Synthesis of DL-Threityl Tetrakis(*p*-anisoate), 3b. DL-Threitol (Sigma, 120 mg, 1 mmol) was esterified with *p*-anisoyl chloride as described above, affording 331 mg (49%) of the ester (**3b**) that was recrystallized from absolute ethanol: mp 120-121 °C; UV (EtOH) 257 nm (ϵ 48 000); IR ($CHCl_3$) 1710, 1600, 1250, 1210, 1170, 1100, 850 cm^{-1}; ^1H NMR (CD_2Cl_2) δ 8.00 (d, J = 8.8 Hz), 7.92 (d, J = 8.7 Hz), 6.91 (d, J = 8.8 Hz), 6.88 (d, J = 8.8 Hz), 3.85 (s); EIMS (70 eV) m/z 658 (M, 0.1), 152 (76.7), 135 (100), 107 (7.6), 92 (15.7), 77 (22.8), 64 (14.9).

Synthesis of 2-Deoxy-D-ribityl Tetrakis(*p*-anisoate), 2b. 2-Deoxy-D-ribose (750 mg) was stirred with sodium borohydride (300 mg) in ethanol (20 mL) for 1 h at room temperature. The solution was acidified with glacial acetic acid and decationized with IR-120 ion-exchange resin (2.1 × 3.4 cm) packed in ethanol. The eluate was evaporated, reevaporated from methanol (3 × 15 mL), and vacuum-dried to remove all borate ester.[17] The residual yellow oil was dissolved in pyridine (2 mL) and added slowly, with shaking, to *p*-anisoyl chloride (0.7 mL) in benzene (3 mL). The reaction mixture was stoppered and left to stand at room temperature overnight and then diluted with water and extracted with diethyl ether. Workup of the organic extract, as described for **1b**, provided 380 mg of **2b**, which was recrystallized from absolute ethanol: $[\alpha]^{25}_D$ -8.4° (*c* 0.11, CH_2Cl_2); mp 134-135 °C; UV (EtOH) 260 nm (ϵ 51 700); IR ($CHCl_3$) 1710, 1610, 1250, 1200, 1170, 1100, 850 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.95 (m), 6.86 (m), 3.85 (s); FDMS (0 mA) m/z 672.

Anal. Calcd for $C_{37}H_{36}O_{12}$: C, 66.06; H, 5.39. Found: C, 65.64; H, 5.28.

(17) Schimmel, S. D.; Hoffee, P.; Horecker, B. L. *Arch. Biochem. Biophys.* **1974**, *164*, 560-570.

Acknowledgment. This work was supported by a grant from the National Institute of Allergy and Infectious Diseases (AI 04769) and, in part, by the Institute of Marine and Coastal Studies and the Freshwater Biomedical Center, both at the University of Southern California. NMR spectra and mass spectra were obtained on instruments supported, respectively, in part, by grants from the National Science Foundation (CHE 79-16100) and the National Institute of General Medical Sciences (GM 27029). We thank the staff of the Catalina Marine Science Center, especially Dr. R. Given and Dr. J. Engle, for assistance in mollusk collection and identification and Dr. L. H. Li and J. W. Culp, The Upjohn Co., for L1210 cytotoxicity data.

Registry No. **1a**, 87697-99-2; **1b**, 87711-06-6; **1c**, 87698-00-8; **2a**, 87698-01-9; **2b**, 87698-02-0; **2c**, 87698-03-1; **3b**, 87698-04-2; erythritol, 149-32-6; *p*-anisyl chloride, 100-07-2; DL-threitol, 6968-16-7; 2-deoxy-D-ribose, 533-67-5.

Deuterium Nuclear Magnetic Resonance Spectroscopy as a Probe of the Stereochemistry of Biosynthetic Reactions: The Biosynthesis of Retronecine

Gunnar Grue-Sørensen and Ian D. Spenser*

Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1. *Received June 3, 1983*

Abstract: The mode of incorporation of ^2H from (*R*)- and from (*S*)-(1-^2H)putrescine into retronecine in *Senecio vulgaris* was determined by ^2H NMR spectroscopy. Retronecine, derived from (*R*)-(1-^2H)putrescine, was labeled with ^2H equally at positions 3-*re*, 5-*re*, 8, and 9-*si*. Retronecine from (*S*)-(1-^2H)putrescine was labeled with ^2H equally at positions 3-*si* and 5-*si*. These results establish the stereochemistry of five of the steps in the biosynthetic conversion of putrescine into retronecine.

The carbon skeleton of retronecine (**8**), the most abundant of the necine bases of the *Senecio* alkaloids,[1] is derived from two C_4 units related to ornithine.[2] Label from ornithine and from putrescine (**1**), its decarboxylation product, is incorporated nonrandomly into retronecine (**8**).[3] A molecule with a C_4-N-C_4 skeleton and C_{2v} symmetry, generated from two putrescine units, is a further intermediate.[3-5] There is some evidence that this nondissymmetric "dimeric" intermediate may be homospermidine (**5**).[5,6] The two routes from putrescine to the pyrrolizidine skeleton, shown in Scheme I, are consistent with the tracer evidence. Beyond the finding that retronecine is derived from L-ornithine[7,8] or L-arginine,[8] rather than from the D enantiomers, stereochemical aspects of retronecine biosynthesis have not hitherto received attention.

We have employed ^2H NMR spectroscopy to determine the stereochemical course of five of the steps of retronecine biosynthesis (Scheme I), involving transformations at the carbon atoms derived from C-1 of putrescine.

Results and Discussion

In two experiments, each with 120 plants of *Senecio vulgaris*, (*R*)-(1-^2H)putrescine dihydrochloride (**9**)[9] (98 atom % ^2H) in admixture with [1,4-^{14}C]putrescine dihydrochloride (experiment 1) and (*S*)-(1-^2H)putrescine dihydrochloride (**10**)[9] (87 atom % ^2H), together with [1,4-^{14}C]putrescine dihydrochloride (experiment 2), were administered by the wick method over a period of 12 days (June 1982). From each experiment a mixture of three alkaloids, senecionine (**11**), seneciphylline (**12**), and retrorsine (**13**), each containing retronecine as the necine base, was isolated.[3] The alkaloid mixture that was obtained contained senecionine, seneciphylline, and retrorsine in a molar ratio of ca. 5:4:1, as determined by ^1H NMR.[10]

The ^2H NMR spectra of the alkaloid mixture (in $CHCl_3$) obtained from each of the two experiments are shown in Figure 1. Chemical shifts were assigned by comparison with the corresponding ^1H NMR chemical shifts of the retronecine moiety of the alkaloids **11**, **12**, and **13** (Table I). Correlation of ^1H NMR spectra of retronecine[11,12] with spectra of 12-membered pyrrol-

(1) Bull, L. B.; Culvenor, C. C. J.; Dick, A. T. "The Pyrrolizidine Alkaloids"; North-Holland Publishing Co.: Amsterdam, 1968.
(2) For a summary of the literature, see ref. 3.
(3) Grue-Sørensen, G.; Spenser, I. D. *Can. J. Chem.* **1982**, *60*, 643-662.
(4) Grue-Sørensen, G.; Spenser, I. D. *J. Am. Chem. Soc.* **1981**, *103*, 3208-3210.
(5) Khan, H. A.; Robins, D. J. *J. Chem. Soc., Chem. Commun.* **1981**, 554-556.
(6) Robins, D. J. *J. Chem. Soc., Chem. Commun.* **1982**, 1289-1290.
(7) Reference 3, footnote 2.
(8) Robins, D. J.; Sweeney, J. R. *Phytochemistry* **1983**, *22*, 457-459.
(9) Richards, J. C.; Spenser, I. D. *Can. J. Chem.* **1982**, *60*, 2810-2820.
(10) Molyneux, R. J.; Johnson, A. E.; Roitman, J. N.; Benson, M. E. *J. Agric. Food Chem.* **1979**, *27*, 494-499.

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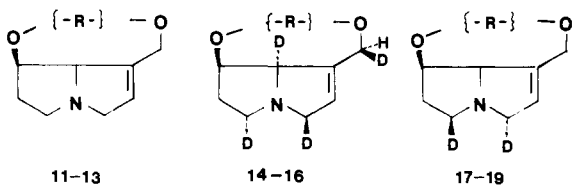
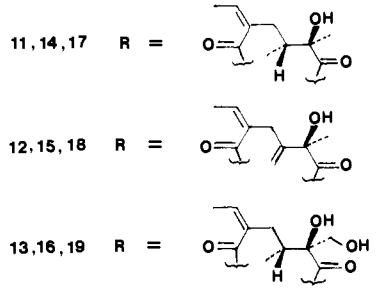




izidine alkaloids containing retronecine,[12,13] together with selective decoupling experiments, facilitated the assignment of the retronecine portion of **11**, **12**, and **13**. Assignment of the ^1H NMR signals from H-3α and H-3β, which has been in dispute,[11,12] was established from nuclear Overhauser effect measurements with senecionine (**11**) in C^2HCl_3. Upon irradiation at 2.50 ppm, a nuclear Overhauser enhancement of 27 ± 5% at 3.23 ppm, 11 ± 5% at 3.36 ppm, and 3 ± 5% at 3.91 ppm was observed. This establishes that of the two absorptions at 3.36 and 3.91 ppm, the former is due to H-3β, which is the shortest distance away from the irradiated H-5β. The signals due to the two prochiral protons at C-9, which in **11**, **12**, and **13** differ by ca. 1.4 ppm, have been assigned on the basis of NMR conformational analysis,[12-14] supported by X-ray diffraction data from 12-membered pyrrolizidine alkaloids. In the ^2H NMR spectrum of the product from experiment 1, the signal at δ 5.42 is due to ^2H at the 9-*si* position and the signal at δ 4.28 is due to ^2H at C-8. This assignment is confirmed by the observation that the retronecine samples, derived from L- and DL-[(*RS*)-5-^{3}H]ornithine, each contained equimolar amounts of tritium at C-8 and at C-9.[3] The signal at δ 3,36, which integrates to two ^2H, is due to ^2H at positions 3β and 5α. In the spectrum of the product from experiment 2, the two signals at δ 3.82 and 2.42 are due to deuterium at positions 3α and 5β, respectively,

The deuterium content at the labeled sites of the enriched samples can be calculated from the ^2H NMR spectra, by employing the natural abundance signal of $C[^2H]Cl_3$ in chloroform as the internal standard and subtracting the contribution due to natural abdundance deuterium in the alkaloids **11–13**. The four labeled sites in the product (**14–16**) from experiment 1 had an average ^2H content of 0,37 atom %; the two labeled sites in the product (**17–19**) from experiment 2 had an average ^2H content of 0.22 atom %,

Thus, the specific incorporation of ^2H from (*R*)-(1-^{2}H)putrescine (experiment 1) into each C_4 unit of retronecine was [0.37/(98/2)] × 100 = 0.76%, a value which is identical, within experimental error, with that calculated from the ^{14}C data (0.75%) (see Experimental Section). This means that no deuterium is lost, relative to ^{14}C, from any of the four sites, C-3, C-5, C-8, and C-9. It follows that none of the transformations in the course of the incorporation of the two C_4 units of putrescine into retronecine (steps a, c or e, f, Scheme I) involve loss of the 1-*re* hydrogen of putrescine.

The specific incorporation of ^2H from (*S*)-(1-^{2}H)putrescine (experiment 2) into each of the two labeled sites, one per C_4 unit,

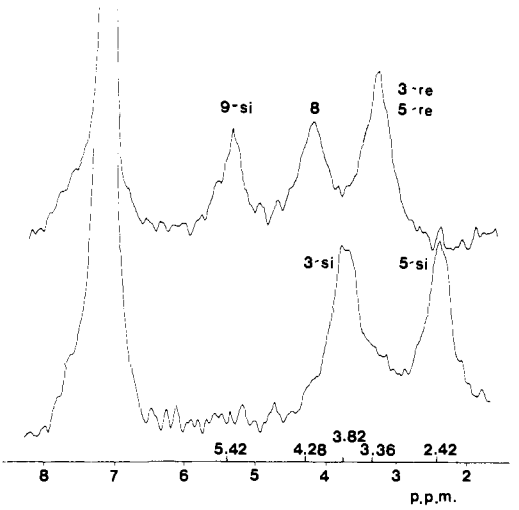


Figure 1. 38.40-MHz ^2H NMR spectra of (top) **14 + 15 +16** (ca. 5:4:1) (36 mg in 1 mL of $CHCl_3$, 75 000 transients) obtained from administration of (*R*)-(1-^{2}H)putrescine dihydrochloride (**9**) and of (bottom) **17 + 18 + 19** (ca. 5:4:1) (62 mg in 1 mL of $CHCl_3$, 78 900 transients) obtained from administration of (*S*)-(1-^{2}H)putrescine dihydrochloride (**10**). Recorded in the Fourier mode on a Bruker WM 250 spectrometer, in 10-mm tubes, with natural-abundance ^2H in $CHCl_3$ (7.25 ppm) as the internal reference. Acqusition time, 1.024 s.

Table I. Incorporation of (*R*)- and (*S*)-(1-^{2}H)Putrescine Dihydrochloride (9 and **10**) into the Retronecine Moiety of Senecionine (**11**), Seneciphylline (**12**), and Retrorsine (**13**): ^2H NMR Analysis

hydrogen atom	^1H NMR chemical shifts,[a] ppm 11	12	13	^2H NMR chemical shifts,[b] ppm expt 1: 14 + 15 + 16 (ca. 5:4:1) from feeding of 9	expt 2: 17 + 18 + 19 (ca. 5:4:1) from feeding of **10**
2	6.16	6.16	6.18		
3-*si* (α)	3.91	3.91	3.92		3.82
3-*re* (β)	3.36	3.36	3.36	3.36[c]	
5-*re* (α)	3.23	3.23	3.23		
5-*si* (β)	2.50	2.50	2.50		2.42
6-*si* (α)	2.10	2.09	2.12		
6-*re* (β)	2.32	2.32	2.36		
7	4.99	4.94	4.98		
8	4.24	4.21	4.25	4.28	
9-*re*	4.01	3.99	4.07		
9-*si*	5.47	5.38	5.48	5.42	

[a] Recorded in C^2HCl_3/Me_4Si at 250 MHz in the Fourier mode on a Bruker WM 250 spectrometer. [b] See caption to Figure 1. [c] This signal integrates to two ^2H.

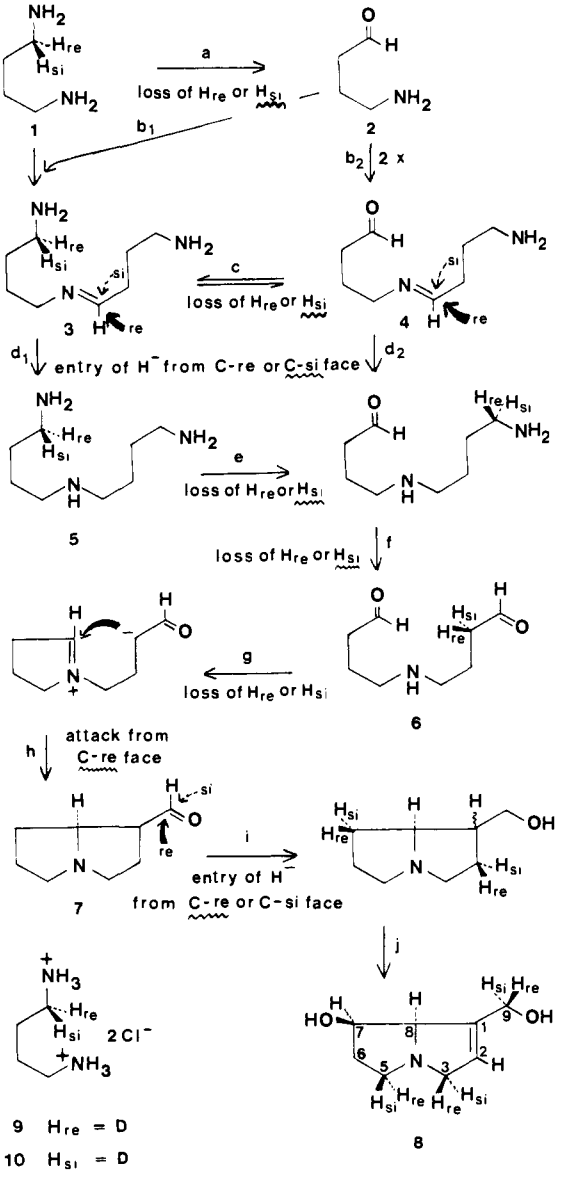
calculated from the ^2H NMR data, was [0.22/(87/2)] × 100 = 0.51%, whereas the value derived from the ^{14}C data was 0.74% (see Experimental Section). Thus, (0.51/0.74) × 100 = 69% of the deuterium, relative to ^{14}C, was retained at the two labeled sites. This result is, at first sight, not in agreement either with the predicted value for retention of $^2H_{si}$, 100%,[15] or with the predicted value for loss of $^2H_{si}$ in the conversion of (*S*)-(1-^{2}H)putrescine into 4-aminobutanal (**2**), which, by way of an intermediate with C_{2v} symmetry, such as **5**, would lead to retronecine retaining 50% ^2H, relative to ^{14}C, at C-3 and C-5.

A possible explanation for this apparent discrepancy may be found in the existence of an intramolecular $^1H/^2H$ isotope effect in the oxidation, catalyzed by diamine oxidase, of (*S*)-(1-^{2}H)-putrescine to nonlabeled 4-aminobutanal (**2**) by removal of $^2H_{si}$

(11) Culvenor, C. C. J.; Heffernan, M. L.; Woods, W. G. *Aust. J. Chem.* **1965**, *18*, 1605–1624.
(12) Reference 1, pp 40–54.
(13) Culvenor, C. C. J.; Woods, W. G. *Aust. J. Chem.* **1965**, *18*, 1625–1637.
(14) Culvenor, C. C. J. *Tetrahedron Lett.* **1966**, 1091–1099.

(15) If homospermidine were an obligatory intermediate, and its formation from putrescine were to take place via a displacement mechanism, no loss of ^2H relative to ^{14}C would be predicted. Since the configurations at C-3 and at C-5 of retronecine are the same, such a displacement reaction would have had to take place with net retention (e.g., 2 × inversion) of configuration. Such a mechanism is, to our knowledge, unprecedented for amine functions.

Scheme I, Biosynthetic Route from Putrescine into Retronecine and Its Stereochemical Ambiguities[a]



[a] The stereochemical questions answered in this investigation are printed in boldface (e.g., H_{Si}). (Stereochemical ambiguities associated with j: loss of 7-*re* or 7-*si* proton; oxygen insertion at C-7 with retention or inversion; loss of 2-*re* or 2-*si* proton; syn or anti dehydrogenation at C-1,2.)

or to (*S*)-4-amino(4-^{2}H)butanal [(*S*)-(4-^{2}H)-**2**], by removal of the homotopic, but isotopically distinct, $^1H_{si}$. Such an intramolecular isotope effect ($k_{H_{si}}/k_{D_{si}} = 3.5$) is observed in this oxidation, catalyzed by hog kidney diamine oxidase,[16,17] The synthesis of (*S*)-(4-^{2}H)-**2** would then be favored over that of **2**, and this would give rise to retronecine with a retention of ^{2}H, relative to ^{14}C (69%), higher than expected (50%). Furthermore, both deuteriated centers of the ^{2}H-labeled product (**17**–**19**) from experiment 2, C-3 and C-5, have the deuterium in the *si* position, as expected if a "dimer" with C_{2v} symmetry served as an intermediate. There is therefore strong evidence that the "dimerization" takes place via an oxidation–condensation–reduction sequence and that the *si*-hydrogen is lost, stereospecifically, from the site, destined to become C-3 or C-5 of retronecine, of one of the two putrescine-derived C_4 units, but not of the other.

The *re*-hydrogen, on the other hand, is retained at both C-3 and C-5 (experiment 1). An intermediate, such as the imine **3** or **4**, derived from (*R*)-(1-^{2}H)putrescine, would carry deuterium at the imine carbon atom as well as at the *re* site of the sp^3 carbon adjacent to the imine nitrogen. Reduction of the imine function by hydride attack from the C-*re* face would result in a secondary amine one of whose α-carbon atoms would be labeled at the *re* site while the other would be labeled at the *si* site. Incorporation of such a deuteriated species into retronecine by way of an intermediate with C_{2v} symmetry would yield an alkaloid sample labeled with deuterium at the positions 3α, 3β, 5α, and 5β, in the ratio 1:1:1:1. This is not the labeling pattern that is observed in the product obtained from (*R*)-(1-^{2}H)putrescine (experiment 1). Reduction of the imine function by hydride attack from the C-*si* face would result in a secondary amine with deuterium at the *re* site of both α-carbon atoms. This, in turn, would yield retronecine deuteriated only at C-3β and C-5α, the two *re* sites. This is indeed observed. It follows that hydride attack takes place from the C-*si* face of the C=N bond.

Deuterium enters positions C-8 and C-9 of retronecine when (*R*)-(1-^{2}H)putrescine serves as a precursor but not when (*S*)-(1-^{2}H)putrescine is the substrate. Stereospecific loss of the *si* proton from each of the terminal carbon atoms of the C_4–N–C_4 chain points to the intermediacy of the dialdehydeamine (**6**). This compound has been employed in a facile "biogenetically modeled" synthesis of the pyrrolizidine skeleton.[6,18,19]

Retronecine, derived from (*R*)-(1-^{2}H)putrescine (experiment 1), carries label at the *si* site of the primary alcohol group, C-9. This stereochemistry is consistent with attack by a hydride donor from the C-*re* face of the C=O bond of an aldehyde intermediate, such as **7**.

We have determined the stereochemical outcome of all the transformations (steps a, c or e, d, f, and i) in the course of retronecine biosynthesis, which occur at the four carbon atoms of retronecine that are derived from the α-carbon atoms of putrescine. The results support the biosynthetic sequence shown in Scheme I.

The stereochemisry of another transformation (step h) follows from the structure of the alkaloid. Several other stereochemical questions remain to be resolved (steps g and j).

Experimental Section

Plant Material and Administration of Labeled Compounds. *S. vulgaris* plants were collected on the McMaster campus and propagated as described earlier.[3] In two experiments, carried out concurrently, labeled compounds were administered by the wick technique over 12 days in June 1982. One hundred twenty plants were used in each experiment: experiment 1, (*R*)-(1-^{2}H)putrescine dihydrochloride[9] (**9**) (98 atom % ^{2}H, 88 mg) in admixture with [1,4-^{14}C]putrescine dihydrochloride[20] (12.5 μCi); experiment 2, (*S*)-(1-^{2}H)putrescine dihydrochloride[9] (**10**) (87 atom % ^{2}H, 308 mg) in admixture with [1,4-^{14}C]putrescine dihydrochloride[20] (26 μCi).

Isolation and Purification of Senecio Alkaloids. A mixture of three alkaloids, senecionine (**11**), seneciphylline (**12**), and retrorsine (**13**), was isolated and purified by the method described in an earlier paper.[3] After recrystallization (CH_3OH) to constant activity, the alkaloids **11**, **12**, and **13** were present in a molar ratio of ca. 5:4:1, as determined by ^{1}H NMR.[10] The specific activity was calculated from an average molecular weight (M_r) of M_r(**11**) × 0.5 + M_r(**12**) × 0.4 + M_r(**13**) × 0.1 = 336. Experiment 1: yield 36 mg; specific activity 7.7 × 10^5 dpm/mmol; specific incorporation per C_4 unit[21] 0.75%. Experiment 2: yield 62 mg; specific activity 4.5 × 10^5 dpm/mmol; specific incorporation per C_4 unit[21] 0.74%.

^{1}H NMR spectra were recorded in the Fourier mode on a Bruker WM 250 spectrometer, in 5-mm tubes, in C^2HCl_3/Me_4Si solutions. NOE measurements were performed with a saturated solution of senecionine (**11**) in C^2HCl_3 that had been degassed through three freeze–pump–thaw cycles. NOE values were obtained from the integrals of the observed peaks in the "enhanced" spectrum, measured with the irradiating field

(16) Callery, P. S.; Nayar, M. S. B.; Jakubowski, E. M.; Stogniew, M. *Experientia* **1982**, *38*, 431–433.
(17) Richards, J. C.; Spenser, I. D. *Tetrahedron* **1983**, in press.
(18) Babor, K.; Ježo, I.; Kalāč, V.; Karvaš, M. *Chem. Zvesti* **1959**, *13*, 163–169.
(19) Leonard, N. J.; Blum, S. W. *J. Am. Chem. Soc.* **1960**, *82*, 503–504.
(20) Nominal specific activity 74 mCi/mmol; New England Nuclear.
(21) Specific incorporation per C_4 unit = (molar specific activity of isolated alkaloids)/(molar specific activity of administered putrescine × 2) × 100.

on, as compared with the integrals in the normal spectrum. The irradiating field was gated off during acquisition of the fid.

^{2}H NMR spectra were recorded in the Fourier mode on a Bruker WM 250 spectrometer, in 10-mm tubes. Details are shown in Figure 1.

Acknowledgments. This work was supported by a grant from the Natural Sciences and Engineering Research Council of Canada. We are indebted to Thelma Leech, M.Sc., Greenhouse Supervisor, McMaster University, for providing greenhouse facilities for our experiments and to Brian G. Sayer, Department of Chemistry, for recording NMR spectra.

Registry No. **1**, 110-60-1; **2**, 4390-05-0; **3**, 87556-53-4; **4**, 87556-54-5; **5**, 4427-76-3; **6**, 87556-55-6; **7**, 87556-56-7; **8**, 480-85-3.

Thermal Isomerization of Quadricyclane to Norbornadiene Catalyzed by Copper(II) and Tin(II) Salts

D. J. Fife, K. W. Morse, and W. M. Moore*

Contribution from the Department of Chemistry and Biochemistry, Utah State University, UMC 03, Logan, Utah 84322. *Received May 10, 1983*

Abstract: Copper(II) salts and tin(II) chloride show exceptional heterogeneous catalytic behavior in converting quadricyclane to norbornadiene in benzene. The heterogeneous catalysis mechanism is described by the adsorption of quadricyclane on the salt surface by a combination of a one-site and a two-site coordination. The two-site-coordination process results in the formation of $C_7H_8X_2$ (X = Cl or Br) as a side product when $CuCl_2$ or $CuBr_2$ are used as catalysts. The rate constant for the disappearance of quadricyclane is much greater when $CuCl_2$ or $CuBr_2$ ($\sim 10^{-2}$ min^{-1} cm^{-2}) is used than when $CuSO_4$ ($\sim 10^{-4}$ min^{-1} cm^{-2}) is used.

The reversible valence isomerization of norbornadiene[1] (NBD) to quadricyclane[2] (Q) has received considerable attention as an attractive system for solar chemical energy storage.[3-5] Our studies have primarily involved the photosensitized isomerization of NBD to Q by copper(I) complexes.[6] During these investigations it was observed that anhydrous copper(II) salts catalyzed the reverse isomerization of Q to NBD. This was extremely interesting in that previous studies[5,7-11] have focused on more exotic and expensive catalysts (e.g., $[(CF_3)_2C_2S_2]_3Mo$,[5] $[Rh(CO)_2Cl]_2$,[8] $(CH_2{=}CHCN)_2Ni$,[9] cobalt(II) porphyrins,[5,8] $[(NBD)RhCl]_2$,[10] and $[M(NO)_2(CH_3CN)_4](BF)_4)_2$ with M = Mo or W[11]).

Recently it was reported that a solution of $SnCl_2$ and $(Ph_3P)SnCl_2$ in deuterated methanol catalyzed the isomerization of Q to NBD.[7] However, a benzene solution of Q in contact with $SnCl_2$ was observed to be inactive.[7] In view of our findings with $CuCl_2$, we assume that stannous chloride dihydrate was used. Indeed, we have found that $SnCl_2{\cdot}2H_2O$ does not catalyze the conversion of Q to NBD in benzene. Anhydrous $SnCl_2$ in benzene does catalyze the isomerization with the desired catalytic properties: (1) rapid and specific conversion of Q to NBD and (2) insolubility in the reaction medium.

Table I. Summary of Catalytic Properties of $CuCl_2$, $CuBr_2$, $SnCl_2$, and $CuSO_4$ in the Conversion of Quadricyclane, Q, to Norbornadiene, NBD, in Benzene

added salt	change in catalytic surface	remarks on kinetics
$CuCl_2{\cdot}2H_2O$, $CuSO_4{\cdot}5H_2O$, $SnCl_2{\cdot}2H_2O$	none	no reaction
$CuCl_2$	brown to white	−rate Q > +rate NBD, $C_7H_8Cl_2$ formed (−rate Q/rate NBD decreases with surface area of salt, with very small surface areas −rate Q ≃ +rate NBD)
$CuBr_2$	black to white	−rate Q ≫ +rate NBD; $C_7H_8Br_2$ formed (−rate Q/rate NBD decreases with surface area of salt, with very small surface areas −rate Q ≃ +rate NBD)
$CuSO_4$	none	−rate Q = +rate NBD
$SnCl_2$	none	−rate Q = +rate NBD

Experimental Procedures

Materials. All materials were purchased commercially. Spectral grade benzene was dried by anhydrous cupric sulfate prior to the kinetic experiments. Anhydrous $CuCl_2$ was prepared by heating it in an oven at 160 °C for several hours. Anhydrous $CuSO_4$ was similarly heated prior to use. Powdered anhydrous $CuSO_4$ of approximately 400–600 mesh was used. The anhydrous $CuCl_2$ and $CuBr_2$ were 120–200 mesh and 50–70 mesh, respectively. Anhydrous $SnCl_2$ was used as purchased with the size of the crystals varying greatly from 2.5 to 0.2 mm.

Conversion Rates. Dried benzene was added to a predetermined amount of copper(II) or tin(II) salt weighed in a nitrogen-dried 10-mL volumetric flask. Quadricyclane dissolved in benzene was then added to the volumetric flask, with approximately 10–15 s required to achieve mixing. The heterogeneous solution was continuously stirred except for 5- to 10-s intervals when ~0.3 μL of solution was withdrawn for analysis.

(1) Bicyclo[2.2.1]hepta-2,5-diene.
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