Ground State Stereoelectronic Effects of Silicon: A Comparison of the Effects of Synperiplanar and Antiperiplanar Silicon on C−O Bond Lengths at the β Position

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Received November 17, 1994®

Results from low-temperature crystal structure analyses of β-trimethylsilyl esters with synperiplanar and antiperiplanar geometry are reported. These studies reveal a significant response of the C(alkyl)−O(ester) bond length to the electron demand of the ester function when the β-trimethylsilyl substituent is antiperiplanar to the ester. However, when the geometry is synperiplanar, the C−O bond lengths are not significantly different from those of the corresponding nonsilylated derivatives. This is interpreted in terms of more effective overlap between the σ_{C-Si} orbital and the σ^*_{C-O} antibonding orbital in the antiperiplanar geometry than in the synperiplanar geometry.

Introduction

The stabilizing influence of a silicon substituent on electron deficient centers at the β position is a remarkable electronic effect and is central to the chemistry of silicon-containing organic compounds.[1,2] Lambert and co-workers have demonstrated the magnitude of this effect in solution by studying the solvolyses of β-silicon-substituted esters.[3−6] They have measured the rates of unimolecular solvolyses of esters substituted with a trimethylsilyl group at the β position and compared these with the corresponding silicon-free esters. Notable findings from these studies are as follows. (a) The relative rates of reaction of **1** (with the trimethylsilyl substituent anti to the ester leaving group) *vs* the silicon-free analogue **2** are 10^{12}:1, which indicates that the β-silicon stabilizes the intermediate secondary carbenium ion by a remarkable 18 kcal/mol relative to H. (b) There is a marked dependence of the reaction rate upon the Si−C−C−O dihedral angle; it is maximal when these two groups are antiperiplanar[4] (10^{12}) and significantly less when these groups are gauche (10^4) or synperiplanar[5] (10^5) *vs* silicon-free analogues. (c) A secondary α-deuterium isotope effect $k_H/k_D = 1.17(1)$ for the solvolysis of **3** is observed.[6] These studies support the involvement of a classical cation **4** on the reaction pathway, in which the silicon substituent stabilizes the positive charge substantially by hyperconjugation. We have shown from accurate X-ray structural studies on a selected range of β-trimethylsilyl esters[7] that there are also significant ground state effects when a silicon substituent is disposed β to a leaving group. For example, when the Si−C−C−O dihedral angle is close to 180° as in **5** and **6**, then the C−O bond is lengthened; however, when the Si−C−C−O angle is gauche, the C−O bond is shorter and essentially the same as the nonsilylated analogue. We proposed that the origin of these effects was the result of σ−σ^* "hyperconjugative-like" interactions between the C−Si σ orbital and the C−O σ^* orbital. Further evidence for this type of interaction was provided by studies on a series of conformationally mobile β-trimethylsilyl esters **7**.[8] We found that the diaxial conformation **7a** (allowing maximum overlap between the σ_{C-Si} and the σ^*_{C-O} orbitals) was preferred over the diequatorial conformation **7b**, a result which contrasted with that predicted from molecular mechanics calculations.

We were interested in investigating the influence of β-silicon on the structural parameters of adjacent ester substituents having a synperiplanar relationship between the C−Si bond and the C−O bond and comparing these with the ground state effects observed in the antiperiplanar geometry. Accordingly, we chose to prepare the *endo*-3-(trimethylsilyl)-*endo*-2-norborneol **8** in order to perform structural studies on selected ester derivatives. The reactivity of this system to unimolecular solvolysis is already known, and it is significantly less reactive than substrates with an antiperiplanar geometry between the ester function and the trimethylsilyl group. The model compounds **9**[17] and **10**[17] with *p*-nitrobenzoate and 2,4-dinitrobenzoate esters, respectively, were chosen for study, and in addition, the 2,4-dinitrobenzoate derivative **11**[17] with antiperiplanar geometry was prepared for comparison purposes.

Results

endo-3-(Trimethylsilyl)-*endo*-2-norborneol **8** was prepared as reported by Lambert *et al.*,[5] The *p*-nitro- and 2,4-dinitrobenzoate derivatives **9** and **10** were prepared from **8** using standard methods. The antiperiplanar ester **11** was prepared from the 5-*tert*-butyl-*anti*-trimethylsilyl alcohol **12**.[7] The dinitro ester **11** proved to be relatively unstable to elimination; however, crystals suitable for X-ray analysis were successfully obtained by crystallization from pentane at low temperatures.

Molecular Structures

The structures of **9** and **11** were determined at 130 K to remove unwanted thermal effects. The ester **10** underwent a destructive phase change below 180 K. Therefore, the structure was determined at 213 K. The structures of **9**−**11** are shown in Figures 1−3 and were

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® Abstract published in *Advance ACS Abstracts*, April 15, 1995.

(1) Colvin, E. *Silicon in Organic Synthesis*; Butterworths Monographs in Chemistry; Butterworth: Boston, 1981.

(2) Lambert, J. B. *Tetrahedron* **1990**, *46*, 2677.

(3) Lambert, J. B.; Wang, G.-T.; Finzel, R. B.; Teramura, D. H. *J. Am. Chem. Soc.* **1987**, *109*, 7838.

(4) Lambert, J. B.; Wang, G.-T. *J. Phys. Org. Chem.* **1988**, *1*, 169.

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(6) Lambert, J. B.; Emblidge, R. W.; Malany, S. *J. Am. Chem. Soc.* **1993**, *115*, 1317.

(7) White, J. M.; Robertson, G. B. *J. Org. Chem.* **1992**, *57*, 4638.

(8) Kuan, Y. L.; White, J. M. *J. Chem. Soc., Chem. Commun.* **1994**, 1195.

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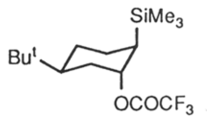
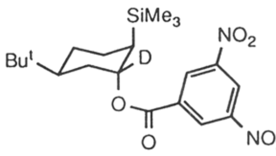
Chart 1



(1)

(2)



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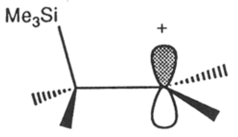

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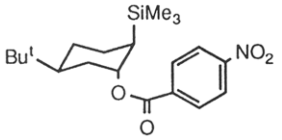

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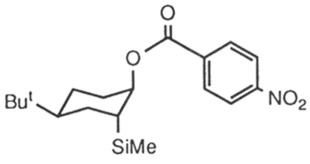

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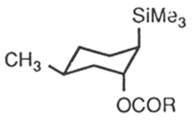
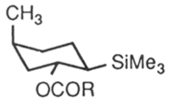
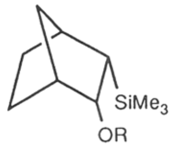


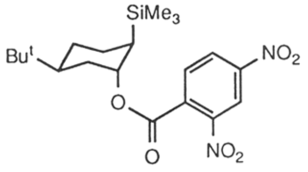
(7a)



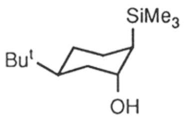
(7b)



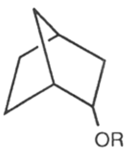
(8) R = H
(9) R = OCO-p-nitrobenzoate
(10) R = OCO-2,4-dinitrobenzoate



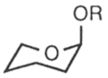
(11)



(12)



(13) R = OCO-p-nitrobenzoate
(14) R = OCO-2,4-dinitrobenzoate



(15)

drawn using ORTEPII[9] to depict 50% ellipsoids. Hydrogen atoms which were refined with isotropic thermal parameters are omitted for clarity. Selected bond lengths, bond angles, and dihedral angles are presented in Tables 1 and 2. Structures of the silicon-free analogues **13**[10] and **14**[11] were also determined at 130 K, and these will be reported elsewhere. The bond angles of the two norborneol-derived esters **9** and **10** (Table 1) suggest significant steric interactions between the trimethylsilyl substituent and the adjacent ester substituent; Si−C(3)−C(2) = 121.59(14) and 118.16°(11) for **9** and **10**, respectively. Twisting about the C(2)−C(3) bond away from the idealized synperiplanar geometry in both structures, Si−C(3)−C(2)−O(1) = −17.5(2) and −9.4(2)° for **9** and **10**, respectively, is also observed and presumably acts to minimize steric repulsion. The geometry of the rigid norborneol framework is essentially identical for **9** and **10**. However, the orientation of the phenyl ring as defined by the dihedral angle O(1)−C(8)−C(9)−C(10) differs significantly between the two structures; whereas for **9** the phenyl ring is nearly coplanar with the carboxylate function, in structure **10**, these two groups are essentially orthogonal. In structure **11**, inspection of

Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for Compounds 9 and 10

	9	10[a]
C(2)−O(1)	1.464(2)	1.457(2)
Si−C	1.888(2)	1.897(2)
Si−CH3 (av)	1.863	1.863
C(4)−C(3)−Si	119.54(14)	119.31(11)
C(2)−C(3)−Si	121.59(14)	118.16(11)
O(1)−C(2)−C(1)	112.6(2)	113.37(14)
O(1)−C(2)−C(3)	110.3(2)	109.66(11)
C(1)−C(2)−C(3)	104.4(2)	104.00(13)
C(4)−C(3)−C(2)	102.0(2)	101.93(13)
C(7)−C(4)−C(5)	101.5(2)	101.5(2)
C(7)−C(4)−C(3)	100.6(2)	101.33(14)
C(5)−C(4)−C(3)	110.8(2)	110.46(14)
C(4)−C(5)−C(6)	103.0(2)	102.9(2)
C(1)−C(6)−C(5)	103.3(2)	103.2(2)
C(4)−C(7)−C(1)	94.4(2)	93.73(14)
Si−C(3)−C(2)−O(1)	−17.5(2)	−9.4(2)
C(1)−C(2)−C(3)−C(4)	−2.4(2)	1.9(2)
C(1)−C(2)−C(3)−Si	−138.7(2)	−130.97(13)
C(6)−C(1)−C(2)−O(1)	−47.5(2)	−49.9(2)
O(1)−C(8)−C(9)−C(10)	163.4(2)	86.9(2)
C(9)−C(8)−O(1)−C(2)	−174.5(2)	175.33(12)

[a] For the enantiomer.

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[9] Johnson, C. K. ORTEP. Report ORNL-3794; Oak Ridge National Laboratories: Oak Ridge, TN, 1965.

[10] White, J. M.; Green, A. J. *Acta Crystallogr., Sect. C*, submitted for publication, 1994.

[11] White, J. M.; Green, A. J. *Acta Crystallogr., Sect. C*, in press.

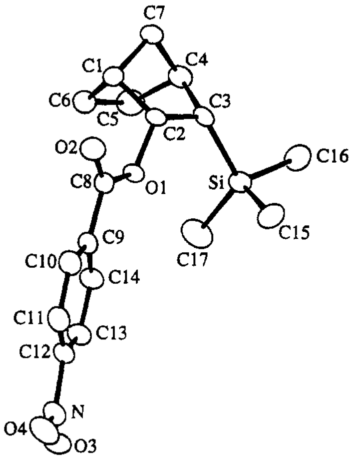

Figure 1. Thermal ellipsoid plot for **9**. Ellipsoids are drawn at the 50% probability level.

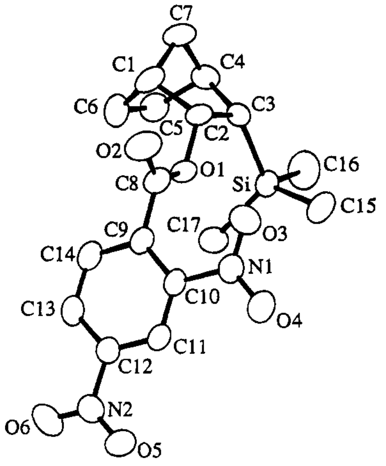

Figure 2. Thermal ellipsoid plot for **10**. Ellipsoids are drawn at the 50% probability level.

Table 2. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg) for Compound 11

O(1)–C(2)	1.497(2)	C(1)–C(2)	1.516(2)
Si–C(1)	1.906(2)	Si–CH3 (av)	1.867
Si–C(2)–C(1)	113.09(12)	Si–C(2)–C(3)	116.28(12)
O(1)–C(1)–C(2)	109.63(13)	O(1)–C(1)–C(6)	105.20(13)
C(1)–C(2)–C(3)	111.4(2)	C(2)–C(3)–C(4)	113.1(2)
C(3)–C(4)–C(5)	111.7(2)	C(4)–C(5)–C(6)	108.8(2)
C(5)–C(6)–C(1)	114.3(2)		
O(1)–C(1)–C(2)–Si(1)	−155.29(11)	C(6)–C(1)–C(2)–Si(1)	86.8(2)
Si(1)–C(2)–C(3)–C(4)	−81.6(2)	C(1)–C(2)–C(3)–C(4)	50.0(2)
C(2)–C(3)–C(4)–C(5)	−56.5(2)	C(3)–C(4)–C(5)–C(6)	56.3(2)
C(4)–C(5)–C(6)–C(1)	−53.5(2)	C(5)–C(6)–C(1)–C(2)	50.0(2)
C(6)–C(1)–C(2)–C(3)	−46.4(2)	O(1)–C(1)–C(2)–C(3)	71.5(2)
O(1)–C(1)–C(6)–C(5)	−70.4(2)		

Table 2 confirms the presence of angle strain at the C(1), C(2), C(3), and C(6) cyclohexane carbon centers. This manifests itself as a flattening of the ring in the region of the trimethylsilyl and dinitrobenzoate substituents [C(6)–C(1)–C(2)–C(3) = −46.4(2)°] and a substantial opening of the Si–C–C angles. As a consequence, the Si–C(2)–C(1)–O(1) dihedral angle in **11** is reduced from 180 to −155.29(11)°.

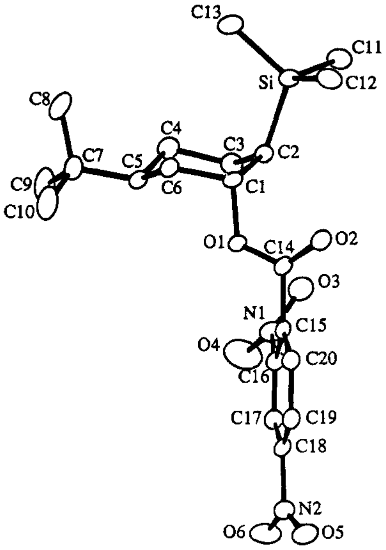

Figure 3. Thermal ellipsoid plot for **11**. Ellipsoids are drawn at the 50% probability level.

It is evident from an inspection of Table 1 that the presence of a β-trimethylsilyl substituent with synperiplanar geometry has no significant effect on the ester C–O bond length. For example, the C(2)–O(1) bond lengths for **9** and **10** do not differ significantly from the C(2)–O(1) length in the corresponding nonsilylated derivatives **12** and **13**. However, the C–O bond length for the β-trimethylsilyl-substituted ester **11** with antiperiplanar geometry is somewhat longer. The (non-methyl) C–Si bond lengths of **9** and **10** are both significantly shorter than the (non-methyl) C–Si bond length of **11**.

Discussion

The C–O bond lengths for **9** and **10** are not significantly different from that observed in the nonsilylated derivatives **12** (1.456(3) Å[11]) and **13** (1.465(2) Å[10]), and also, they are not significantly different from each other. Given that the pK_a values for the corresponding carboxylic acids *p*-nitrobenzoic acid and 2,4-dinitrobenzoic acid (3.44 and 1.4, respectively) differ by 2 log units, this bond length equality indicates a very weak response of the C–O bond lengths to the electron demand of the ester substituent. In contrast, the C–O bond length for **11** is very long, 1.497(2) Å, compared to that expected for a secondary 2,4-dinitrobenzoate ester[12] of *ca.* 1.47 Å. Furthermore, the C–O bond length for **11** is also significantly longer than the C–O bond lengths observed for structures **5** and **6** which differ from **11** by having a (*p*-nitrobenzoyl)oxy substituent antiperiplanar to a β-trimethylsilyl substituent. This comparison suggests a strong response of the C–O bond length to the electron demand of the ester substituent when the groups are antiperiplanar. In fact, a comparison of the C–O bond lengths of esters **5**, **6**, and **11** with the C–O bond lengths observed for the reported series of axial tetrahydropyranyl acetals[13] **15** indicates a similar response of the C–O bond lengths for both series of compounds to the electron demand of the OR group. This suggests that, in the optimum geometry, a C–Si bond has a similar donor ability to a p-type oxygen lone pair. This is a conclusion that we have also arrived at on the basis of our conformational studies on esters **8**.[8] This apparent similarity in donor abilities of a C–Si bond and an oxygen lone pair is not surprising in view of the fact that the

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(12) Allen, F. H.; Kirby, A. J. *J. Am. Chem. Soc.* **1984**, *106*, 6197.

(13) Briggs, A. J.; Glenn, R.; Jones, P. G.; Kirby, A. J.; Ramaswamy, P. *J. Am. Chem. Soc.* **1984**, *106*, 6200.

Table 3. Crystal Data and Structure Refinement for 9−11

	9	**10**	**11**
empirical formula	$C_{17}H_{23}NO_4Si$	$C_{17}H_{22}N_2O_6Si$	$C_{20}H_{30}N_2O_6Si$
formula weight	333.45	378.5	422.55
temperature (K)	130	213(1)	130
radiation	Mo Kα	Mo Kα	Mo Kα
crystal system	monoclinic	monoclinic	triclinic
space group	$P2_1/n$	$P2_1$	$P\bar{1}$
a (Å)	6.7760(9)	6.2920(10)	6.290(2)
b (Å)	34.342(3)	11.526(2)	13.3800(10)
c (Å)	7.699(2)	13.280(2)	13.291(2)
α (deg)	90.00	90.00	88.610(8)
β (deg)	107.09(2)	101.97(2)	85.65(2)
γ (deg)	90.00	90.00	77.470(10)
volume (Å^3)	1712.5(5)	942.1(3)	1088.8(4)
Z	4	2	2
density (calculated) (mg/m^3)	1.293	1.334	1.289
absorption coefficient (mm^{-1})	0.156	0.160	0.146
F(000)	712	400	452
crystal size (mm)	0.6 × 0.4 × 0.1	0.3 × 0.4 × 0.4	0.5 × 0.1 × 0.1
θ range for data collection (deg)	2.37−27.49	2.36−32.47	2.18−29.96
index ranges	$0 \le h \le 8$	$-2 \le h \le 9$	$-2 \le h \le 8$
	$-44 \le k \le 44$	$-3 \le k \le 17$	$-18 \le k \le 18$
	$-9 \le l \le 8$	$-20 \le l \le 20$	$-18 \le l \le 18$
reflections collected	7605	6064	6749
no. of observed reflections	2689	3903	3487
criterion for observed	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
independent reflections	3591 [R(int) = 0.0322]	4423 [R(int) = 0.0340]	6201 [R(int) = 0.0344]
data/restraints/parameters	3591/0/301	4423/1/323	6201/0/364
goodness-of-fit on F^2	1.092	1.063	0.903
final R indices [$I > 2\sigma(I)$]	R1 = 0.0445, $R2_w$ = 0.1131	R1 = 0.0356, $R2_w$ = 0.0942	R1 = 0.0456, $R2_w$ = 0.1017
R indices (all data)	R1 = 0.0710, $R2_w$ = 0.1347	R1 = 0.0414, $R2_w$ = 0.0977	R1 = 0.1139, $R2_w$ = 0.1137
weighting scheme where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0492P)^2 + 1.3607P]$		$w = 1/[\sigma^2(F_o^2) + (0.0663P)^2 + 0.0000P]$
extinction method	SHELXL		
extinction coefficient	0.0008(9)		
absolute structure parameter		0.15(9)	
maximum shift (esd)	0.356	0.070	0.001
largest diff peak and hole (e Å^{-3})	0.313 and −0.392	0.260 and −0.207	0.39 and −0.26

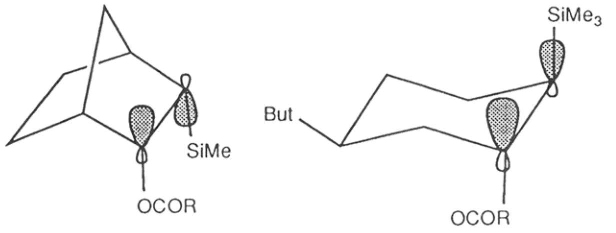

Figure 4. Comparison of the $\sigma_{C-Si}-\sigma^*_{C-O}$ interaction for syn- and antiperiplanar geometries.

vertical ionization potentials of a C−Si bond and an oxygen lone pair are very similar.[14]

Conclusion

These results suggest that the ground state effects of β-silicon with synperiplanar geometry, as measured by the response of the ester C−O bond length, are small by comparison with those of antiperiplanar silicon. This is very likely the result of the much poorer overlap between the σ_{C-Si} orbital and the neighboring σ^*_{C-O} orbital in the synperiplanar geometry as compared to the antiperiplanar geometry (Figure 4), resulting in a much weaker $\sigma-\sigma^*$ interaction. Also consistent with this is the significant lengthening of the C−Si bonds of **5**, **6**, and **11** relative to the C−Si bond lengths of **9** and **10**. Given the demonstrated relationship between a C−O bond length and the reactivity of this C−O bond toward heterolysis, these results nicely complement the solution reactivity studies of Lambert *et al.*[5]

Experimental Section

(a) Synthesis. Melting points were determined on a Gallenkamp melting point apparatus, and infrared spectra were run on a Perkin-Elmer 983G infrared spectrometer. NMR spectra were run on a Varian Unity-300 spectrometer operating at 299.9 MHz for ^{1}H spectra and 75 MHz for ^{13}C spectra or on a JEOL FX-90Q spectrometer.

endo-3-(Trimethylsilyl)-*endo*-2-norborneol **8** was prepared as previously described[5] and was obtained as a clear oil in 75% yield.

Preparation of the Esters 9−11. The ester compounds were prepared by the general procedure described for the preparation of **11**, except that, in the case of **9**, *p*-nitrobenzoyl chloride was used in place of 2,4-dinitrobenzoyl chloride.

***r*-5-*tert*-Butyl-*c*-2-(trimethylsilyl)cyclohexan-*t*-yl 2,4-Dinitrobenzoate (11).** To a solution of 2,4-dinitrobenzoyl chloride (0.09 g, 0.39 mmol) in pyridine (5 mL) was added a solution of alcohol **10** (0.07 g, 0.31 mmol) in pyridine (1 mL). The resulting suspension was stirred overnight at room temperature and then diluted with water (40 mL). The mixture was extracted with ether (3 × 30 mL), and the combined extracts were washed with 1 M HCl (2 × 50 mL), water (2 × 50 mL), and aqueous sodium bicarbonate (1 × 50 mL), dried ($MgSO_4$), and evaporated down to a pale yellow solid. Recrystallization from pentane gave colorless needles of **11** (0.1 g, 83%): mp 91−93 °C; ^{1}H NMR δ ($CDCl_3$) 8.4−8.8 (2H, m), 7.8−8.1 (1H, d, J = 8 Hz), 5.5−5.7 (1H, bs), 2.2−0.95 (8H, m), 0.8 (9H, s), 0.1 (9H, s); ^{13}C NMR δ ($CDCl_3$) 162.4, 148.9, 133.4, 131.6, 127.06, 119.4, 78.35, 41.62, 32.2, 29.8, 29.2, 27.2, 24.4, 22.4, −0.95; λ_{max} (Nujol) 1712 (s), 1538 (s), 1298 (s), 1251 (s), 875 (s), 831 (s) cm^{-1}.

***endo*-3-(Trimethylsilyl)-2-norbornyl *p*-nitrobenzoate 9:** white plates from pentane (91%); mp 85−86 °C; ^{1}H NMR δ

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($CDCl_3$) 8.1–8.35 (4H, m), 5.69 (1H, ddd, J = 1.2, 4.4, 7.8 Hz), 2.64 (1H, bs), 2.4 (1H, bs), 1.85–1.2 (8H, m), 0.07 (9H, s); ^{13}C NMR δ ($CDCl_3$) 162.4, 150.3, 136.1, 130.5, 123.5, 80.56, 42.08, 40.80, 40.17, 35.67, 26.41, 20.95, 0.07; λ_{max} (Nujol) 1717 (s), 1526 (s), 1282 (s), 1247 (s), 870 (s), 835 (s) cm^{-1}.

***endo*-3-(Trimethylsilyl)-2-norbornyl 2,4-dinitrobenzoate (10):** white blocks from pentane (32%); mp 98–99 °C; ^1H NMR δ ($CDCl_3$) 8.86 (1H, d, J = 2.2 Hz), 8.55 (1H, dd, J = 2.2, 8.3 Hz), 7.83 (1H, d, J = 8.3 Hz), 5.68 (1H, dddd, J = 1.2, 4.4, 6.6 Hz), 2.83 (1H, bs), 2.37 (1H, bs), 1.75–1.2 (8H, m), −0.03 (9H, s); ^{13}C NMR δ ($CDCl_3$) 163.94, 148.59, 147.39, 134.35, 130.24, 127.82, 119.88, 82.85, 41.75, 40.65, 40.07, 35.24, 26.47, 20.66, −0.06; λ_{max} (Nujol) 1734 (s), 1547 (s), 1286 (s), 1246 (s), 873 (s), 835 (s) cm^{-1}.

(b) Crystallography. Diffraction data were recorded on an Enraf-Nonius CAD4f diffractometer operating in the $\theta/2\theta$ scan mode. Crystal temperatures were maintained at 130(1) K for **9** and **11** and 213(1) K for **10** using an Oxford Cryostream cooling device. Data were corrected for Lorentz and polarization effects. Structures were solved by direct methods (SHELXS-86)[15] and were refined on F^2 (SHELXL93).[16] Crystal data and refinement details for **9**–**11** are listed in Table 3.

Acknowledgment. Our thanks go to the Australian Research Council Large Grants Scheme for financial support.

Supplementary Material Available: ^1H and ^{13}C NMR spectra of **9**, **10**, and **11** (6 pages). This material is contained in libraries on microfiche, immediately follows 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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(17) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.