(135.6 g, 147 mol). To the ice-cold, stirred mixture was added concentrated sulfuric acid (64 mL) in small portions. The reaction mixture was refluxed for 3 h, basified with 25% NaOH (575 mL), diluted with water, and steam-distilled and the distillate (7 L) was extracted with benzene. The combined benzene extract was dried (Na_2SO_4), refluxed for 30 min with *p*-toluenesulfonyl chloride (15.3 g, 0.080 mol), poured into ice water (300 g), and acidified (Congo Red end point) with concentrated HCl. The aqueous phase was washed with benzene, basified with 6 N NaOH to pH 10, and extracted with CH_2Cl_2. The combined CH_2Cl_2 extract was dried (Na_2SO_4), distilled to remove solvent, and vacuum distilled to remove quinoline (head temperature 128 °C at 1.4 mm). The distillate (6.99 g) solidified to orange-brown crystals: GLC (215 °C, 30 mL/min) **3** 9.5, **9** 10.2, **1** 12. Integration of the peak areas indicated 23% of dimethylquinolines (**3** + **9**) and 75% of **1** (5.2 g, 0.034 mol, 9.0%) which was purified and isolated by preparative GLC [(232 °C, 200 mL/min) quinoline 39, **3** 46, **9** 48.5, **1** 67] to give **1**: mp 78.6–79.6 °C; UV_{max} (95% EtOH) 291 nm (ϵ 3810), 297.5 (3740), 303.5 (5110), 310.5 (4680), 317.5 (8220); NMR (100 MHz, $DCCl_3$) δ 3.40 (s, 4), 7.44 (dd, $J_{23} = 4$, $J_{34} = 8$ Hz, H-3), 7.51 (s, H-5), 7.86 (s, H-8), 8.25 (dd, $J_{24} = 2$, $J_{34} = 8$ Hz, H-4), 8.86 (dd, $J_{23} = 4$, $J_{24} = 2$ Hz, H-2); at 270 MHz ($DCCl_3$) the methylene protons were separated by 0.0093 ppm; high-resolution MS *m/e* 155.07346 (calcd for $C_{11}H_9N$, 155.07354) (M^+).

Anal. Calcd for $C_{11}H_9N$: C, 85.13; H, 5.85; N, 9.02. Found: C, 85.21; H, 5.75; N, 9.11.

7,8-Dihydro-6*H*-cyclopenta[*g*]quinoline (2). A Skraup cyclization was carried out in a manner identical with that reported above, using the following conditions: **6** (8.5 g, 64 mmol), ferrous sulfate heptahydrate (2.5 g, 9.0 mmol), 5-nitroindan (7.5 g, 46 mmol), boric acid (4.4 g, 71 mmol), glycerol (28 g, 0.30 mol), concentrated H_2SO_4 (13 mL); reflux time, 4 h. The yellow solid (0.84 g) obtained as a crude product was chromatographed on a column of alumina (Woelm, neutral) with $HCCl_3$ as eluant to give 0.26 g (2.4%) of white crystalline **2**: mp 77.4–78.0 °C (lit.[14] mp 79–80.5 °C); GLC (220 °C, 29 mL/min) **2** 16.2, no peaks corresponding to **6** (5.9) or 5-nitroindan (9.9); IR ($HCCl_3$) 2950, 2850, 870 cm^{-1}; UV_{max} (95% EtOH) 307 nm (ϵ 6010), 310 (5000), 320 (9000); NMR (60 MHz, $DCCl_3$) δ 2.25 (m, 2), 3.12 (t, 4), 7.18–8.97 (m, 5); high-resolution MS *m/e* 169.08936 (calcd for $C_{12}H_{11}N$, 169.08920) (M^+); picrate mp 274–275 °C dec (95% EtOH) (lit.[14] mp 269–271 °C).

Subsequent fractions from the column chromatography afforded a small amount of yellow oil, considered to be **8**: GLC (220 °C, 29 mL/min) **8** 18; NMR (60 MHz, $DCCl_3$) δ 2.25 (m, 2), 3.16 (m, 4), 7.15–8.95 (m, 5) (lit.[14] mp 43–44.5 °C, picrate mp 190–191 °C).

6,7-Dimethylquinoline (3). A Skraup cyclization was carried out in a manner identical with that reported above, using the following conditions: **7** (60.0 g, 0.495 mol), ferrous sulfate heptahydrate (16.2 g, 0.058 mol), 4-nitro-*o*-xylene (47.9 g, 0.317 mol), boric acid (28.5 g, 0.461 mol), glycerol (179 g, 1.94 mol), concentrated H_2SO_4 (84 mL); reflux time, 4 h. The red-brown residual oil (65.7 g) obtained as a crude product was vacuum distilled to give 57.8 g (74.3%) of 6,7-dimethylquinoline (**3**) and 5,6-dimethylquinoline (**9**): bp 100–107 °C (1.8 mm) [lit.[15a] bp 152–160 °C (15 mm)]; GLC (215 °C, 30 mL/min) **3** 10.2, **9** 11. Separation of the product mixture by preparative GLC [(235 °C, 200 mL/min) **3** 56, **9** 59] gave white crystalline **3**: NMR (60 MHz, CCl_4) δ 2.41 (s, 3), 2.44 (s, 3), 7.1–8.1 (m, 4), 8.8 (m, 1, H-2). Obtained similarly was **9**: NMR (60 MHz, CCl_4) δ 2.47 (s, 3), 2.53 (s, 3), 7.1–8.5 (m, 4), 8.8 (m, 1, H-2).

Basicity Measurements. Basicities were determined at 25.00 ± 0.02 °C by our previously reported procedure,[5] using a Beckman Century SS-1 pH meter. The end point and half-neutralization potential were determined graphically. All runs were carried out in duplicate, with a precision of ±1 mV.

Acknowledgment. The 100-MHz NMR spectra were obtained by Dr. Robert E. Lundin, U.S. Department of Agriculture, Berkeley, Calif., through the courtesy of Dr. Roy Teranishi. The 270-MHz NMR data were obtained at Brandeis University through the courtesy of Dr. JoAnne Stubbe on an instrument supported by grants from the Research Corporation and the U.S. Public Health Service (Grant GM-20168). We thank Dr. Walter J. McMurray, Yale University School of Medicine, for the high-resolution mass spectra. The assistance of Dr. Kurt L. Loening, Chemical Abstracts Service, Columbus, Ohio, with nomenclature is gratefully acknowledged. We thank Dr. Peter M. Wege II for summer stipends to F.J.W. and R.A.B.

Registry No. **1**, 70891-81-5; **2**, 7193-31-9; **3**, 20668-33-1; **4**, 13353-49-6; **5**, 55716-66-0; **6**, 24425-40-9; **7**, 95-64-7; **8**, 70891-82-6; **9**, 20668-30-8; benzocyclobutene, 694-87-1; 4-nitrobenzocyclobutene, 52961-81-6; 4-nitro-*o*-xylene, 99-51-4.

Notes

Volume Profile of the Degenerate Equilibration of a Classical Norbornyl Ion

W. J. le Noble,*[1] S. Bitterman, and P. Staub

Department of Chemistry, State University of New York, Stony Brook, New York 11794

F. K. Meyer and A. E. Merbach*[1]

Institute de Chimie, Minerale et Analytique, Faculté des Sciences, Université de Lausanne, Lausanne, Switzerland

Received February 12, 1979

In 1965, we reported that the hydrolysis of *exo*-2-norbornyl tosylate in aqueous acetone is characterized by an activation volume about 3–4 cm^3/mol less negative than that of the endo epimer and that the latter reaction is closely similar in its response to pressure to that of cyclopentyl tosylate.[2] Some time later we published a similar difference between the hydrolyses of the epimeric 3-substituted bicyclo[3.1.0]hexanes,[3] this time with the endo derivative less sensitive to pressure. These results are in agreement with the concept of σ participation, and we interpreted them in terms of the controversial[4] nonclassical ions, in which the positive charge is equally divided between two or more carbon atoms because of symmetry. Reduced volume contractions were subsequently observed in various solvolytic reactions involving phenyl participation as well.[5]

The argument is based on the Drude–Nernst equation,

---

[1] Authors to whom correspondence should be addressed.

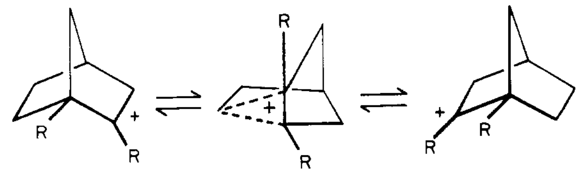
[2] W. J. le Noble and B. L. Yates, *J. Am. Chem. Soc.*, **87**, 3515 (1965).

[3] W. J. le Noble, B. L. Yates, and A. W. Scaplehorn, *J. Am. Chem. Soc.*, **89**, 3751 (1967).

[4] H. C. Brown, "The Nonclassical Ion Problem", with comments by P. von R. Schleyer, Plenum Press, New York, N.Y., 1977.

[5] W. J. le Noble and B. Gabrielsen, *Tetrahedron Lett.*, 45 (1970); *ibid.*, 3417 (1971); C. Yamagani and A. Sera, *Chem. Lett.*, 741 (1972).

Scheme I



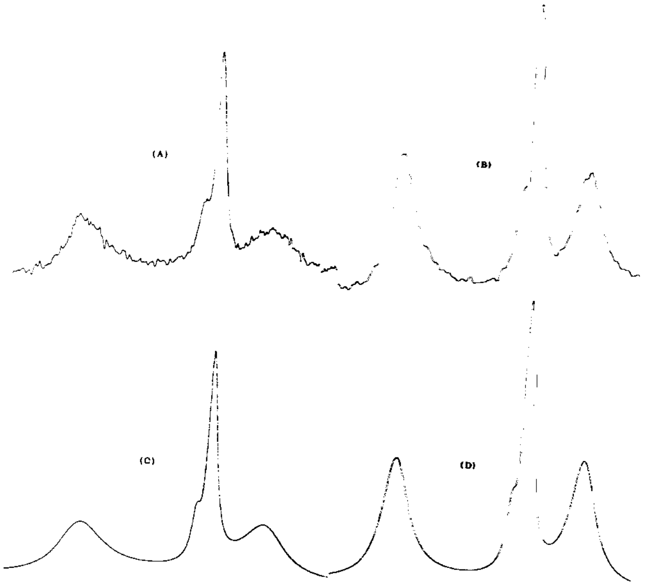


Figure 1. Methoxy region at 277 K and at 0.1 (A) and at 200 MPa (B) and the corresponding simulated spectra (C and D).

according to which the volume decrease accompanying the solvation of a charged species ("electrostriction") is proportional to the square of the charge.[6] We supported this reasoning by referring to listings of the ionization volumes of acids and bases, which tend to show that $\Delta(V_i)$ for monovalent species is most negative if the ions generated have a single atom carrying the charge and that even greater contractions result if multiply charged ions are produced. However, this argument is subject to the ever-current question about the validity of applying observations concerning equilibria to kinetic problems. It was not possible then directly to determine the volume effect of the smearing out of an ionic charge under conditions very similar to those prevailing, for example, in the norbornyl parents. In principle, this could be done by measuring the effect of pressure on the rate of equilibration of a pair of known classical 2-norbornyl ions (Scheme I); in the transition state, the charge is presumably dispersed exactly as in the nonclassical ion.[7] Several norbornyl ions subject to such degenerate equilibration were known or have been reported since then;[8] however, in each instance, the equilibration rate can only be measured at low temperatures, at atmospheric pressure, and by means of NMR signal coalescence techniques. Two recent developments, however, have now begun to move this reaction within range of high-pressure scrutiny.

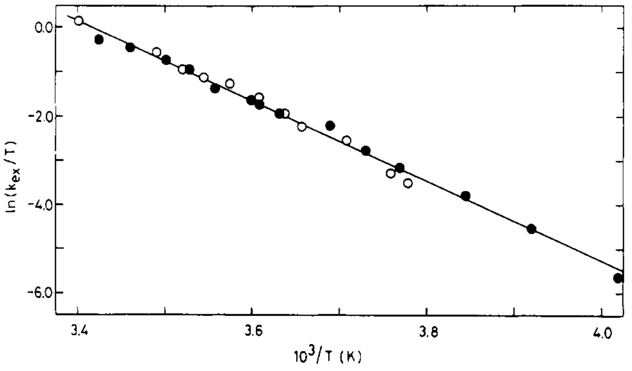


Figure 2. Eyring plot for the rearrangement of the 1,2-dimethoxy-2-norbornyl cation: (○) Varian T-60-A; (●) Bruker WP-60.

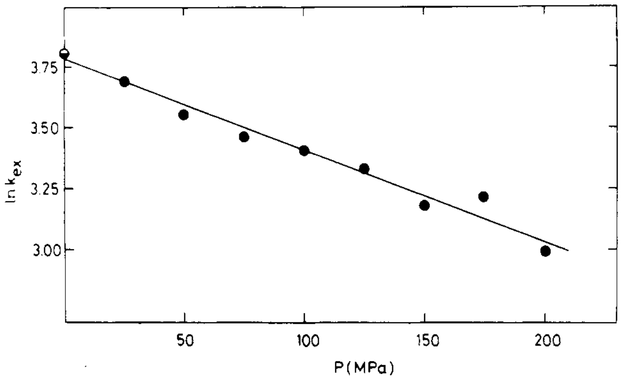


Figure 3. Rate of 1,2-dimethoxy-2-norbornyl cation rearrangement as a function of pressure at 277 K.

Table I. Rates of 1,2-Dimethoxy-2-norbornyl Cation Rearrangement as a Function of Pressure at 277.0 K[a,b]

P, MPa	k_{exptl}, s^{-1}	P, MPa	k_{exptl}, s^{-1}
0.1	45	175.0	25
50.0	35	125.0	28
100.0	30	75.0	32
150.0	24	25.0	40
200.0	20	0.1	45

[a] Data are given in the order in which experiments have been performed. [b] Typical line widths for the reference ranged between 2.4 and 3 Hz. Temperature stability ±0.1 K.

First, Nickon and co-workers have reported[9] that the equilibration of the 1,2-dimethoxy-2-norbornyl ions is especially slow, with a coalescence temperature for the methoxy NMR signals somewhat above 0 °C. This consideration is important because the combination of high pressures and low temperatures places severe restrictions on solvents and probe designs. Secondly, we have recently succeeded[10] in the construction of NMR equipment suitable for the measurement of spectra with a resolution of 1.5 Hz at pressures up to 200 MPa,[11] over a temperature range of −10 to +80 °C and with a temperature control of 0.1 °C.

Experimental Section

The precursor 1,2,2-trimethoxynorbornane was prepared as described by Nickon.[9] A solution was made in fluorosulfonic acid (0.1 M); the methyl fluorosulfonate signal so produced was used as both chemical shift (δ 4.2) and line-width reference; each measurement made use of 500–1200 scans. The temperature was determined with a calibrated platinum resistance thermometer,[12]

---

(6) See, e.g., W. J. le Noble, "High Pressure Chemistry", H. Kelm, Ed., D. Reidel Publishing Co., Boston, Mass., 1978, p 325 ff.

(7) The C_s symmetry of the transition state is required by microscopic reversibility if the Wagner–Meerwein rearrangement is concerted.

(8) R = *p*-anisyl: P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, *J. Am. Chem. Soc.*, **85**, 479 (1963); R = phenyl: G. A. Olah and G. Liang, *ibid.*, **96**, 195 (1974); R = methyl: T. S. Sorensen and K. Ranganayakulu, *Tetrahedron Lett.*, 2447 (1972).

(9) A Nickon and Y. Lin, *J. Am. Chem. Soc.*, **91**, 6861 (1969).

(10) W. L. Earl, H. Vanni, and A. E. Merbach, *J. Magn. Reson.*, **30**, 571 (1978).

(11) Unit recommended by IUPAC. One megapascal (10^6 newton/m^2) is 10 bars (hence, approximately 10 atm).

and the ^1H NMR spectra were measured by means of FT techniques with a Bruker WP-60 spectrometer; an external ^{19}F lock was used. The rate data were determined from the line broadening of the two exchanging methoxy signals at δ 4.90 and 3.77 at 3.8 °C; the spectra were simulated between δ 3.5 and 5.2 by the use of Delpuech's method[13] (see Figure 1).

Results and Discussion

The atmospheric pressure results, measured both at Stony Brook and in Lausanne, agree very well with those reported by Nickon; they show (see Figure 2) that $\Delta H^{\ddagger} = 18.1 \pm 0.3$ kcal/mol and $\Delta S^{\ddagger} = 14.8 \pm 1.2$ eu between −25 and +20 °C. The high-pressure data are shown in Table I. The rate at 3.7 °C is evidently strongly depressed by the application of hydrostatic pressures. The data can be fitted to $\Delta V^{\ddagger} = -RT\ \delta \ln k/\delta p$ by use of the linear approximation as shown in Figure 3, and this gives the result that $\Delta V^{\ddagger} = +8.7 \pm 0.5$ cm^3/mol.

This result demonstrates that the partial volume of the nonclassical structure is indeed larger than that of the limiting classical ions as postulated earlier. The numerical result is not directly comparable to the earlier difference $\Delta\Delta V^{\ddagger}$ of 3.5 cm^3/mol. It is tempting to ascribe the larger difference found in the present experiment to the facts that it presumably considers free and fully developed ions, whereas the solvolytic measurement dealt with transition states likely to resemble ion pairs, and that the charge in the transition state of the equilibration may be even more highly dispersed than that leading to the nonclassical 2-norbornyl ion because of the methoxy groups. The difference in medium renders the further pursuit of a *quantitative* comparison unprofitable at this stage; however, there can be little doubt about the *qualitative* conclusion that charge delocalization in the 2-norbornyl ion does indeed lead to an expansion in volume.

Acknowledgment. The authors express their gratitude for support by the U.S. National Science Foundation (Grant No. CHE7726634) and by the Swiss National Science Foundation (Grant No. 2.921-0.77). Professor Alex Nickon kindly provided us with unpublished details of his synthetic work.

Registry No. 1,2,2-Trimethoxynorborane, 26391-31-1; fluorosulfonic acid, 7789-21-1; methyl fluorosulfonate, 421-20-5; 1,2-dimethoxy-2-norbornyl cation, 26327-58-2.

---

(12) A 1218 Special 2 resistor of 100 ω from Heraeus was used: F. K. Meyer and A. E. Merbach, *J. Phys. E*, in press.

(13) J. Chrisment, J. J. Delpuech, and P. Rubini, *Mol. Phys.*, 27, 1663 (1974).

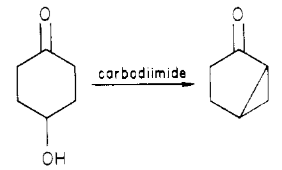
Synthesis of an Unusual Carbodiimide

R. R. Hiatt,* Min-Jen Shaio, and Fawzi Georges

Department of Chemistry, Brock University, St. Catharines, Ontario, Canada L2S 3A1

Received January 30, 1979

The preparation of a series of cyclopropyl ketones by the reaction of keto alcohols with cyclohexylcarbodiimide[1] suggested the possibility of a novel asymmetric synthesis. Reaction, say, of 4-hydroxycyclohexanone with a chiral carbodiimide of known configuration might yield bicyclo[3.1.0]hexan-2-one with predictable geometry.



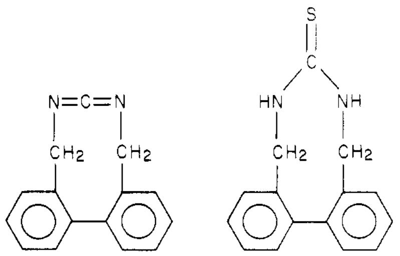
(1)

While preparation of a carbodiimide from an optically active amine presented no synthetic difficulties, models indicated that such a reagent would exhibit little steric control. A cyclic carbodiimide constructed from a restricted rotamer of biphenyl seemed to offer both more chance of success and more interesting chemistry. While carbodiimides have allene-like chirality, some structural constraint is necessary to prevent racemization by nitrogen inversion.

We report here on the feasibility of synthesis of such a carbodiimide, taking as a model an achiral analogue, and peripherally on the bicyclo ketone preparation using a chiral, but acylic, reagent.

Results

The key intermediate, 2,2′-bis(aminomethyl)biphenyl, in the projected synthesis of the nine-membered cyclic carbodiimide, a dibenzo[*e*,*g*](1,3)diazonine (I) was prepared from diphenic acid in fair yield by either of two routes: (1) reduction of diphenic acid diamide with an excess of boron hydride; (2) $LiAlH_4$ reduction of 2,2′-bis(azidomethyl)biphenyl, prepared conventionally from dimethyl diphenate.

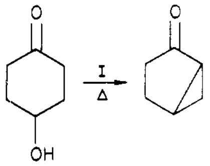


I II

All attempts to prepare the cyclic urea from the diamine failed. Reaction of diamine with CS_2 proceeded smoothly, however, to yield the cyclic thiourea (II), which was fully characterized.

Dehydrosulfurization of II with mercuric oxide[2] gave I, albeit impure. IR and ^1H NMR gave spectra consistent with I, with no extraneous peaks. Mass spectrometric analysis showed the contaminant to be elemental sulfur (S_8). Attempts to remove this impurity were unsuccessful.

In addition to the spectral evidence, compound I, although not pure, gave chemical evidence of being a carbodiimide. In particular, it was used (1) to prepare an acyl anhydride, and (2) to prepare bicyclo[3.1.0]hexan-2-one from 4-hydroxycyclohexanone (eq 2) in fair yield. Thus



(2)

the feasibility of synthesis of a nine-membered ring cyclic carbodiimide has been established.

Our enthusiasm for repeating the synthesis with chiral starting material was dampened by concurrent results

---

(1) P. C. Alexandre and F. Rouessac, *Bull. Soc. Chim. Fr.*, 5, 1837 (1971).

(2) H. G. Khoranz, *Chem. Rev.*, **53**, 146 (1953); W. Weith, *Ber. Dtsch. Chem. Ges.*, 7, 10, 1306 (1874).

0022-3263/79/1944-3265$01.00/0