

A STUDY OF SEVERAL 1,3-CYCLOBUTANEDIYLS
BY FT-IR AND COMPUTATIONAL TECHNIQUES

Thesis by
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ABSTRACT

We have studied the photolytic decomposition of 2,3-diazabicyclo[2.2.1]hept-2-ene (Closs' azo) by FT-IR spectroscopy. While no transient species were detected, the photolysis product was exclusively bicyclopentane, as compared to Closs' result of 1:30 cyclopentene: bicyclopentane. The reasons for this difference are unclear; it may be due to our choice of argon for a matrix material. It has been previously shown that argon increases ISC rates compared to the first row elements.

We have also studied the photolytic decomposition of 1,4-diethyl-2,3-diazabicyclo[2.1.1]hex-2-ene. In this case, we have evidence that an intermediate exists, probably the diazenyl biradical formed by cleavage of a C-N bond. This intermediate has been detected by its decay to the starting diazene with a half-life of roughly 2 min. During the course of this investigation, the 1,4-diethyl diazene has been synthesized using a slight variation of methods previously developed in our group.

We have partially redesigned the FT-IR spectrometer in order to facilitate our investigations. Specifically, we have used a lens and mirror system to allow for photolysis inside the spectrometer of compounds deposited on the Displex window. This adaptation greatly reduces the time required for spectral acquisition.

Finally, we have undertaken an *ab initio* study of the biradical 1,3-diethenyl-1,3-cyclobutanediyl at the Hartree-Fock level. The results of the study show a high concentration of spin density on the ring carbons of the triplet. This difference with experimental results might be ameliorated by an inclusion of configuration interaction, specifically an MCSCF treatment.

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INTRODUCTION

Biradicals have been proposed as intermediates and transition states in reactions for some time¹. As early as 1934, Chambers and Kistiakowsky² proposed their existence while studying the thermolysis of cyclopropane. The class is often defined by the possession of two electrons in degenerate, or nearly degenerate orbitals. Usually, a biradical can be related to a cyclic closed-shell molecule by the homolytic cleavage of a single bond. This paradigm



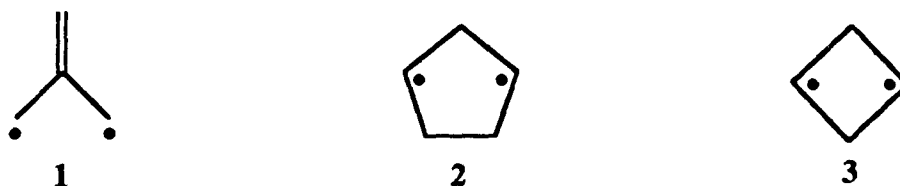
explains the enormous interest generated in the field of biradicals: they allow the study of the elementary processes that comprise the formation of a C-C bond. Insight into such fundamental processes is the goal of physical organic chemistry.

Biradicals, by definition, have two low lying spin states, a singlet and a triplet. These two states may have very different structures and reactivities. This is important because the direct examination of biradicals requires that they be intermediates, and not transition states; that is, that they lie in a local minimum of their potential energy surface. In general, "singlet biradicals" have little or no barrier to closure to form the corresponding closed shell molecule³; an important exception is the class of derivatives of trimethylenemethane (TMM)⁴. Therefore, only biradicals with triplet ground states have been directly observed⁵. One is consequently limited to biradicals with triplet ground states for most spectroscopic studies.

One of the first instances of the direct observation (by physical methods) of biradicals was the detection of TMM (1) by Dowd⁷. Other "delocalized" biradicals have been characterized since then; but, it was not until 1975 that Closs⁸ observed the first "localized" or non-conjugated biradical (2). These biradicals are somewhat more interesting in that their

unpaired electrons reside essentially completely on the two radical carbons. The interaction between radical centers is an important topic of research; the 1,3-biradicals provide the closest approach of the two radicals⁹. Further, since straight chain 1,3-biradicals (such as trimethylene) are generally quite floppy, cyclic biradicals are much more structurally defined, and are therefore often studied.

Theoretical studies¹⁰ have shown that the triplet states of cyclic 1,3-biradicals (in particular, 1,3-cyclopentandiyls (2) and 1,3-cyclobutandiyls (3)) experience a surprising



counter-balance between through-space coupling and through-bond coupling between the two radical centers. This rationalizes the observed triplet ground state of several such molecules^{8,11}. The study of several of these molecules is presented here.

Biradicals, with very few exceptions, require special conditions to be observed spectroscopically. These conditions are usually fulfilled by matrix isolation. Matrix isolation techniques have been important for the study of reactive intermediates for several years¹². Matrix isolated species are separated from themselves and other reactive species by a rigid cage of inert solvent atoms or molecules at a low temperature. These conditions force stringent requirements on the decay of reactive species (provided they do not react with the matrix): 1) they must decay intramolecularly, and 2) they must decay by a pathway that requires very little activation energy. For spectral purposes, matrix isolation forces the species of interest (except for very small molecules, *e.g.* CO, NH₃) to be in its lowest rotational and vibrational states, thereby simplifying the interpretation of their spectra.

The drawbacks of matrix isolation include the following. The very low temperatures involved (typically 5-20 K) require either liquid helium (or worse, liquid hydrogen) coolant

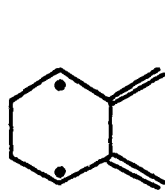
systems that are very large and expensive in terms of coolant, or large helium refrigeration units. Both alternatives are bulky and somewhat cumbersome to use. More importantly, the "inert" matrix material often packs around the species of interest in several different ways, producing "matrix site effects". That is, the species of interest are not all chemically equivalent; and, therefore, they have slightly different properties. These differences manifest themselves in the broadening or splitting of spectral lines and the non-exponentiality of decay traces. Sometimes this problem can be eased by "annealing" the matrix at a higher temperature, but this technique rarely eliminates these effects.

Specific examples of matrix isolation techniques are quite varied and depend on the desired experiment. Electron spin resonance (ESR) experiments often freeze a solution of a precursor to the desired intermediate in an organic solvent, preferably one that is a glass at the desired temperature¹³. Examples are cyclohexane and 2-methyltetrahydrofuran (MTHF). Infrared spectra, on the other hand, would be very difficult in these matrices since the matrices themselves are good absorbers in the infrared region of the spectrum. Typically, species to be analyzed by infrared spectroscopy (or their precursors) are mixed in the gas phase with argon, nitrogen, or another inert gas and sprayed onto a cryogenically refrigerated window. This is the technique which has been used in the work presented here.

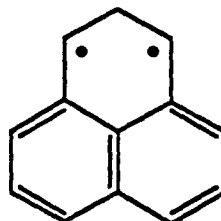
While ESR is a powerful technique for observing triplet biradicals, the structural information gained from it is rather sketchy. Infrared spectroscopy, on the other hand, is usually considered the ideal technique for determining structural parameters. The problem is that infrared spectroscopy requires orders of magnitude more concentrated a sample than ESR. This can obviously pose difficulties in attempted infrared observations of reactive intermediates, which may be difficult to generate in high concentrations.

It is possible that the above problem is the reason that only two examples of infrared observation of biradicals have been reported. The first was recorded by Roth *et al.*¹⁴, who

observed the infrared spectrum of 2,3-dimethylene-1,4-cyclohexanediyl (4), a derivative of tetramethyleneethane. More recently, Michl¹⁵ has studied the infrared spectra of various isotopomers of a bridged 1,8-naphthoquinodimethane (5). In both cases, the biradicals under



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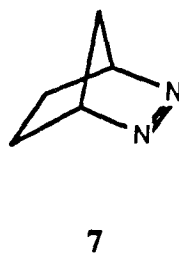
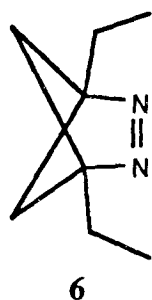


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study were delocalized biradicals. In this work, we attempt the infrared study of localized 1,3-biradicals. To our knowledge, such a study has not been previously reported.

In spite of the difficulties with infrared spectroscopy mentioned above, several instrumental advances have made these studies much more practical. Foremost among these is Fourier Transform Infrared Spectroscopy (FT-IR)¹⁶. The typical FT-IR instrument has several advantages over a grating spectrometer. Most importantly, the signal-to-noise ratio of an FT-IR instrument is higher for a given measurement time. This is mainly because of the simultaneous measurement of all frequencies in the spectrum that occurs in FT-IR (the multiplex advantage). Another advantage of an FT-IR spectrometer is the improvement in frequency accuracy that it affords, due to a laser reference used in the instrument (the Connes advantage¹⁷). This advantage can be very important when analyzing spectra of mixtures of substances. Another useful advance, though not restricted solely to FT-IR technology, is the digitalization of the spectrum in a computer, allowing many sophisticated spectral processing operations to be performed rather easily.

The specific biradicals studied here are 1,3-cyclopentanedyl (2) (first observed by Closs⁸) and 1,3-diethyl-1,3-cyclobutanediyl (first observed in our laboratories^{11,18}). These two biradicals have been generated from their corresponding 1,2-diazene precursors (6,7)¹⁹.



The biradicals have been shown to have triplet ground states, both by experiment^{8,11} and by the theoretical studies previously mentioned¹⁰. It was hoped, therefore, that these biradicals could be observed directly by FT-IR spectroscopy. An effort could then be made to determine their precise structures.

This study is the first such of "localized" or non-conjugated biradicals, to our knowledge. During the course of the study, some of the reasons for this seeming neglect became evident. Foremost, the biradicals in question are hydrocarbons; they have no strong chromophores in the infrared. This is a consequence of the very low polarity of C-C and C-H single bonds. As a result, the minimum concentration of these biradicals necessary for detection by FT-IR spectroscopy is higher than for most other molecules. Also, it has recently been noted that argon, our choice of matrix material due chiefly to convenience, may cause unforeseen problems. According to Michl²⁰, argon enhances the intersystem crossing (ISC) rates of biradicals 2.3 times over those for hydrocarbon matrices. This effect is presumably due to spin-orbit coupling. The impact of this study is that any triplet formed in an argon matrix essentially has its Arrhenius A factor for the conversion back to the singlet multiplied by a factor of 2.3. In other words, the triplet decays considerably faster. In spite of these problems, we feel that the study of this class of biradicals is well justified. Several theoretical studies of these species have been done^{10,21,22}; we feel they require experimental data for confirmation.

RESULTS AND DISCUSSION

Matrix Isolation of 2,3-Diazabicyclo[2.2.1]hept-2-ene (7).

The study of this 1,3-biradical precursor was chosen as a starting point in our investigations for several reasons. Most important was its ease of handling. It was stable at room temperature and had a high vapor pressure enabling the use of simple gas mixture techniques to produce a sample for matrix deposition. Also of relatively high importance was its availability; the other 1,3-biradical precursors we wished to study were only available in milligram quantities and were produced in arduously long syntheses. This compound, however, was easily prepared²³ and was available in high purity in our laboratories. It was therefore decided that this compound would be a good test of our equipment and procedures.

A sample of the diazene (7) was mixed with argon (1:1000) in a gas manifold. This mixture was deposited onto a 20 K CsI window at a rate of 13 mmol/h. After 3 h, the deposition was halted and the matrix was cooled to 10 K. (Further details of the procedures described here may be found in the Experimental Section.) An FT-IR spectrum of the matrix isolated compound was taken (Figure 1). The major peaks are at 2993 cm^{-1} , 2964 cm^{-1} (C-H stretches); 1445 cm^{-1} (C-N stretch); 1282 cm^{-1} , 1255 cm^{-1} , 1197 cm^{-1} , and 1122 cm^{-1} (C-C stretches). Impurities include the peaks at 2152 cm^{-1} , 1709 cm^{-1} , 1612 cm^{-1} , 1396 cm^{-1} , 1237 cm^{-1} , and 1231 cm^{-1} (organic impurities in the manifold); 3755 cm^{-1} , 3728 cm^{-1} , 3642 cm^{-1} , 1614 cm^{-1} , 1602 cm^{-1} , 1599 cm^{-1} , and 1593 cm^{-1} (H_2O in the matrix); 2347 cm^{-1} , and 2340 cm^{-1} (CO_2 in the matrix).

The matrix isolated sample of the diazene was photolyzed with a 1000 watt Hg(Xe) lamp through Schott UG-11, KG-5, and WG-305 filters. This filter combination passes light between 310 and 380 nm. The photolysis was completed in 200 s. Examination of the FT-IR

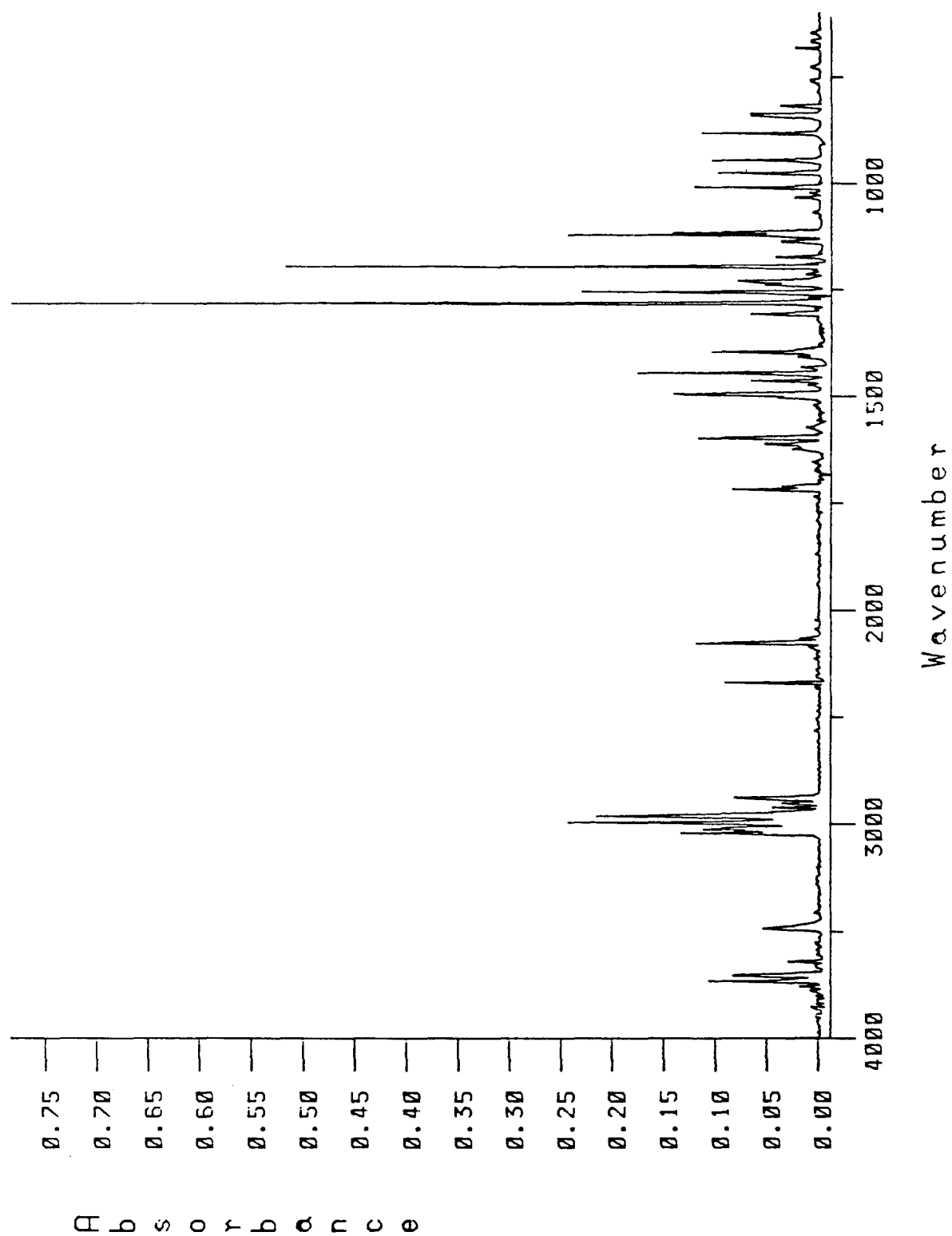


Figure 1. FT-IR Spectrum of 2,3-Diazabicyclo[2.2.1]hept-2-ene (7).

spectrum of the photolyzed matrix (Figure 2) shows virtually none of the azo precursor. The product has major peaks at 3072 cm^{-1} , 2972 cm^{-1} , 2941 cm^{-1} , 2866 cm^{-1} (C-H stretches); 1276 cm^{-1} , 1215 cm^{-1} (C-C stretches); 916 cm^{-1} , and 786 cm^{-1} (ring deformations).

A search for transient species was carried out. Beginning 170 s after the completion of photolysis, several spectra were taken in rapid succession. In no case did any of these spectra show any difference (other than atmospheric water and carbon dioxide) from the final product spectrum recorded an hour later. We estimate that transients of 2% or more of the photolysis product could have been detected. This implies (assuming all azo decomposition proceeded through the triplet biradical) that the biradical half-life in argon is much less than 60 s; or, that very little of the decay takes place through the triplet. This conflicts somewhat with the estimation by Closs⁸ of a 1500 s half-life in a hydrocarbon matrix. It may be that the actual formation of the triplet biradical is an unlikely occurrence under direct photolysis and that only a very low concentration of triplet is ever produced.

The expected products of photolysis of this compound are bicyclo[2.1.0]pentane (**8**) (arising from closure of the 1,3-biradical) and cyclopentene (**9**) (resulting from a 1,2-hydrogen



8



9

shift in the biradical). The FT-IR spectra of authentic samples of both possible products are shown in Figures 3 and 4. Note that the spectrum of bicyclopentane has major peaks at 3069 cm^{-1} , 2978 cm^{-1} , 2940 cm^{-1} , 2867 cm^{-1} (C-H stretches); 1276 cm^{-1} , 1214 cm^{-1} (C-C stretches); 915 cm^{-1} , and 784 cm^{-1} (ring deformations), corresponding well with the photolysis product spectrum. The spectrum of the photolysis product and cyclopentene were compared in an attempt to determine the fraction of cyclopentene produced in the photolysis. Note especially the large peak at 699 cm^{-1} in the spectrum of cyclopentene. Figure 5 is an

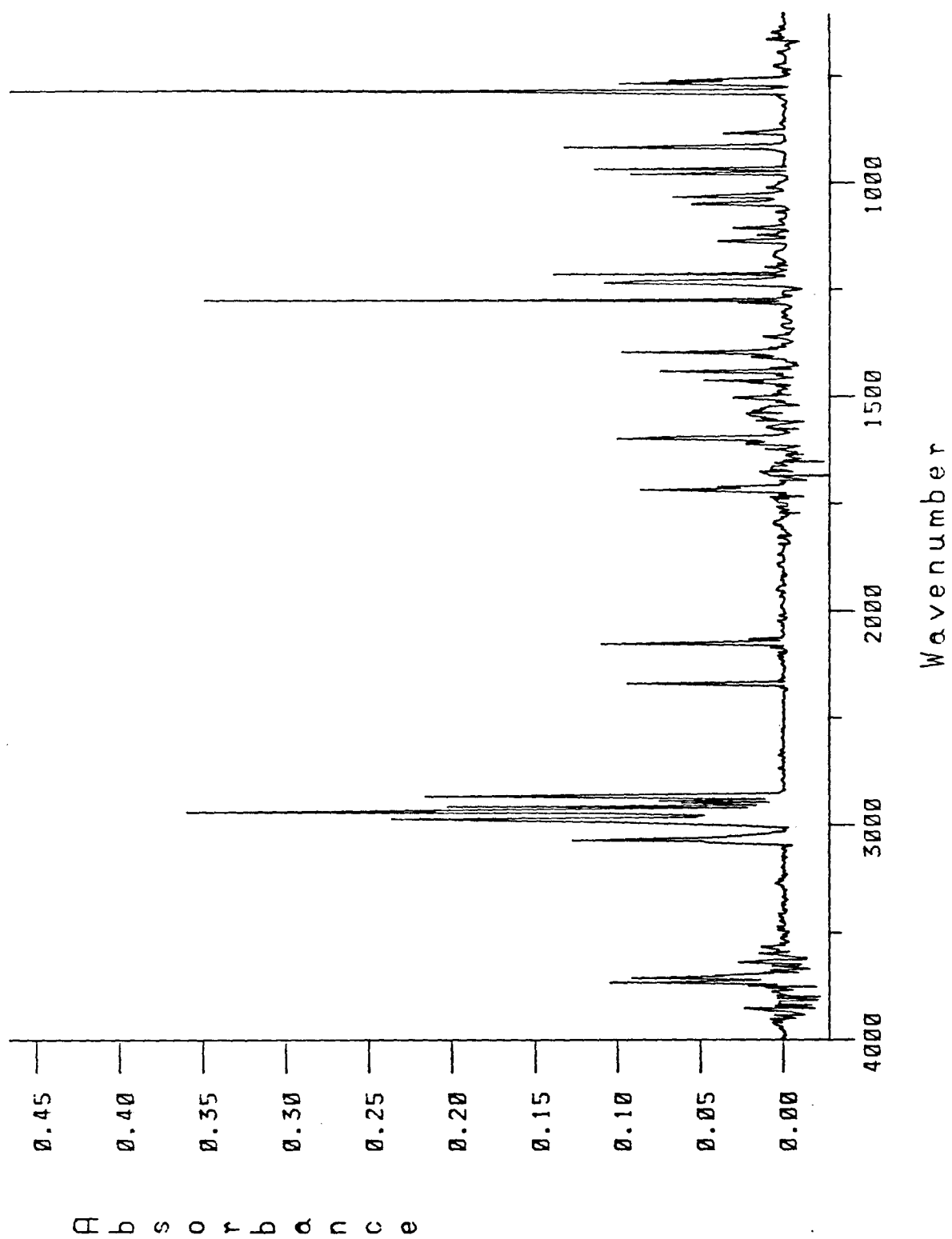


Figure 2. FT-IR Spectrum of Photolyzed 2,3-Diazabicyclo[2.2.1]hept-2-ene (7).

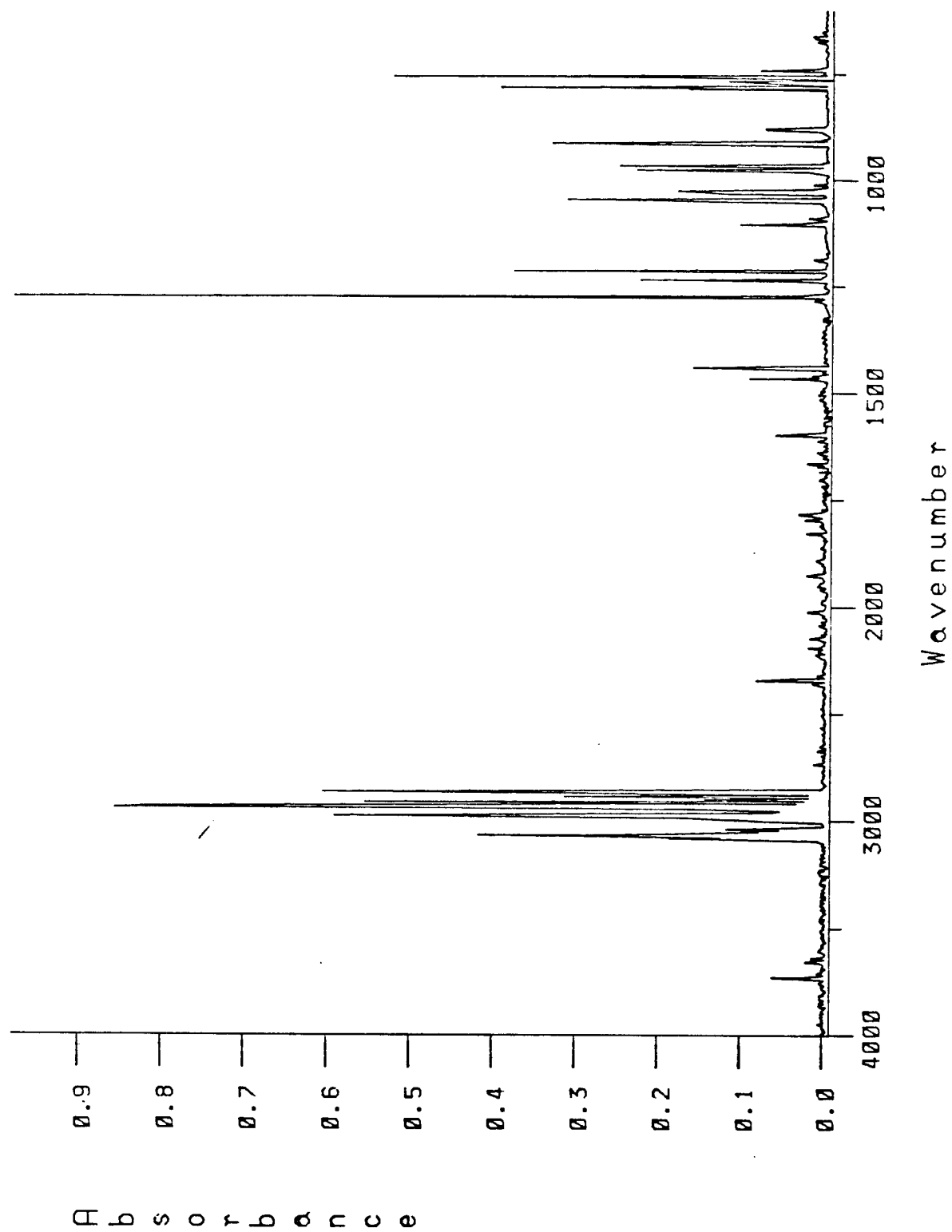


Figure 3. FT-IR Spectrum of Bicyclopentane (8). Note the similarity to Figure 2.

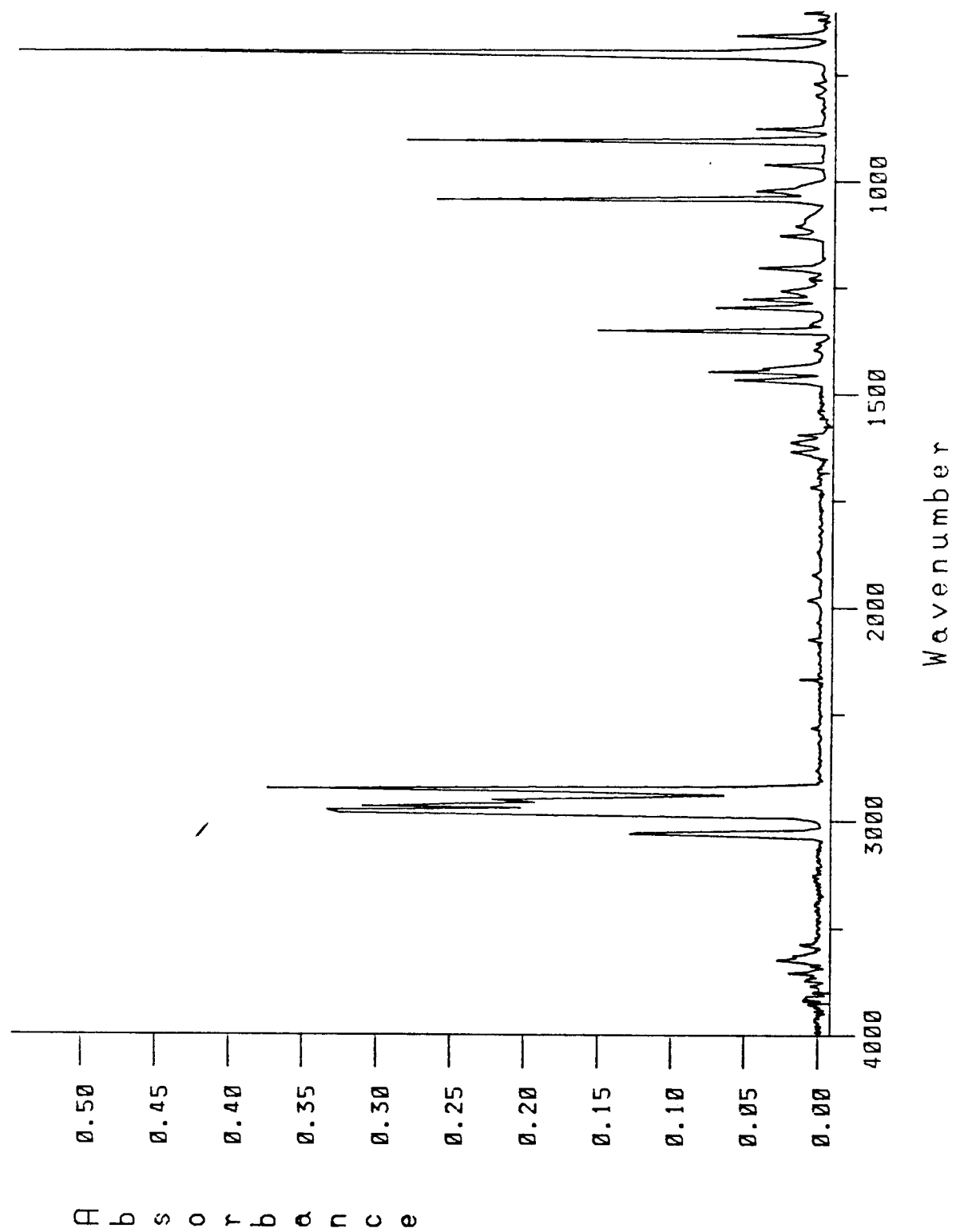


Figure 4. FT-IR Spectrum of Cyclopentene (9). Note the large peak at 699 cm^{-1} .

expansion of this region for both cyclopentene and the photolysis product. It is clearly seen that there is no evidence of cyclopentene in the product. In contrast, Closs found a 1:30 ratio of cyclopentene:bicyclopentane in his study⁸. In our study we have calculated an upper limit for this ratio of 1:200.

The diazene (7) was also used for preliminary tests on our new photolysis equipment (see below). It was chosen primarily for its availability. The experimental procedures used were identical with those given above except for the photolysis itself, which required 10 min to destroy roughly 30% of the original sample. FT-IR spectra were taken in succession beginning 29 s after photolysis. A spectrum of the partially photolyzed azo compound is shown in Figure 6; the region between 600 and 900 cm^{-1} is expanded in Figure 7. Once again, the absence of cyclopentene is evident, although 1:200 is still the upper limit for the product ratio (cyclopentene:bicyclopentane) found for the photolysis. No evidence for transients was found.

What are the reasons for the differences between our results and those of Closs? For one, our study was done in an argon matrix, while his was carried out in a hydrocarbon matrix. Michl²⁰ has shown that argon causes significantly higher intersystem crossing (ISC) rates between triplet and singlet compared to hydrocarbons. Therefore, any triplet biradical formed in our experiment would be relatively more likely to revert to the singlet. Also, ESR being a very sensitive technique, it is possible that in neither case was triplet biradical produced in large enough quantities to be observed by FT-IR. Closs' detection of the triplet biradical and our failure to detect it are then explained by the relative sensitivities of ESR and IR spectroscopies. The difference in photolysis products between our experiments and those of Closs might also be rationalized by the difference in matrix material. Closs⁸ reported a strong ESR doublet signal, presumably caused by hydrogen abstraction from the matrix. A second hydrogen abstraction by the matrix from the cyclopentyl radical would form cyclopentene. The

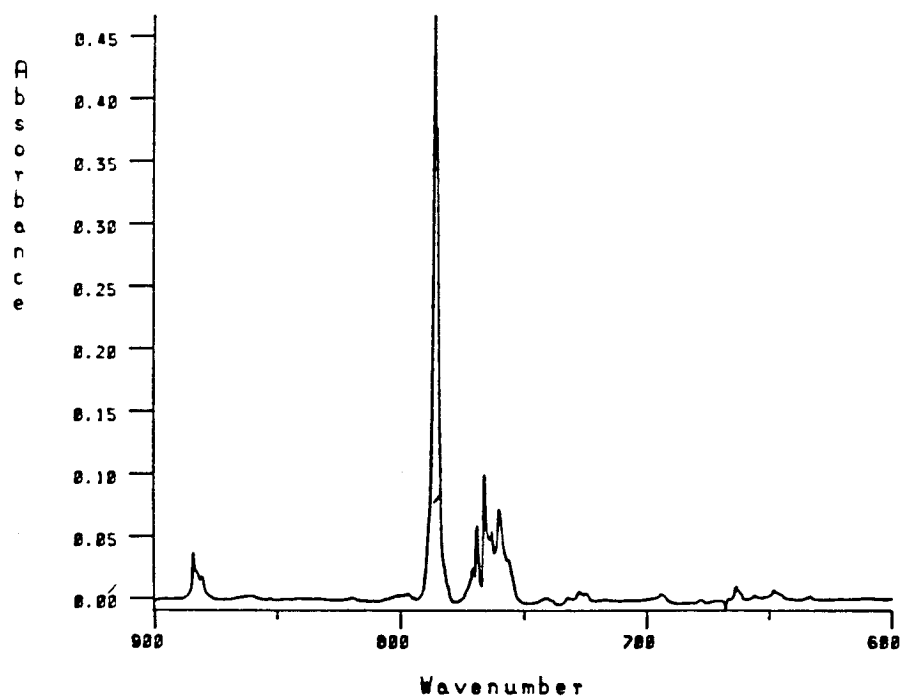
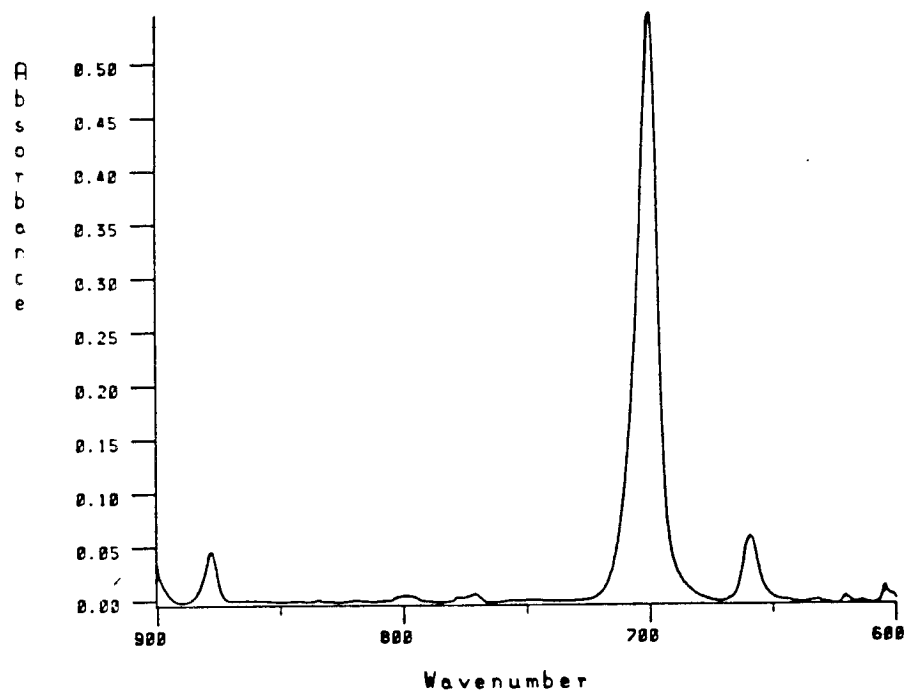


Figure 5. Comparison of FT-IR Spectra of Cyclopentene (9) and Product from the Photolysis of 7.

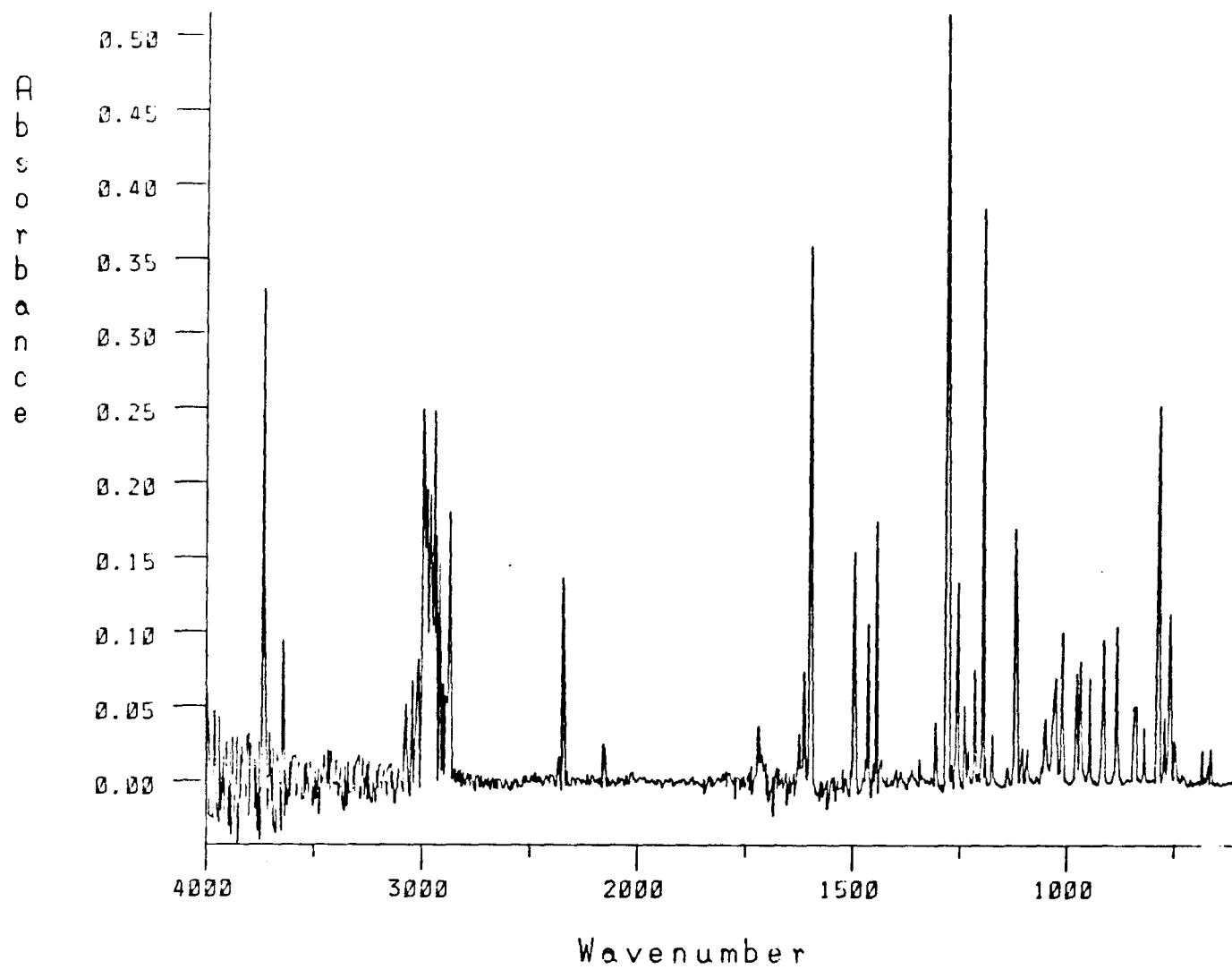


Figure 6. Spectrum of 7 Photolyzed with New Photolysis Equipment.

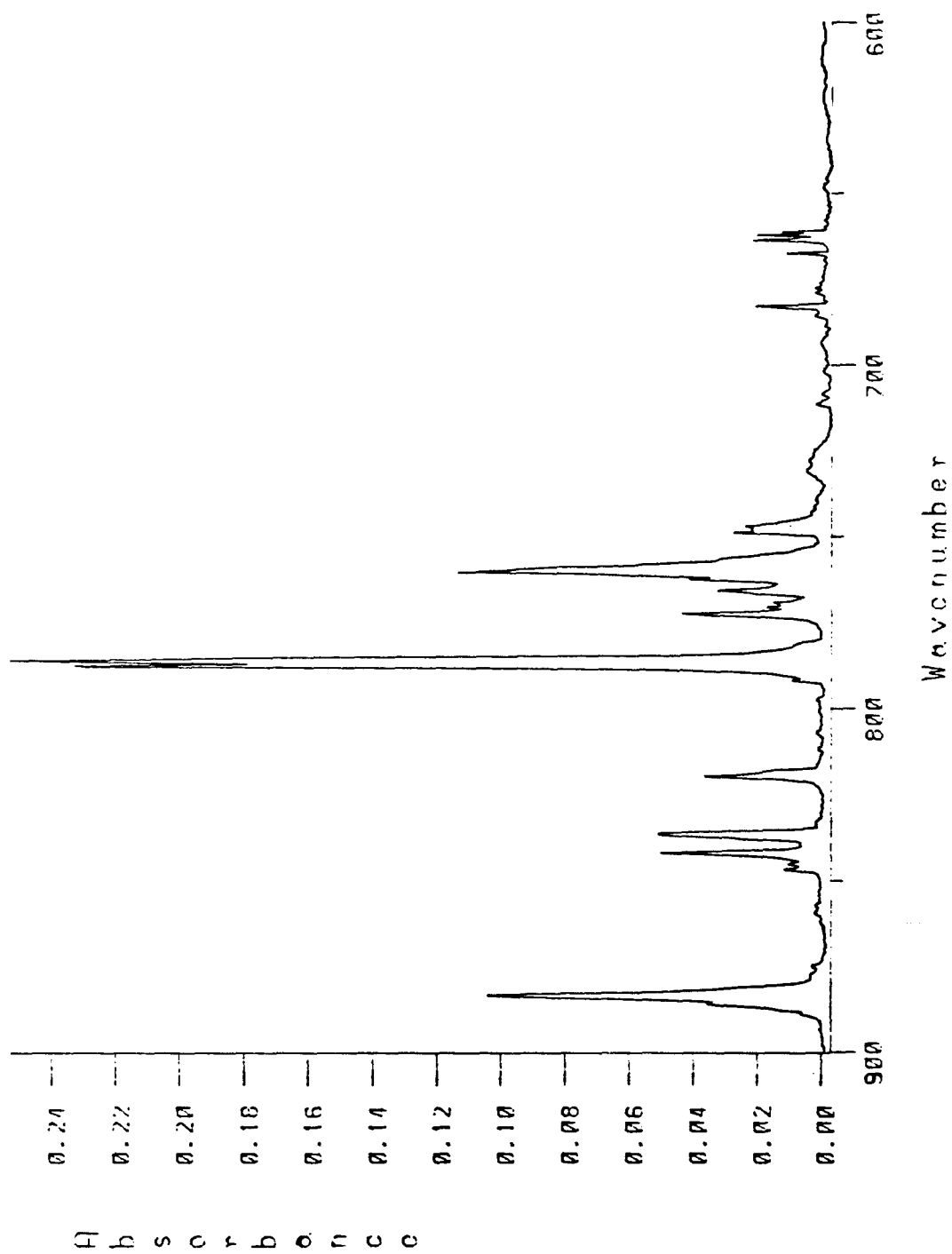


Figure 7. Expansion of Figure 6 Between 900 and 600 cm^{-1} .

driving force for this second hydrogen abstraction is the formation of the cyclopentene double bond.

Although the above explanations have by no means been thoroughly established, we can find no equally plausible alternatives. Further investigations of these effects may include the repetition of our experiment using a hydrocarbon matrix; however, these effects lie somewhat out of our primary interest of observation of 1,3-biradicals.

Matrix Isolation of 1,4-Diethyl-2,3-diazabicyclo[2.1.1]hex-2-ene (6).

The successful study of 2,3-diazabicyclo[2.2.1]hept-2-ene encouraged us to attempt the study of the 1,3-cyclobutanediyls that have been observed by ESR in our laboratories. The first of these biradicals chosen for study was the 1,3-diethyl derivative^{11c,18}. Unlike the parent compound²⁴ (1,3-cyclobutanediyl), this biradical has been observed by ESR^{11c,18}. It was presumed that the ethyl substituent would stabilize the biradical relative to the dimethyl derivative. The azo precursor (6) is stable at room temperature and quite volatile, allowing simple gas handling techniques for preparing a matrix mixture.

A sample of the azo precursor (6) was mixed with argon (1:1000) in a gas manifold and deposited onto a 20 K CsI window at a rate of 13 mmol/h. After 3 h, the deposition was halted and the matrix was cooled to 10 K. (Further details of the procedures described here may be found in the Experimental Section.) An FT-IR spectrum was taken of the matrix isolated azo compound (Figure 8). The major peaks are at 2979 cm⁻¹, 2945 cm⁻¹, 2887 cm⁻¹ (C-H stretches); 1459 cm⁻¹, 1379 cm⁻¹ (C-C stretches); and 1271 cm⁻¹ (C-N stretch). Impurities include the peaks at 2152 cm⁻¹, 1709 cm⁻¹, 1612 cm⁻¹, 1396 cm⁻¹, 1237 cm⁻¹, and 1231 cm⁻¹ (organic impurities in the manifold); 3755 cm⁻¹, 3728 cm⁻¹, 3642 cm⁻¹, 1614 cm⁻¹, 1602 cm⁻¹, 1599 cm⁻¹, and 1593 cm⁻¹ (H₂O in the matrix); 2347 cm⁻¹, and 2340 cm⁻¹ (CO₂ in the matrix).

The matrix was photolyzed with a 1000 watt Hg(Xe) lamp through Schott UG-11, KG-5, and WG-305 filters. This filter combination passes light between 310 and 380 nm. The matrix was photolysed for 7 min, resulting in the destruction of roughly 70% of the azo precursor. A spectrum of the matrix after photolysis is given in Figure 9. The remaining azo compound peaks were digitally subtracted to give the spectrum of pure products (Figure 10). The region of the spectrum between 1500 and 600 cm⁻¹ for Figures 8 and 10 is shown in

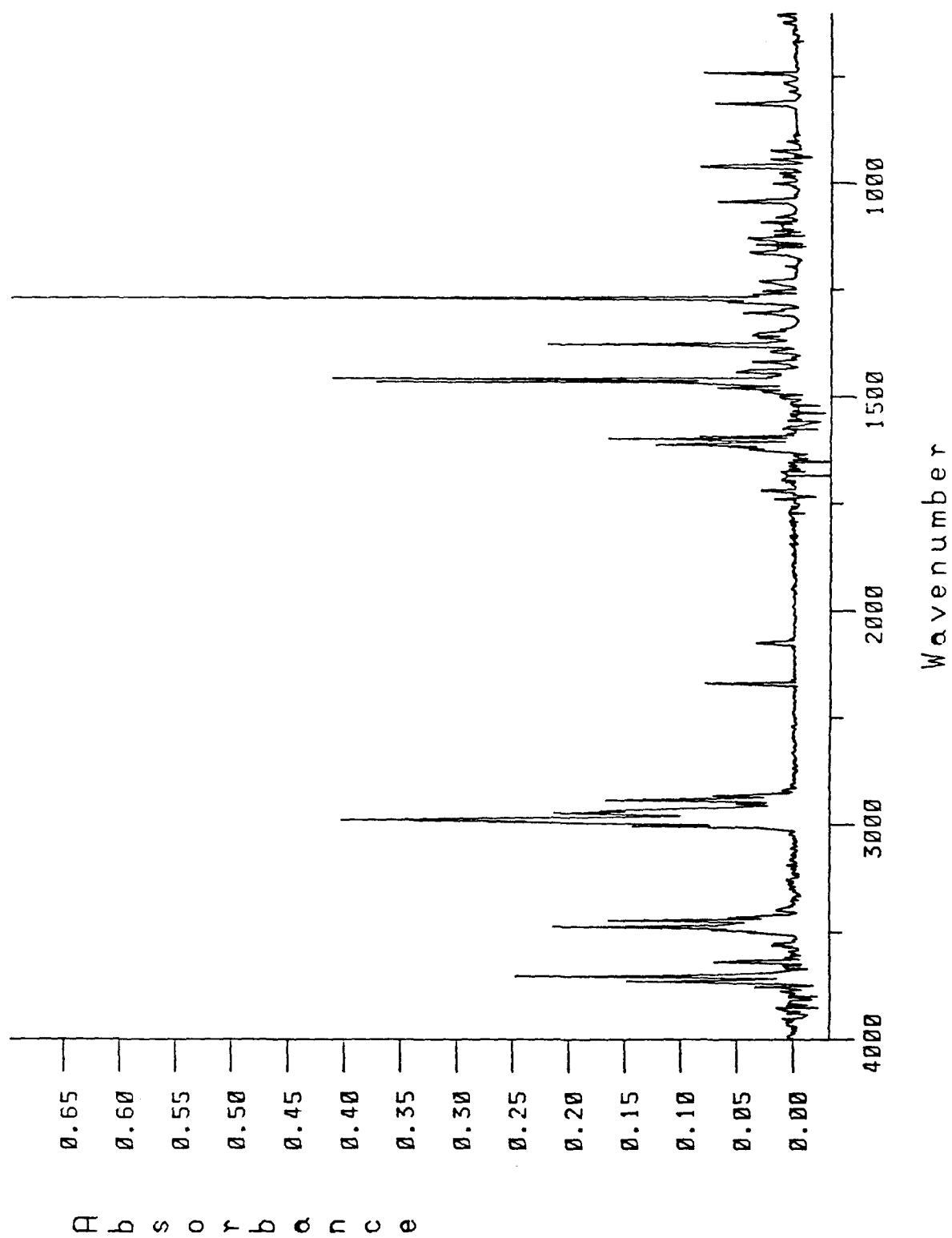


Figure 8. FT-IR Spectrum of 1,4-Diethyl-2,3-diazabicyclo[2.1.1]hex-2-ene (6).

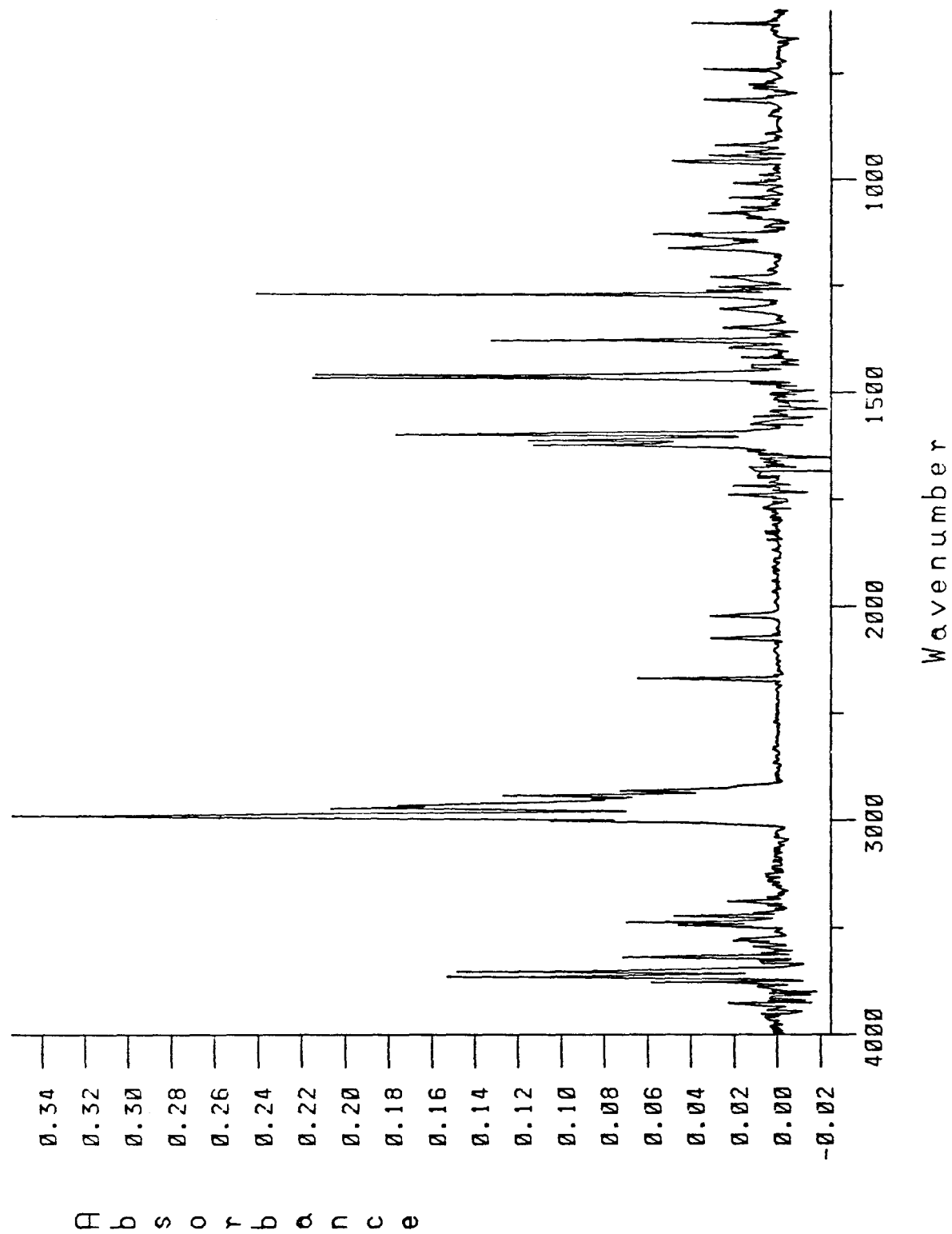


Figure 9. FT-IR Spectrum of Photolysis Product of 6.

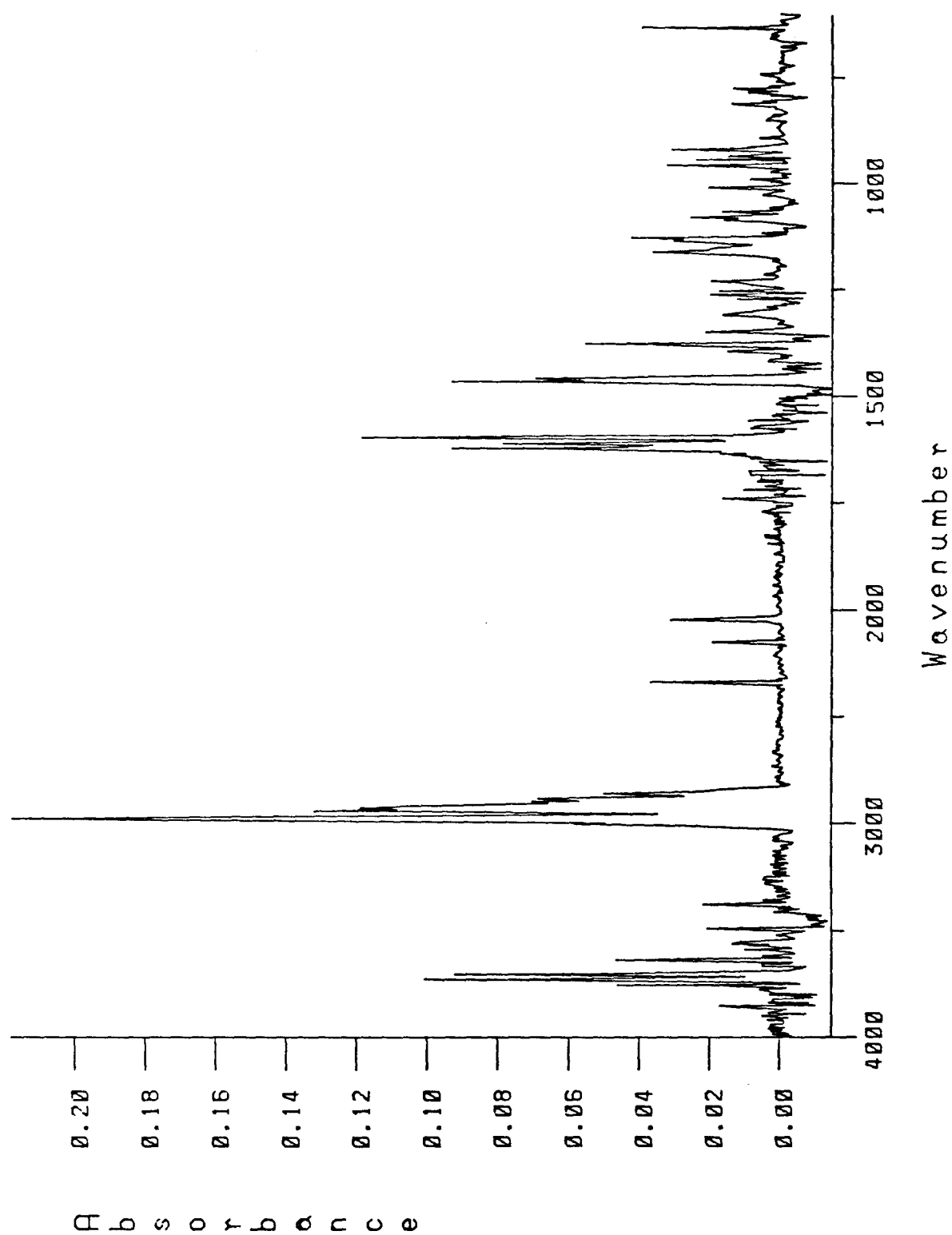
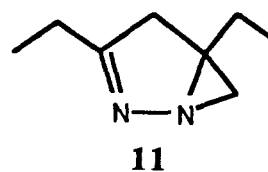
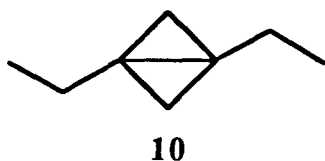


Figure 10. FT-IR Spectrum of Photolysis Product After Subtraction of 6.

Figure 11. Note the major peaks at 2981 cm^{-1} , 2945 cm^{-1} (C-H stretches); and 1378 cm^{-1} (C-C stretch). The obvious expected product of this photolysis is 1,4-diethylbicyclobutane (10). No authentic sample of this compound was available to compare with the product spectrum; however, evidence exists that points to the bicyclobutane as the major product. A study of the vibrational spectrum of the parent bicyclo[1.1.0]butane has been published²⁵. The normal coordinate analysis therein lists frequencies at 2896 cm^{-1} (C-H stretch), 1113 cm^{-1} (C-H bend), 1110 cm^{-1} (ring flex), and 735 cm^{-1} (ring twist). All these absorptions should be found in the diethyl derivative. The corresponding frequencies in the photolysis product spectrum are 2901 cm^{-1} , 1137 cm^{-1} , 1129 cm^{-1} , and 633 cm^{-1} . This correspondence is suggestive that 1,4-diethylbicyclobutane (10) is the major product, although 3,5-diethyl-1,2-diazabicyclo[3.1.0]hex-2-ene (11) is a possibility.



Beginning 150 s after the completion of photolysis, a time-series of FT-IR spectra of the photolyzed matrix were taken. Upon subtraction one from another, a very startling feature became apparent: the amount of starting material increased with time. This increase was significant, amounting to 2-3% of the original sample. This effect was visible in all subtracted spectra, for an example see Figure 12. For a plot of the total increase *versus* time, see Figure 13. We feel this is a real effect, not instrumental error. The increase is greatest immediately after photolysis and declines thereafter (see Figure 13). Also, close examination of the spectra showed that several peaks from the azo precursor grew back, not the largest one (in Figure 12) alone. Unfortunately, no peaks could be seen to have disappeared over time. We conclude from this data that some unknown intermediate is being formed and decaying to the starting azo compound.

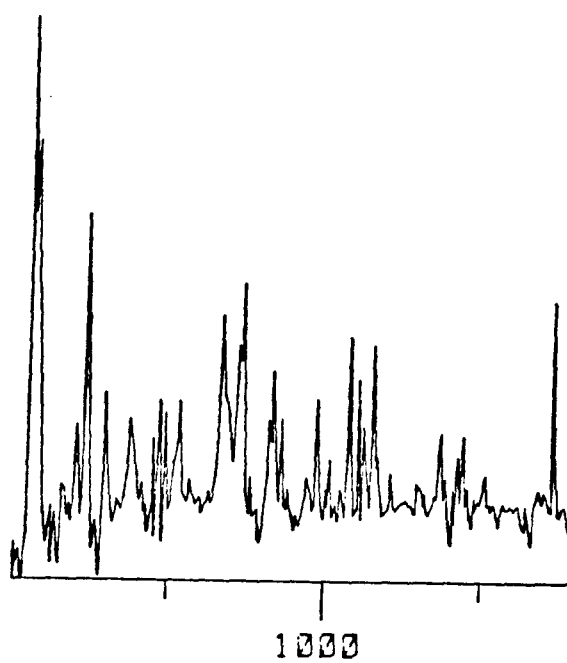
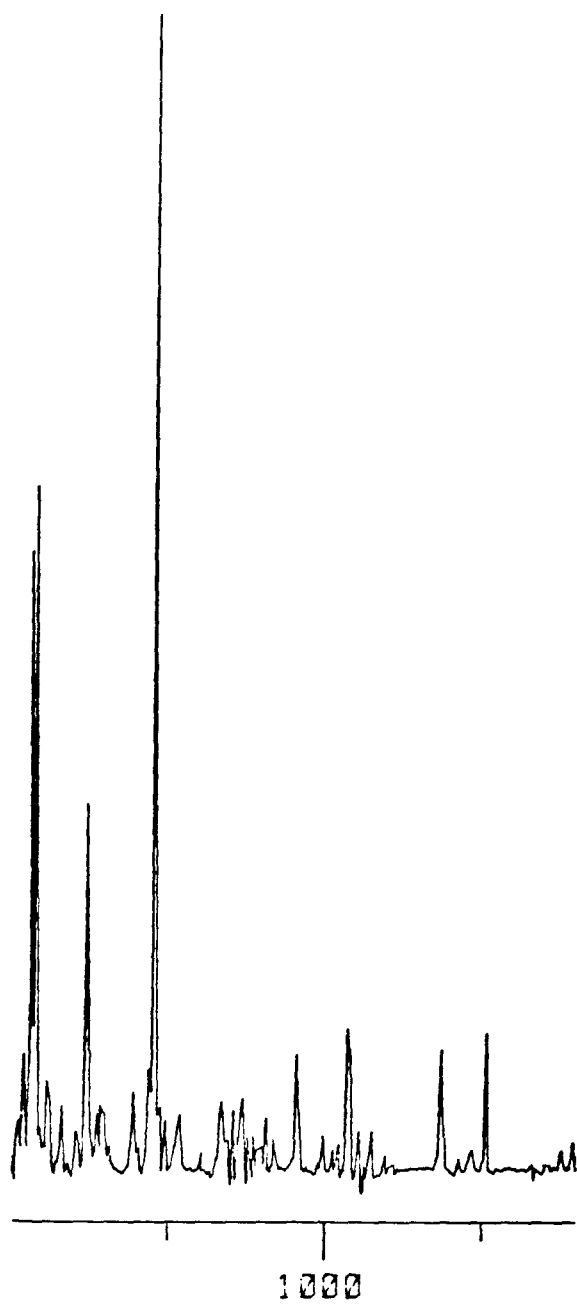


Figure 11. Figures 8 and 10 Between 1500 and 600 cm^{-1} .

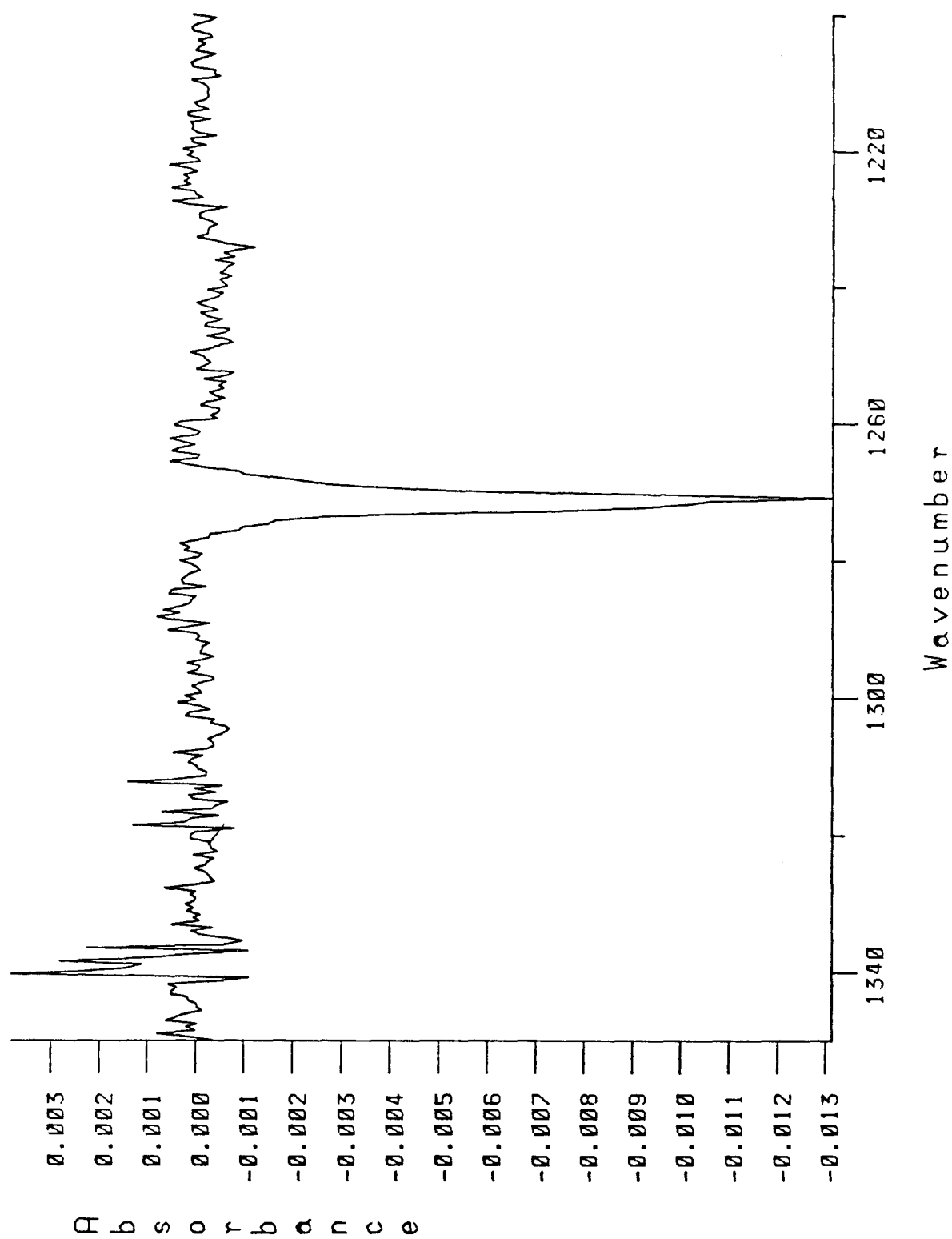


Figure 12. Subtracted FT-IR Spectrum from Two Consecutive Scans After the Photolysis of 6. Negative peaks indicate an increase in concentration over time. The peak at 1337 cm^{-1} is due to atmospheric water.

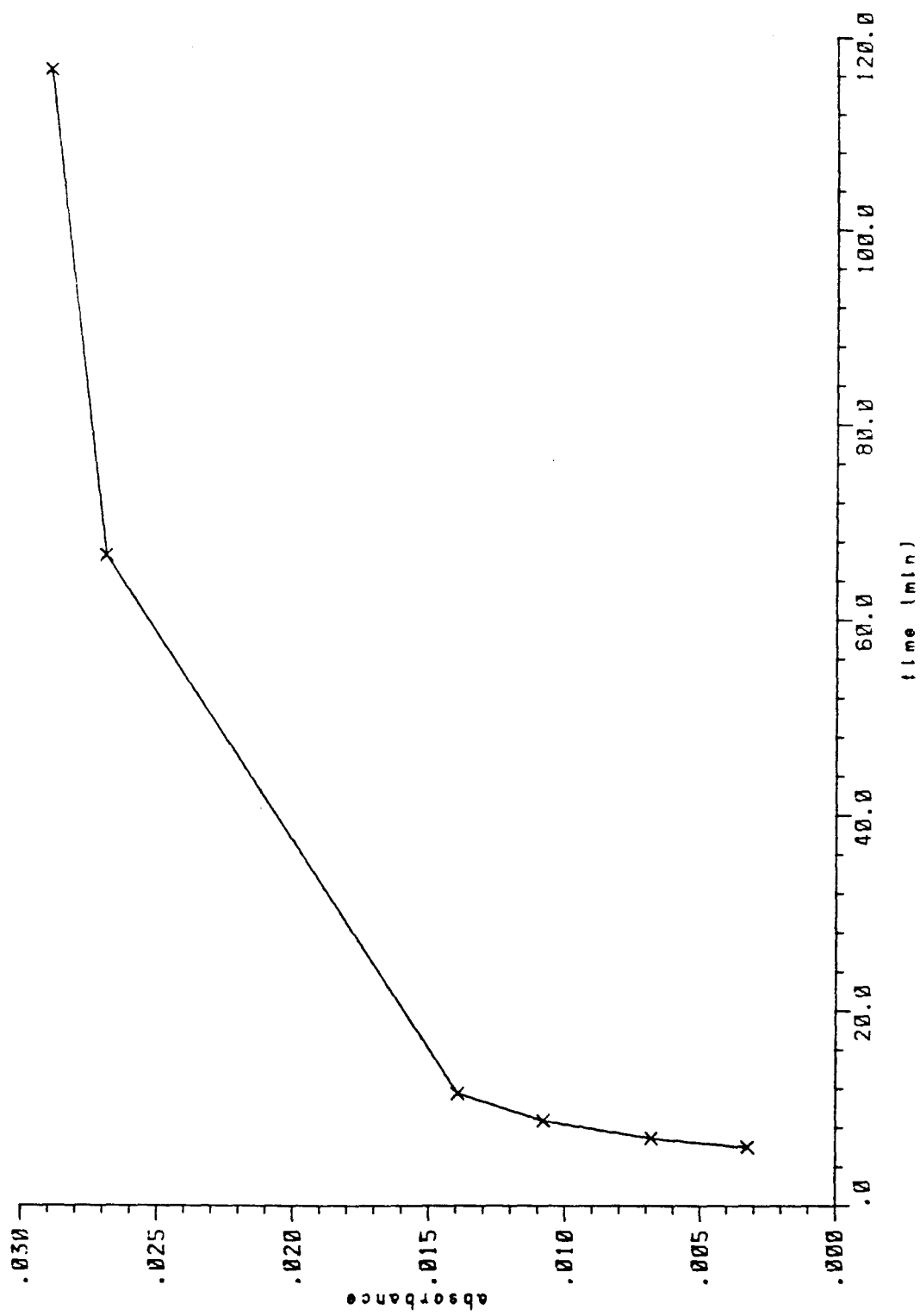
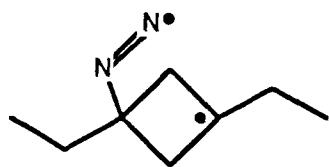


Figure 13. Growth of Absorption at 1271 cm⁻¹ Over Time.

An effort was made to understand the kinetics of the formation of the azo precursor. Simple first and second order decay plots are given as Figures 14 and 15. Unfortunately, but somewhat typically, the reaction is not simply first (or second) order. We believe that this is another instance (among many) of matrix site effects on reaction kinetics^{8,26,27}. Initial rates are high; the signal growth has an initial half-life of roughly 1-2 min. After one hour, no appreciable further change is evident in the spectrum.

The exact nature of the intermediate in this reaction is intriguing. We envision two possibilities. In the first, photolysis results in cleavage of only one C-N bond, resulting in a diazenyl biradical (12). This biradical could then close to form the azo precursor. The diazenyl biradical should produce a strong infrared band between 1400 and 1600 cm^{-1} . Unfortunately, water vapor in the spectrometer cavity introduces very large amounts of noise in that region. The second possibility is that two bond cleavage takes place upon photolysis; the intermediate is therefore our goal: 1,3-diethyl-1,3-cyclobutanediyl (13). This biradical could



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13



14

then attack the extruded nitrogen molecule to reform the starting azo compound. Evidence for this is the presumed low IR activity of the hydrocarbon biradical due to its lack of polarity, accounting for our failure to observe it. Nevertheless, this is negative evidence and as such it is not particularly persuasive. In either case, the singlet biradical would react much too quickly for us to observe it in this manner; the biradical must have a triplet ground state.

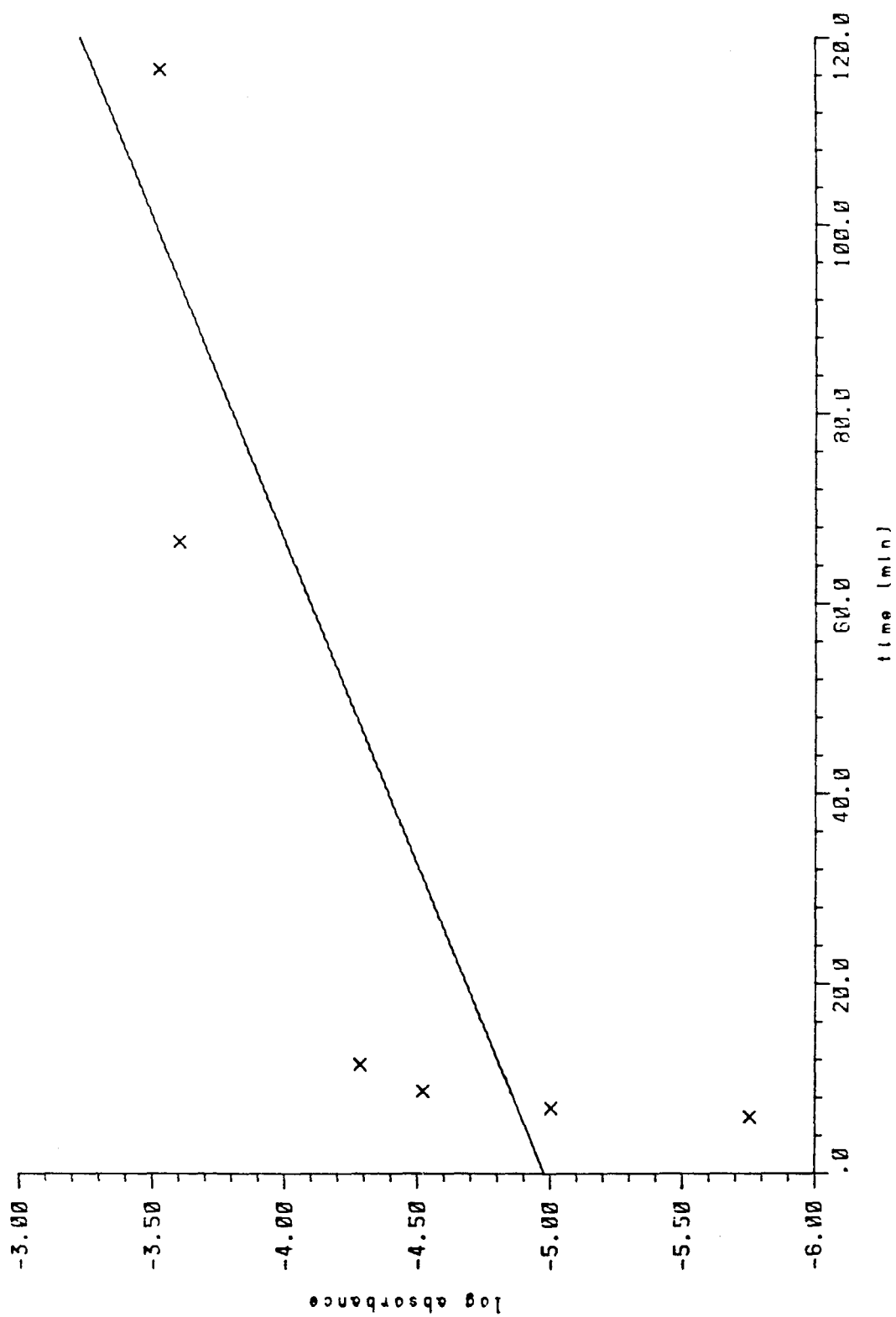


Figure 14. First Order Kinetic Plot of 1271 cm^{-1} Growth. Note extreme non-linearity.

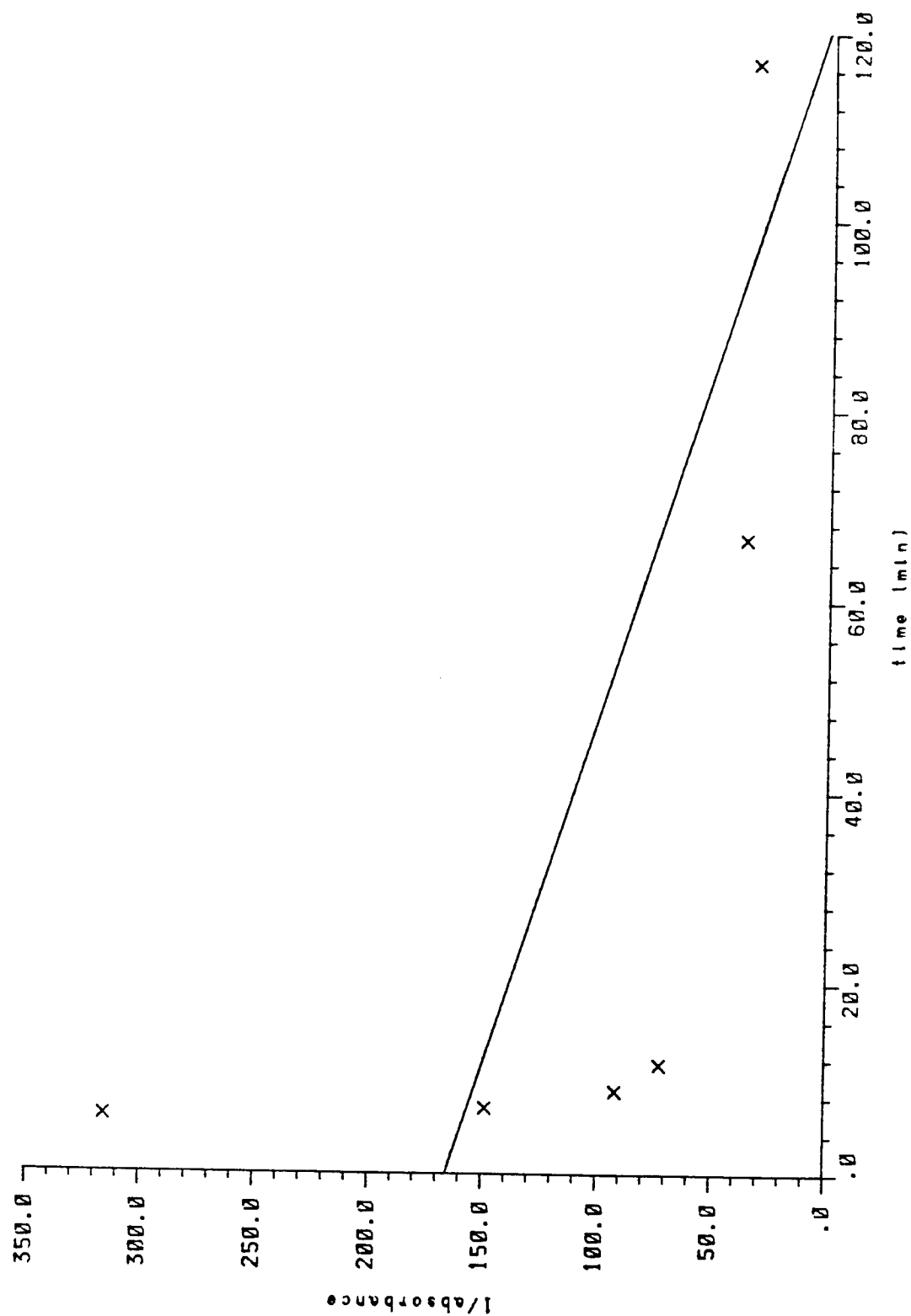


Figure 15. Second Order Kinetic Plot of 1271 cm^{-1} Growth. Note extreme non-linearity.

An attempt was made to confirm our indirect observation of an intermediate in the photolysis of **6** using our newly constructed photolysis arrangement (see below). The conditions of the experiment are those described above, with the exception of the photolysis time, which was 20 min and resulted in the destruction of 55% of the diazene. FT-IR spectra were recorded in succession, beginning 21 s after photolysis.

The product of the photolysis is identical to that found from previous studies; it may be 1,3-diethylbicyclo[1.1.0]butane (**10**) or 3,5-diethyl-1,2-diazabicyclo[3.1.0]hex-2-ene (**11**) (see Figure 16). Unfortunately, no transients were detected in this experiment. This is some cause for concern as to whether the previous results were in error. It does not, however, rule out the possibility of their correctness for several reasons. First, it may be that the low rate of photolysis with our current experimental setup causes an undetectable concentration of the intermediate to be present under steady state conditions. Also, an accidental corruption of one of the data files by the experimenter resulted in a fairly narrow time baseline over which to compare data.

We hope to correct these deficiencies in the future by using a higher concentration of diazene (1:200 or more), thereby allowing a higher concentration of intermediate to be formed. Other possibilities for progress include laser photolysis and an attempt to repeat our original experiment with the previous photolysis setup. These experiments should clear up the question of the existence of the intermediate, if not its identity.

A diazene related to **6** is the diethenyl compound (**14**). It can be made by a slight deviation from our synthesis of **6**. The biradical produced from its photolysis (**15**) should be more stable. In the future, we would like to study it and other more stable biradicals such as and the dimethylene (**16**) compound. These biradicals would very likely be stable at our matrix temperatures, allowing their spectra to be recorded at leisure.

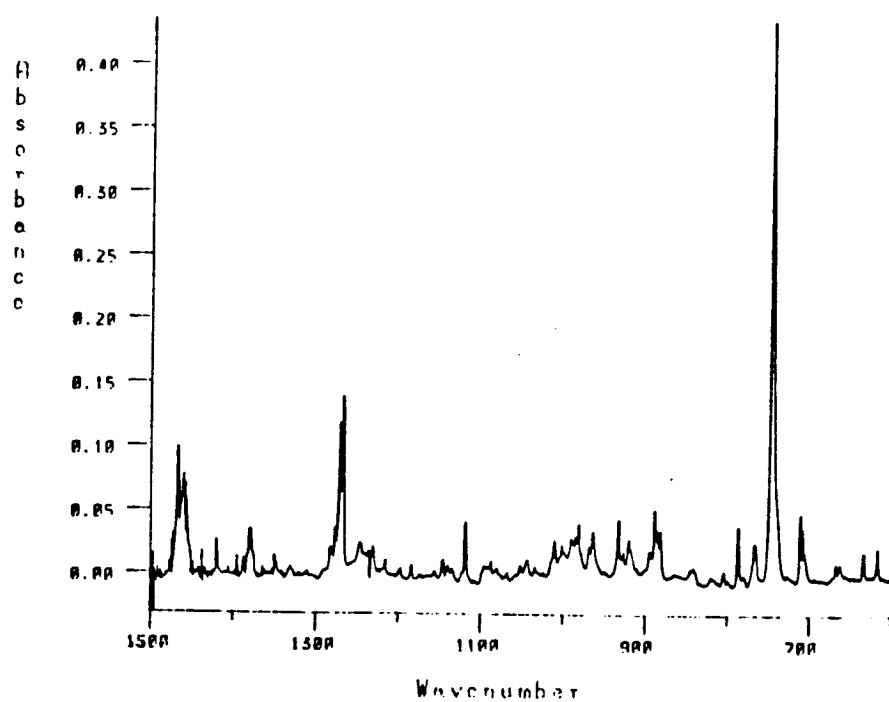
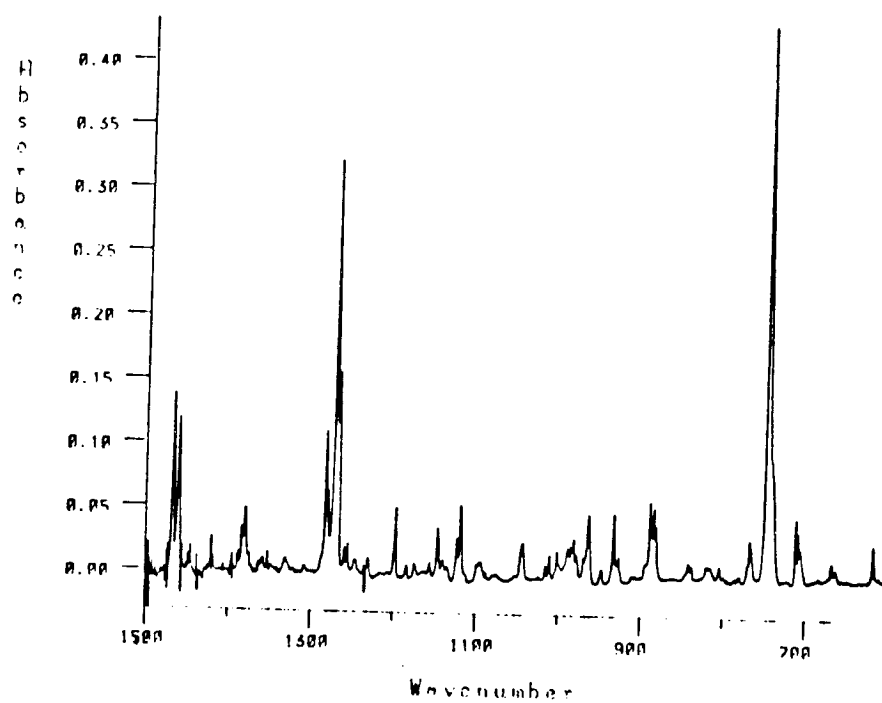
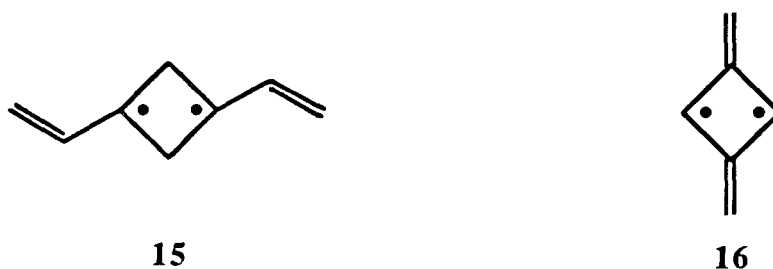


Figure 16. Diazene 6 Before and After Photolysis: 1500 to 600 cm^{-1} .



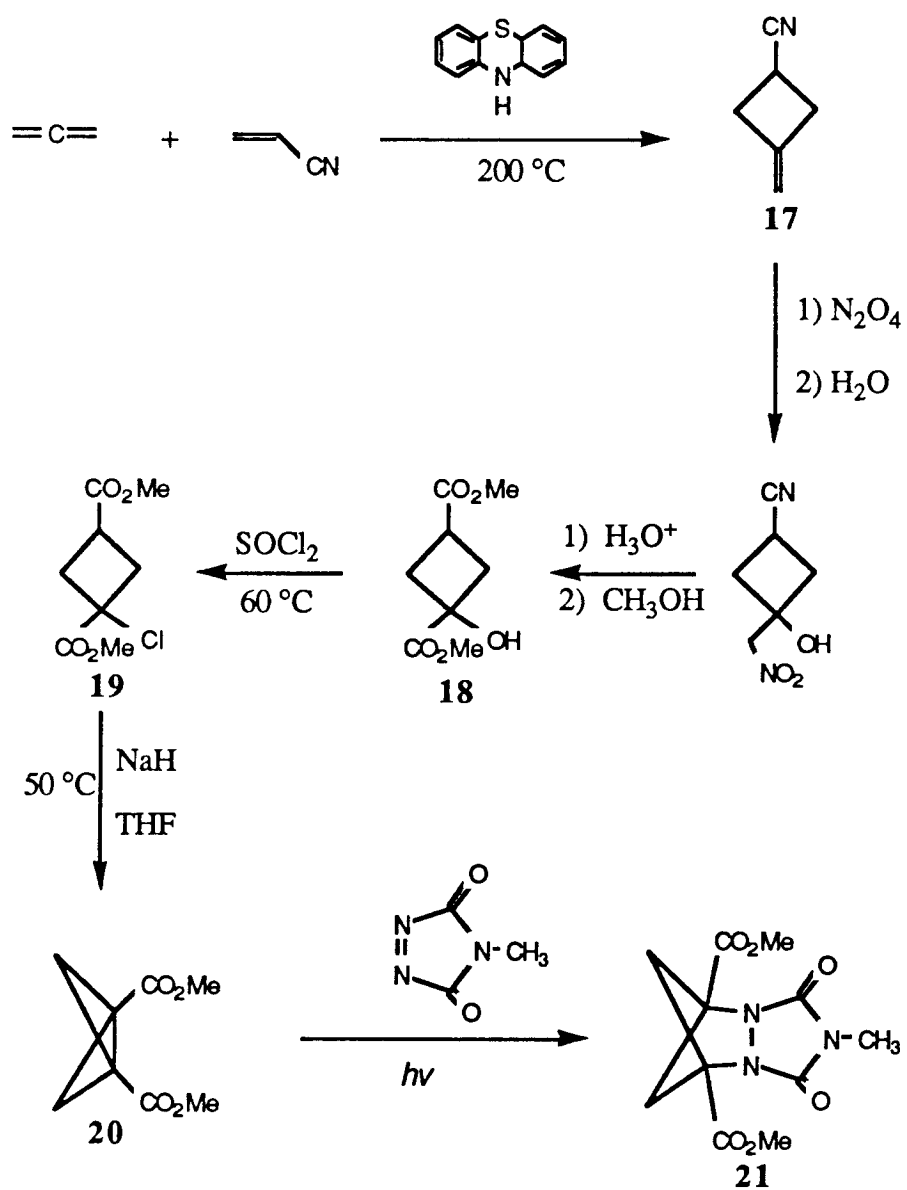
Synthesis

A synthesis of one of the above azo compounds, 1,4-diethyl-2,3-diazabicyclo[2.1.1]hex-2-ene (**6**), has been developed in our laboratories^{11c,18}. In order to conduct further FT-IR research of this compound, we attempted a large scale (~.5 g) synthesis of it. The synthesis used (see Schemes I and II) was a slight variation of that presented in Jain *et al.*^{11c}

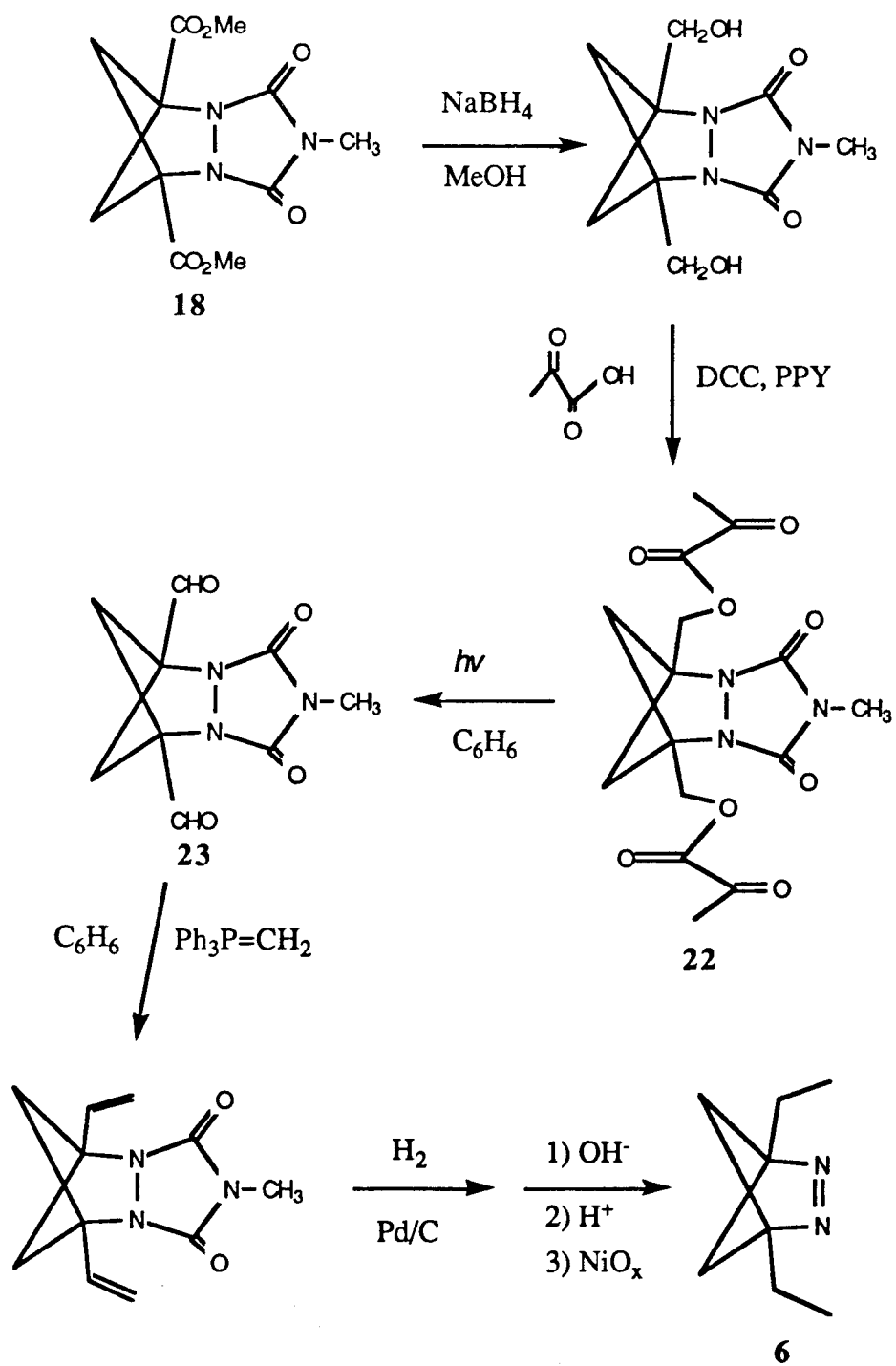
The steps outlined in Scheme I are fairly simple and are detailed in the Experimental Section²⁸. The resultant diester (**21**) was easily reduced to the corresponding diol. Formation of the pyruvate diester^{11c,29} (**22**), however, was more difficult, and low yields were sometimes obtained, probably due to the facile reversion to the diol. The photolytic rearrangement to the dialdehyde^{11c,30} (**23**), followed by a Wittig coupling to give the diene, gave the most difficulty in the synthesis.

The root of the problem was almost certainly the extreme water sensitivity of the dialdehyde. This series of reactions (photolysis followed by Wittig) was run several times with very limited success (yields ~8-12%). After precautions were taken to keep exposure to air to

Scheme I



Scheme II



an absolute minimum, a yield of 24% was obtained and the combined product was carried on into the synthesis. The diene was first hydrogenated with a standard Pd/C catalyst and H₂ gas.

The standard method of preparing this azo had previously been the generation of a copper-azo complex by oxidation of the semicarbazide *in situ* with CuBr^{11c}. It was decided that a cleaner method would be isolation of the semicarbazide (taking care not to form the corresponding hydrazine during hydrolysis), followed by oxidation to the azo compound with nickel peroxide^{11b}. The solvent was pumped away from the product at -45°C; and the azo compound was vacuum transferred away from any impurities.

Instrumental Modifications

The difficulty with atmospheric water and carbon dioxide absorptions in the FT-IR spectrometer cavity has been previously mentioned. We have undertaken a redesign of our experimental equipment in order to ameliorate this problem. In essence, we have made it possible to perform photolysis while the matrix isolation apparatus is inside the nitrogen-purged spectrometer cavity. This arrangement might remove several other troublesome aspects of our current setup. Among these are unstable spectral baselines due to imperfect realignment of the matrix in the spectrometer, and the ~200 s time delay between photolysis and spectra due to the necessity of moving the matrix from the photolysis equipment to the FT-IR instrument.

A schematic diagram of our new setup is given in Figure 17. A 100 cm focal length quartz lens is used to collimate the light from our photolysis source. The light is reflected from a diagonal mirror onto the matrix window, which has been tilted 45° with respect to both photolysis and infrared scanning beams. This arrangement allows photolysis and accumulation of spectra without disturbing the matrix isolation apparatus. One drawback to this setup is the loss of FT-IR signal caused by the angle of the matrix window. This does not seem particularly troublesome. Of further concern is the efficiency of the focussed UV photolysis beam.

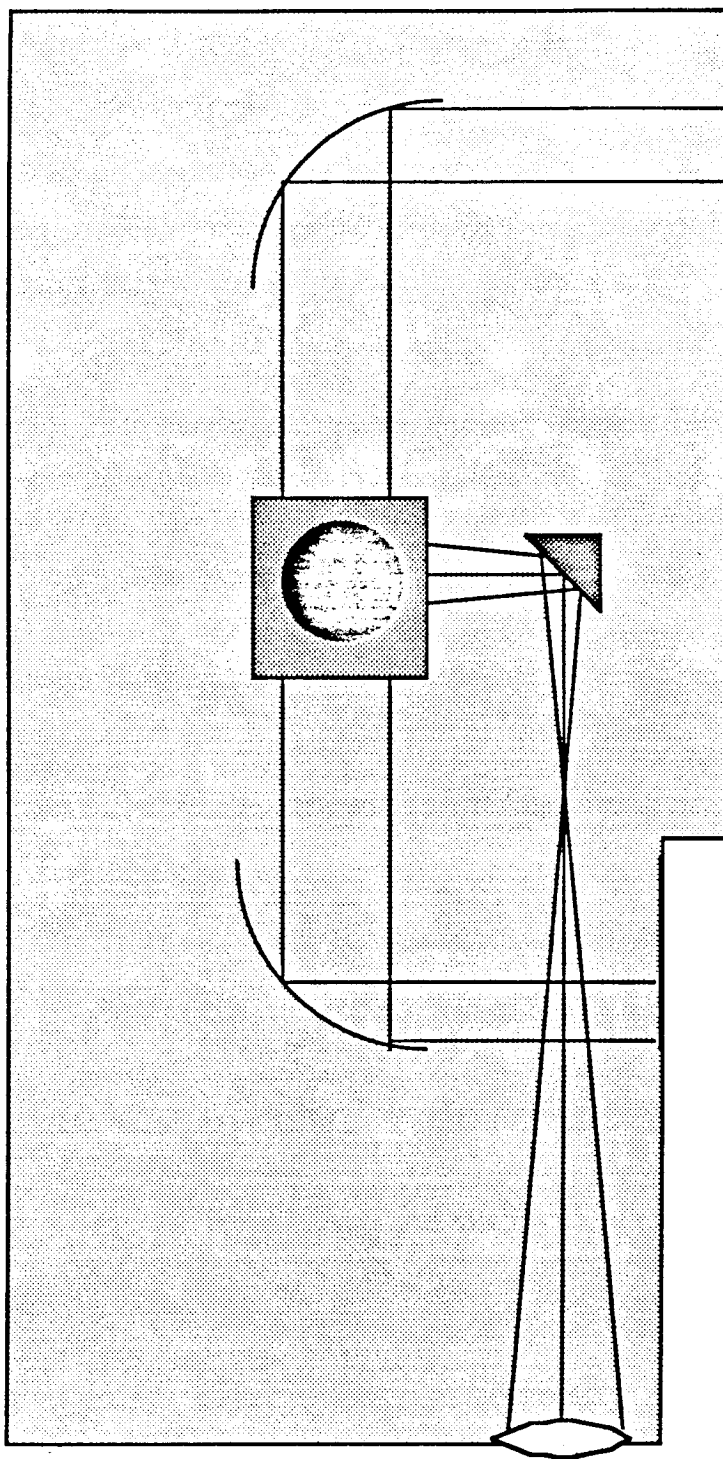


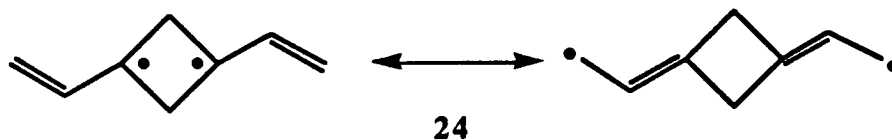
Figure 17. Schematic Diagram of Improvements Made to the FT-IR Spectrometer Cavity.
(To scale, 1:3)

During preliminary experiments with Closs' azo (see above), the efficiency of photolysis inside the spectrometer was estimated at approximately 20% relative to the previous arrangement outside the spectrometer. Most of this effect may be attributed to the fact that our photolysis lamp is not a point source. The beam's focus therefore depends strongly on the distance between the sample and the nearest lens.

The light path of the UV photolysis beam is shown on Figure 18. The prefocussing lens is a 100 mm focal length, 2" diameter, quartz lens. The lens in the instrument wall is similar (Oriel part # 41765). The diagonal mirror is 2" in diameter aluminum front surface coated glass (CVI Laser Inc. part # B20AL). The mirror mount is Oriel part # 19283.

Computational Studies of 1,3-Dietheny-1,3-cyclobutanediyl

In order to verify our group's deductions from experimental data regarding the electronic structure of our biradicals (1,3-cyclobutanediyls), we decided to pursue an *ab initio* study of the 1,3-diethenyl biradical. This study was undertaken in conjunction with Chem 120c. The biradical in question is notable in that the radical electrons are delocalized by the double bonds (24). The study was conducted at the Hartree-Fock level for the triplet, and at the GVB(1/2)



level for the singlet. The integrals were calculated using molecular symmetry (C_{2h}) with the Goddard group's HONDOSYM program³¹. The HF calculations were carried out with the Goddard group's GVB2.5 program³².

Because of the size of the molecule to be studied, geometry optimization was ruled out at the beginning. The geometry was constructed from the optimized geometry of cyclobutane-diyl¹⁸ and the experimental geometry of the allyl radical³³. The adopted bond lengths were as follows: 1.048Å for ring C-C bonds; 1.086Å for C_{2,4}-H bonds; 1.428Å for allyl C-C bonds; 1.069Å for allyl C-H bonds. Bond angles were as follows: $\angle C_2-C_1-C_4 = 93.41^\circ$; \angle allyl chain = 124.6° ; ring $\angle H-C-H = 107.6^\circ$; central $\angle H-C-C = 117.7^\circ$; terminal $\angle H-C-H = 118.2^\circ$. The molecule is planar except for the hydrogens on the ring. The basis set chosen for this study was the valence double- ζ (VDZ) set of Dunning *et al*³⁴. The molecule has a total of 92 basis functions with this basis set.

The molecule that was chosen for study proved especially difficult to converge. In fact, this molecule could not be converged in a previous attempt by our group using a variety of programs. Our method of convergence follows. First, one electron orbitals for each symmetry type were partially converged. The virtuals produced in that procedure having bonding characteristics were selected by chemical intuition; these orbitals were filled two at a time. The previously converged core was frozen, and the next two orbitals were converged. The core was then unfrozen and reoptimization allowed to take place. This technique was adequate for the orbitals representing the C 1s core and those representing the C-C bonds, but the C-H bonds could not be added in this manner. These orbitals were altered by hand to enhance their H character, and were filled all at once. The wavefunction was then converged until the sum of squares of the differences in coefficients was $< 10^{-13}$. The absolute energies of the triplet and singlet states were calculated to be -308.48649961 and -308.48489614 hartree respectively. The singlet-triplet gap was found to be 1.026 kcal/mol at the HF level, triplet being the ground state.

The in-plane " σ " core orbitals of the triplet are shown in Figure 19. The more interesting " π " out-of-plane orbitals of the triplet are shown in Figure 20. The singly occupied orbitals for

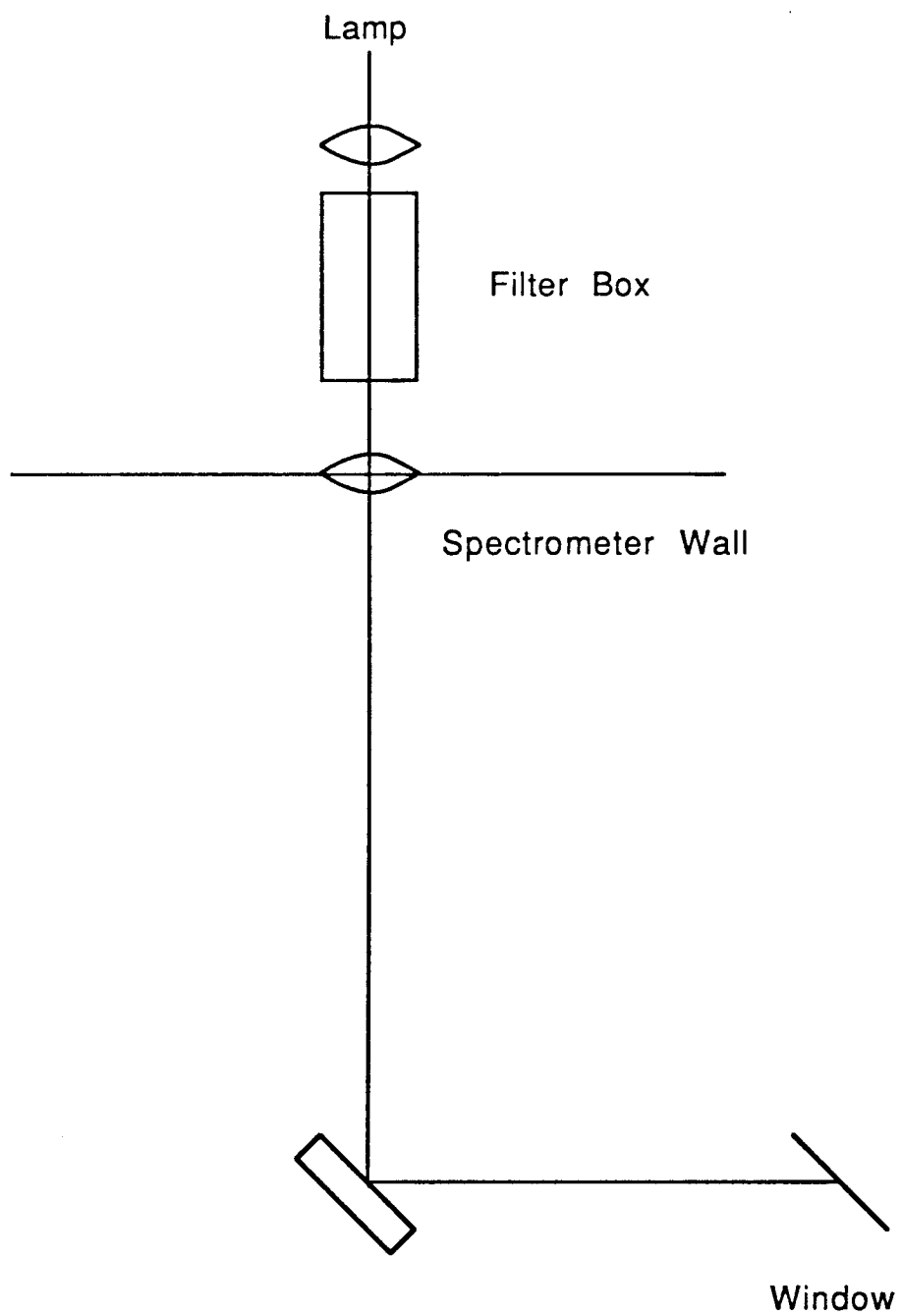


Figure 18. Light Path of the New Photolysis Arrangement.

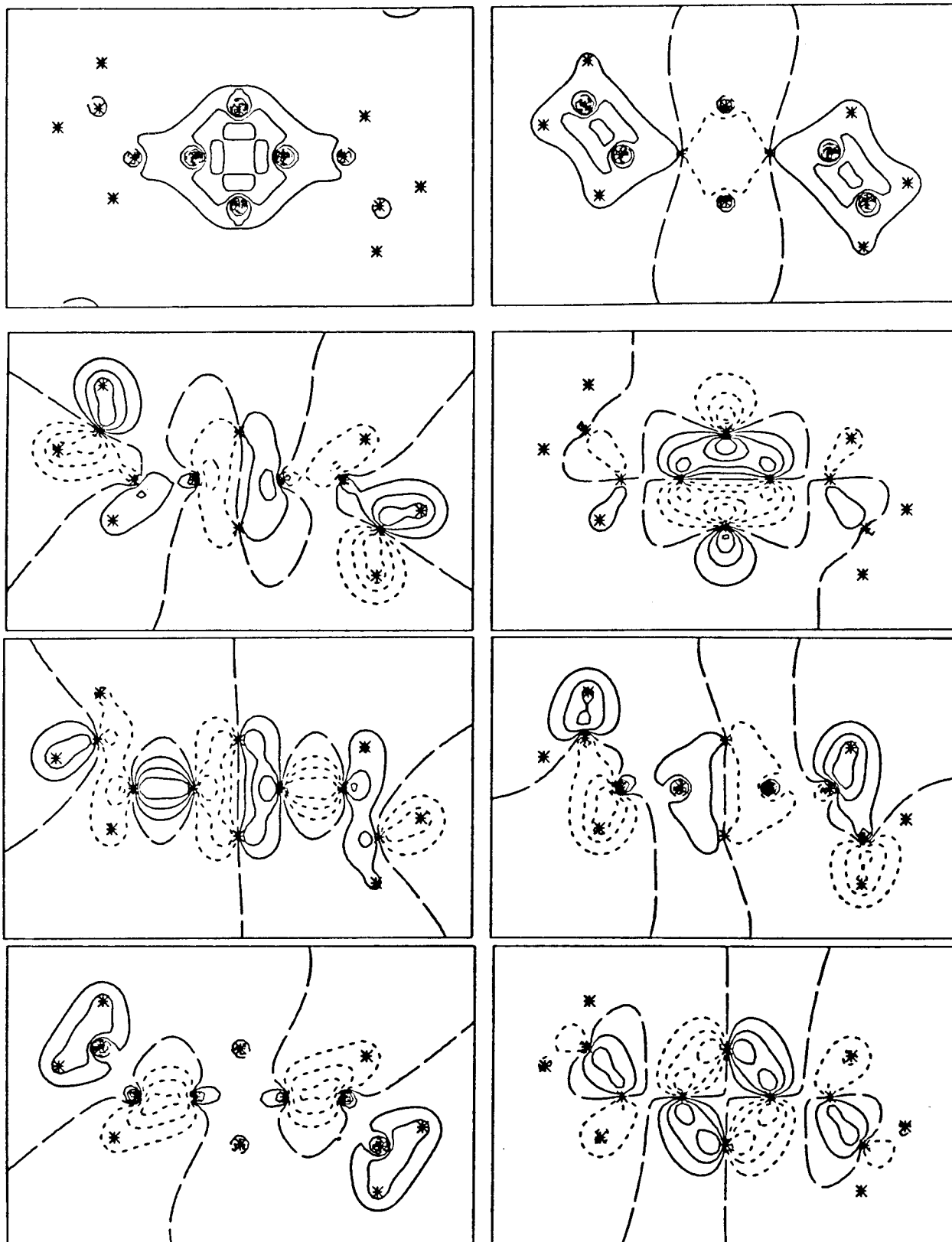


Figure 19. In-plane (σ) Orbitals of the Triplet. Carbon Framework Plane is Shown.

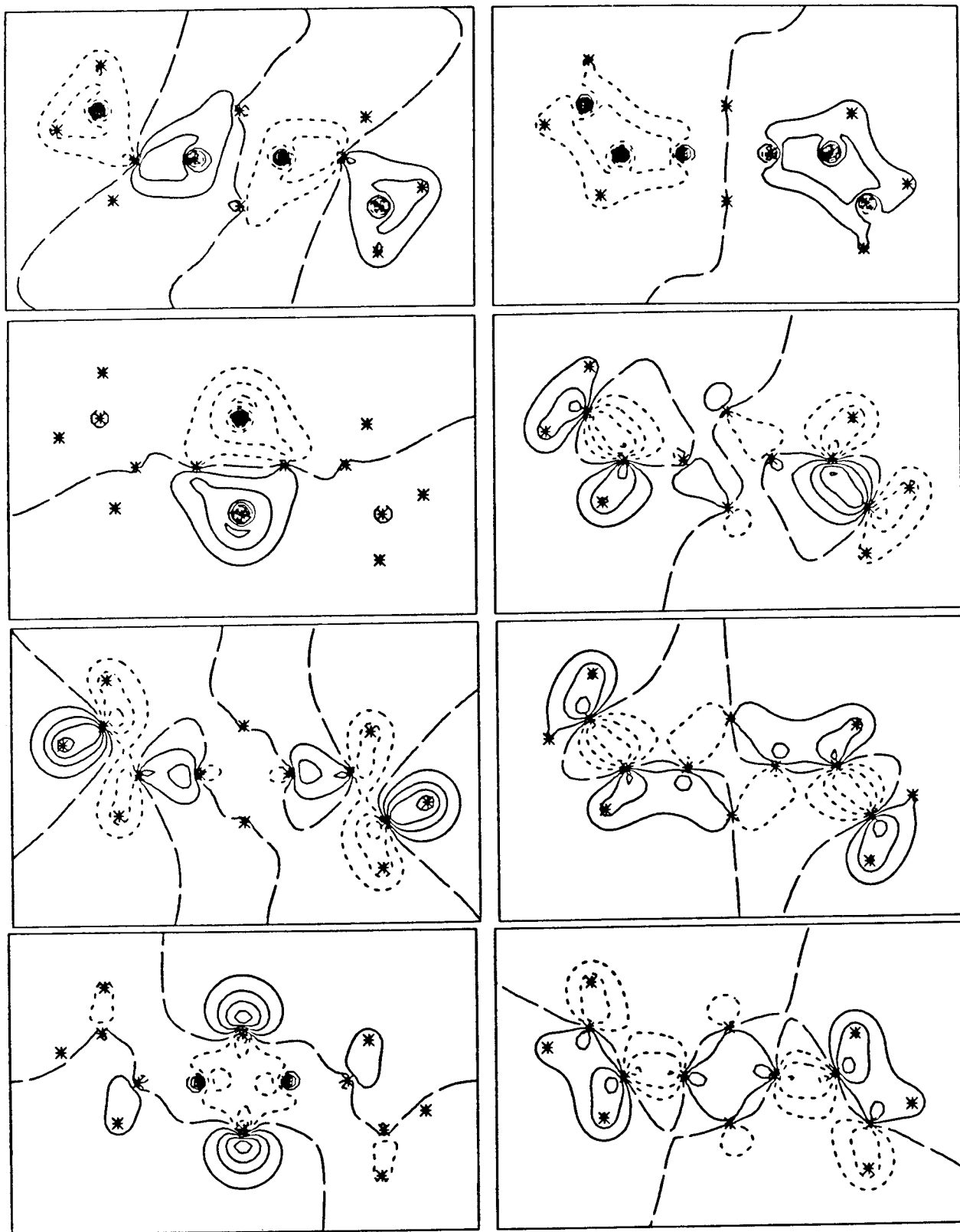


Figure 19. (cont.)

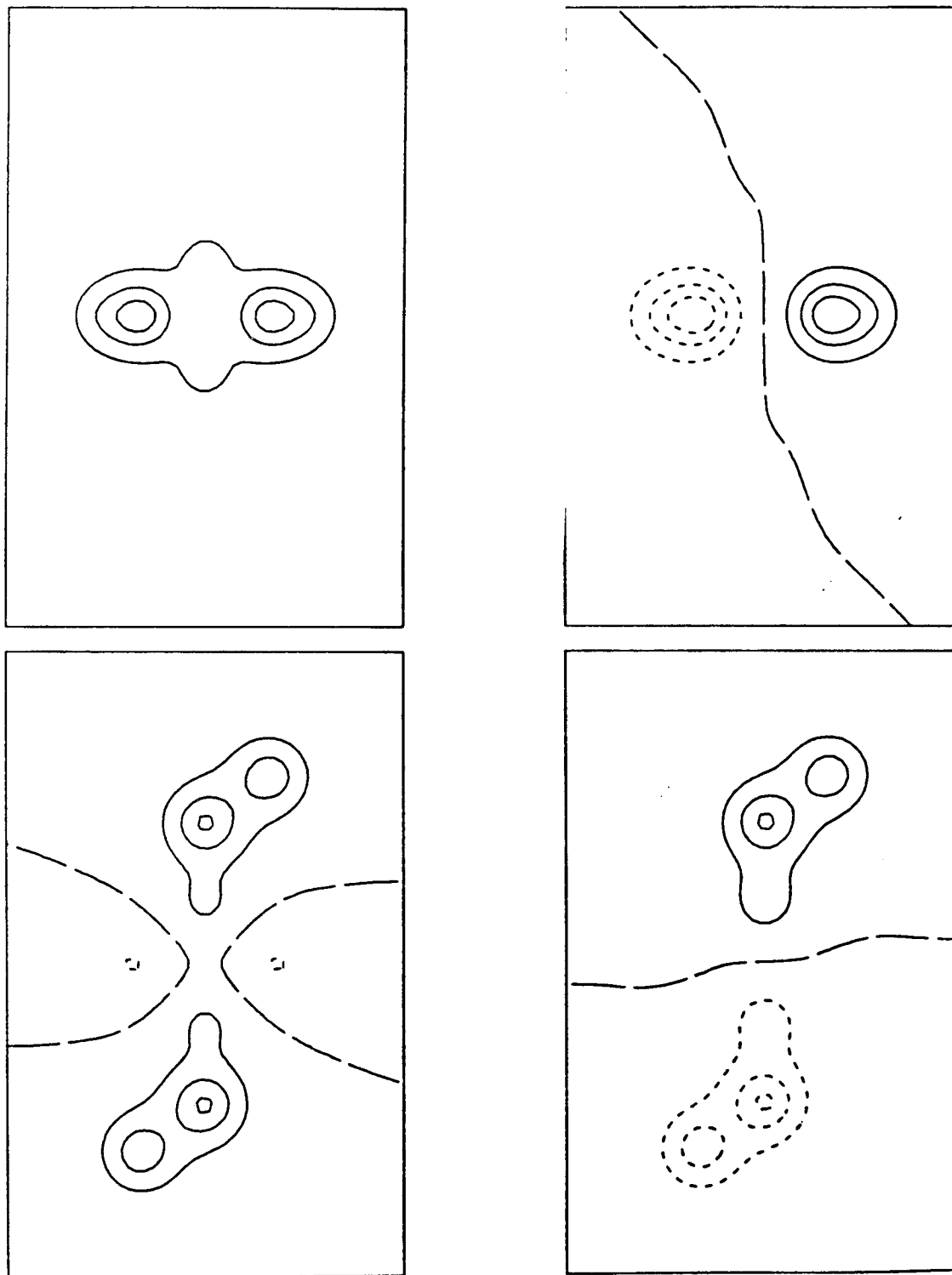


Figure 20. Out-of-plane (π) Orbitals of the Triplet (.5Å above carbon framework plane).

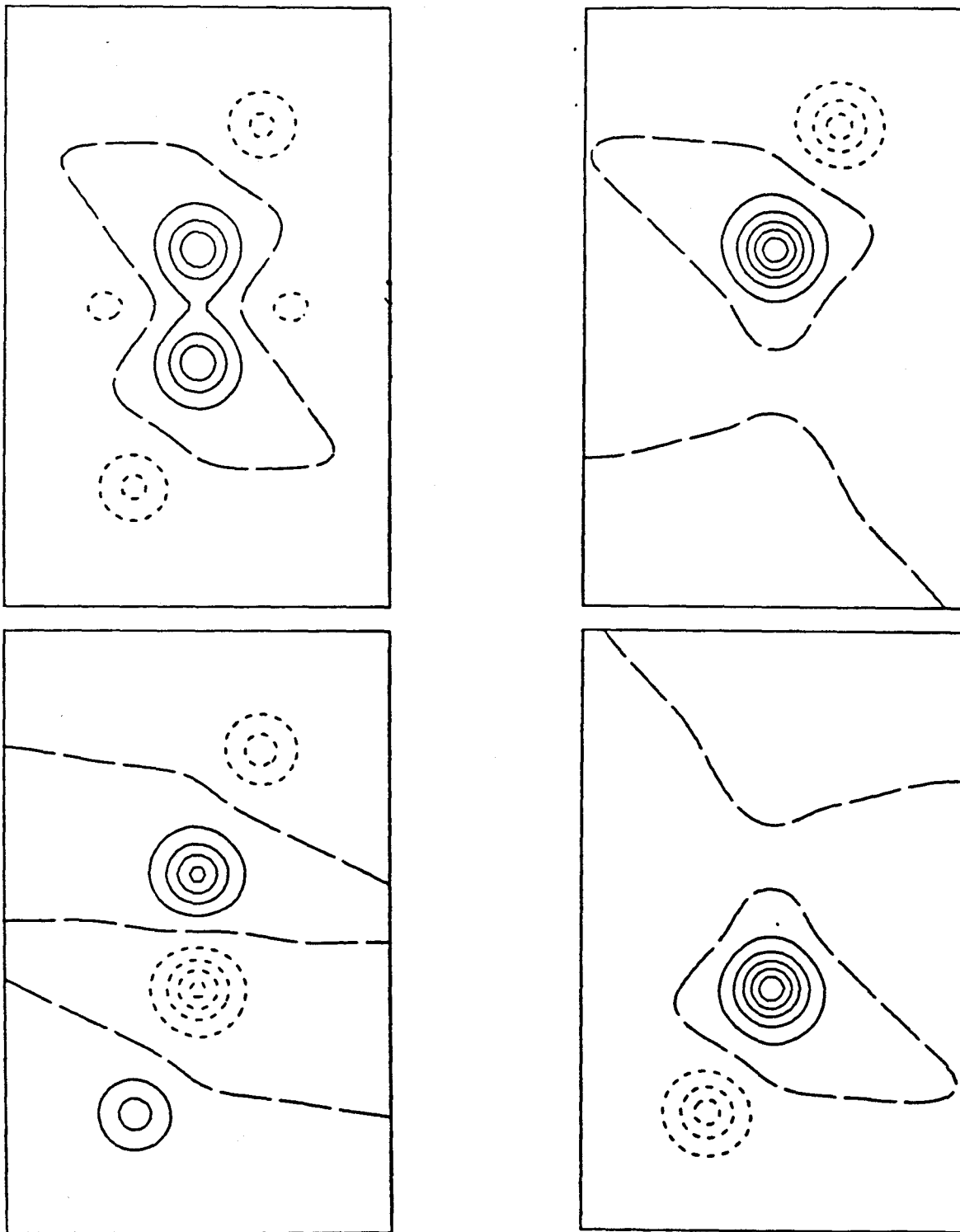


Figure 21. Singly Occupied Orbitals, Triplet on Left ($.5\text{\AA}$ above carbon framework plane).

both the triplet and the singlet are shown in Figure 21. Note the strong polarization in the C-C π -bonding orbital which forces the radical electrons (both singlet and triplet species) to be localized on the ring. These results seem to contradict our ESR results²⁷, which indicate a lower spin density on the ring carbons. This may be a problem with the level of theory; the fact that allyl radical cannot be properly geometry optimized at the HF level³⁵ is cause for suspicion.

The converged HF wavefunction is not our ultimate goal; we plan some CI studies in the future. Of particular interest is a full MCSCF treatment of the " π " orbitals, keeping the " σ " core frozen. As a preliminary to this study, we have determined the energy change under the following conditions. The triplet " σ " core was frozen, and the " π " system was optimized for a singlet. The reverse experiment was also performed. The energy change between the two systems was 7.66 cal/mol using the triplet core for the singlet, and 2.07 cal/mol using the singlet core for the triplet. These small numbers seem to justify our assumption that the " σ " core may be legitimately frozen while MCSCF studies are carried out. Our goals from these studies include insights into the interaction between the radical electrons and a precise determination of the singlet-triplet energy gap.

EXPERIMENTAL SECTION

General: ^1H NMR spectra were recorded on a Varian EM-390 spectrometer.

Preparative gas chromatography was performed on a Varian Model 920 chromatograph equipped with a 1/4" x 10' column packed with 10% VCW 982 on 80-100 mesh Chromosorb WAW-DCMS and a thermal conductivity detector.

Tetrahydrofuran was distilled from benzophenone ketyl before use. Diethyl ether used for extractions was USP grade. All other solvents were reagent grade and were used as received except where noted. Linde UHP argon was used as received. Flash chromatography³⁶ was done on silica columns.

Bicyclo[2.1.0]pentane (8).

To 1.02g (4.26 mmol) of 2,3-diazabicyclo[2.2.1]hept-2-ene copper bromide (prepared by Moon Chang using the method of Gassman and Mansfield²³) was added 10 ml concentrated aqueous ammonium hydroxide and 10 ml distilled water. The resulting suspension was extracted with 5 portions of 20 ml diethyl ether. The combined extracts were dried over sodium sulfate, filtered, and the ether was removed by rotary evaporator. The remaining solid was transferred to a 100 ml pyrolysis bulb. The bulb was cooled to 78 K, evacuated, and heated to 180 °C for 8 h. The bulb was then cooled to -40 °C and the product was vacuum transferred into another vessel. The product was pure by NMR. ^1H NMR (CDCl_3): δ 0.55 (m, 2H), 1.40 (m, 4H), 2.05 (m, 2H).

1-Cyano-3-methylenecyclobutane (17).

This compound was prepared by the method of Jain *et al.*^{11c,18,28}. To a 1 l stainless

steel bottle (bomb) was added 250 ml (3.80 mol) acrylonitrile (CAUTION: CANCER SUSPECT AGENT), 2.58 g (12.9 mmol) phenothiazine (a radical scavenger), and 250 ml benzene. The bomb was cooled in a -78 °C bath. Allene (~60 ml, 43.3 g, 1.081 mol) was condensed in a test tube at -78 °C and cannulated into the bomb. The bomb was sealed and shaken at 200 °C for 11 h. The bomb was cooled to 25 °C over 9 h. Benzene and excess acrylonitrile were distilled off at atmospheric pressure; the remaining solvent was removed at 100 torr. The cyclobutane (58.94g, 708 mmol) was distilled at 66-68.5 °C at 18 torr. Isolated yield = 56.4%.

1,3-Dicarbomethoxy-1-hydroxycyclobutane (18).

This compound was prepared by the method of Jain *et al.*^{11c,18}. The nitrile (17) (26.25 g, 282 mmol) and a stir bar were added to 600 ml dichloromethane in a 1 l three-necked round bottomed flask. The flask was equipped with an ice condenser and an addition funnel. Cold dichloro- methane (95 ml, 0 °C) was added to the addition funnel, which was sealed with a septum. Oxygen was bubbled for 80 min through dinitrogen tetroxide (24 ml, $\rho = 1.45$ g/ml, 35 g, 380 mmol) which had been condensed in a test tube at 0 °C. The N₂O₄ was cannulated into the addition funnel. The nitrile (17) solution was refluxed and the contents of the addition funnel were added over 60 min. The mixture was refluxed an additional 30 min. The excess NO₂ was removed by flushing the apparatus with nitrogen for 10 min. A 10 ml portion of water was added, and the mixture refluxed for 30 min. Excess NO₂ was again removed with nitrogen. The mixture was dried over sodium sulfate, filtered, rotovapped, and the green oil was added with 300 ml conc. HCl and a stir bar to a 500 ml round bottomed flask. A reflux condenser was attached and the mixture heated to 95-100 °C for 90 min. The aqueous HCl was removed by distillation; the residue was extracted with 23 portions of 100 ml diethyl ether. The ether extracts were combined, dried, and rotovapped. The recovered

red-brown oil was added to 600 ml methanol, 3 ml conc. sulfuric acid, and a stir bar in a 1 l round bottomed flask. The flask was equipped with a condenser and the mixture was refluxed for 17 h. The methanol was removed by rotary evaporator. The residue was cooled (0 °C), and added with 40 ml ice water to a separatory funnel. The aqueous solution was extracted with 6 portions of 100 ml diethyl ether. The ether layers were combined and washed with 4 portions of 50 ml sat. aqueous sodium bicarbonate, then with 50 ml water. The ether layers were dried, and the ether was removed by rotary evaporator. The residue was distilled (1.5 torr, 102-140 °C) to give 13.43 g of a slightly yellowish oil. Yield = 25.3%.

1,3-Dicarbomethoxy-1-chlorocyclobutane (19).

This compound was prepared by the method of Jain *et al.*^{11c,18}. The alcohol (18) (13.43 g, 71.4 mmol) and a stir bar were added to a 100 ml round bottomed flask. Pyridine (6.6 ml) was added, and the mixture was cooled in an ice bath. Thionyl chloride (5.6 ml, (ρ = 0.98, 6.5 g), 82 mmol) was added slowly via pipette. The flask was equipped with a reflux condenser and heated at 60 °C for 100 min. The temperature was then raised to 90 °C for 30 min. The reaction mixture was cooled and extracted with 10 portions of 40 ml diethyl ether. The product was dried, rotovapped, and distilled at 96-104 °C (~2 torr) to give a brown oil (10.02 g). Yield = 68.0%.

1,3-Dicarbomethoxybicyclobutane (20).

The compound was prepared by the method of Jain *et al.*^{11c,18}. A portion of sodium hydride (1.50 g, 60% in oil, 37.5 mmol) was washed 8 times with pentane and once with THF in a 100 ml three-necked round bottomed flask. A stir bar and 40 ml THF were added. The flask was equipped with a reflux condenser and an addition funnel containing the chloride (19) (4.93 g, 23.9 mmol) and 15 ml THF. The apparatus was flushed with nitrogen for 10 min and

the reaction was carried out under nitrogen. The flask was heated to 49-51 °C and the chloride solution was added dropwise over 40 min. After addition, the reaction mixture was stirred at 50 °C for 60 min. The mixture was cooled, and sat. aqueous NaCl (1.6 ml) was added dropwise to neutralize excess hydride. The mixture was then added to 8 ml water and 45 ml diethyl ether in a separatory funnel and the aqueous layer was discarded. The ether layer was washed 4 times with 4 ml portions of water, dried over sodium sulfate, and rotovapped to give 2.63 g of a green-brown oil. Yield (crude product) = 64.7%.

1,7-Dicarbomethoxy-4-methyl-2,4,6-triazatricyclo[5.1.1.0^{2,6}]nonane-3,5-dione (21).

This compound was prepared by the method of Jain *et al.*^{11c,18}. A dichloromethane solution of the bicyclobutane (20) (2.63 g, 15.4 mmol) and *N*-methyltriazolinedione (2.18 g, 19.3 mmol) was photolyzed with a Hanovia 450 watt medium pressure mercury arc lamp equipped with a Pyrex filter. The photolysis was conducted for a total of 90 min. The solvent was removed by rotary evaporator; recrystallization from ethyl acetate yielded 2.78 g white, cubic crystals. Yield = 63.7%. ¹H NMR (CDCl₃): δ 2.26 (d, 2H), 2.68 (d, 2H), 3.04 (s, 3H), 3.83 (s, 6H).

1,7-Bis(dihydroxymethyl)-4-methyl-2,4,6-triazatricyclo[5.1.1.0^{2,6}]nonane-3,5-dione.

The diester (21) (.989 g, 3.49 mmol) was dissolved in 40 ml methanol and added with a stir bar to a 100 ml round bottomed flask. The flask was equipped with a reflux condenser and degassed five times with dry nitrogen. Sodium borohydride (1.387 g, 36.7 mmol) was added to the stirred solution over 10 min, producing vigorous gas evolution. The flask was heated to reflux for 2 h, cooled, and neutralized to pH paper with 3 N HCl (~10 ml). The methanol was

removed by rotary evaporator; and the remaining water was lyophilized overnight. The resultant white solid was powdered with a mortar and pestle, and added to the top of a silica flash column³⁶. Flash chromatography (dichloromethane:ethanol 9:1) resulted in 497 mg of clear oil. Yield = 62.7%.

1,7-Bis(pyruvylloxymethyl)-4-methyl-2,4,6-triazatricyclo[5.1.1.0^{2,6}]nonane-3,5-dione (22).

This compound was prepared by the method of Jain *et al*^{11c,18,29}. The above diol (497 mg, 2.19 mmol) was dissolved in 40 ml freshly distilled dichloromethane and added to an oven-dried 100 ml round bottomed flask equipped with a stir bar under a nitrogen atmosphere. Portions of PPY (67 mg, .45 mmol), pyruvic acid (835 mg, 9.48 mmol), and DCC (1.859 g, 9.01 mmol) were added in sequence to the stirred reaction mixture. The white precipitate that formed on stirring for 10 min was removed by filtration. The filtrate was concentrated to ~2 ml and flash chromatography³⁶ was used (dichloromethane:ethyl acetate 1:1) to purify the product. Removal of solvents gave 691 mg of a light brown solid. Yield = 85.9%.

1,7-Diethenyl-4-methyl-2,4,6-triazatricyclo[5.1.1.0^{2,6}]nonane-3,5-dione.

This compound was prepared by the method of Jain *et al*^{11c,18,30}. The diester (22) (725 mg, 1.97 mmol) was dissolved in 1 l freshly distilled benzene and photolyzed with a 450 W Hanovia lamp equipped with a Pyrex filter in an oven-dried 1 l photolysis vessel under argon for 4 h. The resulting solution was concentrated by rotary evaporator under nitrogen in an oven-dried 2 l round bottomed flask to ~120 ml. The concentrate was cannulated into a 250 ml round bottomed flask containing the following solution.

The 250 ml (oven-dried) flask was equipped with a stir bar and Ph₃P(CH₃)(Br) (2.114 g, 5.922 mmol) and 100 ml freshly distilled benzene were added. Under a nitrogen atmo-

sphere, n-BuLi (3.584 ml, 1.6 M in hexane, 5.734 mmol) was added by syringe. The solution was allowed to stir at room temperature for 3 h.

The reaction mixture was allowed to stir for 40 min, then 60 ml 1.5 N HCl was added. The mixture was stirred for 5 min. The layers were separated, and the aqueous layer was extracted with two 35 ml portions of dichloromethane. The organic layers were combined and washed with 40 ml sat. aq. NaHCO₃ and 40 ml water. The organic layer was dried over MgSO₄ and the solvent was removed by rotary evaporator. Flash chromatography³⁶ was performed (pentane:ethyl acetate 7:4). The product was 102 mg of yellow oil. Yield = 23.6%.

1,7-Diethyl-4-methyl-2,4,6-triazatricyclo[5.1.1.0^{2,6}]nonane-3,5-dione.

The above diene (100 mg, .447 mmol) was added with 5 ml ethyl acetate under a nitrogen atmosphere to a 25 ml pear-shaped flask equipped with a stir bar. A ~50 mg portion of Pd/C was added. The system was partially evacuated, and ~50 ml hydrogen gas was added via balloon. The mixture was stirred at room temperature for 2 h. The catalyst was removed by filtration with Celite. The filtrate was concentrated by rotary evaporator, then flash chromatography³⁶ was performed (pet. ether:ethyl acetate 7:3). The product was 64 mg of yellow oil. Yield = 63.6%.

1,4-Diethyl-4-methyl-2,3-diazabicyclo[2.1.1]hex-2-ene (6).

To 8 ml degassed isopropanol in a 25 ml pear-shaped flask was added the diethyl urazole (61 mg, .273 mmol) and a stir bar. A pellet of KOH (171 mg, 87.1%, 3.05 mmol) was added under nitrogen. The flask was equipped with a reflux condenser and heated to ~80 °C for 50 min. The mixture was cooled to room temperature and ~4 ml degassed 3 N HCl was added. Decarboxylation was observed. The solution was neutralized with ~9 ml degassed 1 N

NH₄OH, extracted with three 5 ml portions of freshly distilled dichloromethane, and dried over MgSO₄. The solvents were removed by rotary evaporator. The resulting oil was dissolved in 5 ml dichloromethane and cannulated into a solution of 987 mg NiO_x (freshly activated) in 5 ml freshly distilled dichloromethane in a 25 ml round bottomed flask equipped with stir bar. The mixture was stirred for 30 min and the NiO_x was filtered away with a fine frit. The dichloromethane was removed under vacuum at -45 °C. The clear oil (~10 mg) was vacuum transferred at 0 °C. Yield = 24%.

Low Temperature Matrix Isolation Apparatus.

The apparatus used has been described extensively elsewhere³⁷; however, a brief description will be included here for completeness. The apparatus is of conventional design¹² employing an Air Products Displex CSW-202 DMX-1E closed cycle helium refrigerator unit with rotating optical shroud. The entire apparatus is constructed on a mobile cart, allowing access to photolysis and spectrometer equipment. High vacuum ($\sim 10^{-7}$ torr) is achieved with an Edwards Mk. 2 Diffstak oil diffusion pump. Temperature control is maintained with an Air Products Displex -E heater/controller unit equipped with an iron-doped gold/chromel thermocouple (2-300 K \pm 0.1 K). Matrix gas mixtures were prepared using standard manometric techniques in a glass vacuum manifold. Manifold pressures were measured with a Pennwalt Model 1500 absolute pressure gauge (0-800 torr). Matrix gas and gas mixture deposition rates were controlled with a Granville-Phillips variable leak valve. An inner CsI window was used, and outer KBr (for IR spectroscopy) and Suprasil I (for UV photolysis) windows were used. Photolysis was carried out with an Oriel 6295 Hg(Xe) source equipped with an f/0.7 quartz lens. Photolyses inside the FT-IR spectrometer were carried out with the equipment listed above under **Instrumental Modifications**.

FT-IR Spectroscopy.

A Mattson Instruments Sirius 100 sample compartment cover was modified to permit access of the Displex optical shroud³⁷. In order to maintain an efficient nitrogen purge of the spectrometer and cell compartment, a clear vinyl cover was taped to the optical shroud with vinyl tape and affixed to the modified sample compartment cover by means of a detachable Velcro seal cemented around the perimeter of the access hole. A positive dry nitrogen gas pressure was produced from a regulated high pressure liquid nitrogen dispenser dewar.

For a typical matrix isolation FT-IR experiment, the Displex apparatus, gas handling manifold, and flexible connecting line to the matrix gas cylinder were exhaustively outgassed by warming with a heat gun for 24 h prior to gas admission. A vacuum of better than 10^{-6} torr was established immediately before gas admission. The sample vapor was admitted through a greaseless Teflon joint and the desired gas mixture in argon was prepared by standard manometric techniques. The gas mixture was allowed to equilibrate for 24 h prior to deposition.

The Displex compressor was switched on and the temperature controller adjusted to 20 K. Once the inner CsI window temperature had cooled to 77 K, the high vacuum valve isolating the cold head from the diffusion pump was closed to prevent back-streaming of diffusion pump oil to the optical window. The sample window was allowed to equilibrate for approximately 60 min at 20 K prior to deposition. During this period, and after the appropriate nitrogen purge time, the background interferogram (of the empty cell) for the experiment was accumulated to achieve a stable baseline.

To begin a deposition, the manifold stopcock leading to the Granville-Phillips variable leak valve was opened together with the high vacuum isolation valve (Nupro) to the deposition port on the cold head. The deposition rate was adjusted with the Granville-Phillips leak valve to the appropriate flow rate and checked periodically. The optical shroud was then rotated and deposition begun. Deposition progress was monitored by FT-IR at appropriate intervals.

Once deposition was complete, the window temperature was slowly lowered to 10 K and the spectrum of the matrix isolated material recorded.

Photolysis was carried out through the back of the CsI inner window. The photolysis beam was focussed onto a circle of approximately 1 cm in diameter resulting in power densities of roughly 100 watt/cm². Progress of photochemical transformations was monitored by FT-IR at appropriate time intervals. A reproducible alignment of the sample window and infrared beam was necessary for a constant baseline.

FT-IR Spectra Workup.

Workup of FT-IR absorbance spectra was achieved using Mattson Instruments FT-IR software. All spectra were ratioed and processed using a background interferogram of the IR cell recorded prior to sample deposition. All absorbance spectra were carefully corrected using interactive subtraction software for interfering residual atmospheric impurities not removed in the nitrogen purge [e.g. H₂O (g), CO₂ (g)]. Ice bands [H₂O (s)] resulting from ice formation on the liquid nitrogen cooled HgCdTe (MCT) detector over the course of an experiment were also judiciously corrected. Baseline inclination and baseline rolls were carefully corrected with appropriate baseline correction software. The narrow half-band widths of matrix isolated species ($\leq 2\text{ cm}^{-1}$) make these corrections straightforward. Difference FT-IR spectra are presented to demonstrate changes in the species present over time. Difference spectra are presented as $A - B = C$ where A and B are the spectra to be subtracted and C is the resulting difference spectrum.

Matrix Isolation of Cyclopentene (9) and Bicyclo[2.1.0]pentane (8).

A 1:800 (1:500) gas mixture of cyclopentene (bicyclopentane) in argon was allowed to equilibrate in the Displex manifold. The mixture was deposited onto the 20 K CsI window at a

rate of 13 mmol/h over approximately 3 h. The CsI window temperature was lowered to 10 K and the sample spectrum was recorded after 60 min nitrogen purge time.

Matrix Isolation of 2,3-Diazabicyclo[2.2.1]hept-2-ene (7).

A 1:1000 gas mixture of the azo compound (7) (prepared by Moon Chang) in argon was allowed to equilibrate in the Displex manifold. The mixture was deposited onto the 20 K CsI window at a rate of 13 mmol/h over approximately 3 h. The CsI window temperature was lowered to 10 K and the sample spectrum was recorded after 60 min nitrogen purge time. The matrix was photolyzed with light from a 1000 watt Hg(Xe) source through an outer Suprasil I window and through the back of the inner CsI window using Schott UG-11, KG-5, and WG-305 filters. This combination of filters transmits light between 310 and 380 nm. Photolysis time for 99+% conversion was 200 s. A time series of spectra were recorded beginning 170 s after the completion of the photolysis. Several 30 s scans were taken, followed by several of longer duration. A final spectrum was taken 60 min after photolysis.

Matrix Isolation of 1,4-Diethyl-2,3-diazabicyclo[2.1.1]hex-2-ene (6).

The procedure given above for 2,3-diazabicyclo[2.2.1]hept-2-ene (7) was used with the following changes. The azo compound was prepared by Rakesh Jain and purified by preparative gas chromatography. The photolysis time was 7 min resulting in roughly 70% destruction of the azo compound. Scans were begun 150 s after photolysis was ended. The final scan was taken 120 min after photolysis.

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