**Table II.** Some Experimental Values of $\Delta S^{\ddagger}_{\text{sie}}$ for Hydrolytic Reactions in Light and Heavy Water

| Reactant | $\Delta H^{\ddagger}$, kcal mol$^{-1}$ |  | $\Delta S^{\ddagger}$, cal mol$^{-1}$ deg$^{-1}$ |  |  |  |  |
|---|---|---|---|---|---|---|---|
|  | $H_2O$ | $D_2O$ | $H_2O$ | $D_2O$ | $k_{H_2O}/k_{D_2O}$ | $\Delta S^{\ddagger}_{\text{sie}}$ | Ref |
| *O*-(Chloroacetyl)-salicylic acid[a] | 14.62 ± 0.08 | 14.84 ± 0.08 | −23.58 ± 0.27 | −24.51 ± 0.27 | 2.35 | −0.9 | *d* |
| Methyl trifluoro-acetate[b] | 10.60 ± 0.03 | 10.48 ± 0.05 | −32.3 ± 0.3 | −34.0 ± 0.4 | 3.48 | −1.7 | *e* |
| Ethyl trifluoro-acetate[b] | 10.53 ± 0.03 | 11.08 ± 0.03 | −34.5 ± 0.3 | −35.1 ± 0.3 | 3.54 | −0.6 | *e* |
| *tert*-Butyl trifluoro-acetate[b] | 25.44 ± 0.06 | 26.08 ± 0.05 | +13.7 ± 0.5 | +15.5 ± 0.0 | 1.19 | +1.8 | *e* |
| α-Bromoisobutyrate | 28.96 | 29.86 | +20.6 | +23.2 | 1.26 | +2.6 | *f* |
| 2,4-Dinitrophenyl-acetate[c] | 12.04 | 9.49 | −37.2 | −48.8 | 1.48 | −11.6 | *g* |

[a] 10% v/v dioxane, pH 6. [b] Neutral solution. [c] 10% v/v dioxane, pH 5.6. [d] Reference 7. [e] Reference 8. [f] Reference 9a. [g] Reference 10.

Since $m_1$ is usually much larger than $m_2$ or $m_3$, and if $x$ or $y$ are not very large, then the first and last terms in eq 6 are approximately equal. This equation becomes

$$\Delta S^{\ddagger}_{\text{sie}} = \Delta S^{\ddagger}_{\text{tr}(D_2O)} - \Delta S^{\ddagger}_{\text{tr}(H_2O)} = 6.8604x(\log m_2/m_3) \quad (7)$$

where $\Delta S^{\ddagger}_{\text{sie}}$ is defined as the solvent isotope effect on the translational entropy of activation due to differences in solvation between the reactant(s) and the activated complex. Values of $\Delta S^{\ddagger}_{\text{sie}}$ calculated for light and heavy water by assigning interger values to $x$ in eq 7 are listed in Table I. They were calculated on the basis that the degree of solvation of reactant and the association of solvent are the same for both isotopes. That is, the values of $x$, $y$, and $n$ are equal for $H_2O$ and $D_2O$. Although the values of $\Delta S^{\ddagger}_{\text{sie}}$ given in Table I are not very great, they have a pronounced effect on the ratio $k_{H_2O}/k_{D_2O}$. Furthermore, the sign of $\Delta S^{\ddagger}_{\text{sie}}$ can be used as evidence to indicate whether additional solvent is bound or released in the activated state. When solvent is released $x$ is negative and the values of $\Delta S^{\ddagger}_{\text{sie}}$ are positive. However, when solvent is bound, $x$ is positive and $\Delta S^{\ddagger}_{\text{sie}}$ negative. To verify these findings some experimental evidence is cited below.

So far two systems have been studied in this laboratory,[7,10] but examples also can be found in the literature.[8,9] We measured the activation parameters for *O*-(chloroacetyl)salicylic acid at several pH and pD values.[7] The most reliable measurements were obtained in the pH- or pD-independent region 4.5–8. The results at pH 6 (pD 6.4) are listed in Table II. The raw data were analyzed by computer techniques using the least-squares method. Within experimental error the activation enthalpy is slightly greater for the $D_2O$ system as expected. However, the entropy term is more negative. If a portion of the large negative entropy of activation for this system is caused by solvation, then the activated state must be more polar and upon activation additional solvent becomes bound.[14] This means that, according to eq 7, $\Delta S^{\ddagger}_{\text{sie}}$ should be negative. The result in Table II for $\Delta S^{\ddagger}_{\text{sie}}$ is −0.9 eu. With reference to Table I, this suggests approximately three additional units of water are bound in the transition state. This finding for *O*-(chloroacetyl)salicylic acid is sustantiated by the results for the neutral hydrolysis of methyl and ethyl trifluoroacetates as reported in the literature.[8] These esters (Table II) have negative $\Delta S^{\ddagger}$ and $\Delta S^{\ddagger}_{\text{sie}}$ values which suggests additional solvent is bound in the activated state. It is interesting to note that the methyl ester hydrolyzes slower in $D_2O$ even though it has a lower $\Delta H^{\ddagger}$ than in $H_2O$. Therefore, the slower rate in $D_2O$ is due entirely to a decrease in $\Delta S^{\ddagger}$. According to Table I, five or six additional solvent units are bound in the transition state for this ester.

In contrast with systems having negative entropies, *tert*-butyl trifluoroacetate[8] and α-bromoisobutyrate[9] listed in Table II have positive $\Delta S^{\ddagger}$ and positive $\Delta S^{\ddagger}_{\text{sie}}$ values. On the basis of these positive values, it can be postulated that solvent is released when these systems attain a transition condition. The fact that solvent is lost during activation tends to lower the $k_{H_2O}/k_{D_2O}$ ratio to near unity.

In conclusion, it can be said that thermodynamic activation parameters must be closely scrutinized before any firm conclusions can be drawn as to the mechanistic significance of the value of $k_{H_2O}/k_{D_2O}$. The characterization of a chemical reaction by solvent isotope studies appears to involve changes in enthalpy and entropy, and both must be weighed accordingly. In the past only differences in activation enthalpy have been considered and correlated with zero-point energies, whereas our present calculations infer that differences in activation entropies also must be considered. If additional solvent (compared to the reactant) is translated over the free-energy barrier, the translational entropy contribution to the rate constant will be less in the heavier isotopic solvent. On the other hand, if solvent is lost during transition, the entropy contribution to the rate constant will be greater in the heavier isotopic solvent.

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## The Tricyclo[3.2.0.0$^{2,7}$]hept-3-yl (3-Psinortricyclyl) Cation[1]

*Sir:*

The highly strained *exo*- and *endo*-tricyclo[3.2.0.0$^{2,7}$]-hept-3-yl systems (**3** and **5**) provide structures whose

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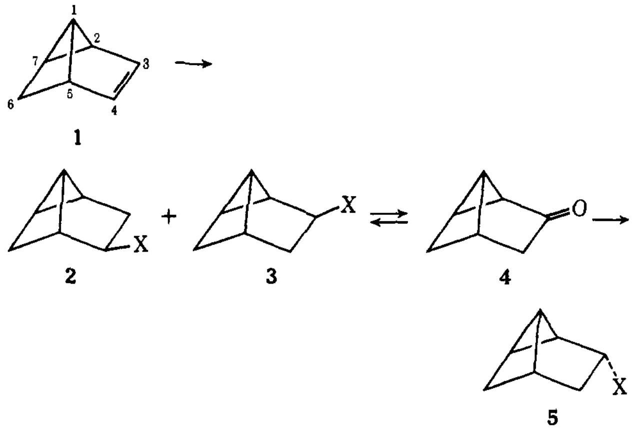
(14) K. J. Laidler, "Chemical Kinetics," McGraw-Hill, New York, N. Y., 1965, Chapter 5, p 228.

(1) The name "psinortricyclyl" (for "pseudonortricyclyl") is intro-

solvolyses could, in principle, proceed *via* several carbonium ion rearrangement pathways. These include a degenerate and a nondegenerate cyclopropylcarbinyl–cyclopropylcarbinyl isomerization, as well as homoallylic ring openings. This communication reports results which show that, in fact, hydrolysis proceeds predominantly with retention of structure and with no apparent dependence of rate or product distribution on configuration.

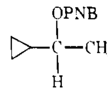
7-Norbornadienyl chloride was converted to olefin **1**[2] which was hydroborated to give a 92% yield (from starting chloride) of alcohols **2**-OH[3] and **3**-OH[4] in a 73:27 ratio, respectively, separable by preparative glpc on Carbowax columns. Oxidation of **3**-OH with $CrO_3$–pyridine gave tricyclic ketone **4**, identical with the material prepared independently by irradiation of 5-norbornenone.[5] Metal hydride reduction of **4** gave **3**-OH and **5**-OH (59:41, respectively, using $LiAlH_4$ in ether; 37:63, respectively, using $NaBH_4$ in methanol). Hydrogenation of **3**-OH and **5**-OH (10% Pd/C, 95% EtOH) produced *exo*- and *endo*-norborneol, respectively. Esters **3**-OPNB (mp 68.5–69.5°) and **5**-OPNB (mp 96.0–97.0°) were prepared routinely.



Titrimetric rate constants for **3**-OPNB and **5**-OPNB are listed in Table I along with that estimated for the parent cyclopropylmethylcarbinyl–OPNB. Hydrolysis of either epimer proceeded with 9–11% ion pair return to unreactive esters (*vide infra*), and the values in Table I are sums of the hydrolysis and ion pair return rate constants ($k_t = k_s + k_{ip}$). Nmr examination of recovered ester after *ca.* one solvolysis half-life failed to reveal any contamination of either epimer by the other, indicating that the similarity in rates for **3**-OPNB and **5**-OPNB is not due to rapid interconversion of one to the other followed by hydrolysis. The rate data in Table I imply that the degree of cyclopropyl participation in the 3-psinortricyclyl systems is equal to that in the secondary cyclopropylmethylcarbinyl analog. Since the former systems contain a rigid, nearly "bisected" geometry, as well as substitution at both β carbons of the three-membered ring, they might have been expected to solvolyze more rapidly than the model. Probably angle strain at the developing reaction site exerts a mildly retarding effect on the rate.[6]

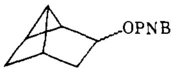
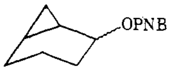
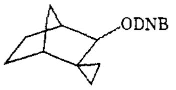
The exo–endo rate ratio for the 3-psinortricyclyl system is compared with related values in Table II.[7]

**Table I.** Hydrolysis Rates for Some Cyclopropylcarbinyl *p*-Nitrobenzoates in 70% Acetone at 99.6°

| Compd | $10^5k$, sec$^{-1}$ |
|---|---|
| **3-OPNB** | 2.94 ± 0.06[a] |
| **5-OPNB** | 4.59 ± 0.06[a] |
|  $\triangleright-\overset{\text{OPNB}}{\underset{\text{H}}{\text{C}}}-CH_3$ | 2.0[b] |

[a] Average of 2–3 runs. [b] Estimated from data in: P. von R. Schleyer and G. W. Van Dine, *J. Amer. Chem. Soc.*, **88**, 2321 (1966); K. Rubenstein, Ph.D. Dissertation, University of Wisconsin, 1967.

**Table II.** Epimeric Rate Ratios for Some Secondary Cyclopropylcarbinyl Derivatives

| Compound | $\frac{k_{\text{exo (cis)}}}{k_{\text{endo (trans)}}}$ | Solvent | *T*, °C |
|---|---|---|---|
|  OPNB | 0.64 | 70% acetone | 99.6 |
|  OPNB | 0.76[a] | 80% acetone | 79.0 |
|  ODNB | 2.6[b] | 70% acetone | 100 |

[a] See K. Rubenstein, Table I, footnote *b*. [b] Reference 6.

The insensitivity of rate to configuration is common to these systems. It now seems clear that such conformationally rigid cyclopropylcarbinyl systems behave analogously to freely rotating counterparts.[8] The cyclopropane ring is able to overlap with the developing p orbital equally efficiently from either configuration and stereospecific transcoplanar (unsymmetrical homoallyl) cyclopropane bond participation is unimportant.[9]

As shown in Table III, the hydrolysis product distribution from either epimer is essentially the same. It consists mainly of unrearranged tricyclic alcohols and homoallylic bicyclo[3.2.0]heptenols.[10] This strongly

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duced for this ring system as a convenient reminder of its isomeric relationship to the nortricyclyl system.

[2] H. C. Brown and H. M. Bell, *J. Amer. Chem. Soc.*, **85**, 2324 (1963).

[3] The chemistry of the 4-psinortricyclyl system will be reported separately. Initial observations show that *exo*-4-psinortricyclyl tosylate is extremely reactive and that it ionizes to the nortricyclyl cation.

[4] Satisfactory analyses and/or high-resolution mass spectra were obtained for all new compounds.

[5] J. Ipaktschi, *Tetrahedron Lett.*, 2153 (1969). The author wishes to thank Dr. Ipaktschi for personal communication of unpublished material.

[6] An analogous effect has been noted for spirocyclopropylcarbinyl systems: C. F. Wilcox and R. G. Jesaitis, *Tetrahedron Lett.*, 2567 (1967).

[7] The equilibrium between **3**-OH and **5**-OH (aluminum isopropoxide–isopropyl alcohol–acetone (trace), 99.6°) is 63:37, respectively, established from either side. By inference, the free-energy difference between the corresponding esters is negligibly small. On this basis, there is no significant "ground-state effect" manifested in their relative rates.

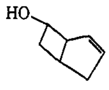
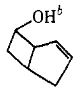
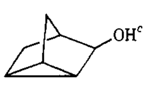
[8] See P. von R. Schleyer and G. W. Van Dine, Table I, footnote *b*.

[9] Conformationally mobile systems exhibit decidedly larger epimeric rate ratios, with little cross-over between the different ions involved; *cf.* C. D. Poulter, E. C. Friedrich, and S. Winstein, *J. Amer. Chem. Soc.*, **92**, 4274 (1970); K. B. Wiberg and T. Nakahira, *Tetrahedron Lett.*, 3759 (1970), and references therein; *cf.* also N. A. LeBel and J. E. Huber, *J. Amer. Chem. Soc.*, **85**, 3193 (1963).

[10] Structure proof is based on oxidation to the known ketone[11] and hydrogenation to known alcohols.[12]

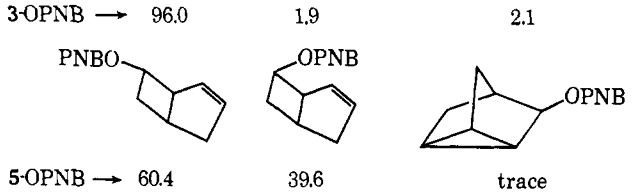
[11] D. I. Schuster, M. Axelrod, and J. Auerbach, *Tetrahedron Lett.*, 1911 (1963).

**Table III.** Hydrolysis Products from **3**-OPNB and **5**-OPNB in 70% Aqueous Acetone[a]

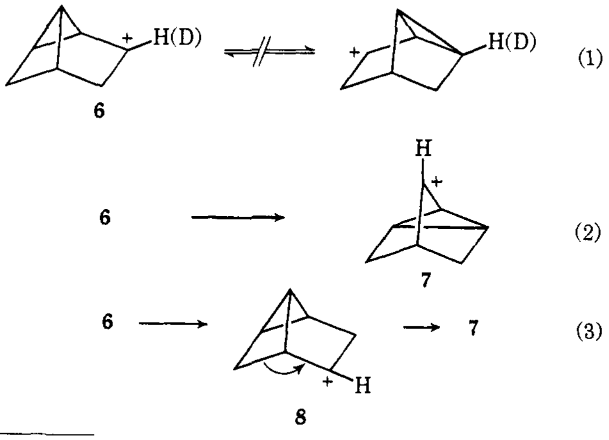
| Ester | **5**-OH | **3**-OH |  |  |  | Unknown[d] |
|---|---|---|---|---|---|---|
| **3**-OPNB | 61.5 | 4.5 | 22.5 | 2.3 | 2.8 | 6.4 |
| **5**-OPNB | 62.1 | 5.3 | 22.8 | 1.7 | 2.1 | 6.0 |

[a] Relative per cent yields; absolute yields of alcohols were *ca.* 100% based on unreturned ester. Solutions were 0.02 *M* in ester and 0.08 *M* in 2,6-lutidine, under which conditions all products were stable. [b] Identified only by gc peak enhancement with authentic material. [c] A trace of 5-norbornenol would not have been detected. [d] One peak on gc.

suggests a common product-determining intermediate(s) in the solvolyses. However, **3**-OPNB and **5**-OPNB apparently ionize, at least partially, to separate ion pairs, as the ion-pair return product distributions are different.



Degenerate cyclopropylcarbinyl–cyclopropylcarbinyl isomerization has been noted in several instances during solvolysis of some systems,[13a–c] but occurs to a very small extent, or not at all, in others.[13d,14] The isomerization proceeds by inversion of configuration at the $\beta$-cyclopropyl carbon.[13b] The 3-psinortricyclyl cation appears well suited stereochemically for the isomerization (eq 1). However, when **3**-OPNB-$\alpha$-*d* or **5**-OPNB-$\alpha$-*d* was hydrolyzed under kinetic control, no protium incorporation (<3%) could be detected by nmr at the $\alpha$ position of recovered **5**-OH.[15] Formation of a small amount of product derived from the nortricyclyl ion **7** may result from nondegenerate cyclopropylcarbinyl–cyclopropylcarbinyl isomerization (eq 2). An alternative, though unlikely, mechanism involves vicinal hydride transfer to give the 4-psinortricyclyl cation **8** which rearranges to **7**[3] (eq 3). Appropriate labeling should discern the correct pathway.



The present results show that neither mode of the cyclopropylcarbinyl–cyclopropylcarbinyl isomerization prevails over kinetically controlled solvent capture of **6**, even though there is probably a large driving force for formation of **7**.[16] This is perhaps surprising in light of the nearly total (degenerate) scrambling during hydrolysis of dehydroadamantyl dinitrobenzoate.[13c] However, it is not yet clear whether cyclobutyl carbonium ions are requisite intermediates.[13c,17] Such intermediates in the present case should be highly strained.

**Acknowledgments.** The author is grateful to Professor W. L. Mock for the use of his equipment, to Professor D. Schuster for unpublished spectral data, and to Professors H. G. Richey, Jr. and P. von R. Schleyer for helpful discussions.

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(12) F. F. Nelson, Ph.D. Dissertation, University of Wisconsin, 1960.

(13) (a) R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver, and J. D. Roberts, *J. Amer. Chem. Soc.*, **81**, 4390 (1959); (b) K. B. Wiberg and G. Szeimies, *ibid.*, **90**, 4195 (1968); **92**, 571 (1970); (c) J. E. Baldwin and W. D. Foglesong, *ibid.*, **90**, 4303 (1968); (d) R. R. Sauers, J. A. Beisler, and H. Feilich, *J. Org. Chem.*, **32**, 569 (1967).

(14) See K. Rubenstein, Table I, footnote *b*.

(15) Recovered *exo*-bicyclo[3.2.0]hept-2-en-7-ol integrated for 1.0 vinyl hydrogen.

(16) The psinortricyclene ring system may be estimated to have a free energy greater than that of nortricyclene by at least 13.6 kcal/mol [*cf.* P. von R. Schleyer, *J. Amer. Chem. Soc.*, **80**, 1700 (1958); A. Diaz, M. Brookhart, and S. Winstein, *ibid.*, **88**, 3133 (1966)]. Using carbonyl stretching frequencies to account for the strain incurred by introduction of trigonal centers, one may estimate that **7** has 5.5 kcal/mol more angle strain than **6**. On this basis, **7** is still favored over **6** by better than 8 kcal/mol.

(17) (a) J. E. Baldwin and W. D. Foglesong, *J. Amer. Chem. Soc.*, **90**, 4311 (1968); (b) C. Trindle and O. Sinanoglu, *ibid.*, **91**, 4054 (1970).

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## On the Mechanism of Paterno–Büchi Reaction of Alkanals

*Sir:*

The Paterno–Büchi reaction, the photocycloaddition of carbonyl compounds to olefins, has been applied to a variety of substrates,[1] and contributions have been made by several groups in elucidating its mechanism.[2,3] However, few attempts have been made to analyze the stereochemistry and mechanism of photochemical addition of alkanals to simple olefins. Evidence is now presented that indicates the intermediacy of an exciplex between the $^1$n–$\pi^*$ of the aldehyde and

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(1) For a review on the photocycloaddition of carbonyl compounds to unsaturated systems, see D. R. Arnold, *Advan. Photochem.*, **6**, 301 (1968).

(2) For more recent work on the photochemical addition of alkanones to olefins, see (a) N. J. Turro, P. Wriede, J. C. Dalton, D. R. Arnold, and A. Glick, *J. Amer. Chem. Soc.*, **89**, 3950 (1967); (b) N. J. Turro, P. Wriede, and J. C. Dalton, *ibid.*, **90**, 3274 (1968); (c) N. J. Turro and P. Wriede, *ibid.*, **90**, 6863 (1968); **92**, 320 (1970); (d) J. A. Barltrop and H. A. Carless, *Tetrahedron Lett.*, 3901 (1968).

(3) For the mechanism of Paterno–Büchi reaction of aromatic carbonyl compounds see: (a) R. A. Caldwell and S. P. Jones, *J. Amer. Chem. Soc.*, **91**, 5184 (1969); (b) I. H. Kochevar and P. J. Wagner, *ibid.*, **92**, 5742 (1970); (c) N. C. Yang, R. L. Loeschen, and D. Mitchell, *ibid.*, **89**, 5465 (1967).