J. Am. Chem. Soc. 1987, 109, 4407–4408

and favors enolization with structures in which this angle approximates 90°. Table II gives the steric energy (kilocalories per mole, relative to global minimum) of the lowest energy conformer with said dihedral angle within the angular window specified.

As expected, structures having low-energy conformers with α-hydrogens close to 90° are the ones most prone to enolization. However, the relationship is qualitatively correct for the data only with the 25° angular window. A slightly smaller window (20°) makes the nine-ring prediction exclusively benzylic metalation (vs. experimental 25% enolization), and a slightly larger window (30°) makes the seven-ring prediction exclusively enolization (vs. experimental <1% enolization). Thus, the sensitivity of the results to the precise window size renders this model problematic.

A second model (model 2) attempts to assess the ease of enolization by measuring the excess steric energy necessary to attain the stereoelectronically preferred 90° O═C—C—H alignment. We used an arbitrarily large 1000 kJ/mol and 1-fold torsional restraint to force the α-hydrogens of each conformer to approximate the desired 90° torsion angle, and the resulting minimized energies (relative to the global minimum) of the lowest energy structures thus found are summarized in Table II.

With model 2, the correlations with experiment are rather good given the simplistic nature of our treatment. Furthermore, the results are not strongly dependent on the precise magnitude of the torsional restraint. Finally, we would like to note that application of this model to the twistanone system[2a] gives an excess strain of only 0.3 kcal/mol for the kinetically more acidic (by 290:1) hydrogen and 7.4 kcal/mol for the less acidic one.

Acknowledgment. We thank the National Science Foundation for financial support.

Formation of 1,3,4,5-Tetraphenyl-2,6,7-trioxabicyclo[3.2.1]oct-3-ene from the Ozonolysis of 1,2,3,4-Tetraphenyl-1,3-cyclopentadiene. First [3 + 4] Addition of a Carbonyl Oxide Moiety to an α,β-Unsaturated Carbonyl Group

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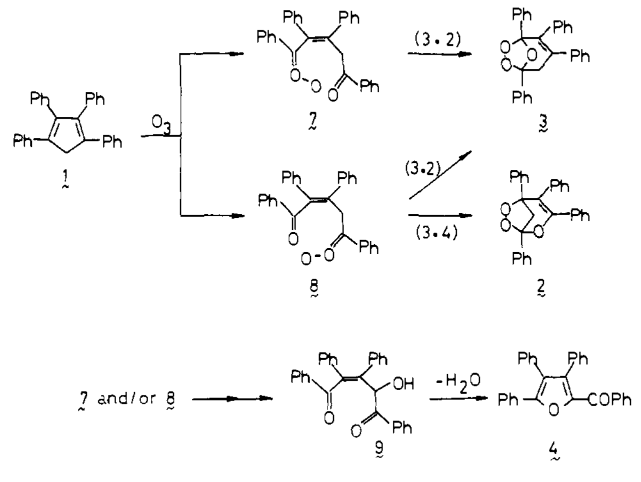
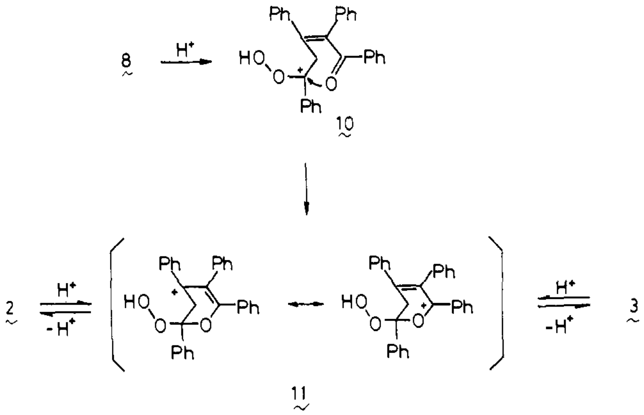
Carbonyl oxides, being key intermediates in the ozonolysis of olefins, have attracted much attention.[1] The most well-known feature of their chemistry is the 1,3-dipolar cycloaddition to a carbonyl group affording 1,2,4-trioxolane (final ozonide). It is therefore surprising that only one clear-cut example is known, to our knowledge, for the reaction of carbonyl oxide with α,β-unsaturated carbonyl compound: the ozonolysis of 2,3-di-*tert*-butyl-1,3-butadiene on polyethylene, which proceeds via formaldehyde oxide and *tert*-butyl 1-*tert*-butylvinyl ketone, yields 3-*tert*-butyl-3-(1-*tert*-butylvinyl)-1,2,4-trioxolane in good yield.[1f] If a formal [3 + 4] addition of carbonyl oxide to α,β-unsaturated carbonyl could occur instead of a [3 + 2] addition, a 1,2,4-trioxacyclohept-5-ene would be produced in place of the isomeric 3-vinyl-1,2,4-trioxolane. We report herein that this is certainly observed in the ozonolysis of 1,2,3,4-tetraphenyl-1,3-cyclopentadiene (**1**).[2,3]

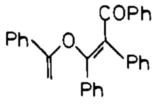
Scheme I



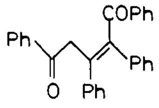
Scheme II



The reaction of **1** with 1 equiv of ozone in methylene chloride afforded a mixture of two isomeric peroxides **2** and **3** in 27% yield, the **2**:**3** ratio being 3:7 (Scheme I).[4] In good agreement with this assignment, treatment of the cyclic peroxide **2** with triphenylphosphine gave a mixture of the ketone **5**[5] and the diketone **6** in



5



6

yields of 45% and 35%, respectively, while only the diketone **6**[6]

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(2) In the concerted cycloaddition of a 4π-electron 1,3-dipole to a dipolarophile having 4π electrons, [3 + 4] addition is thermally disallowed by orbital symmetry and, consequently, the alternative [3 + 2] mode is always preferred.[3a] Very recently, however, Huisgen discovered that the addition of thiocarbonyl ylide to tetracyanoethylene, which proceeds stepwise, provides the [3 + 4]-addition product together with the [3 + 2]-addition product.[3b]

(3) (a) Crabb, J. N.; Storr, R. C. In *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Vol. 2. (b) Huisgen, R.; Mloston, G.; Langhals, E. *J. Am. Chem. Soc.* **1986**, *108*, 6401; *J. Org. Chem.* **1986**, *51*, 4087.

(4) **2**: mp 125–127 °C (from methanol); ^{1}H NMR δ 3.63 (d, *J* = 11 Hz, 1 H), 4.17 (d, *J* = 11 Hz, 1 H), 7.50–9.00 (m, 20 H); ^{13}C NMR δ 51.415 (1 C, C-8), 87.449 (1 C, C-5), 107.779 (1 C, C-1), 118.751 (1 C, C-4), 126.280–136.550 (24 C), 150.375 (1 C, C-3); mass spectrum, *m/e* 418 (M^+). Anal. Calcd for $C_{29}H_{22}O_3$: C, 83.23; H, 5.26. Found: C, 83.27; H, 5.29. **3**: mp 116–119 °C (from methanol); ^{1}H NMR δ 3.63 (d, *J* = 18 Hz, 1 H), 4.03 (d, *J* = 18 Hz, 1 H), 7.50–8.70 (m, 20 H); ^{13}C NMR δ 42.111 (1 C, C-4), 108.506 (1 C, C-5 or C-1), 109.032 (1 C, C-1 or C-5), 125.886–139.570 (26 C); mass spectrum, *m/e* 418 (M^+). Anal. Calcd for $C_{29}H_{22}O_3$: C, 83.23; H, 5.26. Found: C, 83.27; H, 5.29.

(5) **6**: mp 124–126 °C (from methanol); ^{1}H NMR δ 4.44 (d, *J* = 3 Hz, 1 H), 4.79 (d, *J* = 3 Hz, 1 H), 6.90–7.65 (m, 18 H), 7.89–8.16 (m, 2 H); IR 1660, 1640, 1600, 1490, 1442, 1312, 1263, 1214, 1175, 1116, 1070, 1011 cm^{-1}. Anal. Calcd for $C_{29}H_{22}O_2$: C, 86.57; H, 5.47. Found: C, 86.62; H, 5.41.

(6) Rio, G.; Fellion, Y. *Tetrahedron Lett.* **1962**, 1213.

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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]

Acknowledgment. We thank Dr. Kevin J. McCullough of Heriot-Watt University and Prof. Karl Griesbaum of Universität Karlsruhe for useful discussions.

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Structures of Cyclic C_4H_4 Radical Cations

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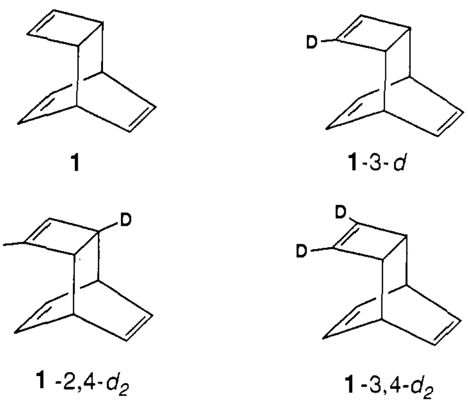
It is now generally agreed that the C_4H_4 ions observed as fragmentation products in the mass spectra of larger organic molecules can have either linear or cyclic structures and that mixtures of both are commonly obtained.[1] Bowers and co-workers have pointed out that the *m/z* 26:27 peak ratio in 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]



1 **1**-3-*d* **1**-2,4-d_2 **1**-3,4-d_2

Figure 1.

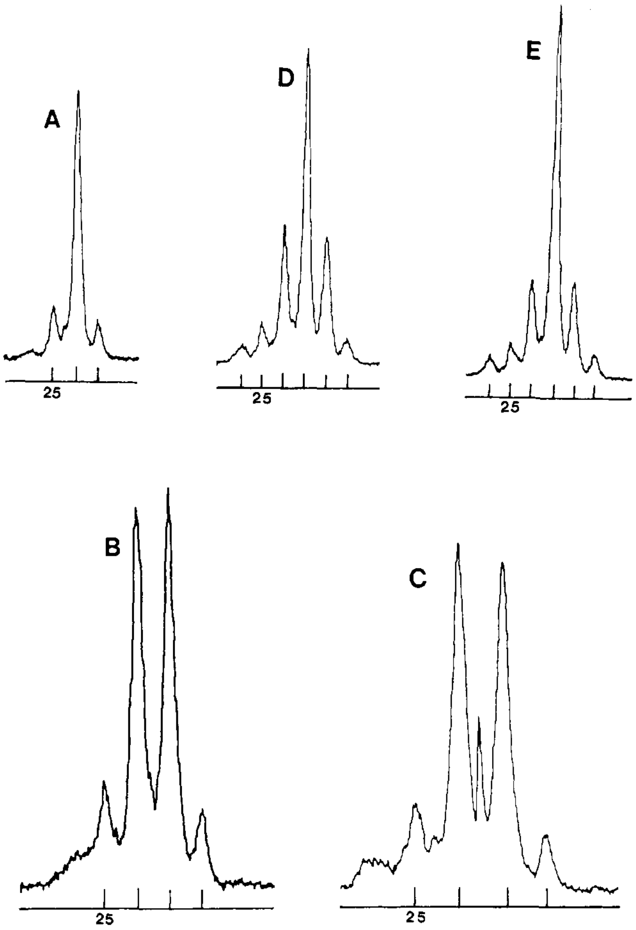


Figure 2. *m/z* 24–28 region of the CAD spectra of the $C_4H_nD_{4-n}$ ions from the precursors shown in Figure 1. The collision gas was helium for all samples except C. Precursors to the $C_4H_nD_{4-n}$ ions were as follows: A, **1**; B, **1**-*3-d*; C, **1**-*3-d* (collision gas was N_2); D, **1**-*3,4-d*$_2$;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