mol^{-1}. $\Delta(\Delta G^{\ddagger}) = -7.6$ kcal mol^{-1} so that $c = 0.53 \pm 0.04$. This is a lower value than found for the other systems and suggests a smaller amount of reduction in the transition state. It is clear that c depends on the nature of the complex, and it may be that a relationship $\Delta G^{\ddagger} = c\Delta G_1^{\circ} + c'\Delta G_2^{\circ}$ will be found to be more appropriate when more extensive and precise kinetic and thermodynamic data become available.

There is not the same correlation between the values of $\Delta H^{\ddagger}$ and ΔH_2° for reduction. $\Delta(\Delta H_2^{\circ})$ can be estimated from data in ref 21 to be slightly less than -15 kcal mol^{-1}, while $\Delta(\Delta H^{\ddagger})$ is $+5.2$ kcal mol^{-1}. There is also no enthalpy correlation in the reactions of *trans*-$\mathrm{Pt(CN)_4Br_2{}^{2-}}$ with bromide and hydroxide. While $\Delta(\Delta H^{\ddagger})$ = *ca.* 12 kcal mol^{-1}, $\Delta(\Delta H_2^{\circ})$ is negligible. Whether this absence of an enthalpy correlation is general or not remains to be seen, but it may be significant that both these examples include reactions for which unusual entropies of activation are obtained. Thus $\Delta S^{\ddagger}$ for the reaction of hydroxide with *trans*-$\mathrm{Pt(CN)_4Br_2{}^{2-}}$ is unusually positive, while that for the reaction of *trans*-$\mathrm{Pt(en)(tet)Cl_2{}^{2+}}$ with bromide is unusually negative. The only other reaction of the latter type for which such a value is observed is that of iodide with *trans*-$\mathrm{Pt(C_2O_4)_2Cl_2{}^{-}}$,[3a] which also has a correspondingly low value of $\Delta H^{\ddagger}$. Both these cases might be exceptional in having much less $\mathrm{Pt^{IV}}$–Cl bond breaking in the transition state coupled with a much less favorable probability of electron transfer of some sort.

The reaction of iodide with *trans*-$\mathrm{Pt(en)_2Cl_2{}^{2+}}$ shows no sign of a [Pt(II)]-independent rate term, and the value of the rate constant for direct attack must, therefore, be less than *ca.* 2 M^{-1} sec^{-1} at 25° and $\mu = 1.0$ M. This is less than one-tenth of the rate constant for direct attack on *trans*-$\mathrm{Pt(en)(tet)Cl_2{}^{2+}}$. As might be expected, the more bulky amine ligand causes more rapid reduction in addition to stabilizing the reduced form thermodynamically, the latter being shown by the nonexistence of *trans*-$\mathrm{Pt(en)(tet)I_2{}^{2+}}$. A similar effect has been noted in the reduction of analogous complexes of platinum(IV) by nitrite.[2b]

The fact that there is no evidence for the formation of *trans*-$\mathrm{Pt(en)(tet)I_2{}^{2+}}$ is probably a consequence of steric factors rather than of electronic ones, since *trans*-$\mathrm{Pt(CN)_4I_2{}^{2-}}$ can be detected in solution although *trans*-$\mathrm{Pt(CN)_4Cl_2{}^{2-}}$ is reduced by iodide about 50 times more rapidly than is *trans*-$\mathrm{Pt(en)(tet)Cl_2{}^{2+}}$.

Finally, there is a strong spectroscopic interaction between *trans*-$\mathrm{Pt(en)(tet)Br_2{}^{2+}}$ and bromide of a similar type to the interactions already observed between bromide and the trans complexes $\mathrm{Pt(en)_2Br_2{}^{2+}}$,[7] $\mathrm{Pt(NH_3)_4Br_2{}^{2+}}$,[11] $\mathrm{Pt(}l\mathrm{\text{-}pn)_2Br_2{}^{2+}}$,[22] and $\mathrm{Pt(CN)_4Br_2{}^{2-}}$.[3b,15] Similar interactions have also been observed between chloride and *trans*-$\mathrm{Pt(en)_2Cl_2{}^{2+}}$[7] and *trans*-$\mathrm{Pt(CN)_4Cl_2{}^{2-}}$[3b] and between iodide and *trans*-$\mathrm{Rh(en)_2I_2{}^{+}}$.[23] None of these interactions appears to be caused by reduction, and no leveling off of the plots of absorbance against halide concentration (characteristic of finite degrees of ion association) is observed. The existence of these interactions is clearly not charge dependent, and it may be quite general. No really satisfactory explanation of their occurrence has been offered.[3b]

Acknowledgment. Acknowledgment is made to the Science Research Council for the award of a Studentship to one of us (D. H. V.) and for grants to buy the spectrophotometers and the stopped-flow assembly.

(22) H. Ito, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jap.*, 42, 1286 (1969).

(23) H. L. Bott, Ph.D. Thesis, London University, 1966.

Pyrolysis of Tetracyclo[5.3.0.0^{2,10}.0^{3,6}]decene-8. A (2′-Vinylcyclopropyl)cyclobutane Rearrangement

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Received May 15, 1970

Abstract: Pyrolysis of tetracyclo[5.3.0.0^{2,10}.0^{3,6}]decene-8 (V) (believed to be 3,6-endo) in the vapor phase (~100 Torr) in a static system at 250° gave three isomeric products in the ratio of 4:2:1. The first of these was tricyclo-[5.2.1.0^{4,10}]deca-2,5-diene (VI). The second was found to be the exo stereoisomer (VIII) of the starting material. The third isomer was not further identified. In a fast-flow system at 550° at a pressure of <1 Torr, the products were VI and 1,2-dihydronaphthalene. From kinetic studies and by deuterium labeling, the formation of VI was shown to involve a shift of the $\mathrm{C_3C_4}$ bond in V to the $\mathrm{C_8}$ position. Thus, this reaction can be regarded as the rearrangement of a (2′-vinylcyclopropyl)cyclobutane system to a 1,4-cyclononadiene.

There are numerous examples of thermal rearrangements in which the normal isomerization (or decomposition) pathways of cyclopropane and cyclobutane rings are modified by the presence of a vinyl group on the ring.[1] When two such rings and a vinyl group are suitably placed in a molecule, it should be

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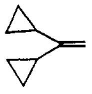
[1] For a recent review, see H. M. Frey and R. Walsh, *Chem. Rev.*, 69, 103 (1969).

possible to create a larger ring by a thermal isomerization. An example would be the isomerization of 1,1-dicyclopropylethylene, I, to II, an eight-membered ring system.[2a] Similarly, it should be possible to construct a nine-membered ring (IV) from a molecule (III) which contains one each of a cyclobutane, a cyclopropane, and a vinyl group, in order. However, there can be a problem if the two rings fail to open simultaneously to provide the necessary allylic stabilization. Thus, the premature occurrence of a vinylcyclopropane rearrangement would shift the double bond to an unfavorable position for the vinylcyclobutane rearrangement.[2b] It is, hence, necessary to place the vinylcyclopropane in a cyclohexane ring so that its isomerization would be degenerate, while the cyclobutane ring should be located so that the sequence of functional groups in III would always be preserved. The simplest structure in which all of these conditions are fulfilled is tetracyclo$[5.3.0.0^{2,10}.0^{3,6}]$decene-8 (V). The serendipitous synthesis of this compound[3] by the photochemical addition of benzene to cyclobutene[4,5] prompted this study of the thermal rearrangements in this system.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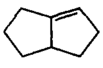
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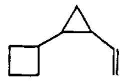
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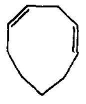
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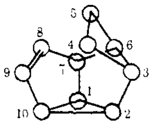
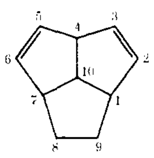


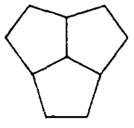
V

Results

Pyrolysis of V in the vapor phase (~100 Torr) at about 250° gave three isomeric products in the ratio of 4:2:1. At low conversions, the mass balance showed that there were no fragmentation products and hardly any condensed material. The major product was identified as tricyclo$[5.2.1.0^{4,10}]$deca-2,5-diene (VI) from the following data. The mass spectrum showed a parent peak at m/e 132 ($C_{10}H_{12}$) and major peaks at m/e 117 and 104. In the infrared spectrum, an intense absorption at 3050 cm^{-1} and a weaker absorption at 1600 cm^{-1} could be attributed to a double bond in a cyclopentane ring.[6] The ultraviolet spectrum showed only end absorption up to 200 nm. In the nmr spectrum (Figure 1a), there were three groups of four protons each centered at τ 4.5, 6.7, and 8.5, respectively. The first of these indicated the presence of four olefinic protons on two double bonds in the molecule. Catalytic hydrogenation over Adam's catalyst at 1 atm gave a product which corresponded to the addition of 2 mol of hydrogen to each mole of VI. Since the physical data (particularly the nmr spectrum) of the hydrogenated product indicated that it was saturated, VI must be a tricyclic compound with two double bonds in it.



VI


VII

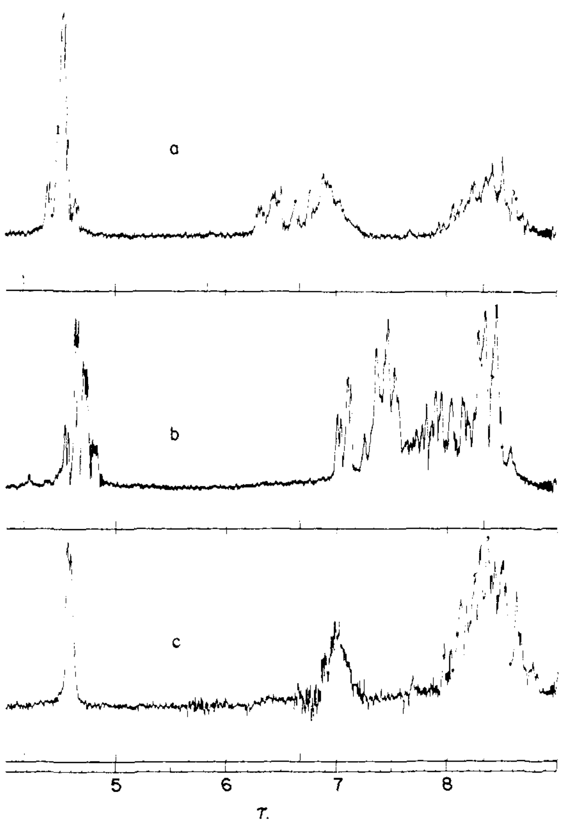


Figure 1. Nmr spectra of pyrolysis products: (a) VI, (b) VIII, (c) X (Varian HA-60 spectrometer; solvent, CCl_4; TMS as internal reference).

Double-irradiation studies[7] on the nmr spectrum showed that the four olefinic protons (2, 3, 5, and 6) belonged to two AB pairs. These were coupled to the single proton (10) at τ 6.4 and the two protons (1 and 7) at τ 6.9.[8] The single proton (6) at τ 6.7, which appeared as a symmetric quartet, was not coupled to the olefinic protons. The tricyclic structure VI would account for all of these features.

Confirmatory evidence was obtained by comparing the hydrogenated product VII to an authentic sample of tricyclo$[5.2.1.0^{4,10}]$decane which was synthesized by

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(2) (a) A. D. Ketley and J. L. McClanahan, *J. Org. Chem.*, **30**, 940 (1965); G. R. Branton and H. M. Frey, *J. Chem. Soc. A*, 1342 (1966). (b) The rearrangements I → II and III → IV are similar only in that both can lead to medium-sized rings. Obviously, the former can occur in two steps while the latter may not.

(3) We shall assume that the cyclobutane ring is fused endo along the 3,6 bond. The stereochemistry of this compound will be discussed in a later section.

(4) R. Srinivasan, *IBM J. Res. Develop.*, in press.

(5) In an earlier communication on this addition [R. Srinivasan and K. A. Hill, *J. Amer. Chem. Soc.*, **87**, 4653 (1965)], we had overlooked this product (see footnote 12, ref 11).

(6) R. N. Jones and C. Sandorfy, *Tech. Org. Chem.*, **9**, 371 (1956).

(7) We thank Dr. B. F. Dowden of the IBM San Jose Research Laboratory for these experiments.

(8) The two halves of the AB pairs were too close together for double irradiation at separate frequencies.

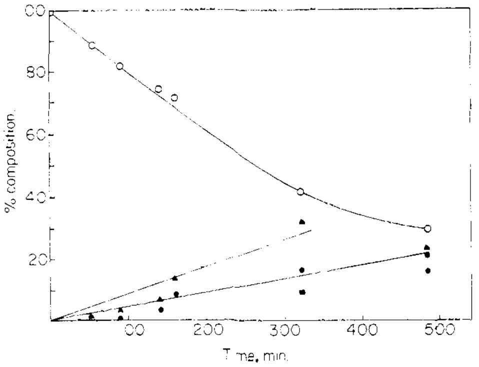
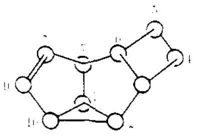


Figure 2. Kinetics of the decomposition of V (pressure ~ 100 Torr; temperature = 248°): ○, V; ●, VIII; ▲, VI; ■, unidentified isomer.

the method of Jacobson.[9,10] The two samples were identical in all respects.

The second product was identified as the exo isomer VIII of the starting material from the following evidence. The mass spectrum showed a parent peak at *m/e* 132. The infrared spectrum closely resembled that of the starting material V in the regions of C—H and C=C stretching absorptions, and showed the same cyclopentene absorptions at 3050 and 1600 cm^{-1}. The maximum in the ultraviolet spectrum at 220 nm (ϵ 2200 cm^2 mol^{-1}) once again paralelled that found in V.[3] This absorption has been attributed to the vinylcyclopropane chromophore in the major photochemical adducts of benzene to olefins.[11,12] In the nmr spectrum there were two olefinic proton absorptions at τ 4.60 and 4.78. Since these data suggested a tetracyclic system, the possibility that the product was a stereoisomer of V was considered.



VIII

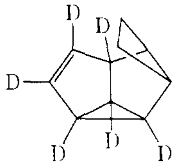
From double-irradiation experiments, it was found that the olefinic protons were strongly coupled to each other (J = 5 Hz) as in the adducts of benzene to *cis*- or *trans*-2-butene.[11] In addition, proton 8 was coupled to one (no. 7) at τ 7.1 (J = 2 Hz), while proton 9 was weakly coupled to one (no. 10?) at τ ~8.4. Thus protons 7, 8, 9, and 10 (which originally belonged to the benzene molecule from which V was made) have nearly the same chemical shifts and coupling constants in VIII, V, and in the major adduct of benzene to *cis*-2-butene. The two remaining benzene protons were believed to be at *ca.* τ 7.4 (since proton no. 7 was strongly coupled to one at higher field, presumably 10 or 6) and τ 8.4, respectively, but they were obscured by the protons derived from the cyclobutene ring. The latter occurred as a broad absorption at τ ~7.4 (2 H) and a complex pattern centered at τ 7.9 (4 H). The nmr spectrum seemed to agree with the proposed structure for VIII. The assignment of the exo configuration of the cyclobutane ring will be discussed in a later section.

The third isomeric product was never obtained entirely free from impurities. It was not identified.

Pyrolysis of V in a flow system was carried out by passing the vapor of the compound at a pressure of ~0.1 Torr over powdered quartz kept at 450°. The product mixture contained VI (50%) and about 20% of 1,2-dihydronaphthalene, which was identified by its ultraviolet, nmr, and mass spectra and by comparison to an authentic sample. There were three other products (one of which was VIII), each of which made up 1–5% of the mixture. One of these was recognized as the unidentified product from the pyrolysis in a static system. VIII was definitely not formed under these conditions.

Kinetic Studies. The disappearance of V and the appearance of the three products during pyrolysis in a static system are plotted in Figure 2. The mass balance was satisfactory even up to 60% reaction.[13] The formation of the exo isomer VIII was linear, with conversion to more than 70%. This shows that the formations of VI and VIII are parallel and not consecutive processes. Separate experiments showed that the exo isomer did not decompose to a detectable extent even at 310° in the time that the pyrolysis of V was essentially complete. The half-life of VI at 260° was about 100 min. The half-life of V at 248° was 244 min. At 310° it was less than 5 min.

Deuterium-Labeling Experiments. In order to follow the transformation of V to VI, the deuterium-labeled compound IX was prepared by the photochemical addition of deuteriobenzene to cyclobutene. The nmr spectrum of this material showed no absorption due to olefinic protons. The spectrum consisted of a broad absorption at τ ~6.8 (2 H) and two complex absorptions at τ 8.1 (3 H) and 8.7 (1 H), respectively. By the pyrolysis of this material in a flow system, a sample of hexadeuterio VI was prepared. Its nmr spectrum (Figure 1b) showed three absorptions at τ 4.6 (1 H), 7.0 (1 H), and ~8.4 (4 H). By comparison to the nmr spectrum of V, these protons were located on the carbons at 2, 1, and (8 + 9), respectively. The product must therefore have the structure X.



IX

The 1,2-dihydronaphthalene that was isolated from this reaction was found to have a nmr spectrum that was entirely identical in its proton distribution with the spectrum of unlabeled 1,2-dihydronaphthalene.

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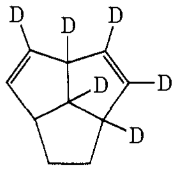
[9] I. T. Jacobson, *Acta Chem. Scand.*, 21, 2235 (1967).

[10] We thank Professor L. A. Paquette of Ohio State University for a sample of this material.

[11] K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, **88**, 2066 (1966).

[12] D. Bryce-Smith, A. Gilbert, and B. H. Orger, *Chem. Commun.*, 512 (1966).

[13] At higher conversions, there was an imbalance between the disappearance of V and the appearance of volatile products that was due mainly to the secondary decomposition of VI.



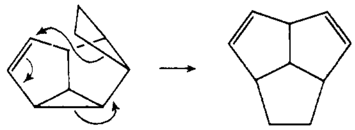
X

It suggested that the deuterium label in the material was randomly distributed among all the possible locations in the molecule.

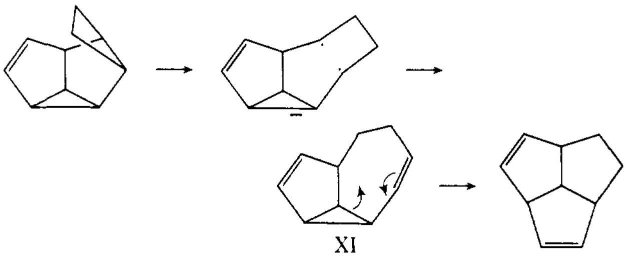
Discussion

The transformation of V to VI appears to be a unimolecular isomerization which can be explained in one of two ways. Both would be consistent with the deuterium-labeling experiment. Mechanism I involves the shift of the 3,4 bond in V to carbon 8 and other electron redistributions which correspond to the (2′-vinylcyclopropyl)cyclobutane rearrangement that was sought. However, this is only one of the formal ways in which this reaction can be viewed. One alternative would be to consider it as a Cope rearrangement in which a cyclobutane ring replaces one of the double bonds in the 1,5-hexadiene system. The second mechanism involves a break in the 3,6 bond in V to give a diradical which could lead to XI by the migration of a hydrogen. The latter can undergo a vinylcyclopropane rearrangement to give VI. Step 1 in this mechanism is plausible and probably is the intermediate step in the formation of the stereoisomeric product, VIII. Step 2 may have a considerable activation energy since it involves the migration of a hydrogen atom. The strongest defect in this mechanism is that if XI is an intermediate, it will, in all likelihood, undergo a Cope rearrangement to the tricyclic product XII.[14] Since there was no evidence for the formation of XII in this system,[15] it seems unlikely that XI would be a precursor to VI.

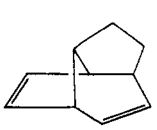
Mechanism I



Mechanism II



XI



XII

The assumption, which has been made earlier, that V has the 3,6-endo structure, can be examined at this point. Molecular models indicate that the isomer of VI which is trans-fused at C_1 and C_7 would be severely strained. The formation of VI by a thermal rearrangement rules out the possibility that it would have a trans-fused structure. On the basis that VI has a crown-shaped structure, it can be deduced that V must either have the 3,6-endo configuration or it must rearrange to the endo structure and then isomerize to VI according to mechanism I. But since the stereoisomer of V about the 3,6 bond is VIII and the latter is not an intermediate in the formation of V (as shown by the kinetics), V must be the 3,6-endo structure and VIII must be the 3,6-exo isomer.

Cyclobutenes can be readily synthesized by the photoisomerization of 1,3-dienes,[16] and the photochemical addition of benzene to cyclobutene is an efficient reaction.[4] Therefore, the possibility exists that reactions analogous to the isomerization of V to VI may have some utility in the synthesis of certain polycyclic compounds. This avenue is being explored at present.

Experimental Section

Preparation of V. A solution of cyclobutene (1.5 g, 28 mmol) in 20 ml of benzene was photolyzed in a quartz tube for 18 hr using a Rayonet RPR-100 reactor[17] fitted with eight 253.7-nm lamps. At the end of this period, the unreacted cyclobutene and benzene were distilled off and reirradiated in a clean quartz tube. This procedure was repeated four times until the benzene distillate was yellow.

The combined residues were distilled *in vacuo* from bulb to bulb to remove the polymeric material. The distillate (1.2 g) was separated on a vapor-phase chromatograph (silicone column, 12 ft long initially, at 100° programmed at 4°/min to 150°) to give V (0.7 g; 20% based on cyclobutene).

The yield of V is affected principally by the loss of cyclobutene during the distillations and by the secondary (sensitized?) photodecomposition of V if the irradiation is prolonged. The initial yield of V can be as high as 60%.[4] *Anal.* Calcd for $C_{10}H_{12}$: C, 90.84; H, 9.16. Found: C, 90.70; H, 9.21.

Pyrolysis of V. In a typical run in a static system, a sample of V (0.125 g) was introduced into a Pyrex bulb (500 ml), pumped down to 0.01 Torr, degassed, and sealed. The bulb was placed in an air bath at 273° for 4 hr. The products were condensed in a cold trap in the bulb and collected. Separation on a gas chromatograph (conditions as above) gave VI (0.064 g, 50%) and VIII (0.018 g 14%).

VI: Mass spectrum (Hitachi Perkin-Elmer RMS-4) *m/e* 132, 131, 117, 115, 104, 103, 91, 78, 77, 51, 39; ir spectrum (Perkin-Elmer Infracord; solvent, CCl_4) 3.28 (s), 3.38 (s), 3.45 (s), 7.40 (m), 10.20 (w), 10.35 (w), 10.81 (s), 11.85 (s), 13.70 (s), 14.00 (s) μ; nmr spectrum (Varian HA-60, HA-100; solvent, CCl_4; TMS as internal reference), see Figure 1. *Anal.* Calcd for $C_{10}H_{12}$: C, 90.84; H, 9.16. Found: C, 90.62; H, 9.34.

VIII: Mass spectrum *m/e* 132, 131, 117, 115, 104, 103, 91, 79, 78, etc.; ir spectrum (solvent, CCl_4) 3.27 (s), 3.40 (s), 3.50 (sh), 7.42 (m), 7.61 (w), 11.00 (m), 14.15 (s) μ; nmr spectrum (solvent, CCl_4; TMS as internal reference), see Figure 1. *Anal.* Calcd for $C_{10}H_{12}$: C, 90.84; H, 9.16. Found: C, 90.83; H, 9.10.

The flow system for pyrolysis consisted of a 200-ml quartz bulb filled with powdered quartz and placed in an electric furance in which its temperature could be maintained to ±5°. The inlet tube was attached to a reservoir which contained a degassed sample

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[14] T. J. Katz and J. J. Cheung, *J. Amer. Chem. Soc.*, **91**, 7772 (1969).

[15] We thank Professor T. J. Katz of Columbia University for providing us with the nmr spectrum of XII.

[16] R. Srinivasan, *J. Amer. Chem. Soc.*, **84**, 4141 (1962); K. J. Crowley, *Tetrahedron*, **21**, 1001 (1965).

[17] Supplied by the Southern New England Ultraviolet Co., Middletown, Conn.

of V (~50 mg). The outlet led to a trap that was cooled in liquid nitrogen and a high-vacuum line. The sample of V distilled over in about 1–2 hr at a few microns of pressure.

For preparative purposes, the crude residue which is obtained by adding benzene to cyclobutene and distilling off the materials which are C_6 or smaller can be used as such; *i.e.*, it is not necessary to purify the sample of V for use in the pyrolysis.

The preparation of hexadeuterio V was carried out in exactly the same way as that of V itself.

Kinetic Studies. Samples of V which were purified by gas chromatography were used. A number of cylindrical bulbs were filled with 2 mg each of V. The bulbs were attached to a high-vacuum line, pumped, degassed, and sealed. After pyrolysis, the bulbs were cooled in liquid nitrogen and opened and 50 μl of cyclohexane was added. The whole of this solution was injected onto a chromatographic column. The reproducibility was ±5%.

Acknowledgment. The author thanks Mrs. Jane Picone for her technical assistance and Dr. J. N. C. Hsu for useful discussions on the interpretation of the nmr spectra.