124.69, 126.25, 126.31, 126.61, 127.65, 128.32, 128.91, 131.33, 131.61, 132.29, 133.82, 135.09, 135.49, 136.24, 137.11, 144.21, 162.79, 164.25, one carbon was not observed; mass spectrum, m/z (relative intensity) 533 (M^+, 19), 215 (52), 115 (100). Anal. Calcd for $C_{27}H_{24}N_4O_4S_2$: C, 60.88; H, 4.54; N, 10.52. Found: C, 60.59; H, 4.60; N, 10.29.

Reaction of 20 with [*N*-(4-Methylphenyl)imino]triphenylphosphorane. To a solution of **20** (0.53 g, 1 mmol) in 25 mL of dry toluene was added [*N*-(4-methylphenyl)imino]-triphenylphosphorane (1.10 g, 3 mmol). The reaction mixture was heated at reflux temperature for 3 h and afterwards at 150 °C in a sealed tube for 12 h. After cooling, the solvent was removed under reduced pressure, and the resulting material was chromatographed (silica gel column; *n*-hexane/ethyl acetate, 7:3) to give **5e** (48%) and **22**.

22: yield 51%; mp 243 °C; yellow prisms (ethyl acetate/*n*-hexane); IR (Nujol) 3267, 1719, 1439, 1336, 1111 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.47 (t, 3 H, J = 7.1 Hz), 2.25 (s, 3 H), 2.41 (s, 3 H), 4.32 (q, 2 H, J = 7.1 Hz), 6.36 (s, 1 H, J = 7.8 Hz), 6.86 (d, 2 H, J = 8.3 Hz), 6.92 (d, 2 H, J = 8.3 Hz), 7.42–7.61 (m, 10 H), 7.71–7.82 (m, 7 H), 13.61 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.36, 18.96, 20.76, 60.95, 111.16, 115.97 (s, d, J_{P-C} = 19.9 Hz), 119.12 (d, J_{P-C} = 12.7 Hz), 119.73, 123.29 (s), 128.64 (s, d, J_{P-C} = 99.9 Hz), 128.82, 129.14 (d, J_{P-C} = 12.1 Hz), 130.22 (s), 130.68, 132.47 (d, J_{P-C} = 2.6 Hz), 132.81 (d, J_{P-C} = 9.8 Hz), 138.07 (s, d, J_{P-C} = 2.3 Hz), 138.66 (s, d, J_{P-C} = 2.9 Hz), 147.47 (s, d, J_{P-C} = 3.0 Hz), 155.67 (s, d, J_{P-C} = 1.5 Hz), 167.06 (s), one carbon was not observed; ^{31}P NMR ($CDCl_3$) δ 10.69; mass spectrum, m/z (relative intensity) 595 (M^+, 25), 183 (100), 108 (30). Anal. Calcd for $C_{38}H_{34}N_3O_2P$: C, 76.62; H, 5.75; N, 7.05. Found: C, 76.55; H, 5.71; N, 6.98.

Preparation of 5-(Ethoxycarbonyl)-3-(4-methylphenyl)-7-methyl-1*H*-pyrido[2,3,4-*de*]quinazoline-2-thione. To a solution of **22** (0.12 g, 0.2 mmol) in 10 mL of dry toluene was added carbon disulfide (1 mL). The mixture was heated at 140 °C in a sealed tube for 8 h. After cooling, the separated solid was isolated by filtration, dried, and recrystallized to give **23**: yield 68%; mp 299–300 °C; colorless prisms (toluene); IR (Nujol) 3296, 1698, 1169 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.27 (t, 3 H, J = 7.1 Hz), 2.44 (s, 3 H), 2.53 (s, 3 H), 4.27 (q, 2 H, J = 7.1 Hz), 7.06 (d, 1 H, J = 8.2 Hz), 7.27 (d, 2 H, J = 8.3 Hz), 7.38 (d, 2 H, J = 8.3 Hz), 7.44 (d, 1 H, J = 8.2 Hz), 7.98 (s, 1 H), 11.52 (s, 1 H), 11.52 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 14.02, 18.26, 21.50, 61.65, 109.40, 113.10 (s), 115.10, 127.85 (s), 128.78, 130.47, 133.56 (s), 133.76, 135.61 (s), 136.62 (s), 138.74 (s), 140.95 (s), 151.19 (s), 165.01 (s), 176.35 (s); mass spectrum, m/z (relative intensity) 377 (M^+, 67), 305 (100), 151 (29). Anal. Calcd for $C_{21}H_{19}N_3O_2S$: C, 66.82; H, 5.07; N, 11.13. Found: C, 66.75; H, 5.00; N, 11.01.

Preparation of the Carbodiimide 21 (R = 4-$CH_3C_6H_4$). Procedure A. To a solution of the bis(iminophosphorane) **4** (1.29 g, 1.75 mmol) in 25 mL of dry methylene chloride was added at room temperature 4-methylphenyl isocyanate (0.23 g, 1.75 mmol) in the same solvent (25 mL) during 4–5 h. Afterwards, the solvent was removed under reduced pressure, the resulting material was dissolved in 30 mL of dry benzene, and carbon disulfide (10 mL) was added. The new reaction mixture was stirred at reflux temperature for 4 h. After cooling, the solvent was removed under reduced pressure, and the resulting material was chromatographed (silica gel column; *n*-hexane/ether, 4:1).

Procedure B. To a stirred solution of **19** (0.30 g, 1 mmol) in 20 mL of dry benzene at 50 °C was added dropwise a solution of [*N*-(4-methylphenyl)imino]triphenylphosphorane (0.36 g, 1 mmol) in the same solvent (20 mL), during 4 h, and the stirring was continued for 1 h. The solvent was removed under reduced pressure, and the resulting material was chromatographed (silica gel column; *n*-hexane/ether, 4:1).

21: yield 71% (procedure A), 65% (procedure B); viscous oil; IR (neat) 2135, 2021, 1727 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40 (t, 3 H, J = 7.1 Hz), 2.32 (s, 3 H), 2.35 (s, 3 H), 4.37 (q, 2 H, J = 7.1 Hz), 7.06–7.18 (m, 6 H), 7.44 (s, 1 H), 7.80 (d, 1 H, J = 2.1 Hz); mass spectrum m/z (relative intensity) 377 (M^+, 100), 345 (21), 91 (65). Anal. Calcd for $C_{21}H_{19}N_3O_2S$: C, 66.82; H, 5.07; N, 11.13. Found: C, 66.73; H, 5.10; N, 11.01.

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Rearrangements of 1,6,7-Trisubstituted 2-Methyl-1,2,3,4-tetrahydroisoquinolinium 2-Methylides

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Chemical behavior of 1,6,7-trisubstituted 2-methyl-1,2,3,4-tetrahydroisoquinolinium 2-methylides **4** was investigated in fluoride-ion induced desilylation reaction of 1,6,7-trisubstituted 2-methyl-2-(trimethylsilyl)-methyl-1,2,3,4-tetrahydroisoquinolinium iodides **3**. The 1-nonsubstituted (**4a,b**) and 1-alkyl-substituted ylides (**4c,d**) gave mixtures of five products (**7–11**), but the 1-phenyl-substituted analogues (**4e,f**) yielded (*E*)- and (*Z*)-2,3-disubstituted 5-benzylidene-1,3-cyclohexadiene-6-spiro-3′-1′-methylpyrrolidines (*E*)-**5** and (*Z*)-**5** and 7,8-disubstituted 3-methyl-1-phenyl-2,3,4,5-tetrahydro-1*H*-3-benzazepines **6**. The mechanisms of the rearrangement are discussed.

Introduction

Ammonium ylide intermediates are usually produced by α-deprotonation of tetraorganoammonium salts under basic conditions, e.g., sodium amide in liquid ammonia.[1] However, it is difficult to prepare 2-methyl-1,2,3,4-tetrahydroisoquinolinium 2-methylides from 2,2-dimethyl-1,2,3,4-tetrahydroisoquinolinium salts because the α-deprotonation occurs on the 1-position in preference to the 2-methyl groups.[2] The ylide anions produced by fluoride-ion induced desilylation of trialkyl[(trimethylsilyl)-methyl]ammonium salts locate regioselectively on the

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(2) Grethe, G.; Lee, H. L.; Uskokovic, M. R. *Tetrahedron Lett.* **1969**, 1937.

0022-3263/92/1957-6711$03.00/0

Table I. 2-Methyl-2-[(trimethylsilyl)methyl]-1,6,7-trisubstituted-1,2,3,4-tetrahydroisoquinolinium Iodides 3

salts	R^1	R^2	reaction time (h)	yield[a] (%)	ratio[b] of cis to trans
3a	H	H	0.5	94	
3b	MeO	H	1	97	
3c	H	Me	1	88	60:40
3d	H	Et	1	89	68:32
3e	H	Ph	0.5	91	74:26
3e-d_3[c]	H	Ph	1	95	67:33
3f	MeO	Ph	0.5	98	62:38

[a] A mixture of the cis and trans isomers. [b] Determined from the proton ratios of ^{1}H NMR. [c] A *N*-CD_3 analogue of **3e**.

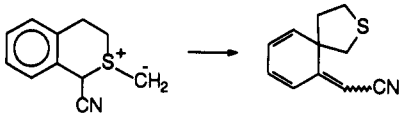
Table II. Melting Points and Selected ^{1}H NMR Data of 1,2,3,4-Tetrahydroisoquinolinium Iodides 3

ammonium salts	mp, °C	^{1}H NMR ($CHCl_3$) δ		
		$Si(CH_3)_3$	$SiCH_2N$	NCH_3
3a	205–206	0.33	3.56 (s)	3.51
3b	214–216	0.36	3.55 (s)	3.52
cis-**3c**	172–173	0.40	3.32, 3.45 (ABq, J = 14.8 Hz)	3.42
trans-**3c**		0.33	*a*	3.49
cis-**3d**	202–203	0.41	3.60, 3.67 (ABq, J = 15.0 Hz)	3.29
trans-**3d**		0.28	*a*	3.63
cis-**3e**	224–227	0.30	2.28, 3.72 (ABq, J = 14.7 Hz)	3.58
trans-**3e**		0.36	*a*	3.16
cis-**3e-d_3**	226–228	0.30	2.28, 3.72 (ABq, J = 14.7 Hz)	
cis-**3f**	202–204	0.30	2.24, 3.81 (ABq, J = 14.7 Hz)	3.60
trans-**3f**	223–227	0.37	3.64, 3.88 (ABq, J = 15.1 Hz)	3.15

[a] These signals were overlapped by signals of the cis isomer and could not be assigned.

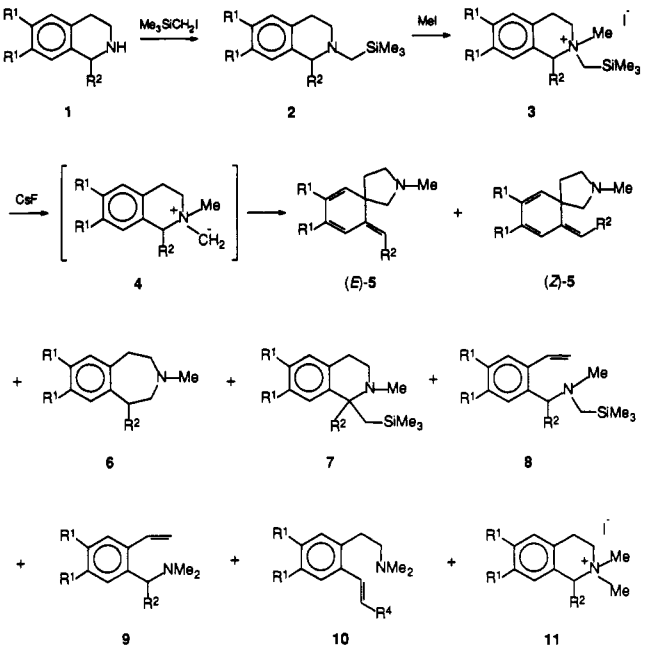
carbons which had bonded with the silyl groups.[3,4] Treatment of 2-alkyl-2-[(trimethylsilyl)methyl]-1,2,3,4-tetrahydroisoquinolinium halides with cesium fluoride may give 2-alkyl-1,2,3,4-tetrahydroisoquinolinium 2-methylides.

Hori and co-workers[5] reported that 1-cyanothioisochromanium 2-methylide rearranged to the spiro compound in a high yield. This suggests that 2-alkyl-

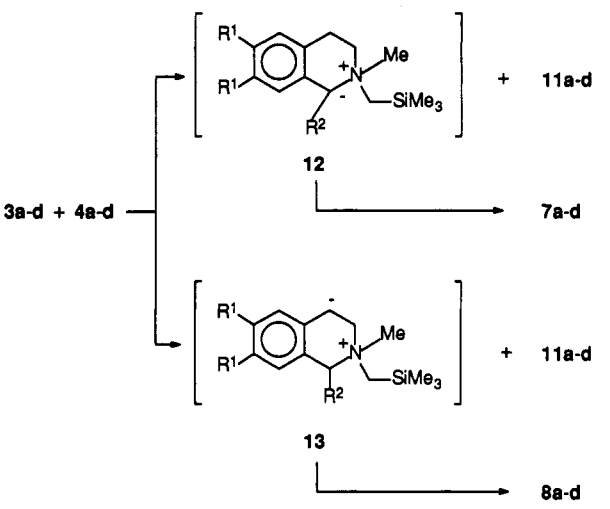


1,2,3,4-tetrahydroisoquinolinium 2-methylides rearrange to 5-methylene-1,3-cyclohexadiene-6-spiro-3′-1′-alkylpyrrolidines. This paper describes the chemical behavior of 2-methyl-1-substituted-1,2,3,4-tetrahydroisoquinolinium 2-methylides.

Scheme I



Scheme II



Results and Discussion

1,6,7-Trisubstituted 2-methyl-2-[(trimethylsilyl)methyl]-1,2,3,4-tetrahydroisoquinolinium iodides (**3**) were prepared from reaction of 1,6,7-trisubstituted 1,2,3,4-tetrahydroisoquinolines (**1**) with (iodomethyl)trimethylsilane followed by quaternization with iodomethane (Table I). The major geometrical isomer of **3f** was assigned to have the cis configuration based on an X-ray crystallographic analysis. That of **3e** was also assigned as the cis by comparison of the chemical shifts of the *N*-methyl (cis > trans) and the trimethylsilyl groups (cis < trans) in ^{1}H NMR spectroscopy, though these relations were reversed in the 1-alkyl-substituted analogues **3c,d**[6] (Table II).

(3) Vedejs, E.; West, F. G. *Chem. Rev.* **1986**, *86*, 941.
(4) (a) Nakano, M.; Sato, Y. *J. Org. Chem.* **1987**, *52*, 1844. (b) Shirai, N.; Sato, Y. *J. Org. Chem.* **1988**, *53*, 194. (c) Sugiyama, H.; Sato, Y.; Shirai, N. *Synthesis* **1988**, 988. (d) Shirai, N.; Sumiya, F.; Sato, Y.; Hori, M. *J. Org. Chem.* **1989**, *54*, 836. (e) Okazaki, S.; Shirai, N.; Sato, Y. *J. Org. Chem.* **1990**, *55*, 334. (f) Shirai, N.; Watanabe, Y.; Sato, Y. *J. Org. Chem.* **1990**, *55*, 2767. (g) Sumiya, F.; Shirai, N.; Sato, Y. *Chem. Pharm. Bull.* **1991**, *39*, 36. (h) Machida, Y.; Shirai, N.; Sato, Y. *Synthesis* **1991**, 117. (i) Kitano, T.; Shirai, N.; Sato, Y. *Synthesis* **1991**, 996. (j) Tanaka, T.; Shirai, N.; Sato, Y. *Chem. Pharm. Bull.* **1992**, *40*, 518. (k) Kitano, T.; Shirai, N.; Sato, Y. *Chem. Pharm. Bull.* **1992**, *40*, 768. (l) Tanaka, T.; Shirai, N.; Sugimori, J.; Sato, Y. *J. Org. Chem.* **1992**, *57*, 5034. (m) Usami, T.; Shirai, N.; Sato, Y. *J. Org. Chem.*, in press.
(5) Hori, M.; Kataoka, T.; Shimizu, H.; Kataoka, M. *Tetrahedron Lett.* **1983**, *24*, 3733.

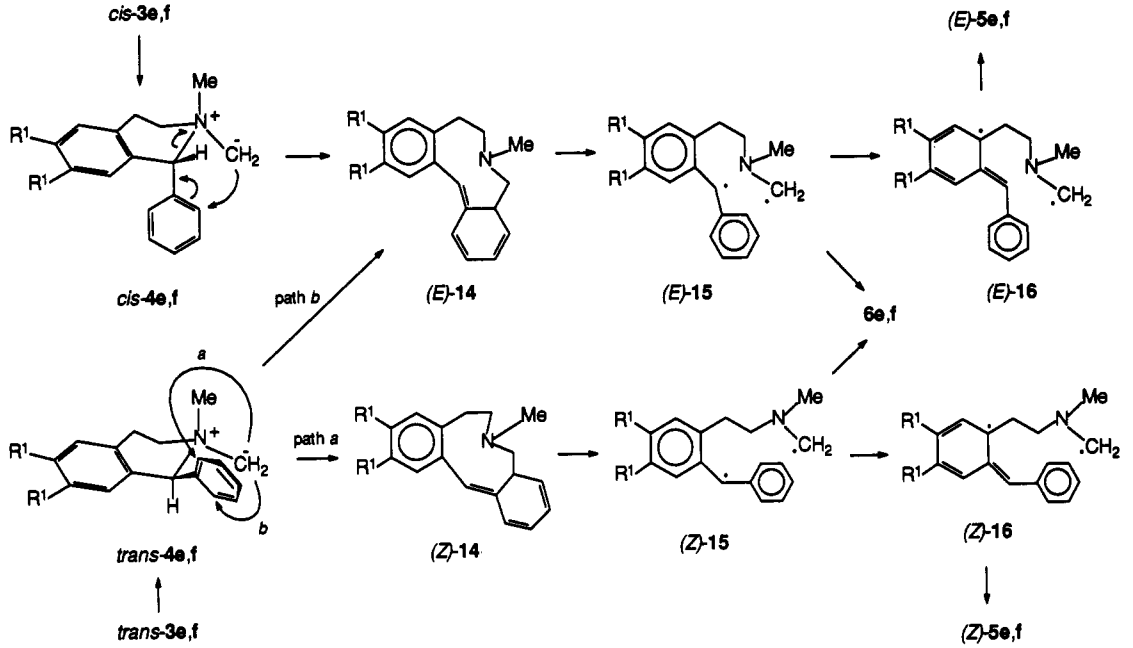
(6) Bernath,[7] Smith,[8] and their co-workers reported that, in quaternization reaction of 1-substituted 2-methyl-1,2,3,4-tetrahydroisoquinolines, the preferred direction of the attacking groups was trans relative to the substitutents at C-1. The chemical shift of *N*-methyl groups of the cis isomers was observed in a slightly higher field than those of trans salts in ^{1}H NMR of 1,2-dialkyl-2-methyl-1,2,3,4-tetrahydroisoquinolines, but the relation of the chemical shifts was reversed in 2-alkyl-2-methyl-1-phenyl-substituted salts.
(7) Bernath, G.; Kobor, J.; Koczka, K.; Radics, L.; Kajtar, M. *Tetrahedron Lett.* **1968**, 225.
(8) Smith, S., Jr.; Elango, V.; Shamma, M. *J. Org. Chem.* **1984**, *49*, 581.

Table III. Reaction of the 1,2,3,4-Tetrahydroisoquinolinium Iodides 3 with CsF in DMF for 3 h at Room Temperature

		product yields[a] (%)							
entry	salt	(*E*)-5	(*Z*)-5	6	7	8	9	10	11[b]
1	**3a**	0	0	0	34	2	3		49
2	**3b**	0	0	0	35	2	3		50
3	*cis*-**3c**	0	0	0	1	14	27	14[c]	30
4	*cis*-**3d**	0	0	0	6	11	20	11[d]	37
5	*cis*-**3e**	17	1	77	0	0	0		*e*
6	**3e**[f]	11	3	75	0	0	0		*e*
7	*cis*-**3e**-d_3	11	2	72	0	0	0		*e*
8	*cis*-**3f**	45	1	49	0	0	0		*e*
9	*trans*-**3f**	15	30	36	0	0	0		*e*

[a] Determined from the proton ratios of ^{1}H NMR of a mixture of the amines. [b] Isolated yield. [c] R^4 = H. [d] R^4 = Me. [e] Not determined. [f] A mixture of cis and trans isomers, 30:70.

Scheme III



Reaction of **3** with cesium fluoride was carried out at room temperature for 3 h in DMF. Products from the reaction of **3a–d** were mixtures of the following four amines and one ammonium salt: 1,6,7-trisubstituted 2-methyl-1-[(trimethylsilyl)methyl]-1,2,3,4-tetrahydroisoquinolines **7**, *N*-methyl-*N*-[(trimethylsilyl)methyl]-α-alkyl-2-vinylbenzylamines **8**, *N*,*N*-dimethyl-α-alkyl-2-vinylbenzylamines **9**, *N*,*N*-dimethyl-2-[2-(1-alkenyl)-4,5-disubstituted phenyl]ethylamines **10**, and 1,6,7-trisubstituted 2,2-dimethyl-1,2,3,4-tetrahydroisoquinolinium iodides **11** (Table III). Amines **7a,b** and salts **11a,b** were the main products in the reaction of **3a,b** having no substituent at the 1-position (entries 1 and 2). In the reaction of 1-alkyl-substituted ammonium salts (**3c,d**), amounts of **8c,d** and **9c,d** were increased with decreasing yields of **7c,d** (entries 3 and 4). Proton transfers from **3a–d** to **4a–d** which were initially formed may give **11a–d**, **12a–d**, and **13a–d** (Scheme II). Then, a [1,2] shift of the (trimethylsilyl)methyl group of **12** gives **7**, and Hofmann elimination of **13** results in **8**. Thus, no presence of the expected spiro amines **5** was observed in these reactions.

In the reaction of 1-phenyl-substituted analogues **3e,f** with cesium fluoride, however, the reaction products changed to mixtures of (*E*)- and (*Z*)-5-benzylidene-2,3-disubstituted-1,3-cyclohexadiene-6-spiro-3′-1′-methylpyrrolidines [(*E*)-**5** and (*Z*)-**5**, Sommelet–Hauser rearrangement products] and 7,8-disubstituted 3-methyl-1-phenyl-2,3,4,5-tetrahydro-1*H*-3-benzazepines (**6**, Stevens rearrangement products) (entries 5–9).

We previously reported that Stevens products in the rearrangement of benzylammonium alkylides were not directly formed by a [1,2] radical rearrangement pathway as previously believed,[9] but were produced by a [2,3] sigmatropic followed by a [1,3] radical rearrangement pathway via 6-[1-(dimethylamino)alkyl]-5-methylene-1,3-cyclohexadienes (isotoluene derivatives).[4e] Because (*E*)-**5**, (*Z*)-**5**, and **6** were only obtained from the 1-phenyl-substituted ylides **4e,f**, it is questionable whether **6** was produced directly from **4** by the [1,2] migration process.

The [2,3] sigmatropic rearrangement of benzylammonium methylides occurred more quickly with no electron-rich benzene rings than with electron-rich rings.[4j] Because the dimethoxy-substituted benzene ring in the tetrahydroisoquinolinium moiety of **4f** is apparently more electron-rich than the 1-phenyl group, it is unlikely that a [2,3] sigmatropic shift of ylide anions to the 4a-carbon (*E*)-**5f** and (*Z*)-**5f**.

A [2,3] sigmatropic rearrangement of **4e,f** to the 1-phenyl groups gives 10,11-disubstituted 6-methyl-4a,5,7,8-tetrahydro-6*H*-dibenzo[*c*,*f*]azonines (**14**, isotoluene derivatives) followed by conversion to (*E*)-**5**, (*Z*)-**5**, and **6** by a radical-dissociation and -recombination process (Scheme III). Aromatization of isotoluene derivatives requires a [1,3] antarafacial proton migration under nonbasic conditions, which is difficult in bicyclic isotoluenes.[4d,g] In the presence

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Scheme IV

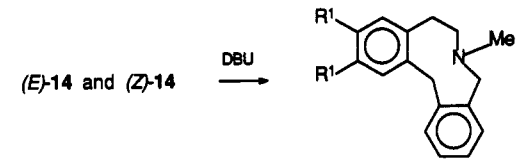

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Table IV. Reaction of the 1,2,3,4-Tetrahydroisoquinolinium Iodides (3) with CsF in the Presence of DBU

			ratio[a]			
salts	additive	total yield (%)	(*E*)-5	(*Z*)-5	6	17
cis-3e		90	13	3	84	0
cis-3e	DBU	90	2	4	18	76
cis-3f		95	47	1	52	0
cis-3f	DBU	85	7	4	9	80

[a] Determined from the proton ratios of ^{1}H NMR.

of a strongly basic amine (e.g., DBU), the aromatization occurs by a proton-dissociation and -recombination pathway.[4h,i] The addition of DBU to the reaction of *cis*-3e,f resulted in formation of dibenzo[*c,f*]azonine derivatives (17) with decreased amounts of (*E*)-5 and 6 (Scheme IV, Table IV). These results appear to indicate that (*E*)-5, (*Z*)-5, and 6 were produced via 14. Salts *cis*-3e,f gave preferentially (*E*)-5e,f (entries 5, 7, and 8 in Table III), and *trans*-3f gave a mixture of (*E*)-5f and (*Z*)-5f in a ratio of 1:2 (entry 9). A proton transfer from the 2-methyl group to the 2-methylide anion in 4 is unlikely.[10] Indeed, when *cis*-2-(trideuteriomethyl)-1-phenyl-2-[(trimethylsilyl)-methyl]-1,2,3,4-tetrahydroisoquinolinium iodide (*cis*-3e-d_3) was similarly treated, all deuterium atoms were observed on the *N*-methyl groups of the rearrangement products (*E*)-5e-d_3, (*Z*)-5e-d_3, and 6e-d_3.

The ylides *cis*-4e,f which formed from *cis*-3e,f rearrange to (*E*)-14; however, in the rearrangement of *trans*-4e,f produced from *trans*-3e,f, paths *a* and *b* are possible giving (*E*)-14 and (*Z*)-14, respectively (Scheme III). The conversion of (*E*)-14 to (*E*)-5 and of (*Z*)-14 to (*Z*)-5 occurs by retaining the configuration via the radical-dissociation and -recombination process. It is known that the Stevens rearrangement of acyl-stabilized ammonium ylides proceeds by a [1,2] radical migration mechanism with retention of the configuration of the chiral migrating group.[11]

Experimental Section

DMF was dried by distillation from BaO under reduced pressure. CsF was dried over P_2O_5 at 170 °C under reduced pressure. ^{1}H NMR spectra were recorded at 100, 270, or 400 MHz. Mass spectra were obtained using either EI or CI ionization. Aluminum oxide (Merck, Aluminumoxide 90, 70–230 mesh) was used for column chromatographies. All melting points and boiling points are uncorrected.

2-[(Trimethylsilyl)methyl]-1,6,7-trisubstituted-1,2,3,4-tetrahydroisoquinolines 2a–f: General Procedure. A mixture of (iodomethyl)trimethylsilane (2.1 g, 10 mmol) and 1,2,3,4-tetrahydroisoquinoline (1a) or a substituted analogue (6,7-dimethoxy- (1b), 1-methyl- (1c), 1-ethyl- (1d), 1-phenyl- (1e), or 6,7-dimethoxy-1-phenyl-1,2,3,4-tetrahydroisoquinoline (1f) (20 mmol)) in DMSO (10 mL) was stirred at 100 °C for 2–3 h. The reaction mixture was poured into water and extracted with diethyl ether. The extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The crude products were chromatographed on aluminum oxide columns (ethyl ether/hexane) and then distilled under reduced pressure or recrystallized from EtOH.

2a: yield 76%; bp 158–159.5 °C (15 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9 H), 2.07 (s, 2 H), 2.52–2.96 (m, 4 H), 3.56 (s, 2 H), 6.90–7.12 (m, 4 H). Anal. Calcd for $C_{13}H_{21}NSi$: C, 71.17; H, 9.65; N, 6.38. Found: C, 71.15; H, 9.90; N, 6.34.

2b: yield 86%; mp 65–67 °C; ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9 H), 2.05 (s, 2 H), 2.52–2.86 (m, 4 H), 3.48 (s, 2 H), 3.83 (s, 6 H), 6.46 (s, 1 H), 6.57 (s, 1 H). Anal. Calcd for $C_{15}H_{25}NO_2Si$: C, 64.47; H, 9.02; N, 5.01. Found: C, 64.26; H, 8.88; N, 4.90.

2c: yield 59%; bp 165–167 °C (10 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.09 (s, 9 H), 1.33 (d, 3 H, *J* = 6.8 Hz), 2.02 and 2.24 (AB-q, 2 H, *J* = 14.6 Hz), 2.61–2.76 (m, 2 H), 2.91 (ddd, 1 H, *J* = 16.0, 8.4, 4.7 Hz), 3.05 (ddd, 1 H, *J* = 11.8, 8.4, 4.4 Hz), 3.69 (q, 1 H, *J* = 6.8 Hz), 7.05–7.30 (m, 4 H). Anal. Calcd for $C_{14}H_{23}NSi$: C, 72.04; H, 9.93; N, 6.00. Found: C, 71.92; H, 10.10; N, 5.98.

2d: yield 60%; bp 171–174 °C (10 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.07 (s, 9 H), 0.91 (t, 3 H, *J* = 7.3 Hz), 1.64–1.78 (m, 2 H), 2.05 and 2.18 (AB-q, 2 H, *J* = 14.7 Hz), 2.59 (ddd, 1 H, *J* = 20.0, 5.2, 5.1 Hz), 2.65 (ddd, 1 H, *J* = 12.5, 5.3, 5.2 Hz), 2.90 (ddd, 1 H, *J* = 20.0, 9.0, 5.3 Hz), 3.16 (ddd, 1 H, *J* = 12.5, 9.0, 5.1 Hz), 3.39 (t, 1 H, *J* = 6.0 Hz), 7.02 (m, 4 H). Anal. Calcd for $C_{15}H_{25}NSi$: C, 72.81; H, 10.18; N, 5.66. Found: C, 72.79; H, 10.16; N, 5.53.

2e: yield 64%; bp 167–170 °C (5 mmHg); ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 9 H), 1.75 and 2.05 (AB-q, 2 H, *J* = 14.7 Hz), 2.50–2.57 (m, 1 H), 2.76–2.90 (m, 1 H), 3.09–3.17 (m, 2 H), 4.31 (s, 1 H), 6.66 (d, 1 H, *J* = 7.9 Hz), 6.94–6.98 (m, 1 H), 7.05–7.11 (m, 2 H), 7.19–7.61 (m, 5 H). Anal. Calcd for $C_{19}H_{25}NSi$: C, 77.23; H, 8.53; N, 4.74. Found: C, 77.52; H, 8.71; N, 4.86.

2f: yield 81%; mp 80–81 °C; ^{1}H NMR ($CDCl_3$) δ 0.02 (s, 9 H), 1.78 and 2.06 (AB-q, 2 H, *J* = 14.5 Hz), 2.49–2.74 (m, 2 H), 2.97–3.10 (m, 2 H), 3.58 (s, 3 H), 3.84 (s, 3 H), 4.26 (s, 1 H), 6.15 (s, 1 H), 6.59 (s, 1 H), 7.20–7.28 (m, 5 H). Anal. Calcd for $C_{21}H_{29}NO_2Si$: C, 70.94; H, 8.22; N, 3.94. Found: C, 70.68; H, 8.08; N, 3.97.

2-Methyl-2-[(trimethylsilyl)methyl]-1,6,7-trisubstituted-1,2,3,4-tetrahydroisoquinolinium Iodides 3a–f: General Procedure. A solution of 2 (10 mmol) and iodomethane (8.5 g, 60 mmol) or iodotrideuteriomethane (8.7 g, 60 mmol) in MeCN (10 mL) was heated at 60 °C for the time listed in Table I. The solvent was removed, and the residue was recrystallized to give 3. The cis-isomers were isolated by repeated recrystallization from a mixture of AcOEt and MeOH, but isolation of the trans-isomers was difficult. The results are summarized in Tables I and II.

Reaction of 3 with Cesium Fluoride: General Procedure A. Ammonium salt 3a–d (2 mmol) was placed in a 30-mL flask equipped with a magnetic stirrer, a septum, and a test tube which was connected to the flask by a short piece of rubber tubing. CsF (1.52 g, 10 mmol) was placed in the test tube. The apparatus was dried under reduced pressure and was flushed with N_2. DMF (10 mL) was added to the flask with a syringe, and then CsF was added from the test tube. The mixture was stirred for 3 h at room temperature. The reaction mixture was poured into 2% $NaHCO_3$ and extracted with ether. The ethereal extract was washed with 2% $NaHCO_3$, dried ($MgSO_4$), and concentrated under reduced pressure to give mixtures of 6,7-disubstituted 2-methyl-1-[(trimethylsilyl)methyl]-1,2,3,4-tetrahydroisoquinolines 7, *N*-methyl-*N*-[(trimethylsilyl)methyl]-α-alkyl-2-vinylbenzylamines 8 and *N,N*-dimethyl-α-alkyl-2-vinylbenzylamines 9, and *N,N*-dimethyl-2-[2-(1-alkenyl)phenyl]ethylamines 10. The yields were determined on the basis of the proton ratios of ^{1}H NMR of the residual oils. The products were separated on an aluminum column (hexane/ether = 100:0 to 1:1) and distilled under reduced pressure. The aqueous layer after ether extraction was concentrated, and the residue was recrystallized from a mixture of EtOAc and MeOH to give 6,7-disubstituted 2,2-dimethyl-1,2,3,4-tetrahydroisoquinolinium iodides 11. The results are summarized in Table III.

Mixture of 7a and 8a: bp 130 °C (17 mmHg, oven temperature of a Büchi Kugelrohr distillation apparatus). Anal. Calcd for $C_{14}H_{23}NSi$: C, 72.04; H, 9.93; N, 6.00. Found: C, 72.01; H, 10.03; N, 5.72.

7a: ^{1}H NMR ($CDCl_3$) δ −0.03 (s, 9 H), 1.10 (dd, 1 H, *J* = 5.7, 15.2 Hz), 1.21 (dd, 1 H, *J* = 15.2, 7.7 Hz), 2.39 (s, 3 H), 2.64–2.72 (m, 2 H), 2.82–2.90 (m, 1 H), 3.11–3.18 (m, 1 H), 3.64 (dd, 1 H,

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J = 7.7, 5.7 Hz), 7.02–7.25 (m, 4 H).

8a: ^{1}H NMR ($CDCl_3$) δ 0.04 (s, 9 H), 1.91 (s, 2 H), 2.16 (s, 3 H), 3.46 (s, 2 H), 5.26 (dd, 1 H, J = 1.7, 11.0 Hz), 5.63 (dd, 1 H, J = 1.7, 17.6 Hz), 7.05–7.32 (m, 4 H), 7.51 (dd, 1 H, J = 8.9, 1.8 Hz).

9a: ^{1}H NMR ($CDCl_3$) δ 2.27 (s, 6 H), 3.48 (s, 2 H), 5.33 (dd, 1 H, J = 11.0, 1.5 Hz), 5.70 (dd, 1 H, J = 17.4, 1.5 Hz), 7.19 (dd, 1 H, J = 17.4, 11.0 Hz), 7.08–7.30 (m, 3 H), 7.56 (dd, 1 H, J = 5.7, 2.2 Hz); exact mass calcd for $C_{11}H_{15}N$ 161.1204, found 161.1193.

11a: mp 192–193 °C (lit.[12] mp 189 °C).

Mixture of **7b** and **8b**: bp 155 °C (15 mmHg, Kugelrohor). Anal. Calcd for $C_{16}H_{27}NO_2Si$: C, 65.48; H, 9.27; N, 4.77. Found: C, 65.40; H, 9.48; N, 4.83.

7b: ^{1}H NMR ($CDCl_3$) δ −0.01 (s, 9 H), 1.07 (dd, 1 H, J = 5.7, 15.2 Hz), 1.16 (dd, 1 H, J = 15.2, 8.0 Hz), 2.37 (s, 3 H), 2.56 (ddd, 1 H, J = 15.9, 5.1, 5.0 Hz), 2.64 (ddd, 1 H, J = 12.8, 5.1, 5.0 Hz), 2.78 (ddd, 1 H, J = 15.9, 8.7, 5.1 Hz), 3.10 (ddd, 1 H, J = 5.1, 8.7, 12.8 Hz), 3.54 (dd, 1 H, J = 8.0, 5.7 Hz), 3.84 (s, 3 H), 3.85 (s, 3 H), 6.53 (s, 1 H), 6.55 (s, 1 H).

8b: ^{1}H NMR ($CDCl_3$) δ 0.05 (s, 9 H), 1.90 (s, 2 H), 2.18 (s, 3 H), 3.42 (s, 2 H), 3.89 (s, 3 H), 3.91 (s, 3 H), 5.18 (dd, 1 H, J = 1.3, 10.6 Hz), 5.52 (dd, 1 H, J = 17.8, 1.3 Hz), 6.87 (s, 1 H), 7.02 (s, 1 H), 7.14 (dd, 1 H, J = 17.8, 10.6 Hz).

9b: ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 6 H), 3.40 (s, 2 H), 3.89 (s, 3 H), 3.91 (s, 3 H), 5.21 (dd, 1 H, J = 1.3, 11.0 Hz), 5.56 (dd, 1 H, J = 1.3, 17.4 Hz), 6.81 (s, 1 H), 7.04 (s, 1 H), 7.08 (dd, 1 H, J = 17.4, 11.0 Hz); exact mass calcd for $C_{13}H_{19}NO_2$ 221.1416, found 221.1399.

11b: mp 247–248 °C (lit.[13] mp 242–243 °C).

Mixture of **7c** and **8c**: bp 130 °C (16 mmHg, Kugelrohor). Anal. Calcd for $C_{15}H_{25}NSi$: C, 72.81; H, 10.18; N, 5.66. Found: C, 72.86; H, 10.37; N, 5.66.

7c: ^{1}H NMR ($CDCl_3$) δ −0.28 (s, 9 H), 1.31 (s, 3 H), 1.34, 1.46 (ABq, 2 H, J = 15.3 Hz), 2.34 (s, 3 H), 2.60–2.66 (m, 1 H), 2.69–2.80 (m, 2 H), 3.03 (ddd, 1 H, J = 15.6, 10.4, 6.6 Hz), 7.00 (d, 1 H, J = 7.5 Hz), 7.07 (td, 1 H, J = 7.5, 1.5 Hz), 7.13 (t, 1 H, J = 7.5 Hz), 7.19 (dd, 1 H, J = 7.5, 1.5 Hz).

8c: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 1.27 (d, 3 H, J = 6.6 Hz), 1.85 (s, 2 H), 2.19 (s, 3 H), 3.63 (q, 1 H, J = 6.6 Hz), 5.26 (dd, 1 H, J = 1.6, 11.0 Hz), 5.58 (dd, 1 H, J = 1.6, 17.5 Hz), 7.20–7.26 (m, 2 H), 7.32 (dd, 1 H, J = 11.0, 17.5 Hz), 7.40 (dd, 1 H, J = 1.6, 7.3 Hz), 7.47 (dd, 1 H, J = 1.9, 7.3 Hz).

Mixture of **9c** and **10c**: bp 90 °C (15 mmHg, Kugelrohor). Anal. Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.78; N, 7.99. Found: C, 82.43; H, 9.80; N, 8.05.

9c: ^{1}H NMR ($CDCl_3$) δ 1.30 (d, 3 H, J = 6.6 Hz), 2.21 (s, 6 H), 3.51 (q, 1 H, J = 6.6 Hz), 5.28 (dd, 1 H, J = 1.5, 17.4 Hz), 5.57 (dd, 1 H, J = 1.5, 11.0 Hz), 7.18–7.28 (m, 3 H), 7.42–7.46 (m, 2 H).

10c: ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 6 H), 2.44–2.49 (m, 2 H), 2.84–2.88 (m, 2 H), 5.31 (dd, 1 H, J = 10.9, 1.4 Hz), 5.65 (dd, 1 H, J = 1.4, 17.3 Hz), 6.99 (dd, 1 H, J = 17.3, 10.9 Hz), 7.15–7.22 (m, 3 H), 7.26–7.50 (m, 1 H).

11c: mp 187–188 °C.[14]

Mixture of **7d** and **8d**: bp 135 °C (12 mmHg, Kugelrohor). Anal. Calcd for $C_{16}H_{27}NSi$: C, 73.49; H, 10.41; N, 5.36. Found: C, 73.35; H, 10.44; N, 5.36.

7d: ^{1}H NMR ($CDCl_3$) δ −0.29 (s, 9 H), 0.71 (t, 3 H, J = 7.5 Hz), 1.24, 1.36 (ABq, 2 H, J = 15.2 Hz), 1.66–1.80 (m, 2 H), 2.28 (s, 3 H), 2.62–2.82 (m, 3 H), 3.00–3.07 (m, 1 H), 6.94–7.18 (m, 4 H).

8d: ^{1}H NMR ($CDCl_3$) δ 0.00 (s, 9 H), 0.67 (t, 3 H, J = 7.4 Hz), 1.68–1.89 (m, 2 H), 1.89 (s, 2 H), 2.17 (s, 3 H), 3.40–3.50 (m, 1 H), 5.24 (dd, 1 H, J = 11.0, 1.6 Hz), 5.55 (dd, 1 H, J = 17.4, 1.6 Hz), 7.18–7.34 (m, 4 H), 7.46–7.48 (m, 1 H).

Mixture of **9d** and **10d**: bp 100 °C (11 mmHg, Kugelrohor). Anal. Calcd for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.26; H, 10.08; N, 7.39.

9d: ^{1}H NMR ($CDCl_3$) δ 0.65 (t, 3 H, J = 7.4 Hz), 1.26–1.44 (m, 2 H), 2.20 (s, 6 H), 3.39 (dd, 1 H, J = 4.2, 9.5 Hz), 5.27 (dd, 1 H, J = 1.5, 10.9 Hz), 5.55 (dd, 1 H, J = 17.3, 1.5 Hz), 7.18–7.28 (m, 3 H), 7.36 (dd, 1 H, J = 7.5, 1.6 Hz), 7.45 (dd, 1 H, J = 1.6, 7.5 Hz).

10d: ^{1}H NMR ($CDCl_3$) δ 1.90 (dd, 3 H, J = 6.6, 1.7 Hz), 2.32 (s, 6 H), 2.44–2.48 (m, 2 H), 2.82–2.86 (m, 2 H), 6.11 (dq, 1 H, J = 6.6, 15.6 Hz), 6.64 (dq, 1 H, J = 15.6, 1.7 Hz), 7.11–7.18 (m, 3 H), 7.39–7.42 (m, 1 H).

11d: mp 165–166 °C, ^{1}H NMR ($CDCl_3$) δ 1.07 (t, 3 H, J = 7.3 Hz), 1.67–1.81 (m, 1 H), 2.35–2.45 (m, 1 H), 3.22–3.39 (m, 2 H), 3.45 (s, 3 H), 3.70 (s, 3 H), 3.81–3.89 (m, 1 H), 4.20–4.26 (m, 1 H), 4.86 (dd, 1 H, J = 9.7, 2.9 Hz), 7.13–7.54 (m, 4 H). Anal. Calcd for $C_{13}H_{20}IN$: C, 49.22; H, 6.35; N, 4.42. Found: C, 49.19; H, 6.50; N, 4.19.

General Procedure B. In a manner similar to that described above, a mixture of **3e** or **3f** (2 mmol) and CsF (1.52 g, 10 mmol) was treated in DMF (10 mL). The residual oil was distilled under reduced pressure to give a mixture of (*E*)- and (*Z*)-5-benzylidene-2,3-disubstituted-1,3-cyclohexadiene-6-spiro-3′-1′-methylpyrrolidines (*E*)-**5** and (*Z*)-**5** and 7,8-disubstituted 3-methyl-1-phenyl-2,3,4,5-tetrahydro-1*H*-3-benzazepines **6**. The yield was determined from the proton ratios of ^{1}H NMR of the distillate. The results are shown in Table III.

Distillation of the residue from *cis*-**3e** (894 mg, 2.04 mmol) gave a mixture (460 mg) of (*E*)- and (*Z*)-5-benzylidene-1,3-cyclohexadiene-6-spiro-3′-1′-methylpyrrolidine [(*E*)-**5e** and (*Z*)-**5e**] and 3-methyl-1-phenyl-2,3,4,5-tetrahydro-1*H*-3-benzazepine (**6e**): bp 130 °C (0.37 mmHg, Kugelrohor). Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07; N, 5.90. Found: C, 86.10; H, 8.13; N, 5.69.

A part of the distillate was separated on a HPLC column (Merck Hibar LiChrosorb NH_2, 250 mm × 10 mm). The mobile phase was hexane on an initial stage at flow rate of 5 mL/min, and the ratio of ether in hexane was increased linearly to 10% in 15 min. The eluent was monitored at a 254-nm UV detector. Fractions of retention time 14.8, 15.7, and 17.2 min were collected and concentrated to give (*Z*)-**5e**, (*E*)-**5e**, and **6e**, respectively.

(*E*)-**5e**: ^{1}H NMR ($CDCl_3$) δ 1.93–2.00 (m, 1 H), 2.09–2.17 (m, 1 H), 2.40 (s, 3 H), 2.60 (d, 1 H, J = 9.5 Hz), 2.73 (d, 1 H, J = 9.5 Hz), 2.76–2.80 (m, 2 H), 5.91–5.98 (m, 3 H), 6.68 (br d, 1 H, J = 9.6 Hz), 6.74 (s, 1 H), 7.18–7.36 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 42.12 (q), 57.11 (t), 48.20 (s), 55.28 (t), 65.86 (t), 116.34 (d), 123.31 (d), 123.45 (d), 126.53 (d), 126.95 (d, 2 C), 128.66 (d), 128.75 (d), 129.75 (d), 129.90 (d), 138.40 (s), 144.30 (s).

(*Z*)-**5e**: ^{1}H NMR ($CDCl_3$) δ 1.63–1.70 (m, 1 H), 1.87 (ddd, 1 H, J = 13.3, 8.1, 5.1 Hz), 2.12 (s, 3 H), 2.22 (ddd, 1 H, J = 13.3, 8.6, 3.5 Hz), 2.65 (d, 1 H, J = 9.4 Hz), 2.72–2.78 (m, 1 H), 2.76 (d, 1 H, J = 9.4 Hz), 5.78–5.90 (m, 3 H), 6.14 (dd, 1 H, J = 0.9, 9.3 Hz), 6.69 (s, 1 H), 7.21–7.32 (m, 5 H); the NOE enhancement (12%) of 4-H (δ 6.14) was observed upon irradiation of the benzylidene protons (δ 6.69); ^{13}C NMR ($CDCl_3$) δ 41.44 (q), 42.86 (t), 47.68 (s), 57.10 (t), 62.88 (t), 117.81 (d), 121.98 (d), 126.53 (d), 127.83 (d, 2 C), 128.17 (d), 128.83 (d), 129.67 (d), 131.17 (d), 133.19 (d), 141.17 (s), 143.03 (s).

6e: ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3 H), 2.37–2.42 (m, 1 H), 2.83–2.92 (m, 3 H), 3.07–3.18 (m, 2 H), 4.36 (d, 1 H, J = 8.4 Hz), 6.66 (d, 1 H, J = 5.9 Hz), 6.99–7.52 (m, 8 H).

Distillation of the residue from **3e**-d_3 (883 mg, 2.00 mmol) gave a mixture (418 mg) of (*E*)- and (*Z*)-5-benzylidene-1,3-cyclohexadiene-6-spiro-3′-1′-(trideuteriomethyl)pyrrolidine [(*E*)-**5e**-d_3 and (*Z*)-**5e**-d_3] and 3-(trideuteriomethyl)-1-phenyl-2,3,4,5-tetrahydro-1*H*-3-benzazepine (**6e**-d_3): bp 130 °C (0.37 mmHg, Kugelrohr). The following signals were not observed in ^{1}H NMR ($CDCl_3$) (*E*)-**5e**-d_3: δ 2.40 (s, 3 H) in (*E*)-**5e**; (*Z*)-**5e**-d_3: δ 2.12 (s, 3 H) in (*Z*)-**5e**; **6e**-d_3: δ 2.39 (s, 3 H) in **6e**.

Distillation of the residue from *trans*-**3f** (1.022 g, 2.05 mmol) gave a mixture (494 mg) of (*E*)- and (*Z*)-5-benzylidene-2,3-dimethoxy-1,3-cyclohexadiene-6-spiro-3′-1′-methylpyrrolidine [(*E*)-**5f** and (*Z*)-**5f**] and 7,8-dimethoxy-3-methyl-1-phenyl-2,3,4,5-tetrahydro-1*H*-3-benzazepine[15] (**6f**): bp 170 °C (0.09 mmHg, Kugelrohor). Anal. Calcd for $C_{19}H_{23}NO_2$: C, 76.74; H, 7.79; N, 4.71. Found: C, 76.51; H, 7.84; N, 4.44.

A part of the distillate was separated on a Hiber LiChrosorb NH_2 column. The mobile phase was a mixture of 60% dichloromethane in hexane at a flow rate of 5 mL/min. The eluent

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was monitored at a 240-nm UV detector. Two fractions of retention time 5.5 and 8–10 min were collected and concentrated to give **6f** and a mixture of (*E*)- and (*Z*)-**5f**, respectively. The mixture of **5f** was separated on the HPLC column. The mobile phase was a mixture 50% ether in hexane for 10 min at flow rate of 5 mL/min, increased linearly to 80% in 2 min. Fractions of (*E*)-**5f** (10.0 min) and (*Z*)-**5f** (13.5 min) were collected.

(*E*)-**5f**: ^{1}H NMR ($CDCl_3$) δ 2.07–2.14 (m, 2 H), 2.40 (s, 3 H), 2.60 (d, 1 H, J = 9.5 Hz), 2.65–2.76 (m, 1 H), 2.79 (d, 1 H, J = 9.5 Hz), 2.84–2.90 (m, 1 H), 3.65 (s, 3 H), 3.66 (s, 3 H), 5.07 (s, 1 H), 6.05 (s, 1 H), 6.45 (s, 1 H), 7.16–7.39 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 42.25 (q), 47.94 (t), 48.14 (s), 55.25 (q), 55.38 (q), 56.93 (t), 76.45 (t), 97.22 (d), 109.98 (d), 122.62 (d), 125.95 (d), 128.26 (d, 2 C), 128.92 (d, 2 C), 138.80 (s), 143.91 (s), 147.30 (s), 150.72 (s).

(*Z*)-**5f**: ^{1}H NMR ($CDCl_3$) δ 1.56–1.62 (m, 1 H), 1.92 (ddd, 1 H, J = 12.9, 7.7, 5.2 Hz), 2.11 (s, 3 H), 2.31 (ddd, 1 H, J = 12.9, 8.5, 3.9 Hz), 2.75 (d, 1 H, J = 9.2 Hz), 2.78–2.83 (m, 1 H), 2.94 (d, 1 H, J = 9.2 Hz), 3.62 (s, 3 H), 3.73 (s, 3 H), 5.02 (s, 1 H), 5.45 (s, 1 H), 6.53 (s, 1 H), 7.13–7.39 (m, 5 H). ^{13}C NMR ($CDCl_3$) δ 41.93 (q), 44.14 (t), 47.69 (s), 55.10 (q), 55.14 (q), 55.59 (t), 72.34 (t), 104.22 (d), 110.79 (d), 126.32 (d), 126.80 (d), 127.56 (d, 2 C), 130.15 (d, 2 C), 139.27 (s), 142.58 (s), 144.47 (s), 148.97 (s).

Reaction of 3e,f with CsF in the Presence of DBU: General Procedure. To a solution of **3e,f** (2 mmol) in DMF (10 mL) prepared in a manner similar to that described in General Procedure A above was added DBU (1.52 g, 10 mmol) by syringe. Then, CsF (1.52 g, 10 mmol) was added and the mixture was stirred for 3 h at room temperature. The mixture was poured into 2% $NaHCO_3$ and extracted with ether. The extract was washed with 2% $NaHCO_3$, dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was chromatographed on an aluminum oxide column (hexane:ether = 19:1).

6-Methyl-5,6,7,8-tetrahydro-13*H*-dibenzo[*c*,*f*]azonine (**17e**): yield 281 mg (59%); bp 200 °C (8 mmHg, Kugelrohor); ^{1}H NMR ($CDCl_3$) δ 2.26 (s, 3 H), 2.71 (t, 2 H, J = 5.9 Hz), 3.03–3.08 (m, 2 H), 3.43 (s, 2 H), 4.25 (s, 2 H), 6.99–7.52 (m, 8 H). Anal. Calcd for $C_{17}H_{19}N$: C, 86.03; H, 8.07, N, 5.90. Found: C, 86.09; H, 8.03; N, 5.85.

10,11-Dimethoxy-6-methyl-5,6,7,8-tetrahydro-13*H*-dibenzo-[*c*,*f*]azonine (**17f**): yield 380 mg (64%); mp 99–100 °C (EtOH, lit.[16] mp 102–104 °C).

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Supplementary Material Available: X-ray crystallographic data for *cis*-**3f**, ^{1}H NMR data of **6f**, **11a–c**, and **17f**, and microanalyses data of **3a**, **3b**, *cis*-**3c**, *cis*-**3d**, *cis*-**3e**, *cis*-**3e**-d_3, and *cis*-**3f** (26 pages). This material is contained in many libraries on microfiche, immediately allows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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Facile Generation and Trapping of α-Oxo-*o*-quinodimethanes: Synthesis of 3-Aryl-3,4-dihydroisocoumarins and Protoberberines

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Fluorodesilylation of *o*-((trimethylsilyl)methyl)benzoyl derivatives **5** in the presence of aromatic aldehydes and alkyl fumarates gives 3-aryl-3,4-dihydroisocoumarins **6** and α-tetralones **10**, respectively. Reaction of **5** with 3,4-dihydroisoquinolinium salts **19** leads to 8-oxoberbines **21**. Using this procedure, racemic hydrangenol, phyllodulcin, tetrahydropalmatine (**22a**), and canadine (**22b**) have been synthesized.

Ever since the firm postulation of *o*-quinodimethanes (oQDM) (**1**) by Cava in 1957,[1] these reactive intermediates have been used to construct a variety of molecular frameworks by inter- or intramolecular [4 + 2] trapping.[2] Many methods for oQDM generation have been developed over the years.[3] A particularly convenient approach, introduced by Ito,[4] entails F^--promoted desilylation to effect a 1,4-elimination in an *o*-((trimethylsilyl)alkyl)benzyltrimethylammonium compound (**2** → **1**). This procedure can be extended to functionalized oQDM which can, in turn, afford usefully functionalized target molecules.[5] For example, α-imino-oQDM (**3a**) generated in such a manner was trapped with suitable dienophiles and the obtained adduct **4a** hydrolyzed to obtain tetralone **4b**.[6] This sequence amounts to a [4 + 2] addition of α-oxo-oQDM (**3b**)

Table I. Synthesis of 3-Substituted 3,4-Dihydroisocoumarins 6 and 7, 1-Tetralones 10, and 3-Arylisocoumarin 11

entry	substrate	dienophile	product (isolated yield, %)
1	**5a**	C_6H_5CHO	**6a** (38)
2	**5a**	*o*-MeC_6H_4CHO	**6b** (38)
3	**5a**	*p*-$MeOC_6H_4CHO$	**6c** (51)
4	**5a**	3,4-$(MeO)_2C_6H_3CHO$	**6d** (62)
5	**5a**	CCl_3CHO	**7** (90)
6	**5b**	*p*-$MeOC_6H_4CHO$	**6e** (50)
7	**5b**	3-$PhCH_2O$-4-$MeOC_6H_3CHO$	**6f** (53)
8	**5a**	*trans*-MeOOCCH=CHCOOMe	**10a** (48)
9	**5a**	*trans*-EtOOCCH=CHCOOEt	**10b** (60)
10	**5a**		**11** (70)

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