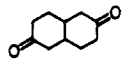
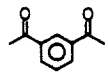
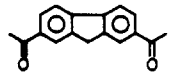
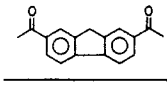
Table I. Hydrolysis Yield of Polymer Ketal Template[a]

Template	Loading (μ mol/g)	Matrix	Yield
	60	DVB	56
	60	DIP	100
	60	DIP	100
	12	DIP	100
	60	DVB	0
	60	DVB	20
	60	DIP	82
	12	DIP	77
	60	DIP	86
	12	DIP	67

[a] See text for conditions.

Table II. Rebinding Ratios and Corrected Selectivities (α)[a]

Template	Rebinding Substrates			
	Ac / 1,3	1,3 / 1,4	1,4 / fl	1,3 / fl
	60 : 40	45 : 55	65 : 35	60 : 40
	40 : 60 ($\alpha_{1,3/Ac}$ = 2.25)	58 : 42 ($\alpha_{1,3/1,4}$ = 1.69)	80 : 20 ($\alpha_{1,4/fl}$ = 2.15)	85 : 15 ($\alpha_{1,3/fl}$ = 3.8)
			75 : 25 ($\alpha_{fl/1,4}$ = 0.62)	70 : 30 ($\alpha_{fl/1,3}$ = 0.64)

[a] Ac = acetophenone; 1,3, 1,4 = 1,3- and 1,4-diacetylbenzene; fl = 2,7-diacetylfluorene. Typical rebinding conditions employed equimolar amounts of competiting ketones in a fourfold excess over the number of available sites on the polymer in refluxing benzene containing a catalytic amount of TSA.

We are continuing our efforts to establish the relative importance of functional group positioning, hydrophilicity and complementary shape in the molecular recognition process.[11]

Acknowledgment. We thank the National Institutes of Health and Hughes Aircraft Corporation for financial support of this work.

Registry No. (S)-(DIP)-(3-(4-ethenylphenyl)-1,5-dioxaspira[5.5]undecane) (copolymer), 100047-21-0; (S)-(DIP)-(6-(4-ethenylphenyl)-2-methyl-2-phenyl-*m*-dioxane) (copolymer), 100047-23-2; (S)-(DIP)-(5,5″-bis(4-ethenylphenyl)hexahydrodispiro[*m*-dioxane-2,2′(1′*H*)-naphthalene-6′(7*H*),2″-*m*-dioxane]) (copolymer), 100047-25-4; (1,4-bis[5-(4-ethenylphenyl)-2-methyl-*m*-dioxan-2-yl]benzene)-(S)-(DIP) (copolymer), 100047-27-6; (S)-(DIP)-(2,7-bis[5-(4-ethenylphenyl)-2-methyl-*m*-dioxan-2-yl]fluorene) (copolymer), 100084-88-6; (DVB)-(3-(4-ethenylphenyl)-1,5-dioxaspira[5.5]undecane) (copolymer), 100047-28-7; (DVB)-(1,4-bis[5-(4-ethenylphenyl)-2-methyl-*m*-dioxan-2-yl]-benzene) (copolymer), 100047-30-1; acetophenone, 98-86-2; 1,3-diacetylbenzene, 6781-42-6; 2,7-diacetylbenzene, 961-27-3; 1,4-diacetylbenzene, 1009-61-6.

(11) For related work regarding molecular recognition of template functionalized polymers, see: Wulff, G.; Heide, B.; Helfmeier, G., preceding paper in this issue. We are grateful for Professor Wulff for an exchange of information prior to publication.

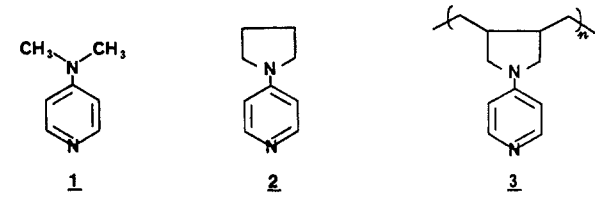
Inverse Phase Transfer Catalysis. First Report of a New Class of Interfacial Reactions

Lon J. Mathias* and Rajeev A. Vaidya†

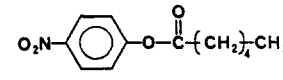
Department of Polymer Science
University of Southern Mississippi
Hattiesburg, Mississippi 39406-0076
Received October 24, 1985

Phase-transfer catalysis has been used to promote a variety of interfacial reactions involving small molecule reactants,[1] polymer synthesis,[2] and polymer modification.[3] All transfer agents employed to date facilitate transport of a water-soluble or solid reactant into an organic phase. We present evidence here for a new class of reactions involving transport of an organic-soluble reactant into an aqueous phase for reaction.

Our approach is based on 4-aminopyridine supernucleophiles. 4-(Dimethylamino)pyridine (DMAP, **1**) and 4-pyrrolidinopyridine



1 **2** **3**



4

(PPY, **2**) have been used to accelerate a variety of homogeneous reactions.[4] We recently synthesized a polymer analogue of PPY[5] that displays *greater* catalytic activity in homogeneous reactions than PPY, the most active of the small molecule supernucleophiles.[6]

The first reaction studied involved the acylation of aqueous racemic alanine with organic-soluble acid chlorides.[7] Table I summarizes the conversions and product yields for fixed reaction times of DMAP-catalyzed and uncatalyzed interfacial reactions. The decanoyl chloride reaction was carried out for 1 h, although complete disppearance of the starting material occurred in less than 10 min with DMAP present. The rate acceleration with

† Present address: E.I. duPont de Nemours & Co., Washington Works, Parkersburg, WV 26102-1217.

(1) Weber, W. P.; Gokel, G. W. "Reactivity and Structure Concepts in Organic Chemistry"; vol. *4*; Springer-Verlag: New York, 1977; Vol. 4.
(2) Rassmussen, J. K.; Smith, H. K. *J. Am. Chem. Soc.* **1981**, *103*, 730.
(3) Mathias, L. J., Carraher, C. E., Eds. *Polym. Sci. Technol.* **1984**, *24*. Plenum Press: NY, 1984.
(4) Hofle, G.; Steglich, W.; Vorbruggen, H. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 569.
(5) Mathias, L. J.; Vaidya, R. A.; Bloodworth, R. H. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 289.
(6) Vaidya, R. A. Ph.D. Dissertation, University of Southern Mississippi, Hattiesburg, MS, 1985.
(7) General procedure for acid chloride–amino acid IPTC reactions: Aqueous 1 N NaOH, 10 mL, and 0.01 mol of the amino acid were stirred in a jacketed reactor thermostated at 0 °C and allowed to thermally equlibrate for 10 min. Catalyst, 0.001 mol, dissolved in 1 mL of methylene chloride was added to catalyzed reactions and 1 mL of solvent was added to control reactions. After 5 min, 0.011 mol of the acid chloride dissolved in 9 mL of cold methylene chloride were added in one portion. Reaction times were counted from this instant. After the required reaction time had elapsed, the methylene chloride was evaporated from the mixture and the aqueous phase was cooled and acidified with cold 0.5 M $KHSO_4$ to pH 2. The reaction products precipitated and were filtered and washed extensively with deionized water. The wet cake was dried at 40 °C in a vacuum oven. The percent acid in the product was determined by using FTIR or ^1H NMR. From the total weight of the product, the amount of the amide and the total amount of acid chloride reacted were calculated.

0002-7863/86/1508-1093$01.50/0

Table I. Interfacial Reaction of Water-Insoluble Acid Chlorides with Aqueous D,L-Alanine

	acid chloride A	catalyst	rxn time	% conversion of A	% amide in prod
1	decanoyl	DMAP	1 h[a]	91	52[b]
		none	1 h	52	60[b]
2	*p*-chlorobenzoyl	DMAP	10 min	85	44[c]
		none	10 min	nil[d]	

[a] The catalyzed reaction was essentially complete in 5-10 min. [b] FTIR spectroscopy was used to quantitate percent amide in product. [c] ^{1}H NMR spectroscopy was used to quantitate percent amide in product. [d] No product could be isolated from the control reaction.

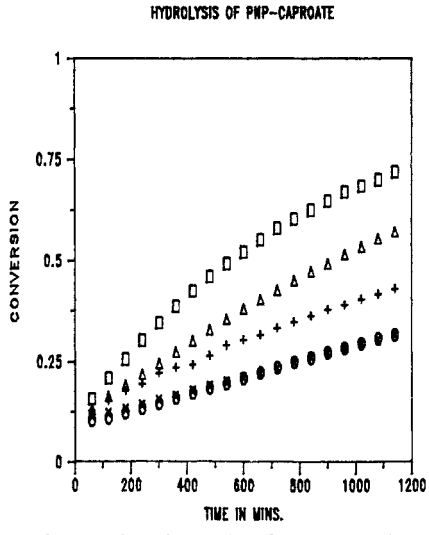


Figure 1. Plots of conversion of **4** vs. time for control (○), PPY (X), and **3** (+) in the excess substrate regime and PPY (△) and **3** (□) in the excess catalyst regime.

DMAP is even more striking for the *p*-chlorobenzoyl chloride. In both cases, competing hydrolysis accounts for conversion of approximately half of the starting material. While no effort has been made to optimize reaction conditions, increasing the concentration of the aqueous reactant should increase both the rate and the yield of the desired reaction.

Further support for inverse phase transfer catalysis (IPTC) was provided by evaluation of relative rates of interfacial hydrolysis of *p*-nitrophenyl caproate (**4**).[8] Figure 1 summarizes hydrolysis kinetics for both PPY and polymer catalyst **3**. Substrate **4** was present as a solution in toluene. Homogeneous hydrolysis of **4** in the absence of toluene (but with all other conditions identical) occurred ca. 10 times faster. This clearly indicates that solubility of **4** is much greater in toluene than in water in this two-phase system and that interfacial transport is the rate-limiting step.

The hydrolysis rate of **4** with PPY in the excess substrate regime was experimentally identical with that of the control. The polymer-catalyzed reaction is clearly faster. In the excess catalyst regime, both PPY and polymer were effective catalysts with the polymer displaying significantly faster conversion.

(8) General procedure for the hydrolysis of *p*-nitrophenyl caproate (**4**). Aqueous 1 N NaOH, 3 mL, was added to a capped glass UV cuvette stirred by a gas-driven magnetic stirrer mounted inside a Perkin-Elmer 320 UV-vis spectrometer.[9] The catalyst was injected as a concentrated solution in methanol. The total amount of methanol injected was the same for PPY and the polymer and was 60 μL in the excess catalyst regime and 3 μL in the excess substrate regime. Control reactions with and without these amounts of methanol were found to have experimentally identical rates. The ratio of substrate to catalyst was 2 in the excess substrate regime and 0.1 in the excess catalyst regime. The substrate (**4**) was injected as a 10-μL dose of a 8.28×10^{-3} g/mL solution in toluene. The contents were momentarily shaken and the toluene droplets rose to the top within minutes. The aqueous phase was stirred at a constant rate without disturbing the organic phase for the duration of the reaction. Absorbance at 400 nm (λ_{max} for *p*-nitrophenoxide ion) was monitored as a function of time.

(9) The stirrer has been described: Vaidya, R. A.; Hermes, R. E.; Mathias, L. J.; Bridges, J. L. *Am. Lab.* (*Fairfield, Conn.*) **1985**, *17*, 84.

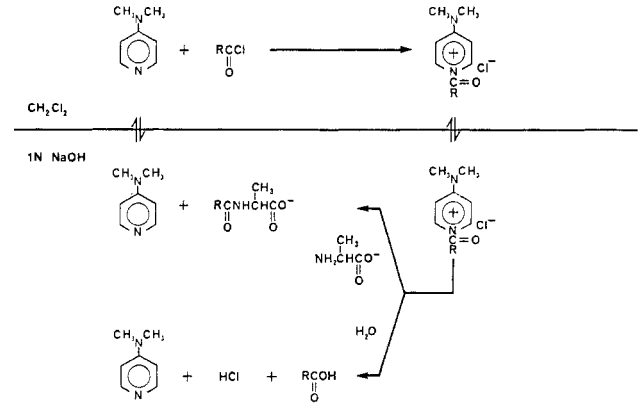


Figure 2. Schematic representation of the IPTC process.

Figure 2 depicts the proposed sequence of steps in the overall inverse phase transfer process. A major difference of this process compared to normal phase transfer catalysis is that the catalyst actually *reacts* with the substrate to generate the charged intermediate which possesses increased solubility in the aqueous phase. This intermediate undergoes phase transport and then reacts with the water-soluble nucleophile or with water to give the two products observed. Regeneration of the neutral supernucleophile and transport back to the organic phase allows true catalytic activity.

Further examination of the proposed mechanism and intermediates is under way along with extension of inverse phase transfer catalysis to additional reactions.

Acknowledgment. We gratefully acknowledge continued financial support for this project from 3M and the donors of the Petroleum Research Fund, administered by the American Chemical Society, and helpful discussions with J. K. Rasmussen, S. M. Heilmann, and C. J. Podsiadly of 3M Central Research Laboratory.

Hyperconjugative Effects of Allylic Substituents Are Not Important in Osmylations

Edwin Vedejs* and Cynthia K. McClure

S. M. McElvain Laboratory of Organic Chemistry
Chemistry Department, University of Wisconsin
Madison, Wisconsin 53706

Received June 4, 1985

Allylic ethers are osmylated with useful selectivity for diastereomer I over II, especially in the case of electron-rich *Z* alkenes.[1,2] This result has been rationalized by Kishi et al.[1] using a reactant-like empirical model, but other explanations based on "perpendicular" transition states have recently appeared.[3] Houk et al. originally suggested that bulky allylic substituents would prefer "anti", "outside", and "inside" positions in that order, σ-acceptors would occupy "inside" or "outside" positions, and the best σ-donor would be "anti" to the electrophile to facilitate olefin HOMO–electrophile LUMO interactions.[3a] Although details were not specified for osmylations, structures **1** and **2** follow as the best transition states for I- or II-selective allylic ether hydroxylations (X = alkoxy, Figure 1). These factors are difficult to evaluate because the mechanism of osmylation is not well defined.[4]

(1) Cha, J. K.; Christ, W. J.; Kishi, Y. *Tetrahedron* **1984**, *40*, 2247.
(2) A different pattern is seen with α,β-unsaturated carbonyl compounds: Stork, G.; Kahn, M. *Tetrahedron Lett.* **1983**, *24*, 3951. Also, ref 1.
(3) (a) Houk, K. N.; Moses, S. R.; Wu, Y.-D.; Rondan, N. G.; Jäger, V.; Schohe, R.; Fronczek, R. *J. Am. Chem. Soc.* **1984**, *106*, 3880. (b) McGarvey, G. J.; Williams, M. J. *Ibid.* **1985**, *107*, 1435.
(4) Schröder, M. *Chem. Rev.* **1980**, *80*, 187. Sharpless, K. B.; Teranishi, A. Y.; Backvall, J.-E. *J. Am. Chem. Soc.* **1977**, *99*, 3120; **1980**, *102*, 4263.

0002-7863/86/1508-1094$01.50/0