can be considered to verify the predictions of the theory of Kawabata,[9] and represents one of the few, direct experimental observations of quantum size effects (see ref 4 for an excellent up to date account of the field) in fine metallic particles, as first discussed some 43 years ago by Fröhlich.[10]

It is also worth noting that a plot of the measured g shift vs. line width yields a reasonably linear correlation (in agreement with the prediction of the theory[9]) which gives an extrapolated $\Delta g_{SO} = 0.026 \pm 0.006$. This corresponds to the experimental value of the contribution of the spin-orbit coupling to the g shift of the bulk, which is reasonably close to the value $\Delta g_{SO} = 0.03$ calculated for bulk silver[6] by Elliot's theory[11] (using $\Delta g_{\text{bulk}} \simeq \Delta g_{SO} \simeq \lambda/\Delta E$, with $\lambda = 0.115$ and $\Delta E = 3.87$ eV).

According to the theory of Kawabata,[9] a C ESR line width of ~25 G corresponds to a silver particle diameter of roughly 10 Å (see Figure 2), a dimension close to that expected for a close-packed, 13-atom silver cluster. This estimate places the ESR data in line with the conclusions drawn from the corresponding optical experiments,[1-3] which used the appearance of the surface plasma absorption as a criterion for establishing the onset of the molecular silver cluster to bulk silver particle transformation. Although the details of these spectra have yet to be deciphered, it would appear that the quantum size effect is being detected in these ESR-optical matrix experiments, and can therefore provide crucial information on the transition metal cluster to bulk metal.

Acknowledgments. I acknowledge the technical assistance of Mr. H. Huber and helpful discussions with Mr. M. Andrews and Mr. S. Mitchell. The generous financial assistance of the Natural Sciences and Engineering Research Council of Canada's Operating Grant Programme, New Ideas Programme, and National Energy Programme, the Connaught Fund, Imperial Oil of Canada, the Lash Miller Chemical Laboratories, and Erindale College for support at various stages of this work is also acknowledged.

References and Notes

(1) G. A. Ozin and H. Huber, *Inorg. Chem.*, **17**, 155 (1978). G. A. Ozin, *Catal. Rev. Sci. Eng.*, **16**, 191 (1977). G. A. Ozin, S. Mitchell, D. McIntosh, J. G. Norman, Jr., and L. Noodleman, *J. Am. Chem. Soc.*, **101**, 3504 (1979). G. A. Ozin and S. Mitchell, *ibid.*, **100**, 6776 (1978); *Inorg. Chem.*, **18**, 2932 (1979).

(2) W. Schulze, H. U. Becker, and D. Leutloff, *J. Phys.*, **C-2**, 7 (1977); W. Schulze, H. U. Becker, and H. Abe, *Chem. Phys.*, **35**, 177 (1978); H. Abe, W. Schulze, and B. Tesche, *ibid.*, **47**, 95 (1980).

(3) T. Welker and T. P. Martin, *J. Chem. Phys.*, **70**, 5683 (1979).

(4) R. F. Marzke, *Catal. Rev. Sci. Eng.*, **19**, 43 (1979).

(5) P. H. Kasai and D. McLeod, Jr., *J. Chem. Phys.*, **55**, 1566 (1971).

(6) (a) M. Smithard, *Solid State Commun.*, **13**, 153 (1973); (b) W. K. Knight, *J. Phys.*, **C-2**, 110 (1977); (c) D. A. Gordon, *Phys. Rev. B*, **13**, 3738 (1976); (d) R. Monot, A. Châtelain, and J. P. Borel, *Phys. Lett. A*, **34**, 57 (1971); *J. Phys.*, **C-2**, 115 (1977); (e) R. Dupree, C. T. Forwood and M. H. A. Smith, *Phys. Status Solidi*, **24**, 525 (1967); (f) R. Monot, C. Narbel and J. P. Borel, *Nuovo. Cimento*, **19**, 253 (1974); (g) C. Taupin, *J. Phys. Chem. Solids*, **28**, 41 (1967); (h) K. Asayama and Y. Oda, *J. Phys. Soc. Jpn.*, **22**, 937 (1967); (i) M. Ya Gen and V. I. Petinov, *Sov. Phys.-JETP (Engl. Transl.)*, **21**, 19 (1965).

(7) R. Kubo, *J. Phys. Soc. Jpn.*, **17**, 975 (1962).

(8) L. P. Gor'kov and G. M. Eliashberg, *Sov. Phys.-JETP (Engl. Transl.)*, **21**, 940 (1965).

(9) A. Kawabata, *J. Phys. Soc. Jpn.*, **29**, 902 (1970).

(10) H. Fröhlich, *Physica*, **6**, 406 (1937).

(11) R. J. Elliot, *Phys. Rev.*, **96**, 266 (1954).

(12) In the ESR experiments, the sample was deposited onto an optically polished sapphire rod (dimensions 1.75 × 0.12 × 0.14 in.) cooled to 10-12 K by means of an Air Products Displex closed cycle helium refrigerator using techniques similar to those described previously.[1] By employing a specially designed telescopic vacuum shroud-furnace assembly, the sample could be lowered into an extension quartz tailpiece, held in the microwave cavity of a standard Varian E4 spectrometer. ESR spectra were recorded in the range of 0-6000 G with microwave powers varied between 0.1 and 10 mW for optimum resolution conditions. UV-visible spectra were recorded on the same sample using a standard Varian Techtron instrument in the range of 190-900 nm.

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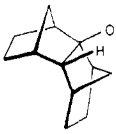
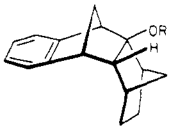
syn,endo-Tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodec-2-ylium Cations. Kinetic and Chemical Consequences of Fusing Norbornyl Systems across Common C_2,C_3 Segments

Sir:

We wish to draw attention to some of the novel structural features of compound **1**, a molecule constructed of two amalgamated norbornyl frameworks having the tertiary substituent simultaneously oriented exo to both bicyclic units. The solvolysis of **1b** proceeds at a rate in excess of that of 2-*tert*-butyl-2-*exo*-norbornyl p-nitrobenzoate,[1] qualifying this substance as the most highly reactive saturated tertiary derivative presently known. Further, **1** is seen to ionize 1.25×10^3 times faster than its benzologue **2** in 80% dioxane, this margin being substantially larger than any heretofore uncovered in norbornyl-benzonorbornenyl structural pairs. The studies involving **1** and **2** supplement extensive previous work on norbornyl cations[2] and, in particular, permit assessment of several aspects of the chemistry of these species not possible before. For example, it is our belief that σ participation in **1** to form either or both of the nonclassical intermediates **4a** and **4b** cannot be important in this system. These canonical structures differ so greatly in energy from their classical counterpart **3** that resonance between them is not considered significant.

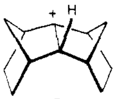


1



2

a, R = H; b, R = PNB; c, R = CH_3 a, R = H; b, R = DNB; c, R = CH_3



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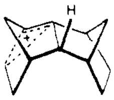
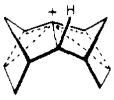


4a



4b

Alcohols **1a** and **2a** were prepared from the corresponding olefins[3] by sequential epoxidation and reduction. The action of lithium in anhydrous ethylenediamine gave **1a**, mp 100-101 °C, in 94% yield, whereas lithium in liquid ammonia-tetrahydrofuran at −40 °C provided **2a**, mp 95-96 °C.[4,5] The esters were obtained by conventional reaction with the appropriate acid chloride in pyridine solution. p-Nitrobenzoate **1b** was solvolyzed in 80% acetone and 80% dioxane. The analogous derivative of **2** proved too unreactive under the same conditions. Consequently, recourse was made to the 3,5-dinitrobenzoate (**2b**), where solubility considerations dictated the use of 80% dioxane as solvent. The kinetic determinations and thermodynamic parameters are summarized in Table I.[6] Product distribution and yield data for both solvolysis and methanolysis are collected in Table II.

Theory and previous experience with solvent polarity effects lead one to expect a slight rate enhancement for **1b** in 80% acetone ($Y = -0.673$) relative to 80% dioxane ($Y = -0.833$).[7] As is clear from Table II, both **1b** and **2b** ionize without skeletal isomerization to return unrearranged alcohol or methyl ether, as well as substantial levels of the internal olefins from which they were originally derived. The factor of 1250 by which the fused benzene ring in **2b** decelerates ionization of the tertiary exo leaving group (at 25°C) is much larger in magnitude than values obtained for either the secondary pair **5**/**6**[8] or the series of tertiary p-nitrobenzoates **7**/**8**.[9] This phenomenon should not be viewed as the result of decreased levels of anchimeric assistance in **2** relative to the model systems, where it is already recognized to be at a low level or nonexistent.[9-11] Rather, molecular models of **1** dramatically reflect the fact that ground states of *syn,endo*-tetracyclo[6.2.1.1^{3,6}.0^{2,7}]dodecanes (e.g.,

Table I. Rate Constants and Activation Parameters Obtained for **1b** and **2b**

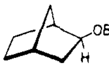
compd	solvent	temp, °C	10^5k, s^{-1} [a]	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	k_{rel}(25 °C)
1b	80% acetone	60.0	22.3			
		50.0	6.67	24.4	−2.3	
		40.0	2.00			
		25.0^b	0.260			2
	80% dioxane	70.0	30.9			
		60.0	8.60			
		50.0	3.33	23.9	−5.5	
		25.0^b	0.127			1
2b	80% dioxane	110.0	13.8			
		100.0	4.69			
		90.0	1.87	25.7	−9.8	
		25.0^b	6.22×10^{-4}			8×10^{-4} [c]

[a] The values represented constitute averages from two independent runs; the activation parameters were calculated with use of all individual rate constants. [b] Extrapolated values calculated on the basis of the activation parameters. [c] Calculated on the assumption that 3,5-dinitrobenzoates solvolyze six times more rapidly than *p*-nitrobenzoates.

Table II. Summary of Solvolysis and Methanolysis Products and Yields[a]

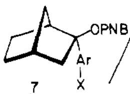
compd	reaction conditions (temp, °C; time, h)	% alcohol[b]	% olefin	% methyl ether	other
1b	80% acetone, 2,6-lutidine (60; 20 h)	21	53		
	80% dioxane, 2,6-lutidine (60; 48 h)	32	68		
	methanol, 2,6-lutidine (65; 32 h)	7	45	21	CH_3OPNB (trace)
2b	80% dioxane, 2,6-lutidine (100; 40 h)	11	59		
	methanol, 2,6-lutidine (90; 100 h)		20	53	

[a] Products were isolated in excellent yields by direct preparative thin layer chromatography of the reaction mixtures (after solvent evaporation) on basic alumina (elution with 4:1 petroleum ether–ether). [b] Alcohols **1a** and **2a** were independently shown not to undergo dehydration under these reaction conditions.



5

6



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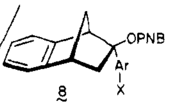


8

k_5/k_6 (25 °C, HOAc) = 17

a, X = *p*-OCH_3 k_7/k_8 (25 °C, 80% acetone) = 10

b, X = H k_7/k_8 (25 °C, 80% acetone) = 27

c, X = *p*-CF_3 k_7/k_8 (25 °C, 80% acetone) = 91

1) are highly congested on the molecular interior (endo surface), principally as the result of severe nonbonded interactions between the inner protons of the two ethano bridges.[12] Substitution by benzo at one of these sites significantly decreases this steric crowding and consequently reduces the ground state energy of **2** relative to **1**, with the usual kinetic consequences. The implication is that **2** ionizes by an unassisted (k_s) pathway without benefit of k_Δ contributions.

Epimeric 2,3-dimethyl-2-norbornyl cations have been directly observed by Olah[13] and Sorensen[14] under superacid conditions and serve as useful model systems to compare with **3**. Addition of either alcohol **1a** or its internal olefin precursor to SO_2ClF-FSO_3H (3:1) in CD_2Cl_2 solution at −110 °C resulted in conversion into the single stable carbocation **3**. Quenching of the solutions by pouring into cold (−78 °C) methanol containing anhydrous potassium carbonate gave **1c** accompanied by lesser amounts of the olefin. The ^1H NMR spectrum of ion **3** (see Figure 1) was observed to be essentially unchanged over the temperature range −90 to 0 °C, except for some line broadening at the extreme low end. Selected experimental ^{13}C spectra of **3** taken over a comparable ΔT are shown in Figure 2. These data convincingly show that **3** experiences rapid 3,2-hydride shift. The C_2-C_3 carbons which appear as a single sharp peak (201.91 ppm) at −15 °C show obvious broadening at −30 °C and are totally time-averaged at −60 °C. Rough estimates place the actual rate of 3,2-exo-hydride shift in **3** at a level slightly faster than those in polymethyl substituted norbornyl systems.[13-15] This phenomenon may find its origin in the greater conformational rigidity of **3** which more effectively orients the empty p-like orbital into the ideal 0° dihedral angle relationship with the adjoining C–H bond.[16]

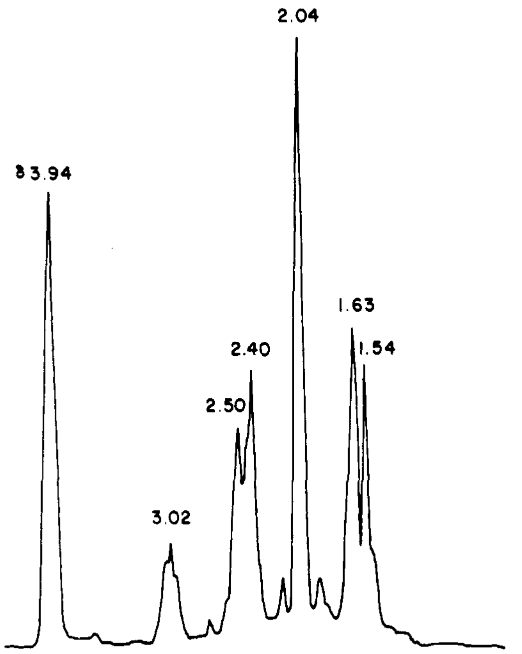


Figure 1. ^1H NMR spectrum (90 MHz) of **3** in FSO_3H-SO_2ClF-CD_2Cl_2 solution at −60 °C.

The exceptionally fast solvolysis rate of **1c** is revealed by direct comparison with **9** and **10**.[1] It is particularly instructive to consider that **1c** is 3 500 000 times more reactive than *tert*-butyl *p*-nitrobenzoate. These results conform to the high ground-state energy of **1c**.

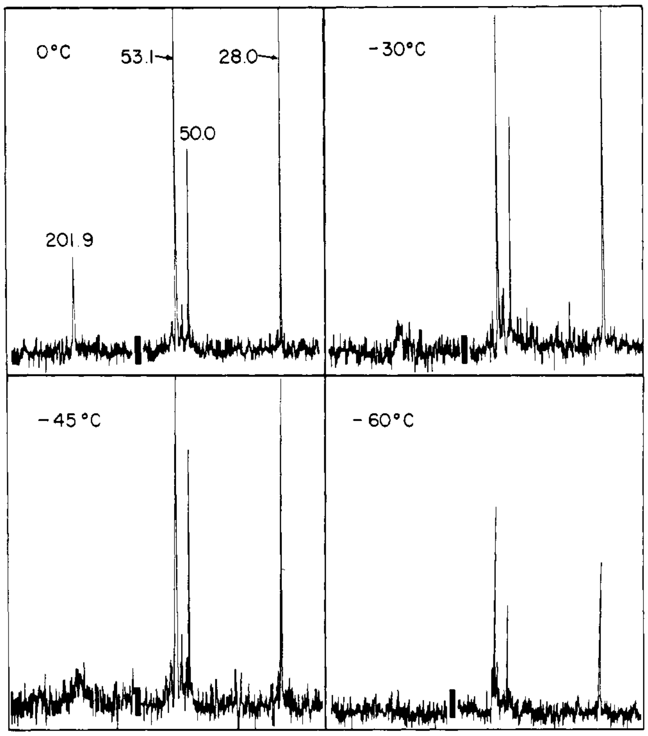
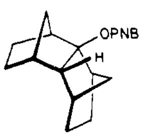
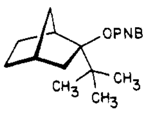


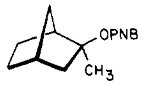
Figure 2. Selected ^{13}C NMR spectra (22.6 MHz) of **3** in FSO$_3$H-SO$_2$ClF-CD$_2$Cl$_2$ solution recorded at the various indicated temperatures.



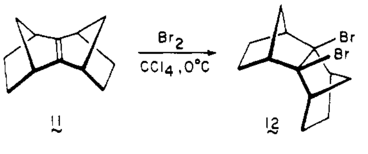
1c
k_{rel}(25°C) 26,000



9
21,000



10
1



A major thrust of norbornyl cation research has involved examination of exo:endo rate ratios. In the present instance, such considerations lose their significance because of the major steric alterations which would accompany the changeover to endo stereochemistry. In this connection, it would seem appropriate to call attention to the fact that the double bond in **11** is preferentially attacked from the exo direction. However, placement of an exo substituent at C$_2$ necessitates that the same stereochemistry be adopted at C$_3$ because of strain. The bromination of **11** to produce cis dibromide **12**[17] exclusively without skeletal rearrangement exemplifies this rationale.[18]

References and Notes

(1) Peters, E. N.; Brown, H. C. *J. Am. Chem. Soc.* **1974,** *96,* 265; **1975,** *97,* 2892.
(2) Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977.
(3) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. J. *J. Am. Chem. Soc.*, in press.
(4) Utilization of lithium in ethylenediamine for the latter system caused overreduction of the benzene ring as expected. Reduction of the eopxide with diisobutylaluminum hydride in ether at room temperature led to **2a** in 62% yield.
(5) Analytical and spectral data for all new compounds were fully compatible with the given assignments.
(6) In the case of **2b**, the infinity titers could not be determined by the indicator method, for the equivalent point was not obvious. Therefore, its first-order rate constants were calculated by use of the theoretical initial concentration.
(7) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; Wiley: New York, 1963; pp 297–299.
(8) Bartlett, P. D.; Giddings, W. P. *J. Am. Chem. Soc.* **1960,** *82,* 1240.
(9) (a) Takeuchi, T.; Brown, H. C. *J. Am. Chem. Soc.* **1968,** *90,* 2693. (b) Brown, H. C.; Ikegami, S.; Liu, K. -T.; Tritle, G. L. *Ibid.* **1976,** *98,* 2531.
(10) Brown, H. C.; Tritle, G. L. *J. Am. Chem. Soc.* **1964,** *86,* 4904; **1968,** *90,* 2689.
(11) Paquette, L. A.; Dunkin, I. R. *J. Am. Chem. Soc.* **1973,** *95,* 3067.
(12) For relevant X-ray crystallographic data, consult Ermer, O. *Angew. Chem.* **1977,** *89,* 833; *Angew. Chem., Int. Ed. Engl.* **1977,** *16,* 798.
(13) Olah, G. A.; Liang, G. J. *J. Am. Chem. Soc.* **1974,** *96,* 189.
(14) (a) Huang, E.; Ranganayakulu, K.; Sorensen, T. S. *J. Am. Chem. Soc.* **1972,** *94,* 1780; (b) Jones, A. J.; Huang, E.; Haseltine, R.; Sorensen, T. S. *Ibid.* **1975,** *97,* 1133.
(15) Huang, L.; Ranganayakulu, K.; Wong, N.; Sorensen, T. S. *J. Am. Chem. Soc.* **1973,** *95,* 1936.
(16) Chandrasekhar, J.; Schleyer, P. v. R. *Tetrahedron Lett.* **1979,** 4057.
(17) Mp 178–180 °C; ^{1}H NMR (δ, CDCl$_3$) 3.18–2.67 (m, 6 H) and 2.40–1.28 (series of m, 10 H); ^{13}C NMR (ppm, CDCl$_3$) 92.07, 55.85, 48.93, and 25.98.
(18) This research was financially supported by a grant from the National Science Foundation (CHE-7900333).

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Book Reviews

Radicals. By D. C. NONHEBEL (University of Strathclyde), J. M. TEDDER (University of St. Andrews), and J. C. WALTON (University of St. Andrews). Cambridge University Press, Cambridge, England. 1979. xvi + 200 pp. $32.50 hardcover; $11.95 paperback.

This book is intended primarily for undergraduate and beginning graduate students. It provides an extensive introduction into the study of free-radical chemistry and detection, but is aimed at a level such that it can be easily read after an introductory course in organic chemistry. It accomplishes these goals admirably, and provides a useful reference survey for the researcher as well. The subject of radical chemistry plays an ubiquitous role in industrial and polymer chemistry, synthesis, and even biochemical processes. The present text provides a valuable introduction to the awareness of free-radical chemistry and the importance of free radicals in these fields. The treatment is mainly oriented toward examples in organic synthesis, although there are numerous sections on the physical detection of radicals, inorganic metal complex radical species, and radical reactions in biochemistry. The text is well written, extensively documented, and clearly outlined with well-chosen subheadings. Extensive tables catch the immediate attention of the reader, providing intriguing comparisons, such as the relative selectivities of radical reactions at various sites on substituted hydrocarbons. The text thoroughly covers traditional subjects such as chain initiation, propagation and termination, and explosive reactions, in terms of the *chemistry.* It is not a text for detailed kinetic treatment of these phenomena. This book gives an excellent appreciation for the overwhelming importance of radicals in chemical synthesis and industrial processes.

Stephen R. Leone, *Joint Institute for Laboratory Astrophysics*

Physical Organic Chemistry through Solved Problems. By JOSEPH B. LAMBERT (Northwestern University). Holden-Day, Inc., San Francisco. 1978. xii + 265 pp. $11.95.

Joseph Lambert has given us a remarkably useful collection of representative, challenging, and instructive problems which have been gleaned from the current literature and several physical organic chemistry texts. Most noteworthy are his clearly thought-out, well-