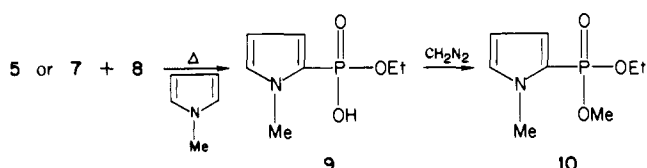


MCPBA. *tert*-Butyl hydroperoxide in acetic acid (25 °C) gave a similar result, although isomer **8** was selectively destroyed during the isolation procedure (evaporation of volatiles, chromatography on silica gel with 5% methanol-chloroform).

When phosphonate **5** was heated in benzene at 80 °C, loss of the P bridge was complete after 1.5 h; a new ³¹P NMR signal at δ +72.3 was assigned to the residual dihydrophosphindole. The only other ³¹P NMR signals were found in the phosphate region (0 to -12 ppm) and apparently arose from reactions of the released metaphosphate. The mixture of phosphonates **7** and **8** gave a similar clean decomposition at 110 °C for 7 h.

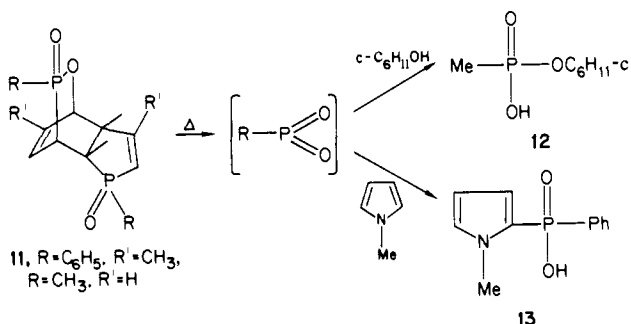
Trapping of the P fragment was accomplished by replacing the inert solvent with methanol (forming MeOPO(OH)(OEt) at 80 °C, 1.5 h) or dicyclohexylamine (forming (C₆H₁₁)₂NPO(OH)(OEt) at 100 °C, 2 h). In each case, the phosphate derivatives were the major products by ³¹P NMR analysis (δ -0.4 and +5.2, respectively) and the signals upfield of δ 0 were eliminated.

The thermolysis of the cyclic phosphonates was also conducted in *N*-methylpyrrole at 110 °C. The product had δ ³¹P +20.0 and accounted for about 80% of the expelled phosphorus. To establish the identity of the product as **9**, it was isolated after esterification with CH₂N₂ and Kugelrohr distillation (90 °C, 0.3 mm). The phosphonate **10** had the expected MS and NMR properties.⁷ The



yield of **10** was reduced to 23% during the isolation procedure, but this value is not representative of the efficiency of the trapping. No β-substitution product was formed. The diethyl ester corresponding to **10** has been previously prepared by another method.⁸

The 5,6-oxaphosphabicyclo[2.2.2]octene system has also been found to be an excellent generator of metaphosphonic anhydrides when the phosphorus bears a carbon substituent. This process was suggested, but not explored, by Kashman and Awerbouch,⁹ who first synthesized such bicyclic compounds. Sigal and Loew¹⁰ later generated mesitylphosphonic anhydride by this approach; the bicyclic precursor was generated by Diels-Alder reactions of mesitylbutadienylphosphinate, but the temperatures required caused prompt decomposition of the intermediates, which were never observed directly. We found that heating **11**¹ in alcohols resulted in virtually complete interception of the expelled P fragment, forming half-esters of phosphonic acids (e.g., **12**, δ ³¹P +28.6).



The process may have synthetic significance for specialized phosphonates. Of significance also was the effective trapping of PhPO₂ by *N*-methylpyrrole, forming **13**¹¹ (isolated as the *p*-

toluidine salt). The ability of metaphosphonic anhydrides to function as electrophilic substitution agents in solution has not previously been recognized, although the cyclization of *o*-biphenylmetaphosphonic anhydride¹² when formed at 600-800 °C is another example of electrophilic substitution. Other applications of the phosphorylating ability of this species are under study.

Acknowledgment. Support of this work by grants from the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the U.S. Army Research Office is gratefully acknowledged.

(11) Calcd for C₁₁H₁₂NO₂P (M⁺) 221.0606, found, *m/z* 221.0607; ¹H NMR (CDCl₃) δ 3.30 (NCH₃), 5.6-7.3 (3 H, m, =CH), 7.3-7.9 (5 H, Ar H); ¹³C NMR (CDCl₃) δ 35.4 (CH₃), 110.6 (d, *J* = 12.1 Hz, C-4), 111.8 (d, *J* = 112.0 Hz, C-2), 123.7 (d, *J* = 12.1 Hz, C-5), 127.3 (d, *J* = 19.8 Hz, C-3), 130.0 (d, *J* = 9.0 Hz, phenyl ortho C), 128.1 (d, *J* = 13.2 Hz, phenyl meta C), 130.4 (phenyl para C, ipso C not observed); δ ³¹P NMR (CDCl₃) +9.8.

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Structure of the C₄H₆CH₃⁺ Cation. ¹³C and ¹H NMR Spectroscopic Investigation of Equilibrium Isotope Effects in Deuterated Methylcyclobutonium Ions¹

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The dominant structure in the dynamic equilibrium of the 1-methylcyclobutyl/1-methylcyclopropylcarbonyl cation² (C₄H₆CH₃⁺) **1** has been in dispute for more than a decade.²⁻⁵ Recently two different structures have been suggested for **1** on the basis of ¹³C NMR spectroscopic studies.^{4,5} These structures are an sp³ hybridized cyclobutyl cation⁴ and a bicyclobutonium ion, considered to be either a single minimum or a set of fast equilibrating less symmetric cations claimed to be indistinguishable from the symmetric one.⁵

A comparison of the deuterium equilibrium isotope effects (EIE)⁶ in cation **1** and in related model cations **2** and **3** appeared suitable to clarify the controversy concerning the structure of **1**.

The ¹H and ¹³C NMR spectra of a mixture of **1** and CD₂-labeled **1** (**1-d₂**) show isotopic perturbation for the averaged signal of the three methylene groups, whereas the other peaks are unaffected. The peak for the nondeuterated methylene groups in **1-d₂** is shifted upfield compared to the unlabeled ion **1** between 1.45 (-80 °C) and 1.22 ppm (-56 °C) in the ¹³C NMR, and between 0.043 (-110 °C) and 0.041 ppm (-90 °C) in the ¹H NMR spectrum. This indicates a definite EIE on a fast rearrangement of *degenerate* cations.

In the C₄H₅DCH₃⁺ cation (**1-d**) the signal for the proton geminal to deuterium moves downfield between 0.099 (-110 °C) and 0.063 ppm (-50 °C) whereas the remaining methylene protons show a small upfield shift. The EIE is observed most clearly in the ¹³C NMR spectrum of a mixture of **1-d** and **1** (Figure 1a). The triplet (*J*_{CD} = 25.3 Hz) of the deuterated carbon in **1-d** is shifted downfield between 0.898 (-80 °C) and 0.670 ppm (-46

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(b) Saunders, M.; Telkowsky, L. A.; Kates, M. R. *J. Am. Chem. Soc.* 1977, 99, 8070. (c) Telkowski, L. A. Ph.D. Dissertation, Yale University, New Haven, CT, 1975.

(7) Calcd for C₈H₁₄NO₂P (M⁺) 203.0711, found, *m/z* 203.0713; ¹H NMR (CDCl₃) δ 1.30 (t, *J* = 6.8 Hz, CH₂CH₃), 3.7 (s, NCH₃), 3.75 (d, ³*J*_{PH} = 9.4 Hz, OCH₂), 4.10 (2 H, m, OCH₂), 5.9-7.4 (3 H, m, =CH); ¹³C NMR (CDCl₃) δ 16.3 (d, *J* = 6.6 Hz, CH₂CH₃), 36.3 (NCH₃), 52.2 (d, *J* = 5.5 Hz, OCH₂), 61.7 (d, *J* = 5.5 Hz, OCH₂), 107.6 (d, *J* = 224.4 Hz, C-2), 111.8 (d, *J* = 11.0 Hz, C-4), 123.6 (d, *J* = 15.4 Hz, C-5), 129.3 (d, *J* = 23.0 Hz, C-3); ³¹P NMR (CDCl₃) δ +19.4.

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(10) Sigal, I.; Loew, L. *J. Am. Chem. Soc.* 1978, 100, 6394.

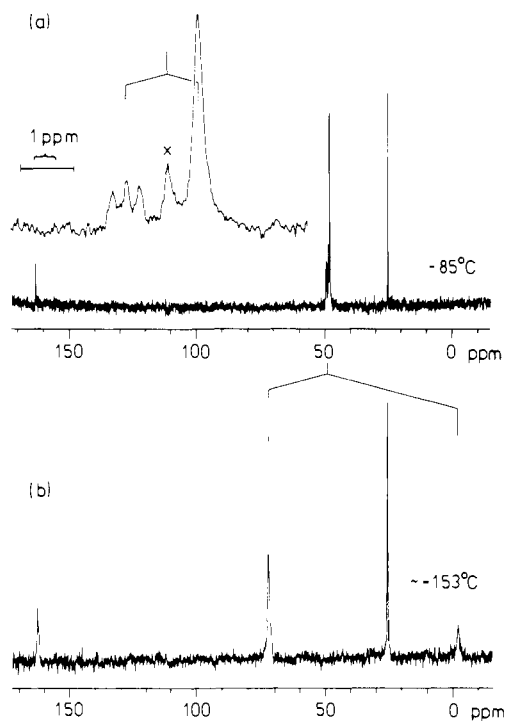


Figure 1. ^{13}C NMR spectra, 100.6 MHz, of $\text{C}_4\text{H}_5\text{DCH}_3^+$ cation with unlabeled cation (x) for reference in $\text{SO}_2\text{ClF}/\text{SO}_2\text{F}_2$ (2:1) at (a) -85°C and (b) $\sim -153^\circ\text{C}$. Upper trace shows expansion of methylene peaks at -85°C .

$^\circ\text{C}$) and the signal for the two methylene carbons in **1-d** moves upfield between 0.607 (-80°C) and 0.536 ppm (-46°C) as compared to **1**. The downfield shift of the deuterated carbon, corrected for an intrinsic (upfield) shift, has twice the size of the upfield shift, indicating a two-site fast exchange taking place between a double-populated downfield site and a single-populated upfield site in the frozen-out species.

At -153°C the ^{13}C NMR spectra of **1-d**, **1-d₂**, **1**, and mixtures of **1-d/1** (Figure 1b) and **1-d₂/1** have basically the same appearance (except for intrinsic isotope shifts). The methylene carbons are decoupled into two broad peaks at 71.3 and -2.8 ppm (ratio 2:1). The equilibrium averaging the methylene groups is frozen out and consequently the isotopic perturbation of this process is no longer observable. In addition there can be no equilibrium between the postulated unsymmetrical species,⁵ which if present should show isotopic perturbation.

The structure of **1** can be derived by correlating the *direction* of the EIE in the averaged spectra of **1** with the shift and intensity of the two types of methylene groups in the frozen out spectra. The averaged deuterated carbons are shifted downfield toward the two methylene groups and the averaged protonated carbons move upfield toward the one methylene group at -2.8 ppm. According to isotope effect theory⁷ the mean of the force constants of the two hydrogens at the upfield carbon must be lower than the C-H bond force constants at the two low-field methylene carbons.

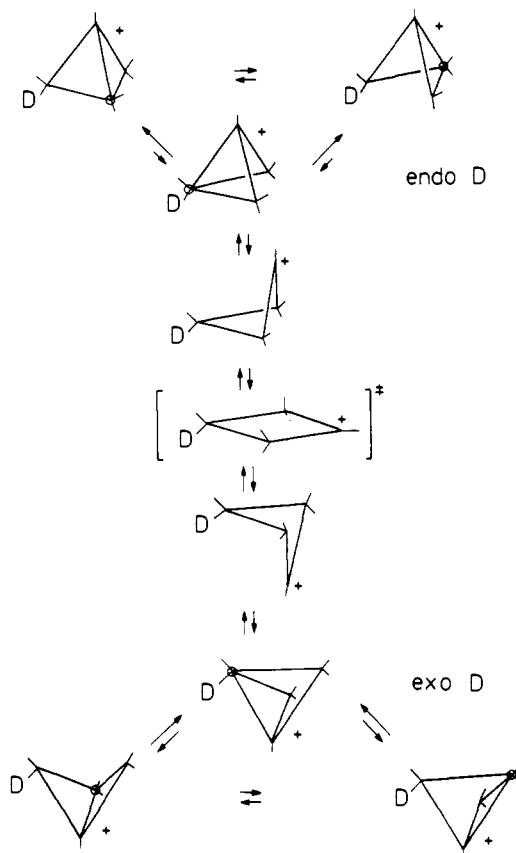
Table I shows the three types of static structures **2-4** and criteria for their distinction: relative intensity and chemical shift and relative C-H bond force constants for the two types of methylene groups. The α/γ -EIE in the threefold degenerate β,β' , 1-trimethylcyclopropylcarbinyl cation is of opposite sign as in **1** and the averaged carbons frozen out at -154°C with the expected intensity/shift ratio (Table I).⁸ This rules out a cyclopropylcarbinyl-type structure **2** for cation **1**.

A puckered cyclobutyl-type structure **3** for cation **1** cannot be excluded from the intensity/shift ratio of the methylene carbons,

Table I. Relative CH_2 Chemical Shifts and C-H Bond Force Constants

2	3	4
2 CH_2 (upfield, tight) 1 CH_2 (downfield, less tight)	2 CH_2 (downfield, less tight) 1 CH_2 (upfield, tight)	2 CH_2 (downfield, tight) 1 CH_2 (upfield, less tight, averaged)

Scheme I. Equilibration of Deuterated Bicyclobutonium Ions^a



^a Direction and size of isotope effects are indicated by relative size of arrows. Exchanging exo and endo D via planar cyclobutyl cation is observed only for the 1- CH_3 cation.

although the extremely high field position for one methylene carbon could not be rationalized.⁴ The relative strength of C-H bond force constants at the two different methylene carbons in cyclobutyl cations was derived from β -deuterium isotope effects on the ^{13}C NMR chemical shift in static 1-phenylcyclobutyl- β - d_1 and $-\beta,\beta$ - d_2 cations. These cations show small temperature-independent downfield shifts for the C^+ carbons compared to the unlabeled ion, indicating less hyperconjugative stabilization in the β -deuterated ions.⁹ As a consequence of hyperconjugation, the β -C-H bonds have lower force constants and lower zero point energy than the γ -C-H bonds. In a degenerate rearrangement of cyclobutyl cations protons would therefore prefer the (low field) β -position and deuterium the (upfield) γ -position, thus an upfield shift for deuterated methylene carbons is predicted. The opposite direction is observed in **1**, consequently a cyclobutyl-type structure **3** can be excluded.

The direction of all EIE's observed in the **1** (deuterium preferred in the low-field position) is the same as was observed in the

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bicyclobutoniumion- d_2 ,¹⁰ where the EIE is an average of a large effect preferring deuterium in the low-field (endo)¹¹ position and a smaller one preferring deuterium in the upfield (exo)¹¹ position. The size of the isotope splitting in the ¹³C NMR spectrum of **1-d** corresponds to the arithmetic mean of the two isotope effects which are different in size and sign in the *exo*- and *endo*-C₄H₆D⁺ cations.¹⁰

Taking into account the adequate intensity/chemical shift ratio and the fundamental coincidence of the EIE's in **1** with those in the parent ion, it can be concluded that the minimum-energy structure for **1** is the methylbicyclobutonium ion structure **4**. At higher temperatures the degenerate equilibrium of three bicyclobutonium ions is principally perturbed to different sides by *endo* and *exo* deuterium (Scheme I). However, contrary to the C₄H₇⁺ cation, the geminal protons at the averaged methylene carbons are not distinct in C₄H₆CH₃⁺. Averaging of the geminal protons occurs by inversion via a planar cyclobutyl cation transition state,¹² thus leading to averaged *exo/endo* EIE's in the C₄H₆CH₃⁺ cation.

The *endo* C-H bond at the pentacoordinated carbon has a much lower bond force constant than the other *endo* proton bonds. Vibrations are less hindered because bridging drains electron density particularly out of this C-H bond.^{12,13} This resembles the transition state of an α primary KIE ($k_H/k_D > 1$) in an S_E2 reaction.¹⁴ The *endo* proton would be the leaving group and the bridging carbon the incoming electrophile. The reverse applies for the *exo* C-H bonds, which are to be more hindered to bending vibration due to crowding at the pentacoordinated carbon. This inverse effect can be compared with an α secondary KIE ($k_H/k_D < 1$).⁷

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft.

Registry No. **1**, 96347-33-0; **2**, 14973-56-9; **3**, 19067-43-7; **4**, 96347-32-9; D₂, 7782-39-0; 1-methylcyclobutyl cation, 19394-14-0; (1-methylcyclopropyl)carbinyl cation, 27761-35-9.

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(2-Alkynylethenyl)ketenes: A New Benzoquinone Synthesis

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We wish to report the generation and chemistry of the heretofore unknown (2-alkynylethenyl)ketenes, specifically those of general structure **2**. Such compounds are accessible from the corresponding alkynylcyclobutenones **1**. The ketenes thus generated are envisaged to undergo ring closure to the unique zwitterions **3** and **4** and these, in turn, proceed to products **5** and **6** via transfer of the trimethylsilyl group.¹ Significantly, the formation of **5** constitutes a new and potentially general quinone synthesis.

The results of this study are outlined in Scheme I and Table I. The 4-alkynyl-2,3-dimethoxy-4-(trimethylsilyloxy)cyclobutenones **1a-e** were thermolyzed in refluxing *p*-xylene (135 °C) to give both five- and six-membered ring products. The ring closure pathway is influenced by the substituent R. Specifically, electron-with-

Scheme I

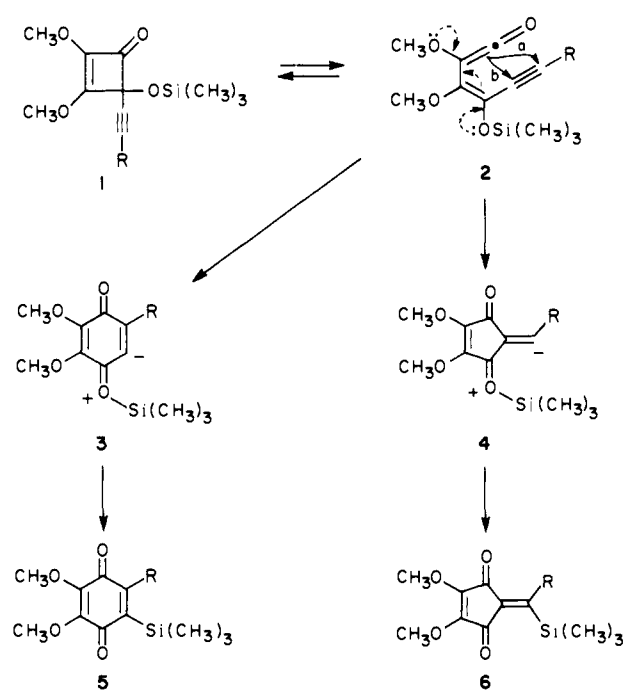


Table I

R	Isolated Yields (%)	
	5	6
a, CO ₂ C ₂ H ₅		33 ^a
b, C ₆ H ₅	13 ^b	52
c, <i>n</i> -C ₄ H ₉	75	
d, CH ₂ C ₆ H ₅	74	
e, CH ₂ OSi(CH ₃) ₃	80	

^aA yield of 43% was obtained starting from a chromatographed (silica gel) sample of the cyclobutenone **1a**. However, the yield of **1a** was only 21% after chromatography due to hydrolysis. ^b**5b** and **6b** could not be separated by chromatography; instead the mixture was reduced with sodium dithionite. The hydroquinone of **5b** was then separated from **6b** by chromatography and later reoxidized to **5b** with Ag₂O. The yield of **5b** is based on the isolated yield of its hydroquinone.

drawing groups favor the formation of cyclopentenediones **6** and electron-releasing groups favor the quinones **5**. The structures of these products are based upon spectral (Table II) and chemical properties. For example, the quinones **5b-e** all show a positive leucomethylene blue test and can be easily reduced to their corresponding hydroquinones upon treatment with sodium dithionite.

The proposed mechanism for the conversion of **1** to **5** and **6** is provided in Scheme I. The cyclobutenones **1** would be anticipated to be in equilibrium with the (2-alkynylethenyl)ketenes **2** at 135 °C. These ketenes are viewed as undergoing ring closure to **3** and/or **4**.^{2,3} As is indicated by the product distributions, the mode of ring closure (path a vs. path b) is dictated by the electronic influence of the alkyne substituent, R. Transfer of the trimethylsilyl group to the negative site then gives the products

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(1) The corresponding diradical structure is also a viable possibility. See ref 5.