δ 1.9 (s) and 2.1 (s)[11] (3H), 3.8 (s) and 3.9 (s)[11] (3H), 7.2-7.8 (m, 11 H); MS m/z (relative intensity) 315 (M^+, 66), 273 (100), 257 (26), 241 (19), 228 (22). The crude product was dissolved in 50 mL of THF to which was added 0.1 mL (6 mmol) of H_2O and 0.93 g (8.3 mmol) of potassium *tert*-butoxide, the mixture was refluxed for 24 h, and an additional 0.3 g (2.7 mmol) of potassium *tert*-butoxide was added followed by refluxing for 48 h. The THF was evaporated under vacuum and the residue taken up in 50 mL of methylene chloride and 50 mL of H_2O. The layers were separated, and the organic layer was dried over anhydrous sodium sulfate and the methylene chloride evaporated under vacuum. Column chromatography of the residue using carbon tetrachloride on 15 g of silica gel gave 0.35 g of 11 (1.3 mmol, 39% from 8): mp 157-159 °C (heptane); ^1H NMR ($CDCl_3$, 300 MHz) δ 3.78 (s, 3 H), 5.12 (s, 1 H), 6.87 (d, J = 8.4 Hz, 1 H), 6.94 (d, J = 7.5, 1 H), 7.00 (d, J = 8.4 Hz, 1 H), 7.0-7.3 (m, 5 H), 7.38 (dd, J = 8.4 Hz, 1 H), 7.53 (d, J = 8.4 Hz, 1 H), 7.65 (d, J = 7.5 Hz, 1 H); ^{13}C NMR ($CDCl_3$, 75 MHz) 55.95, 110.69, 119.36, 120.19, 122.58, 123.09, 123.83, 127.53, 127.74, 128.01, 128.38, 129.99, 132.32, 133.39, 141.44, 151.45, 151.70, 156.23; MS m/z (relative intensity), 273 (M^+, 100), 258 (12), 257 (14), 230 (9) 228 (8), 202 (5). Anal. Calcd for $C_{19}H_{15}NO$: C, 83.49; H, 5.53; N, 5.12; O 5.85. Found: C, 83.61; H, 5.87; N, 5.04; O, 5.39.

Preparation of 9*H*-Tribenz[*b*,*d*,*f*]azepine (2) from Reaction of 5-Acetyl-10-bromo-5*H*-dibenz[*b*,*f*]azepine (6) with Potassium *tert*-Butoxide and 1,3-Cyclohexadiene (12) Followed by Hydrolysis with Potassium *tert*-Butoxide and Water. 5-Acetyl-10-bromo-5*H*-dibenz[*b*,*f*]azepine (6; 3.0 g, 9.5 mmol) and 1.47 g (13 mmol) of potassium *tert*-butoxide were placed in 24 mL of 1,4-cyclohexadiene (12), and the mixture was refluxed for 21 h. The cyclohexadiene was distilled from the reaction mixture. The residue was dissolved in 20 mL of 2-methoxyethyl ether (diglyme), 2.4 g (21 mmol) of potassium *tert*-butoxide was added, and the mixture was refluxed for 18 h.[12] Water (50 mL) was added to the reaction mixture, and the mixture cooled in an ice bath to yield one large piece of black solid. The black solid was dissolved in methylene chloride, the solution dried over anhydrous sodium sulfate, and the solvent was removed under vacuum. Column chromatography of the residue using toluene on 40 g of silica gel yielded 0.89 g (3.6 mmol, 39% from 6) of 9*H*-tribenz[*b*,*d*,*f*]azepine (2): mp 220 °C (ethanol); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.29 (s, 1 H), 6.89 (d, J = 7.6 Hz, 2 H), 7.12 (dd, 2 H), 7.22 (dd, 2 H), 7.4-7.8 (m, 6 H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 119.71, 124.09, 127.72, 128.43, 130.08, 130.15, 132.68, 139.34, 150.99; MS m/z (relative mass), 243 (M^+, 100), 215 (11), 202 (3), 189 (3), 120 (9). Anal. Calcd for $C_{18}H_{13}N$: C, 88.85; H, 5.38; N, 5.75. Found: C, 88.94; H, 5.48; N, 5.53.

If the hydrolysis was performed in refluxing THF (in place of diglyme), a mixture of 14 and 2 was obtained. No attempts were made to maximize the yield of 14. Column chromatography of this mixture using toluene on silica gel resulted in partial separation. 14: mp 158 °C from ethanol (decomposes with bubbling to 2 as evidenced by ^1H and ^{13}C NMR of decomposition product); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.65 (m, 4 H), 4.08 (s, 2 H), 4.99 (s, 1 H), 6.54 (dd, 2 H), 6.69 (d, 2 H), 7.01 (dd, 2 H), 7.08 (dd, 2 H), 7.25 (d, 2 H); ^{13}C NMR ($CDCl_3$, 75 MHz) 25.95, 42.55, 119.80, 123.57, 126.47, 128.02, 131.74, 134.98, 142.42, 148.41; MS m/z (relative intensity), 243 (100), 215 (12), 202 (3), 189 (4), 120 (10). Anal. Calcd for $C_{20}H_{17}N$: C, 88.52; H, 6.31; N, 5.16. Found: C, 88.28; H, 6.58; N, 5.06.

(12) The mixture was refluxed in a vessel open to the atmosphere, and water for the hydrolysis is presumably absorbed from the atmosphere.

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Fluoride Ion Promoted Reactions of α-Halo Silanes: Synthesis of Stilbenes, Epoxides, Cyclopropanes, Benzazepines, and Phthalidylisoquinolines

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Reaction of α-halo silanes 1 with CsF in DMF affords stilbenes 5. In the presence of added aldehydes, epoxides 6 are obtained, while with electron-deficient olefins the corresponding cyclopropanes 7 are formed. A similar reaction of 1a with iminium compounds 8 in HMPA leads to 2-phenyl-3-benzazepines 12, whereas 1b or 17 furnishes phthalidylisoquinolines 15.

We have initiated studies on synthetic utilization of organosilanes having suitably placed electrofugic groups.[1] Reactions of such substrates with a negatively charged silaphile, like F^- or OR^-, can afford carbanion equivalents of reactive intermediates; e.g., carbenoids may be obtained from α-halo silanes. This approach is useful for halogenated and vinylcarbenes,[2] but with other precursors (1, $R^1 = R^2 \neq$ halogen or doubly bonded carbon) side reactions, shown in Scheme I, tend to ingress to a large extent.[3,4] In fact, our attempts to generate and trap phenylcarbenes in this manner were unsuccessful until it was found that dipolar aprotic solvents particularly favor the desired reaction course.[1] We now report these results in detail along with a significant extension wherein iminium compounds are used for capturing the reactive intermediates.

Results and Discussion

Reaction of 1a with CsF (1.5 mmol) in solvents like DME and THF led only to protodesilylation, but in DMF the *trans*-stilbene (5a) was formed in 89% yield. The product 5a can arise by dimerization of carbene 4a or through reaction of the anion 3a with the halide 1a as

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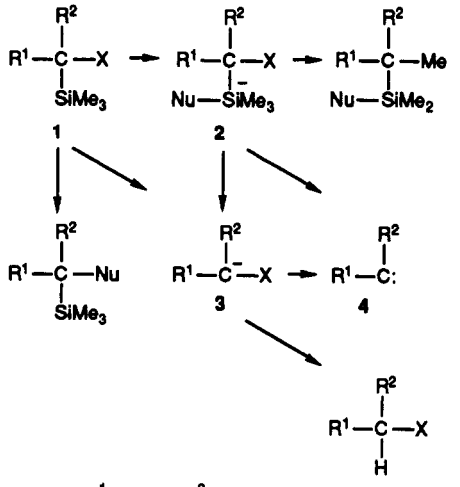
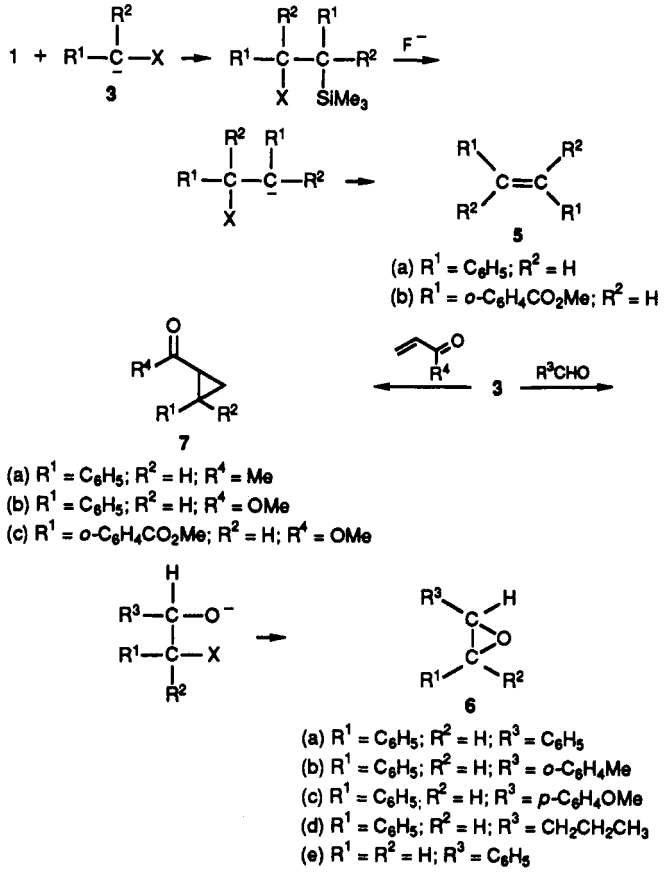
Scheme I



(a) $R^1 = C_6H_5$; R^2 = H; X = Br
(b) R^1 = o-$C_6H_4CO_2Me$; R^2 = H; X = Br
(c) $R^1 = R^2$ = H; X = Cl

Scheme II



(a) $R^1 = C_6H_5$; R^2 = H
(b) R^1 = o-$C_6H_4CO_2Me$; R^2 = H

(a) $R^1 = C_6H_5$; R^2 = H; R^4 = Me
(b) $R^1 = C_6H_5$; R^2 = H; R^4 = OMe
(c) R^1 = o-$C_6H_4CO_2Me$; R^2 = H; R^4 = OMe

(a) $R^1 = C_6H_5$; R^2 = H; $R^3 = C_6H_5$
(b) $R^1 = C_6H_5$; R^2 = H; R^3 = o-C_6H_4Me
(c) $R^1 = C_6H_5$; R^2 = H; R^3 = p-C_6H_4OMe
(d) $R^1 = C_6H_5$; R^2 = H; $R^3 = CH_2CH_2CH_3$
(e) $R^1 = R^2$ = H; $R^3 = C_6H_5$

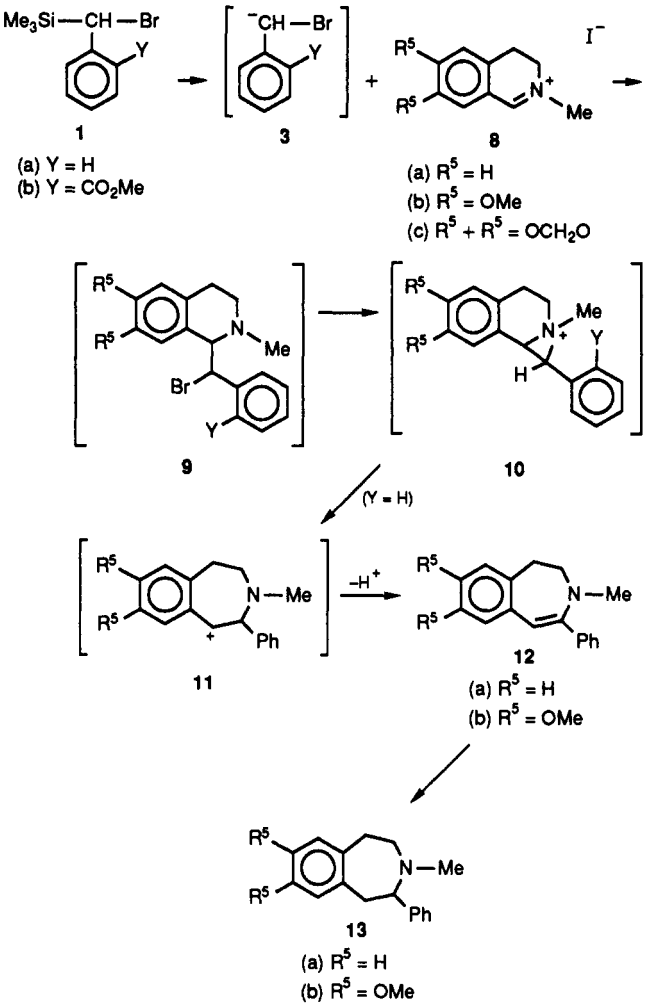
shown in Scheme II.[5] Reaction of **1b** with CsF afforded **5b** in 76% yield. On the basis of this result, stilbene formation by carbene dimerization can be discounted because if free carbene **4b** (R^1 = $OC_6H_4CO_2Me$; R^2 = H) was formed it would have been intramolecularly trapped by the o-carbomethoxy group.[6]

When reaction of **1a** with CsF was carried out in the presence of 1.5 equiv of benzaldehyde, a cis/trans mixture of epoxides **6a** was obtained in 87% yield.[7] Reaction of

Table I. Synthesis of Stilbenes 5, Epoxides 6, and Cyclopropanes 7

entry	reactant	addendum	product	isolated yield (%)
1	1a		5a	89 (trans only)
2	1b		5b	76 (trans only)
3	1a	C_6H_5CHO	6a	87 (50:50)[7]
4	1a	o-MeC_6H_4CHO	6b	55 (46:54)
5	1a	p-$MeOC_6H_4CHO$	6c	58 (50:50)
6	1a	$CH_3CH_2CH_2CHO$	6d	60 (37:63)
7	1c	C_6H_5CHO	6e	60
8	1a	CH_2=CHCOMe	7a	50
9	1a	CH_2=$CHCO_2Me$	7b	59 (27:73)
10	1b	CH_2=$CHCO_2Me$	7c	54 (42:58)

Scheme III



(a) Y = H
(b) Y = CO_2Me

(a) R^5 = H
(b) R^5 = OMe
(c) $R^5 + R^5 = OCH_2O$

(a) R^5 = H
(b) R^5 = OMe

(a) R^5 = H
(b) R^5 = OMe

1c with benzaldehyde afforded **6e** in 60% yield. Ketones like cyclohexanone and acetone reacted inefficiently (5–10% yield) with **1a** and **1c**. Addition of 1.5 equiv of methyl vinyl ketone or methyl acrylate to the reaction mixture gave cyclopropanes **7** in yields shown in Table I. These adducts can arise via carbene **4** or from **3** by tandem addition/cycloelimination. However, carbene intermediacy is disfavored by the formation of cyclopropane **7c** from the

(5) Although in the figures the reactions are shown with the anion **3**, they might as well emanate from its precursor pentavalent silyl intermediate **2**. (a) Majetich, G.; Casares, A.; Chapman, D.; Behnke, M. *J. Org. Chem.* **1986**, *51*, 1745. (b) Pernez, S.; Hamelin, J. *Tetrahedron Lett.* **1989**, *30*, 3419.

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(7) The cis/trans ratio in epoxides and cyclopropanes was estimated from the ^1H NMR of the mixtures on the basis that three-membered ring protons or CO_2Me protons cis to the adjoining phenyl group appear upfield: Imuta, M.; Ziffer, H. *J. Org. Chem.* **1979**, *44*, 2505. The cis/trans ratio in **7a** could not be determined due to overlap of relevant proton signals.

Table II. Synthesis of Benzazepines 12 and Phthalidylisoquinolines 15

entry	reactant	iminium compd	product	isolated yield (%)
1	1a	8a	12a	53
2	1a	8b	12b	47
3	1b	8a	15a	57 (14:43)[a]
4	1b	8b	15b	52 (12:40)
5	17a	8a	15a	66 (38:28)
6	17a	8b	15b	76 (39:37)
7	17b	8b	15c	76 (46:30)
8	17b	8c	15d	74 (41:33)

[a] Isolated yields of threo and erythro isomers, respectively.

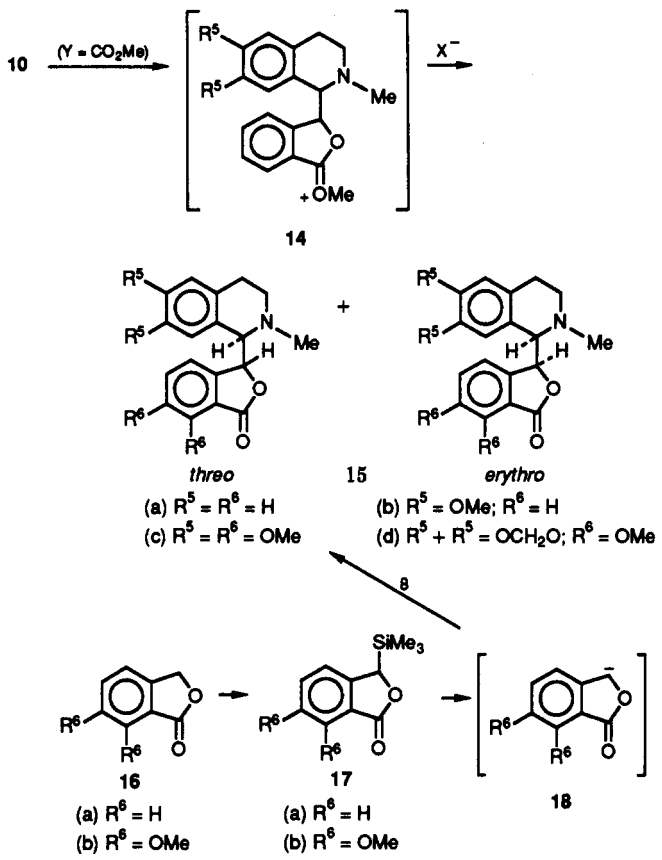
carbomethoxy-bearing substrate **1b**, in a yield comparable to that of **7b** from **1a**.[6]

Treatment of a mixture of silane **1a** and iminium compounds **8a** or **8b** with CsF in HMPA at 120 °C furnished benzazepines **12a** and **12b** in 53 and 47% yields, respectively. The benzazepine can be formed by addition of anion **3** to the iminium salts and subsequent ring closure to aziridinium intermediate **10** (Scheme III). The latter can then furnish **12** by ring opening and proton loss from the carbonium ion **11**. It is interesting to note that **10** can also ring open in an alternate sense to give 4,5-dihydro-1-phenyl-3-methyl-1*H*-3-benzazepine or 1-benzylidene-*N*-methyl-1,2,3,4-tetrahydroisoquinoline.[8] Since clear distinction between **12** and the latter compounds could not be made on the basis of NMR spectra, structures **12a** and **12b** for the isolated products were confirmed by reduction to tetrahydrobenzazepines **13a** and **13b**. The compound **13a** had been prepared earlier, and the mp of its hydrochloride corresponded with the reported value.[9] The structure of **13b** was confirmed from its mass spectrum, which was devoid of peaks at M − 91 and M − 57, expected from 1-benzyltetrahydroisoquinolines and tetrahydro-1-phenyl-3-benzazepines, respectively.[8] Furthermore, in conformity[8] with a tetrahydro-2-phenyl-3-benzazepine structure, a prominent fragment at M − 133 (45%) was observed. The present approach provides a useful access to 2-phenyl-3-benzazepines, which have considerable medicinal interest[10] and constitute the skeleton of the rhoeadine group of alkaloids.[11] It is especially significant because earlier attempts to procure 2-phenyl-3-benzazepines through reaction of **8** with phenylcarbenes generated from diazo precursors were unsuccessful.[12]

The reaction of *o*-carbomethoxy-substituted silane **1b** with iminium compounds **8a** or **8b** led to phthalidylisoquinolines **15a** and **15b**, respectively. These products were obtained as mixtures of threo and erythro isomers that could be readily separated by chromatography. This change of the reaction course can be rationalized in the following terms. The aziridine ring in the intermediate **10** is opened by attack of the carbomethoxy oxygen to give **14**, which evolves to the product **15** as shown in Scheme IV.

We have also explored the use of fluorodesilylation for coupling of 3,4-dihydroisoquinolinium salts with phthalides. Ever since the early work of Perkin and Robinson[13] on this short route to phthalidylisoquinoline alkaloids,[14]

Scheme IV



many modifications have been introduced to improve its efficiency.[15-19] Since its main drawback[15,17] is product instability under the strongly basic conditions used for deprotonation of **16**, silyl precursors **17** seemed attractive.

In the event, reaction of **17** with **8** proceeded smoothly, using 2 equiv of cesium fluoride in DMF solvent, to give the desired alkaloids (Table II). This approach is comparatively more efficient, e.g., earlier best procedures afforded **15b** and **15c** in 30 and 22% yields.[17]

The required silyl derivatives **17** can be obtained in nearly quantitative yields from phthalides **16** by treatment with LDA/THF followed by trimethylsilyl chloride. It is not necessary to isolate pure **17**, and the subsequent coupling reactions can be carried out with the crude silylation products. It is interesting to note that the anions derived from 3-arylphthalides are reported[20] to undergo O-silylation in contrast to the present case where only C-silylated products are formed.

Experimental Section

Instrumentation. All melting points were determined with a Thomas-Hoover capillary melting point apparatus and are

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uncorrected. Infrared spectra (IR) were recorded on a Perkin-Elmer 1420 grating spectrophotometer. The proton nuclear magnetic resonance spectra (^{1}H NMR) were measured with a Varian spectrometer, Model EM 390. In the NMR spectrum of cis/trans mixtures, the reference for integral ratios is δ 7.0–8.0 region signals representing the total number of aromatic protons present in the mixture. Mass spectra were determined with a VG micromass 70/70F instrument at 70 eV. Chromatographic separations were carried out on Harrison Research Chromatotron, Model 7924, using silica gel 60 PF 254. Liquid analytical samples were obtained by Kugelrohr distillation using a Buchi GKR-50 instrument.

General Chemicals and Inert Reaction Media. All solvents were distilled/dried prior to use by standard methods.[21] THF and DME were distilled from sodium benzophenone ketyl immediately prior to use. Diisopropylamine and trimethylsilyl chloride were freshly distilled from CaH_2. BuLi was prepared by known procedure.[22] CsF was dried in a reaction vessel by pumping it down to 1 Torr and waving over an open flame for 2 min. After the vessel was cooled, the lumps of CsF were finely powdered with use of a fire-polished glass rod. All solvent extracts were dried over Na_2SO_4. All preparations and reactions involving air- and moisture-sensitive orgaometallic intermediates or CsF were conducted under an atmosphere of dry, oxygen-free nitrogen.

Methyl 2-[Bromo(trimethylsilyl)methyl]benzoate (1b). A solution of methyl 2-[(trimethylsilyl)methyl]benzoate[23] (3 g, 13.5 mmol) in CCl_4 (25 mL) was refluxed (3 h) with NBS (2.4 g, 13.5 mmol) under illumination (60-W tungsten lamp). After being cooled, it was filtered and the solvent was evaporated in vacuo. The resultant liquid was purified by flash chromatography (mobile phase, petroleum ether) to yield **1b** as a colorless oil (3.86 g, 95%). ^{1}H NMR (CCl_4): δ 0.00 (s, 9 H, $SiMe_3$); 3.85 (s, 3 H, CO_2Me); 5.88 (s, 1 H, ArCH); 7.1–8.0 (m, 4 H, ArH). MS *m/e*: M^+ 300, 302 (1:1). Anal. Calcd for $C_{12}H_{17}BrO_2Si$: C, 47.84; H, 5.64. Found: C, 47.80; H, 5.64.

General Procedure for Fluorodesilylation. A. A solution of α-halosilane (1 mmol) and electrophile (1.5 mmol) in DMF (10 mL) was stirred (5 h) with anhydrous CsF (1.5 mmol) under nitrogen at room temperature. The reaction mixture was then poured into benzene (25 mL), washed with water (30 mL × 3), and dried. The solvent was distilled off and the residue chromatographed to get pure products.

B. A solution of α-halosilane (1 mmol) in HMPA (25 mL) containing the electrophile (1 mmol) and CsF (1.5 mmol) was stirred, under nitrogen, at 120 °C for 1.5 h. The cooled reaction mixture was worked up as in A.

Stilbene (5a): obtained from **1a**[24] in 89% yield by procedure A, mp 123–124 °C (lit.[25] mp 124 °C).

2,2′-Dicarbomethoxystilbene (5b): secured from **1b** in 76% yield by procedure A, mp 103–104 °C. ^{1}H NMR (CCl_4): δ 3.92 (s, 6 H, CO_2Me×2); 7.10–8.00 (m, 10 H, ArH and C=CH). MS *m/e*: M^+ 296. Anal. Calcd for $C_{18}H_{16}O_4$: C, 72.94; H, 5.40. Found: C, 72.96; H, 5.10.

Stilbene Oxide (6a).[7] Reaction of **1a** and benzaldehyde by procedure A furnished **6a** (87%). ^{1}H NMR ($CDCl_3$): δ 3.84 (s, 2 H, ArCH, trans); 4.34 (s, 2 H, ArCH, cis); 7.10–7.80 (m, 20 H, ArH). MS *m/e*: M^+ 196.

2-*o*-Tolyl-3-phenyloxirane (6b): obtained in 55% yield from **1a** and *o*-tolualdehyde by procedure A. ^{1}H NMR (CCl_4): δ 2.22 (d, 3.36 H, *J* = 3 Hz, Me, trans); 2.35 (s, 2.64 H, Me, cis); 3.02 (m, 2 H); 3.69 (d, 0.54 H, *J* = 1.5 Hz); 3.93 (d, 0.54 H, *J* = 1.5 Hz); 4.28 (s, 0.92 H). MS *m/e*: M^+ 210. Anal. Calcd for $C_{15}H_{14}O$: C, 85.71; H, 6.66. Found: C, 85.55; H, 6.68.

2-*p*-Anisyl-3-phenyloxirane (6c). Reaction of **1a** and *p*-anisaldehyde by procedure A afforded **6c** in 58% yield. ^{1}H NMR (CCl_4): δ 3.74 (s, 2 H, ArCH, trans); 3.92 (s, 6 H, OMe); 4.40 (s, 2 H, ArCH, cis); 7.05–7.60 (m, 18 H, ArH). MS *m/e*: M^+ 226. Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.64; H, 6.19. Found: C, 79.60; H, 6.15.

2-*n*-Propyl-3-phenyloxirane (6d): obtained in 60% yield from **1a** and *n*-butyraldehyde by procedure A. ^{1}H NMR (CCl_4): δ 0.73–1.71 (m, 14 H, propyl); 2.78 (m, 1.26 H, propyl-CH, trans); 3.1 (m, 0.74 H, propyl-CH, cis); 3.47 (d, 1.26 H, *J* = 3 Hz, ArCH, trans); 3.93 (d, 0.74 H, *J* = 6 Hz, ArCH, cis); 7.27 (m, 10 H, ArH). MS *m/e*: M^+ 162. Anal. Calcd for $C_{11}H_{14}O$: C, 81.48; H, 8.64. Found: C, 81.46; H, 8.63.

Styrene Oxide (6e). (Chloromethyl)trimethylsilane **1c** (122 mg, 1 mmol) and benzaldehyde (424 mg, 3 mmol) were stirred (4 h) in DMF (12 mL) at 80 °C under nitrogen in the presence of CsF (228 mg, 1.5 mmol). Usual workup afforded the styrene oxide (**6e**; 72 mg, 60%). ^{1}H NMR (CCl_4): δ 2.79 (dd, 2 H); 3.13 (dd, 2 H); 3.90 (dd, 2 H); 7.28 (m, 10 H, ArH).[26]

1-Phenyl-2-acetylcyclopropane (7a):[27] secured in 50% yield from **1a** and methyl vinyl ketone by procedure A. ^{1}H NMR (CCl_4): δ 1.03–2.73 (m, 14 H, cyclopropyl and methyl); 7.03–7.52 (m, 10 H, ArH). MS *m/e*: M^+ 160. Anal. Calcd for $C_{11}H_{12}O_2$: C, 82.50; H, 7.50. Found: C, 82.30; H, 7.50.

1-Phenyl-2-carbomethoxycyclopropane (7b):[28] obtained in 59% yield from **1a** and methyl acrylate by procedure A. ^{1}H NMR (CCl_4): δ 1.02–1.92 (m, 6 H, cyclopropyl); 2.22–2.53 (m, 2 H, ArCH); 3.50 (s, 1.62 H, CO_2Me, cis); 3.72 (s, 4.38 H, CO_2Me, trans); 7.12–7.82 (m, 10 H, ArH). MS *m/e*: M^+ 176. Anal. Calcd for $C_{11}H_{12}O_2$: C, 75.00; H, 6.81. Found: C, 74.80; H, 6.80.

1-(2′-Carbomethoxyphenyl)-2-carbomethoxycyclopropane (7c): obtained from **1b** and methyl acrylate in 54% yield by procedure A. ^{1}H NMR (CCl_4): δ 1.10–2.40 (m, 6 H, cyclopropyl); 2.74–3.24 (m, 2 H, ArCH); 3.35 (s, 2.52 H, cyclopropyl-CO_2Me, cis); 3.72 (s, 3.48 H, cyclopropyl-CO_2Me, trans); 3.92 (s, 6 H, $ArCO_2Me$); 7.02–8.0 (m, 8 H, ArH). MS *m/e*: M^+ 234 (10); 203 (5); 148 (100); 144 (3); 117 (4); 116 (34). IR (neat): ν 3050; 1730 cm^{-1}. Anal. Calcd for $C_{13}H_{14}O_4$: C, 66.66; H, 5.98. Found: C, 66.65; H, 5.98.

4,5-Dihydro-2-phenyl-3-methyl-1*H*-3-benzazepine (12a). Reaction of the silane **1a** (1 mmol) with iminium compound **8a**[29] (1 mmol) in presence of CsF (1.5 mmol) by procedure B afforded the benzazepine **12a** as an oil (53%). ^{1}H NMR ($CDCl_3$): δ 2.60 (s, 6 H, NMe); 2.85–3.05 (m, 2 H, CH_2); 3.15–3.35 (m, 2 H, CH_2); 5.70 (s, 1 H, =CH); 7.00–7.60 (m, 9 H, ArH). MS *m/e*: M^+ 235. IR ($CHCl_3$): ν 1640 cm^{-1}. Anal. Calcd for $C_{17}H_{17}N$: C, 86.80; H, 7.23; N, 5.95. Found: C, 86.77; H, 7.23; N, 5.94.

4,5-Dihydro-7,8-dimethoxy-2-phenyl-3-methyl-1*H*-3-benzazepine (12b): secured from **1a** and iminium compound **8b**[29] in 47% yield by procedure B, mp 165–167 °C (hexane). ^{1}H NMR ($CDCl_3$): δ 2.68 (s, 3 H, NMe); 2.86–3.11 (m, 2 H, CH_2); 3.22–3.46 (m, 2 H, CH_2); 3.88 (s, 3 H, OMe); 3.92 (s, 3 H, OMe); 5.72 (s, 1 H, =CH); 6.79, 6.85 (s, s, 2 H, C_6H and C_9H); 7.33–7.81 (m, 5 H, ArH). MS *m/e*: M^+ 295. IR (KBr pellet): ν 1618 cm^{-1}. Anal. Calcd for $C_{19}H_{21}NO_2$: C, 77.28; H, 7.11; N, 4.74. Found: C, 77.26; H, 7.10; N, 4.75.

2,3,4,5-Tetrahydro-2-phenyl-3-methyl-1*H*-3-benzazepine (13a). Dry HCl gas was passed for 1 h through a solution of the benzazepine **12a** (83 mg) in dry ether (70 mL). The solid that separated out was filtered, dissolved in methanol (10 mL), and treated with sodium borohydride (100 mg). The solvent was distilled off, and to the residue aqueous Na_2CO_3 was added. The organic material was taken up in ether, washed with water, and dried. The solvent was removed to furnish **13a** as an oil (75 mg). ^{1}H NMR ($CDCl_3$): δ 2.55 (s, 3 H, NMe); 2.1–3.6 (m, 7 H, CH_2×3, CH); 6.9–7.4 (m, 9 H, ArH). Hydrochloride mp 212–213 °C (lit.[9] mp 215 °C).

2,3,4,5-Tetrahydro-7,8-dimethoxy-2-phenyl-3-methyl-1*H*-3-benzazepine (13b). The benzazepine **12b** was reduced as in the previous text to **13b**, mp 156–157 °C (methanol). ^{1}H NMR ($CDCl_3$): δ 2.10 (s, 3 H, NMe); 2.20–3.55 (m, 7 H, CH_2×3, CH); 3.82 (s, 3 H, OMe); 3.90 (s, 3 H, OMe); 6.62, 6.72 (s, s, 2 H, C_6H and C_9H); 7.20–7.62 (s, 5 H, ArH). MS *m/e*: 297 (M^+); 282 (100);

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254 (40); 179 (25); 178 (35); 164 (45). Anal. Calcd for $C_{19}H_{23}NO_2$: C, 76.76; H, 7.74; N, 4.71. Found: C, 76.71; H, 7.73; N, 4.70. Hydrochloride mp 204-205 °C.

2-Methyl-1-phthalidyl-1,2,3,4-tetrahydroisoquinoline (15a). Reaction of **1b** with iminium compound **8a** by procedure A afforded *threo*-**15a** (14%), mp 130-131 °C (lit.[15] mp 132-133 °C), and *erythro*-**15a** (43%), mp 100-101 °C (lit.[15] mp 100-102 °C). ^{1}H NMR of both isomers corresponded with literature data.[15] These could also be secured through reaction of 3-silylphthalide **17a** with **8a**.

6,7-Dimethoxy-2-methyl-1-phthalidyl-1,2,3,4-tetrahydroisoquinoline (15b). Reaction of **1b** with iminium compound **8b** by procedure A afforded *threo*-**15b** (12%), mp 156-157 °C (lit.[17] mp 159 °C), and *erythro*-**15b** as an oil (40%). ^{1}H NMR of both isomers corresponded with literature values.[17] These could also be secured through reaction of 3-silylphthalide **17a** with **8b**.

3-(Trimethylsilyl)phthalide (17a). Into a flame-dried 100-mL two-necked round-bottom flask equipped with a stir bar and a septum cap was introduced THF (10 mL) and diisopropylamine (0.84 mL, 6 mmol). It was cooled to -78 °C, and a 2.8 M solution of BuLi in hexane (2.14 mL, 6 mmol) was added via a syringe. After 15 min, a solution of phthalide **16a**[30] (0.536 g, 4 mmol) in THF (5 mL) was added. The resulting orange-red solution was further stirred for 30 min at -78 °C and the reaction quenched with trimethylsilyl chloride (0.76 mL, 6 mmol). The reaction mixture was gradually allowed to come to room temperature, poured into water (30 mL), and extracted with ether (100 mL × 3). The combined organic extract was washed with water and dried. The solvent was removed under reduced pressure to afford the silylphthalide **17a** as a yellow oil, giving a single spot on TLC (0.772 g, 93.6%). ^{1}H NMR (CCl_4): δ 0.00 (s, 9 H, $SiMe_3$), 5.15 (s, 1 H, ArCH); 7.28-7.85 (m, 4 H, ArH). Its attempted chromatographic purification led to decomposition.

3-(Trimethylsilyl)-6,7-dimethoxyphthalide (17b). Reaction of 6,7-dimethoxyphthalide (**16b**,[31] 0.194 g, 1 mmol) with LDA (1.5 mmol) in THF (10 mL) followed by addition of trimethylsilyl chloride (0.19 mL, 1.5 mmol), as in the previous text, afforded **17b** as a light yellow solid (0.256 g, 96%), mp 110-112 °C. ^{1}H NMR ($CDCl_3$): δ 0.00 (s, 9 H, $SiMe_3$); 3.82 (s, 3 H, OMe); 4.04 (s, 3 H, OMe); 5.1 (s, 1 H, ArCH); 6.90 (d, 1 H, J = 9 Hz, ArH); 7.26 (d, 1 H, J = 9 Hz, ArH).

General Procedure for Reaction of Silylphthalides 17 with Dihydroisoquinoline Methiodides 8. These reactions were carried out according to procedure A using 2 equiv of CsF and stirring at room temperature for 15 h.

(±)-Cordrastine (15c). The alkaloid **15c** was obtained in 76% yield by reaction of the phthalide **17b** (266 mg) with isoquinolinium salt **8b** (400 mg).

***threo*-15c**: 184 mg, 46%, mp 155-156 °C (lit.[15] mp 156-157 °C). R_f: 0.66 (silica gel, benzene:methanol = 9:1). ^{1}H NMR ($CDCl_3$): δ 2.53 (m, 4 H, C_3 and C_4 H's); 2.7 (s, 3 H, NMe); 3.78, 3.85, 3.95 (3 s, 12 H, 4×OMe); 4.15 (d, 1 H, J = 3.2 Hz, C_1H); 5.68 (d, 1 H, J = 3.2 Hz, C_9H); 6.46 (s, 1 H, ArH); 6.81 (s, 1 H, ArH); 7.14 (d, 1 H, J = 8 Hz, ArH); 7.41 (d, 1 H, J = 8 Hz, ArH).

***erythro*-15c**: 120 mg, 30%, mp 107-108 °C (lit.[15] mp 110-114 °C) R_f: 0.55 (silica gel, benzene:methanol = 9:1). ^{1}H NMR ($CDCl_3$): δ 2.3-3.2 (m, 4 H, C_3 and C_4 H's); 2.63 (s, 3 H, NMe); 3.74 (s, 3 H, OMe); 3.96 (s, 3 H, OMe); 3.98 (s, 3 H, OMe); 4.12 (s, 3 H, OMe); 4.14 (d, 1 H, J = 3.3 Hz, C_1H); 5.69 (d, 1 H, J = 3.3 Hz, C_9H); 6.47 (s, 1 H, ArH); 6.7 (d, 1 H, J = 8 Hz, ArH); 6.73 (s, 1 H, ArH); 7.28 (d, 1 H, J = 8 Hz, ArH).

(±)-Hydrastine (15d). Reaction of the phthalide **17b** (266 mg) with isoquinolinium salt **8c**[14c] (381 mg) afforded the alkaloid **15d** in 74% yield.

***threo*-15d**: 158 mg, 41%, mp 149-151 °C (lit.[14c] mp 150-154 °C). R_f: 0.68 (silica gel, benzene:methanol = 9:1). ^{1}H NMR ($CDCl_3$): δ 2.35-3.3 (m, 4 H, C_3 and C_4 H's); 2.55 (s, 3 H, NMe); 3.95 (s, 3 H, OMe); 4.1 (s, 3 H, OMe); 4.15 (d, 1 H, J = 3 Hz, C_1H); 5.67 (d, 1 H, J = 3 Hz, C_9H); 5.92 (s, 2 H, OCH_2O); 6.48 (s, 1 H, ArH); 6.86 (s, 1 H, ArH); 7.23 (d, 1 H, J = 8 Hz, ArH); 7.41 (d, 1 H, J = 8 Hz, ArH).

***erythro*-15d**: 126 mg, 33%, mp 136-137 °C (lit.[14c] mp 136-140 °C). R_f: 0.49 (silica gel, benzene:methanol = 9:1). ^{1}H NMR ($CDCl_3$): δ 2.2-3.1 (m, 4 H, C_3 and C_4 H's); 2.55 (s, 3 H, NMe); 3.92 (s, 3 H, OMe); 4.1 (s, 3 H, OMe); 3.98 (d, 1 H, J = 3.6 Hz, C_1H); 5.52 (d, 1 H, J = 3.6 Hz, C_9H); 5.93 (s, 2 H, OCH_2O); 6.34 (s, 1 H, ArH); 6.6 (s and d overlapping, 2 H, ArH); 7.18 (d, 1 H, J = 8 Hz, ArH).

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Synthesis of Alkynyl(phenyl)iodonium Triflates and Their Reaction with Diethyl 2-Aminomalonate

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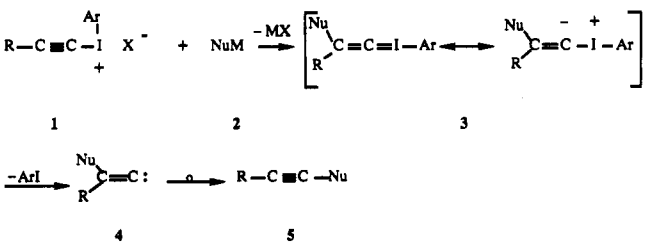
Alkynyl(phenyl)iodonium triflates **9** react with the Li (or K) salt of diethyl 2-[(diphenylmethylene)amino]malonate (**10**) (M = Li or K) to give the corresponding diethyl 2-alkynyl-2-[(diphenylmethylene)amino]malonate (**11**) in 30-95% yield.

The reaction between alkynyl(aryl)iodonium salts **1** and various nucleophiles has been the subject of numerous recent publications.[1,2] Of particular interest are reactions in which the aryliodonium functionality in **1** is formally substituted by the nucleophilic group Nu to give alkynes **5** (Scheme I).[2] It has been postulated[2b-e] that the mechanism of these reactions involves the addition of the nucleophile to the β-position of the polarized triple bond to give an alkylidenecarbene–iodonium ylide **3**. Elimination

Scheme I



of aryl iodide generates the free alkylidene carbene **4**, which rearranges to the alkyne **5**.[3] This course of events

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