1a and **1b** dissolve in hexane or heptane with various amounts of water and at least 1 equiv of added NaAOT to give clear solutions of reversed micelles. Here "excimer" emission occurs at much lower stilbazolium cation concentrations than in homogeneous solutions. For example, for 1×10^{-4} M *trans*-**1a** prominent excimer emission is observed for low water/surfactant ratios (ω) when the concentration ratio, *trans*-**1a**/AOT, is 1/100 or greater. Accompanying the onset of excimer emission is a decrease in $\phi_{t\rightarrow c}$ and production of dimers **2-4** (eq 1). Both $\phi_{t\rightarrow c}$ and the ratio of the major dimers, **2**/**4**, are strongly dependent on ω over the range 10-80. In this range the solution should consist of reversed micelles of similar size and surfactant aggregation number but with quite different amounts of free and ion-associated water.[33-35] Product distributions for **1b** are given in Table I; similar results have been obtained for **1a**. For the higher values of ω in this range the major products are *cis*-**1** and dimer **4**, the products predominating in solution. As ω decreases, the ratio of dimers **2**/**4** increases sharply and the yield of *cis*-**1** decreases; at ω = 10-20 (Table I) the syn head-to-head dimer **2**, which is not produced upon irradiation in homogeneous solution, becomes the dominant photoproduct. Quantum efficiencies for photoreaction of **1a** and **1b** increase from 0.53[36] in dilute aqueous acid to 1.14 and 1.05 for **1a** and **1b** in the reversed micelles with ω = 10. Accompanying the pronounced change in the photodimer ratio as ω is decreased from 80 to 10 is a significant blue shift (from 520 to 490 nm, respectively) and a slight increase in intensity of the excimer fluorescence; only a very slight broadening of the absorption spectrum, compared to the "monomer" spectrum observed in dilute solution, occurs in all cases where the various excimer spectra are observed.[37]

The remarkable change in photodimer ratio as the water-pool composition is varied indicates that the photophysics and photochemistry of **1** are modified by both concentrating and orienting properties of the reversed micelle. Thus in solutions of relatively high ω the water pool increases the local concentration, and the "normal" excimer and photodimer **4** produced in aqueous solutions having high [**1**] are obtained. As ω decreases such that little "free" water is present, the orientation of stilbazolium ions with respect to the charged interface must become more constrained such that

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(32) Irradiation of *cis*-**1b** in reversed micelles (low ω) leads to a preponderance of dimer **4** with smaller amounts of **2** and **3** under conditions where little *trans*-**1b** accumulates (K. Takagi, unpublished results).
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(37) Fluorescence for the "excimer" emission shows two components with decays between 2 and 8 ns; the monomer in dilute solution has $\tau \sim 0.3$ ns. Over the range studied for both **1a** and **1b** the excimer ϕ_f = 0.01-0.02.

the predominant excimer formed fluoresces at shorter wavelength and decays preferentially to dimer **2**. Since there is little spectroscopic evidence of strong association at any concentration of **1** in either homogeneous solution or reversed micelles, it is likely that the orientation is controlled by interaction of the stilbazolium cations with the negatively charged interface rather than to preferential association of the cations in what would be expected to be a Coulombically unfavorable arrangement. The striking increase in selectivity and quantum efficiency to produce a photoproduct not observed in homogeneous solution indicates a degree of topological control of reactivity in the AOT reversed micelles previously associated chiefly with the crystalline state. We are currently extending our studies to other photoreactive ions to determine whether the ability of these charged interfaces to orient ionic reactants is a general and/or tunable property.

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Measurement of Rates and Equilibria for Keto–Enol Tautomerism of Aldehydes Using Horseradish Peroxidase Compound I

Cornelia Bohne,[1a] I. David MacDonald,[1b] and H. Brian Dunford*[1c]

Department of Chemistry, University of Alberta Edmonton, Alberta, Canada T6G 2G2

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Measurement of the relevant kinetic and thermodynamic parameters for keto–enol tautomerism of aldehydes has presented a major challenge, caused mainly by difficulties in measuring the small concentration of the enol form present in most systems.[2] From investigations of the horseradish peroxidase catalyzed reaction of 2-methylpropanal (isobutyraldehyde) and molecular oxygen to form triplet-state acetone and formic acid, it has been established that only the enol form of the aldehyde is reactive with compounds I and II of peroxidase.[3] We report here upon exploitation of this reactivity of enols to measure the rate and equilibrium constants for the keto–enol tautomerism of 2-methylpropanal, propanal, and butanal.

Compound I (HRP-I) was prepared in close to pure form (with only inert native enzyme present as a small contaminant) and introduced into one reservoir of a stopped-flow apparatus (Union Giken Model RA-601).[4] 2-Methylpropanal, solubilized in up to 0.59 M aqueous ethanol, was placed into the other reservoir. All reactions were studied at 35.0 °C, pH 7.4, and ionic strength 0.67 M. K_2SO_4 was used as an inert electrolyte where necessary. Phosphate buffer was used; it catalyzes the keto–enol conversion. The relevant equations are

$$\text{phosphate} + \text{keto} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{enol} + \text{phosphate} \quad (1)$$

$$H_2O \rightleftharpoons H_2O \quad (K_{hyd})$$

hydrate

$$K_{enol} = \frac{[enol]}{[keto]} = \frac{k_1}{k_{-1}} \quad (2)$$

$$[aldehyde]_{tot} = [keto] + [hydrate] + [enol] \simeq [keto] + [hydrate] \quad (3)$$

$$K_{hyd} = \frac{[hydrate]}{[keto]} = \frac{[aldehyde]_{tot} - [keto]}{[keto]} \quad (4)$$

$$\therefore [keto] = \frac{[aldehyde]_{tot}}{1 + K_{hyd}} \quad (5)$$

Molecular oxygen does not play any role in the elementary reactions described here, only in the overall reaction.[3]

With enol in excess with respect to compound I a pseudo-first-order reaction is observed at 411 nm, the isosbestic point between native enzyme and compound II,

$$-d[HRP\text{-}I]/dt = k_{obsd}[HRP\text{-}I] = k_{app}[enol][HRP\text{-}I] \quad (6)$$

where the units of k_{obsd} are s^{-1} and of k_{app} are $M^{-1}\ s^{-1}$. From eq 2, 5, and 6,

$$k_{obsd} = k_{app}[enol] = \frac{k_{app}K_{enol}[aldehyde]_{tot}}{1 + K_{hyd}} \quad (7)$$

A plot of k_{obsd} vs. total aldehyde concentration is linear with the slope equal to $k_{app}K_{enol}/(1 + K_{hyd})$. Thus if the equilibrium constants are known, the rate constant for the reaction of compound I with enol, k_{app}, can be calculated. This approach was valid for 2-methylpropanal and propanal but not for butanal because of its low solubility. The values of k_{app} are of the order of $5 \times 10^6\ M^{-1}\ s^{-1}$.

More complicated but more revealing behavior is observed when compound I is in excess of enol. Now the consumption of compound I consists of an initial burst in which the equilibrium pool of enol is consumed rapidly, followed by a slow zero-order reaction in which the rate-limiting step is the keto–enol conversion. The steady-state approximation is valid in the zero-order region and it can be shown that

$$-d[HRP\text{-}I]/dt = \frac{k_1[aldehyde]_{tot}[phosphate]}{1 + K_{hyd}} = k_{zo} \quad (8)$$

where k_1 is the second-order rate constant for the conversion of keto to enol, catalyzed by phosphate, and k_{zo} is the experimentally determined zero-order rate constant ($M\ s^{-1}$). For fixed $[aldehyde]_{tot}$ a plot of k_{zo} vs. [Phosphate] is linear; similarly for fixed phosphate a plot of k_{zo} vs. $[aldehyde]_{tot}$ is linear. Therefore k_1 is calculated readily if K_{hyd} is known. Unfortunately, some measurements of K_{hyd} in the literature are inconsistent or obtained under different experimental conditions.[5] The multiplication factor $(1 + K_{hyd})$ therefore has not been applied to the values reported in Table I. We define new parameters K'_{enol} and k'_1 which are the ones listed in Table I.

$$K'_{enol} = K_{enol}/(1 + K_{hyd}); \quad k'_1 = k_1/(1 + K_{hyd}) \quad (9)$$

The factor $(1 + K_{hyd})$ cancels in the determination of k_{-1}. By calibration of the stopped-flow apparatus, the amount of compound I disappearing in the initial burst can be determined; this provides a measure of the equilibrium concentration of enol and hence of the equilibrium constant K'_{enol}. Since both k'_1 and K'_{enol} have been determined, k_{-1} can be calculated. A similar approach was used for propanal and butanal for which no experimentally determined constants appear in the literature. Results are summarized in

(1) (a) Instituto de Quimica, Universidade de São Paulo, C.P. 20.780, São Paulo, S.P., Brasil. Supported by the exchange program Natural Sciences and Engineering Research Council (Canada) and Conselho Nacional de Desenvolvimento Científico e Technôlogico (Brasil). (b) Alberta Heritage Foundation for Medical Research Scholar. (c) Supported by operating Grant A1248 from N.S.E.R.C.

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