VII. It is presumed that VIb and VIc react *via* the proposed[1] type-II-like cleavage and hence this reaction should prove to be general for properly substituted aromatic N-heterocycles.

F. R. Stermitz, W. H. Huang
Department of Chemistry, Colorado State University
Fort Collins, Colorado 80521

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Base-Catalyzed Deuterium Exchange of Bicyclo[2.2.1]heptanones[1]

Sir:

There has recently been considerable interest in the investigation of rates of base-catalyzed deuterium exchange of ketones,[2] the stereochemistry of protonation of enolates and other anions,[3] and the selectivity of deuterium exchange in bicyclic ketones.[4] This communication reports measurements of the rates and stereochemistry of base-catalyzed deuterium exchange in representative bicyclo[2.2.1]heptan-2-ones and application of these studies to the preparation of selectively deuterated compounds in this series.

The rates of deuterium uptake of the ketones in 2:1 dioxane–D_2O containing NaOD at 25.0° were monitored by mass spectrometry; in all cases there was a relatively rapid uptake of a first deuterium, followed by the slower incorporation of a second deuterium. No trideuteration was observed. The stereochemistry of the first deuterium was found to be *exo* in all cases by isolating monodeuterated ketone, reducing with $LiAlH_4$, isolating the predominant epimeric alcohol, and examining the characteristic nmr spectrum.[4a,c] The ketones examined were norcamphor (**1**), camphor (**2**), dehydronorcamphor (**3**), and benzodehydronorcamphor (**4**). The relative rates of deuterium uptake at various positions (all relative to the *endo*-3 position of **1**) are summarized in Chart I and the measured rate constants and *exo*:*endo* rate ratios are given in Table I. The kinetic procedure involved removing samples at intervals and quenching the base with dilute nitric acid. The ketones were extracted into pentane and each sample was purified by gas chromatography. Rates of deuterium uptake were calculated by the variation in the mass distribution of the molecular ion peaks of the ketones in their mass spectra. In several cases the two ketones were deuterated competitively in the same reaction solution and separated into the individual components by vpc for mass analysis.

The detailed steps of the exchange are not established and no attempt is made herein to interpret the observed rates of exchange in terms of specific processes at the molecular level.[5] As examples of the complexities involved there are dissenting views as to whether proton abstraction from ketones by bases such as deuteroxide[2e] and methoxide[6] leads to transition states and/or intermediates with the character of enols[2e] or enolates,[6] and it has been further suggested that ketonization of the enolate of 4-*t*-butylcyclohexanone with deuterioacetic acid–D_2O occurs with initial attack both on carbon and oxygen and that the final stereochemistry of the ketone is different for the two pathways.[7] Further work is in progress to clarify the mechanism of the exchange.

Chart I. Relative Rates of NaOD-Catalyzed Deuterium Exchange of Ketones at 25.0° in 2:1 Dioxane–D_2O

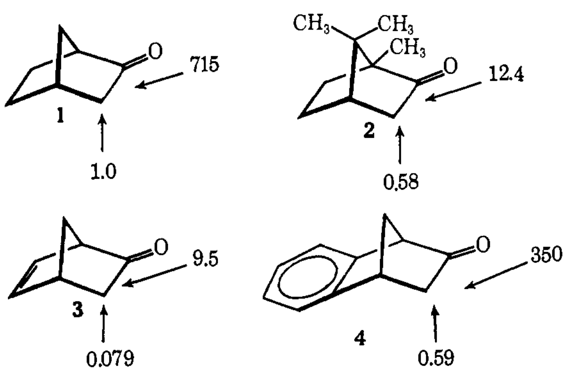

Table I. Second-Order Rate Constants of NaOD-Catalyzed Deuterium Exchange of Ketones at 25.0° in 2:1 Dioxane–D_2O

Ketone	k_2 (l. M^{-1} sec^{-1})[a,b]	*exo*:*endo*
1 *exo*	5.48×10^{-2}	715
endo	7.67×10^{-5}	
2 *exo*	9.50×10^{-4}	21
endo	4.46×10^{-5}	
3 *exo*	7.30×10^{-4}	120
endo	6.06×10^{-6}	
4 *exo*	2.68×10^{-2}	595
endo	4.50×10^{-5}	

[a] Second-order rate constants were obtained by dividing the measured pseudo-first-order rate constants by the base concentration, and were invariant with concentration in the range 0.08–0.004 *M* used. [b] Rates were reproducible with maximum deviations of ±10%. Competition experiments verified the relative orders of reactivity between **1** and **4** *exo*, **1** and **4** *endo*, and **1** and **2** *endo*.

With this caveat in mind the relative reactivities and *exo*:*endo* rate ratios of **1–4** would appear to be of significance to the relationship between structure and reactivity in these compounds and may be profitably examined in more detail.

A preference for *exo* exchange in **1** would have been predicted on steric grounds but the magnitude of the selectivity is perhaps surprisingly large. For comparison the *exo*:*endo* ionization rate ratio for norbornyl brosylate is 1600,[8a] and there is a >5000:1 preference for *exo* hydration of the norbornyl cation.[8a] Free radical chlorination of norbornane with sulfuryl chlo-

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[1] Presented at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, Abstracts, ORGN 42.

[2] (a) C. Rappe and W. H. Sachs, *Tetrahedron*, **24**, 6287 (1968); (b) W. Th. van Wijnen, H. Steinberg, and Th. J. de Boer, *Rec. Trav. Chim. Pays-Bas*, **87**, 844 (1968); (c) A. A. Bothner-By and C. Sun, *J. Org. Chem.*, **32**, 492 (1967); (d) E. N. Marvell, G. J. Gleicher, D. Sturmer, and K. Salisbury, *ibid.*, **33**, 3393 (1968); (e) J. Warkentin and C. Barnett, *J. Amer. Chem. Soc.*, **90**, 4629 (1968); (f) H. W. Amburn, K. C. Kauffman, and H. Schechter, *ibid.*, **91**, 530 (1969); (g) F. G. Bordwell and R. G. Scamehorn, *ibid.*, **90**, 6749 (1968); (h) J. Hine, K. G. Hampton, and B. C. Menon, *ibid.*, **89**, 2664 (1967).

[3] F. Johnson, *Chem. Rev.*, **68**, 375 (1968); (b) H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **90**, 6091 (1968); (c) R. A. Abramovitch, M. M. Rogić, S. S. Singer, and N. Venkateswaran, *ibid.*, **91**, 1571 (1969).

[4] A. F. Thomas and B. Willhalm, *Tetrahedron Lett.*, 1309 (1965); (b) J. M. Jerkunica, S. Borčić, and D. E. Sunko, *ibid.*, 4465 (1965); (c) A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Amer. Chem. Soc.*, **89**, 68 (1967).

[5] Professor L. K. Montgomery (private communication) has independently made considerable progress in dissecting the various steps involved in these exchange reactions.

[6] J. F. Bunnett and L. A. Retallick, *J. Amer. Chem. Soc.*, **89**, 423 (1967).

[7] H. O. House, B. A. Terfertiller, and H. D. Olmstead, *J. Org. Chem.*, **33**, 935 (1968).

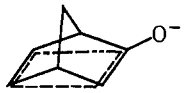
[8] (a) S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *J. Amer. Chem. Soc.*, **87**, 376 (1965); (b) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

ride favors formation of *exo*- over *endo*-norbornyl chloride by a factor of about 20.[8b] The steric effect of the *syn*-7-methyl group in **2** considerably reduces the rate of *exo* exchange and shows a much smaller effect on the *endo* rate, but as already has been observed qualitatively, there is still a residual preference for *exo* exchange.[4a,c]

The low reactivity of **3** relative to **1** is contrary to the report[4b] of previous authors (who used somewhat different conditions), and the similarity of the *exo*:*endo* rate ratios of **1**, **3**, and **4** shows that the steric effect of the *endo*-5,6 hydrogens in **1** is not the dominant factor governing its reactivity relative to **3** and **4**. By careful control of the reaction conditions, it has been found possible to selectively deuterate **3** in the *exo* position.[9] Similarly, **4** can be prepared with predominant *exo*-deuterium substitution[11] despite previous[12] intimations to the contrary.[13]

The differences in reactivity among **1**, **3**, and **4** likely reflect the simultaneous operation of a number of effects. Variations in the geometry of the ketones that lead to decreasing internal bond angles would impair enolate formation by increasing the strain in the sp^2-hybridized intermediates, while the same decrease in internal angles would tend to increase the acidity of the protons due to the increased s character of the external orbitals.[14] Results with cyclopropyl ketones suggest that the former effect is dominant.[2a,b,f]

Homoallyl[15] and homobenzyl[16] stabilization would have been expected to accelerate the rate of anion formation from **3** and **4**, respectively, as would the inductive effect[2g] of the unsaturated groupings. More extensive delocalization to give the "antiaromatic" bishomocyclobutadiene-type of structure would have been destabilizing.[17,18]



Thus a variety of factors, including ring strain, homoconjugation, hydridization, steric blocking, inductive effects, and torsional effects[19] apparently contribute to the observed relative reactivities of these ketones. A number of investigations are under way in these laboratories to elucidate the respective contributions of these effects.

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[9] Dehydronorcamphor (3) (0.112 g) was dissolved in 10 ml of a 0.0363 *N* solution of NaOD in 2:1 dioxane–D$_2$O and was maintained at 25° for 55 hr. The reaction mixture was poured into a solution of 5 ml of 0.25 *N* HNO$_3$, 25 ml of water, and 25 ml of pentane and after extraction into pentane, the ketone was purified by gas chromatography. The mass spectrum of the ketone indicated 1% d_0, 94% d_1, and 5% d_2 species. Reduction of the deuterated ketone with lithium aluminum hydride and purification by vpc gave *endo*-bicyclo[2.2.1]hept-5-en-2-ol whose nmr spectrum showed the complete absence of the heptet assigned[10] to the *exo*-3 H at δ 1.97 (CCl$_4$) and the collapse of the couplings of this proton.

[10] J. C. Davis, Jr., and T. V. Van Auken, *J. Amer. Chem. Soc.*, **87**, 3900 (1965).

[11] Benzodehydronorcamphor (4) (0.233 g) was treated as above with a reaction time of 2 hr. The mass spectrum of the purified ketone indicated 2% d_0, 97% d_1, and 1% d_2 species. The nmr spectrum of the corresponding *endo* alcohol showed the complete absence of the heptet at δ 2.20 in the nondeuterated compound which can be assigned to the *exo*-3 H as above. Norcamphor was monodeuterated under similar conditions. The couplings of the nmr absorption of the *exo*-2 H at δ 4.08 in the derived *endo* alcohol were not resolved at 60 MHz (*cf.* ref 4a) but at 100 MHz, with irradiation of the bridgehead hydrogens at 2.1, showed a broad doublet with the expected 3 cycle coupling to the *endo*-3 H.

[12] R. Caple, F. M. Hsu, and C. S. Ilenda, *J. Org. Chem.*, **33**, 4111 (1968).

[13] Dr. H. Tanida (private communication) has independently measured the rate of hydrogen exchange of **4** and has not only found a preference for *exo* exchange, but has also prepared specifically *exo*-deuterated **4**.

[14] A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *J. Amer. Chem. Soc.*, **91**, 529 (1969).

[15] For leading references see M. Hanack and H.-J. Schneider, *Angew. Chem. Intern. Ed. Engl.*, **6**, 666 (1967).

[16] For leading references see H. Tanida, H. Ishitobi, T. Irie, and T. Tsushima, *J. Amer. Chem. Soc.*, **91**, 4512 (1969).

[17] The possibility of antiaromatic destabilization of the 7-norbornenyl anion was discussed by R. Breslow, lecture at the 21st Organic Chemistry Symposium, Salt Lake City, Utah, June 1969, Abstracts, p 139; see also, R. Breslow, J. Brown, and J. J. Gajewski, *J. Amer. Chem. Soc.*, **89**, 4383 (1967).

[18] For a possible stabilized bishomocyclobutadienyl dication see J. B. Lambert and A. G. Holcomb, *ibid.*, **91**, 1572 (1969). For contrary evidence in the benzo derivative see H. Tanida and T. Tsushima, *Tetrahedron Lett.*, 3647 (1969).

[19] P. von R. Schleyer, *J. Amer. Chem. Soc.*, **89**, 701 (1967); see, however, the experimental results in ref 1.

Thomas T. Tidwell
Department of Chemistry, University of South Carolina
Columbia, South Carolina 29208

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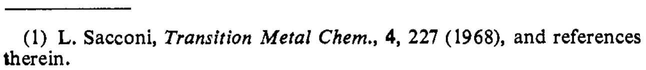
A Possible Low-Spin Five-Coordinate Nickel(II) Complex with Predominantly Nitrogen and Oxygen Donor Atoms

Sir:

Five-coordinated nickel(II) complexes may be either diamagnetic or paramagnetic which until recently was thought to depend on the particular donor atoms involved. Ligands with low π-bond-forming ability (*i.e.*, oxygen, nitrogen, etc.) were thought to form only paramagnetic complexes whereas ligands with high π-bond-forming ability (*i.e.*, sulfur, phosphorus, etc.) give rise to diamagnetic complexes.[1]

We wish to report here the synthesis and characterization of a green nickel(II) complex containing a pentadentate ligand which we believe may be the first example of a diamagnetic five-coordinate structure where oxygen serves as two of the donor atoms. Schiff bases formed from substituted salicylaldehydes (X–Sal) and bis(2-aminoethyl) sulfide (DAES) serve as the pentadentate ligand (structure Ia), hereafter referred to as X–SalDAES.



Ia, $n = 2$; Z = S
b, $n = 3$; Z = S
c, $n = 2$; Z = N–H
d, $n = 3$; Z = N–H

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[1] L. Sacconi, *Transition Metal Chem.*, **4**, 227 (1968), and references therein.