a mixture of THF-CH_3CN-H_2O for 3 days in the presence of catalytic amounts of *p*-toluenesulfonic acid. TLC analysis of the reaction mixture showed the expected presence of all four possible trans products resulting from addition to the asymmetric double bond of **11**. The total yield was 74%, with the more polar pair of diastereoisomers (**13a,b**) predominating [R_f 0.32 and 0.46 in ethyl acetate–hexane (3:2)]. This pair of isomers and the less polar pair were separated and resolved into their components by either preparative TLC or high-performance LC. The yields of the diastereoisomers comprising the more polar pair were 29% and 18%, respectively. At this point, the structural differentiation between the two possible regioisomeric sets **13** and **14** was impossible to make. Only after the elimination reaction were we able to assign structures unambiguously as a result of the different positions of the double bonds. It was fortunate that the addition of the ArSeX reagent showed some degree of regioselectivity since the major pair of adducts corresponded to the desired diastereoisomers **13a** and **13b**.[13] Oxidation of **13a** and **13b** with *m*-CPBA at room temperature for 15 min followed by refluxing in $CHCl_3$ (2 h) in the presence of Et_2NH afforded **15a** and **15b**, respectively. Compounds **15a** and **15b** have very similar NMR spectra which conclusively support the assigned structures. Compound **15a** was obtained as a foam: mp 74–80 °C;[12] $[\alpha]^{23}_D$ +17.5° (*c* 0.1, $CHCl_3$); NMR (acetone-d_6) δ 3.00 (br s, 1, OH, D_2O exchanged), 3.25 (m, 2, $NHCH_2CHOH$), 4.00 (m, 1, $NHCH_2CHOH$), 4.75 (m, 3, H-4′, H-5′, H-5′a), 4.98 (dd, 1, $CHOHCH{=}CHN$, J = 10, J' = 5 Hz), 5.86 (m, 2, H-2′, H-3′), 6.12 (d, 1, H-1′, J = 6 Hz), 6.30 (d, 1, $CHOHCH{=}CHN$, J = 10 Hz), 6.70 (br t, 1, $NHCH_2$, J = 5 Hz, D_2O exchanged), 7.20–7.60 (m, 9, aryl), 7.80–8.20 (m, 6, aryl). Compound **15b** was also obtained as a foam: mp 77–82 °C;[12] $[\alpha]^{23}_D$ −71.5° (*c* 0.1, $CHCl_3$); NMR (acetone-d_6) δ 3.10 (br s, 1, OH, D_2O exchanged), 3.30 (m, 2, $NHCH_2CHOH$), 4.20 (m, 1, $NHCH_2CHOH$), 4.80 (m, 3, H-4′, H-5′, H-5′a), 5.00 (dd, 1, $CHOHCH{=}CHN$, J = 10, J' = 2 Hz), 5.90 (m, 2, H-2′, H-3′), 6.20 (d, 1, H-1′, J = 6 Hz), 6.30 (d, 1, $CHOHCH{=}CHN$, J = 10 Hz), 6.80 (br t, 1, $NHCH_2$, J = 5 Hz, D_2O exchanged), 7.20–7.70 (m, 9, aryl), 7.80–8.20 (m, 6, aryl). The well-resolved, first-order nature of these spectra in the downfield region from δ 5 to 7 confirmed the assignment of the structures for this pair of diastereoisomers. In addition, after D_2O exchange, the CH_2 signal of the C-4 carbon of the aglycon was greatly simplified whereas the vinyl hydrogen at C-7 remained unchanged. Decoupling experiments likewise corroborated the assignment. These two diastereoisomers differ only in the absolute configuration of the hydroxyl group at C-5 as evidenced from their different specific rotations and coupling constants ($J'_{5,6}$) in the NMR. Oxidation and thermal elimination of ArSeOH performed on the other diastereoisomeric pair (**14a** and **14b**) gave the expected products (**16a** and **16b**) which showed NMR spectra consistent with the different location of the double bond. Again both spectra were nearly identical and data from only one of the diastereoisomers is given: NMR ($CDCl_3$) δ 2.50 (br s, 1, OH), 3.20–3.40 (m, 2, CH_2N), 4.10 (m, 1, CHOH), 4.60 (m, 3, H-4′, H-5′, H-5′a), 4.90 (dd, 1, $HNCH{=}CHCHOH$, J = 10, J' = 5 Hz), 5.85 (m, 3, $HNCH{=}CHCHOH$, H-2′, H-3′), 6.80 (d, 1, $NHCH{=}$, J = 8 Hz, D_2O exchanged), 7.20–7.50 (m, 9, aryl), 7.70–8.10 (m, 6, aryl). An important difference between the two sets of regioisomers (**15a,b** vs. **16a,b**) is the chemical shift observed for the vinyl hydrogen adjacent to the heterocyclic nitrogen. In diastereoisomers **15a** and **15b**, this signal is significantly lower, absorbing at δ 6.30. This observation can be explained in terms of the magnetic anisotropic effect resulting from the close proximity of the vinyl hydrogen to the furanose ring oxygen in the expected most stable anti configuration of these nucleosides.[14] The corresponding signal in **16a** and **16b** appears at δ 5.85 which compares very well with the resonance of the equivalent proton in the aglycon **8** at δ 5.82.

Deprotection of nucleosides **15a** and **15b** by the standard procedure in methanol saturated with ammonia afforded the corresponding target compounds **4a** and **4b** in ca. 80% yield. Compound **4a** was obtained as a lyophilized powder: mp 75–78 °C;[12] IR (KBr) 1660 cm^{-1}; $[\alpha]^{23}_D$ +62° (*c* 0.1, MeOH); NMR (CD_3OD–D_2O) δ 5.13 (dd, 1, J = 10, J' = 4 Hz), 5.48 (m, 6-Hz wide, 1, H-1′), 6.25 (d, 1, J = 10 Hz); M^+· 620 (penta-Me_3Si derivative). Compound **4b** was also obtained as a lyophilized powder: mp 66–69 °C;[12] IR (KBr) 1660 cm^{-1}; $[\alpha]^{23}_D$ −28.5° (*c* 0.1, MeOH); NMR (CD_3OD–D_2O) δ 5.12 (dd, 1, J = 10, J' = 1 Hz), 5.52 (d, 1, H-1′, J = 6 Hz), 6.20 (d, 1, J = 10 Hz); mass spectrum, *m/e* 620 (M^+·, penta-Me_3Si derivative).

Compound **11** was deblocked in the same manner as **15a** and **15b** to afford the free nucleoside **12**. Preliminary biological testing indicated that all three compounds (**4a**, **4b**, and **12**) were more potent than THU (**1**) as cytidine deaminase inhibitors. A detailed discussion of their activity will be reported elsewhere.

Registry No. **4** (isomer 1), 75430-93-2; **4** (isomer 2), 75421-07-7; **5**, 72331-40-9; **6**, 71098-88-9; **7**, 75421-08-8; **8**, 75421-09-9; **10**, 22860-91-9; **11**, 75421-10-2; **12**, 75421-11-3; **13** (isomer 1), 75421-12-4; **13** (isomer 2), 75444-05-2; **14** (isomer 1), 75421-13-5; **14** (isomer 2), 75444-06-3; **15** (isomer 1), 75421-14-6; **15** (isomer 2), 75421-15-7; **16** (isomer 1), 75421-16-8; **16** (isomer 2), 75421-17-9.

(13) This favorable regioselectivity is perhaps related to a preferential attack by water on the initially formed episelenonium intermediate from the least hindered and most hydrophilic side of the molecule.

(14) Zemlicka, J.; Horwitz, J. P. *J. Am. Chem. Soc.* 1975, *97*, 4089.

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Selenium-Stabilized Carbanions.[1] Acidity of Allyl and Vinyl Sulfides and Selenides

Summary: The rates of deprotonation of vinyl and allyl aryl sulfides with amide bases show that allyl sulfides are kinetically more acidic than allyl selenides, whereas vinyl sulfides are less acidic than vinyl selenides.

Sir: The scattered information available on the acidifying effect of phenylthio and phenylseleno substituents on α-hydrogens indicates that sulfur stabilizes carbanions slightly more effectively than does selenium.[2] In contrast, molecular orbital calculations have predicted that $HSeCH_2^-$ should be approximately 4 kcal/mol more stable than

(1) For previous papers see: (a) H. J. Reich, F. Chow, and S. K. Shah, *J. Am. Chem. Soc.*, **101**, 6638 (1979); (b) H. J. Reich, S. K. Shah, and F. Chow, *ibid.*, **101**, 6648 (1979); (c) H. J. Reich, *J. Org. Chem.*, **40**, 2570 (1975).

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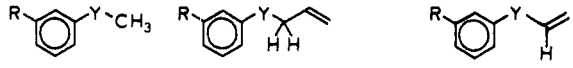
Table I. Substituent Effects in the Formation of α-Lithio Methyl, Allyl, and Vinyl Sulfides and Selenides



1 2 3

	1	2	3	
base	LiTMP	LDA	LiTMP	LDA
temp, °C	−56	−78	−78	−78
$k_{S/Se}$[a] (R = H)		7.5	0.37	0.21[b]
(R = CF_3)	3.8[c]		0.42	0.3[b]
$k_{CF_3/H}$[a] (Y = S)	22.4[c]		16.7	92[b]
(Y = Se)		11.7	14.9	64[b]

[a] Relative rates of deprotonation: $k_{RH}/k_{R'H}$ = log M_{RH}/log $M_{R'H}$, where M_{RH} and $M_{R'H}$ are the mole fractions of components RH and R'H remaining when the reaction was quenched. [b] Equilibrium constants $K_{S/Se}$ and $K_{CF_3/H}$, where K = [R'H][RLi]/[RH][R'Li]. [c] Reference 1a.

$HSCH_2^-$ relative to the protonated forms.[3] We report here on additional systems in which the phenylthio compound is more easily deprotonated and the first examples where the phenylseleno compound is more acidic under both kinetic and thermodynamic conditions.

In the course of our exploratory studies on the preparation of a variety of selenium-stabilized carbanions,[1] we have measured several relative kinetic and thermodynamic acidities under typical synthetic conditions: lithium diisopropylamide (LDA) or lithium 2,2,6,6-tetramethylpiperidide (LTMP) in THF–hexane. Our studies were carried out by treating a mixture of two compounds at low temperature with a deficiency of amide base, followed by derivatization using methyl iodide or trimethylchlorosilane. Control experiments showed that proton transfer between lithium reagents did not occur for the aryl methyl (LTMP),[1a] aryl allyl (LDA), and aryl vinyl (LTMP) selenides and sulfides, but equilibration did take place when the vinyl derivatives were deprotonated with LDA. In each case, derivatization was faster than deprotonation or equilibration. It seems likely that the mechanism of the equilibration involves reversible proton transfer between the vinyllithium reagents and diisopropylamine rather than between the two lithium reagents, since equilibration was very slow when the more basic and hindered LTMP was used. The achievement of equilibrium was confirmed by approach from both sides.

The rate of deprotonation of the vinyl sulfides[4] and selenides[5] with LDA was strongly depressed by the presence of excess amine. Thus phenyl vinyl sulfide is half deprotonated in 10 min at −78 °C, while after 75 min, the reaction has proceeded only to ~60%. It is reasonable to postulate that a 1:1 complex between LDA and diisopropylamine is a much weaker base than LDA itself. These observations can be put to synthetic use: when phenyl vinyl sulfide or selenide and a *catalytic* amount of diisopropylamine is treated with 1 equiv of *n*-butyllithium, the deprotonation is rapid and complete in a few minutes.[6] With 1.3 equiv of LDA in THF, phenyl vinyl selenide is deprotonated to the extent of 80–95% in 3 h.

The substituent effects we have measured are summarized in Table I. As in the other published S/Se comparisons, the sulfur derivative was more rapidly deprotonated for $ArYCH_3$[1a] and $PhYCH_2CH{=}CH_2$.[1c] *For the vinyl sulfides and selenides, however, the selenium compound is more acidic.* This was the case for the kinetic acidities with LTMP, as well as for the equilibrium constants measured with LDA.

Several factors which enter into the relative stabilization of negative charge by sulfur and selenium are as follows: (1) selenium is a larger and more polarizable atom and thus disperses charge more effectively; (2) sulfur is more electronegative and hence better stabilizes charge by an inductive effect; (3) conjugative interactions (either with the Y–Ph antibonding orbital or with d orbitals) should be more favorable for sulfur. The only other reported case in addition to the vinyl system in which a selenium compound is more acidic than the sulfur analogue is that of selenophene and thiophene (isotopic exchange α to sulfur and selenium in Me_2SO/KO-*t*-Bu, k_S/k_{Se} = 0.67[7]), for which the carbanionic center is also in an orbital with approximately sp^2 hybridization. These are exactly the types of carbanions that should be best stabilized by the greater inductive effect[8] of sulfur, yet the selenium compounds are slightly more acidic. A possible explanation for these results is that conjugative interactions control the delicate balance between sulfur and selenium. The systems for which the negative charge is in an orbital having high p character (e.g., allyl, propargyl,[2b] allenyl,[2b] and phenacyl[2c]) can be well stabilized by conjugative interactions with the heteroatom, and hence the sulfur compounds are more acidic.[9] For these systems where the situation is not favorable for conjugation (e.g., vinyl, thiophene, and selenophene), the greater polarizability of selenium dominates. It would be desirable to make the sulfur/selenium comparison in other systems where well-defined geometric constraints enforce a pyramidal geometry of the carbanion to determine if the trends we have detected here are general.

Theoretical studies have consistently ruled out any *major* d orbital stabilization of a lone pair on carbon by second-row elements.[3,10] The extensive pK_a measurements by Bordwell and co-workers, however, have provided ex-

(2) (a) Isotopic exchange of $PhYCH_3$ (in KNH_2/NH_3), $k_{S/Se}$ = 10 [A. I. Shatenshtein and H. A. Gvozdeva, *Tetrahedron*, **25**, 2749 (1969)]. (b) Base-catalyzed isomerization of $PhYCH_2C{\equiv}CH$ to $PhYCH{=}C{=}CH_2$ (NaOEt/EtOH), $k_{S/Se}$ = 6.14, and $PhYCH{=}C{=}CH_2$ to $PhYC{\equiv}CCH_3$, $k_{S/Se}$ = 4.8 [G. Pourcelot and C. Georgoulis, *Bull. Soc. Chim. Fr.*, 866 (1964); G. Pourcelot and J.-M. Cense, *ibid.*, 1578 (1976)]. (c) Acidity of $PhCOCH_2YPh(Me_2SO)$, $K_{S/Se}$ = 32 [F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. E. Drucker, J. Gerhold, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, *J. Org. Chem.*, **42**, 326 (1977)]. (d) Relative acidity of $(PhY)_2CH_2$ (RLi/THF), $\Delta pK_a \approx 2$ [D. Seebach and N. Peleties, *Angew. Chem.*, **81**, 465 (1969); *Chem. Ber.*, **105**, 511 (1972)].

(3) J.-M. Lehn, G. Wipff, and J. Demuynck, *Helv. Chim. Acta*, **60**, 1239 (1977).

(4) Phenyl vinyl sulfide has been deprotonated with LDA/THF/HMPA [R. C. Cookson and P. J. Parsons, *J. Chem. Soc., Chem. Commun.*, 990 (1976); B. Harirchian and P. Magnus, *ibid.*, 522 (1977)].

(5) Phenyl vinyl selenide has been deprotonated with LDA/THF [S. K. Shah, Ph.D. Thesis, University of Wisconsin—Madison, 1977; H. J. Reich in "21st Annual Report on Research Under Sponsorship of the Petroleum Research Fund", American Chemical Society, Washington, D.C., 1977] with LDA/HMPA/THF [M. Sevrin, J. Denis, and A. Krief, *Angew. Chem.*, **90**, 550 (1978)], and with $KN(i\text{-}Pr)_2$ [S. Raucher and G. A. Koolpe, *J. Org. Chem.*, **43**, 3794 (1978)].

(6) *n*-Butyllithium is not a satisfactory base for the high-yield deprotonation of phenyl vinyl sulfide and selenide since considerable addition to the double bond occurs.

(7) A. I. Shatenshtein, N. N. Magdesieva, Y. I. Ranneva, I. O. Shapiro, and A. I. Serebryanskaya, *Teor. Eksp. Khim.*, **3**, 343 (1967); *Chem. Abstr.*, **68**, 58799 (1968).

(8) Fluorine substituents dramatically stabilize pyramidal carbanions but may actually destabilize planar anions: A. Streitwieser, Jr., and F. Mares, *J. Am. Chem. Soc.*, **90**, 2444 (1968).

(9) The wide range of solvents used for these studies (THF, EtOH, Me_2SO, NH_3) indicates that the nature of the solvent does not have a dramatic effect on the relative acidity of sulfides and selenides.

(10) A. Streitwieser, Jr., and J. E. Williams, Jr., *J. Am. Chem. Soc.*, **97**, 191 (1975); F. Bernardi, I. G. Csizmadia, A. Mangini, H. B. Schlegel, M.-H. Whangbo, and S. Wolfe, *ibid.*, **97**, 2209 (1975); J.-M. Lehn and G. Wipff, *ibid.*, **98**, 7498 (1976); W. T. Borden, E. R. Davidson, N. H. Anderson, A. D. Denniston, and N. D. Epiotis, *ibid.*, **100**, 1604 (1978).

amples of strikingly similar structural effects between classically conjugating groups such as carbonyl or phenyl and various sulfur functionalities.[1c,11] The data in Table I on the *m*-trifluoromethyl substituent effects also indicate efficient transmission of negative charge by sulfur and selenium. The two point Hammet ρ values ($\sigma_{m\text{-}CF_3} = 0.43$) are 3.14 (kinetic) for $ArSCH_3$,[1a] 2.48 (kinetic) for ArSe–allyl, 2.83 (kinetic) and 4.75 (thermodynamic) for ArS–vinyl, and 2.73 (kinetic) and 4.20 (thermodynamic) for ArSe–vinyl. These values are quite comparable to those for kinetic acidities (ρ = 1.2–4[12]) in systems where the carbanion formed is directly conjugated with the aryl ring. They are smaller than the equilibrium ρ value of 7.4 estimated by Bordwell and co-workers[13] for toluenes in the highly dissociating solvent Me_2SO. The high ρ values observed for our vinyl systems suggest that the transmission coefficient for S and Se may be considerably higher here than the value (0.4) found for acidities of $ArYCH_2CO_2H$.[14] It is interesting to note that the introduction of a CF_3 group five bonds away introduces in each case we have studied a much larger perturbation than exchange of directly bonded sulfur by selenium.

The present results are limited by two factors: lithium reagents are being compared under conditions that do not promote ion pair separation, and kinetic acidities are used as a probe of carbanion stability. However, these approximate techniques are still the only ones that can be used for systems which are weakly acidic and for which the carbanions have limited stability.

Acknowledgment. We thank Dr. S. K. Shah and P. D. Clark for carrying out exploratory experiments on the deprotonation of vinyl selenides and the National Science Foundation and the National Institutes of Health for financial support.

Registry No. Phenyl allyl sulfide, 5296-64-0; phenyl allyl selenide, 14370-82-2; phenyl vinyl sulfide, 1822-73-7; *m*-(trifluoromethyl)-phenyl vinyl sulfide, 75599-82-5; phenyl vinyl selenide, 35167-28-3; *m*-(trifluoromethyl)phenyl vinyl selenide, 75599-83-6.

(11) F. G. Bordwell, J. E. Bares, J. E. Bartmess, G. J. McCollum, M. Van Der Puy, N. R. Vanier, and W. S. Matthews, *J. Org. Chem.*, **42**, 321 (1977).

(12) (a) Isotopic exchange of toluenes (lithium cyclohexylamide in cyclohexylamine), ρ = 4.0 [A. Streitwieser and H. F. Koch, *J. Am. Chem. Soc.*, **86**, 404 (1964)]. (b) Rate of deprotonation of diphenylaryl methanes (PhLi, THF), ρ = 2.2 [P. West, R. Waack and J. I. Purmort, *J. Organomet. Chem.*, **19**, 267 (1969)]. (c) Rate of deprotonation of 1-arylpropynes (*n*-BuLi/Et_2O), ρ = 1.3 [J. Y. Becker, *ibid.*, **118**, 247 (1976)].

(13) F. G. Bordwell, D. Algrim, and N. R. Vanier, *J. Org. Chem.*, **42**, 1817 (1977); D. Algrim, J. E. Bares, J. C. Branca, and F. G. Bordwell, *ibid.*, **43**, 5024 (1978). Note that acetophenones show a ρ of 3.55 in Me_2SO: F. G. Bordwell and F. J. Cornforth, *ibid.*, **43**, 1763 (1978).

(14) O. Exner in "Advances in Linear Free Energy Relationships", N. B. Chapman and J. Shorter, Eds., Plenum Press, New York, 1972, p 25.

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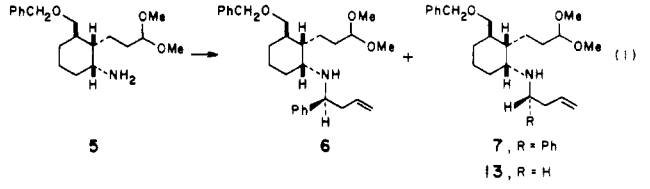
A New Method for Stereoselective Piperidine Annulation. Directing the 2-Azonia-[3,3]-Sigmatropic Rearrangement by Irreversible Hydrolysis[1]

Summary: A new method for stereoselective piperidine annulation is described involving the cyclization and subsequent [3,3]-sigmatropic rearrangement of (5,5-dimethoxypentyl)-3-butenylamines.

Sir: New strategies for forming carbon–carbon bonds under mild conditions, which exploit the facile 2-azonia-[3,3]-sigmatropic rearrangement (e.g., **2** ⇄ **3**), have been described recently from this laboratory.[1-3] One of our central objectives in this area is the development of new procedures for "directing" the 2-azonia-[3,3]-sigmatropic rearrangement such that it is irreversible (e.g., **2** → **3**) in the desired direction. A possible method for achieving this control is outlined in Scheme I. The basic strategy is to conduct the iminium ion rearrangement in the presence of sufficient H_2O such that the amine salts, rather than the iminium ions, are the major components of the mixture and to design the system such that hydrolysis of the starting iminium ion **2** is more readily reversible (via intramolecularity) than that of the desired product iminium ion **3**.[4] In this communication we demonstrate the viability of this strategy and illustrate its preparative value for stereoselective piperidine annulation.

The reaction was first explored with phenylbutenylamines **6**[5] and **7**, which were prepared in a 2:1 ratio and 65% yield by sequential treatment of primary amine **5**[1] with benzaldehyde and allylmagnesium bromide, followed by chromatographic separation on silica gel (eq 1). When



a benzene solution (0.02 M) of the major amine acetal **6** was heated at reflux for 12 h in the presence of 0.95 equiv of *d*-10-camphorsulfonic acid monohydrate and ~3 equiv of H_2O, and the reaction was quenched at 5 °C with $NaBH_4$ and methanol, the 2-allyl-*cis*-decahydroquinolines **8** and **9** were formed in a ratio of 20:1[6] (crude yield ~65%) together with small amounts of unrearranged materials[7]

(1) Part 4 in the series "Synthesis Applications of Directed 2-Azonia-[3,3]-Sigmatropic Rearrangements". For Part 3 see: Overman, L. E.; Fukaya, C. *J. Am. Chem. Soc.* **1980**, *102*, 1454.

(2) Overman, L. E.; Kakimoto, M. *J. Am. Chem. Soc.* **1979**, *101*, 1310. Overman, L. E.; Kakimoto, M.; Okawara, M. *Tetrahedron Lett.* **1979**, 4041.

(3) For a recent review of [3,3]-sigmatropic rearrangements of iminium ions see: Heimgartner, H.; Hansen, H.-J.; Schmid, H. In "Iminium Salts in Organic Chemistry", Part 2; Böhme, H., Viehe, H. G., Eds.; Wiley: New York, 1979; pp 655–732.

(4) That such an approach would be possible was apparent in the original report by Geissman of the 2-azonia-[3,3]-sigmatropic rearrangement: Horowitz, R. M.; Geissman, T. A. *J. Am. Chem. Soc.* **1950**, *72*, 1518.

(5) **6**: IR (film) 3400, 1670, 1425, 1120, 990, 910 cm^{-1}; ^1H NMR (60 MHz, $CDCl_3$) δ 7.3 (apparent s, Ph), 7.27 (apparent s, Ph), 6.0–5.4 (m, CH_2=CH), 5.4–4.8 (m, CH_2=CH), 4.5–4.3 (m, $CH(OR)_2$), 4.35 (s, $PhCH_2O$), 3.65 t, J = 6 Hz, PhCHN), 3.35 (s, OCH_3), 3.27 (d, J = 7 Hz, CH_2O), 2.5–2.8 (m, CHN), 2.37 (apparent t, J = 7 Hz, CH_2CH=CH_2); ^{13}C NMR (23 MHz, $CDCl_3$) 145.2, 138.9, 135.9, 128.3, 128.2, 127.5, 127.2, 126.9, 117.3, 105.0, 73.7, 73.1, 58.9, 52.6, 50.3, 43.6, 42.7, 37.1, 30.2, 29.0, 27.8, 22.8, 19.9; mass spectrum, m/z (isobutane CI, relative %) 452 (33), 420 (100), 378 (15), 131 (11), 91 (23). **8**: IR (film) 1645, 1455, 995, 915 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 7.1–7.5 (m, Ph), 5.60–5.82 (m, CH=CH_2), 5.08 (d, J = 17.3 Hz, (Z) =CH_2), 5.05 (d, J = 9.9 Hz, (E) =CH_2), 4.50 (AB q, $\Delta\nu_{AB}$ = 18.9 Hz, J_{AB} = 12.1 Hz, $PhCH_2O$), 3.47 (d, J = 7.0 Hz, CH_2O), 3.02 (m, $w_{h/2}$ = 17 Hz, CHN), 2.82 (m, $w_{h/2}$ = 20 Hz, CHN); ^{13}C NMR (63 MHz, $CDCl_3$) δ 138.6 (s, ipso Ph), 135.8 (d, CH=CH_2), 128.3 (d, *o*-Ph), 127.6 (d, *m*-Ph), 127.4 (d, *p*-Ph), 117.0 (t, CH=CH_2), 73.1 (t, OCH_2Ph), 72.6 (t, CH_2O), 51.0 (d, C-2), 49.1 (d, C-8a), 41.1 (t, CH_2CH=), 39.1 (d, C-4a), 37.1 (d, C-5), 31.8 (t), 27.8 (t), 25.4 (t), 23.6 (t), 21.1 (t); mass spectrum, m/z (isobutane CI, relative %) 300 (100), 258 (49), 107 (20), 91 (25).

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