Conversion of *syn*-Sesquinorbornene to a 4,5-Dihydro-1,2,3-oxadiazole 3-Oxide Derivative

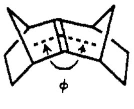
Stephen F. Nelsen,*,† Mark F. Teasley,† and Menahem Kaftory*,‡

S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, and Department of Chemistry, Technion—Israel Institute Technology, Haifa Haifa 32 000, Israel

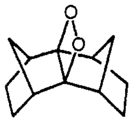
Received March 31, 1988

Reaction of *syn*-sesquinorbornene (1) with $NOPF_6$ gives the formal 1,3 cycloadduct of O=NN=O to the double bond, 5 which is the first reported 4,5-dihydro-1,2,3-oxadiazole 3-oxide derivative. No 5 was detected upon reaction of 1 with NO, and the vicinal nitro, nitroxy adduct 8 is the major product. X-ray crystallographic structures are reported for 5 and 8.

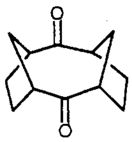
Derivatives of *syn*-sequinorbornene, 1, have been of particular interest because their central double bonds are significantly endo pyramidalized. X-ray structures of six derivatives[1-3] have given ϕ values in the range 164.5–162° (out of plane deformation angles 15.5–18°). The reasons for endo pyramidalization at the olefinic carbons have been summarized and extended by Houk and co-workers.[4] Not surprisingly, the double bond of 1 is unusually reactive, and reagents add to the exo face of the olefin.[1,4,5] Paquette and Carr[5d] attempted to prepare the dioxetane 2 (expected isomer shown) by dye-sensitized photooxygenation. The photooxygenation was unusually slow, and they succeeded in isolating the cleavage product, diketone 3, along with epoxide 4 by using some sensitizers, but no dioxetane was detected.



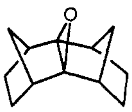
1



2



3



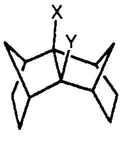
4

Because the cation radical of 1 clearly reacts with oxygen in cyclic voltammetry experiments,[5e] we investigated the products produced from 1 and $(2,4\text{-}Br_2\text{-}C_6H_3)_3N^+SbCl_6^-$, which proved to be numerous. The principal products isolated in addition to 3 and 4 contained chlorine, and we were also unable to detect dioxetane. The $SbCl_6^-$ counterion of the oxidant used was apparently reacting with intermediates produced under the reaction conditions, so we next tried reacting 1 with the commercially available oxidant $NOPF_6$. These experiments also failed to produce any dioxetane, but they did give a low yield of a heterocyclic compound of unexpected structure, which is the subject of this report.

Results and Discussion

Reaction of 1 with $NOPF_6$ in methylene chloride at −78 °C with O_2 bubbling through the solution required approximately 2 equiv of $NOPF_6$ for consumption of 1. Polymeric materials that were not investigated were major products, and NMR of both the crude product and material eluted from silica gel showed the presence of diketone 3 (but not epoxide 4), as well as a new compound 5, which was purified by TLC on silica gel, filtration through alumina to remove yellow impuries, and recrystallization in up to 19% yield based on 1 (see the Experimental Section for details of the conditions).

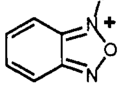
Both the proton and carbon NMR spectra indicated that 5 had the sesquinorbornene structure intact, but that the plane of symmetry perpendicular to the double bond of 1 had been broken, that is, that 5 has general structure A.



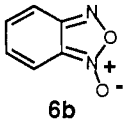
A

Analysis and mass spectroscopy established its empirical formula as $C_{12}H_{16}N_2O_2$, so X, Y have the empirical formula $(NO)_2$. Compound 5 is colorless, presumably ruling out the presence of C nitroso groups, which show weak visible absorption. Strong IR bands at 1484 and 1450 cm^{-1} indicated that π bonding was present, as did near UV absorption (maxima at 261, 268, and 276 nm, with ϵ about 4000). The nitrogens are, as expected, different by ^{15}N NMR. Chemical shifts of δ −37.4 and −188.2 (upfield from nitromethane reference) were observed, indicating that their bonding is quite different. We were unable to assign a structure with confidence, even with all of these spectral data.

Vicinal *C*-nitroso compounds are apparently always less stable than isomeric heterocyclic species. Katritzky and co-workers[6] showed that benzofuroxan is benzo-2,1,3-oxadiazole 1-oxide, and that 6a and 6b interconvert rapidly on the NMR time scale at higher temperatures. The



6a



6b

---

[1] Watson, W. H.; Galloy, J.; Bartlett, P. D.; Roof, A. A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2022.

[2] (a) Paquette, L. A.; Charimilund, P.; Böhm, M. C.; Gleiter, R. Bass, L. S.; Clardy, J. *J. Am. Chem. Soc.* **1983**, *105*, 3136. (b) Paquette, L. A.; Hayes, P. C.; Charimilund, P.; Böhm, M. C.; Gleiter, R.; Blount, J. F. *Ibid.* **1983**, *105*, 3148.

[3] Hagenbuch, J. P.; Vogel, P.; Pinkerton, A. A.; Schwarzenbach, D. *Helv. Chim. Acta* **1981**, *64*, 1818.

[4] (a) Houk, K. N.; Rondan, N. G.; Brown, F. K.; Jorgensen, W. L.; Madura, J. D.; Spellmeyer, D. C. *J. Am. Chem. Soc.* **1983**, *105*, 5980. (b) Houk, K. N.; Rondan, N. G.; Brown, F. K. *Isr. J. Chem.* **1983**, *23*, 3.

[5] (a) Bartlett, P. D.; Roof, A. A. M.; Subramanyam, R.; Winter, W. J. *J. Org. Chem.* **1984**, *49*, 1875. (b) Paquette, L. A.; Carr, R. V. C.; Böhm, M. C.; Gleiter, R. *J. Am. Chem. Soc.* **1980**, *102*, 1186. (c) Paquette, L. A.; Ohkata, K.; Carra, R. V. C. *Ibid.* **1980**, *102*, 3303. (d) Paquette, L. A.; Carr, R. V. C. *Ibid.* **1980**, *102*, 7553. (e) Nelsen, S. F.; Teasley, M. F. *J. Org. Chem.* **1986**, *51*, 3474.

[6] Harris, R. K.; Katritzky, A. R.; Oksne, S.; Bailey, A. S.; Paterson, W. G. *J. Chem. Soc.* **1963**, 197.

† University of Wisconsin.

‡ Technion—Israel Institute of Technology.

0022-3263/88/1953-5930$01.50/0

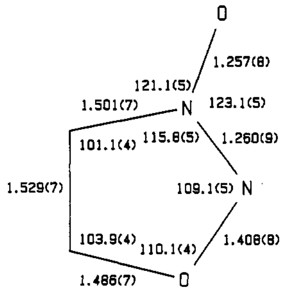
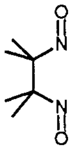
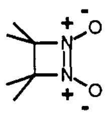


Figure 1. Bond lengths and angles for the heterocyclic ring of **5**.

activation energy for this interconversion is 14 kcal/mol at room temperature.[7] The analogous compound with the benzo ring replaced by two methyl groups (dimethylfuroxan) has a much higher barrier for interconversion of such isomers and shows no dynamic behavior by NMR, although Katritzky has reported seeing slow interconversion for an unsymmetrical example.[8] Oxidation of 1,2-bis(hydroxylamino)tetramethylethane does not give the dinitroso compound **7a**, but azo dioxide **7b**, which is also

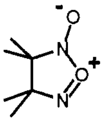


7a

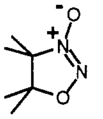


7b

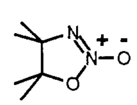
formed when 3,3,4,4-tetramethyldiazetidene 1-oxide is oxidized.[9] Bond strength additivities predict that **7a** ought to be more stable,[10] and it has been suggested that there may be an orbital symmetry problem for converting **7b** to **7a**. Heating **7b** decomposes it to a complex mixture of products,[10b] but there is no evidence that **7a** is produced. An azo dioxide fused to sesquinorbornene would be especially strained, and we did not believe we could conclusively rule out for **5** structure B, *N′*-alkoxy diimide *N*-oxide C, or acinitramine D on the basis of the spectral data, especially since no examples of any derivatives of B–D are known. Neither MNDO nor AM1 semiempirical MO calculations[11] on the parent compounds of B–D with all hydrogen substituents (empirical formulae $C_2H_4N_2O_2$) give B to be a very reasonable structure. B is calculated to be 58.2 kcal/mol less stable than C by AM1 and 58.0 kcal/mol by MNDO. B is also calculated to be less stable than its diazetidene dioxide isomer, **7b**, with all hydrogen substituents, by 10.0 kcal/mol with AM1 and 8.5 kcal/mol with MNDO. These calculations also predict the parent dinitroso compound of **7a** to be far more stable than the diazetidene dioxide isomer **7b**, by 87.7 kcal/mol with AM1 and 58.9 kcal/mol with MNDO, so their reliability for this group of compounds is certainly not established. C and D are calculated to be comparable in stability, D being 1.7 kcal/mol less stable by AM1 and 3.3 kcal/mol more stable by MNDO.



B

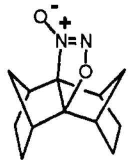


C

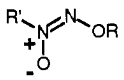


D

X-ray crystallography established **5** as being the C derivative shown. Compound **5** is the first reported 4,5-dihydro-1,2,3-oxadiazole-3-oxide, although acyclic N′-oxygen-substituted diimide *N*-oxides have received some study.[12] The bond lengths in angstroms and bond angles in degrees for the heterocyclic ring of **5** are shown in Figure 1. The atoms of the oxadiazole ring of **5** (those shown in the figure) are within experimental error of lying in a plane. In contrast to **5**, the NO bonds are cis (see E) in the two *N′*-tosyloxy[13a,b] and one *N′*-alkoxy[13c,d] acyclic diimide *N*-oxides we located in the Cambridge Data File. The N=N distance of **5**, at 1.260 Å, is only slightly longer than the 1.22–125-Å range for alkylated azo compounds,[14] and shorter than the 1.292 Å observed for azo dioxide **7b**, which was the shortest of seven azo dioxides[15] we located in the Cambridge Data File. It is also shorter than the 1.283 and 1.270 Å reported for acyclic cis *N′*-alkoxy diimide *N*-oxides,[13c,d] but close to the 1.252 Å of *trans*-di-*tert*-butyl diimide.[16] The exocyclic $N^+–O^-$ bond length of **5** at 1.257 Å is within the range reported for azo dioxides, 1.250 Å for **7b**, and 1.260–1.267 Å for six others, and close to those found for its acyclic analogues.[13c,d] The endocyclic N–O bond length of **5**, at 1.408 Å, is that expected for an NO single bond,[14] and somewhat longer than the O–N distance of 1.366 and 1.383 Å found for the cis acyclic *N′*-alkoxy diimide *N*-oxides[13c,d] and the 1.380 Å of *trans*-di-*tert*-butyldiimide.[16] Other details of the structure of **5** are given in the Experimental Section.



5



E

Compound **1** shows a reversible one electron oxidation wave in methylene chloride containing 0.1 M tetra-*n*-bu-

---

[7] (a) Dahlqvist, K. I.; Forsen, S. *J. Magn. Reson.* **1970**, *2*, 61. (b) Anet, F. A. L.; Yavari, I. *Org. Magn. Reson.* **1976**, *8*, 158.

[8] Boulton, A. J.; Gray, A. C. G.; Katritzky, A. R. *J. Chem. Soc.* **1965**, 5958, footnote 8.

[9] (a) Singh, P.; Boocock, D. G. B.; Ullman, E. F. *Tetrahedron Lett.* **1971**, 3935. (b) Ullman, E. F.; Call, L.; Tseng, S. S. *J. Am. Chem. Soc.* **1973**, *95*, 1677.

[10] (a) Snyder, J. P.; Heyman, M. L.; Suciu, E. N. *J. Org. Chem.* **1975**, *40*, 1395. (b) Singh, P. *Ibid.* **1975**, *40*, 1405. (c) Greene, F. D.; Gilbert, K. E. *Ibid.* **1975**, *40*, 1409.

[11] (a) MNDO: Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899 and 4907. (b) AM1: Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[12] (a) Freeman, J. P. *J. Org. Chem.* **1963**, *28*, 2508. (b) Stevens, T. E. *Ibid.* **1964**, *29*, 311. (c) Freeman, J. P.; Lillwitz, L. D. *Ibid.* **1970**, *35*, 3107. (d) Woodward, R. B.; Wintner, C. *Tetrahedron Lett.* **1969**, 2689. (e) For an extensive review, see: Yandovskii, V. N.; Gidaspov, B. V.; Tselinskii, I. V. *Russ. Chem. Rev.* **1980**, *49*, 237 (translation of *Uspeckhii Khemii* **1980**, *49*, 449).

[13] (a) Maskill, H.; Murray-Rust, P.; Thompson, J. T.; Wilson, A. A. *J. Chem. Soc., Chem. Commun.* **1980**, 788. (b) White, E. H.; Todd, M. J.; Ribi, M.; Ryan, T. J.; Sieber, A. A. F.; Dickerson, R. E.; Bordner, J. *Tetrahedron Lett.* **1970**, 4467. (c) Aebischer, B. M.; Hanssen, H. W.; Vasella, A. T.; Schweizer, W. B. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2139. (d) Cherepinskii-Malov, V. D.; Marchenko, G. A.; Mukhametzyanov, A. S. Buzyki, B. I. *Bull. Acad. Sci., USSR Div. Chem. Sci.* **1985**, *34*, 871 (translation of *Isv. Akad. Nauk. SSSR, Ser. Khim.* **1985**, 954.

[14] Allmann, R. *The Chemistry of Hydrazo, Azo, and Azoxy Groups*; Patai, S., Ed.; Wiley: New York, 1975; Part 1, p 23, where the standard NO single bond length for sp^2 hybridized N is taken as 1.41 Å (p 28).

[15] Prout, K.; Stothard, V. P.; Watkin, D. J. *Acta Crystallogr., Sect. B* **1978**, *B34*, 2602.

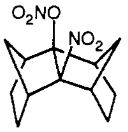
[16] Ogle, C. A.; VanderKooi, K. A.; Mendenhall, G. D.; Lorprayoon, V.; Cornilsen, B. C. *J. Am. Chem. Soc.* **1982**, *104*, 5114.

Table I. Conditions for Reaction of 1 with $NOPF_6$[a]

1, mg (mM)	$NOPF_6$, mg (eqiv)	yield of 5, %	yield of 3, %
160 (100)	350 (2)	12	10
160 (100)	350 (2)	19	
320 (200)	370 (1)	3	
245 (150)	550 (2)	8	6

[a] In CH_2Cl_2 at −78 °C with O_2 bubbling through the solution.

tylammonium tetrafluoroborate as supporting electrolyte and formal potentials $E°'$ vs SCE are 1.61 V (ΔE_{pp} 0.089 V) at room temperature and 1.56 V (ΔE_{pp} 0.088 V) at −78 °C. Although the electron transfer from 1 to NO^+ is endothermic, some $1^{\bullet+}$ and neutral NO should be formed upon mixing 1 with $NOPF_6$. There is experimental precedent for $NOPF_6$ having enough oxidizing power to generate the cation radical from an olefin of very similar $E°'$. $NOPF_6$ rapidly catalyzes the oxygenation of biadamantylidene[17] ($E°'$ 1.62 V at room temperature) to its dioxetane, a reaction that proceeds by an olefin cation radical chain mechanism. Reaction of 1 with gaseous NO in methylene chloride gave almost exclusively a single product, 8, whether or not the solvent was carefully deaerated, although 8 was only isolated in 31% yield after TLC purification. No 5 was detected in these reactions. The structure of 8 was verified by X-ray crystallography to be the vicinal nitronitroxy adduct, A (X = NO_2, Y = ONO_2). Pure NO does not react with alkenes, but the traces of NO_2 present catalyze addition to initially give nitrosonitro alkanes, which catalyze further disproportionation of NO to N_2 and NO_2, giving a complex autocatalytic chain reaction from which nitronitrates are produced from tetraalkylolefins.[18] An ORTEP view of 8 is shown as Figure 3 (supplementary material). The ONO_2 distances are about 0.01 Å shorter than those in the carbon-bound NO_2 group, as expected from previously reported structures containing nitroxy groups.[19] The nitro and nitroxy groups are almost perpendicular, the normals to their mean planes forming an angle of 74.8°. The O_2NO,NO_2 distance is 2.577 Å, indicating some bonding interaction, although both NO_2 groups are planar within experimental error, so the interaction must be quite weak.



8

Conclusion

Our data do not allow us to comment usefully on the mechanism for formation of the unique heterocyclic ring of 5, except that cation radicals are probably involved, because no 5 was seen in reaction of 1 with NO. The overall reaction converting 1 to 5 is formally a 1,3-cycloaddition of the unstable dimer O=NN=O to the double bond, which lacks any close precedent.[20]

Experimental Section

Preparation of 5. Solutions of *syn*-sesquinorbornene (1) at the concentrations indicated in Table I were cooled to −78 °C and saturated with a stream of O_2 bubbling through a syringe needle. The indicated amount of $NOPF_6$ was added as a solid, and the reactions were monitored by TLC (hexane/silica gel) until 1, R_f 0.8, was consumed, at which point some solid $NOPF_6$ remained. The reaction mixtures were poured into aqueous Na_2CO_3 solution and extracted with pentane. Poor mass balances were observed after drying over $MgSO_4$, filtration, and evaporation, and additional polymeric material was removed by filtration of pentane solutions through alumina. ^1H NMR spectra of crude material showed minor amounts of 3 and no 4, but the major product observed was 5. Preparative TLC on silica gel using 15% ethyl acetate in hexane separated 5 (R_f 0.11), although multiple elutions were sometimes necessary. Some samples were contaminated with yellow material, which was removed by filtration of pentane solutions through alumina. Recrystallization from pentane gave analytically pure material: mp 214–217 °C dec; MS, *m/e* obsd 220.1230 (2), calcd 220.1212; obsd 160.1265 (P − N_2O_2, 32), calcd 160.1252 for $C_{12}H_{16}$; IR 3032 (m), 3002, 2976 (m), 2931 (m), 2905, 2874, 1723, 1484 (s), 1450 (s), 1348, 1322 (m) cm^{-1} (other bands in fingerprint region); UV (C_6H_{12}) 262 (ϵ 4320), 268 (ϵ 4600), 276 (ϵ 3710) nm; ^1H NMR δ ($CDCl_3$) 3.02 (m, 2 H), 2.83 (m, 2 H), 2.14 (m, 6 H), 1.65 (m, 4 H), 1.47 (br d, J = 10.9 Hz, 2 H); ^{13}C NMR δ ($CDCl_3$) 102.2 (C_q), 95.6 (C_q), 46.9 (CH), 43.5 (CH_2), 43.4 (CH), 23.4 (CH_2), 22.9 (CH_2); ^{15}N NMR δ vs CH_3NO_2 (CD_3NO_2) −37.4, −188.2. Anal. Obsd for $C_{12}H_{16}N_2O_2$: C, 65.46; H, 7.44; N, 12.69. Calcd: C, 65.43; H, 7.32; N, 12.72.

Crystallography of 5: orthorhombic space group *Pbca*; a = 12.296 (6), b = 14.209 (7), and c = 12.200 (6) Å; the calculated density for Z = 8 is 1.373 g/cm³. The structure was solved by MULTAN80[21] and refined by SHELX.[22] The refinement was performed in a full-matrix least-squares procedure anisotropically for the heavy atoms, isotropically for the H atoms. The agreement factors are R = 0.084 and R_w = 0.102 for 1181 observed reflections [$F_o > 1.5\sigma(F_o)$] (out of 1702 measured unique reflections) {$w = 1.0740/[\sigma^2(F_o) + 0.0086(F_o)^2]$}.

Preparation of 8. Compound 1 (80 mg, 0.50 mmol) in 10 mL of CH_2Cl_2 (50 mM) was deaerated by bubbling N_2 through it for 1 h at −78 °C, and gaseous NO which had been passed through a column of silica gel at −78 °C was bubbled through the solution, which turned light blue. After 1 was consumed (followed by TLC on silica gel/hexane) NO was flushed from the reaction flask with N_2. Evaporation gave 130 mg of green oil, which was mainly 8 by ^1H NMR analysis. TLC with 15% ethyl acetate/hexane separated 8, R_f 0.44, 41 mg (31%). Repetition under the same conditions except without deoxygenation gave crude product, which was almost pure 8, but increased the yield after TLC only to 42 mg. Recrystallization gave pure 8 (25%): mp 120 °C dec (evolution of brown gas); IR 3035, 2997, 2929, 2893, 1636 (s), 1540 (s), 1468, 1349, 1302 (m), 1286 (s) cm^{-1} (other bands in fingerprint region); ^1H NMR δ ($CDCl_3$) 3.08 (br s, 2 H), 3.04 (br s, 2 H), 2.82 (br d, J = 10.8 Hz, 2 H), 2.22 (m, 4 H), 1.72 (m, 6 H); ^{13}C NMR δ ($CDCl_3$) 109.9 (C_q), 105.7 (C_q), 48.7 (CH), 47.1 (CH_2), 45.2 (CH), 25.4 (CH_2), 24.5 (CH_2). Anal. Obsd for $C_{12}H_{16}N_2O_5$: C, 54.03; H, 6.09; N, 10.20. Calcd: C, 53.73; H, 6.01; N, 10.44.

Crystallography of 8: triclinic space group $P1$; a = 11.639 (6), b = 7.678 (4), and c = 7.384 (4) Å; α = 114.47 (3), β = 90.40 (3), and γ = 93.22 (3)°; the calculated density for Z = 8 is 1.487 g/cm³. The crystal structure was solved by MULTAN80[21] and refined by SHELX.[21] The refinement was performed in a full-matrix least-squares procedure anistropically for the heavy atoms, and isotropically for the H atoms. The agreement factors are R = 0.051 and R_w = 0.058 for 1543 observed reflections [$F_o > 1.5\sigma(F_o)$] (out of 1832 measured unique reflections) {$w = 1.3351/[\sigma^2(F_o) + 0.0015(F_o)^2]$}.

---

(17) Nelsen, S. F.; Akaba, R. *J. Am. Chem. Soc.* **1981**, *103*, 2096.

(18) (a) Rees, Y.; Williams, G. H. *Adv. Free Radical Chem.* **1969**, *3*, 199. (b) Ogata, N. *Oxidation in Organic Chemistry*; Trahanovsky, W. S., Ed.; Wiley: New York, 1978; Part C, p 309.

(19) (a) Couldwell, C. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1527. (b) Halfpenny, J.; Small, R. W. H. *Ibid.* **1978**, *B34*, 3452.

(20) For reviews of synthetic methods for making azoxy compounds, see ref 12c and Yandovskii, V. N.; Gidaspov, B. V.; Tselinskii, I. V. *Russ. Chem. Rev.* **1981**, *50*, 237 (translation of *Uspeckhii Khemii* **1981**, *50*, 296).

(21) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, S. P.; Woolfson, M. M. MULTAN 80, "A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data"; Universities of York, England, and Louvain, Belgium.

(22) Sheldrick, G. M. SHELX, Program for Crystal Structure Determination, University of Cambridge, 1976.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial financial support for this research.

Registry No. 1, 73321-28-5; 3, 113428-76-5; 5, 116970-46-8; 8, 116970-47-9.

Supplementary Material Available: Stereoscopic views of structures and packing diagrams, atomic coordinates and heavy atom bond lengths, bond angles, and anisotropic temperature coefficients for 5 and 8 (9 pages). Ordering information is given on any current masthead page.

Transport of Uranyl Ion through Liquid Membrane Mediated by Macrocyclic Polycarboxylate in Combination with Hydrophobic Quaternary Ammonium Cation

Yoshiaki Kobuke,* Iwao Tabushi,† Kohki Oh, and Takao Aoki

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

Received September 6, 1988

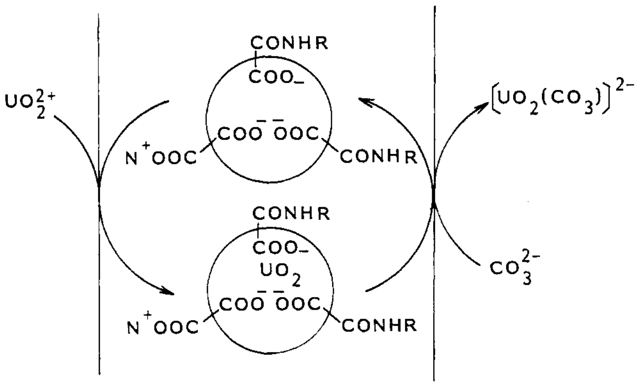
Macrocyclic polycarboxylates affording planer hexadentation to uranyl ion were prepared from a hexaester of 27-membered carboxylic acids. One to three *tert*-butyl moieties were introduced systematically into the macrocyclic skeleton by using ethyl *tert*-butyl malonate in the synthesis. The *tert*-butyl ester functionality was selectively cleaved and converted into the amide of hydrophobic aliphatic amines. The remaining three to five ethyl esters were then hydrolyzed into carboxylic acids that satisfy the hexadentation by three carboxylates attached to different carbon atoms in the macrocycle. These polycarboxylates were combined with hydrophobic quaternary ammonium salts to form complexes with each other, which partitioned preferentially into the organic phase. The 1:1 complex functioned as the real carrier molecule for the uranyl transport through the chloroform liquid membrane. The uranyl ion was transported smoothly against the concentration gradient by the use of carbonate gradient. The efficiency of quaternary salts followed a decreasing order of hydrophobicity: trioctylmethyl > cetyltrimethyl > lauryltrimethyl > benzyltrimethyl > tetraethyl. Among the series of amide carriers, diamide tetracarboxylate **3h** gave the fastest transport rate; then the relative order **3l** > **3g** > **3m** > **3i** was observed, illustrating the combined effect of hydrophobic–hydrophilic balance and stereochemical requirement.

Introduction

Since the discovery of ionophores, the transport of ionic species through the membrane[1] mediated by these ionophores has gained special attention that covers a wide range of interest, including mimicking biologically important phenomena, development of ion-selective electrodes, separation of metal ions or amino acids, applications to a waste water treatment, and others.[2–7]

One of the least studied but most important examples of such ions might be uranium, especially that present in seawater as an extremely dilute solution. The total amount, 4×10^9 tons, is ca. 1000-fold of the amount existing in the mines all over the free world.[8] However, the concentration, 3.3 ppb almost uniformly in all oceans, is too low to be easily extracted and efficient ways of concentrating uranyl species are now under current investigations.[9–11] The most successful approach so far is adsorption onto chelating resins.[12–18] The problem is a small overall adsorption rate mainly limited by the low uranyl concentration and a small equilibrium adsorption by the competing metal ions sometimes in a large excess. Membrane transport may give an attractive alternative. Here, the uranyl ion is transferred into a membrane phase by complexation with appropriate "uranophile"[19–26] type carrier molecules and moves across the membrane and then is liberated into another aqueous phase by the dissociation. For efficient UO_2^{2+} concentration it is necessary to transport UO_2^{2+} against its own concentration gradient across the membrane by applying other chemical potential differences in the opposite direction across the membrane (see Scheme I). Then, the uranyl species is accumulated into the other receiving aqueous phase. This procedure may be promising for the spontaneous concentration of

Scheme I



---

† Deceased March 22, 1987.

(1) McMurry, W.; Begg, R. W. *Arch. Biochem. Biophys.* **1959**, *84*, 546–548.
(2) Lehn, J. M. *Struct. Bonding (Berlin)* **1973**, *16*, 1–69.
(3) Simon, W.; Morf, W. E.; Meier, P. C. *Struct. Bonding (Berlin)* **1973**, *16*, 113–160.
(4) Pressman, B. C. *Annu. Rev. Biochem.* **1976**, *45*, 501–530.
(5) Izatt, R. M., Christensen, J. J., Ed. *Synthetic Multidentate Macrocyclic Compounds*; Academic Press: New York, 1978.
(6) Ovchinnikov, Y. A. *Eur. J. Biochem.* **1979**, *94*, 321–336.
(7) Wright, J. K.; Seckler, R.; Overath, P. *Annu. Rev. Biochem.* **1986**, *5*, 225–248.
(8) Davies, R.; Kennedy, J.; McIlroy, R.; Spence, R. *Nature (London)* **1964**, *203*, 1110–1115.
(9) Tabushi, I.; Kobuke, Y. *Mem. Fac. Eng. Kyoto Univ.* **1984**, *46*, 51–60.
(10) Tabushi, I.; Kobuke, Y. *Israel J. Chem.* **1985**, *25*, 217–227.
(11) Tabushi, I.; Kobuke, Y.; Nishiya, T. *Nature (London)* **1979**, *280*, 665–666.

0022-3263/88/1953-5933$01.50/0 © 1988 American Chemical Society