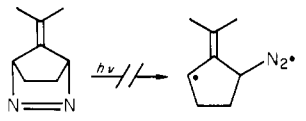
A second possibility is internal conversion to the lowest singlet state. However, the 280-ps lifetime increases to ~900 ps at 77 K. Since the rate of internal conversion is expected to be approximately temperature independent, this process probably makes only a small contribution to the total quenching rate.

Other possible pathways that cannot yet be ruled out include direct ring-closure, **1S*** → *ground-state* **2**, and ring-opening, **1S*** → 3-isopropylidenepenta-1,4-diene.

Although an excited diazenyl biradical **5***, derived by cleavage of only one bond of **3**, might be compatible with the 280-ps lifetime, independent chemical evidence[18] opposes such an intermediate in the photolysis of **3**.



3 **5**

Because of the methyl and methylene substituents in **1S**, the main *absorption* maximum should lie slightly to the red of 289 nm, predicted theoretically[8] for the S → S* ($^1E' \rightarrow {}^1A_1$) transition of the parent trimethylenemethane singlet. Although we have not yet observed the absorption spectrum of **1S** directly, the observed fluorescence maximum at 430 nm, ~60 nm beyond the onset of the band progression (Figure 2), and the assumption of the absorption and fluorescence spectra[9b] mirror-image relationship are in agreement with theoretical predictions[8] of an absorption band near 300 nm.

Registry No. 1, 32553-01-8; **2**, 72447-89-3; **3**, 31689-32-4.

Supplementary Material Available: Experimental details (1 page). Ordering information is given on any current masthead page.

(18) (a) Cichra, D. A.; Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 8507. (b) Cichra, D. A.; Duncan, C. D.; Berson, J. A. *Ibid.* **1980**, *102*, 6527.

S_N2 Displacements at 2-Norbornyl Brosylates

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Inverting nucleophile displacements at 2-norbonyl derivatives are rare,[1] and none of the recorded examples has been studied kinetically. The reluctance of *exo*-2-norbornyl derivaties to undergo S_N2 displacements[2,3] has been discussed in terms of steric hindrance to endo attack by nucleophiles[1c,2,5] but is also explicable by the high rate of unimolecular ionization. Quantitative data are required to solve this problem. We report that S_N2 displacements by azide ion at *exo*- and *endo*-2-norbornyl brosylates

Scheme I

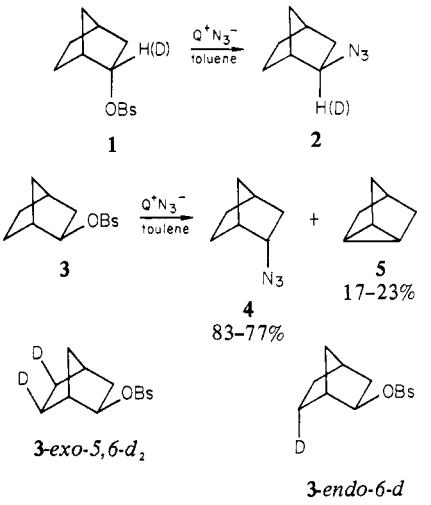

Table I. Second-Order Rate Constants for Alkyl Azide Formation from Alkyl Brosylates and Tributylhexadecylphosphonium Azide ($Q^+N_3^-$) in Toluene

ROBs	run no.	temp., °C	$[ROBs]_0$, M	$[Q^+N_3^-]_0$, M	elim, %	10^3k, M s^{-1}
1	1	65	0.02	0.025		2.17 ± 0.08[c]
	2	65	0.04	0.025		2.10 ± 0.06
	3	65	0.02	0.05		1.54 ± 0.06
	4	65	0.02	0.025[a]		1.50 ± 0.04
	5	65	0.02	0.0125		2.67 ± 0.13
	6	40	0.02	0.025		0.151 ± 0.007
		27.5[b]	0.02	0.025		0.034
2	7	65	0.02	0.025	17	1.90 ± 0.05
	8	65	0.02	0.05	10	1.50 ± 0.04
	9	40	0.02	0.025	23	0.101 ± 0.002
		27.5[b]	0.02	0.025		0.019
6	10	40	0.02	0.025	5	5.75 ± 0.15
	11	27.5	0.02	0.025	7	1.33 ± 0.05
7	12	27.5	0.02	0.025		74.6 ± 1.7
8	13	27.5	0.02	0.025		3.46 ± 0.07
9	14	27.5	0.02	0.025	6	16.3 ± 0.6

[a] Q^+OTs^- (0.025 M) added. [b] Calculated from data at higher temperatures. [c] Errors are standard deviations from a least-squares treatment. The results of duplicate runs agreed within these limits.

proceed at similar rates which indicate substantial (though not excessive) steric hindrance.

The reactions of *endo*-2-norbornyl brosylate (**1**) (Scheme I) with tributylhexadecylphosphonium azide[7] ($Q^+N_3^-$) in toluene at 40–65 °C afforded >97% of *exo*-2-norbornyl azide (**2**).[8] The analogous treatment of the deuterated brosylate **1**-d_2 did not lead to scrambling of the label (^2H NMR), thus excluding the intervention of 2-norbornyl cations. Rates were measured by quantitative IR analysis of the 2-norbornyl azide **2**.[9] Second-order kinetics, rate = $k[\mathbf{1}][Q^+N_3^-]$, were followed beyond 80% conversion. The rate constants (Table I) were independent of the initial concentration of **1** (runs 1 and 2) but decreased with increasing concentration of $Q^+N_3^-$ (runs 1, 3, and 5). Addition of

(1) (a) Cristol, S. J.; Brindell, G. D. *J. Am. Chem. Soc.* **1954**, *76*, 5699. (b) Nickon, A.; Hammons, J. H. *Ibid.* **1964**, *86*, 3322. (c) Schaefer, J. P.; Weinberg, D. S. *J. Org. Chem.* **1965**, *30*, 2635, 2639. (d) Tanigawa, Y.; Kanamaru, H.; Murahashi, S. I. *Tetrahedron Lett.* **1975**, 4655. (e) Brown, H. C.; Krishnamurthy, S. *J. Am. Chem. Soc.* **1973**, *95*, 1669. *Tetrahedron* **1979**, *35*, 5671. (f) Fischer, W.; Grob, C. A.; von Sprecher, G. *Helv. Chim. Acta* **1980**, *63*, 806.

(2) Grob, C. A.; Lutz, E. *Helv. Chim. Acta* **1981**, *64*, 153.

(3) *endo*-2-Norbornyl derivaties are more susceptible to inverting displacement;[1b,c,f] even the solvolyses of *endo*-2-norbornyl tosylate appear to be weakly solvent assisted.[4]

(4) (a) Winstein, S.; Trifan, D. S. *J. Am. Chem. Soc.* **1952**, *74*, 1147, 1154. (b) Harris, J. M.; Mount, D. L.; Raber, D. J. *Ibid.* **1978**, *100*, 3139. (c) Bentley, T. W.; Bowen, C. T.; Morten, D. H.; Schleyer, P. v. R. *Ibid.* **1981**, *103*, 5466.

(5) Steric hindrance to ionization has been invoked to explain the high solvolytic exo:endo rate ratios of 2-norbornyl derivatives.[6]

(6) Brown, H. C. "The Nonclassical Ion Problem", with comments by P. v. R. Schleyer; Plenum, New York, 1977; Chapter 8.

(7) Landini, D.; Maia, A.; Montanari, F. *J. Am. Chem. Soc.* **1978**, *100*, 2796. *Nouv. J. Chim.* **1979**, *3*, 575. We obtained $Q^+N_3^-$ by repeated exchange of Q^+Br^- in ether with 4 M NaN_3 in water. The residual Q^+Br^- was <1%.

(8) We have not been able to separate *exo*- and *endo*-2-norbornyl azide by VPC. Configurations were assigned by NMR (2-H of **2**: br t, J = 4–6 Hz, at δ 3.44; 2-H of **4**: dt, J = 10 and 4 Hz, at δ 3.89) and by catalytic hydrogenation (PtO_2 toluene). The azide obtained from **1** gave 97.8% of *exo*- and 2.2% of *endo*-2-norbornylamine. With the azide obtained from **3**, the exo:endo ratio of the amines was 2.6:97.4.

(9) The absorption of alkyl azides at 2100 cm^{-1} was sufficiently resolved from the absorption of $Q^+N_3^-$ at 2000 cm^{-1}. Calibration curves of the pure alkyl azides were established in the presence of the appropriate concentration of $Q^+N_3^-$ to account for an eventual overlap of the absorption bands.

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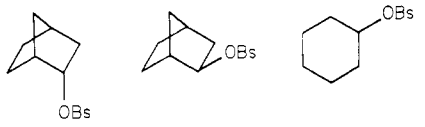
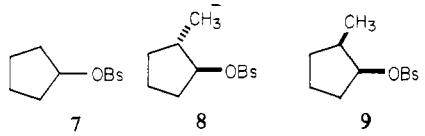
Scheme II



	1	3	6
RR ($Q^+N_3^-$, 27.5 °C)	0.026	0.014	1.0
RR (trifluoroacetolysis, 25 °C)[12]	1.5	1730	1.0



	7	8	9
RR ($Q^+N_3^-$, 27.5 °C)	56	2.6	12.3
RR (trifluoroacetolysis, 25 °C)[12]	8.9	24	

Q^+OTs^- had the same effect as increasing the concentration of $Q^+N_3^-$. Analogous observations with other substrates[7,10] have been attributed to association of the quaternary salts in weakly polar solvents.

exo-2-Norbornyl brosylate (**3**) and $Q^+N_3^-$ yielded 77–83% of *endo*-2-norbornyl azide (**4**) (contaminated with <3% of the exo-isomer **2**[8]) and 17–23% of nortricyclene (**5**). Only traces of norbornene were found. Substitution and elimination were treated as parallel second-order reactions; the rate constants in the table refer to the formation of **4**. The proton abstraction from **3** was explored with the aid of 6-position *d* labels. With the assumptions $(k_H/k_D)_{exo} = (k_H/k_D)_{endo} = Y$ and $k_{H,endo}/k_{H,exo} = k_{D,endo}/k_{D,exo} = p$, we obtain $Y = 1.6$ and $p = 1.3$. Our results agree closely with Nickon's data ($Y = 1.6, p = 1.5$) for the *tert*-butoxide-induced 1,3-elimination.[11]

So that the reactivity of **1** and **3** in direct displacement reactions with $Q^+N_3^-$ could be assessed, the brosylates **6–9** were included in our study (Scheme II and Table I). Cyclohexyl brosylate (**6**) reacted ca. 50 times faster than the 2-norbornyl brosylates, quite in contrast to the relative rates of trifluoroacetolysis.[12] The superiority of cyclopentyl over cyclohexyl derivatives in S_N2 reactions[13] was confirmed with **7** and $Q^+N_3^-$. For an evaluation of steric effects we studied *trans*- and *cis*-2-methylcyclopentyl brosylates (**8**, **9**). Both **8** and **9** showed clean inversion and depressed rates, as compared to **7**. The cis-isomer **9** (in which departure of the brosylate is sterically hindered) was ca. 5 times faster than the trans-isomer **8** (where the methyl group is in the way of the approaching nucleophile). These effects appear to balance more evenly in the reactions of **1** and **3** with $Q^+N_3^-$, whose rates differ by a factor less than 2.

The S_N2 reactivity of the 2-norbornyl brosylates (**1**, **3**) is moderate if compared to sterically unhindered substrates (**6**, **7**). On the other hand, **1** and **3** react at least 500 times faster than the seriously congested 2-adamantyl brosylate (**10**). An upper limit[14] for the reaction of **10** with $Q^+N_3^-$ in toluene at 65 °C is $k = (4.4 \pm 0.6)10^{-6}$ M s^{-1}. Inspection of Scheme II strongly suggests that the deviant behavior of **1** and **3** in solvolyses is not due to large differences in k_s but to the fast unimolecular ionization (k_c or k_Δ) of **3**.

Registry No. **1**, 840-89-1; **2**, 22526-51-8; **3**, 840-88-0; **4**, 81940-38-7; **5**, 279-19-6; **6**, 18939-93-0; **7**, 4596-40-1; **8**, 36367-81-4; **9**, 81940-39-8; **10**, 38680-00-1; *endo*-2-norbornylamine, 31002-73-0; *exo*-2-norbornylamine, 7242-92-4.

(10) Landini, D.; Maia, A.; Montanari, F.; Pirisi, F. M. *J. Chem. Soc., Perkin Trans. 2* **1980**, 46.

(11) Nickon, A.; Werstiuk, N. H. *J. Am. Chem. Soc.* **1967**, *89*, 3914, 1915, 3917.

(12) The rates of trifluoroacetolysis refer to the corresponding tosylates: Roberts, D. D.; Hendrickson, W. *J. Org. Chem.* **1969**, *34*, 2415. Nordlander, J. E.; Gruetzmacker, R. R.; Kelly, W. J.; Jindal, S. P. *J. Am. Chem. Soc.* **1974**, *96*, 181.

(13) (a) Streitwieser, A., Jr. "Solvolytic Displacement Reactions"; McGraw Hill: New York, 1962. (b) Elias, H.; Krutzig, S. *Chem. Ber.* **1966**, *99*, 1026. (c) Chang, W.-S.; Elias, H. *Ibid.* **1970**, *103*, 842. Gounelle, Y.; Solgadi, D. *Bull. Soc. Chim. Fr.* **1973**, 3019.

(14) The reaction of 2-adamantyl brosylate with $Q^+N_3^-$ was second order but afforded 82% of 2-adamantyl azide and 18% of 2-adamantyl bromide. The most probable source of bromide ion is nucleophilic displacement at the para position of the brosylate. Therefore the rate constant contains an unknown contribution of S_NAr. These complications are avoided with 2-adamantyl tosylate which, however, requires elevated temperatures: $k \approx 9.5 \times 10^{-5}$ M s^{-1} at 111 °C in toluene; $k = (1.48 \pm 0.02) \times 10^{-4}$ M s^{-1} at 114 °C in ethylbenzene. The stereochemistry of these reactions remains to be elucidated.

Stereochemical Control of Intramolecular Conjugate Addition. A Short, Highly Stereoselective Synthesis of Adrenosterone

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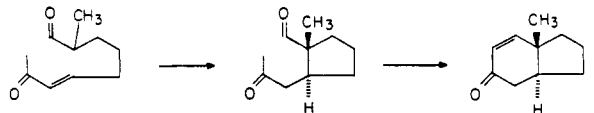
We have recently demonstrated the use of the intramolecular Michael addition to control vicinal stereochemistry in the construction of trans-fused hydrindans, i.e., **1** → **3**.[1]



1 **2** **3**

We report here the application of this method to a short synthesis of adrenosterone. The synthesis of the key intermediate, *trans*-hydrindenone **10**, is outlined below (Scheme I).

Alkylation of the dianion of ethyl 2-methylacetoacetate[2] with allyl bromide (tetrahydrofuran, 0 °C → room temperature) provided **5** (68% yield, bp 76–78 °C (12 mmHg)), which was ketalized (ethylene glycol, *p*-toluenesulfonic acid, benzene, 74% yield) to give **6**, bp 64–66 °C (0.05 mmHg).[3] Ozonolysis of **6** (methanol, −78 °C, triphenylphosphine, 93% yield) afforded aldehydo ester **7**, which was treated with dimethyl 3-methoxy-2-(oxopropyl)phosphonate[4] (K_2CO_3, benzene, room temperature, 79% yield) to provide enone ester **8**.[5] Reduction of **8** (lithium aluminum hydride, tetrahydrofuran, −40 °C → room temperature, 95% yield) furnished the corresponding unsaturated diol, which was oxidized by using the Ratcliffe modification[6] of the Collins oxidation[7] to produce **9** in 70–80% yield.

Cyclization of **9** with 1.5 equiv of zirconium tetra-*n*-propoxide (0.04 M in benzene, room temperature) followed by treatment with 2 equiv of sodium methoxide furnished *trans*-hydrindenone **10**, mp 80–81 °C (ether/petroleum ether), in 63% yield (found: C, 65.40; H, 7.55). ^{1}H NMR and VPC analysis of the reaction product showed a 25:1 trans/cis ratio of hydrindenone **10** and its cis-fused isomer.[8,9]

(1) Stork, G.; Shiner, C.; Winkler, J. *J. Am. Chem. Soc.* **1982**, *104*, 310.

(2) Huckin, S. N.; Weiler, L. *J. Am. Chem. Soc.* **1974**, *96*, 1082.

(3) Infrared data are listed in cm^{-1}. ^{1}H NMR data are reported in δ, downfield from Me_4Si. ^{13}C NMR data are reported in δ, with $CHCl_3$ as a reference standard. **6**: IR (film) 1720, 1640; ^{1}H NMR (80 MHz) 1.18 (d, J = 7 Hz, 3 H), 1.24 (t, J = 7 Hz, 3 H), 1.6–2.3 (m, 4 H), 2.80 (q, J = 7 Hz, 1 H), 3.96 (s, 4 H), 4.13 (q, J = 7 Hz, 2 H), 4.92 (br d, J = 10 Hz, 1 H), 5.03 (br d, J = 8 Hz, 1 H), 5.6–6.1 (m, 1 H); ^{13}C NMR (20.1 MHz) 12.26, 13.90, 27.13, 34.11, 46.91, 60.01, 65.35, 110.97, 113.95, 138.34, 172.92; MS (CI–ME) 229 (M + 1).

(4) Corey, E. J.; Kwiatkowsky, G. *J. Am. Chem. Soc.* **1966**, *88*, 5652.

(5) **8**: IR (film) 1735, 1695, 1630; ^{1}H NMR (80 MHz) 1.18 (d, J = 7 Hz, 3 H), 1.25 (t, J = 7 Hz, 3 H), 1.8–2.5 (m, 4 H), 2.80 (q, J = 7 Hz, 1 H), 3.41 (s, 3 H), 3.97 (br s, 4 H), 4.15 (s, 2 H), 4.14 (q, J = 7 Hz, 2 H), 6.24 (d, J = 16 Hz, 1 H), 6.99 (dt, J = 7, 16 Hz, 1 H); MS (CI–ME) 301 (M + 1).

(6) Ratcliffe, R.; Rodehorst, R. *J. Org. Chem.* **1970**, *35*, 4000.

(7) Collins, J.; Hess, W. *Org. Synth.* **1972**, *52*, 5.

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