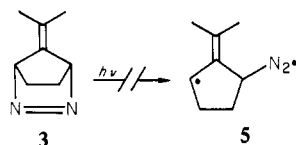


A second possibility is internal conversion to the lowest singlet state. However, the 280-ps lifetime increases to  $\sim 900$  ps at 77 K. Since the rate of internal conversion is expected to be approximately temperature independent, this process probably makes only a small contribution to the total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

Other possible pathways that cannot yet be ruled out include direct ring-closure,  $1S^* \rightarrow$  ground-state **2**, and ring-opening,  $1S^* \rightarrow$  3-isopropylidene-penta-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<sup>18</sup> opposes such an intermediate in the photolysis of **3**.



Because of the methyl and methylene substituents in **1S**, the main absorption maximum should lie slightly to the red of 289 nm, predicted theoretically<sup>8</sup> for the  $S \rightarrow S^*$  ( ${}^1E' \rightarrow {}^1A_1$ ) 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,  $\sim 60$  nm beyond the onset of the band progression (Figure 2), and the assumption of the absorption and fluorescence spectra<sup>9b</sup> mirror-image relationship are in agreement with theoretical predictions<sup>8</sup> 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-norbornyl derivatives are rare,<sup>1</sup> and none of the recorded examples has been studied kinetically. The reluctance of *exo*-2-norbornyl derivatives to undergo  $S_N2$  displacements<sup>2,3</sup> has been discussed in terms of steric hindrance to *endo* attack by nucleophiles<sup>1c,2,5</sup> 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

(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. *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 derivatives are more susceptible to inverting displacement;<sup>1b,e,f</sup> even the solvolyses of *endo*-2-norbornyl tosylate appear to be weakly solvent assisted.<sup>4</sup>

(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.<sup>6</sup>

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

## Scheme I

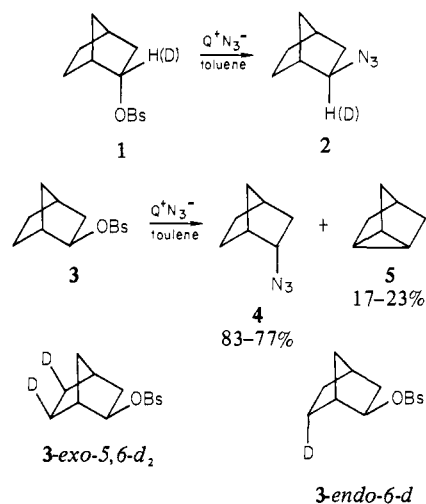


Table I. Second-Order Rate Constants for Alkyl Azide Formation from Alkyl Brosylates and Tributylhexadecylphosphonium Azide ( $Q^+N_3^-$ ) in Toluene

ROBs	run no.	temp., °C	[ROBs] <sub>0</sub> , M	[ $Q^+N_3^-$ ] <sub>0</sub> , M	elim, %	$10^3 k$ , M s <sup>-1</sup>
<b>1</b>	1	65	0.02	0.025		$2.17 \pm 0.08^c$
	2	65	0.04	0.025		$2.10 \pm 0.06$
	3	65	0.02	0.05		$1.54 \pm 0.06$
	4	65	0.02	0.025 <sup>a</sup>		$1.50 \pm 0.04$
	5	65	0.02	0.0125		$2.67 \pm 0.13$
	6	40	0.02	0.025		$0.151 \pm 0.007$
<b>2</b>	7	65	0.02	0.025	17	$1.90 \pm 0.05$
	8	65	0.02	0.05	10	$1.50 \pm 0.04$
	9	40	0.02	0.025	23	$0.101 \pm 0.002$
<b>6</b>	10	40	0.02	0.025	5	$5.75 \pm 0.15$
	11	27.5	0.02	0.025	7	$1.33 \pm 0.05$
<b>7</b>	12	27.5	0.02	0.025		$74.6 \pm 1.7$
<b>8</b>	13	27.5	0.02	0.025		$3.46 \pm 0.07$
<b>9</b>	14	27.5	0.02	0.025	6	$16.3 \pm 0.6$

<sup>a</sup>  $Q^+OTs^-$  (0.025 M) added. <sup>b</sup> Calculated from data at higher temperatures. <sup>c</sup> 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.

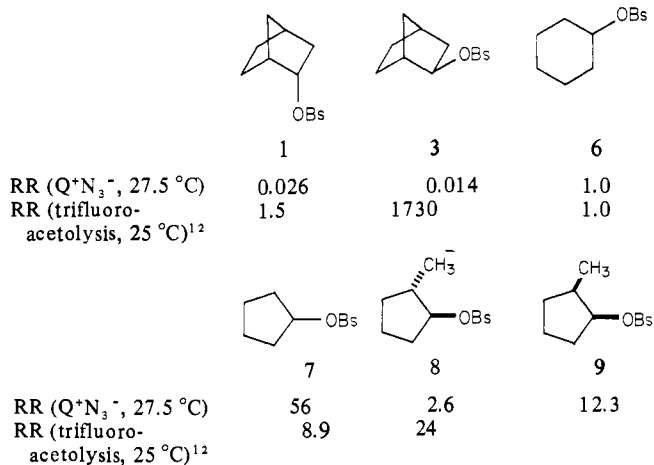
The reactions of *endo*-2-norbornyl brosylate (**1**) (Scheme I) with tributylhexadecylphosphonium azide<sup>7</sup> ( $Q^+N_3^-$ ) in toluene at 40–65 °C afforded >97% of *exo*-2-norbornyl azide (**2**).<sup>8</sup> The analogous treatment of the deuterated brosylate **1-d<sub>2</sub>** did not lead to scrambling of the label (<sup>2</sup>H NMR), thus excluding the intervention of 2-norbornyl cations. Rates were measured by quantitative IR analysis of the 2-norbornyl azide **2**.<sup>9</sup> Second-order kinetics, rate =  $k[1][Q^+N_3^-]$ , 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

(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  $\delta$  3.44; 2-H of **4**: dt,  $J = 10$  and 4 Hz, at  $\delta$  3.89) and by catalytic hydrogenation (PtO<sub>2</sub> 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<sup>-1</sup> was sufficiently resolved from the absorption of  $Q^+N_3^-$  at 2000 cm<sup>-1</sup>. 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.

## Scheme II



Q<sup>+</sup>OTs<sup>-</sup> had the same effect as increasing the concentration of Q<sup>+</sup>N<sub>3</sub><sup>-</sup>. Analogous observations with other substrates<sup>7,10</sup> have been attributed to association of the quaternary salts in weakly polar solvents.

*exo*-2-Norbornyl brosylate (3) and Q<sup>+</sup>N<sub>3</sub><sup>-</sup> yielded 77–83% of *endo*-2-norbornyl azide (4) (contaminated with <3% of the *exo*-isomer 2<sup>8</sup>) 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 ( $k_H/k_D$ )<sub>exo</sub> = ( $k_H/k_D$ )<sub>endo</sub> = *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.<sup>11</sup>

So that the reactivity of 1 and 3 in direct displacement reactions with Q<sup>+</sup>N<sub>3</sub><sup>-</sup> 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.<sup>12</sup> The superiority of cyclopentyl over cyclohexyl derivatives in S<sub>N</sub>2 reactions<sup>13</sup> was confirmed with 7 and Q<sup>+</sup>N<sub>3</sub><sup>-</sup>. 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<sup>+</sup>N<sub>3</sub><sup>-</sup>, whose rates differ by a factor less than 2.

The S<sub>N</sub>2 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<sup>14</sup> for the reaction of 10 with Q<sup>+</sup>N<sub>3</sub><sup>-</sup> in toluene at 65 °C is  $k = (4.4 \pm 0.6)10^{-6} \text{ M s}^{-1}$ . Inspection of Scheme II strongly suggests that the deviant behavior of 1 and 3 in solvolyses is not due to large differences in *k<sub>s</sub>* but to the fast unimolecular ionization (*k<sub>c</sub>* or *k<sub>d</sub>*) 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.

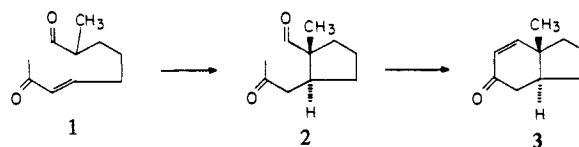
### Stereochemical Control of Intramolecular Conjugate Addition. A Short, Highly Stereoselective Synthesis of Adrenosterone

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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.<sup>1</sup>



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<sup>2</sup> 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).<sup>3</sup> Ozonolysis of 6 (methanol, –78 °C, triphenylphosphine, 93% yield) afforded aldehyde ester 7, which was treated with dimethyl 3-methoxy-2-(oxopropyl)phosphonate<sup>4</sup> (K<sub>2</sub>CO<sub>3</sub>, benzene, room temperature, 79% yield) to provide enone ester 8.<sup>5</sup> 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<sup>6</sup> of the Collins oxidation<sup>7</sup> 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). <sup>1</sup>H NMR and VPC analysis of the reaction product showed a 25:1 *trans*/*cis* ratio of hydrindenone 10 and its *cis*-fused isomer.<sup>8,9</sup>

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

(11) Nickon, A.; Werstik, 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.; Gruetzmaeker, 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<sup>+</sup>N<sub>3</sub><sup>-</sup> 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<sub>N</sub>Ar. These complications are avoided with 2-adamantyl tosylate which, however, requires elevated temperatures:  $k \approx 9.5 \times 10^{-5} \text{ M s}^{-1}$  at 111 °C in toluene;  $k = (1.48 \pm 0.02) \times 10^{-4} \text{ M s}^{-1}$  at 114 °C in ethylbenzene. The stereochemistry of these reactions remains to be elucidated.

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

(3) Infrared data are listed in cm<sup>-1</sup>. <sup>1</sup>H NMR data are reported in  $\delta$ , downfield from Me<sub>4</sub>Si. <sup>13</sup>C NMR data are reported in  $\delta$ , with CHCl<sub>3</sub> as a reference standard. 6: IR (film) 1720, 1640; <sup>1</sup>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); <sup>13</sup>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; <sup>1</sup>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).

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