or alternatively the symmetry observed in some β-diketone structures is the result of statistical disorder.

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Supplementary Material Available: Table of anisotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

A New Approach to Asymmetric Synthesis of Polycycles on the Basis of *o*-Quinodimethane Generation

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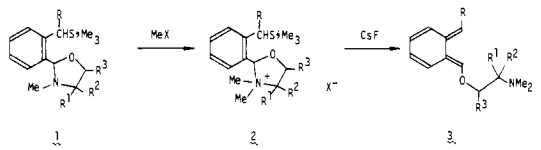
Abstract: The fluoride anion induced 1,4 elimination of 2-[*o*-[1-(trimethylsilyl)alkyl]phenyl]-3,3-dimethyloxazolidinium salts generates (*E*,*E*)-α-alkyl-α′-[2-(dimethylamino)alkyl]-*o*-quinodimethane intermediates, which are trapped stereoselectively with dienophiles to give polycycles. Intramolecular cyclization of 2-[*o*-[1-(trimethylsilyl)hept-6-enyl]phenyl]-3,3-dimethyl-4-(*R*)-methyl-5(*R*)-phenyloxazolidinium triflate at 0 °C produces a 3:1 diastereoisomeric mixture of 6-[2(*R*)-(dimethylamino)-1(*R*)-phenylpropoxyl]-*trans*-octahydrophenanthrene, which is converted by hydrogenolysis on Pd/C to *trans*-octahydrophenanthrene with $[\alpha]_D$ +46.6° (50% ee). Similarly, intramolecular cyclization of 2-[*o*-[1-(trimethylsilyl)hept-6-enyl]phenyl]-3,3-dimethyl-4(*S*)-methoxymethyl-5(*S*)-phenyloxazolidinium triflate produces, after hydrogenolysis on Pd/C, *trans*-octahydrophenanthrene with $[\alpha]_D$ −51.1° (55% ee). The enantioselection in the cycloaddition with *o*-quinodimethane intermediate may be accounted for on the basis of π-stacking interaction in the Diels–Alder transition state.

A variety of methodologies[1] have so far been developed to generate in situ *o*-quinodimethane and applied to synthesize polycycles including steroidal structures by their cycloaddition reactions. However, a generation of *o*-quinodimethanes with electron-donating heteroatom substituents[2] at the α position, which may be expected to exert higher regioselectivity and higher reactivity in Diels–Alder cycloaddition, has been scarcely known. In the preceding papers[3], we reported a mild and efficient generation of *o*-quinodimethanes by the fluoride anion induced 1,4-elimination of *o*-[1-(trimethylsilyl)alkyl]benzyltrimethylammonium halides. The methodology for the generation of *o*-quinodimethanes has been successfully extended to 2-[*o*-[1-(trimethylsilyl)alkyl]phenyl]-3,3-dimethyloxazolidinium salts (**2**),



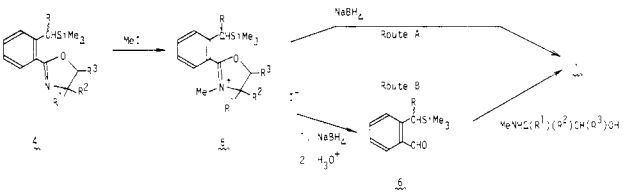
1 **2** **3**

a, R = H; R^1 = R^2 = Me; R^3 = H
b, R = R^1 = R^2 = H; R^3 = Me
c, R = $-(CH_2)_4CH{=}CH_2$; R^1 = R^2 = H; R^3 = Me
d, R = $-(CH_2)_4CH{=}CH_2$; R^1 = R^2 = H; R^3 = (*R*)-Ph
e, R = $-(CH_2)_4CH{=}CH_2$; R^1 = (*S*)-Me; R^2 = H; R^3 = (*R*)-Ph
f, R = $-(CH_2)_4CH{=}CH_2$; R^1 = (*R*)-Me; R^2 = H; R^3 = (*R*)-Ph
g, R = $-(CH_2)_4CH{=}CH_2$; R^1 = (*S*)-CH_2OMe; R^2 = H; R^3 = (*S*)-Ph
h, R = $-(CH_2)_4CH{=}CH_2$; R^1 = (*R*)-Ph; R^2 = R^3 = H
i, R = $-(CH_2)_4CH{=}CH_2$; R^1 = (*S*)-CH_2Ph; R^2 = R^3 = H
j, R = H; R^1 = (*S*)-Me; R^2 = H; R^3 = (*R*)-Ph

leading to the formation of (*E*,*E*)-α-alkyl-α′-[2-(dimethylamino)alkoxy]-*o*-quinodimethane intermediates (**3**).

In this paper, we describe a synthesis of polycycles by the inter- and intramolecular cycloadditions of **3**. Of special interest is that

Scheme I



a, R = H; R^1 = R^2 = Me; R^3 = H
b, R = R^1 = R^2 = H; R^3 = Me
c, R = $-(CH_2)_4CH{=}CH_2$; R^1 = R^2 = Me; R^3 = H
d, R = $-(CH_2)_4CH{=}CH_2$; R^1 = R^2 = H; R^3 = Me

some 2-[*o*-[1-(trimethylsilyl)alkyl]phenyl]-3,3-dimethyloxazolidinium salts (**2**) with a phenyl substituent at the C-5 on the oxazolidinium ring were cyclized enantioselectively via the corresponding *o*-quinodimethanes to afford polycycles. This reaction, which is the first use of *o*-quinodimethane in asymmetric synthesis, may present a new approach to asymmetric synthesis of polycycles. The 2-(dimethylamino)alkoxy substituent of **3**, which conferred high reactivity in reactions with dienophiles and brought about the asymmetric induction, was easily removed after the reactions.

Results and Discussions

Preparation of the requisite oxazolidines **1**[4] for the generation of *o*-quinodimethanes **3** could be carried out via quaternization and reduction of the corresponding 2-[*o*-[(trimethylsilyl)-methyl]phenyl]oxazolines (**4**) and 2-[*o*-[1-(trimethylsilyl)alkyl]phenyl]oxazolines (**4**, R = alkyl), which were accessible from alkylations at the silicon-stabilized carbanion of **4** R = H[4a] (route A in Scheme I). Thus, 2-[*o*-[(trimethylsilyl)methyl]phenyl]-3,4,4-trimethyloxazolidine (**1a**) and 2-[*o*-[1-(trimethylsilyl)-hept-6-enyl]phenyl]-3,5-dimethyloxazolidine (**1c**) were prepared

(1) Oppolzer, W., *Synthesis*, **1978**, 793.
(2) Sammes, P. G. *Tetrahedron* **1976**, *32*, 405.
(3) (a) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 863. (b) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1981**, *103*, 476.
(4) (a) Gschwend, H. W.; Hamdan, A. *J. Org. Chem.* **1975**, *40*, 2008. (b) Nordin, I. C. *J. Heterocycl. Chem.* **1966**, *3*, 531. (c) Meyers, A. I.; Nabeya, A.; Adickes, H. W.; Politzer, I. R.; Malone, G. R.; Kovelesky, A. C.; Nolen, R. L.; Portnoy, R. C. *J. Org. Chem.* **1973**, *38*, 36.

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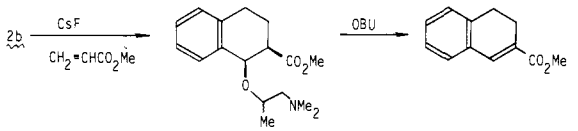
in satisfactory yields. However, this direct route (A) to the oxazolidine precursors **1** often gave rise to a mixture containing a byproduct, which arose from the reductive ring opening of the oxazolidine.[4c] Moreover, route A was not applied to the preparation of optically active 2-[*o*-[1-(trimethylsilyl)alkyl]phenyl]-5-phenyloxazolidines (**1d–g**), which possess an asymmetric carbon at the C-5 of the oxazolidine ring, because the quaternization of the corresponding 2-[*o*-[1-(trimethylsilyl)alkyl]phenyl]-5-phenyloxazolines (**4**) was accompanied with the racemation.

A more general and practical preparation[5] of **1** was performed by the reaction of 2-(methylamino) alcohol with *o*-[1-(trimethylsilyl)alkyl]benzaldehydes (**6**) (route B), which were available in high yield[4c] via reduction and hydrolysis of 2-[*o*-[1-(trimethylsilyl)alkyl]phenyl]-3,4,4-trimethyloxazolinium iodide (**5**).

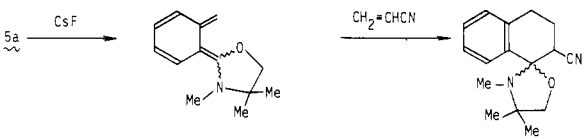
A regio- and stereoselective intermolecular cycloaddition of **3** is demonstrated by the trapping of **3** with methyl acrylate. When 2-[*o*-[(trimethylsilyl)methyl]phenyl]-3,3,5-trimethyloxazolidinium iodide (**2b**) was reacted with CsF in acetonitrile in the presence of methyl acrylate at room temperature, a 1:1diastereoisomeric mixture of *cis*-1-[2-(dimethylamino)-1-methylethoxy]-2-(methoxycarbonyl)-1,2,3,4-tetrahydronaphthalene (**7b**) was produced



7b 8b

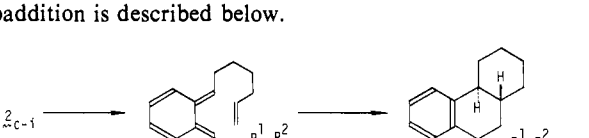
in ca. 90% yield, uncontaminated with its regioisomeric cycloadducts. Treatment of **7b** with DBU afforded 2-(methoxycarbonyl)-3,4-dihydronaphthalene (**8b**).

As might be expected, 2-[*o*-(trimethylsilylmethyl)phenyl]oxazolinium salts (**5**) were also precursors for the generation of α-heteroatom-substituted *o*-quinodimethanes. Specifically, treatment of 2-[*o*-[(trimethylsilyl)methyl)]phenyl]-3,4,4-trimethyloxazolinium iodide (**5a**) with CsF in the presence of



9a 10a

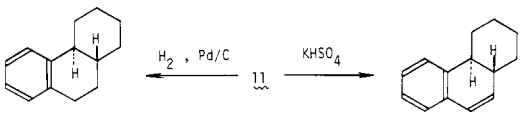
acrylonitrile afforded a cycloadduct (**10a**) as a diastereoisomeric mixture in a good yield, which may be derived from Diels–Alder addition of *o*-quinodimethane intermediate **9a**. However, 2-[*o*-[1-(trimethylsilyl)hept-5-enyl]phenyl]-3,4,4-trimethyloxazolinium iodide (**5c**) was not intramolecularly cyclized on treatment with CsF, unlike 2-[*o*-[1-(trimethylsilyl)hept-6-enyl]-phenyl]oxazolidinium salts (**2c–i**), of which intramolecular cycloaddition is described below.



3c-i 11c-i

On treatment with CsF in acetonitrile at room temperature, 2-[*o*-[1-(trimethylsilyl)alkenyl]phenyl]oxazolidinium salts (**2c**, **2d**[6]**–2i**) thus prepared were intramolecularly cyclized to polycycles **11** in satisfactory yields. This finding is interestingly compared with the fact that the generation of α-(hex-5-enyl)-*o*-quinodimethane from *o*-[1-(trimethylsilyl)hept-6-enyl]benzyltrimethylammonium salt at the same temperature afforded octahydrophenanthrene in only low yield with the spiro dimer predominating.[3a]

For instance, when 2-[*o*-[1-(trimethylsilyl)hept-6-enyl]-phenyl]-3,3,5-trimethyloxazolidinium iodide (**2c**) was stirred with a suspension of CsF (2- to 3-fold excess) in acetonitrile at room temperature overnight, 8,9-*trans*-6-[2-(dimethylamino)-1-methylethoxy]octahydrophenanthrene (**11c**) was produced as a 1:1 diastereoisomeric mixture (80%). Removal of the 2-(dimethylamino)-1-methylethoxy substituent in **11c** was achieved



12 13

by hydrogenolysis with 10% Pd/C in acetic acid containing 2% of aqueous 70% $HClO_4$ (40 kg/cm^2 of H_2, room temperature, 12 h) to give *trans*-octahydrophenanthrene (**12**)[3a] in 75% overall yield from **2c**, which was contaminated by a few percent of the C-9 epimer. The 2-(dimethylamino)-1-methylethoxy substituent was also removed by heating in benzene containing $KHSO_4$ with 2–3% of aqueous 70% $HClO_4$ to give *trans*-hexahydrophenanthrene (**13**) in 76% yield.

The formation of 1:1 mixtures of two diastereoisomers of cis cycloadduct **7b** and of trans cycloadduct **11c** mentioned above may be rationalized by assuming inter- and intramolecular Diels–Alder reactions with *o*-quinodimethane intermediates **3b** and **3c** through the endo and exo transition state, respectively, in which dienophiles approach equally either of the two enantiotopic faces of the reacting diene moiety of **3**. If this assumption is correct, the proper choice of 2-(dimethylamino)alkoxy substituents on **3** might lead to the asymmetric formation of polycycles. It was actually found that some 2-[*o*-[1-(trimethylsilyl)hept-6-enyl]phenyl]-3,3-dimethyl-5-phenyloxazolidinium salts (**2d**,[6] **2e**, **2f**, and **2g**) were cyclized enantioselectively via the corresponding **3** to give polycycles with asymmetric induction.

The intramolecular cyclization of 2-[*o*-[1-(trimethylsilyl)-hept-6-enyl]phenyl]-3,3-dimethyl-4(*R*)-methyl-5(*R*)-phenyloxazolidinium triflate (**2f**) at 0 °C, which was prepared via the reaction of **6**, R = C_6H_{11}, with (−)-pseudoephedrine, produced 6-[2(*R*)-(dimethylamino)-1(*R*)-phenylpropoxy]-*trans*-octahydrophenanthrene (**11f**) as a mixture of two diastereoisomers. The NMR singlets at δ 2.12 and 2.25, which are ascribed to methyl protons on nitrogen of **11f**, in a 3:1 ratio indicate the degree of asymmetric induction. The removal of the 2-(dimethylamino)-alkoxy substituent from **11f** by hydrogenolysis on Pd/C gave *trans*-octahydrophenanthrene (**12**) in 73% overall yield, which showed $[\alpha]^{19}_D$ +46.6° (*c* 1.11, C_6H_{12}). On the other hand, two diastereoisomers of **11f** were separated by preparative TLC on silica gel, and the major diastereoisomer was treated with H_2 on Pd/C to give an optically pure *trans*-octahydrophenanthrene (**12**): mp 41.5–42.0 °C; $[\alpha]^{19}_D$ +92.9° (*c* 1.06, C_6H_{12}). The rotation also indicated that the cycloadduct **11f** consisted of a 75:25 ratio of diastereoisomers.

Similarly, intramolecular cyclization of 2-[*o*-[1-(trimethylsilyl)hept-6-enyl]phenyl]-3,3-dimethyl-4(*S*)-methoxymethyl-5-(*S*)-phenyloxazolidinium triflate (**2g**), which was prepared from **6** (R = C_6H_{11}) and (1*S*,2*S*)-(+)-1-phenyl-2-(methylamino)-3-methoxypropanol, afforded *trans*-octahydrophenanthrene (**12**) with $[\alpha]^{19}_D$ −51.1° (*c* 1.02, C_6H_{12}), after hydrogenolysis on Pd/C. Asymmetric induction in the cyclizations of some 2-[*o*-[1-(trimethylsilyl)hept-6-enyl]phenyl]-3,3-dimethyloxazolidinium salts (**2c–i**) are summarized in Table I. As seen in Table I, a phenyl substituent at the C-5 on the oxazolidinium ring of **2** (**2d–g**) remarkably increased the asymmetric induction in the intramolecular Diels–Alder cycloaddition via **3**. Phenyl and benzyl substituents at the C-4 on the oxazolidinium ring of **2** (**2h** and **2i**) have no significant effect on the enantioselection in the intramolecular cycloaddition.

(5) Neelakantan, L. *J. Org. Chem.* **1971**, *36*, 2256.
(6) Hydrolysis of **2d**, which was prepared via route B, produced α-(*R*)-[(dimethylamino)methyl]benzyl alcohol with $[\alpha]^{19}_D$ −64.9° (*c* 2.0, EtOH) (cf. $[\alpha]_D$ −65° *Chem. Abstr.* **1945**, *39*, 1172).

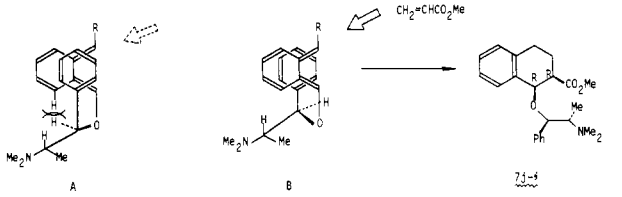
Table I. Intramolecular Cyclizations of 2-[*o*-[1-(Trimethylsilyl)hept-6-enyl]phenyl]-3,3-dimethyloxazolidinium Salts (**2**)

oxazolidinium salt (**2**)			reaction	*trans*-octahydrophenanthrene (**12**)		
C-4	C-5	X	temp, °C	yield, %	$[\alpha]^{19}_D$ (C_6H_{12})	% ee[a]
	Me	I (**2c**)	20	75[b]		
	(*R*)-Ph	I (**2d**)	20	75[b]	+25.8 (*c* 1.18)	28
	(*R*)-Ph	I (**2d**)	0	73[b]	+31.6 (*c* 1.35)	34
(*S*)-Me	(*R*)-Ph	I (**2e**)	20	73[b]	+36.3 (*c* 1.31)	39
(*S*)-Me	(*R*)-Ph	OTf (**2e**)	20	70[c]	+33.4 (*c* 1.20)	36
(*R*)-Me	(*R*)-Ph	OTf (**2f**)	20	78[c]	+40.5 (*c* 1.14)	44
(*R*)-Me	(*R*)-Ph	OTf (**2f**)	0	73[c]	+46.6 (*c* 1.11)	50
(*S*)-$MeOCH_2$	(*S*)-Ph	OTf (**2g**)	0	71[c]	−51.1 (*c* 1.02)	55
(*R*)-Ph		I (**2h**)	20	49	−0.8 (*c* 1.06)	
(*S*)-$PhCH_2$		I (**2i**)	20	56	−1.7 (*c* 1.79)	

[a] % ee was calculated on the basis of the maximum rotation $[\alpha]^{19}_D$ 92.9° (*c* 1.06, C_6H_{12}). [b] Overall yield based upon oxazolidinium salt **2**. [c] Overall yield based upon oxazolidine precursor **1**.

On the other hand, the intermolecular cycloaddition of 2-[*o*-[(trimethylsilyl)methyl]phenyl]-3,3-dimethyl-4(*S*)-methyl-5-(*R*)-phenyloxazolidinium triflate (**2j**), which was prepared from **6** (R = H) and (−)-ephedrine, with methyl acrylate afforded a 2:1 diastereoisomeric mixture of *cis*-1-[2(*S*)-(dimethylamino)-1-(*R*)-phenylpropoxy]-2-(methoxycarbonyl)-1,2,3,4-tetrahydronaphthalene (**7j**) in 92% yield. The major diastereoisomer **7j**-i, which was separated by preparative TLC on silica gel, was treated with H_2 on Pd/C followed by hydrolysis (4 molar equiv of KOH in $MeOH/H_2O$, room temperature, 10 h) to furnish 1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (**14**)[7] with the *R* configuration as determined by comparison with the known rotation and configuration of **14**.[8] Consequently, the major diastereoisomer of **7j** was assigned to the 1(*R*),2(*R*) configuration depicted in **7j**-i.

Although the absolute configuration of **11** and/or **12** produced has not been determined, the enantioselection in the Diels–Alder cycloaddition via *o*-quinodimethane intermediates may be accounted for in accordance with Trost's observation[9] that π-stacking interactions may serve as a steric steering group to direct the incoming dienophile to one of the two enantiotopic faces of the diene. The two conformations A and B depicted below may be



envisioned for the π-stacking interaction in the present Diels–Alder cycloaddition. Inspection of molecular models reveals that the former encounters a severe nonbonded interaction between the aromatic hydrogen and the benzylic hydrogen adjacent to the ether oxygen as indicated in A and the latter would be favored.

Experimental Section

Material. (−)-Ephedrine hydrochloride and (−)-pseudoephedrine were commercially available. 2(*R*)-(Methylamino)phenethyl alcohol $[[\alpha]^{20}_D$ −79.6° (*c* 1.0, EtOH)] and 2(*S*)-(methylamino)-3-phenylpropanol $[[\alpha]^{20}_D$ +22.0° (*c* 1.0, EtOH)] were prepared from D-α-phenylglycine and L-phenylalanine, respectively, via N-formylation[10] and $LiAlH_4$ reduction.[11] 2-(Methylamino)-1(*R*)-phenylethanol $[[\alpha]^{20}_D$ −40.7° (*c* 1.3, EtOH)] was prepared by $LiAlH_4$ reduction of the *N*-methylamide of D-(−)-mandelic acid.[12] (1*S*,2*S*)-(+)-1-Phenyl-2-(methylamino)-3-methoxypropanol $[[\alpha]^{23}_D$ +61.3° (*c* 1.5, $CHCl_3$); bp 117 °C (0.1 torr)] was prepared by N-formylation[10] and $LiAlH_4$ reduction[11] of (1*S*,2*S*)-(+)-1-phenyl-2-amino-3-methoxypropanol $[[\alpha]^{24}_D$ +26.4° (*c* 1.7, $CHCl_3$)], which was synthesized according to the reported procedure.[13] 2-[*o*-[(Trimethylsilyl)methyl]phenyl]-4,4-dimethyloxazoline (**4a**) and 2-[*o*-[(trimethylsilyl)methyl]phenyl]-5-methyloxazoline (**4b**) were prepared by lithiation and silylation[14] of the corresponding 2-(*o*-tolyl)oxazolines[15] on the basis of the reported procedure.

Preparation of 2-[*o*-[1-(Trimethylsilyl)hept-6-enyl]phenyl]-5-methyloxazoline (4d). To a stirring solution of 9.12 g (36.9 mmol) of **4b** in 60 mL of ether, 1.5 molar equiv of *n*-BuLi (1.6 M hexane solution) was added at 0 °C. After 30 min, 2 molar equiv of HMPA and then 11.6 g (55.4 mmol) of 5-hexenyl iodide were added to the resultant deep red solution at 0 °C and stirred overnight at room temperature. The reaction mixture was quenched by adding aqueous $NaHCO_3$ and extracted with ether. The ether extract was distilled to give **4d**: bp 110 °C (0.1 torr); 85% yield; IR (neat) 840, 855, 910, 990, 1250, 1640 cm^{-1}; NMR ($CDCl_3$) δ 0.03 (s, 9 H), 1.51 (d, *J* = 5.3 Hz, 3 H), 1.08–2.23 (m, 8 H), 3.40 (t, *J* = 7 Hz, 1 H), 3.35–4.43 (m, 2 H), 4.63–5.14 (m, 3 H), 5.48–6.23 (m, 1 H), 6.83–7.83 (m, 4 H). Anal. Calcd for $C_{20}H_{31}NOSi$: C, 72.91; H, 9.48; N, 4.25. Found: C, 72.77; H, 9.65; N, 4.50.

2-[*o*-[1-(Trimethylsilyl)hept-6-enyl]phenyl]-4,4-dimethyloxazoline (4c): bp 110 °C (0.1 torr); 89% yield; IR (neat) 840, 850, 910, 990, 1245, 1640 cm^{-1}; NMR ($CDCl_3$) δ 0.03 (s, 9 H), 1.38 (s, 6 H), 0.93–2.18 (m, 8 H), 3.33 (t, *J* = 7.5 Hz, 1 H), 3.98 (s, 2 H), 4.68–5.13 (m, 2 H), 5.33–6.08 (m, 1 H), 6.83–7.73 (m, 4 H). Anal. Calcd for $C_{21}H_{33}NOSi$: C, 73.42; H, 9.68; N, 4.08. Found C, 73.56; H, 9.90; N, 3.92.

Preparation of 2-[*o*-[1-(Trimethylsilyl)hept-6-enyl]phenyl]-3,5-dimethyloxazolidine (1c). To a solution of 2.26 g (6.86 mmol) of **4d** in 7 mL of acetonitrile was added 2.84 g (20 mmol) of methyl iodide, and the solution was heated at 40–50 °C for 4 h. The reaction mixture was evaporated in vacuo and then washed twice with a mixture of ether–hexane. The residue was dissolved in 10 mL of methanol and cooled down to −78 °C, to which 0.13 g (3.43 mmol) of $NaBH_4$ was added with vigrous stirring for 5 min. The reaction mixture was quenched with aqueous K_2CO_3 and extracted with ether. The ether extract was distilled to afford **1c**: bp 115 °C (0.1 torr); 77% yield; IR (neat) 835, 850, 910, 1010, 1245, 1638 cm^{-1}; NMR ($CDCl_3$) δ 0.00 (s, 9 H), 0.80–3.00 (m, 10 H), 1.17–1.40 (m, 3 H), 2.10–2.20 (m, 3 H), 3.20–3.60 (m, 1 H), 3.95–4.60 (m, 1 H), 4.60–5.10 (m, 3 H), 5.15–6.10 (m, 1 H), 6.85–7.70 (m, 4 H). Anal. Calcd for $C_{21}H_{35}NOSi$: C, 73.00; H, 10.21, N, 4.05. Found: C, 73.11; H, 10.35; N, 3.98.

According to the above procedure, oxazolidines **1a** and **1b** were prepared in 75–85% yields from oxazolines **4a** and **4b**, respectively.

2-[*o*-[(Trimethylsilyl)methyl]phenyl]-3,4,4-trimethyloxazolidine (1a): bp 82 °C (0.1 torr); IR (neat) 840, 1240, 1600 cm^{-1}; NMR ($CDCl_3$) δ

(7) The compound **7j**-i was converted by hydrogenolysis on Pd/C and then alkaline hydrolysis to 1,2,3,4-tetrahydronaphthalene-2-carboxylic acid (**14**) with $[\alpha]^{22}_D$ +37.24° (*c* = 1.23, $CHCl_3$), which corresponds to 67.1% ee from the known optically pure (*R*)-**14**, $[\alpha]^{22}_D$ +55.5° (*c* 1.4, $CHCl_3$).[8]

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0.03 (s, 9 H), 1.12 and 1.25 (two s, 6 H), 2.18 (s, 3 H), 2.38 (s, 2 H), 3.73 (s, 2 H), 5.03 (s, 2 H), 6.75–7.60 (m, 4 H). Anal. Calcd for $C_{16}H_{27}NOSi$: C, 69.28; H, 9.81; N, 5.05. Found: C, 69.44; H, 10.01, N, 4.95.

2-[*o*-[(Trimethylsilyl)methyl]phenyl]-3,5-dimethyloxazolidine (1b): bp 85 °C (0.1 torr); IR (neat) 840, 1240, 1600 cm^{-1}; NMR ($CDCl_3$) δ 0.00 (s, 9 H), 1.20 and 1.27 (two d, J = 6 Hz, 3 H), 2.09 and 2.12 (two s, 3 H), 2.16 (broad s, 2 H), 2.30–3.55 (m, 2 H), 3.90–4.50 (m, 1 H), 4.76 (broad s, 1 H), 6.70–7.65 (m, 4 H). Anal. Calcd for $C_{15}H_{25}NOSi$: C, 68.41; H, 9.57; N, 5.32. Found: C, 68.58; H, 9.44; N, 5.11.

***o*-[1-(Trimethylsilyl)hept-6-enyl]benzaldehyde (6, $R = C_6H_{11}$)**. A solution of 11.5 g (33.5 mmol) of 2-[*o*-[1-(trimethylsilyl)hept-6-enyl]-phenyl]-4,4-dimethyloxazoline (**4c**) and 14.2 g (100 mmol) of methyl iodide in 35 mL of acetonitrile was heated at 40–50 °C for 7 h. The reaction mixture was evaporated in vacuo and triturated with ether to give 2-[*o*-[1-(trimethylsilyl)hept-6-enyl]phenyl]-3,4,4-trimethyl-oxazolinium iodide (**5c**) in 90% yield. Next, to a vigorously stirred solution of 6.0 g (12.4 mmol) of the oxazolinium iodide in 70 mL of ethanol was added a solution of 0.23 g (6.2 mmol) of $NaBH_4$ and 2.5 g (24.8 mmol) of triethylamine in 20 mL of ethanol at −78 °C in 30 s, with stirring for another 30 s. To the reaction solution was added 40 mL of aqueous 5% HCl, and then the solution was warmed to room temperature over 3 h. The mixture was diluted with 50 mL of water and extracted with hexane. The hexane extract was distilled to furnish *o*-[1-(trimethylsilyl)hept-6-enyl]benzaldehyde (**6**, R = C_6H_{11}): bp 75 °C (0.1 torr); 75% yield; IR (neat) 850, 1250, 1640, 1695 cm^{-1}; NMR($CDCl_3$) δ −0.07 (s, 9 H), 1.05–2.15 (m, 8 H), 3.55 (dd, 1 H), 4.70–5.10 (m, 2 H), 5.40–6.15 (m, 1 H), 7.05–7.90 (m, 4 H), 10.38 (s, 1 H). Anal. Calcd for $C_{17}H_{26}OSi$: C, 74.39; H, 9.55. Found: C, 74.61; H, 9.80.

***o*-[(Trimethylsilyl)methyl]benzaldehyde (6, R = H)**: bp 80 °C (2 torr); IR (neat) 850, 1245, 1690 cm^{-1}; NMR ($CDCl_3$) δ 0.00 (s, 9 H), 2.68 (s, 2 H), 6.97–7.88 (m, 4 H), 10.21 (s, 1 H). Anal. Calcd for $C_{11}H_{16}OSi$: C, 68.69; H, 8.39. Found: C, 68.57; H, 8.51.

Preparations of 2-[*o*-[1-[(trimethylsilyl)methyl]alkyl]phenyl]oxazolidines (1) from *o*-[1-(trimethylsilyl)alkyl]benzaldehydes and methylamino alcohols were performed in 87–95% yields according to the reported procedure.[5]

2-[*o*-(Trimethylsilyl)phenyl]-3,4(*S*)-dimethyl-5(*R*)-phenyloxazolidine (1j): mp 51–52 °C; IR (neat) 850, 1245, 1600 cm^{-1}; NMR ($CDCl_3$) δ 0.00 (s, 9 H), 0.70 (d, J = 6.5 Hz, 3 H), 2.23 (s, 3 H), 3.40 and 3.49 (two s, 2 H), 2.70–3.30 (m, 1 H), 4.85 (s, 1 H), 5.00 (d, J = 8.2 Hz, 1 H), 6.85–7.90 (m, 9 H). Anal. Calcd for $C_{21}H_{29}NOSi$: C, 74.28; H, 8.61; N, 4.13. Found: C, 74.57; H, 8.86; N, 3.99.

2-[*o*-[1-(Trimethylsilyl)hept-6-enyl]phenyl]-3-methyl-5(*R*)-phenyl-oxazolidine (1d): bp 150 °C (0.1 torr); IR (neat) 850, 910, 990, 1245, 1635 cm^{-1}; NMR ($CDCl_3$) δ −0.04 (s, 9 H), 0.70–2.35 (m, 8 H), 2.20 and 2.22 (two s, 3 H), 2.35–2.90 (m, 1 H), 3.05–3.35 (m, 1 H), 3.70 (m, 1 H), 4.65–6.00 (m, 5 H), 6.80–7.85 (m, 9 H). Anal. Calcd for $C_{26}H_{37}NOSi$: C, 76.61; H, 9.15; N, 3.44. Found: C, 76.48; H, 9.30; N, 3.55.

2-[*o*-[1-(Trimethylsilyl)hept-6-enyl]phenyl]-3-methyl-4(*S*)-methyl-5-(*R*)-phenyloxazolidine (1e): bp 120 °C (0.1 torr); IR (neat) 835, 850, 908, 1020, 1250, 1640 cm^{-1}; NMR ($CDCl_3$) δ 0.00 and 0.08 (two s, 9 H), 0.85 (d, J = 6 Hz, 3 H), 1.15–2.20 (m, 8 H), 2.27 and 2.30 (two s, 3 H), 2.60–2.80 (m, 2 H), 4.70–5.15 (m, 3 H), 5.23 (d, J = 7.5 Hz, 1 H), 5.45–6.15 (m, 1 H), 6.70–7.50 (m, 9 H). Anal. Calcd for $C_{27}H_{39}NOSi$: C, 76.91 H, 9.32; N, 3.32. Found: C, 76.80; H, 9.51; N, 3.29.

2-[*o*-[1-(Trimethylsilyl)hept-6-enyl]phenyl]-3-methyl-4(*R*)-methyl-5-(*R*)-phenyloxazolidine (1f): bp 120 °C (0.1 torr); IR (neat) 835, 850, 907, 1040, 1250, 1640 cm^{-1}; NMR ($CDCl_3$) δ 0.00 (s, 9 H), 1.25 (d, J = 6 Hz, 3 H), 1.10–2.15 (m, 8 H), 2.17 (s, 3 H), 2.30–3.15 (m, 2 H), 4.57–5.07 (m, 3 H), 5.20 (d, J = 4.5 Hz, 1 H), 5.35–6.10 (m, 1 H), 6.90–7.85 (m, 9 H). Anal. Calcd for $C_{27}H_{39}NOSi$: C, 76.91; H, 9.32; N, 3.32. Found: C, 76.99; H, 9.48; N, 3.11.

2-[*o*-[1-(Trimethylsilyl)hept-6-enyl]phenyl]-3-methyl-4(*S*)-methoxy-methyl-5(*S*)-phenyloxazolidine (1g): bp 135–140 °C (0.1 torr); IR (neat) 840, 855, 910, 1040, 1245, 1635 cm^{-1}; NMR ($CDCl_3$) δ −0.3 (s, 9 H), 1.03–2.00 (m, 8 H), 2.15 (s, 3 H), 2.43–2.93 (m, 2 H), 3.14 (s, 3 H), 3.50 (d, J = 5.3 Hz, 2 H), 4.50–4.93 (m, 3 H), 5.10 (d, J = 4.5 Hz, 1 H), 5.20–5.70 (m, 1 H), 6.85–7.75 (m, 9 H). Anal. Calcd for $C_{28}H_{41}NO_2Si$: C, 74.45; H, 9.15. Found: C, 74.71; H, 8.99.

2-[*o*-[1-(Trimethylsilyl)hept-6-enyl]phenyl]-3-methyl-4(*R*)-phenyl-oxazolidine (1h): bp 160 °C (0.1 torr); IR (neat) 835, 850, 907, 990, 1245, 1635 cm^{-1}; NMR ($CDCl_3$) δ −0.01 (s, 9 H), 0.70–2.25 (m, 8 H), 2.08 (s, 3 H), 2.55–3.05 (m, 1 H), 3.15–4.35 (m, 3 H), 4.70–5.05 (m, 2 H), 5.04 and 5.12 (two s, 1 H), 5.37–6.10 (m, 1 H), 6.90–6.95 (m, 9 H). Anal. Calcd for $C_{26}H_{37}NOSi$: C, 76.61; H, 9.15; N, 3.44. Found: C, 76.88; H, 9.02; N, 3.32.

2-[*o*-[1-(Trimethylsilyl)hept-6-enyl]phenyl]-3-methyl-4(*S*)-benzyl-oxazolidine (1i): bp 170 °C (0.1 torr); IR (neat) 850, 908, 1040, 1250, 1640 cm^{-1}; NMR ($CDCl_3$) δ −0.05 (s, 9 H), 0.80–2.05 (m, 8 H), 2.10 (s, 3 H), 2.35–3.15 (m, 3 H), 3.60–3.85 (m, 2 H), 4.60–5.03 (m, 2 H), 4.78 and 4.86 (two s, 1 H), 5.35–6.05 (m, 1 H), 6.70–7.70 (m, 4 H), 7.28 (s, 5 H). Anal. Calcd for $C_{27}H_{39}NOSi$: C, 76.91; H, 9.32; N, 3.32. Found: C, 77.02; H, 9.33; N, 3.58.

2-[*o*-[1-[(Trimethylsilyl)methyl]alkyl]oxazolidinium salts (2) were prepared by reacting the corresponding oxazolidine with 3 molar equiv of methyl iodide in acetonitrile at 40–50 °C for 4–7 h or with 1.5 molar equiv of methyl triflate in methylene chloride at room temperature for 2–3 h, followed by solvent evaporation. The oxazolidinium salts **2** (ca. 90% yield) thus prepared were washed with hexane, and used for further reactions without purification.

2-[*o*-[(Trimethylsilyl)methyl]phenyl]-3,3,5-Trimethyloxazolidinium Iodide (2b): IR (KBr disk) 840, 1135, 1240, 1600 cm^{-1}; NMR (CD_3CN) δ 0.03 (s, 9 H) 2.46 and 2.50 (two d, J = 6 Hz, 3 H), 2.15–2.55 (m, 2 H), 2.67 and 2.72 (two s, 3 H), 3.26 and 3.30 (two s, 3 H), 4.05–5.10 (m, 3 H), 6.26 and 6.31 (two s, 1 H), 7.00–7.77 (m, 4 H).

2-[*o*-[1-(Trimethylsilyl)hept-6-enyl]phenyl]-3,3,4(*S*)-trimethyl-5(*R*)-phenyloxazolidinium iodide (2e): IR (KBr disk) 840, 850, 920, 1005, 1245, 1635 cm^{-1}.

Cycloaddition of 2-[*o*-[(Trimethylsilyl)methyl]phenyl]-3,3,4(*S*)-trimethyl-5(*R*)-phenyloxazolidinium Triflate (2j) with Methyl Acrylate. To a suspension of 0.95 mL (10.5 mmol) of methyl acrylate and 1.58 g (10.4 mmol) of CsF in 7 mL of acetonitrile was added a solution of **2j** (3.5 mmol) in 12 mL of acetonitrile at 0 °C, and the mixture was stirred at 0 °C for 5 h and then at room temperature for 8 h. The mixture was evaporated in vacuo, and the residue was triturated with aqueous Na_2CO_3 and extracted with ether. The ether extract was dried over $MgSO_4$ and evaporated to afford *cis*-1-[2(*S*)-(dimethylamino)-1(*R*)-phenylpropoxy]-2-(methoxycarbonyl)-1,2,3,4-tetrahydronaphthalene (**7j**) as a light yellow solid in 92% yield. NMR spectrum showed that **7j** consisted of a 2:1 diastereoisomer mixture, which were separated by preparative TLC on silica gel (3:2 hexane–acetone). The major diastereomer, **7j**-i: 55% yield; TLC R_f = 0.58; NMR ($CDCl_3$) δ 1.00 (d, J = 6.0 Hz, 3 H), 2.05 (s, 6 H), 1.60–3.10 (m, 6 H), 3.72 (s, 3 H), 4.33 (d, J = 7 Hz, 1 H) 4.77 (br d, $J \simeq$ 2.3 Hz, 1 H), 6.25–7.50 (m, 9 H). The minor diastereomer, **7j**-ii: ~20% yield; TLC, R_f 0.53; NMR ($CDCl_3$) δ 0.83 (d, J = 6 Hz, 3 H), 1.88 (s, 6 H), 3.67 (s, 3 H), 4.50 (br d, $J \simeq$ 2.3 Hz, 1 H). **7j**: Anal. Calcd for $C_{23}H_{29}NO_3$: C, 75.17; H, 7.95; N, 3.81. Found: C, 75.03; H, 8.08; N, 3.93.

In an autoclave, a mixture of **7j** (500 mg), 10% Pd/C (250 mg), and 70% aqueous $HClO_4$ (150 μL) in 5 mL of acetic acid was stirred overnight under 60 kg/cm^2 of hydrogen gas. The reaction mixture was filtered, and the filtrate was added to 15 mL of H_2O and extracted with hexane. The hexane extract was distilled to give 2-(methoxycarbonyl)-1,2,3,4-tetrahydronaphthalene (200 mg, 77%), which was identified by comparison of IR spectrum with that of the authentic sample.[3a]

A solution of **7j** (500 mg) and DBU (30 mg) in 3 mL of acetonitrile was heated at 50–60 °C for 6 h. The mixture was poured into 5% aqueous HCl and then extracted with hexane. The hexane solution was evaporated and the residue was subjected to preparative GLC to afford 2-(methoxycarbonyl)-3,4-dihydronaphthalene[3a] in >90% yield.

Cycloaddition of 2-[*o*-[(Trimethylsilyl)methyl]phenyl]-3,3,5-trimethyloxazolidinium iodide (2b) with methyl acrylate was carried out according to the procedure described above to afford a 1:1 diastereoisomer mixture of *cis*-1-[2-(dimethylamino)-1-methylethoxy]-2-(methoxycarbonyl)-1,2,3,4-tetrahydronaphthalene (**7b**) in 90% yield, which were separated by preparative TLC on silica gel (2:1 hexane–acetone). **7b**-i (42%): TLC R_f 0.41; NMR ($CDCl_3$) δ 0.95 (d, J = 5.7 Hz, 3 H), 2.20 (s, 6 H), 1.85–3.00 (m, 7 H), 3.70 (s, 3 H), 3.75–4.05 (m, 1 H), 4.88 (d, J = 2.5 Hz, 1 H), 6.90–7.50 (m, 4 H). **7b**-ii (40%): TLC R_f 0.29; NMR ($CDCl_3$) δ 1.10 (d, J = 5.7 Hz, 3 H), 2.01 (s, 6 H), 1.85–3.00 (m, 7 H), 3.65 (s, 3 H), 3.65–4.05 (m, 1 H), 4.85 (d, J = 2.5 Hz, 1 H), 6.90–7.50 (m, 4 H). **7b**: Anal. Calcd for $C_{17}H_{25}NO_3$: C, 70.07; H, 8.65; N, 4.81. Found: C, 70.28; H, 8.41; N, 4.55.

Cycloaddition of 2-[*o*-[(Trimethylsilyl)methyl]phenyl]-3,4,4-trimethyloxazolinium iodide (5a) with acrylonitrile was carried out according to the procedure for the cycloaddition of **2j**, producing a 1:1 stereoisomeric mixture of oxazolidine (**10a**) in 89% yield. The stereoisomers of **10a** were separated by preparative TLC on silica gel (5:1 hexane–acetone). **10a**-i (46%): TLC R_f 0.40; IR (neat) 2240 cm^{-1}; NMR ($CDCl_3$) δ 1.25 (s, 6 H), 2.12 (s, 3 H), 1.9–2.5 (m, 2 H), 2.6–3.1 (m, 3 H), 3.6–4.1 (m, 2 H), 6.8–7.5 (m, 4 H). **10a**-ii (40%): TLC R_f 0.35; IR (neat) 2240 cm^{-1}; NMR ($CDCl_3$) δ 1.21 (s, 6 H), 1.98 (s, 3 H), 2.05–2.35 (m, 2 H), 2.6–3.1 (m, 3 H), 3.80 (br s, 2 H), 6.8–7.5 (m, 4 H). **10a**: Anal. Calcd for $C_{16}H_{28}N_2O$: C, 74.96; H, 7.86; N, 10.93. Found: C, 75.08; H, 7.75; N, 10.66. The structure of **10a** was estab-

lished by hydrolysis of **10a** with 5% aqueous HCl at 80 °C for 30 min, producing 2-cyano-1-tetralone.

Intramolecular Cycloaddition of 2-[*o*-[1-(Trimethylsilyl)hept-5-enyl]-phenyl]-3,3-dimethyl-5(*R*)-phenyloxazolidinium Iodide (2d). To a stirred suspension of 0.46 g (3 mmol) of CsF in 5 mL of acetonitrile was added 0.83 g (1.5 mmol) of the oxazolidinium iodide **2d** in 7 mL of acetonitrile at room temperature in 30 min, and the mixture was stirred overnight. The reaction mixture was evaporated in vacuo, and aqueous Na_2CO_3 was added to the residue, followed by ether extraction. The ether extract was dried over $MgSO_4$ and evaporated to give crude 8,9-*trans*-6-[2-(dimethylamino)-1(*R*)-phenylethoxy]octahydrophenanthrene (**11d**) (460 mg, 88%), which consisted of a 2:1 diastereoisomer mixture, as determined from NMR spectrum.

The diastereoisomer mixture of **11d** was separated by preparative TLC on silica gel (2:1 hexane–acetone). The major diastereoisomer, **11d-i** (53%): TLC R_f 0.52; NMR($CDCl_3$) δ 0.60–2.50 (br m, 12 H), 2.29 (s, 6 H), 2.55 (m, 2 H), 4.15–4.32 (m, 1 H), 4.68 (dd, 1 H), 6.90–7.70 (m, 9 H). The minor diastereoisomer, **11d-ii** (28%, TLC R_f 0.45), exhibited a singlet at δ 2.22, which was ascribed to methyl group on the nitrogen. **11d**: Anal. Calcd for $C_{24}H_{31}NO$: C, 82.47; H, 8.94; N, 4.01. Found: C, 82.59; H, 9.18; N, 4.13.

In an autoclave, a mixture of **11d** (460 mg), 70% aqueous $HClO_4$ (100 μL), and 10% Pd/C (250 mg) in 5 mL of acetic acid was stirred overnight under 60 kg/cm^2 of hydrogen gas. After the reaction mixture was filtered, the filtrate was diluted with 30 mL of H_2O and extracted with hexane. The hexane extract was washed with 5% aqueous HCl and brine and distilled to give *trans*-octahydrophenanthrene (**12**) (210 mg[3g], 86%), $[\alpha]^{19}_D$ +31.6° (*c* 1.35, C_6H_{14}). Similarly, the hydrogenolysis of the major diasteroisomer **11d-i** on Pd/C afforded optically pure *trans*-octahydrophenanthrene (**12**): bp 60 °C (0.1 torr); mp 41.5–42.0 °C; $[\alpha]^{19}_D$ +92.9° (*c* 1.06, C_6H_{14}).

On the other hand, a mixture of **11d** (460 mg), $KHSO_4$ (150 mg), and 70% aqueous $HClO_4$ (100 μL) in 3 mL of benzene was refluxed for 3 h. The reaction mixture was added to aqueous Na_2CO_3 and extracted with ether. The ether extract was washed with 5% aqueous HCl and brine and evaporated. The residue was subjected to preparative TLC on silica gel with hexane solvent (R_f 0.63) to furnish 8,9-*trans*-hexahydrophenanthrene (**13**) (210 mg, 87%): bp 95 °C (0.1 torr). **13**: ^{1}H NMR ($CDCl_3$) δ 1.00–2.60 (m, 10 H), 5.68 (br d, J = 9.0 Hz, 1 H), 6.42 (dd, J = 9.0, 2.3 Hz, 1 H), 6.80–7.30(m, 4 H); ^{13}C NMR ($CDCl_3$ with Me_4Si) δ 26.50 (2 C), 28.55, 32.78, 39.64, 42.07, 123.39, 126.01, 126.32, 127.17, 127.25, 134.72, 135.53, 139.42. Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.53; H, 8.73. Intramolecular cycloadditions of **2c–i** were performed according to the procedure described above, and the cycloadducts **11c–i** thus produced were converted to *trans*-octahydrophenanthrene by hydrogenolysis on Pd/C.

8,9-*trans*-6-[2-(Dimethylamino)-1-methylethoxy]octahydrophenanthrene (11c): bp 125 °C (0.1 torr); 80%; NMR($CDCl_3$) δ 1.12 and 1.20 (two d, J = 6 Hz, 3 H), 0.35–2.50 (br m, 12 H), 2.14 (s, 6 H), 2.25 (m, 2 H), 3.40–3.80 (m, 1 H), 4.20–4.42 (m, 1 H), 6.70–7.35 (m, 4 H). Anal. Calcd for $C_{19}H_{29}NO$: C, 79.39; H, 10.17; N, 4.87. Found C, 79.51; H, 10.30; N, 4.59.

8,9-*trans*-6-[2(*S*)-(Dimethylamino)-1(*R*)-phenylpropoxy]octahydrophenanthrene (11e) (83%): NMR ($CDCl_3$) δ 0.97 and 1.04 (two d, J = 6 Hz, 3 H), 2.00 and 2.09 (two s, 6 H), 0.50–2.95 (br m, 13 H), 4.03–4.25 (m, 1 H), 4.32 and 5.04 (two d, J = 7.5 Hz, 1 H), 6.70–7.50 (m, 9 H). Anal. Calcd for $C_{25}H_{33}NO$: C, 82.60; H, 9.15; N, 3.85. Found: C, 82.88; H, 9.19; N, 3.62.

8,9-*trans*-6-[2(*R*)-(Dimethylamino)-1(*R*)-phenylpropoxy]octahydrophenanthrene (11f) (90%): NMR ($CDCl_3$) δ 0.76 (d, J = 6 Hz, 3 H), 0.50–3.15 (br m, 13 H), 2.12 and 2.25 (two s, 6 H), 3.95–4.15 (m, 1 H), 4.32 (d, J = 8.3 Hz, 1 H), 6.65–7.40 (m, 9 H). Anal. Calcd for $C_{25}H_{33}NO$: C, 82.60; H, 9.15, N, 3.85. Found: C, 82.41; H, 9.38; N, 4.02.

8,9-*trans*-6-[3-Methoxy-2(*S*)-(dimethylamino)-1(*S*)-phenylpropoxy]octahydrophenanthrene (11g) (crude product, 85% yield): NMR ($CDCl_3$) δ 2.24 and 2.38 (two s, 6 H), 2.96 and 3.02 (two s, 3 H).

8,9-*trans*-6-[2(*R*)-(Dimethylamino)-2-phenylethoxy]octahydrophenanthrene (11h) (58%): NMR ($CDCl_3$) δ 0.70–2.60 (br m, 12 H), 2.23 (s, 6 H), 3.10–4.00 (m, 4 H), 6.90–7.50 (m, 9 H). Anal. Calcd for $C_{24}H_{31}NO$: C, 82.47; H, 8.94; N, 4.01. Found: C, 82.63; H, 9.18; N, 4.15.

8,9-*trans*-6-[2(*S*)-(Dimethylamino)-3-phenylpropoxy]octahydrophenanthrene (11i) (64%): NMR ($CDCl_3$) δ 0.70–2.70 (br m, 12 H), 2.38 (s, 6 H), 2.70–2.90 (m, 3 H), 3.48–3.65 (m, 2 H), 4.14–4.30 (m, 1 H), 6.90–7.50 (m, 9H). Anal. Calcd for $C_{22}H_{33}NO$: C, 82.60; H, 9.15; N, 3.85. Found: C, 82.84; H, 9.33; N, 4.05.

Intramolecular Hydrogen Abstraction from Triplet States of 2,4,6-Triisopropylbenzophenones: Importance of Hindered Rotation in Excited States[1]

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Abstract: Photochemically initiated benzocyclobutenol formation from a variety of 4′-substituted (4′-X) 2,4,6-triisopropylbenzophenones **1a–f** (**a**, X = OMe; **b**, X = Me; **c**, X = H; **d**, X = CO_2Me; **e**, X = CF_3; **f**, X = CN) as well as from 2,4,6-trimethylbenzophenone (**3a**) and 2,4,6-triethylbenzophenone (**3b**) was studied. The quantum yields of the benzocyclobutenols **2a–f** ranged from 0.60 for **2c** to 0.06 for **2f** in benzene. By usual Stern–Volmer quenching and sensitization methods using diene as quencher or sensitizer, various photokinetic data for these ketones, i.e., triplet lifetime (τ_T) and its temperature dependence (E_a and log A), rate constant for intramolecular hydrogen abstraction from *o*-isopropyl methine hydrogens (k_r) and its isotope effect (k_H/k_D), rate constant for bimolecular triplet quenching (k_2) with hydrogen donors (Bu_3SnH, mesitylene, and cyclooctane), and intersystem crossing yield (Φ_T), were estimated. The effect of 4′-substituents (4′-X) on k_r (or τ_T) was unusual for a series of compounds **1a–c** and **1e** in that k_r decreased in going from **1a** (X = OMe) to **1e** (X = CF_3). This novel substituent effect was interpreted on the basis of hindered rotation in the excited state around the bond linking the 2,4,6-triisopropylphenyl and carbonyl groups. This interpretation was nicely supported by the results obtained for E_a (unusually large, e.g., E_a = 9.0 kcal/mol for **1c**), k_H/k_D (1.5 for **1c**), and k_2 (increased in going from **1a** to **1e**). It is deduced that an increased $n\pi^*$ character of aromatic ketone triplets results in an increased barrier to rotation (viz., an increased double-bond character) about the C_{Ar}—C(=O) single bond in the triplet excited state.

Introduction

o-Alkyl phenyl ketones belong to a typical class of photochromic compounds. Upon absorption of light they can reversibly generate a synthetically very useful intermediate called *o*-xylylene (a typical diradicaloid hydrocarbon).[2] Some of them, however, are known to photocyclize to give highly strained benzocyclobutenols, usually

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