Table I. Kinetic Resolution of 1 Using TBHP, L-(+)-DIPT, and Ti(O-*i*-Pr)$_4$[a]

run		substrate 1 R^1	R^2	time, h	slow-reacting (i.e., recovered) enantiomer (*R*)-1[b] yield,[c] %	% ee	$[\alpha]^{25}_D$ (c, $CHCl_3$)	oxidation product 2: yield,[d] %
1	a	H	Me	24	32	>95[e]	+20.8° (1.27)	53
2[f]	b	H	*n*-Am	25	42	>95[g]	+13.8° (1.07)	53[h]
3	c	H	*i*-Pr	25	39	>95[g]	+18.1° (1.04)	55
4	d	H	*t*-Bu	40	41	6[g,i]		58
5	e	H	Ph	40	42	>99[j]	+6.9° (1.13)	44
6	f	Me	*n*-Am	6	40	>95[g]	+7.8° (1.01)	55

[a] The reaction was carried out by using TBHP (0.6 equiv), L-(+)-DIPT (1.2 equiv), and Ti(O-*i*-Pr)$_4$ (1.0 equiv) in CH_2Cl_2 at −21 °C. [b] Absolute configurations were proven by correlation with the corresponding (*R*)-α-hydroxy acids[9] by the following sequence: (1) Ac_2O, C_5H_5N; (2) $NaIO_4$, $RuCl_3 \cdot H_2O$ (cat.), CCl_4–CH_3CN–H_2O (2:2:3); (3) NaOH, H_2O–MeOH. [c] Isolated yields. [d] Determined by ^1H NMR analysis of the crude reaction mixture. [e] Determined by ^1H NMR analysis of the corresponding acetate in the presence of (−)-Pr(DPPM)$_3$ (detection limit ca. 95% ee). [f] The resolution was also effected by using 20% catalyst in the presence of molecular sieves, affording (*R*)-**1b** with >95% ee in 38% isolated yield.[7] [g] Determined by ^1H NMR analysis of the corresponding MTPA ester (detection limit ca. 95% ee). [h] Anomeric mixture of 2:1 ratio. [i] Absolute configuration was not determined. [j] Determined by HPLC analysis of the corresponding benzoate using CHIRALPAK OT(+) (Daicel Chemical Industries, Ltd.).

an enantioselective manner.

The results of the oxidation of various **1** in which a substituent R^2 is a primary, secondary, or tertiary alkyl group or an aromatic group, using TBHP (0.6 equiv), Ti(O-*i*-Pr)$_4$ (1 equiv), and L-(+)-DIPT (1.2 equiv), are summarized in Table I. It can be seen from Table I that highly efficient kinetic resolution occurs in all cases except for **1d**, which has a sterically demanding tertiary alkyl group. When L-(+)-DIPT is employed, the slow-reacting enantiomer is always that shown in eq 1, i.e., when the hydroxyl group is up, the furan ring is on the left. Thus this system adds another example of the feature of predictability with the parent process for kinetic resolution of allylic alcohols.[6] Noteworthy also is the fact that the kinetic resolution of **1** also proceeds effectively by using 20% catalyst in the presence of molecular sieves (see footnote *f* in Table I).[7] In the present reaction, the oxidation products **2** are readily separable by column chromatography on silica gel since (*R*)-**1** and **2** have quite different R_f values on silica gel. However, the isolation of (*R*)-**1** can be carried out more conveniently by treating the crude mixture with base (NaOH, Et_2O, H_2O).[8] Under these conditions, **2** is converted into an unidentified very polar product or products (R_f 0 (hexane–Et_2O, 2:1)).

A typical experimental procedure is represented by preparation of (*R*)-**1b**: To a solution of Ti(O-*i*-Pr)$_4$ (3.68 mL, 12.3 mmol) in CH_2Cl_2 (60 mL) was added L-(+)-DIPT (3.12 mL, 14.8 mmol) at −20 °C. After being stirred for 10 min, the solution was cooled to −30 °C, and racemic **1b** (2.07 g, 12.3 mmol) in CH_2Cl_2 (3 mL) and TBHP (1.99 mL, 7.41 mmol, 3.73 M in CH_2Cl_2) were added to the system. The solution was stirred at −21 °C for 25 h and poured into a mixture of 10% tartaric acid solution (0.5 mL), Et_2O (20 mL), and NaF (3 g). The mixture was stirred vigorously for 3 h at room temperature, and the resulting white precipitate was filtered through a pad of Celite. The filtrate was concentrated to give an oil, which was dissolved in Et_2O (100 mL) and treated with 1 N NaOH (50 mL) for 30 min at 0 °C with vigorous stirring. The ethereal solution was washed with brine, dried ($MgSO_4$), and concentrated to give an oil, which was passed through a short silica gel column to afford (*R*)-**1b** (872 mg, 42% yield).

As starting racemic carbinols **1** can be readily prepared in large quantity from furfural and Grignard reagents, or 2-furyllithium and aldehydes, the optically active compounds **1** are now readily available asymmetric starting materials. Application of the optically active **1** in natural product synthesis and in material science are in progress in our laboratory.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas, Advanced Molecular Conversion, from the Ministry of Education, Science and Culture.

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(6) Thus far, no exception has been reported; cf. ref 4.
(7) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765.
(8) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 5974.
(9) Newman, P. *Optical Resolution Procedures for Chemical Compounds*; Optical Resolution Information Center: New York, 1981; Vol. 2, Part 1.

Molecular Complex Evaluation. A Simultaneous Assay of Binding Using Substrate Mixtures

Summary: An experimental method is described that allows the simultaneous measurement of the extent of molecular complex formation between a ligand and a mixture of different potential substrates. The method is operated by chemically binding the ligand to a polyacrylamide resin and adding a mixture of potential substrates to the resin. By measurement of the concentrations of the substrates both before and after addition of the resin, the decrease in bulk solution concentration of those substrates that bind to the resin-bound ligand can be observed. By determination of the loading of the ligand on the resin, association constants can be determined, assuming competitive binding. As an application of the assay, ristocetin and vancomycin were used as ligands and binding to a number of dipeptides was measured and compared with association constants measured in free solution by a standard titration assay.

Sir: Measurement of association constants (K_a) is an important part of the study of the complexes formed between ligands and substrates (hosts and guests).[1] Common methods of K_a determination involve monitoring the change in some property (UV extinction coefficient, NMR chemical shift, etc.) during the titration of a ligand with a substrate. Disadvantages of the titration method include

(1) Review: Connors, K. A. *Binding Constants*; Wiley: New York, 1987.

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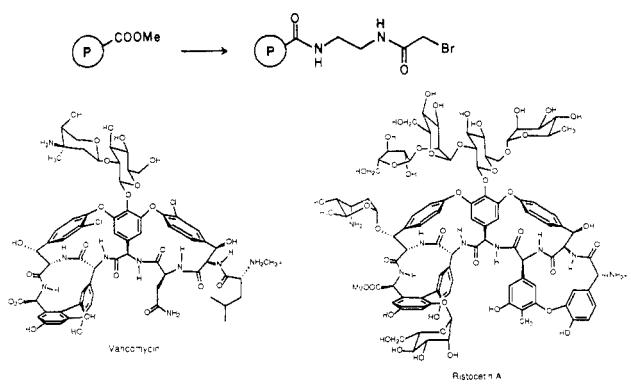

Figure 1.

the necessity of finding a property that is significantly different in the complex and in the free ligand and that is easily measurable at concentrations on the order of the dissociation constant. More direct methods require measurement of the concentrations of the species involved in an equilibration of free and complexed ligands or substrates between two phases and commonly involve partitioning a water-soluble ligand and an organic soluble substrate (or vice versa) between aqueous and organic phases. We describe here a useful new method for evaluating complexation that does not require differential ligand/substrate solubilities and that may be applied to the study of many substrates simultaneously. the method uses a ligand that is covalently bound to an insoluble polymer as one phase and a solution of substrate(s) as the other[2] and allows the direct determination of the relative extent of substrate binding and the approximate measurement of binding constants ranging from 10^2 to 10^8. In the two cases studied, the assay yields binding constants that correlate semiquantitatively with binding results in free solution. We believe the assay described here will facilitate studies of the binding properties of new synthetic ligands for organic substrates.

As the polymer support, we chose a polydimethylacrylamide resin[3] since it is commercially available and easily functionalized and may be used with both aqueous and organic solvents. While a variety of resin activation schemes could be used, depending on the functionality of the ligand to be attached, we converted the polymer beads to a bromoacetyl resin suitable for coupling to nucleophiles (e.g., basic amines) using (1) $NH_2CH_2CH_2NH_2$ and (2) $(BrCH_2CO)_2O$ (Figure 1). We chose, as test ligands, the amine-containing antibiotics ristocetin A and vancomycin, which are known to bind certain C-terminal peptides composed of D-amino acids.[4] These native antibiotics were reacted separately with the bromoacetyl resin (DMF, *i*-Pr_2NEt, 25 °C, 48 h) to yield polymer-bound ristocetin (P-Risto) and vancomycin (P-Vanco). Both ristocetin and vancomycin have a number of sites to which the activated resin bromoacetyl function may have bound, but among the most likely, i.e., the amino and phenolic groups, we believe that the former is the coupling site. Thus, simple phenols (e.g., (*tert*-butyloxycarbonyl)tyrosine benzyl ester) do not couple to the resin when *i*-Pr_2NEt is used (IR analysis of the resin shows no ester stretching band at 1740 cm^{-1}), but basic amines including tyrosine benzyl ester itself do. Under more basic conditions, however, phenols will couple to the bromoacetyl polymer, and K_2CO_3/18-crown-6 in DMF is particularly effective for promoting such couplings.

In any event, the precise nature of the bond is unimportant so long as attachment of the ligand to the resin does not substantially modify the ligand's binding properties (see below). We believe that the primary utility of the assay described here will be for the rapid establishment of binding profiles for new host molecules and that interesting host–guest partners thus found would be studied in more detail by other methods. Generally, new host molecules for use with our assay would be designed in such a way that the functionality used for immobilization would be remote from the substrate-binding site.

After extensive washing of the resin beads, P-Risto and P-Vanco, to remove unbound material,[5] the supported ligands were ready for use in the binding assay. The assay was conducted by first preparing an HPLC-separable mixture of substrates at equal concentrations and measuring the areas of the corresponding HPLC peaks under a standard set of conditions. For our resins, we used a substrate mixture consisting of the N-benzoylated dipeptides GlyGly, D-AlaGly, Gly-D-Ala, D-Ala-D-Ala, D-Ala-L-Ala, D-PheGly, and D-Phe-D-Ala with *N*-benzoyl-L-Ala as an internal standard. The peptides were dissolved in aqueous citrate buffer (pH 5.1, 0.5 mM each), and the corresponding HPLC is shown as trace 1 (Figure 2).[6] To 0.5 mL of this solution was added 10 mg of P-Risto beads, and the mixture was equilibrated by gentle agitation (1 h). As shown in trace 2 and summarized in Table I, the peaks corresponding to certain dipeptides fell dramatically. These dipeptides are the ones that bind most tightly to ristocetin A, and the decreases in peak areas are roughly proportional to the free solution phase ristocetin/dipeptide association energies.[7]

Relative binding may thus be determined by HPLC trace inspection for as many substrates as can be separated provided that the substrates are either all competitively or all noncompetitively bound by the ligand. Even if this condition is not met, those substrates that are substantially bound at the concentration used are easily distinguished from those that are not. For quantitative results, we use the total substrate concentrations ($[SA]_t$, $[SB]_t$,...) and take the HPLC substrate peak areas to be proportional to unbound concentration. With these quantities we can calculate the bound ($[SA]_b$, $[SB]_b$,...) and unbound ($[SA]_u$, $[SB]_u$,...) concentrations of each substrate. If the total concentration of ligand binding sites ($[L]_t$) of the resin is known, the association constants follow directly from the equilibrium expression. Alternatively $[L]_t$ can be determined by adding one or more additional aliquots of the substrate mixture, measuring the HPLC peak areas, and solving the system of linear equations below by least squares. The other least-squares solutions are the concentrations of free ligand binding sites ($[L]_u1$, $[L]_u2$,...) for each substrate mixture aliquot (1, 2,...) added and the

(2) For related work using polymer-bound ligands for competitive binding studies with single substrates, see: Dunn, B. M.; Chaiken, I. M. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 2382. Cox, J. A.; Comte, M.; Fitton, J. E.; DeGrado, W. F. *J. Biol. Chem.* **1985**, *260*, 2527.

(3) Atherton, E.; Clive, D. L. J.; Sheppard, R. C. *J. Am. Chem. Soc.* **1975**, *97*, 6584. Arshady, R.; Atherton, E.; Clive, D. L. J.; Sheppard, R. C. *J. Chem. Soc., Perkin Trans. 1* **1981**, 529.

(4) Reviews: Williams, D. H.; Rajananda, V.; Williamson, M. P.; Boejesen, G. *Top. Antibiot. Chem.* **1980**, *5*, 119. Perkins, H. R. *Pharmacol. Ther.* **1982**, *16*, 181. Williams, D. H. *Acc. Chem. Res.* **1984**, *17*, 364.

(5) Unbound material interferes with the quantitative assay. It is removed by washing 100 mg of resin with seven 10-mL aliquots of distilled water for 24 h each.

(6) Binding to the support was not observed since the same trace was produced if polymer-bound morpholine was added to the peptide mixture.

(7) Binding was measured by UV difference spectroscopy at 283 nm as previously described: Nieto, M.; Perkins, H. R. *Biochem. J.* **1971**, *123*, 773, 789.

Table I. Comparison of Solid-Phase and Solution-Phase Binding Results

supported ligand	peptide substrate	solid-phase assay[a] area loss,[c] %	solid-phase assay[a] assoc energy[d]	titration assay[b] assoc energy[d]
P-Risto	BzGlyGly	24	−5.4 (1.1)[e]	−5.7 (0.2)
P-Risto	Bz-D-AlaGly	71	−6.5 (1.2)[e]	−6.9 (0.4)
P-Risto	BzGly-D-Ala	97	−7.8 (1.2)[e]	−8.2 (0.5)
P-Risto	Bz-D-Ala-D-Ala	>99	−8.5 (1.2)[e]	−9.3 (1.4)
P-Risto	Bz-D-Ala-L-Ala	<1	−3.5 (2.0)[e]	NC[i]
P-Risto	Bz-D-PheGly	69	−6.4 (1.2)[e]	−5.6 (0.2)
P-Risto	Bz-D-Phe-D-Ala	91	−7.2 (1.2)[e]	−7.0 (0.2)
P-Risto	BzGlyGly	78	−4.7 (0.3)[f]	−5.7 (0.2)
P-Risto	Bz-L-AlaGly	6	−0.4 (2.8)[f]	–
P-Risto	BzGly-L-Ala	8	−0.5 (2.7)[f]	–
P-Risto	Bz-L-Ala-L-Ala	2	0.0 (2.9)[f]	NC[i]
P-Risto	Bz-L-Ala-D-Ala	53	−4.0 (0.4)[f]	−4.7 (0.3)
P-Risto	Bz-L-PheGly	50	−4.0 (0.4)[f]	−5.4 (0.6)
P-Risto	Bz-L-Phe-L-Ala	40	−3.7 (0.4)[f]	NC[i]
P-Vanco	BzGlyGly	19	−5.6 (1.3)[g]	−5.4 (0.3)
P-Vanco	Bz-D-AlaGly	49	−6.3 (1.3)[g]	−6.1 (0.1)
P-Vanco	BzGly-D-Ala	61	−6.9 (1.3)[g]	−6.7 (0.1)
P-Vanco	Bz-D-Ala-D-Ala	86	−7.5 (1.3)[g]	−7.2 (0.5)
P-Vanco	Bz-D-Ala-L-Ala	3	−3.8 (2.3)[g]	NC[i]
P-Vanco	Bz-D-PheGly	81	−7.2 (1.3)[g]	−6.9 (0.5)
P-Vanco	Bz-D-Phe-D-Ala	96	−8.3 (1.3)[g]	−8.3 (0.4)
P-Vanco	BzGlyGly	49	−4.5 (0.5)[h]	−5.4 (0.3)
P-Vanco	Bz-L-AlaGly	2	−0.8 (2.9)[h]	–
P-Vanco	BzGly-L-Ala	<1	−0.5 (2.9)[h]	–
P-Vanco	Bz-L-Ala-L-Ala	4	−0.5 (3.4)[h]	NC[i]
P-Vanco	Bz-L-Ala-D-Ala	13	−2.4 (1.8)[h]	−4.6 (0.5)
P-Vanco	Bz-L-PheGly	4	−1.5 (3.3)[h]	NC[i]
P-Vanco	Bz-L-Phe-L-Ala	9	−1.2 (2.4)[h]	–

[a] Assay by UV detection HPLC in pH 5.1 citrate buffer (0.5 mL) with 10 mg of the supported ligand. [b] UV titration assay in same buffer. [c] Percentage of original substrate area lost on initial addition of resin. [d] Association energy (error limit), kcal/mol. [e] Substrates tested simultaneously, resin loading found by least squares to be 0.11 (±0.02) μmol/mg resin. [f] Substrates tested simultaneously with resin loading fixed at 0.11 μmol/mg. [g] Substrates tested simultaneously, loading found to be 0.04 (±0.01) μmol/mg. [h] Substrates tested simultaneously with loading fixed at 0.04 μmol/mg. [i] No complexation observable by UV, dissociation free energies <3.5 kcal/mol could not have been detected.

dissociation constants (K_dA, K_dB,...) for each substrate (A, B,...):[8]

$[L]_t$	$[L]_{u1}$	$[L]_{u2}$...	K_dA	K_dB...	
1.0	-1.0				= $[SA]_{b1}$ + $[SB]_{b1}$ +...
	$[SA]_{u1}/[SA]_{b1}$		-1.0		= 0.0
	$[SB]_{u1}/[SB]_{b1}$			-1.0	= 0.0
	.				
	.				
	.				
1.0		-1.0			= $[SA]_{b2}$ + $[SB]_{b2}$ +...
		$[SA]_{u2}/[SA]_{b2}$	-1.0		= 0.0
		$[SB]_{u2}/[SB]_{b2}$		-1.0	= 0.0
		.			
		.			
		.			

The results for the P-Risto and P-Vanco resins are summarized in Table I. Within our experimental errors,[9] no major differences in binding with either supported or free ligand can be seen. While reproducibility among repeated solid-phase assays is good (±0.3 kcal/mol), errors in HPLC measurements of concentration increase the uncertainty in the absolute values of the association energies to ±1.5 kcal/mol when the resin loading must be simultaneously evaluated. The main problem with the quantitative assay is that a small error in calculation of resin loading ($[L]_t$) can lead to large errors in absolute association energies, and it is advisable to perform several measurements with a single tight-binding substrate to firmly establish $[L]_t$ if quantitative results are desired. While the best way to avoid these errors has yet to be determined, our best results have been obtained by evaluating mixtures of tight- and weak-binding substrates separately and by decreasing (tight binders) or increasing (weak binders) the quantity of beads (and/or the ligand loading) and the concentrations of the substrates to give

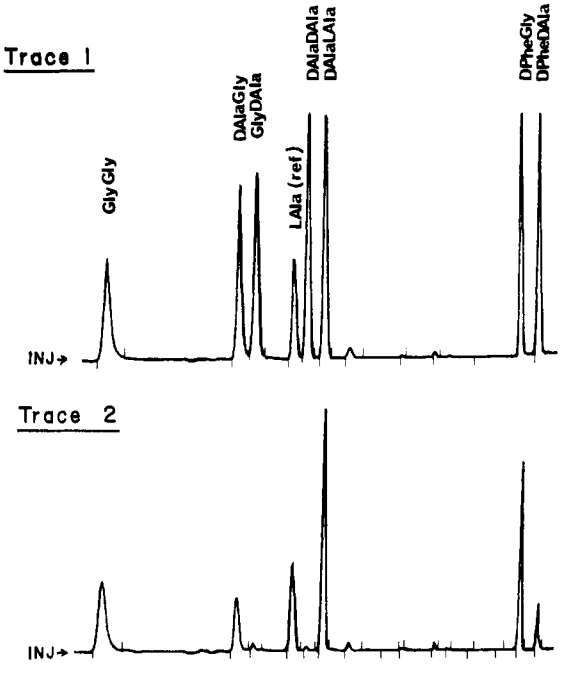

Figure 2.

(8) The stoichiometry of the complexes formed is assumed to be 1:1, and the substrates are assumed to bind competitively.

(9) Energetic errors reported follow from the assumption of a 5% error in the machine-integrated HPLC peaks.

50–95% saturation of the available binding sites. The reader is reminded that the treatment above assumes competitive binding with 1:1 stoichiometry and that the quantitative aspects of this work may not be useful with large, complex ligands having multiple binding sites or the capability of binding multiple substrates.

Most of our results mirror the known properties of ristocetin and vancomycin, but several of the results were unexpected until discovered during the solid-phase assay and confirmed by solution-phase titration experiments. First, D-Phe-D-Ala binds to vancomycin (but not ristocetin) more tightly than the natural substrate sequence D-Ala-D-Ala. Second, L-PheGly shows modest binding to ristocetin (but not vancomycin). Third, an analogous assay in methanol shows that all association constants are reduced, especially those of the phenylalanine-containing dipeptides. Parenthetically we note that the benzoyl dipeptides studied here generally bind more tightly than the corresponding acetyl analogues in water. These findings point to a significant hydrophobic component of the binding energy and demonstrate the utility of the method as an effective screen for finding sets of substrates that bind to a given ligand.[10]

Supplementary Material Available: Experimental details for preparing the bromoacetyl resin, for linking the ligand, and for conducting the assay; a FORTRAN computer program that evaluates binding constants from the HPLC integrations (11 pages). Ordering information is given on any current masthead page.

(10) This work was supported by NIH grant GM37255 and an SERC/NATO postdoctoral fellowship to P.W.S.

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Photocyclization Reactions of 1-Benzyl-1-pyrrolinium Salts by Diradical and Diradical Cation Pathways. Novel Photochemical Pictet–Spengler Cyclizations

Summary: Studies with a series of ortho- and meta-substituted 1-benzyl-1-pyrrolinium perchlorates have uncovered novel, electron-transfer-induced photocyclization processes leading to benzopyrrolizidines and benzindolizidines.

Sir: Mechanistic pathways for electrophilic aromatic substitution activated by single electron transfer (SET) are less common than their two-electron-transfer counterparts.[1] Yet, processes involving generation and coupling of radical cation pairs (Scheme I) could serve as mechanistic models for the design of new reactions of this type, especially in the excited-state manifold where rates of SET can be fast.

In previous efforts probing arene–iminium salt photochemistry, we uncovered isolated examples of reactions of this type. Thus, the low-yielding formation of the arylpyrrolidines **3** by irradiation of the pyrrolinium salts **1** in the presence of toluene or benzene appeared to be a consequence of radical cation pair **2** coupling which weakly competes with cage collapse or cation radical deprotonation.[2] Formation of adducts **3** by this novel pathway occurs only in polar solvents (MeOH vs MeCN) and when alternate reactions of the cation radicals (e.g. R_3Si or R_3Sn group loss) are slow.[2,3]

Scheme I

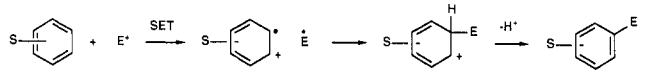
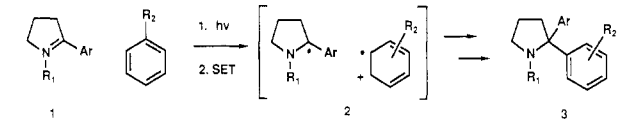


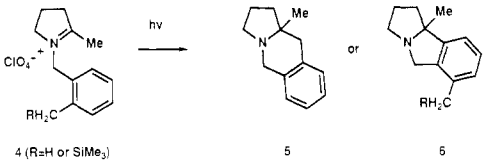
Table I. Photoproduct Distributions from Irradiation of *N*-Benzylpyrrolinium Salts

pyrrolinium salt	irradiation conditions	total yield, %	products (yield, %)
7	direct, MeCN	45	13 (11), 15 (34)
8	direct, MeCN	83	15 (21), 16 (62)
9	direct, MeCN	95	17
8	sensit., Me_2CO	97	16
9	sensit., Me_2CO	97	17
10	direct, MeCN	76	14 (18), 18 (58)
11	direct, MeCN	86	14 (19), 18 (38), 19 (29)
11	direct, MeOH	90	14 (32), 18 (55), 19 (3)
12	direct, MeCN	81	18 (13), 20 (68)
10	sensit., Me_2CO	85	14 (27), 18 (58)
11	sensit., Me_2CO	95	14 (32), 18 (42), 19 (21)
12	sensit., Me_2CO	97	20
21	direct, MeCN	99	25
22	direct, MeCN	99	24 (72), 25 (6), 26 (21)
22	direct, MeOH	99	24 (48), 25 (48), 26 (3)
23	direct, MeCN	90	25 (4), 27 (86)
23	direct, MeOH	90	25 (11), 27 (79)
21	sensit., Me_2CO	99	25
22	sensit., Me_2CO	95	24 (79), 25 (3), 26 (13)
23	sensit., Me_2CO	95	27



1 2 3

The relative rates of electrofugal group loss and radical coupling play a role in intramolecular arene–iminium salt systems. An isolated, yet instructive, example is found in the report that the *N*-xylylpyrrolinium salts **4** photocyclize to produce either the pyrrolizidines **5** or indolizidine **6** depending upon whether or not they contain TMS substitution at the benzylic position.[3,4]



4 (R=H or $SiMe_3$) 5 6

The major purpose of the current study is to explore more fully SET-induced photocyclization reactions related to those shown above. Our aim is to develop a clear understanding of the factors (e.g. excited-state multiplicity, solvent, nature, and location of substituents and nature of electrofugal groups) which influence competition between diradical and cation diradical cyclization modes. Information gained about cyclization regiochemistry and efficiency would also have synthetic implications.[5] For

(1) (a) Cf. Eberson, L.; Radner, F. *Acc. Chem. Res.* **1987**, *26*, 53. (b) Sankararaman, S.; Haney, W. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5235 and references therein.

(2) Borg, R. M.; Heuckeroth, R. O.; Lan, A. J. Y.; Quillen, S. L.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 2728.

(3) Lan, A. J. Y.; Heucheroth, R. O.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 2738.

(4) (a) Competitive diradical and diradical cation cyclization pathways have been detected in allylsilane–iminium salt photocyclizations. (b) Tu, C.-L.; Mariano, P. S. *J. Am. Chem. Soc.* **1987**, *109*, 5287.

0022-3263/88/1953-1590$01.50/0