was obtained from the ozonide **3**. The solvent in the ozonolysis exerted a notable influence on the total yield of the cyclic peroxides, **2** and **3**, although the **2**:**3** isomer ratio (ca. 3:7) was not influenced: CH_2Cl_2 (27%) < CF_3CH_2OH/CH_2Cl_2 (1:3 v/v) (44%) < CH_3CO_2H/CH_2Cl_2 (1:3 v/v) (49%). It should be noted that the ozonide **3** was stable under the reaction conditions, demonstrating that the isomeric peroxide **2** was produced under kinetically controlled conditions.

In the normal sequence of events, two carbonyl oxide intermediates, **7** and **8**, could be formed from the ozonolysis of diene **1**. The normal intramolecular 1,3-dipolar cycloaddition in the intermediate **7** would lead to the formation of the bicyclic ozonide **3**. In the case of the intermediate **8**, however, two recombination modes could be postulated: a [3 + 2] addition leading to the bicyclic ozonide **3** and a [3 + 4] addition leading to the bicyclic endoperoxide **2** (Scheme I). The benzoylfuran **4** would be produced from the carbonyl oxide intermediates, **7** and/or **8**, via the α-hydroxy ketone **9**[7] (Scheme I).

Significant increase in yield of bicyclic peroxides, **2** and **3**, with the concomitant decrease in yield of the benzoylfuran **4** in the ozonolysis in CF_3CH_2OH/CH_2Cl_2 and CH_3CO_2H/CH_2Cl_2 would then imply that solvation of the most polar carbonyl oxide moiety by the protic solvent would enhance the electrophilicity of the carbonyl oxide carbon in the intermediate **8**, thereby facilitating intramolecular cyclization via the cyclic intermediate **11** to yield either the bicyclic endoperoxide **2** or the 1,2,4-trioxolane **3** (Scheme II). This is to some extent confirmed by the fact that trifluoroacetic acid could catalyze the interconversion of the two isomeric peroxides, **2** and **3**. Treatment of either **2** or **3** with 1 equiv of trifluoroacetic acid in methylene chloride at −70 °C for 30 min resulted in the recovery of 60–70% yield of an equilibrium mixture of **2** and **3**, the ratio being ca. 3:2. In this equilibration also, the protonated intermediate **11** is considered to be the key.[8]

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(7) Yates, P.; Stout, G. H. *J. Am. Chem. Soc.* **1954**, *76*, 5110.

(8) Miura, M.; Ikegami, A.; Nojima, M.; Kusabayashi, S.; McCullough, K. J.; Nagase, S. *J. Am. Chem. Soc.* **1983**, *105*, 2414.

Structures of Cyclic C_4H_4 Radical Cations

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It is now generally agreed that the C_4H_4 ions observed as fragmentation products in the mass spectra of larger organic molecules can have either linear or cyclic structures and that mixtures of both are commonly obtained.[1] Bowers and co-workers have pointed out that the m/z 26:27 peak ratio in the collisionally activated dissociation (CAD) spectrum of the C_4H_4 ions can be a useful criterion for determining proportions of linear and cyclic ions;[2] sources expected to give predominantly cyclic ions show a high value (up to 9.0) for this ratio, whereas those expected to give predominantly linear ions exhibit a relative low value (as low as 2.7). The correlation of the m/z 26:27 ratio with the proportion of cyclic ions is consistent with the generally accepted methylenecyclopropene structure for the cyclic ion and vinylacetylene structure for the linear ion.[1,2] The former can fragment easily to two C_2H_2 pieces (m/z 26) whereas the latter fragments more readily to C_2H and C_2H_3 (m/z 25 and 27).[2]

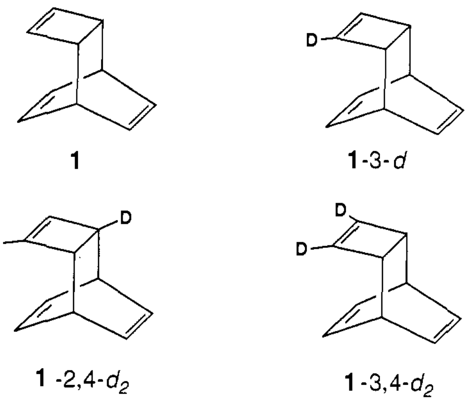

Figure 1.

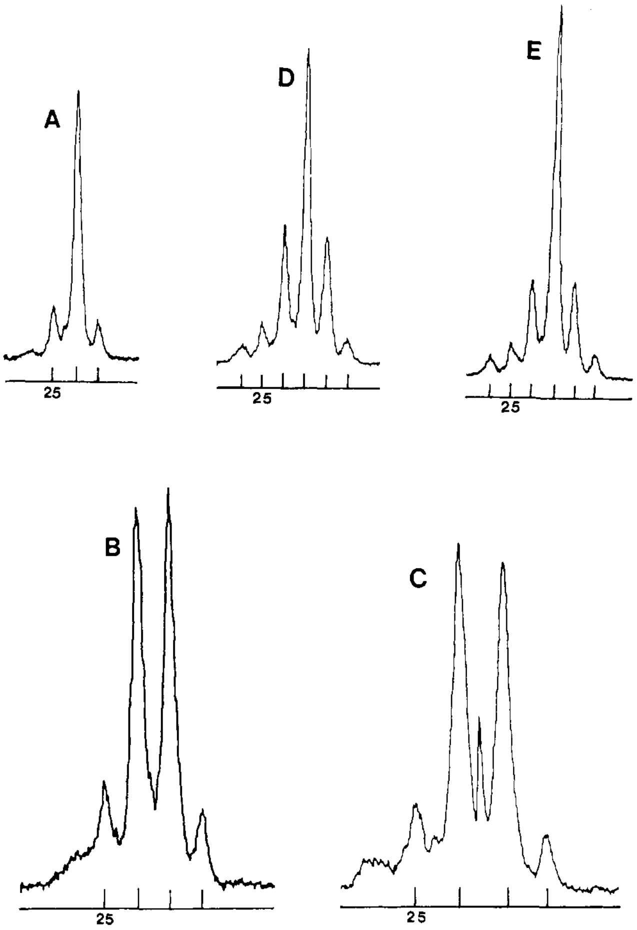

Figure 2. m/z 24–28 region of the CAD spectra of the $C_4H_nD_{4-n}$ ions from the precursors shown in Figure 1. The collision gas was helium for all samples except C. Precursors to the $C_4H_nD_{4-n}$ ions were as follows: A, **1**; B, **1**-*3-d*; C, **1**-*3-d* (collision gas was N_2); D, **1**-*3,4-d*$_2$; E, **1**-*2,4-d*$_2$.

We have been interested in the generation of an alternative cyclic C_4H_4 radical cation—the cyclobutadiene ion. The interest arises from the potential for neutralization of this ion[3] to allow access to both ground and electronic excited states of the theoretically important cyclobutadiene molecule.[4] The sources that we have investigated are all formal Diels–Alder adducts of cy-

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(1) (a) Rosenstock, H. M.; McCulloh, K. E.; Lossing, F. P. *Int. J. Mass Spectrom. Ion Phys.* **1977**, *25*, 327. (b) Baer, T.; Willet, G. D.; Smith, D.; Phillips, J. S. *J. Chem. Phys.* **1979**, *70*, 4076. (c) Lifshitz, C.; Weiss, M. *Int. J. Mass Spectrom. Ion Phys.* **1980**, *34*, 311. (d) Ausloos, P. *J. Am. Chem. Soc.* **1981**, *103*, 3931.

(2) Redeker-Wagner, W.; Illies, A. J.; Kemper, P. R.; Bowers, M. T. *J. Am. Chem. Soc.* **1983**, *105*, 5719.

(3) (a) Danis, P. O.; Wesdemiotis, C.; McLafferty, F. W. *J. Am. Chem. Soc.* **1983**, *105*, 7454. (b) Wesdemiotis, C.; McLafferty, F. W. *Chem. Rev.*, in press.

(4) (a) Whitman, D. W.; Carpenter, B. K. *J. Am. Chem. Soc.* **1980**, *102*, 4272. (b) Whitman, D. W.; Carpenter, B. K. *Ibid.* **1982**, *104*, 6473. (c) Carpenter, B. K. *Ibid.* **1983**, *105*, 1700.

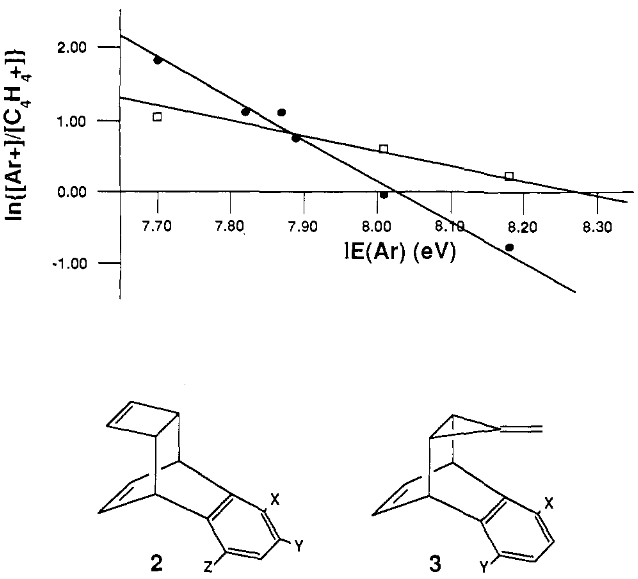

Figure 3. Plot of ln {$[Ar+]/[C_4H_4+]$} vs. IE(Ar) for compounds in the series **2** and **3**. Filled circles correspond to series **2**; substituents studied were X=Y=Z=H; X=Me, Y=Z=H; X=Y=Me, Z=H; X=Z=Me, Y=H; X=Y=Z=Me; X=Z=H, Y=OMe. Open squares correspond to series **3**; substituents studied were X=Y=H; X=Me, Y=H; X=Y=Me.

clobutadiene to an aromatic adjunct, with the prototype being Nenitezscu's hydrocarbon (**1**, Figure 1).[5] The 70-eV electron-ionization mass spectrum of **1** shows m/z 52 as the most intense peak. That this peak is derived from the cyclobutene moiety in **1** and not from fragmentation of the benzene adjunct is shown by deuteriation[6] at C3; **1**-*3-d* shows no more than 0.5% m/z 52—the most intense peak is now m/z 53. The CAD spectrum of the C_4H_3D ion from **1**-*3-d* shows a peak at m/z 26.5, corresponding to the C_4H_3D dication, when nitrogen is used as the collision gas but not when helium is used (Figure 2). Relatively easy formation of the nominally aromatic dication might be expected for cyclobutadiene. All other CAD spectra reported used helium to avoid interference from the dication. The m/z 26:27 ratio in the CAD spectrum of the C_4H_4 ion from **1** is high (>7), consistent with Bowers' criterion for nearly exclusive formation of cyclic ions.[2] We note, however, that this criterion cannot be expected to be useful in differentiating methylenecyclopropene from cyclobutadiene structures since a facile fragmentation of the latter to ions with m/z 26 would also be expected.[7] Double deuteriation[6] of **1** revealed that there cannot be rapid, reversible interconversion between cyclobutadiene and methylenecyclopropene structures; **1**-*2,4-d*$_2$ and its isomer, **1**-*3,4-d*$_2$, gave $C_2H_2D_2$ ions with notably different CAD spectra. The ion from **1**-*3,4-d*$_2$ had peaks at m/z 26, 27, and 28 in a ratio of 1:2.3:0.9 whereas that from **1**-*2,4-d*$_2$ had the same peaks in a ratio of 1:4:1 (Figure 2). Rapid reversible interconversion between cyclobutadiene and methylenecyclopropene structures would have resulted in ions exhibiting the same CAD spectrum.

Further information on the C_4H_4 ion derived from molecules such as **1** was obtained through study[6] of the series **2** (Figure 3). Fragmentation of the molecular ions of these compounds could be expected to give the C_4H_4 ion and the substituted naphthalene ion in a ratio that depended on the relative ionization energies of the C_4H_4 neutral and the naphthalene, according to Stevenson's rule.[8] In fact, a plot of ln {$[Ar^+]/[C_4H_4^+]$} vs. IE(Ar), where $[Ar^+]$ is the relative intensity of the peak with m/z corresponding to the naphthalene ion and IE(Ar) is the ionization energy of the naphthalene,[9] was linear with a slope that depended on the energy of the ionizing electrons but with an intercept on the IE axis that did not. The intercept occurred at 8.02 ± 0.09 eV (Figure 3). The corresponding plot for compounds **3** gave an intercept at 8.28 ± 0.12 eV (Figure 3).[10] It seems reasonable to assume that compounds **3** would be more likely to afford methylenecyclopropene ions and compounds **2** to produce cyclobutadiene ions. To the extent that the intercepts of the Stevenson's rule plots differ by more than the experimental error, there is evidence that these ions retain their structural identity, at least temporarily. One can anticipate that the neutralization-reionization mass spectra[3] might provide more definitive evidence on the lifetimes of these isomeric, cyclic C_4H_4 ions. Experiments to obtain these spectra are in progress.

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[5] Nenitzescu, C. D.; Avram, M.; Pogany, J. J.; Mateescu, G. D.; Farcasian, M. *Stud. Cercet. Chim.* (*Cluj*) **1963**, *11*, 7.

[6] Ray, J. C., Jr., Ph.D. Dissertation, Cornell University, Ithaca, NY, August 1986.

[7] The CAD spectra of the C_4H_4 ions from compounds in series **2** or **3** (Figure 3) are essentially identical.

[8] McLafferty, F. W. *Interpretation of Mass Spectra*, 3rd ed.; University Science Books: Mill Valley, CA, 1980.

[9] Heilbronner, E.; Hoshi, T.; von Rosenberg, J. L.; Hafner, K. *Nouv. J. Chim.* **1977**, *1*, 105. For aromatic hydrocarbons that lack serious nonbonded interactions in the planar geometry, vertical and adiabatic ionization energies are essentially identical: Boschi, R.; Clar, E.; Schmidt, W. *J. Chem. Phys.* **1974**, *60*, 4406.

[10] These intercepts could be identified with ionization energies of the C_4H_4 neutrals; however, some caution is required since the effective ionization energies of the naphthalene fragment and the C_4H_4 fragment will be perturbed by distortion away from their equilibrium geometries during the dissociation of the adduct molecular ion. If one assumed that comparable distortions occurred for the ions from **2** and **3** then the difference in ionization energies of cyclobutadiene and methylenecyclopropene would be equal to the difference between the intercepts for the Stevenson's rule plots. Experiments on the dissociation of butadiene dimer molecular ions suggest that such an assumption is likely to give relative ionization energies to within ±0.05 eV (Tureček, F.; Hanuš, V. *Mass Spec. Rev.* **1984**, *3*, 85). UV photoelectron spectroscopy on cyclobutadiene has revealed that the vertical ionization energy is 8.24 eV and that the adiabatic ionization energy is probably 8.10 eV (Kreile, J.; Münzel, N.; Schweig, A.; Specht, H. *Chem. Phys. Lett.* **1986**, *124*, 140).

Andrimid, a New Peptide Antibiotic Produced by an Intracellular Bacterial Symbiont Isolated from a Brown Planthopper

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Some homopterous insects such as planthoppers and leafhoppers transmit intracellular symbiotic microorganisms to offspring through their eggs.[1] However, their role and the nature of metabolites remain unknown because the microorganisms are difficult to isolate without extracellular contamination.[2] In the following we describe the isolation of andrimid (**1**) from the culture

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[1] Nasu, S. *Nippon Oyo Dobutsu Konchu Gakkaishi* **1965**, *9*, 225.

[2] Nasu, S.; Kusumi, T.; Suwa, Y.; Kita, H. *Appl. Entomol. Zool.* **1981**, *16*, 88.

0002-7863/87/1509-4409$01.50/0