As pointed out by a referee, one equimolar amount of water is also formed in the diazotization of nitramide which will hydrolyze nitronium ion, and the de facto nitrating agent may not be the free nitronium ion, although it is still possible that it is also involved in the overall nitration.

The ability of electronegative substituents in stabilizing diazonium ions was also demonstrated previously by the preparation of isolable fluorodiazonium salts, such as hexafluoroantimonate and hexafluoroarsenate, from *cis*-difluorodiazene and the strong Lewis acid fluorides SbF_5 or AsF_5.[6]

$$FN{=}NF + AsF_5 \rightarrow F^+N{\equiv}NAsF_6^- \xrightarrow{ArH} ArF + HF + AsF_5$$

We have in the course of our studies also attempted fluorination of aromatics such as benzene, toluene, and nitrobenzene with fluorodiazonium hexafluoroarsenate. Clearly FN_2^+ is unable to form F^+; thus, the reaction is expected to be that of displacement by the aromatics. The reactions were carried out at −78 °C in anhydrous hydrogen fluoride solution with careful addition of the solution of the fluorodiazonium ion to excess of the aromatics. The reaction was found to be extremely exothermic even under these conditions, and only trace amounts of fluoroaromatics were formed (analyzed by gas–liquid chromatography and NMR spectroscopy). The fluorodiazonium ion thus seems to be a very strong oxidizing agent and of little practical value for aromatic fluorination.

All reported reactions can be best visualized as displacements of the diazonium ions by the aromatics, either giving the substituted products with simultaneous evolution of nitrogen or by competing reaction on nitrogen with subsequent decomposition of the intermediately formed aryldiazonium ions by the counterions (i.e., cyanide, nitrite, or fluoride).

Acknowledgment. Support of the work at USC by the National Science Foundation and the U.S. Army Research Office, Durham, NC, is greatefully acknowledged.

Registry No. 1, 95512-44-0; 2, 95512-46-2; $PhCH_3$, 108-88-3; $NO^+BF_4^-$, 14635-75-7; H_2NCN, 420-04-2; $SOCl_2$, 7719-09-7; NO_2NH_2, 7782-94-7; $NH_2C(O)OEt$, 51-79-6; $CH_3(CH_2)ONO_3$, 1002-16-0; NC-*o*-C_6H_4Me, 529-19-1; NC-*m*-C_6H_4Me, 620-22-4; NC-*p*-C_6H_4Me, 104-85-8; NO_2-*o*-C_6H_5Me, 88-72-2; NO_2-*m*-C_6H_4Me, 99-08-1; NO_2-*p*-C_6H_4Me, 99-99-0; $FN_2^+AsF_6^-$, 12005-87-7; (*Z*)-FN=NF, 13812-43-6; AsF_5, 7784-36-3.

(6) Christe, K. O.; Wilson, R. D.; Sawodny, W. *J. Mol. Struct.* **1971**, *8*, 245 and references given therein.

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Thermodynamics of Electron Removal from Binorbornylidene and Sesquibicyclooctene

Summary: Binorbornylidene (1) is rearranged to sesquibicyclooctene (2) in $CH_2Cl_2/CF_3CO_2H/(CF_3CO)_2O$ (20:1:1) at room temperature. $1^{+\cdot}$ is both kinetically and thermodynamically destabilized relative to $2^{+\cdot}$ and other Bredt's rule protected radical cations. At −78 °C in the above solvent mixture, it is 9.2 kcal/mol more difficult to oxidize 1 than 2 (electrochemical comparison).

Sir: Ando, Kabe, and Takata[1] found that in contrast to other Bredt's rule protected olefins,[2] binorbornylidene (1)[3] gives a radical cation which is short-lived on the cyclic voltammetry (CV) time scale, so that no reduction wave is observed associated with the $1,1^{+\cdot}$ oxidation wave. Because radical cation lifetimes are often increased in the presence of acid and dehydrating agents,[4] we investigated the CV of 1 in 20:1:1 $CH_2Cl_2/CF_3CO_2H/(CF_3CO)_2O$ containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte (used throughout this work). Although the $1,1^{+\cdot}$ oxidation wave remains completely irreversible at room temperature under these conditions (E_p^{ox} = 2.06 V vs. SCE at 200 mV/s scan rate), 1 is clearly not stable. The $1,1^{+\cdot}$ oxidation wave gradually decreases in size over a period of half an hour and is replaced by a completely reversible oxidation wave at lower potential, $E^{\circ\prime}$ = 1.68 V vs. SCE. As expected from its reversible CV wave, electrochemical oxidation of this solution gives a long-lived radical, which shows ESR splittings for two sets of eight equivalent hydrogens with a(8 H) = 3.9 G (H_a) and a(8 H) = 0.3$_7$ G (H_s) and a g factor of 2.0024. The easily oxidized product from 1 clearly has high symmetry. Stirring 22 mg of 1 in 10 mL of CH_2Cl_2, 0.5 mL of CF_3CO_2H, and 0.5 mL of $(CF_3CO)_2O$ for 5 h, followed by aqueous workup and chromatography on silica gel (hexane eluent) gave two fractions. The first fraction (R_f 0.95, ca. 10 mg) was a 1:3 mixture of 1 and the $E^{\circ\prime}$ = 1.68 V material, which is an isomer of 1 and has a ^{1}H NMR spectrum consisting of a broad singlet at δ 2.48 (H_b) and two broad doublets (separation about 7 Hz) at δ 1.48 and 1.15 (H_a and H_s). From its ESR and NMR data, the rearrangement product can only be sesquibicyclooctene (2).[5] The second fraction (R_f 0.50, 10.2 mg, 29%) shows an IR absorption at 1780 cm^{-1} and has a mass spectrum with major peaks at m/e 302 (M^+, 10%), 188 ($M^+ - HO_2C_2F_3$, 51%), and 160 ($M^+ - HO_2C_2F_3 - C_2H_4$, 32%), indicating that it is a trifluoroacetate. Its ^{1}H NMR spectrum shows δ 2.19 (br s, 2 H), 2.13 (br s, 1 H), 1.8–1.5 (m, 8 H), 1.4–1.1 (m, 10 H). We assign this material as 3, a trifluoroacetic acid adduct of 2 (or conceivably, of 1). A plausible pathway for the conversion of 1 to 2 and 3 is shown in Scheme I. The rearrangement of 1 to 2 is exothermic. Allinger MM2 calculations[6] give 1 as having a 12.8 kcal/mol higher steric energy than 2. We consider the conditions required for the conversion unexpectedly mild. Although the 1 $H^+ \rightarrow$

(1) (a) Ando, W.; Kabe, Y.; Takata, T. *J. Am. Chem. Soc.* **1982**, *104*, 7314. (b) This was also observed in unpublished work from our laboratory by R. Akaba.
(2) (a) Nelsen, S. F.; Kessel, C. R. *J. Am. Chem. Soc.* **1979**, *101*, 2503. (b) Gerson, F.; Lopez, J.; Akaba, R; Nelsen, S. F. *Ibid.* **1981**, *103*, 6716.
(3) Bartlett, P. D.; Ho, M. *J. Am. Chem. Soc.* **1974**, *96*, 627.
(4) Hammerich, O.; Parker, V. D. *Electrochim. Acta* **1973**, *18*, 537.
(5) Systematic names: 1,2,3,4,5,6,7,8-octahydro-1,4:5,8-diethanonaphthalene; tetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradec-2,7-ene. We employ the common nomenclature introduced by Bartlett et al. (Bartlett, P. D.; Blackeney, A. J.; Kimura, M.; Watson, W. H. *J. Am. Chem. Soc.* **1980**, *102*, 1383) for the dimethano bridged compounds, which are called sesquinorbornenes.

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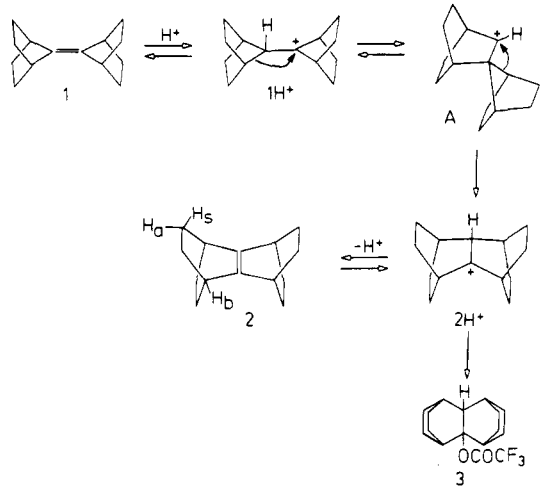

A step is a tertiary to secondary carbonium ion rearrangement, which is normally quite endothermic and causes rearrangements proceeding through such pathways to be rather sluggish, the tertiary cation in this case is a 7-norbornyl cation, making the rearrangement much less endothermic than normal.

The oxidation wave for 1 does become partially reversible at −78 °C, allowing determination of the thermodynamics for electron transfer at this temperature. The relative ease of electron removal from **1**, **2**, and five other tetra-*sec*-alkyl Bredt's rule protected olefins is shown in Figure 1. The numbers shown are differences in free energy for adiabatic electron removal at −78 °C in kcal/mol relative to biadamantylidene ($E^{\circ\prime}$ = 1.59 V); $\Delta\Delta G_e^\circ$ = 23.06 ($E^{\circ\prime}$(olefin) − 1.59)). For the 1,1:2,2-bibicyclic compounds whose structures are shown at the right of the figure, there is a trend toward more difficult electron removal as the number of carbons available to stabilize the positive charge is decreased. The C_{18} olefin is 0.9 kcal/mol harder to oxidize than is the C_{20} olefin, and the C_{16} olefin is 1.1 kcal/mol harder to oxidize than the C_{18} olefin. The C_{14} compound 1 is clearly in a class by itself. It is 8.3 kcal/mol harder to oxidize than its C_{16} homologue and is 9.2 kcal/mol harder than its 1,2:1,2-bibicyclic isomer **2**. 1 is restricted to having the smallest HCC(=)CH angle (α), 98.8° by Allinger's MM2 calculation,[6] and it is possible that olefin cation radicals might be more sensitive to closing α than are neutral olefins, but there is little hint of such an effect in going from the C_{18} bibicyclo[3.3.1]nonylidene (α = 108.9°[6]) to the C_{16} bibicyclo[3.2.1]octylidene (α = 104.6°[6]). Something else is substantially destabilizing $1^{+\cdot}$ relative to the other compounds.

We attribute the difficulty for oxidation of 1 to the remarkable orbital symmetry effect reported in 1973 by Hoffmann, Mollère, and Heilbronner.[7] They pointed out that the upper several filled σ orbitals of the boat cyclohexane portion of a 7-norbornyl system happen to have the wrong symmetry to interact with a p orbital at position 7. Because the size of orbital mixing is inversely proportional to the energy gap between the orbitals, most of the stabilization that alkyl groups can give to the atom to which they are attached which bears an electron-deficient

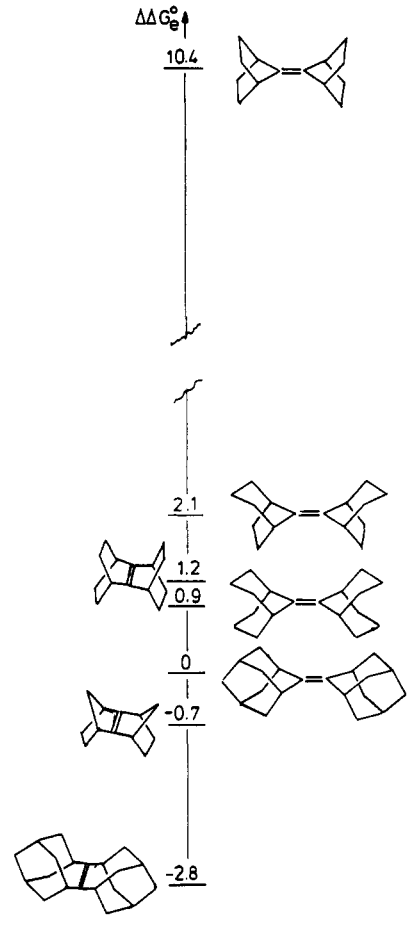

Figure 1. Relative ease of electron removal from Bredt's rule protected olefins at −78 °C. Numbers are in kcal/mol.

p orbital arises from p orbital mixing with the highest filled alkyl group orbitals, which have the smallest energy gap. 7-Norbornyl systems therefore ought to have cations which are destabilized relative to those of other alkyl groups. The predicted inhibition of orbital mixing is easily detected in photoelectron spectra. The oxygen p lone pair of 7-oxanorbornane has a 0.2 eV higher vertical ionization potential than that of the similarly substituted diisopropyl ether, and 7-methylenenorbornane has a 0.25 eV higher vertical ionization potential than does the less substituted methylenecyclopentane.[7] This work shows that the orbital symmetry effect is also important for geometry optimized, solvated neutral to cation radical energy gaps. This is a particularly significant result to establish, as it has now been demonstrated that the majority of the cation-stabilizing differences for different alkyl substituents which are found in the vapor phase are alkyl group polarization effects,[8] which disappear in solution, where solvent is available to be polarized. The orbital symmetry caused destabilization of 7-norbornyl cation obviously does not disappear in solution. Because both neutral olefin and cation radical have a formal 120° α angle preference, this

(6) Allinger, N. L. *J. Am. Chem. Soc.* **1977**, *99*, 8127; Quantum Chemistry Program Exchange, Program 395.
(7) Hoffmann, R.; Mollère, P. O.; Heilbronner, E. *J. Am. Chem. Soc.* **1973**, *95*, 4860.
(8) Taft, R. W.; Taagepera, M.; Abbound, J. L. M.; Wol, E. J.; DeFreez, D. J.; Hehre, W. J.; Bartmess, J. E.; McIVer, R. T., Jr. *J. Am. Chem. Soc.* **1978**, *100*, 7765.

(9) We thank Professor H. Prinzbach and L. and I. Knothe (Freiburg) for generously providing a sample of 1. We thank Mark Teasley for the *syn*-sesquinorbornene point in Figure 1. The fact that this work only consumed 35 mg of 1 is a tribute to the power of cyclic voltammetry in attacking redox problems. We thank the National Science Foundation and the Wisconsin Alumni Research Foundation for financial support of this work.

special destabilization of 7-norbornyl cations is much clearer in these data than it ever could be by considering solvolysis results, in which the effect of flattening at carbon is superimposed on the orbital symmetry effect.[7,9]

Registry No. 1, 51689-29-3; $1^{+\cdot}$, 95484-94-9; 2, 88656-03-5; $2^{+\cdot}$, 95484-95-0; 3, 95484-96-1; 8-(bicyclo[3.2.1]octan-8-ylidene)bicyclo[3.2.1]octane, 95484-97-2; 9-(bicyclo[3.3.1]nonan-9-ylidene)-bicyclo[3.3.1]nonane, 55993-21-0; 2-(2-adamantanylidene)-adamantane, 30541-56-1; tetracyclo[6.2.1.1^{3,6}.0^{2,7}]tetradec-2,7-ene, 73321-28-5; 1,2,3,4,5,6,7,8,9,10,11,12,13,14-tetradecahydro-1,5:3,7:8,12:10,14-tetramethanononalene, 30614-34-7.

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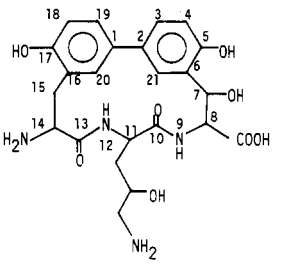
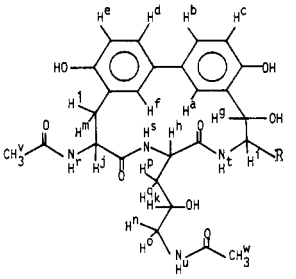
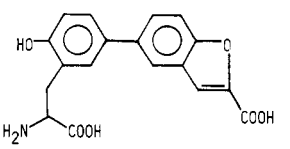


1



2 R = $COOCH_3$

5 R = CH_2OH



3

Structure of WS-43708A, a Novel Cyclic Peptide Antibiotic

Summary: On the basis of chemical and spectroscopic evidence, the antibiotic WS-43708A ($C_{23}H_{28}N_4O_8$) has been shown to be a cyclic peptide (1) containing a biphenyl moiety included in a 15-membered ring.

Sir: WS-43708A (1), recently isolated from *Streptomyces griseorubiginosus* No. 43078, is a novel cyclic peptide with potent antibacterial acctivity.[1] Herein, we report the structure eludication of this antibiotic on the basis of chemical and spectroscopic evidence.

WS-43708A was isolated as colorless needles from dilute HCl (pH 4): $C_{23}H_{28}N_4O_8 \cdot 2HCl$ (FABMS and elemental analysis);[2] mp 205–209 °C dec; $[\alpha]^{20}_D$ −22.5° (*c* 0.1, 1 N HCl); IR (KBr) 3200, 3000–2300, 1690, 1640 cm^{-1}; UV (H_2O) 264 (ε 18 600), 287 nm (sh); UV (0.1 N NaOH) 288 (ε 24 000), 303 nm (sh); positive ninhydrin test. Acetylation of 1 with Ac_2O in MeOH (0 °C), followed by methylation with CH_2N_2 in MeOH (0 °C), gave the diacetyl monomethyl ester 2 (FABMS, *m/z* 587 ($M^+ + 1$)). Hence, one carboxyl and two amino groups are present in 1. The ^{13}C NMR spectrum (D_2O–DCl) of 1 showed in the sp^3-carbon region eight signals including five methine signals attributable to two secondary alcohol carbons (64.4 (d) and 65.2 (d) ppm) and three α-amino acid carbons (50.9 (d), 55.0 (d), and 57.4 (d) ppm), the remainder being three methylene signals (30.4 (t), 37.9 (t), and 44.9 (t) ppm). In the sp^2-carbon region 15 signals were assignable to three carbonyl groups (168.6 (s), 173.2 (s), and 174.0 (s) ppm) and two phenyl rings substituted totally with six substituents (116.4 (d), 116.9 (d), 120.3 (s), 126.2 (d), 127.2 (d), 127.6 (d), 127.9 (s), 130.6 (d), 132.9 (s), 133.0 (s), 152.8 (s), and 154.2 (s) ppm). Extensive spin decoupling (Table I) of the 400-MHz ^1H NMR spectra of 1 and 2 revealed ^1H–^1H relationships as shown in Figure 1, leading to partial structures A, B, and C, which are quite consistent with the ^{13}C NMR data described above.

The partial unit A was confirmed by the fact that hydrolysis of 1 with 6 N HCl (110 °C, 24 h) gave, after chromatography on Toyopearl HW40S, *erythro*-γ-hydroxy-L-ornithine (HCl salt; mp 176–178 °C dec; $[\alpha]^{23}_D$ +10.9° (*c* 1.0, H_2O)) which was identified by comparison with an authentic sample.[3] The partial units B and C can be combined and extended to partial structure B + C (Figure 2) based on the following grounds. The acid hydrolysis described above also gave compound 3 (FDMS, *m/z* 341 (M^+)),[4] which was converted, by acetylation with Ac_2O in MeOH followed by treatment with CH_2N_2 in MeOH, to the monoacetyl trimethyl derivative 4 (high-resolution EIMS, *m/z* 425.1457, calcd for $C_{23}H_{23}NO_7$ 425.1472). The ^1H NMR analysis of 4 with the aid of decoupling (Table I) and NOE experiments (Figure 2) revealed the structure of 3. The genesis of 3 is rationalized by the following, plausible reaction mechanism from the partial units B and C: (1) dehydration of the β-hydroxy amino acid residue in C to the dehydro amino acid; (2) hydrolysis to the keto acid;[5] (3) dehydrative condensation

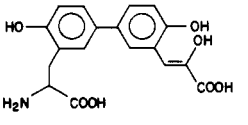
(1) Umehara, K.; Ezaki, M.; Iwami, M.; Yamashita, M.; Hashimoto, S.; Komora, T.; Uchida, I.; Hashimoto, M.; Mine, Y.; Kohsaka, M.; Aoki, H.; Imanaka, H. "Abstracts of Papers", 24th Interscience Conference on Antimicrobial Agents and Chemotherapy, Washington, D.C., 1984, Abstr. No. 1141.

(2) FABMS, *m/z* 489 ($M^+ + 1$) (free base); elemental analysis. Anal. Calcd for $C_{23}H_{28}N_4O_8 \cdot 2HCl \cdot H_2O$: C, 47.65; H, 5.62; N, 9.67; Cl, 12.23. Found: C, 47.80; H, 5.85; N, 9.75; Cl, 12.11.

(3) (a) Mizusaki, K.; Yamamoto, H.; Makizumi, H. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2605. (b) Mizusaki, K.; Makizumi, S. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 470.

(4) ^1H NMR (CD_3OD–D_2O) δ 3.19 (dd, *J* = 7.5, 14 Hz, 1 H), 3.47 (dd, *J* = 5, 14 Hz, 1 H), 4.29 (dd, *J* = 5, 7.5 Hz, 1 H), 7.01 (d, *J* = 8.7 Hz, 1H), 7.49 (m, 2 H), 7.64 (s, 1 H), 7.66 (d, *J* = 8.7 Hz, 1 H), 7.70 (dd, *J* = 2, 8.7 Hz, 1 H), 7.90 (d, *J* = 2 Hz, 1 H).

(5) A subsequent inspection of the acid hydrolysate revealed the presence of keto acid i as a minor product, firmly supporting the mechanism leading to 3: ^1H NMR (CD_3OD–D_2O) δ 3.07 (dd, *J* = 8.8, 14 Hz, 1 H), 3.44 (dd, *J* = 4, 14 Hz, 1 H), 6.93 (d, *J* = 8.7 Hz, 1 H), 7.12 (s, 1 H), 7.32 (d, *J* = 8.7 Hz, 1 H), 7.42 (dd, *J* = 2.5, 8.7 Hz, 1 H), 7.49 (d, *J* = 2.5 Hz, 1 H), 7.59 (dd, *J* = 2.5, 8.7 Hz, 1 H), 7.67 (d, *J* = 2.5 Hz, 1 H).



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