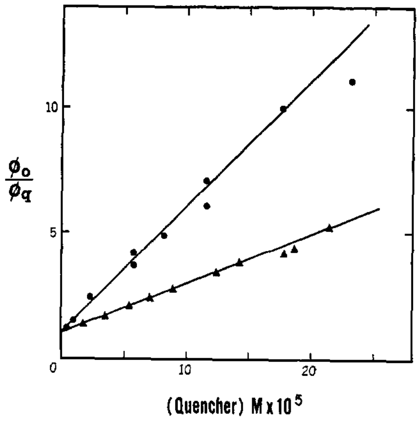

Figure 1. Effect of quencher **1** on the quantum yield of isomerization of *trans*-stilbene sensitized by benzathrone (●) and by anthracene (▲).

plausible geometry might be the twisted form **5** which would owe its stability to the same factors that stabilize nitroxide radicals.

Quenching of benzanthrone (E_T = 47 kcal/mol)[15] and anthracene triplets by **1** was studied quantitatively by observing the effect of **1** on the quantum yields of the sensitized isomerization of *trans*-stilbene. The experimental conditions employed were identical with those in flash photolysis experiments in which the sensitizer triplet lifetimes (τ_s) in the presence of *trans*-stilbene had been determined.[15] Under these conditions quenching should follow eq 1 where subscripts s and t refer to sensitizer and *trans*-stilbene, respectively. Since at

$$\phi_0/\phi_q = (1 + k_{qs}\tau_s[Q])(1 + k_{qt}\tau_t[Q]) \qquad (1)$$

quencher concentrations [Q] of $\leqslant 10^{-4}$ *M* experimental plots of ϕ_0/ϕ_q were linear (Figure 1), one of the terms in eq 1 must be $\sim$1 and can be neglected. This must be the *trans*-stilbene quenching term ($1 + k_{qt}\tau_t[Q]$) because the stilbene triplet lifetime is $< 2 \times 10^{-7}$ sec[10] and the quenching rate constant k_{qt} cannot exceed diffusion control ($< 7 \times 10^9$ M^{-1} sec^{-1}).[15] From the slopes (5.1×10^4 M^{-1} for benzanthrone and 2×10^4 M^{-1} for anthracene) and the respective sensitizer triplet lifetimes ($\tau_s = 3.6 \times 10^{-5}$ and 1.7×10^{-4} sec),[15] rates of energy transfer from sensitizer to **1** (k_{qs}) of 1.4×10^9 M^{-1} sec^{-1} (benzanthrone) and 1.2×10^8 M^{-1} sec^{-1} (anthracene) are calculated. These rates are consistent with the conclusion that E_T for **1** lies near that of anthracene.[16]

Based on the above described efficiency of **1** as a triplet quencher, its short wavelength absorption, and the absence of both singlet quenching and triplet reactivity, we recommend that **1** be considered as a practical alternative to diene triplet quenchers where wavelengths above 300 nm can be employed.

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[15] W. G. Herkstroeter and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 4769 (1966).

[16] A referee's suggestion that ground-state complexing might affect these rates is inconsistent with the absence of changes in the spectra of benzene solutions of anthracene and benzanthrone upon making the solutions 2×10^{-2} *M* in **1**.

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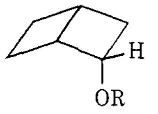
Strained Ring Systems. XIII.[1] Solvolysis of *endo*-Bicyclo[2.2.0]hex-2-yl 3,5-Dinitrobenzoate. A Possible Route to the Homoallylic Δ^3-Cyclohexenyl Cation

Sir:

Of the isomeric bicyclic C_6 ([2.1.0]-5-carbinyl,[2a] [3.1.0]-2-yl,[2a-d] [2.1.1]-5-yl,[2e] and [2.2.0]-2-yl[2f]) and the bicyclo[*m*.2.0]alkyl ([2.1.0]-2-yl, [2.2.0]-2-yl, [3.2.0]-6-yl, and [4.2.0]-7-yl)[3] derivatives, only the literature for the *endo*-bicyclo[2.2.0]hex-2-yl system is presently lacking. We wish to report the results of kinetic and product studies obtained in the solvolysis of *endo*-bicyclo[2.2.0]hex-2-yl 3,5-dinitrobenzoate (**1-ODNB**) in 60% (v/v) aqueous acetone.

The synthesis of **1-ODNB** utilized the previously reported inseparable mixture of **1-OH** and its exo isomer, **2-OH**,[4] which was converted in the usual manner[2e] to



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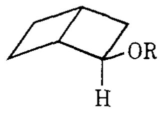

2

the mixture of **1-ODNB** and **2-ODNB** used in this investigation. The kinetic data, determined by the conductance method,[5] and thermodynamic parameters for solvolysis of **1-ODNB** in 60% aqueous acetone are listed in Table I. Applying the factor of 6×10^3 as the difference in rate constants for a tosylate in acetic acid at 50° and a 3,5-dinitrobenzoate in 60% aqueous acetone at 100°[2c] to the acetolysis rate constant of 2-OTs,[2f] we arrive at $k_{endo}/k_{exo} = 8 \times 10^7$ for the bicyclo[2.2.0]hex-2-yl system;[6] this and the rate ratios for the other isomeric bicyclic C_6 derivatives are given in Table II.

The hydrolysis products from **1-ODBN** generated in the presence of *sym*-collidine to eliminate acid-catalyzed rearrangements were most interesting. Not only was the ion-pair return product, *endo*-bicyclo[3.1.0]hex-2-yl ODNB (**3-ODNB**), obtained in substantial quantity but an excess of its alcohol **3-OH** was present when compared to the product results from the solvolysis of **3-ODNB** and its exo isomer, **4-ODNB** (Table III).[7,8]

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[1] For paper XII in this series see R. N. McDonald and R. R. Reitz, *J. Org. Chem.*, in press.

[2] (a) K. B. Wiberg and A. J. Ashe, *J. Amer. Chem. Soc.*, **90**, 63 (1968); (b) E. C. Friedrich and M. A. Saleh, *Tetrahedron Lett.*, 1373 (1971); (c) P. R. Brook, R. M. Ellam, and A. S. Bloss, *Chem. Commun.*, 425 (1968); (d) G. H. Schmid and A. Brown, *Tetrahedron Lett.*, 4695 (1968); (e) K. B. Wiberg, R. A. Fenoglio, V. Z. Williams, and R. W. Ubersax, *J. Amer. Chem. Soc.*, **92**, 568 (1970); (f) R. N. McDonald and C. E. Reineke, *J. Org. Chem.*, **32**, 1878 (1967).

[3] K. B. Wiberg, V. Z. Williams, and L. E. Friedrich, *J. Amer. Chem. Soc.*, **92**, 564 (1970). This reference contains a comparison of the rates of solvolysis of bicyclo[*m*.2.0]alkyl derivatives and the prediction of the large endo/exo rate ratio found for **1** and **2**.

[4] R. N. McDonald and G. E. Davis, *J. Org. Chem.*, **34**, 1916 (1969). A 36:64 mixture of **1-OH** and **2-OH**, respectively, was converted to the mixture of dinitrobenzoates. The solvolytic infinity titer corresponded to 23.2% reaction based on the total amount of **1-** and **2-ODNB** or 64.5% on available **1-ODNB**, assuming that the **1-ODNB**:**2-ODNB** ratio was the same as that of the starting alcohol mixture.

[5] (a) Using a M-D Mini-Cell[5b] coupled to a Beckman RC-18A conductivity bridge; (b) available through R-M Research Products, Inc., Manhattan, Kan. 66502.

[6] The magnitude k_{endo}/k_{exo} in this system readily allowed the use of the mixture of **1-** and **2-ODNB** in the rate studies.

[7] The products from similar hydrolysis of **4-ODNB** (glpc analysis) are the same as obtained from **3-ODNB** within experimental error. The product distribution from **3-ODNB** in this study differs from that

Table I. Solvolysis Rate Data in 60% (v/v) Aqueous Acetone

Compd	Temp, °C	10^4k,[a] sec^{-1}	Av 10^4k, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
1-ODNB	50.0[b]	2.539 ± 0.015	2.52	21.9	−7.5
		2.509 ± 0.007			
	70.0[b]	19.42 ± 0.008	19.5		
		19.64 ± 0.007			
3-ODNB	90.0[c]	0.360 ± 0.006	0.360		
		0.360 ± 0.004			

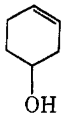
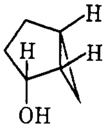
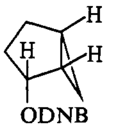
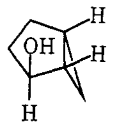
[a] Errors are standard deviations. [b] Conductometric method. [c] Titrimetric method.

Table II. Endo–Exo Rate Ratios for Bicyclic C_6 and Bicyclo[*m*.2.0]alkyl Derivatives

Isomer	k_{endo}/k_{exo}	Ref
[2.1.0]-5-carbinyl	0.86	2a
[3.1.0]-2-yl	1.2	2b
[2.1.1]-5-yl	2.4 × 10^7	2e
[2.2.0]-2-yl	8 × 10^7	2f; this work
[2.1.0]-2-yl	10^7	3
[3.2.0]-6-yl	460	3
[4.2.0]-7-yl	6.5	3

We believe the results of runs 1 and 2 with **3-ODNB** (Table III) show that the only role of *sym*-collidine in these product studies was that of a proton acceptor.

Table III. Products from the 60% (v/v) Aqueous Acetone Solvolysis of **1-ODNB** and **3-ODNB** after 10 Solvolytic Half-Lives[a,b]

Compd	Temp, °C	Run	 **5-OH**	 **3-OH**	 **3-ODNB**	 **4-OH**	% alcohol recovery	**3-OH/4-OH**
1-ODNB	50.0	*c, e*	19[h]	48[h]	(36)[i]	33[h]	90[j]	1.4
3-ODNB	90.0	1[d,e]	14	38		48	85	0.8
		2[d,f]	16	36		48	83	
		3[d,g]	49	22		29	82	

[a] Reference 8. [b] The percentages of **4-OH** and **5-OH** were obtained from glpc (Carbowax 20M capillary column) and nmr analyses, respectively, where these peaks (absorptions) are clearly separated; the per cent of **3-OH** was by difference. These then correlated well with both the total integrated glpc and nmr spectra correcting for overlapping areas. [c] Single product determination. [d] Average of duplicate runs; agreement in duplicates was ±1%. [e] Contained 2 molar equiv of *sym*-collidine. [f] Contained 10 molar equiv of *sym*-collidine. [g] Contained no added base. [h] Per cent of alcohol products. [i] Isolated yield. [j] The **1-** and **2-ODNB** mixture (2.40 mmol) produced 0.41 mmol of alcohol product and 1.72 mmol of a 78:22 mixture of **2-ODNB** and **3-ODNB**, respectively. From these values we calculate that the alcohol product was obtained in 90% yield and the mixture of **2-ODNB** and **3-ODNB** recovered in 89% yield. We further calculate the initial composition of the mixture of **1-ODNB** and **2-ODNB** to be 32:68, respectively, in excellent agreement with the composition of the starting alcohols **1-OH** and **2-OH**.[4]

Since the product studies from **1-ODNB** and **3-ODNB** were done at different temperatures, we have examined the product from **3-ODNB** under the conditions of run 1, Table III, but at 70°. After approximately 4 half-lives, the composition of the alcohol mixture was 32% **3-OH**, 52% **4-OH**, and 16% **5-OH**, in reasonable agreement with runs 1 and 2 for **3-ODNB** at 90°. In fact, the lower temperature effect on this solvolysis and carbonium ion capture by solvent is to increase to a small extent the amount of **4-OH** at the expense of forming **3-OH** with the ratio **3-OH**:**4-OH** decreasing to 0.6.

Any mechanism for the solvolysis of **1-ODNB** must, therefore, account for (1) its relatively fast solvolytic rate, (2) the stereospecific formation of ion-pair return product **3-ODNB**, and (3) the inverse **3-OH**/**4-OH** product ratio found compared to that obtained from **3-ODNB**. Factor 3 rules out the direct conversion of **1-ODNB** to the same ion pair obtained from **3-ODNB** or **4-ODNB**.[2b] We favor the idea of a concerted disrotatory opening of the zero-bridge bond to maintain maximum overlap with the developing p orbital at C_2[3] in the ionization of **1-ODNB**. While this may account for the rapid rate of hydrolysis of **1-ODNB**, it does little to explain the product composition.

Conformational changes in the rather rigid bicyclo[3.1.0]hex-2-yl cation **7** do not appear to account for the differences in product composition obtained from **1-ODNB** and **3-ODNB** or **4-ODNB**. Lacking information about possible differences in the types of ion pairs formed from these systems, we must then consider the reasonable possibility that we are capturing another carbonium ion which may then rearrange to **7**.

We suggest that the first formed intermediate is the homoallylic Δ^3-cyclohexenyl cation–3,5-dinitrobenzoate ion pair **6**. Reaction of **6** with solvent should be preferred from the underside (endo) due to reduced electron density and due to possible solvent-separated ion-pair formation. Solvent attack at C_1 and C_4 would give **3-OH** and **5-OH**, respectively, while ion-pair return would produce **3-ODNB**. Further skeletal and electronic alterations could convert **6** to the proposed

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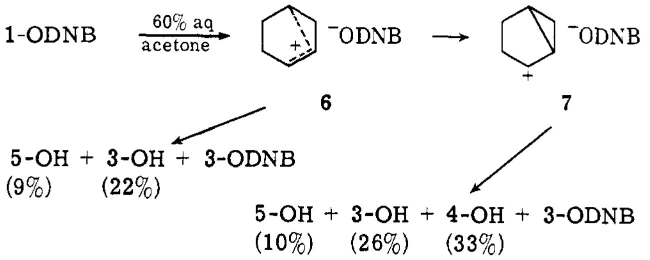
previously reported in 80% aqueous acetone with $CaCO_3$ as the proton scavenger [5-OH (24%), 3-OH (36%), 4-OH (37%), and Δ^2-cyclohexenol (3%)].[2b] This may result from the change in media and/or the use of *sym*-collidine, a soluble base, which functions more efficiently to remove protons from the medium than does the insoluble $CaCO_3$.

(8) All products have been shown to be stable under the reaction conditions used in the presence of *sym*-collidine and its salt from 3,5-dinitrobenzoic acid.

cyclopropylcarbinyl cation–dinitrobenzoate ion pair **7** described for solvolysis and **3**- and **4**-ODNB's.[2b] Reaction of **7** with solvent would produce **3**-OH and **4**-OH, and ion-pair return may produce **3**-ODNB.[9]

If we assume that the product distribution from **7** is the same as that found from **3**-ODNB and that all of alcohol **4**-OH is derived from **7**, the products from ion pair **6** are 22% **3**-OH, 9% **5**-OH, and probably the majority of the ion-pair return product, **3**-ODNB, using the 90° results for **3**-ODNB. This requires a reasonable lifetime and stability of **6** even though the configuration changes required for the conversion of **6** to **7** appear to be small.



Hanack and Keberle[10] reported that the buffered acetolysis of Δ^3-cyclohexenyl tosylate (**5**-OTs) gave a small amount of [3.1.0] products, **3**-OAc and **4**-OAc, along with major amounts of **5**-OAc and Δ^2-cyclohexenyl acetate. We have found that in buffered acetic acid 17% of a mixture of **3**-OAc and **4**-OAc is converted to **5**-OAc after 47 hr at 75° which gives a first-order rate constant of about 1×10^{-6} sec^{-1} for this rearrangement. This requires that *ca.* 40% of the **3**-OAc and **4**-OAc produced from **5**-OTs would have rearranged during the 168-hr acetolysis period at 70.00°.[10] The combined yield of **3**-OAc and **4**-OAc should then be considered to be a minimum of 11%. However, since the ratio of **3**-OAc/**4**-OAc from the acetolysis of **5**-OTs is 0.55,[10] it appears that these products are produced from the cyclopropylcarbinyl cation in **7**.[11]

At least two factors may account for the ability to enter the potential well of the homoallylic cation in **6** from **1**-ODNB but not from **5**-OTs: (1) the increased energy in the [2.2.0] system compared to the Δ^3-cyclohexenyl system due to strain and/or (2) the marked increase in *Y* value and nucleophilicity in the solvent systems used with these two substrates (buffered acetic acid for **5**-OTs and *sym*-collidine buffered 60% aqueous acetone for **1**-ODNB). With respect to factor 2, we have found that **5**-OH is the only alcohol product from **5**-OTs in *sym*-collidine buffered 60% aqueous acetone at 50° after 24 hr. However, this result may only reflect the increased nucleophilicity of this solvent system compared to buffered acetic acid.

Acknowledgments. Support of this research by the National Science Foundation (GP-7818, GP-10691) is gratefully acknowledged.

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[9] The benzoate ester of **1**-OH is stable to the solvolytic conditions which negates any **1**-ODNB → **3**-ODNB by a direct acid-catalyzed rearrangement as found with **1**-OAc.[4]

[10] M. Hanack and W. Keberle, *Chem. Ber.*, **96,** 2937 (1963).

[11] In the Δ^3-cyclohexenyl–cyclohexyl system, $k_{\text{unsat}}/k_{\text{sat}} = 2.4$ is found for tosylate acetolysis; ref 10 and H. C. Brown and G. Ham, *J. Amer. Chem. Soc.*, **78,** 2735 (1956).

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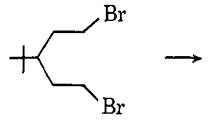
New Conformationally Stable 4-*tert*-Butyl-1-silacyclohexanes and Stereochemistry of Insertion of Dimethylsilylenes into the Silicon-Hydrogen Bond

Sir:

The stereochemistry of reactions on a silicon center has been studied mainly by using optically active 1-naphthylphenylmethylsilyl derivatives prepared first by Sommer and Frye.[1,2] However, it became necessary to look for other aliphatic silicon compounds suitable for the stereochemical study of certain reactions as the dimethylsilylene insertion into the Si–H bond reported in this paper. Accordingly, we have prepared the first conformationally stable 4-*tert*-butyl-1-silacyclohexane derivatives. Numerous stereochemical studies on the corresponding carbon analogs, 4-*tert*-butylcyclohexanes, have been published since the first proposal of the *tert*-butyl function as a holding group.[3]

3-*tert*-Butyl-1,5-dibromopentane (**1**), bp 98–99° (3 mm),[4] was prepared by a five-step synthesis from *p*-*tert*-butylphenol. The reaction of the di-Grignard reagent of **1** with methyldichlorosilane and with methyltrichlorosilane afforded 1-methyl-4-*tert*-butyl-1-silacyclohexane (**2**, cis/trans = 1.0)[5] and 1-methyl-4-*tert*-butyl-1-chloro-1-silacyclohexane (**3**, cis/trans = 1/2.3), respectively.



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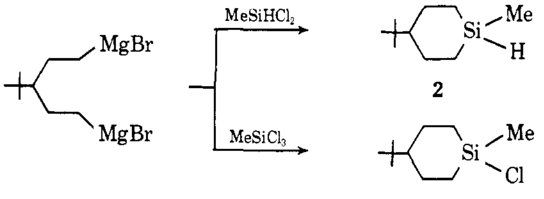

By alcoholysis of **3** or of **2** catalyzed by palladium on charcoal, a number of alkoxy derivatives were prepared. The isopropoxysilane proved the most convenient for separation of cis and trans isomers by preparative glc. These isomeric alkoxy derivatives were then reduced to **2** with LiAlH_4 stereospecifically (retention of configuration) as in reduction of optically active alkoxysilanes.[2] Several derivatives of **2** were prepared; nmr data for these compounds are listed in Table I.[6]

The structures of **2a** and **2b** were assigned from $\text{Si}HCH_2$ coupling constants. Thus, irradiation of the SiCH_3 signal of **2b** revealed $J_{\text{Si}H(\text{ax})-\text{C}H(\text{ax})}$ and $J_{\text{Si}H(\text{ax})-\text{C}H(\text{eq})}$ to be 6.5 and 1.7 Hz, respectively, and $J_{\text{Si}H(\text{eq})-\text{C}H(\text{ax})}$ to be *ca.* 1.0 Hz for **2a**. The axial methyl

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[1] L. H. Sommer and C. L. Frye, *J. Amer. Chem. Soc.*, **81,** 1013 (1959).

[2] L. H. Sommer, "Stereochemistry, Mechanism and Silicon," McGraw-Hill, New York, N. Y., 1965.

[3] S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, **77,** 5562 (1955).

[4] C. R. Johnson and D. McCants, Jr., *ibid.*, **87,** 1109 (1965).

[5] Throughout the paper, cis and trans are defined with respect to 4-*tert*-butyl and 1-methyl groups. Suffix **a** is added to the cis compounds and **b** to the trans.

[6] Satisfactory elemental analyses and parent peaks (M^+) in mass spectra were obtained for each isomer of **4**, **5**, **7**, and **8**, and for cis–trans mixtures of **2**, **3**, **6**, **9**, and **10**.