COMPUTATIONAL AND MATRIX ISOLATION STUDIES OF (2- AND 3-FURYL)METHYLENE

Vincent A. McDermott

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Master of Science

1994

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To Whom It May Concern:

Enclosed is a copy of my Thesis, Computational and Matrix Isolation Studies of (2- and 3-)Furylmethylene, for the degree of Master of Science from the University of Pennsylvania. A copy of my thesis is provided IAW AR 621-1, Chapter 3-6.

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(2- and 3-)Furylmethylene

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GO ARMY !

ABSTRACT

COMPUTATIONAL AND MATRIX ISOLATION STUDIES OF (2- AND 3-FURYL)METHYLENE

Vincent A. McDermott

Professor William P. Dailey

(2- and 3-Furyl)methylene were investigated using both *ab initio* molecular orbital calculations and matrix isolation spectroscopy. Initial approaches to 2-furylmethylene were via the diazirine precursor. However, its synthesis was never realized. We therefore formed the diazo precursor for both compounds and purified them in preparation for matrix isolation. *Ab initio* calculations on 2-furylmethylene predict that the $\phi = 0°$ conformer **2.2** to be more stable than the $\phi = 180°$ conformer **2.1** in both the singlet and triplet states. Additionally, the energy barrier for ring fragmentation of the singlet carbene is predicted to be ~ 2.5 Kcal/mol. For 3-furylmethylene, two different levels of theory predict the opposite ground state multiplicity. Photolysis of 2-furyldiazomethane in a N_2 matrix results in ring fragmentation of the furan ring. Photolysis (Ar matrix) and flash vacuum pyrolysis prior to deposition on an Ar matrix of 3-furyldiazomethane is proposed to give the same product(s); however, the product(s) have yet to be identified.

Conclusive identification of the corresponding carbene was not realized using either 2- or 3-furyldiazomethane as the precursor. Further calculations and matrix isolation studies on these carbenes are planned.

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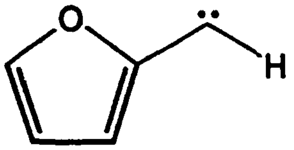
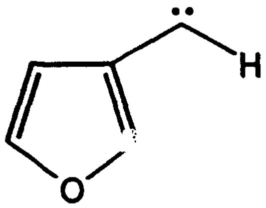
Chapter 1 A Review of the Chemistry of (2- and 3-Furyl)methylenes and an Introduction to Present Investigations

1.0 Introduction

In an effort to better understand the physical and chemical properties of (2- and 3-furyl)methylene **1.1** and **1.2**, *ab initio* calculations and matrix isolation studies of their respective diazo precursors were conducted .



1.1
2-furylmethylene



1.2
3-furylmethylene

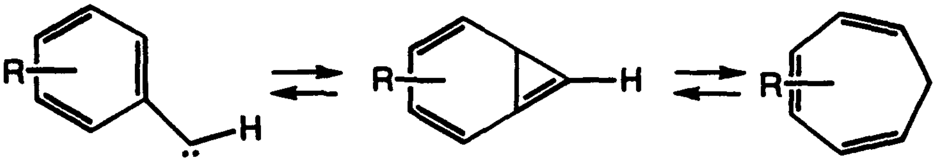
Before presenting the results of this work, a review of the previous studies on these compounds is presented.

1.1 Background and Review

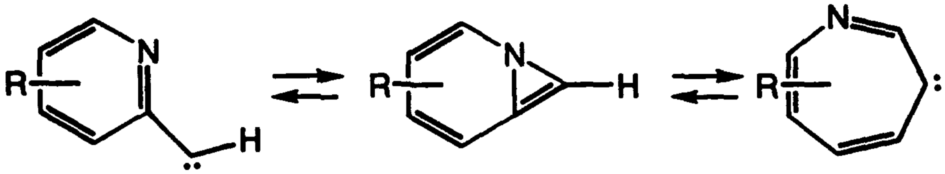
A number of research groups have conducted various experiments on (2- and 3-furyl)methylene [1-9]. However, none of these groups have studied these carbenes under matrix isolation conditions.

Shechter [1] studied the pyrolysis of diazo(2- and 3-furyl)methane and several substituted analogs in an attempt to observe carbene rearrangement products similar to those found with arylmethylenes (Scheme 1.1) and (2-pyridyl)methylenes (Scheme 1.2).

Scheme 1.1 Rearrangement of Arylmethylene

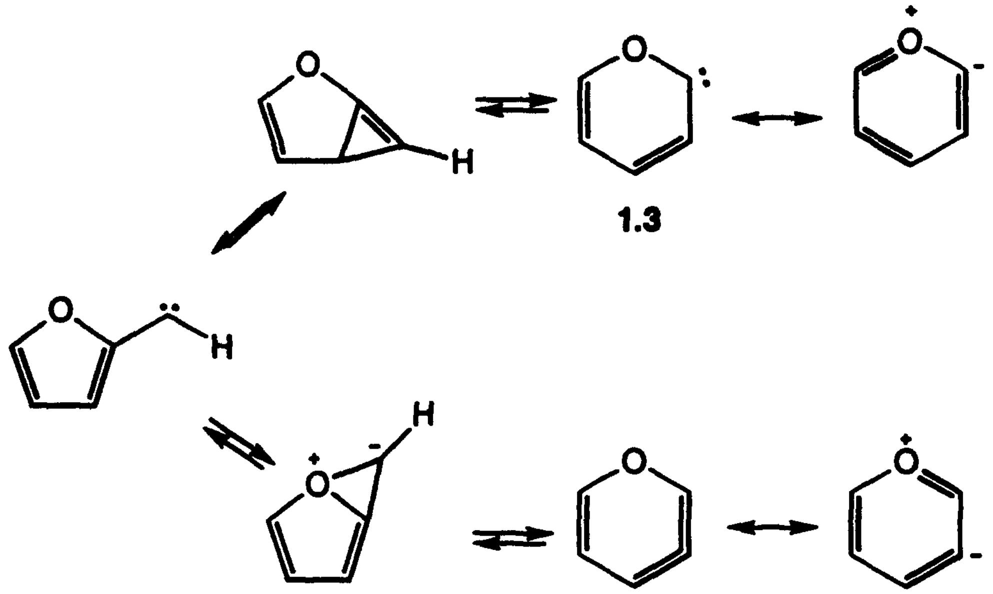


Scheme 1.2 Rearrangement of (2-Pyridyl)methylene



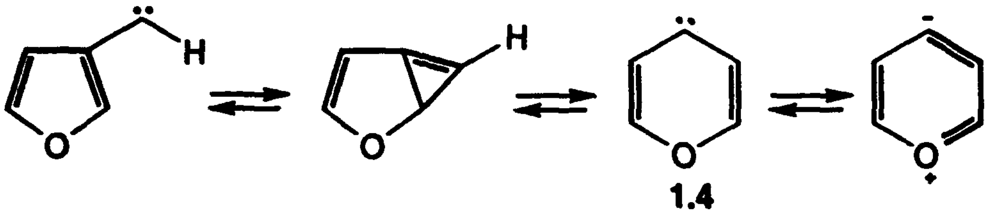
The carbenes were generated by pyrolysis of the corresponding tosylhydrazone sodium salts. He proposed that the above rearrangements may be extended to the (2- and 3- furyl)methylenes, suggesting that 2-furylmethylene could isomerize to 2-pyranylidene **1.3** or rearrange to a cyclic allene derivative (Scheme 1.3).

Scheme 1.3 Proposed Isomerization of 2-Furylmethylene



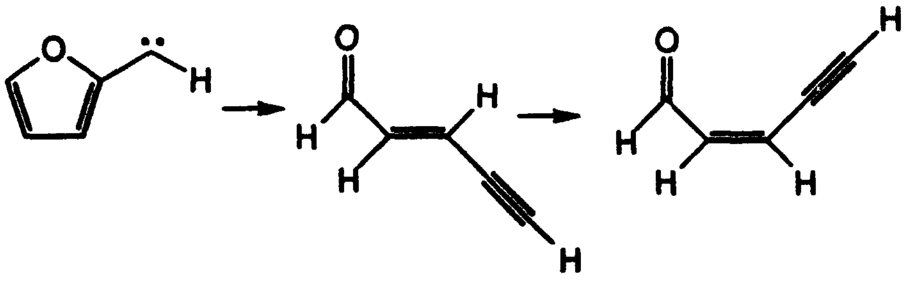
Similarly, 3-furylmethylene could rearrange to give 4-pyranylidene **1.4** (Scheme 1.4).

Scheme 1.4 Proposed Isomerization of 3-Furylmethylene

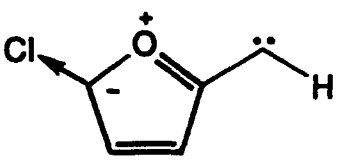


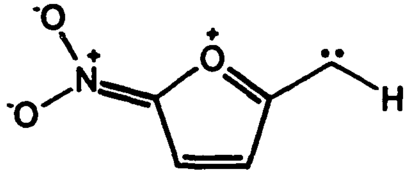
However, Shechter reports that none of the rearranged carbene products were detected for either the (2- or 3-furyl)methylene. With the 2-furylmethylene derivatives, he discovered cis- and trans-2-penten-4-ynal derivatives resulting from ring opening of the furan ring (Scheme 1.5).

Scheme 1.5 Ring Opening of 2-Furylmethylene



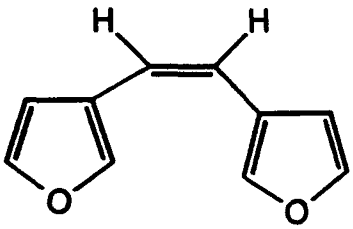
With the parent 2-furylmethylene, the ring opened product was obtained in 60% yield (81:19, cis:trans). Substitution of alkyl or aryl groups on the carbene carbon, and/or the 5 position of the furan ring caused only a small decrease in yield for the ring opened products. Migration of hydrogen α to the carbene was only a very minor process, less than 4%, thus suggesting that ring fragmentation is a very facile process. With electron-withdrawing groups in the 5 position, a significant decrease in the yields of ring opened products was found. Shechter explains that this might be caused by an increase in the strength of the C-O bond in the furan ring because of electronic induction or delocalization as shown below.



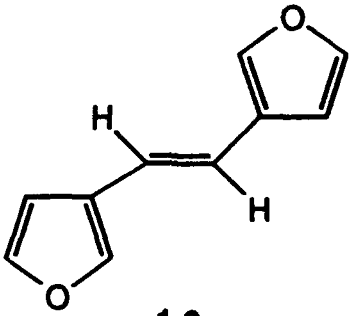


Additionally, some trapping studies were done to determine if the carbene was a discrete intermediate. Pyrolysis of sodium furfural tosylhydrazone in cyclooctane resulted in ring opened products and the C-H insertion product (> 7%), while pyrolysis in styrene gave the cyclopropane (6%). Although the cyclopropane could also arise from 1,3-addition of diazomethane to the double bond and subsequent loss of nitrogen, Shechter suggests that these results support the carbene intermediate.

Pyrolysis of sodium furfural tosylhydrazone gave the cis- and trans-1,2-di(3-furyl)ethylenes **1.5** and **1.6** in a 47:53 ratio with a yield of 29%.



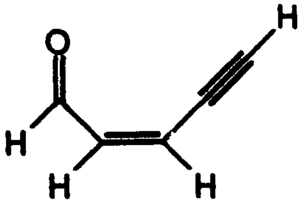
1.5



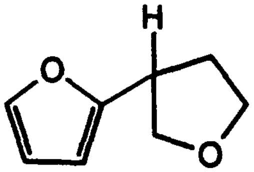
1.6

These products are said to result from reaction of the carbene and the diazo compound. Pyrolysis of sodium 3-furaldehyde tosylhydrazone in 1,1-diphenylethylene yielded 43% of the cyclopropane product along with 10% of the ethylenes, thus supporting a carbene intermediate.

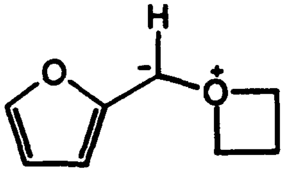
Kirmse[4] studied the chemistry of 2-furylmethylene generated via photolysis of the tosylhydrazone sodium salt and the diazo compound in a solution of oxetane, methanol, or an oxetane/methanol mixture. In a solution of oxetane, the major product (>90%) observed upon photolysis of both the tosylhydrazone and the diazo compound was the cis isomer of the ring opened product **1.7** and an oxetane ring enlarged product **1.8** resulting from Stevens rearrangement of the ylid **1.9**. No C-H insertion or oxetane ring opened products were observed.



1.7

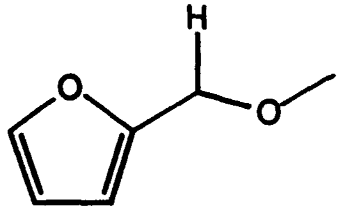


1.8

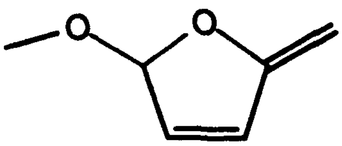


1.9

Photolysis in methanol gave a mixture of three products for both the tosylhydrazone salt and the diazo compound. The two new products are shown below with their respective yields.



1.10
(~40%)

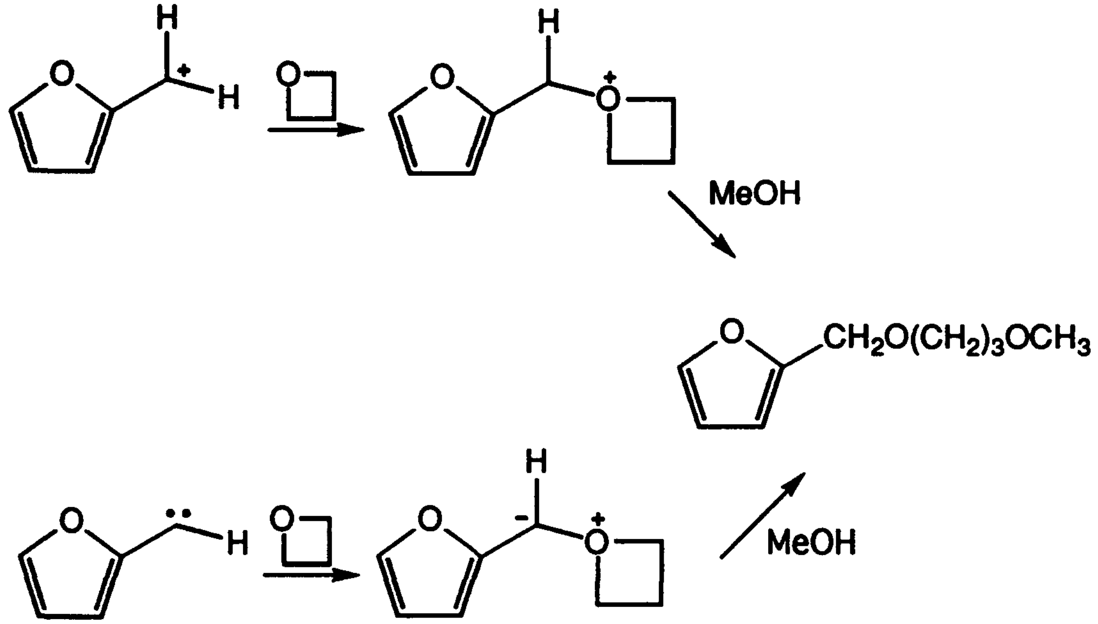


1.11
(~26%)

The major product **1.10** is suggested to arise from O-H insertion of the carbene on methanol or from electrophilic attack of methanol on the protonated form of the carbene at the carbene carbon. The other new product **1.11** is claimed to result from electrophilic attack of methanol on the protonated carbene at the 5-position of the furan ring. The third product was the ring opened product **1.7** in approximately 37% yield.

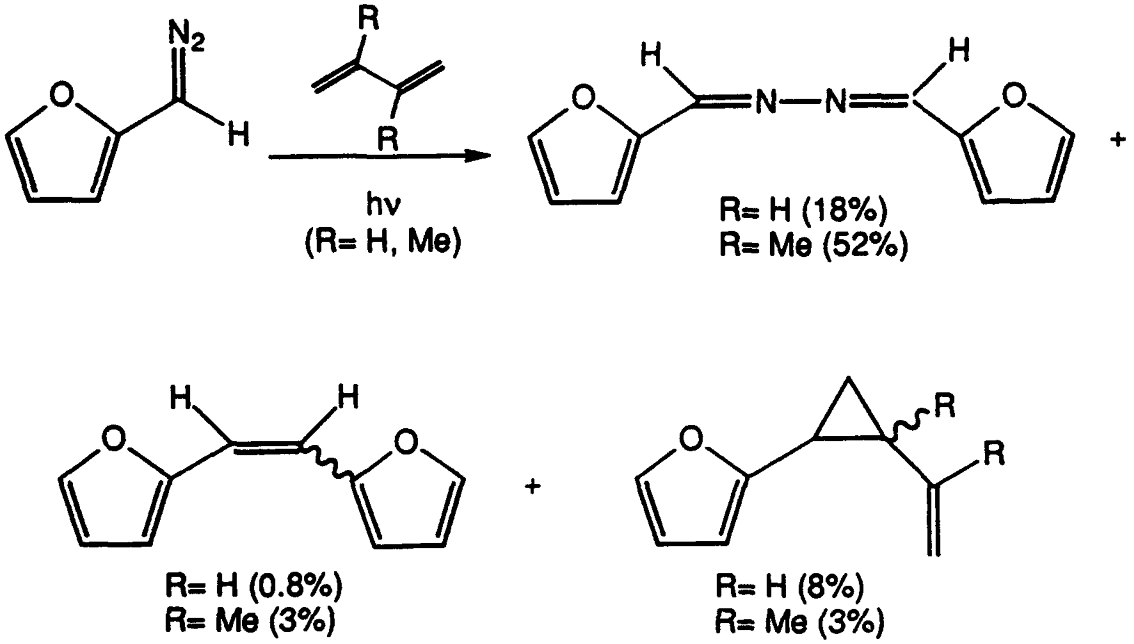
Upon photolysis in a mixture of oxetane and methanol all four of the products previously mentioned as well as a fifth product said to arise via one of two pathways were observed (Scheme 1.6).

Scheme 1.6 Proposed Pathways for the Formation of the Oxetane Ring Opened Product



Maas [2] studied the heteroaromatic Cope rearrangement of 1-furyl-2-vinylcyclopropane. This compound was generated via photolysis of 2-furyldiazomethane in 1,3-butadiene and 2,3-dimethyl-1,3-butadiene (Scheme 1.7).

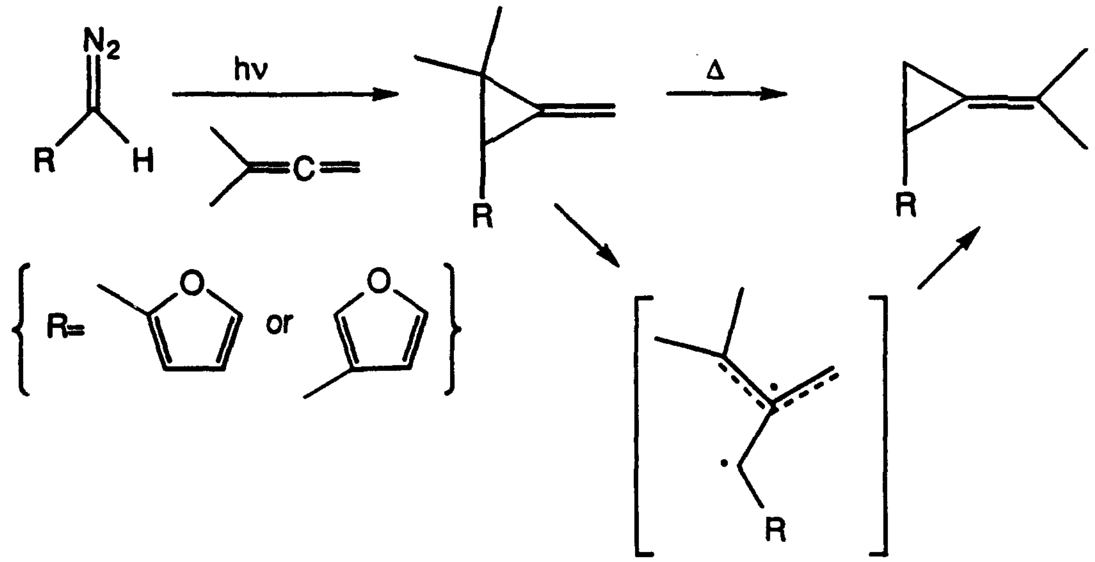
Scheme 1.7 Photolysis of 2-Furyldiazomethane in 1,3-Butadiene and 2,3-Dimethyl-1,3-butadiene



All yields shown are based on the hydrazone precursor to the diazo compound. Consistent with previous results, Maas had difficulty obtaining the carbene addition product.

Creary conducted a study of the radical stabilizing ability of several aromatic groups [3]. Two of the compounds he studied were based on the carbene addition of (2- and 3-furyl)methylene to 1,1-dimethylallene. The resulting cyclopropanes were heated and their rearrangement rates were compared to give a measure of the aromatic groups' ability to stabilize the biradical transition state (Scheme 1.8).

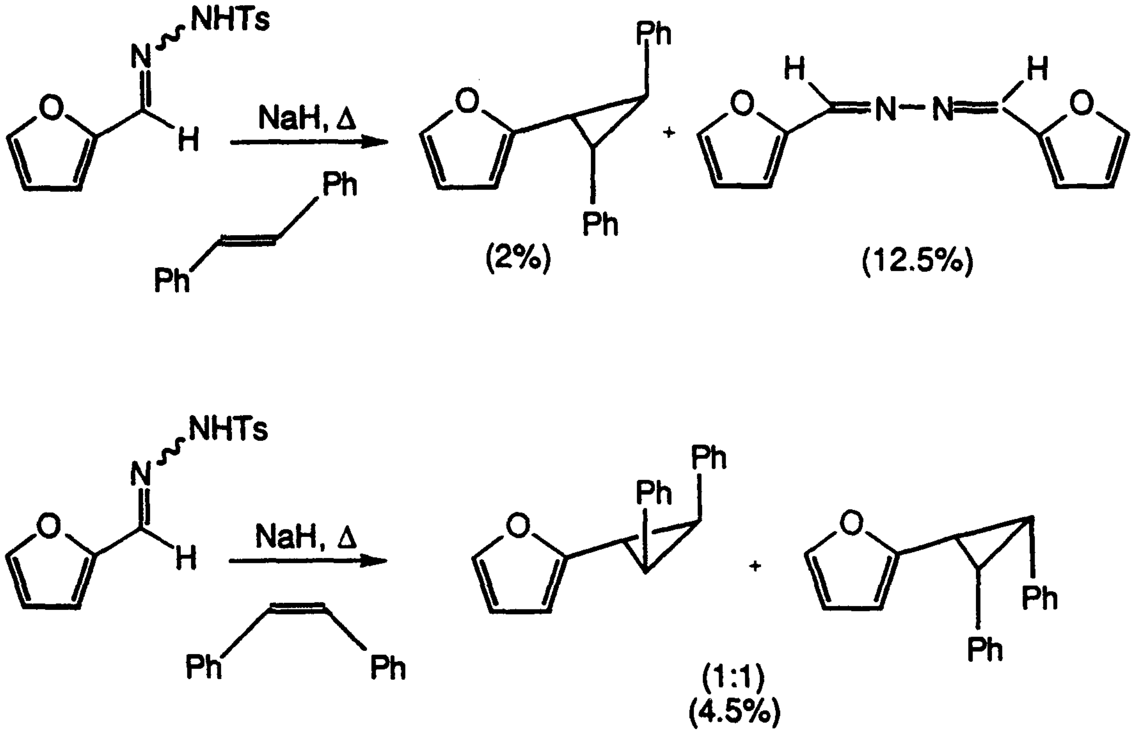
Scheme 1.8 Photolysis of (2- and 3-Furyl)methylene in 1,1-Dimethylallene and Subsequent Thermal Rearrangement



No yields were reported for either the (2- or 3-furyl)compounds. The photolyses were carried out in the ether solution used for the oxidation of the corresponding hydrazone. The 2-furyl derivative has a very high stabilizing ability attributed to the delocalization of the radical within the furan ring, similar to the argument used for the furan ring to undergo electrophilic substitution preferentially at the 2-position versus the 3-position.

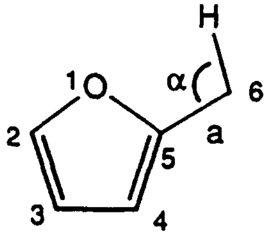
Saito has published several reports on the chemistry of 2-furylmethylene [3,5-9]. The most relevant of these reports with respect to the present research is his study on the multiplicity of carbenes with pyrrole and furan moieties [5]. In this report, he examined the reaction of 2-furylmethylene with cis- and trans-stilbene. His results are shown in Scheme 1.9.

Scheme 1.9 Thermolysis of Furfural Tosylhydrazone in the Presence of cis- and trans-Stilbene.



Based on the products above, Saito concludes that cyclopropane formation proceeds in a stereospecific manner indicating that the multiplicity of 2-furylmethylene is a singlet. He also reports molecular orbital calculations using the MNDO method for both the singlet and triplet (Table 1.1).

Table 1.1 Saito's MNDO Calculations on 2-Furylmethylene



Multiplicity	Singlet	Triplet
Heat of Formation (Kcal/mol)	81.2	63.7
Bond length a (Å)	1.4	1.34
Bond Angle α	123.2°	165.2°
π Electron Density on Carbene Carbon	0.193	1.012
Dihedral Angle * (C_4-C_5-C_6-H)	180.0°	180.0°
Charge on Carbene Carbon	-0.039	-0.169

* Two planar conformations are postulated (dihedral angle = 0° or 180°). The data reported is for the more stable conformer.

Saito's MNDO calculations predict that the carbene is a ground state triplet. He reconciles the apparent discrepancy with solution trapping studies by reference to previous workers results. A report by Trozzollo et al. [10] suggests that despite the triplet ground state of arylcarbenes, they still undergo stereospecific addition reactions due to the higher reactivity of the singlet carbene.

1.2 Discussion

All of the previous reports on 2-furylmethylene suggest that it is a very labile carbene that readily undergoes ring fragmentation to give 2-penten-4-ynal. The best yield reported for a product resulting from a carbene intermediate was 10%, as noted by Kirmse (Figure 1.8).

For 3-furylmethylene, no ring opened products are reported, and experiments to trap the carbene by Shechter gave the carbene addition product in reasonable yield (43%).

Since none of the previous reports had attempted matrix isolation studies on (2- and 3-furyl)methylene, it was our hope that we might be able to isolate and identify these carbenes under matrix isolation conditions.

1.3 References for Chapter 1

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(2) Maas, G.; Hummel, C. *Chem. Ber.* **1980**, *113*, 3679-3696.

(3) Creary, X.; Mehrsheikh-Mohammadi, M. E.; McDonald, S. *J. Org. Chem.* **1989**, *54*, 2904-2910.

(4) Kirmse, W.; Lelgemann, R.; Friedrich, K. *Chem. Ber.* **1991**, *124*, 1853-1863.

(5) Saito, K.; Ushida, T.; Fushihara, H.; Yamashita, Y.; Tanaka, S.; Takahashi, K. *Heterocycles* **1990**, *31*, 115-122.

(6) Saito, K.; Fushihara, H.; Sato, T.; Ishihara, H.; Takahashi, K. *Heterocycles* **1989**, *29*, 1537-1543.

(7) Saito, K.; Sato, T.; Ishihara, H.; Takahashi, K. *Bull. Chem. Soc. of Jpn.* **1989**, *62*, 1925-1929.

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(9) Saito, K.; Ishihara, H. *Heterocycles* **1986**, *24*, 1291-1294.

(10) Trozzolo, A. M.; Wasserman, E. I.; Moss, R. A.; Jones, M. *Carbenes*; Wiley: 1975.

Chapter 2 Computational Investigations of (2- and 3-Furyl)methylene

2.0 Introduction

To aid the characterization of (2- and 3-furyl)methylene, a number of *ab initio* calculations were performed on the singlet and triplet states of these carbenes. Additionally, calculations were carried out on a number of potential reactive intermediates and products for each carbene. As previously noted, Saito [1] (Table 1.1) has reported MNDO calculations on 2-furylmethylene. More recently Herges [2] has reported MNDO calculations on the different conformations of 2-furylmethylene as well as the transition state leading to the rearrangement product. These reports will be discussed during the presentation of our calculations.

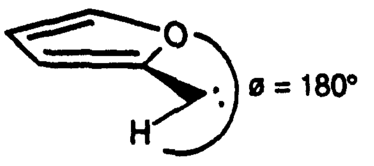
The principle use of these calculations was to compare the calculated IR spectra for (2- and 3-furyl)methylene with the results observed from our matrix isolation studies. This is expected to provide evidence for the multiplicity of these carbenes, as well as potential carbene rearrangement products.

The results of these calculations are presented here for reference during the experimental section of Chapter 5. All of the calculations presented in this chapter and in the respective appendices were carried out by Professor William P. Dailey using Gaussian 92/DFT. [3]

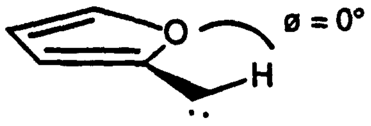
Finally, since this thesis does not represent an end to the research in this area a number of calculations are yet to be performed.

2.1 Computational Investigations of 2-Furylmethylene

Based on previous reports by Saito [1] and Herges [2], calculations were performed on the two planar conformers **2.1** and **2.2** of the carbene in both the singlet and triplet state (Appendix 1).



2.1



2.2

Additionally, calculations were performed on the transition state for the singlet **2.1** enroute to the ring opened product (Appendix 2), and the ring opened product, cis-2-penten-4-ynal, (Appendix 3)

Simple HF calculations using the 6-31G* basis set + ZPE (zero point energy correction applied) predict **2.2** to be more stable in both the singlet and triplet carbene as well as in the transition state. The relative energy difference between the two conformations of the singlet is 1.8 Kcal/mol, for the triplet it is 0.2 Kcal/mol, and for the transition state it is 6.1 Kcal/mol (Appendix 1). Herges [2] reports a relative energy difference of 2.7 Kcal/mol between the two conformations of the singlet using MNDO calculations. Higher level calculations are planned for both conformations in order to better predict the singlet-triplet gap and the transition state leading to ring opening .

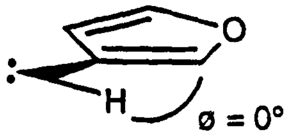
Higher level calculations for singlet **2.1** (Appendix 1) and the respective transition state (Appendix 2) enroute to the ring opened product predict a relative energy barrier of 6.6 Kcal/mol (QCISD(T)/6-311G**) and 6.8 Kcal/mol

(MP4SDTQ/6-311G**) after applying zero point energy corrections. If we assume that similar high level calculations will affect the energy barrier for the more stable conformer **2.2** calculated at the HF/6-31G* level in the same way as they did for **2.1**, then the predicted energy barrier is only 2.3 Kcal/mol (based on QCISD(T)/6-311G**) and 2.5 Kcal/mol (based on MP4SDTQ/6-311G**) for **2.2**. This low energy barrier accounts for the low yields reported by previous researches for carbene type products.

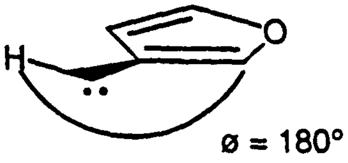
Geometry and frequency calculations were also performed on both conformations of the singlet and triplet (Appendix 1) as well as the ring opened product, cis-2-penten-4-ynal (Appendix 3).

2.2 Computational Investigations of 3-Furylmethylene

Similar calculations were conducted for 3-furylmethylene. Again, we investigated two possible planar conformers **2.3** and **2.4**.



2.3



2.4

For the two conformations of the singlet (Appendix 4), simple HF calculations using the 6-31G* basis set, with zero point energy correction applied, predict **2.4** to be more stable by 1.7 Kcal/mol.

An interesting observation was made while investigating the singlet triplet gap for **2.4** (Appendix 4). The predicted ground state multiplicity of the carbene is found to be dependent on the level of calculation. Calculations using QCISD(T)/6-311G** + ZPE predict the triplet to more stable by 2.9 Kcal/mol. However, calculations using MP4SDTQ/6-311G** + ZPE predict the singlet to be more stable by 5.0 Kcal/mol. This difference in energies is much larger than typically observed when comparing results from these two levels of theory.

Frequency and geometry calculations were also conducted on both conformations of the singlet carbene (Appendix 4), the triplet carbene **2.4** (Appendix 4), and several possible products resulting from rearrangement of the carbene (Appendix 5). These rearrangement products will be discussed in Chapter 5.

No previous reports on *ab initio* calculations for 3-furylmethylene were found in the literature.

2.3 References for Chapter 2

(1) Saito, K.; Ushida, T.; Fushihara, H.; Yamashita, Y.; Tanaka, S.; Takahashi, K. *Heterocycles* **1990**, *31*, 115-122.

(2) Herges, R. *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 255-276.

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Appendix 1

Ab Initio Calculations for 2-Furylmethylene

Table 2.1 Calculated Vibrational Spectrum of Singlet 2-Furylmethylene (ø = 180°) using HF/6-31G* [a]

Calculated	Scaled	Relative Intensity
239	215	.01
426	383	.03
576	518	.2
698	628	0
762	686	.04
818	736	.01
885	797	.2
966	869	.02
980	882	.2
1045	941	.01
1066	959	0
1114	1003	.3
1152	1037	.3
1233	1110	.01
1282	1154	.3
1359	1223	.1
1435	1292	.2
1557	1401	1
1601	1441	.04
1748	1573	.3
3192	2873	.4
3438	3094	0
3449	3104	0
3467	3120	.01

[a] *Frequencies in* cm^{-1}. All calculated frequencies were scaled by a factor of 0.9.

Table 2.2 Calculated Zero Point and Ground State Energies for Singlet 2-Furylmethylene (ø = 180°).[a]

Zero Point Energy	49.3 (Kcal/mol)
Ground State Energy HF	-266.38466 (au)
Ground State Energy MP4SDTQ	-267.38313 (au)
Ground State Energy QCISD(T)	-267.37981 (au)

[a] Zero point energy and ground state energy HF calculated using 6-31G* basis set, Ground state energy MP4SDTQ and QCISD(T) calculated using 6-311G** basis set. (1 au = 627.5 Kcal/mol)

Figure 2.5 Chem3D Rendering of Singlet 2-Furylmethylene (ø = 180°) calculated using MP2/6-31G*.

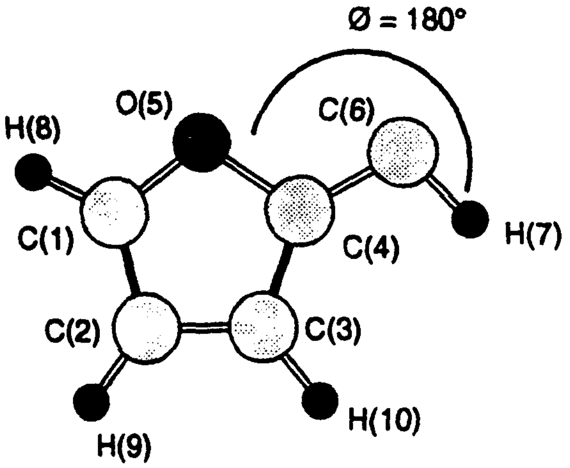


Table 2.3 Bond Distances for Singlet 2-Furylmethylene (ø = 180°) calculated using MP2/6-31G*.[a]

Atom Type and Number	Bond Distance/Angle
rC(1)-C(2)	1.389
rC(1)-O(5)	1.328
rC(1)-H(8)	1.083
rC(2)-C(3)	1.393
rC(2)-H(9)	1.082
rC(3)-C(4)	1.412
rC(3)-H(10)	1.083
rC(4)-O(5)	1.412
rC(4)-C(6)	1.388
rC(6)-H(7)	1.107
øC(2)-C(1)-O(5)	112.032
øC(2)-C(1)-H(8)	131.711
øO(5)-C(1)-H(8)	116.260
øC(1)-C(2)-C(3)	105.256
øC(1)-C(2)-H(9)	126.053
øC(3)-C(2)-H(9)	128.695
øC(2)-C(3)-C(4)	108.844
øC(2)-C(3)-H(10)	127.412
øC(4)-C(3)-H(10)	123.752
øC(3)-C(4)-O(5)	106.090
øC(3)-C(4)-C(6)	137.476
øO(5)-C(4)-C(6)	116.434
øC(1)-O(5)-C(4)	107.781
øC(4)-C(6)-H(7)	105.455

[a] Distances are in angstroms, Angles are in degrees.

Table 2.4 Calculated Vibrational Spectrum of Singlet 2-Furylmethylene ($\phi = 0°$) using HF/6-31G* .[a]

Calculated	Scaled	Relative Intensity
239	215	0
405	365	.03
572	515	0
686	617	.03
754	679	.03
843	759	.2
889	800	.2
952	857	.05
977	879	.3
1052	947	0
1071	964	0
1112	1001	.3
1137	1023	.1
1231	1108	.03
1263	1137	.2
1348	1213	.05
1429	1286	.2
1563	1407	1
1602	1442	.2
1753	1578	.4
3209	2888	.3
3443	3099	0
3458	3112	.01
3469	3122	.01

[a] Frequencies in cm^{-1}. All calculated frequencies were scaled by a factor of 0.9.

Table 2.5 Calculated Zero Point and Ground State Energy for Singlet 2-Furylmethylene (ø = 0°).[a]

Zero Point Energy	49.3 (Kcal/mol)
Ground State Energy	-266.38752 (au)

[a] Zero point and ground state energy calculated using HF/6-31G*. (1 au = 627.5 Kcal/mol)

Figure 2.6 Chem3D Rendering of Singlet 2-Furylmethylene (ø = 0°) calculated using HF/6-31G*.

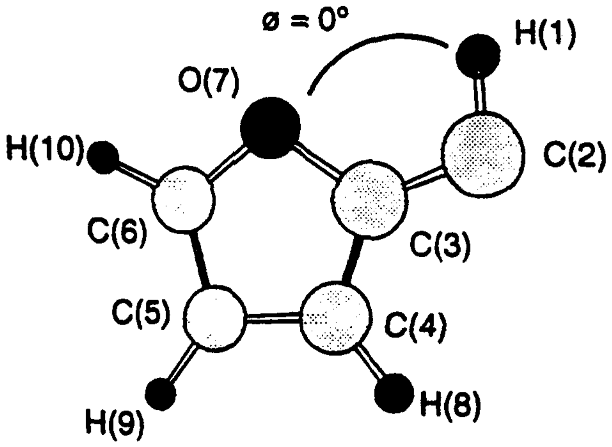


Table 2.6 Bond Distances for Singlet 2-Furylmethylene (ø = 0°) calculated using HF/6-31G*.[a]

Atom Type and Number	Bond Distance/Angle
rH(1)-C(2)	1.091
rC(2)-C(3)	1.395
rC(3)-C(4)	1.374
rC(3)-O(7)	1.395
rC(4)-C(5)	1.407
rC(4)-H(8)	1.070
rC(5)-C(6)	1.362
rC(5)-H(9)	1.069
rC(6)-O(7)	1.304
rC(6)-H(10)	1.071
øH(1)-C(2)-C(3)	108.877
øC(2)-C(3)-C(4)	128.762
øC(2)-C(3)-O(7)	124.562
øC(4)-C(3)-O(7)	106.683
øC(3)-C(4)-C(5)	108.372
øC(3)-C(4)-H(8)	123.521
øC(5)-C(4)-H(8)	128.113
øC(4)-C(5)-C(6)	104.520
øC(4)-C(5)-H(9)	128.739
øC(6)-C(5)-H(9)	126.749
øC(5)-C(6)-O(7)	112.628
øC(5)-C(6)-H(10)	130.591
øO(7)-C(6)-H(10)	116.789
øC(3)-O(7)-C(6)	107.806

[a] Distances are in angstroms, Angles are in degrees.

Table 2.7 Calculated Vibrational Spectrum of Triplet 2-Furylmethylene (ø = 180°) using HF/6-31G*.[a]

Calculated	Scaled	Relative Intensity
259	233	.08
389	350	.08
512	461	.4
587	528	.2
661	595	.02
733	660	.9
747	672	.02
792	713	.6
927	834	.6
928	835	.06
944	850	.3
1009	908	.3
1090	981	.6
1168	1051	.1
1273	1146	.7
1338	1204	1
1414	1273	.5
1502	1352	.06
1516	1364	.04
1629	1466	.1
3429	3086	.06
3442	3098	.08
3451	3106	.06
3476	3128	.08

[a] Frequencies in cm^{-1}. All calculated frequencies were scaled by a factor of 0.9.

Table 2.8 Calculated Zero Point and Ground State Energy for Triplet 2-Furylmethylene (ø = 180°).[a]

Zero Point Energy	47.5 (Kcal/mol)
Ground State Energy	-266.42413 (au)

[a] Zero point and ground state energy calculated using HF/6-31G*. (1 au = 627.5 Kcal/mol)

Figure 2.7 Chem3D Rendering of Triplet 2-Furylmethylene (ø = 180°) calculated using HF/6-31G*.

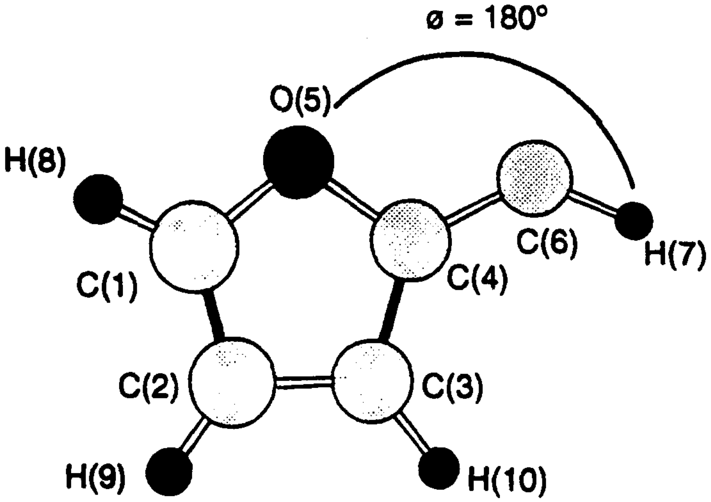


Table 2.9 Bond Distances for Triplet 2-Furylmethylene (ø = 180°) calculated using HF/6-31G*.[a]

Atom Type and Number	Bond Distance/Angle
rC(1)-C(2)	1.364
rC(1)-O(5)	1.351
rC(1)-H(8)	1.068
rC(2)-C(3)	1.414
rC(2)-H(9)	1.071
rC(3)-C(4)	1.405
rC(3)-H(10)	1.070
rC(4)-O(5)	1.365
rC(4)-C(6)	1.378
rC(6)-H(7)	1.069
øC(2)-C(1)-O(5)	110.969
øC(2)-C(1)-H(8)	132.745
øO(5)-C(1)-H(8)	116.293
øC(1)-C(2)-C(3)	106.323
øC(1)-C(2)-H(9)	126.235
øC(3)-C(2)-H(9)	127.448
øC(2)-C(3)-C(4)	106.433
øC(2)-C(3)-H(10)	127.889
øC(4)-C(3)-H(10)	125.682
øC(3)-C(4)-O(5)	108.445
øC(3)-C(4)-C(6)	131.682
øO(5)-C(4)-C(6)	119.879
øC(1)-O(5)-C(4)	107.837
øC(4)-C(6)-H(7)	131.416

[a] Distances are in angstroms, Angles are in degrees.

Table 2.10 Calculated Vibrational Spectrum of Triplet 2-Furylmethylene ($\phi = 0°$) using UHF/6-31G*.[a]

Calculated	Scaled	Relative Intensity
253	228	.06
383	345	.04
496	446	.5
585	527	.2
657	591	.03
729	656	.6
740	666	.06
799	719	.4
930	837	.05
937	843	.1
952	857	.3
987	888	.4
1090	981	.3
1164	1048	.06
1277	1149	.4
1334	1201	1
1408	1267	.4
1496	1346	.01
1524	1372	.03
1629	1466	.1
3431	3088	.04
3444	3100	.04
3455	3110	.04
3476	3128	.06

[a] Frequencies in cm^{-1}. All calculated frequencies were scaled by a factor of 0.9.

Table 2.11 Calculated Zero Point and Ground State Energy for Triplet 2-Furylmethylene (ø = 0°).[a]

Zero Point Energy	47.4 (Kcal/mol)
Ground State Energy	-266.42422 (au)

[a] Zero point and ground state energy calculated using HF/6-31G*. (1 au = 627.5 Kcal/mol)

Figure 2.8 Chem3D Rendering of Triplet 2-Furylmethylene (ø = 0°) calculated using UHF/6-31G*.

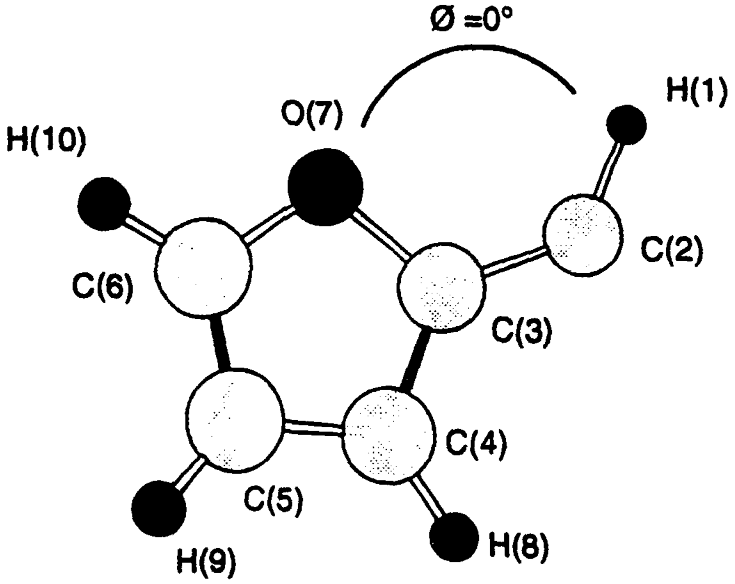


Table 2.12 Bond Distances for Triplet 2-Furylmethylene (ø = 0°) calculated using UHF/6-31G*.[a]

Atom Type and Number	Bond Distance/Angle
rH(1)-C(2)	1.069
rC(2)-C(3)	1.378
rC(3)-C(4)	1.402
rC(3)-O(7)	1.369
rC(4)-C(5)	1.414
rC(4)-H(8)	1.070
rC(5)-C(6)	1.365
rC(5)-H(9)	1.071
rC(6)-O(7)	1.353
rC(6)-H(10)	1.068
øH(1)-C(2)-C(3)	132.832
øC(2)-C(3)-C(4)	131.542
øC(2)-C(3)-O(7)	119.968
øC(4)-C(3)-O(7)	108.496
øC(3)-C(4)-C(5)	106.505
øC(3)-C(4)-H(8)	125.523
øC(5)-C(4)-H(8)	127.980
øC(4)-C(5)-C(6)	106.377
øC(4)-C(5)-H(9)	127.440
øC(6)-C(5)-H(9)	126.186
øC(5)-C(6)-O(7)	110.939
øC(5)-C(6)-H(10)	132.785
øO(7)-C(6)-H(10)	116.282
øC(3)-O(7)-C(6)	107.690

[a] Distances are in angstroms, Angles are in degrees.

Appendix 2

Ab Initio Calculations for Transition State

[2-Furylmethylene → cis-2-Penten-4-ynal]

Table 2.13 Calculated Zero Point and Ground State Energies for Transition State [2-Furylmethylene → cis-2-penten-4-ynal] (ø = 180°).[a]

Zero Point Energy	47.3 (Kcal/mol)
Ground State Energy HF	-266.35794 (au)
Ground State Energy MP4SDTQ	-267.36909 (au)
Ground State Energy QCISD(T)	-267.36606 (au)

[a] Zero point energy and ground state energy HF calculated using 6-31G* basis set, Ground state energy MP4SDTQ and QCISD(T) calculated using 6-311G** basis set. (1 au = 627.5 Kcal/mol)

Figure 2.9 *Chem3D Rendering of the Transition State* [2-Furylmethylene → cis-2-penten-4-ynal] (ø = 180) calculated using MP2/6-31G*.

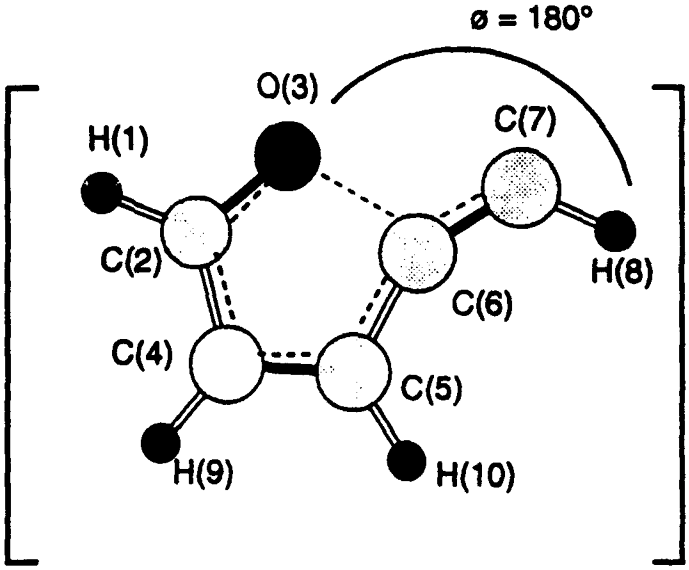


Table 2.14 Bond Distances for the Transition State [2-Furylmethylene → cis-2-penten-4-ynal] (ø = 180°) calculated using MP2/6-31G*.[a]

Atom Type and Number	Bond Distance/Angle
rH(1)-C(2)	1.091
rC(2)-O(3)	1.273
rC(2)-C(4)	1.421
rC(4)-C(5)	1.368
rC(4)-H(9)	1.082
rC(5)-C(6)	1.422
rC(5)-H(10)	1.086
rC(6)-C(7)	1.289
rC(7)-H(8)	1.085
øH(1)-C(2)-O(3)	118.569
øH(1)-C(2)-C(4)	126.163
øO(3)-C(2)-C(4)	115.275
øC(2)-C(4)-C(5)	107.069
øC(2)-C(4)-H(9)	125.366
øC(5)-C(4)-H(9)	127.569
øC(4)-C(5)-C(6)	115.571
øC(4)-C(5)-H(10)	125.144
øC(6)-C(5)-H(10)	119.290
øC(5)-C(6)-C(7)	150.805
øC(6)-C(7)-H(8)	123.687

[a] Distances are in angstroms, Angles are in degrees.

Table 2.15 Calculated Zero Point and Ground State Energies for Transition State [2-Furylmethylene → cis-2-penten-4-ynal] (ø = 0°).[a]

Zero Point Energy	47.5 (Kcal/mol)
Ground State Energy	-266.36794 (au)

[a] Zero point and ground state energy calculated using HF/6-31G*. (1 au = 627.5 Kcal/mol)

Figure 2.10 Chem3D Rendering of Transition State [2-Furylmethylene → cis-2-penten-4-ynal] (ø = 0°) calculated using HF/6-31G*.

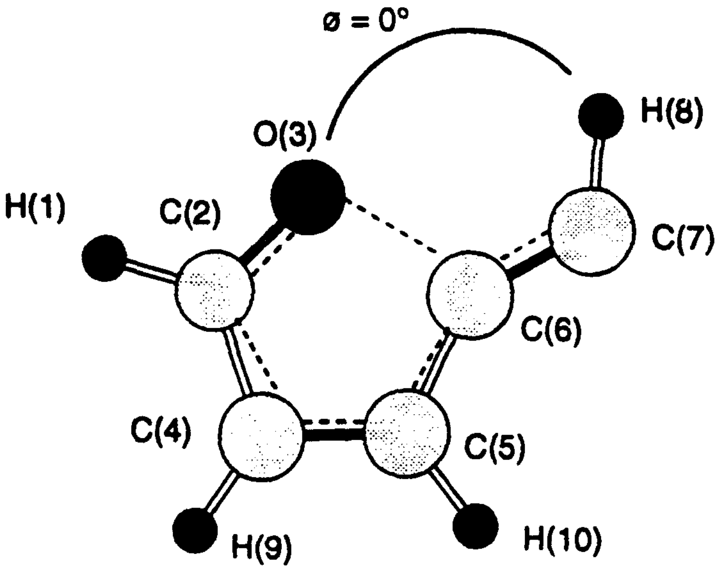


Table 2.16 Bond Distances for Transition State [2-Furylmethylene → cis-2-penten-4-ynal] (ø = 0°) calculated using HF/6-31G*.[a]

Atom Type and Number	Bond Distance/Angle
H(1)-C(2)	1.081
C(2)-O(3)	1.232
C(2)-C(4)	1.419
C(4)-C(5)	1.355
C(4)-H(9)	1.070
C(5)-C(6)	1.408
C(5)-H(10)	1.072
C(6)-C(7)	1.288
C(7)-H(8)	1.074
H(1)-C(2)-O(3)	119.524
H(1)-C(2)-C(4)	124.312
O(3)-C(2)-C(4)	116.169
C(2)-C(4)-C(5)	107.097
C(2)-C(4)-H(9)	125.555
C(5)-C(4)-H(9)	127.354
C(4)-C(5)-C(6)	116.382
C(4)-C(5)-H(10)	125.752
C(6)-C(5)-H(10)	117.870
C(5)-C(6)-C(7)	142.633
C(6)-C(7)-H(8)	122.252

[a] Distances are in angstroms, Angles are in degrees

Appendix 3

Ab Initio Calculations for cis-2-Penten-4-ynal

Table 2.17 Calculated Vibrational Spectrum of cis-2-penten-4-ynal using HF/6-31G*.[a]

Calculated	Scaled	Relative Intensity
90	81	.1
152	137	0
296	266	0
305	275	0
520	468	.1
558	502	.2
791	712	.3
831	748	.2
861	775	.2
886	797	0
975	878	.6
1074	967	0
1129	1016	0
1152	1037	.1
1356	1220	0
1550	1395	.1
1579	1421	.1
1831	1648	.9
2012	1811	.8
2407	2166	.1
3170	2853	1
3351	3016	0
3373	3036	.1
3666	3299	.3

[a] Frequencies in cm^{-1}. All calculated frequencies were scaled by a factor of 0.9.

Table 2.18 Calculated Zero Point Energy for cis-2-penten-4-ynal.[a]

Zero Point Energy	48.5 (Kcal/mol)

[a] Zero point energy calculated using HF/6-31G*.

Figure 2.11 Chem3D Rendering of cis-2-penten-4-ynal using HF/6-31G* .

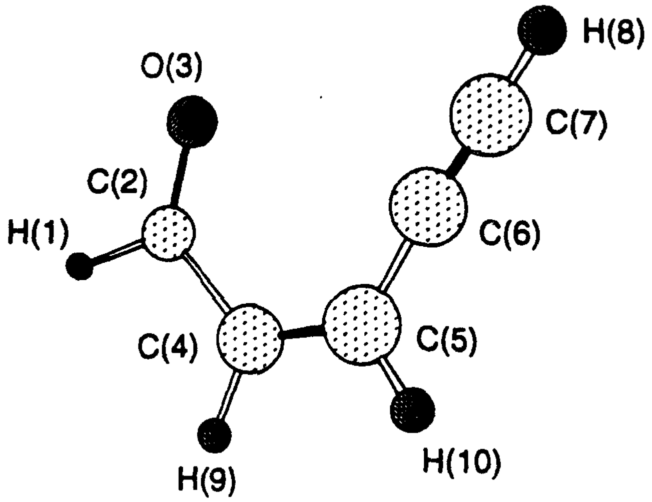


Table 2.19 Bond Distances for cis-2-penten-4-ynal calculated using HF/6-31G*.[a]

Atom Type and Number	Bond Distance/Angle
rH(1)-C(2)	1.094
rC(2)-O(3)	1.189
rC(2)-C(4)	1.483
rC(4)-C(5)	1.329
rC(4)-H(9)	1.076
rC(5)-C(6)	1.432
rC(5)-H(10)	1.077
rC(6)-C(7)	1.188
rC(7)-H(8)	1.057
øH(1)-C(2)-O(3)	120.341
øH(1)-C(2)-C(4)	114.175
øO(3)-C(2)-C(4)	125.488
øC(2)-C(4)-C(5)	126.043
øC(2)-C(4)-H(9)	115.704
øC(5)-C(4)-H(9)	118.260
øC(4)-C(5)-C(6)	127.487
øC(4)-C(5)-H(10)	118.015
øC(6)-C(5)-H(10)	114.504
øC(5)-C(6)-C(7)	175.468
øC(6)-C(7)-H(8)	178.154

[a] Distances are in angstroms, Angles are in degrees.

Appendix 4

Ab Initio Calculations for 3-Furylmethylene

Table 2.20 Calculated Vibrational Spectrum of Singlet 3-Furylmethylene (ø =180°) using HF/6-31G*.[a]

Calculated	Scaled	Relative Intensity
236	212	0
380	342	.03
563	507	.02
679	611	.1
732	659	.06
764	688	.2
862	776	.2
943	849	.1
1019	917	0
1041	937	.03
1057	951	.03
1100	990	.1
1182	1064	.06
1221	1099	.01
1286	1157	.9
1381	1243	0
1481	1333	.05
1525	1373	.01
1674	1507	1
1742	1568	.01
3163	2847	.6
3442	3098	0
3481	3133	0
3495	3146	0

[a] *Frequencies in* cm^{-1}. All calculated frequencies were scaled by a factor of 0.9.

Table 2.21 Calculated Zero Point and Ground State Energies for Singlet 3-Furylmethylene (ø =180°).[a]

Zero Point Energy	49.2 (Kcal/mol)
Ground State Energy HF	-266.37898 (au)
Ground State Energy MP4SDTQ	-267.36923 (au)
Ground State Energy QCISD(T)	-267.36760 (au)

[a] Zero point energy and ground state energy HF calculated using 6-31G* basis set, Ground state energy MP4SDTQ and QCISD(T) calculated using 6-311G** basis set. (1 au = 627.5 Kcal/mol)

Figure 2.12 Chem3D Rendering of Singlet 3-Furylmethylene (ø =180°) calculated using HF/6-31G*.

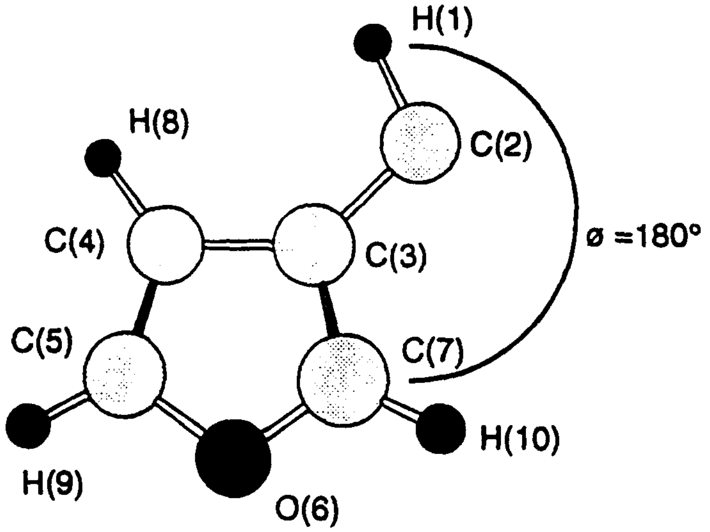


Table 2.22 Bond Distances for Singlet 3-Furylmethylene (ø =180°) calculated using HF/6-31G*.[a]

Atom Type and Number	Bond Distance/Angle
rH(1)-C(2)	1.094
rC(2)-C(3)	1.423
rC(3)-C(4)	1.461
rC(3)-C(7)	1.368
rC(4)-C(5)	1.330
rC(4)-H(8)	1.071
rC(5)-O(6)	1.373
rC(5)-H(9)	1.067
rO(6)-C(7)	1.309
rC(7)-H(10)	1.069
øH(1)-C(2)-C(3)	108.510
øC(2)-C(3)-C(4)	135.271
øC(2)-C(3)-C(7)	121.005
øC(4)-C(3)-C(7)	103.726
øC(3)-C(4)-C(5)	106.417
øC(3)-C(4)-H(8)	127.055
øC(5)-C(4)-H(8)	126.534
øC(4)-C(5)-O(6)	110.274
øC(4)-C(5)-H(9)	134.516
øO(6)-C(5)-H(9)	115.214
øC(5)-O(6)-C(7)	107.430
øC(3)-C(7)-O(6)	112.156
øC(3)-C(7)-H(10)	130.281
øO(6)-C(7)-H(10)	117.569

[a] Distances are in angstroms, Angles are in degrees.

Table 2.23 Calculated Vibrational Spectrum of Singlet 3-Furylmethylene (ø = 0°) using HF/6-31G*.[a]

Calculated	Scaled	Relative Intensity
240	216	.04
387	348	.1
552	496	.3
681	613	.06
730	657	.07
734	660	.01
863	777	.2
945	851	.1
1024	922	.01
1027	924	.05
1058	952	.01
1096	986	.1
1201	1081	.03
1217	1095	.1
1286	1157	1
1390	1251	.01
1480	1332	.05
1529	1376	.02
1669	1502	.9
1739	1565	.02
3145	2831	.6
3455	3110	.01
3461	3115	.01
3498	3148	.01

[a] Frequencies in cm^{-1}. All calculated frequencies were scaled by a factor of 0.9.

Table 2.24 Calculated Zero Point and Ground State Energies for Singlet 3-Furylmethylene (ø = 0°).[a]

Zero Point Energy	49.2 (Kcal/mol)
Ground State Energy	-266.37626 (au)

[a] Zero point and ground state energy calculated using HF/6-31G*. (1 au = 627.5 Kcal/mol)

Figure 2.13 Chem3D Rendering of Singlet 3-Furylmethylene (ø = 0°) calculated using HF/6-31G*.

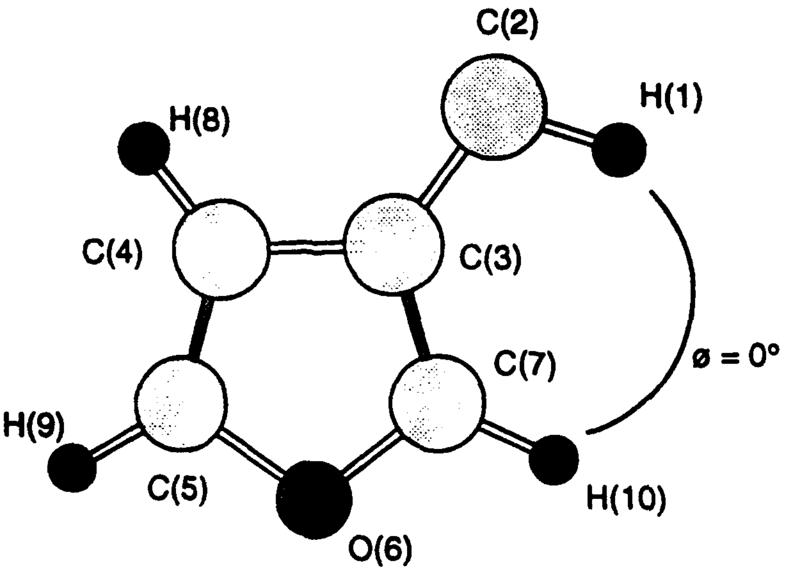


Table 2.25 Bond Distances for Singlet 3-Furylmethylene (ø = 0°) calculated using HF/6-31G*.[a]

Atom Type and Number	Bond Distance/Angle
rH(1)-C(2)	1.095
rC(2)-C(3)	1.428
rC(3)-C(4)	1.456
rC(3)-C(7)	1.368
rC(4)-C(5)	1.330
rC(4)-H(8)	1.070
rC(5)-O(6)	1.373
rC(5)-H(9)	1.067
rO(6)-C(7)	1.309
rC(7)-H(10)	1.071
øH(1)-C(2)-C(3)	107.132
øC(2)-C(3)-C(4)	127.957
øC(2)-C(3)-C(7)	128.269
øC(4)-C(3)-C(7)	103.782
øC(3)-C(4)-C(5)	106.613
øC(3)-C(4)-H(8)	126.076
øC(5)-C(4)-H(8)	127.319
øC(4)-C(5)-O(6)	110.086
øC(4)-C(5)-H(9)	134.735
øO(6)-C(5)-H(9)	115.186
øC(5)-O(6)-C(7)	107.468
øC(3)-C(7)-O(6)	112.060
øC(3)-C(7)-H(10)	131.227
øO(6)-C(7)-H(10)	116.719

[a] Distances are in angstroms, Angles are in degrees.

Table 2.26 Calculated Vibrational Spectrum of Triplet 3-Furylmethylene (ø =180°) using UHF/6-31G*.[a]

Calculated	Scaled	Relative Intensity
290	261	.01
367	330	0
444	400	.4
575	518	.4
618	556	.3
676	608	.1
729	656	.06
815	734	1
913	822	.7
934	841	.04
970	873	.2
1033	930	.02
1116	1004	.9
1180	1062	.2
1309	1178	.5
1349	1214	.8
1399	1259	.04
1450	1305	.2
1603	1443	.2
1639	1475	.2
3433	3090	.1
3437	3093	.04
3472	3125	.1
3477	3129	0

[a] Frequencies in cm^{-1}. All calculated frequencies were scaled by a factor of 0.9.

Table 2.27 Calculated Zero Point and Ground State Energies for Triplet 3-Furylmethylene (ø =180°).[a]

Zero Point Energy	47.5(Kcal/mol)
Ground State Energy MP4SDTQ	-267.35858 (au)
Ground State Energy QCISD(T)	-267.36962 (au)

[a] Zero point energy calculated using UHF/6-31G* , Ground state energies calculated using 6-311G** basis set. (1 au = 627.5 Kcal/mol)

Figure 2.14 Chem3D Rendering of Triplet 3-Furylmethylene (ø = 180°) calculated using MP2/6-31G*.

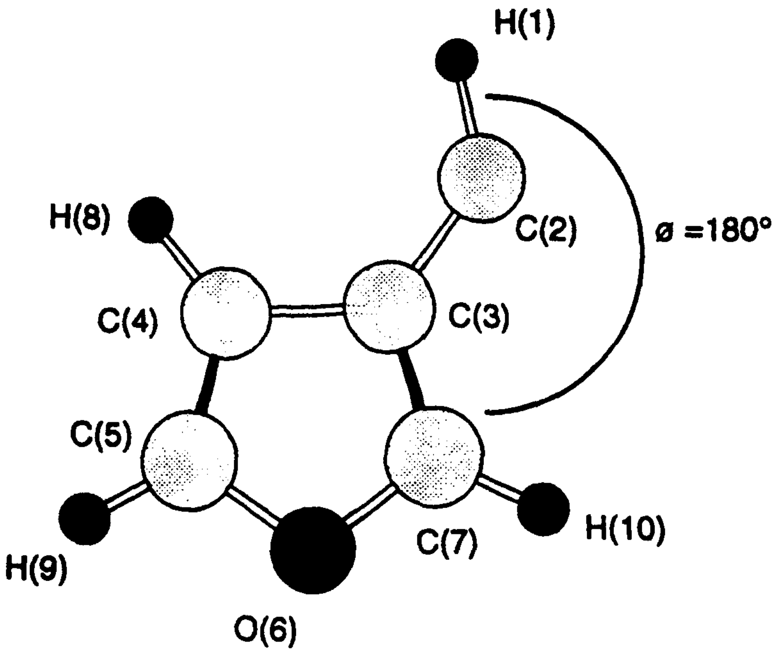


Table 2.28 Bond Distances for Triplet 3-Furylmethylene (ø =180°) calculated using UHF/6-31G*.[a]

Atom Type and Number	Bond Distance/Angle
rH(1)-C(2)	1.070
rC(2)-C(3)	1.398
rC(3)-C(4)	1.453
rC(3)-C(7)	1.390
rC(4)-C(5)	1.346
rC(4)-H(8)	1.070
rC(5)-O(6)	1.351
rC(5)-H(9)	1.068
rO(6)-C(7)	1.354
rC(7)-H(10)	1.067
øH(1)-C(2)-C(3)	132.369
øC(2)-C(3)-C(4)	128.171
øC(2)-C(3)-C(7)	127.559
øC(4)-C(3)-C(7)	104.277
øC(3)-C(4)-C(5)	106.400
øC(3)-C(4)-H(8)	126.829
øC(5)-C(4)-H(8)	126.775
øC(4)-C(5)-O(6)	111.498
øC(4)-C(5)-H(9)	132.406
øO(6)-C(5)-H(9)	116.100
øC(5)-O(6)-C(7)	107.223
øC(3)-C(7)-O(6)	110.608
øC(3)-C(7)-H(10)	132.486
øO(6)-C(7)-H(10)	116.912

[a] Distances are in angstroms, Angles are in degrees.

Appendix 5

Ab Initio Calculations for Potential 3-Furylmethylene Rearrangement Products

Table 2.29 Calculated Vibrational Spectrum of 2-Oxabicyclo[3.1.0]hexa-3.5-diene using HF/6-31G*.[a]

Calculated	Scaled	Relative Intensity
348	313	.1
465	419	.1
589	530	.1
758	682	.7
778	700	.2
831	748	0
887	798	.5
921	829	1
956	860	.2
1047	942	0
1082	974	.2
1109	998	0
1156	1040	.1
1174	1057	.4
1250	1125	.2
1281	1153	.2
1429	1286	.1
1496	1346	0
1722	1550	.8
1885	1697	.4
3350	3015	.4
3437	3093	0
3460	3114	0
3469	3122	.1

[a] Frequencies in cm^{-1}. All calculated frequencies were scaled by a factor of 0.9.

Table 2.30 Calculated ZPE for 2-Oxabicyclo[3.1.0]hexa-3,5-diene.[a]

Zero Point Energy	49.9 (Kcal/mol)

[a] Zero point energy calculated using HF/6-31G*.

Figure 2.15 Chem3D Rendering of 2-Oxabicyclo[3.1.0]hexa-3,5-diene calculated using HF/6-31G*.

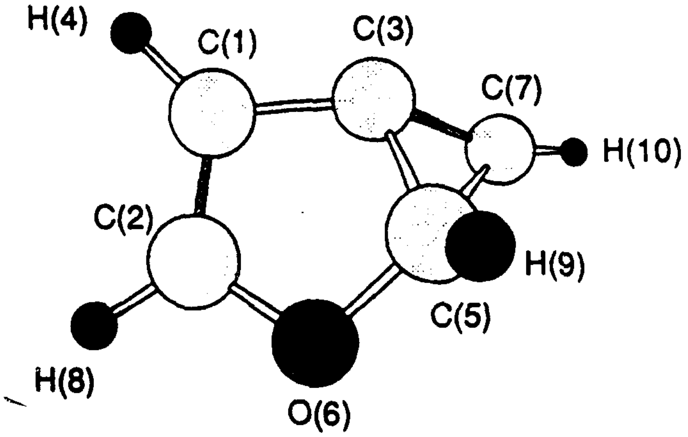


Table 2.31 Bond Distances for 2-Oxabicyclo[3.1.0]hexa-3,5-diene calculated using HF/6-31G*.[a]

Atom Type and Number	Bond Distance/Angle
rC(1)-C(2)	1.339
rC(1)-C(3)	1.456
rC(1)-H(4)	1.068
rC(2)-O(6)	1.343
rC(2)-H(8)	1.072
rC(3)-C(5)	1.455

Continued on next page

Table 2.31 Bond Distances for 2-Oxabicyclo[3.1.0]hexa-3,5-diene calculated using HF/6-31G*.^{a} (Continued)

Atom Type and Number	Bond Distance/Angle
rC(3)-C(7)	1.300
rC(5)-O(6)	1.446
rC(5)-C(7)	1.468
rC(5)-H(9)	1.075
rC(7)-H(10)	1.069
øC(2)-C(1)-C(3)	101.511
øC(2)-C(1)-H(4)	127.487
øC(3)-C(1)-H(4)	130.260
øC(1)-C(2)-O(6)	117.104
øC(1)-C(2)-H(8)	127.662
øO(6)-C(2)-H(8)	115.107
øC(1)-C(3)-C(5)	108.626
øC(1)-C(3)-C(7)	144.623
øC(5)-C(3)-C(7)	64.108
øC(3)-C(5)-O(6)	102.247
øC(3)-C(5)-C(7)	52.816
øC(3)-C(5)-H(9)	128.922
øO(6)-C(5)-C(7)	121.63
øO(6)-C(5)-H(9)	109.968
øC(7)-C(5)-H(9)	126.835
øC(2)-O(6)-C(5)	105.900
øC(3)-C(7)-C(5)	63.076
øC(3)-C(7)-H(10)	145.890
øC(5)-C(7)-H(10)	146.903

^{a} Distances are in angstroms, Angles are in degrees.

Table 2.32 Calculated Vibrational Spectrum of 4-Pyranylidene using HF/6-31G*.[a]

Calculated	Scaled	Relative Intensity
327	294	.2
400	360	0
613	552	0
665	599	.1
718	646	0
915	824	.1
983	885	0
1014	913	.3
1062	956	.2
1115	1004	0
1117	1005	.1
1119	1007	0
1165	1049	0
1344	1210	.1
1351	1216	0
1456	1310	.3
1579	1421	.1
1588	1429	.2
1660	1494	.3
1785	1607	1
3358	3022	.2
3360	3024	.02
3427	3084	.2
3431	3088	.05

[a] Frequencies in cm^{-1}. All calculated frequencies were scaled by a factor of 0.9.

Table 2.33 Calculated Zero Point Energy for 4-Pyranylidene.[a]

Zero Point Energy	50.8 (Kcal/mol)

[a] Zero point energy calculated using HF/6-31G*.

Figure 2.16 Chem3D Rendering of 4-Pyranylidene calculated using HF/6-31G*.

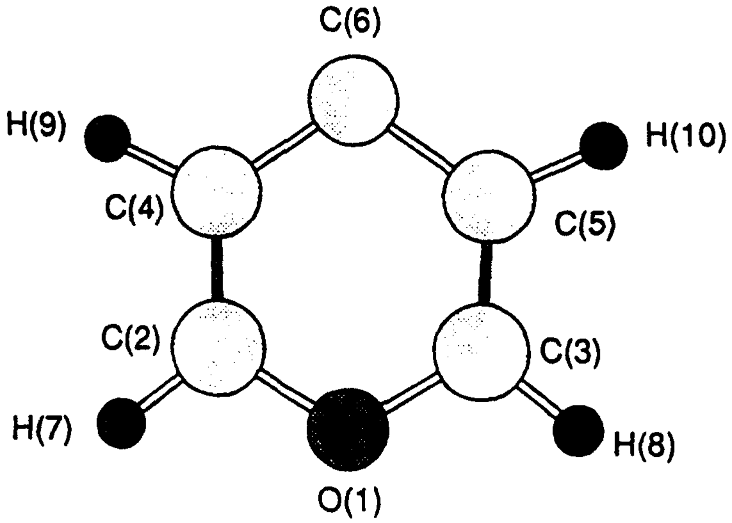


Table 2.34 Bond Distances for 4-Pyranylidene calculated using HF/6-31G*.[a]

Atom Type and Number	Bond Distance/Angle
rO(1)-C(2)	1.327
rO(1)-C(3)	1.327
rC(2)-C(4)	1.343
rC(2)-H(7)	1.072
rC(3)-C(5)	1.343
rC(3)-H(8)	1.072
rC(4)-C(6)	1.441
rC(4)-H(9)	1.076
rC(5)-C(6)	1.441
rC(5)-H(10)	1.076
øC(2)-O(1)-C(3)	118.678
øO(1)-C(2)-C(4)	122.477
øO(1)-C(2)-H(7)	111.456
øC(4)-C(2)-H(7)	126.072
øO(1)-C(3)-C(5)	122.479
øO(1)-C(3)-H(8)	111.455
øC(5)-C(3)-H(8)	126.072
øC(2)-C(4)-C(6)	122.953
øC(2)-C(4)-H(9)	116.980
øC(6)-C(4)-H(9)	120.071
øC(3)-C(5)-C(6)	122.953
øC(3)-C(5)-H(10)	116.984
øC(6)-C(5)-H(10)	120.071
øC(4)-C(6)-C(5)	110.470

[a] Distances are in angstroms, Angles are in degrees.

Table 2.35 Calculated Vibrational Spectrum of Methylenecyclopropene Derivative using HF/6-31G*.[a]

Calculated	Scaled	Relative Intensity
154	139	0
194	175	0
266	239	0
428	385	0
558	502	0
775	698	.1
835	752	0
857	771	.2
945	851	0
1042	938	0
1074	967	.1
1095	986	0
1152	1037	0
1175	1058	.1
1271	1144	.1
1505	1355	0
1565	1409	0
1652	1487	.95
1880	1692	1
1972	1775	.4
3144	2830	.4
3383	3045	0
3475	3128	0
3521	3169	0

[a] Frequencies in cm^{-1}. All calculated frequencies were scaled by a factor of 0.9.

Table 2.36 Calculated Zero Point Energy for Methylenecyclopropene Derivative .[a]

Zero Point Energy	48.5 (Kcal/mol)

[a] Zero point energy calculated using HF/6-31G*.

Figure 2.17 Chem3D Rendering of Methylenecyclopropene Derivative calculated using HF/6-31G*.

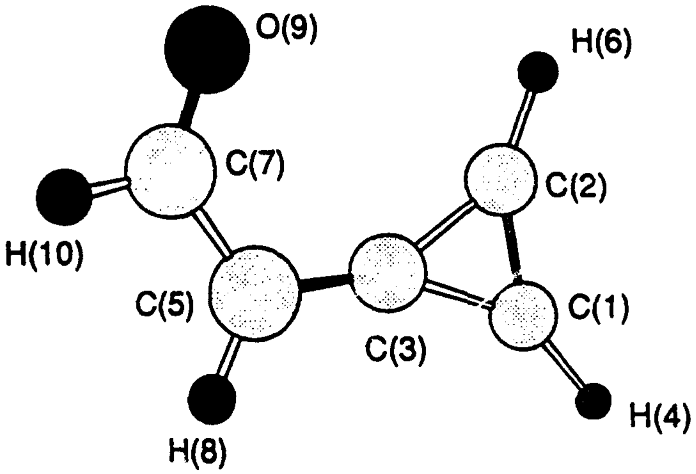


Table 2.37 Bond Distances for Methylenecyclopropene Derivative calculated using HF/6-31G*.[a]

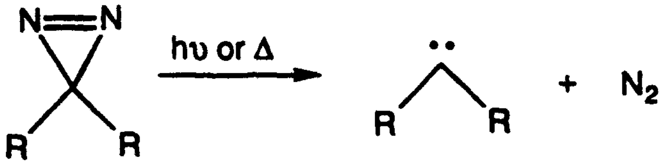
Atom Type and Number	Bond Distance/Angle
rC(1)-C(2)	1.310
rC(1)-C(3)	1.407
rC(1)-H(4)	1.068
rC(2)-C(3)	1.405
rC(2)-H(6)	1.067
rC(3)-C(5)	1.342
rC(5)-C(7)	1.451
rC(5)-H(8)	1.074
rC(7)-O(9)	1.202
rC(7)-H(10)	1.096
øC(2)-C(1)-C(3)	62.127
øC(2)-C(1)-H(4)	149.15
øC(3)-C(1)-H(4)	148.723
øC(1)-C(2)-C(3)	62.351
øC(1)-C(2)-H(6)	150.129
øC(3)-C(2)-H(6)	147.527
øC(1)-C(3)-C(2)	55.523
øC(1)-C(3)-C(5)	154.743
øC(2)-C(3)-C(5)	149.737
øC(3)-C(5)-C(7)	119.127
øC(3)-C(5)-H(8	120.954
øC(7)-C(5)-H(8)	119.925
øC(5)-C(7)-O(9)	125.663
øC(5)-C(7)-H(10)	114.775
øO(9)-C(7)-H(10)	119.570

[a] Distances are in angstroms, Angles are in degrees

Chapter 3 Approaches to 2-Furyldiazirine

3.0 Introduction

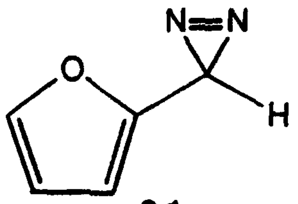
Our initial approach to 2-furylmethylene was via the diazirine precursor. Diazirines are cyclic isomers of diazo compounds which, like the diazo compound, readily decompose to give a carbene and a molecule of nitrogen. [1]



However, unlike the diazo compound, they are more stable towards electrophiles, nucleophiles, and cycloadditions. As such, they are frequently used as a precursor for carbenes.

3.1 Background

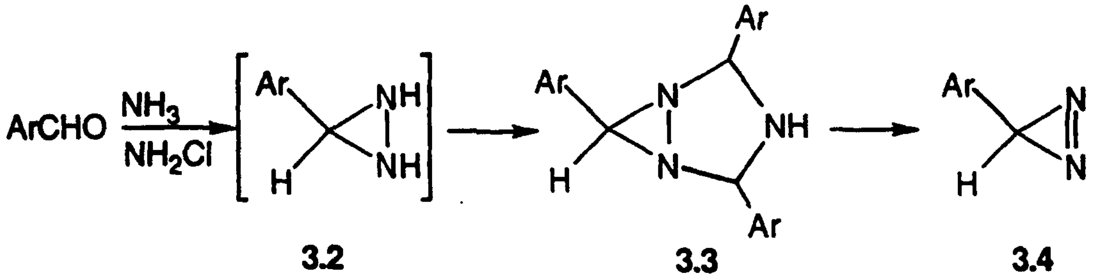
We decided to chose 2-furaldehyde as the starting point for our diazirine synthesis. A number of reports have appeared in the literature regarding the synthesis of diazirines. However, there are only a few reports of diazirines synthesized from aryl aldehydes [2-4]. No literature precedent was found for the synthesis of 3-(2-furyl)-3H-diazirine **3.1**.



3.1

In general, synthesis of diazirines from aldehydes involves reaction of ammonia and chloramine to generate the diaziridine **3.2**. Chloramine is generated *in-situ* from the reaction of ammonia and t-butylhypochlorite. The diaziridine reacts further under the reaction conditions to give the bicyclic compound **3.3** (Scheme 3.1).

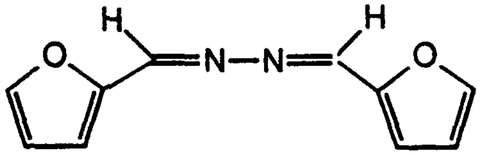
Scheme 3.1 Synthesis of Diazirines from Aryl Aldehydes



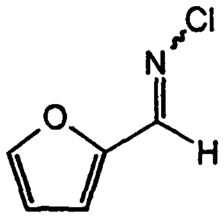
These bicyclic compounds are mixtures of two to three stereoisomers due to the chiral centers at the ring carbons. [5] Oxidative cleavage of **3.3** generates the diazirine **3.4**. Yields for this reaction with benzaldehyde and various *m*-substituted derivatives are between 26 and 45%. [2]

3.2 Results

In order to test the feasibility of this reaction starting with 2-furaldehyde we decided to isolate the bicyclic intermediate **3.3** (Ar = 2-furyl), before proceeding with the oxidation to give the diazirine. Our first attempts were based on the procedures reported by Nielsen [5] and Leblanc [3]. Nielsen reports a yield of 42% for **3.3** (Ar = phenyl). Leblanc does not isolate the bicyclic compound, but reports 24% yield for **3.4** (Ar = *m*-methoxymethylene phenylether). Results with 2-furaldehyde indicate possible formation of the azine **3.5** and/or imine **3.6** along with recovered starting material. The desired bicyclic compound **3.3** (Ar = 2-furyl) was not detected.



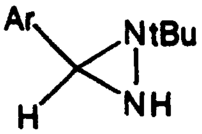
3.5



3.6

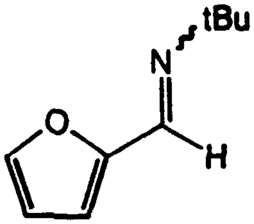
We then examined the procedure reported by Stevens [4] where **3.3** (Ar = phenyl) is obtained in 19% yield. Before attempting this on 2-furaldehyde, we checked this procedure using benzaldehyde and obtained **3.3** (Ar = phenyl) in 8% yield. Reaction with 2-furaldehyde again resulted in mostly recovered starting material and either the azine **3.5** or the imine **3.6**.

Our next attempt was based on the procedure by Knowles [2]. This synthesis uses t-butylamine and hydroxylamine-*O*-sulphonic acid to form the diaziridine **3.7** which is oxidized, *in-situ* ,using t-butyl hypochlorite to give the diazirine.



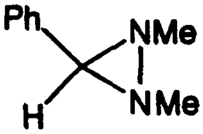
3.7

Results with 2-furaldehyde indicate formation of t-butylimine **3.8** and recovered starting material.



3.8

Other attempts to prepare the diazirine were based on the formation of a substituted diaziridine that could be oxidatively cleaved or "deprotected" to give the diazirine. The starting point for this approach was based on the synthesis of 1,2-dimethyl-3-phenyldiaziridine **3.9** reported by Coates. [6]

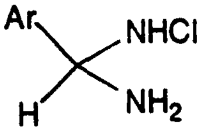


3.9

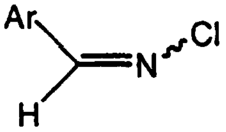
Synthesis of **3.9** is reported in 39% yield by the addition of methylamine and periodic acid to a solution of benzaldehyde. We attempted several modifications of this procedure starting with benzaldehyde and using t-butylamine and benzylamine in place of methylamine. Results indicated formation of the appropriate imine and recovered starting material.

3.3 Discussion

Attempts to synthesize the bicyclic intermediate **3.3** (Ar = 2-furyl) using chloramine resulted in formation of the azine **3.5** and/or the imine **3.6** (Ar = 2-furyl). Knowles [2] suggests that when chloramine is used as the aminating reagent, ring closure of the diamine **3.10** is competitive with elimination of ammonia to give the imine **3.11**.



3.10



3.11

The azine **3.5** (Ar = furyl) is also reported as a side product in Knowles' synthesis of diazirine **3.4** (Ar = *p*-methoxyphenyl). This product may be a result of the electron-rich character of these ring systems which enhance the nucleophilicity of the simple imine formed from the initial condensation of 2-furaldehyde with ammonia.

Failure to achieve a diaziridine similar to **3.9**, with benzyl or t-butyl groups versus methyl is probably a result of steric factors.

Unable to synthesize the diazirine from 2-furaldehyde, we decided to use the known diazo compound, 2-furyldiazomethane, to generate the carbene. Attempts to make the diazirine may be revisited in our future investigations of 2-furylmethylene.

3.4 References for Chapter 3

(1) For a comprehensive review on diazirines see: *Chemistry of Diazirines*; Liu, M. T. H., Ed.; CRC Press: Boca Raton, 1987; Vol. I and II.

(2) Smith, R. A. G.; Knowles, J. R. *J.C.S. Perkin II* **1975**, 686-694.

(3) Leblanc, P.; Gerber, G. E. *Can. J. Chem.* **1984**, *62*, 1767-1771.

(4) Bradley, G. F.; Evans, W. B.; Stevens, I. D. R. *J.C.S. Perkin II* **1977**, 1214-1220.

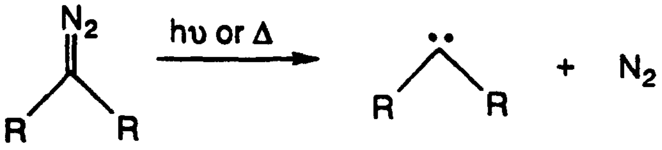
(5) Nielsen, A. T.; Moore, D. W.; Atkins, R. L.; Mallory, D.; DiPol, J.; LaBarge, J. M. *J. Org. Chem.* **1976**, *41*, 3221-3229.

(6) Chang, Z.-Y.; Coates, R. M. *J. Org. Chem.* **1990**, *55*, 3475-3483.

Chapter 4 Synthesis of 2- and 3- Furyldiazomethane

4.0 Introduction

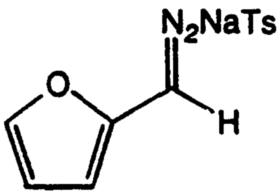
Diazo compounds decompose to the respective carbene and a molecule of nitrogen with an energy of activation around 30 Kcal/mol. [1]



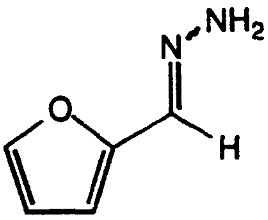
They are readily prepared and, like diazirines, they are frequently used as a source of carbene.

4.1 Background

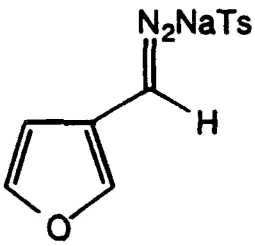
Both 2- and 3-furyldiazomethane are known compounds which have been prepared in one of two ways. They can be generated by the photolysis or pyrolysis of the tosylhydrazone salt [2-4] **4.1** and **4.3** or by oxidation of the hydrazone [4-7] **4.2** and **4.4** .



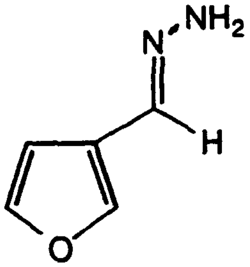
4.1



4.2



4.3



4.4

2-Furyldiazomethane is reported to be an unstable red oil with a half-life of two hours in n-pentane (25° C, in the dark) characterized as follows: IR absorption for the diazo group 2070 (s) cm^{-1}, and λ_{max} (Et_2O) 504 nm, $\varepsilon \sim 38$ [5]. No characterization of 3-furyldiazomethane was found in the literature.

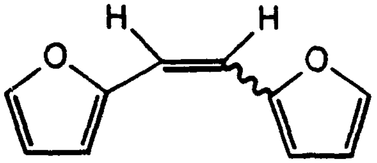
Photolysis or thermolysis of the tosyl hydrazone salt generates the diazo compound which then, under the high temperature conditions, readily loses nitrogen to afford the carbene.

Oxidation of **4.2** and **4.4** is usually accomplished with manganese dioxide. Yields for the reaction are reported to be low. Subsequent reactions of the diazo compound are then carried out in the same solution used for the oxidation.

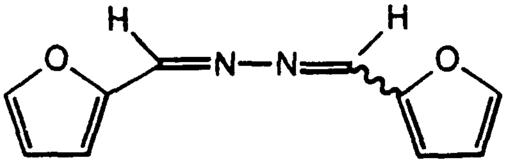
In all of the previous reports, there was no attempt to purify the two diazo compounds. In order to conduct matrix isolation studies on the corresponding carbenes, we needed to develop a method to purify the diazo compounds. Thus we decided to form the diazo compounds via oxidation of **4.2** and **4.4,** and then to purify to them under low temperature and pressure conditions.

4.2 Results

Following Wolffs' procedure, [8] addition of an ether solution of 2-furaldehyde to excess hydrazine hydrate (10%) gave the hydrazone **4.2**, after distillation, in over 80% yield. Oxidation of the hydrazone was accomplished using activated manganese dioxide in ether at 0° C [6]. Yields for this reaction could not be determined due to the volatility of the diazo compound. This diazo solution was then immediately purified via dynamic transfer under high vacuum using a series of cold traps. The diazo compound that was collected was a dark red solid at -78° C. It was effectively stored at -78° C in the dark for over four weeks. If the diazo compound was allowed to warm to room temperature, the red solid immediately melted and began to bubble, indicating loss of nitrogen, and formed a yellow crystalline solid. The major product identified was a mixture of cis- and trans-1,2-di(2-furyl)ethylene **4.5**[9] in a 2:1 ratio (cis:trans) along with a very small amount of azine **4.6** and starting material **4.2**.

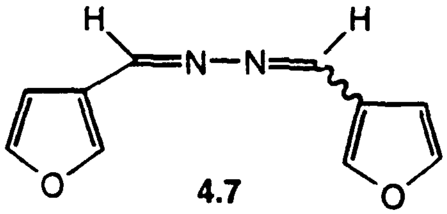


4.5



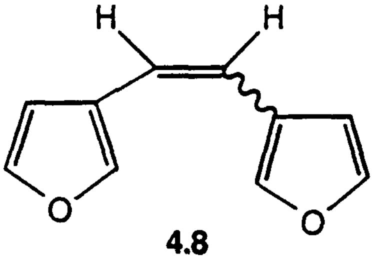
4.6

A modification of this procedure was used for the preparation of 3-furyldiazomethane. The two isomers of the hydrazone **4.4** were obtained in 90% yield using 20% excess hydrazine hydrate. However, the hydrazone proved to be an unstable liquid, readily decomposing at room temperature to azine **4.7**[10].



4.7

The hydrazone was, therefore, immediately oxidized to the diazo compound using the same conditions used for 2-furylhydrazone. However, purification of the resulting diazo compound was also more difficult. Conditions for the purification required adjusting the temperature and pressure for the dynamic transfer. Additionally, the transfer was done in the dark. The resulting diazo compound was a dark red solid. Storage in the dark at -78° C resulted in slow decomposition of the diazo compound. However, it was easily repurified under vacuum. If allowed to warm to room temperature the same results noted for 2-furyldiazomethane were observed. Analysis of the resulting yellow crystalline solid indicate the major product to be a mixture of cis- and trans-1,2-di-(3-furyl)ethylene **4.8** [3,11] along with a small amount of the azine **4.7** [10].



4.8

This mixture was separated using column chromatography with hexane [3,11] as an eluent in order to better assign the ^1H NMR peaks observed for the mixture.

4.3 Discussion

Both 2- and 3-furyldiazomethane were purified in preparation for matrix isolation experiments. As noted previouly, no reports for their purification were found in the literature.

During the preparation of **4.2** and **4.4**, both isomers (cis and trans with respect to the C-N double bond) were obtained in approximately a 3:1 ratio for **4.2** and a 10:1 ratio for **4.4**. Both sets of peaks are reported in the experimental section, however, we did not attempt to identify which set of peaks belong to the cis or trans isomer. No ^{1}H NMR data for either of these compounds was found in the literature.

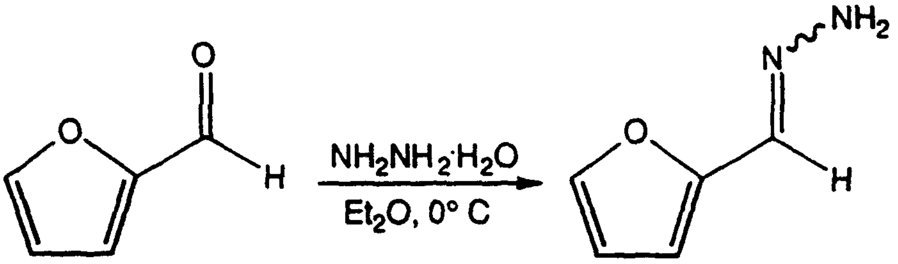
An interesting observation found with both 2- and 3-furyldiazomethane is that both compounds, when neat, decompose at room temperature to give the ethylenes **4.5** and **4.8** respectively. The ethylenes might be formed via one of two reaction pathways or a combination of the two. One pathway involves simple dimerization of the resulting carbene, the other is the reaction of the carbene and the diazo compound.

4.4 Experimental Procedure

General

All reagents used are commercially available and were used without further purification unless otherwise noted. Activated manganese dioxide was purchased from Aldrich. Proton and carbon magnetic resonance spectra were taken in $CDCl_3$ with a Bruker 500 and 250 MHz spectrometer. Chemical shifts are in δ units with an internal standard of $CDCl_3$ at 7.24 ppm for proton and 77 ppm for carbon. Infrared spectra were run on a Perkin-Elmer 1430 instrument.

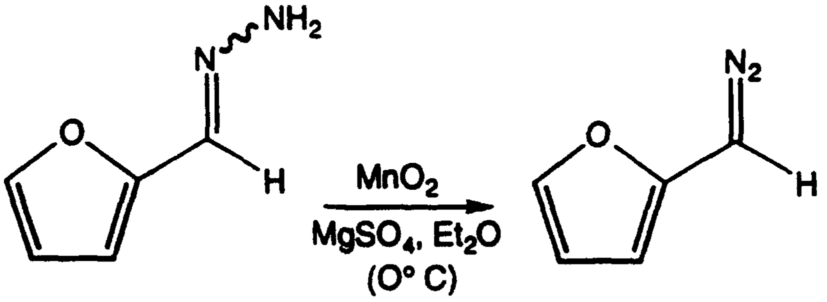
Preparation of 2-Furylhydrazone



Hydrazine hydrate (28.67 g, 0.57 mol) was added to a 250 mL round bottom flask and cooled in an ice bath. Freshly distilled 2-furaldehyde (50.0 g, 0.52 mol) was dissolved in 50 mL of anhydrous ether. The aldehyde solution was added dropwise over a 1 hr period to the hydrazine hydrate while stirring and maintaining the temperature between 0° and 5° C. After addition of the aldehyde solution, the reaction was left to stir for another 2.5 hr at 0° - 5° C. The resulting lemon yellow solution was dried overnight using sodium sulfate. The solution was then decanted from the sodium sulfate and the ether removed under reduced pressure. The hydrazone was distilled (50° C, 110 mTorr) to afford 47.60 g (83%) of 2-furylhydrazone.

IR (neat) 3380 (b), 1495 (m), 1150 (s), 1015 (s), 930 (s), 670 (s) cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ Major isomer; 7.62 (s,1H, C=N H), 7.40 (d, 1H, J = 1.6Hz, 5-furyl H), 6.44 (d, 1H, J = 3.3 Hz, 3-furyl H), 6.41 (dd, 1H, J = 3.3 and 1.7 Hz, 4-furyl H), 5.65 (bs, 2H, NH_2). Minor isomer; 7.50 (d, 1H, J = 1.6 Hz, 5-furyl H), 7.15 (s, 1H, C=N H), 6.62 (d, 1H, J = 3.5 Hz, 3-furyl H), 6.49 (dd, 1H, J = 3.5 and 1.7 Hz, 4-furyl H), 6.29 (bs, 2H, NH_2).

Preparation of 2-Furyldiazomethane



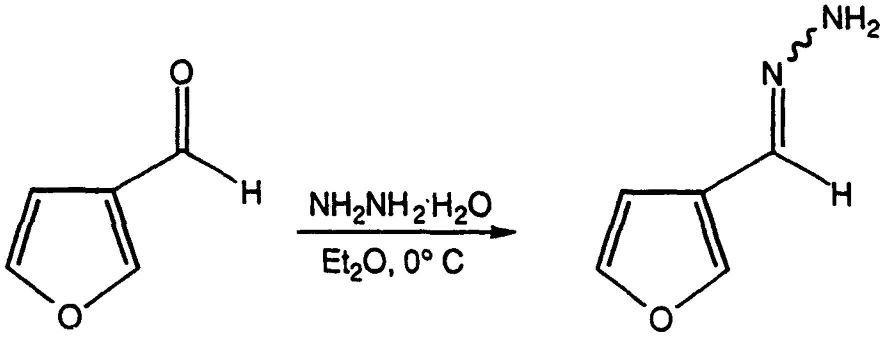
2-Furylhydrazone (0.51 g, 5 mmol) and 5 mL of anhydrous ether were added to a 100 mL round bottom flask and cooled in an ice bath (0° C). Activated manganese dioxide (1.65 g, 19 mmol) and magnesium sulfate (0.05 g, 0.04 mmol) were added to the aldehyde solution and the solution was stirred, under argon, for 30 min while maintaining the temperature at 0° C. After 30 min., the dark red solution was filtered through a fritted funnel into a 100 mL round bottom flask cooled to 0° C. This dark red solution was immediately fractionated under vacuum at approximately 10 mTorr using a series of two cold traps while maintaining the diazo solution at 0° C. Initially, the traps were at -30° C and -196° C until most of the ether was removed and a red color was observed in the -196° C trap. The first trap was then cooled to -78° C. The transfer was complete after approximately one hour. The product in the -78° C trap was a dark red solid that was maintained at -78° C for use in our matrix isolation studies.

Spectroscopic data is provided from a preliminary run of this experiment. The -78° C trap containing the diazo compound was allowed to warm to room temperature, leaving a yellow crystalline solid. The major product identified was a mixture of cis-1,2-di(2-furyl)ethylene and trans-1,2-di(2-furyl)ethylene in a 2:1 ratio respectively.

cis-1,2-Di(2-furyl)ethylene: ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.43 (d, 2H, J = 1.7 Hz, 5-furyl H), 6.81 (d, 1H, J = 3.3 Hz, 3-furyl H), 6.44 (dd, J = 1.8 and 3.3 Hz, 4-furyl H), 6.18 (s, 1H, vinyl H)

trans-1,2-Di(2-furyl)ethylene: ^{1}H NMR (250 MHz, CDCl$_3$) δ 7.36 (d, 1H, J = 1.6 Hz, 5-furyl H), 6.79 (s, 1H, vinyl H), 6.39 (dd, 1H, J = 1.8 and 3.3 Hz, 4-furyl H), 6.30 (d, 1H, J = 3.3 Hz, 3-furyl H)

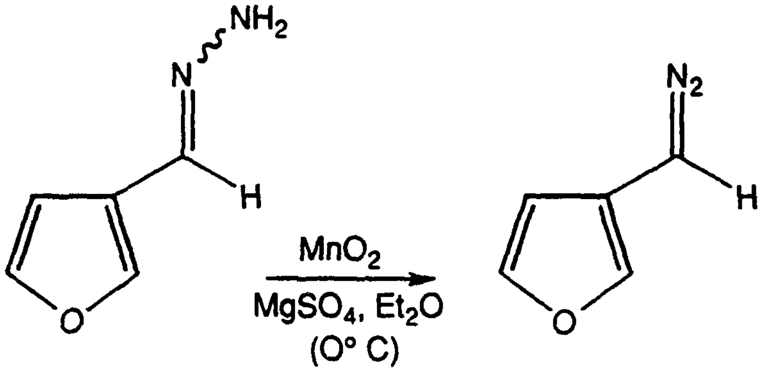
Preparation of 3-Furylhydrazone



Hydrazine hydrate (1.82 g, 36 mmol) was added to a 50 mL round bottom flask and cooled in an ice bath. Freshly distilled 3-furaldehyde (2.9 g, 30 mmol) was dissolved in approximately 5 mL of anhydrous ether. The aldehyde solution was added dropwise over a 1 hr period to the hydrazine hydrate while stirring and maintaining the temperature between 0° and 5° C. After addition of the aldehyde solution, the reaction was left to stir for another 2 hr at 0° - 5° C. The resulting light yellow solution was dried overnight using sodium sulfate. The solution was decanted from the sodium sulfate and the ether removed under reduced pressure. The hydrazone (2.97 g, 90%) was used without further purification for the oxidation to the diazo compound.

IR (neat) 3420 (m), 2250 (m), 1645 (m), 1515 (m), 1160 (s), 1065 (m), 1020 (m), 875 (s), 785 (s) cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ Major isomer; 7.67 (s, 1H, C=N H), 7.51 (d, 1H, J = .6 Hz, 2-furyl H), 7.36 (m, 1H, 5-furyl H), 6.66 (d, 1H, J = 1.4 Hz, 4-furyl H), 5.38 (bs, 2H, NH_2). Minor isomer (all peaks not identified); 7.92 (s,1H, C=N H), 7.47 (d, 1H, J = 1.6), 6.56 (d, 1H, J = 0.9 Hz).

Preparation of 3-Furyldiazomethane



3-Furylhydrazone (2.97 g, 27 mmol) and 5 mL of anhydrous ether were added to a 100 mL round bottom flask and cooled in an ice bath (0° C). Activated manganese dioxide (8.93 g, 103 mmol) and magnesium sulfate (0.33 g, 3 mmol) were added to the aldehyde solution and the solution was stirred in the dark, under argon, for 30 min while maintaining the temperature at 0° C. After 30 min., the dark red solution was filtered, again in the dark, through a fritted funnel into a 100 mL round bottom flask cooled to -78° C. This dark red solution was immediately fractionated under vacuum, in the dark, at approximately 1 mTorr using a series of two cold traps (-78° C and -196° C) while maintaining the diazo solution at -30° C. After two hours, the product in the 100 mL round bottom flask was a dark red solid, the -78° C trap contained a small amount of red solid along with a colorless solid, and the -196° C trap contained a white solid. The red solid remaining in the original 100 mL round bottom flask was fractionated a second time. Again the diazo compound was maintained at -30° C and transferred to a -196° C trap in the dark for 6 hours at a pressure of 4 x 10^{-4} Torr. The product in the -196° C trap was a dark red solid that was maintained at -78° C for use in our matrix isolation studies. Note that this product was purified immediately prior to each deposition by warming the trap to -30° C and transferring a small amount of material into a -78° C trap until the -30° C trap was a dark red solid. Conditions for this purification were typically one hour at a pressure of 2 - 5 x 10^{-4}. The material collected in the -78° C trap was usually a light red/orange color.

Spectroscopic data is provided for the material collected in the -78° C trap from one of these purifications. The major product identified, after allowing the trap to warm to room temperature was a mixture of cis-1,2-di(3-furyl)ethylene and trans-1,2-di(3-furyl)ethylene in approximately a 1.1:1 ratio. The ethylenes were separated on silica gel with hexane as an eluent.

cis-1,2-Di(3-furyl)ethylene: IR ($CDCl_3$) 3180 (m), 3010 (m), 2960 (m), 2300 (s), 2250 (m), 1440 (s), 1380 (s), 1040 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (s, 2H, 2-furyl H), 7.33 (m, 2H, 5-furyl H), 6.40 (d, 2H, J = 1.1 Hz, 4-furyl H), 6.27 (s, 2H, vinyl H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 142.66, 141.44, 119.87, 110.53 (not all carbons were identified).

trans-1,2-Di(3-furyl)ethylene: IR ($CDCl_3$) 2350 (w), 1390 (w), 1160 (w), 1080 (w), 1030 (w), 960 (w), 880 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 (m, 2H, 2-furyl H), 7.37 (d, 2H, J = 1.5 Hz, 5-furyl H), 6.66 (s, 2H, vinyl H), 6.58 (d, 2H, J = 1.1 Hz, 4-furyl H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 143.63, 140.34, 124.46, 118.21, 107.28.

4.5 References for Chapter 4

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4.6 Spectra Relevant to Chapter 4

Figure 4.1 IR (neat) 2-Furylhydrazone.

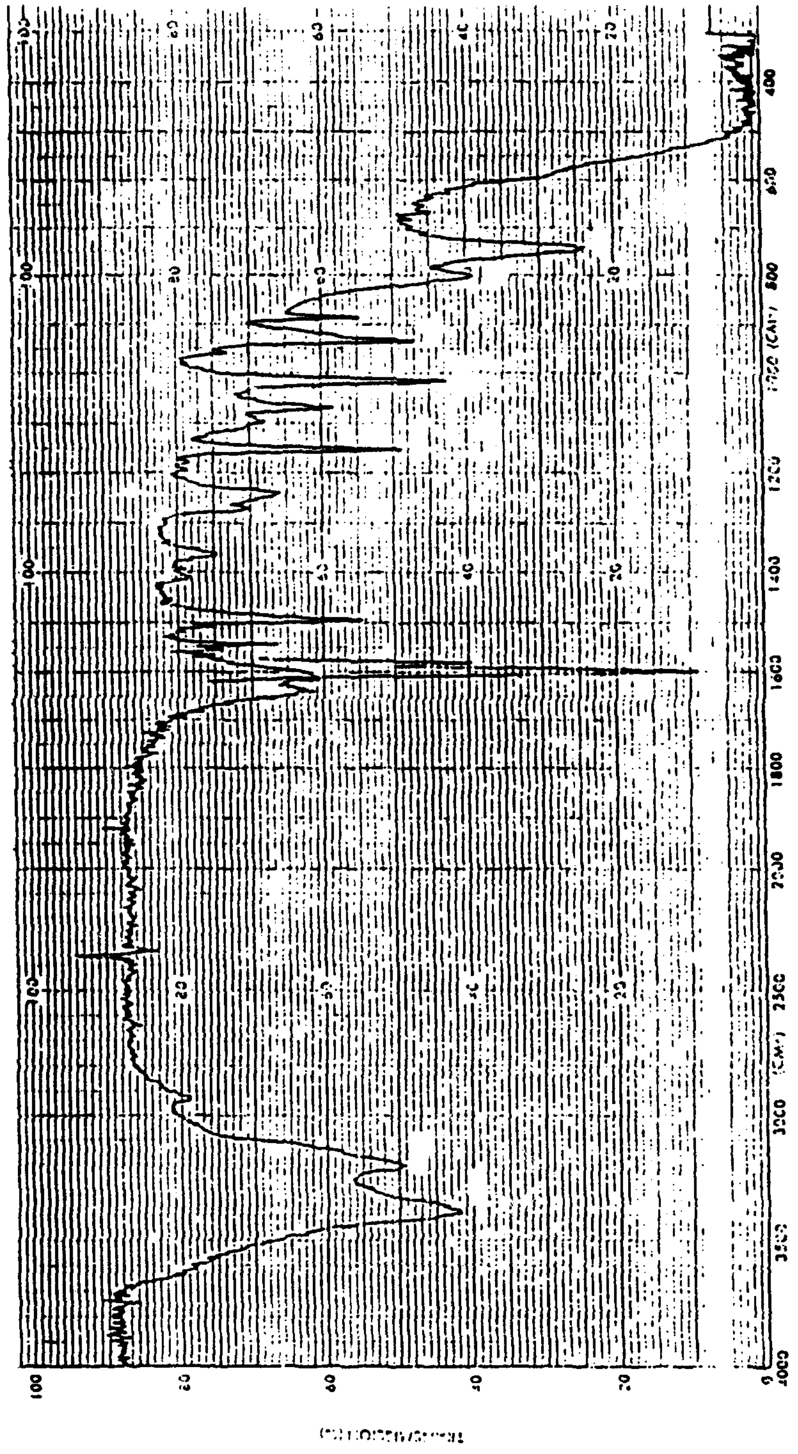


Figure 4.2 ^{1}H NMR (CDCl$_3$, 250 MHz) 2-Furylhydrazone.

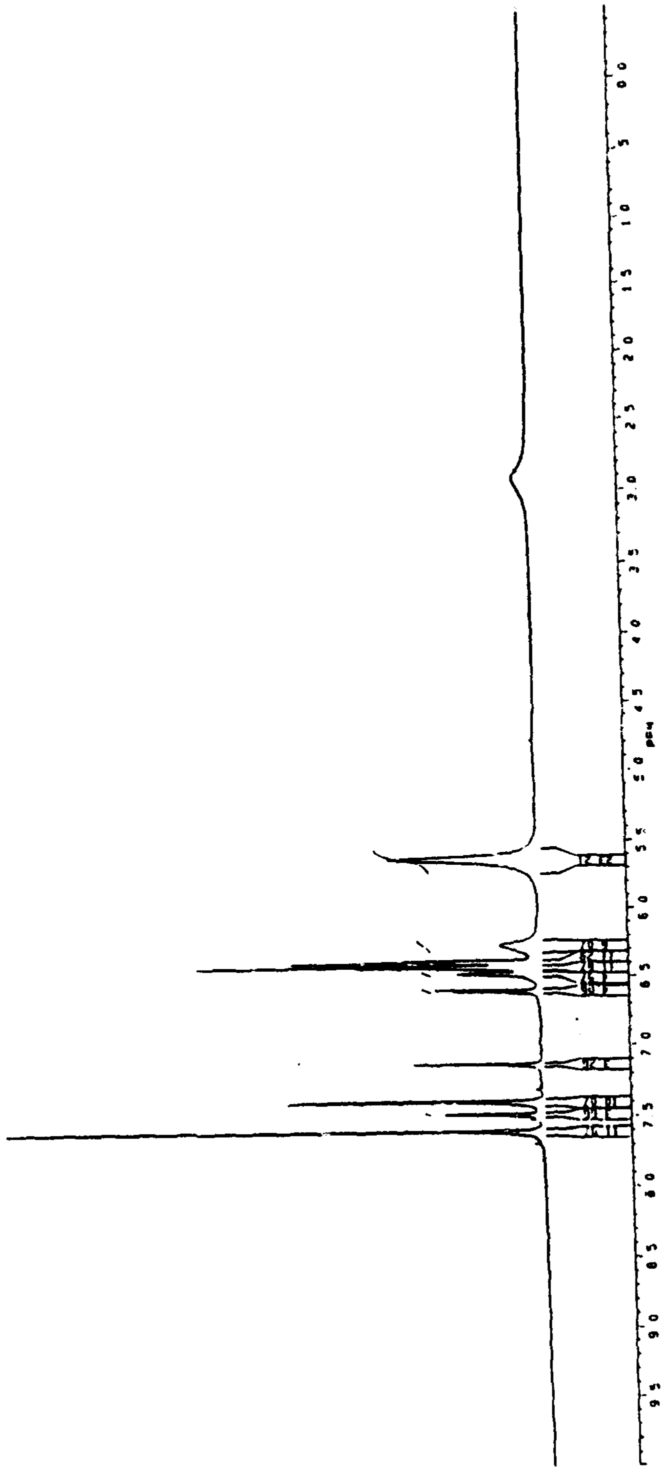


Figure 4.3 ^1H NMR ($CDCl_3$, 250 MHz) cis- and trans-Di(2-Furyl)ethylene.

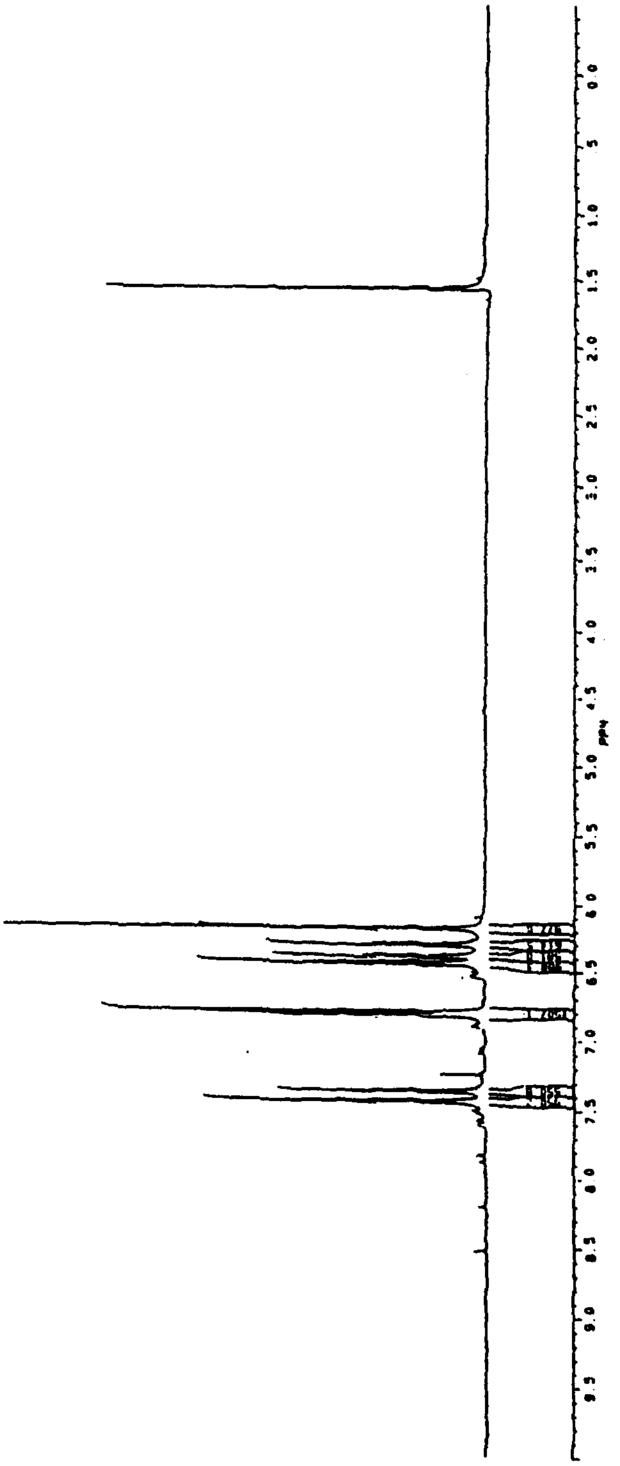


Figure 4.4 IR ($CDCl_3$) 3-Furylhydrazone.

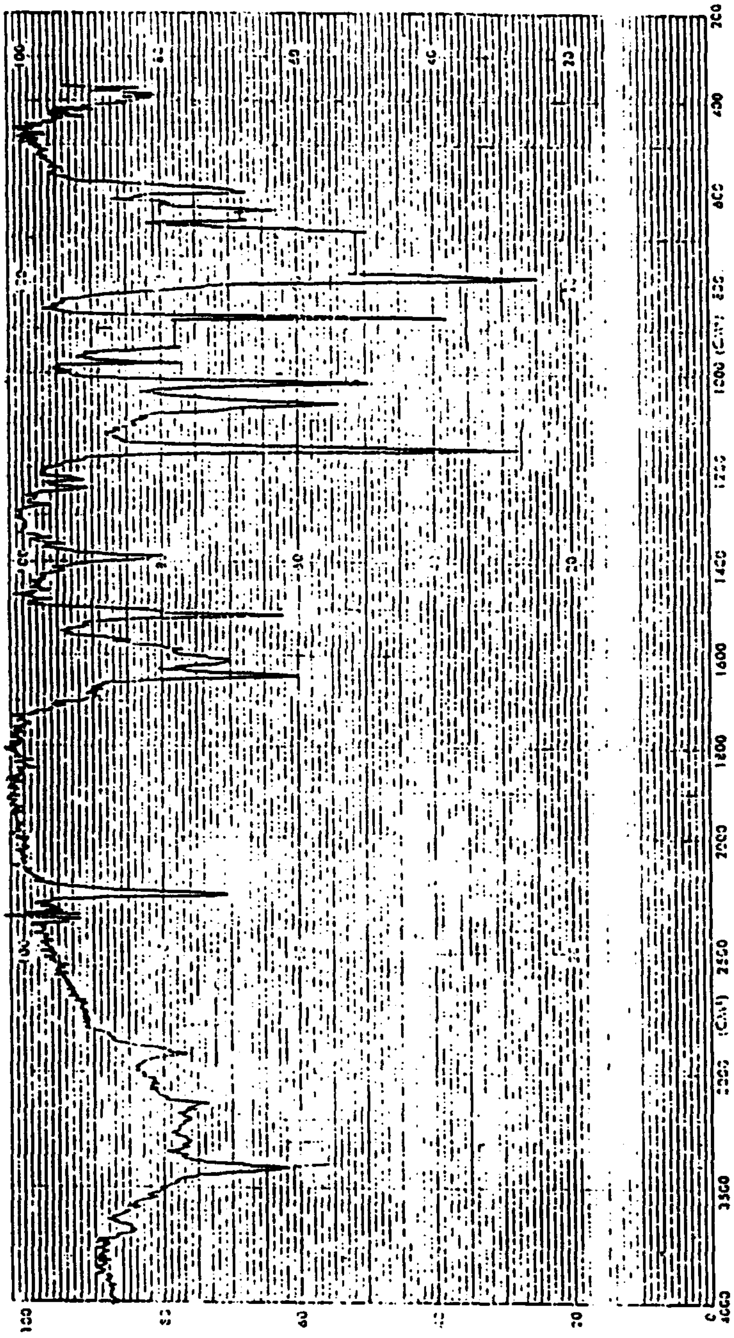


Figure 4.5 ^{1}H NMR ($CDCl_3$, 250 MHz) 3-Furylhydrazone.

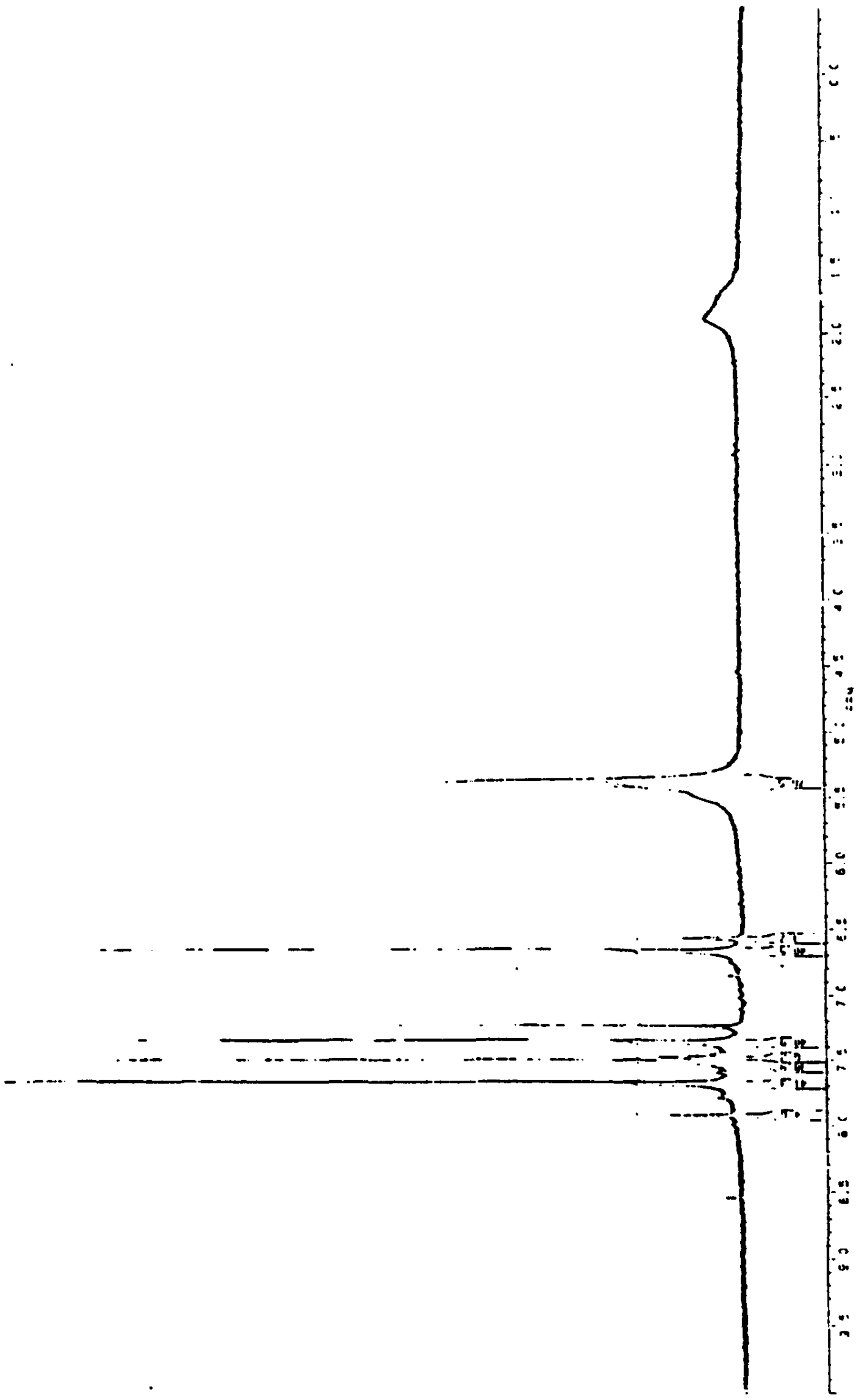


Figure 4.6 IR (CDCl3) cis-Di(3-Furyl)ethylene.

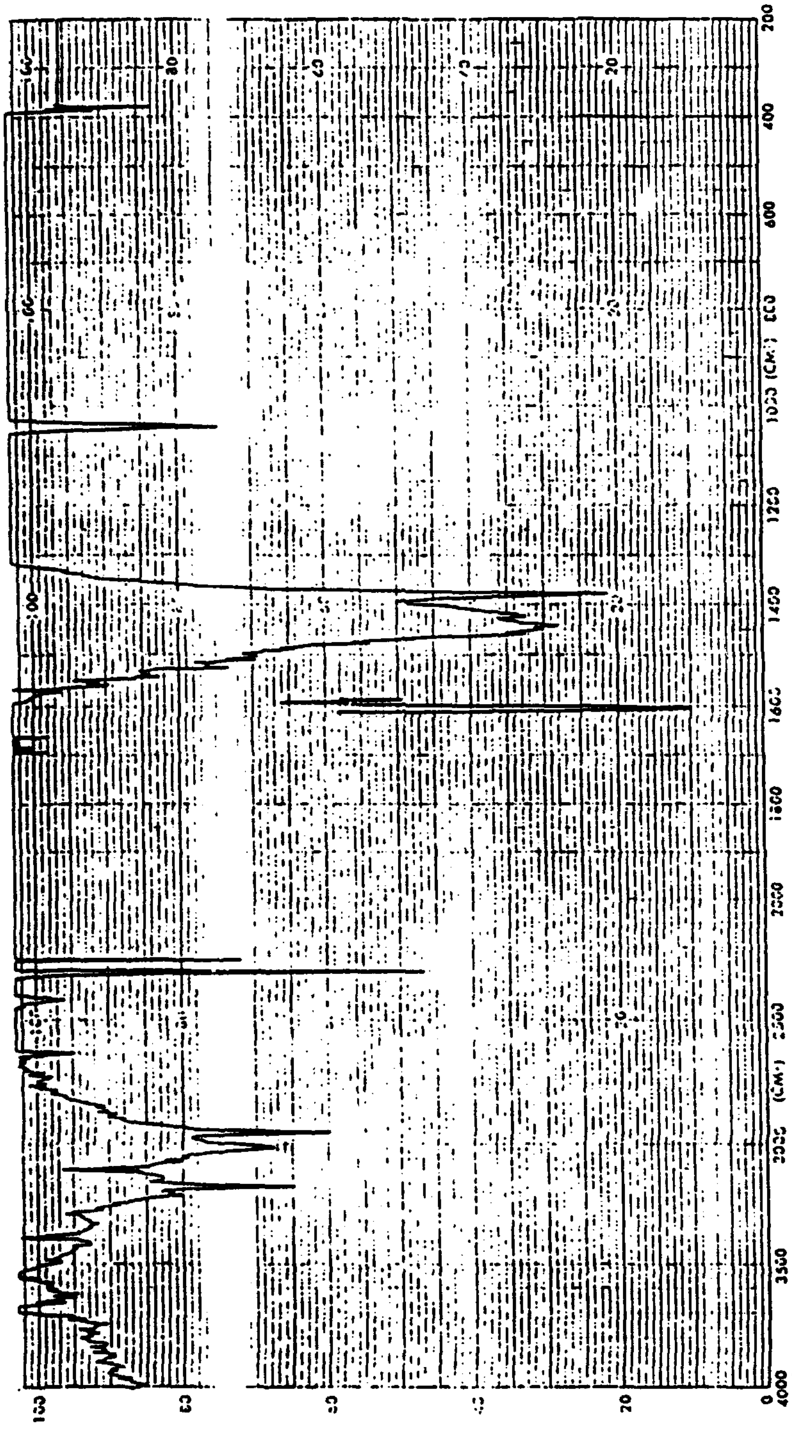


Figure 4.7 ^{1}H NMR (CDCl$_3$, 500 MHz) cis-Di(3-Furyl)ethylene.

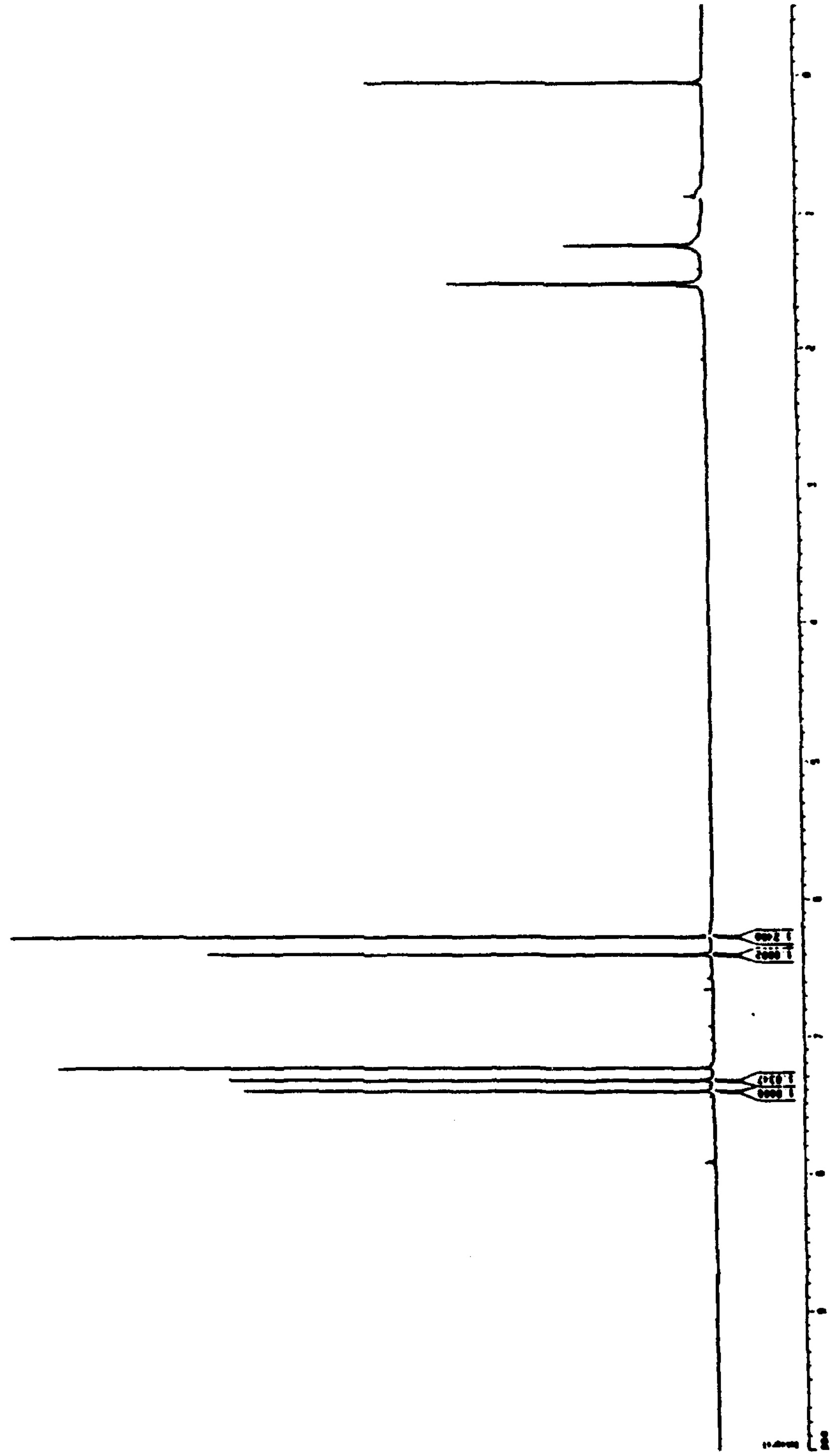


Figure 4.8 ^{13}C NMR ($CDCl_3$, 500 MHz) cis-Di(3-Furyl)ethylene.

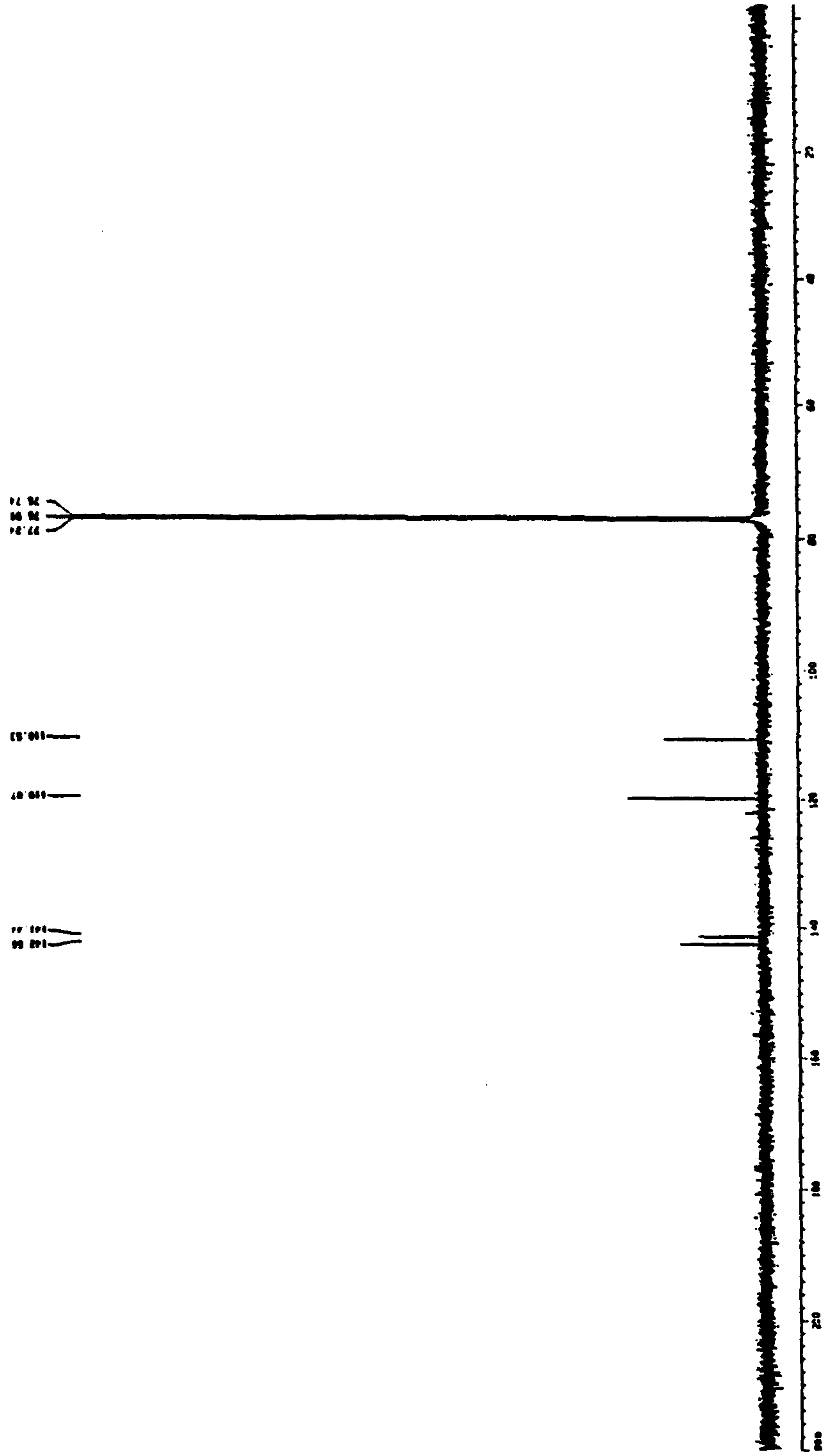


Figure 4.9 IR (CDCl3) trans-Di(3-Furyl)ethylene.

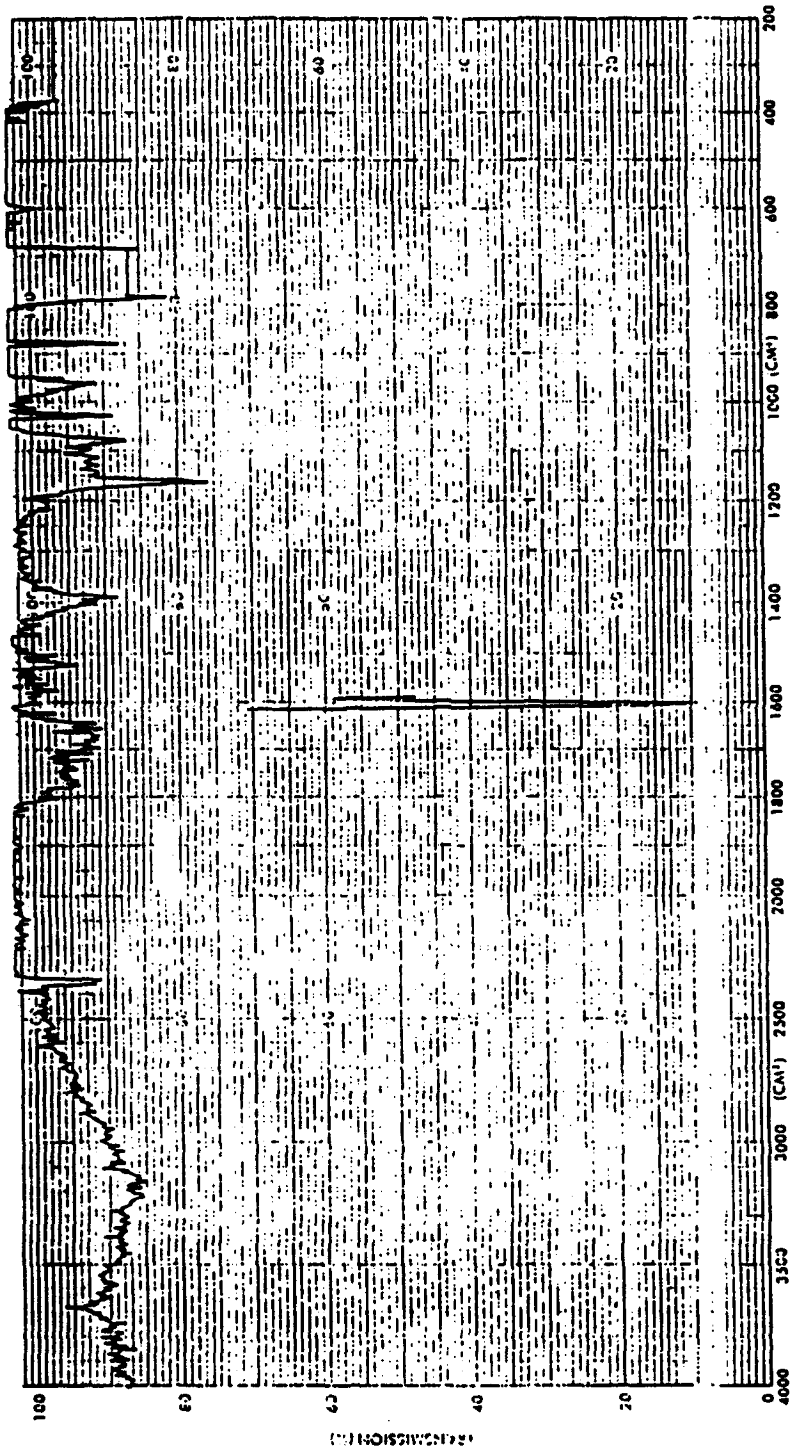


Figure 4.10 ^{1}H NMR ($CDCl_3$, 500 MHz) trans-Di(3-Furyl)ethylene.

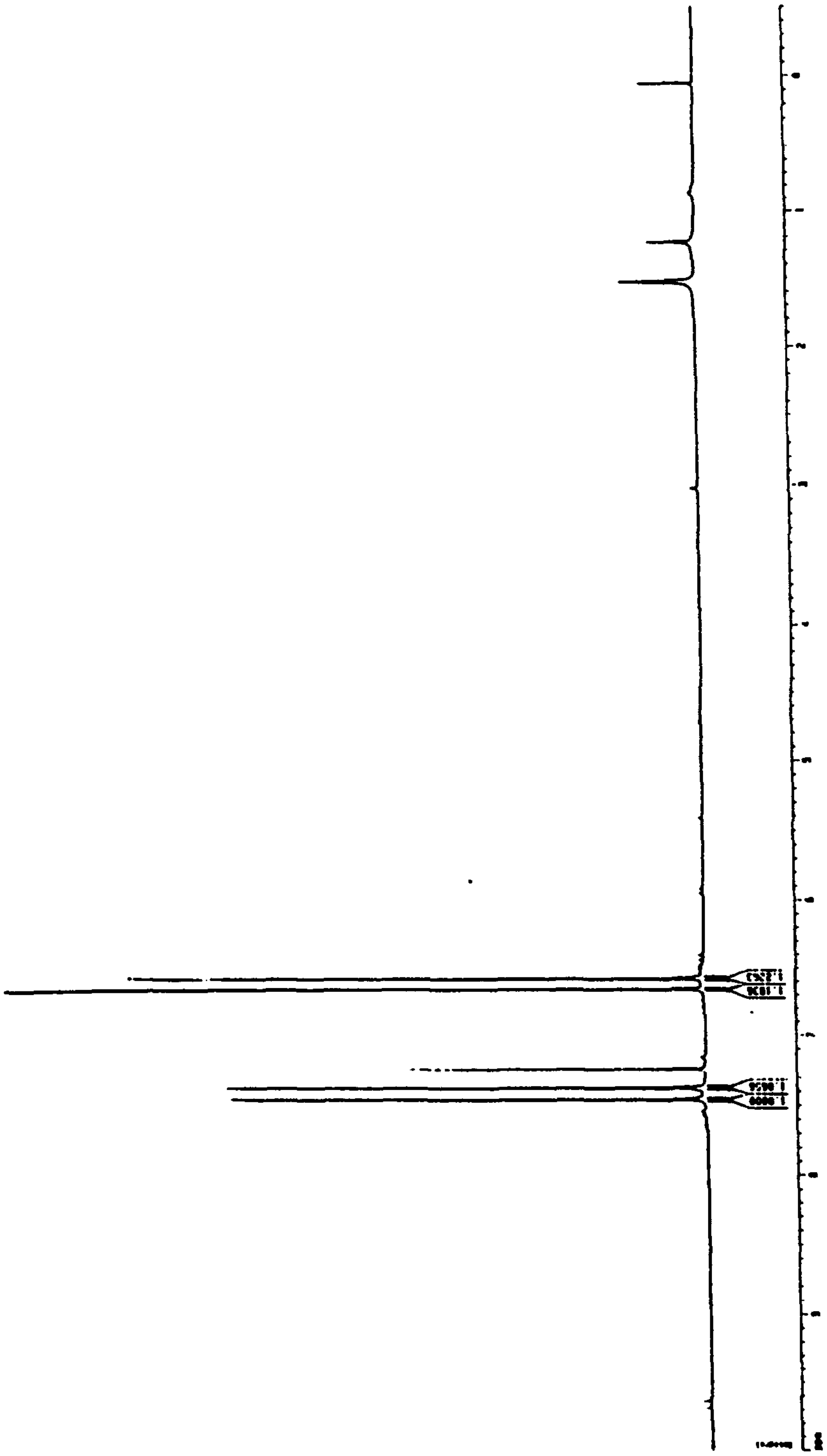


Figure 4.11 ^{13}C NMR ($CDCl_3$, 500 MHz) trans-Di(3-Furyl)ethylene.

Chapter 5 Matrix Isolation Studies of 2- and 3-Furyldiazomethane

5.0 Introduction

Neither (2- nor 3-furyl)methylene have been characterized using matrix isolation spectroscopy. MNDO calculations, previously noted, have been used to predict the multiplicity and conformation of 2-furylmethylene [1,2]. No reports on the multiplicity of 3-furylmethylene were found.

It was our goal to directly observe and characterize these carbenes under matrix isolation conditions using FTIR spectroscopy. A brief background on the technique of matrix isolation will be given before discussing the results of our ongoing investigations.

5.1 Background

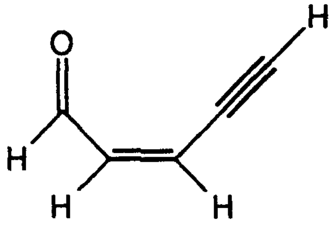
Matrix isolation is a powerful technique for the study of reactive intermediates [3]. There are three types of matrices which have been used to study carbenes: inert gas matrices, organic glasses, and powder matrices. They differ in the method used to generate the matrix and the spectroscopic technique used to characterize the matrix isolated compound. The present work used inert gas matrices. This technique involves codeposition of a noble gas, usually argon, or nitrogen and a carbene precursor onto a spectroscopic window cooled to 4-20 K under high vacuum (10^{-5} Torr). In this way the reactive molecules are physically separated from one another in a rigid, inert medium. Inert gas to carbene ratios are typically 500 - 2000, thus preventing intermolecular reactions of the carbene. Carbenes are found to be thermally stable in argon matrices if the barrier for rearrangement is higher than several Kcal/mol [3]. The most widely used carbene precursors for matrix isolation are diazirines and diazo compounds.

5.2 Results

We conducted several experiments on matrix isolated (2- and 3-furyl)diazomethane. We investigated the photolysis of 2-furyldiazomethane in both argon and nitrogen matrices. The results of the experiment with a nitrogen matrix are reported. Photolysis of 3-furyldiazomethane was conducted in an argon matrix. Additionally, the pyrolysis of 3-furyldiazomethane just prior to deposition on an argon matrix was investigated. All products were characterized using FTIR spectroscopy. The observed spectra were compared to either known data or the data from our computational investigations.

Before discussing the results of these experiments, a few general comments on IR spectroscopy under matrix conditions are given. Band positions of matrix isolated compounds closely match those found in the gas phase, however, the bands appear as sharp lines due to the loss of rotational freedom in the frozen matrix. Also, a fundamental band may appear as several closely spaced peaks (± 1 - 2 cm^{-1}). This is usually caused by matrix site effects, where the different forces exerted on the molecule due to its packing within the matrix can perturb a fundamental stretch or bend.

Photolysis of 2-furyldiazomethane in a nitrogen matrix using a monochromatic light source at a wavelength of 360 nm for a total of 58 hours resulted in almost complete loss of the characteristic diazo stretch at 2079 cm^{-1}. The peaks that were observed to grow in during the photolysis best match those reported by Shechter [4] and from our calculations (Chapter 2, Appendix 3) for the ring opened product **5.1**.



5.1

None of the calculated peaks for either conformation (ø = 0° and 180°) of the singlet or triplet carbene were positively identified.

After completion of the photolysis, the matrix was allowed to warm while collecting the products in a -196° C trap. Proton NMR analysis of these products match those reported for both the cis and trans isomers of the ring opened product [4].

Photolysis of 3-furyldiazomethane in an argon matrix using a monochromatic light source at a wavelength of 280 nm for a total of 24 hours resulted in almost complete loss of the characteristic diazo stretch at 2069 cm^{-1}. The product(s) from this photolysis were not positively identified. The largest peak at 1689 cm^{-1} suggests some type of carbonyl compound.

Upon completion of the photolysis, the matrix was allowed to warm and the product(s) were collected as before, however, proton NMR analysis of the product(s) collected were also inconclusive. After the matrix was warmed a dark brown solid was found on the inside of the matrix head. This material was collected and found to be insoluble in $CHCl_3$, CH_3CN, and DMSO. No further analysis of this material was performed.

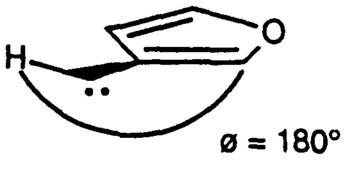
Flash vacuum pyrolysis of 3-furyldiazomethane just prior to matrix isolation was conducted at three different temperatures (250° C, 300° C, 350° C). As the temperature was increased with each experiment, the characteristic diazo stretch at 2070 cm^{-1} disappeared. The major peaks observed were very similar to those found with photolysis. Again the largest peak identified was at 1688 cm^{-1}.

The material from these depositions was collected while warming the matrix as before. Proton NMR analysis of the material collected was also inconclusive. As noted for the photolysis of 3-furyldiazomethane, a dark brown material was found inside the matrix after warming to room temperature. This material was also insoluble in $CHCl_3$, CH_3CN, and DMSO. Further analysis of this material was not performed.

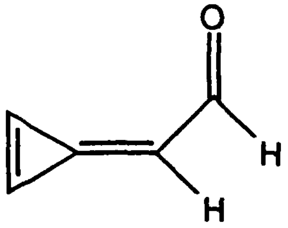
5.3 Discussion

Photolysis of 2-furyldiazomethane in a nitrogen matrix indicates that the resulting carbene undergoes ring fragmentation despite the low temperatures of the matrix (10 K). This is not surprising based on our calculations (Chapter 2, Section 2.1) which predict an energy barrier for the transition state of this ring fragmentation of only 2.3 or 2.5 Kcal/mol. Both the IR and proton NMR data support the formation of the ring opened product. Further investigations of 2-furylmethylene derivatives are planned with the attempt to stabilize the carbene and prevent ring fragmentation.

Results from the photolysis and thermolysis of 3-furyldiazomethane in an argon matrix are inconclusive. The peaks that grew in and the peaks that disappeared with photolysis are very similar to those observed from the pyrolysis experiment. We performed *ab initio* calculations on both conformations of the singlet and triplet carbene (Chapter 2, Appendix 4), as well as a number of possible reactive intermediates resulting from the rearrangement of the carbene (Chapter 2, Appendix 5). The results of these calculations provided us with the expected IR frequencies for these compounds. Comparison of these results with the bands identified from our experiments does not provide conclusive evidence for the formation of any one of these products. The experimental results are most consistent with a mixture of singlet carbene (ø = 180°) **5.2** and the substituted methylenecyclopropene **5.3**.

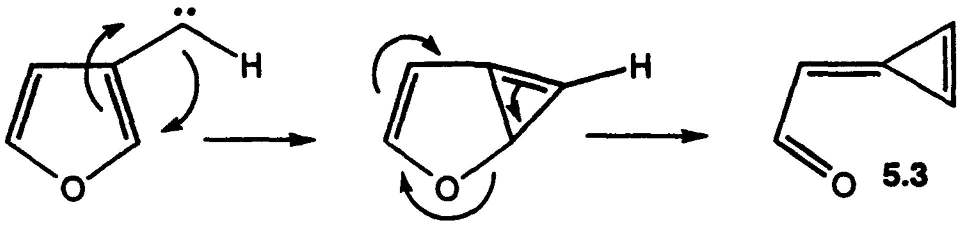


5.2



5.3

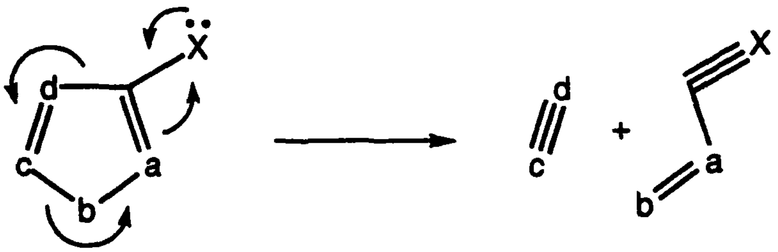
The major peaks predicted using *ab initio* calculations for **5.2** are 2847, 1507, and 1157 cm^{-1} and for **5.3** they are 2830, 1775, 1692, and 1487 cm^{-1}. The peaks observed from both photolysis and thermolysis of the diazo compound are 1746, 1688, 1650, 1515, 1495, 1154, and 703 cm^{-1}. Compound **5.3** may be formed according to the following mechanism:



5.3

Due to their thermal instability, only a few examples are reported for di- and tri-substituted methylenecyclopropenes [5]. Thus if 5.3 is one of the products, it is not surprising that we were unable to isolate it from the matrix. The parent compound methylenecyclopropene has been isolated using an argon matrix [6]. The major IR peaks reported for it are 1770, 1518, 904, 754, 664 cm^{-1}. However, this compound is extremely reactive and readily polymerizes far below room temperature.

We also examined the possibility of ring fragmentation similar to that found in other heterocyclic systems with a nitrene or carbene at the β-position of the five membered ring [1,7].



Previous reports of this type of fragmentation involve formation of nitrogen or a nitrile at the c-d fragment; however there is one report where the c-d fragment is acetylene [7]. Ring fragmentation of this type for 3-furylmethylene would generate acetylene and propynal [8], but neither of these compounds were observed in the matrix-isolation IR spectra or the NMR spectra of the material removed from the matrix. We will continue investigations of this system in order to determine the products observed upon photolysis and thermolysis.

5.4 Experimental

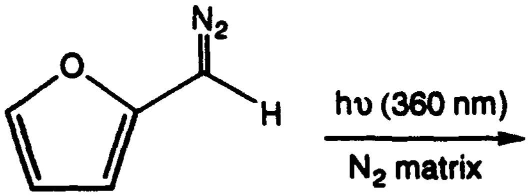
General

An Air Products closed-cycle helium refrigeration system and compressor provided cryogenic temperatures down to 10 K. Flow rate of the inert gas through the cold trap and onto the cold finger was controlled with a variable leak valve and measured by a differential pressure gauge. IR spectra were recordered on an IBM Instruments Inc. IR/97 FTIR spectrometer at 0.5 cm^{-1} resolution. Spectra were obtained by ratioing the single beam spectra of the compound with a single beam spectra of Ar or N_2 taken under similar conditions. Monochromatic photolysis was accomplished using a 75 watt xenon lamp with an effective radiation of ± 10 nm. Photolysis of the diazo compounds was through a quartz window on the matrix shroud directly on the side of the Cs-I window containing the matrix, thus preventing the Cs-I window from acting as a filter. Baseline smoothing and spectral subtraction were accomplished using the computer graphics program. Spectral subtraction was performed by zeroing those peaks that remained unchanged after photolysis. These peaks are reported as impurities, typically water or CO_2. The resulting spectra show positive peaks where material grew in with photolysis and negative peaks where material disappeared with photolysis.

Typical Procedure for Matrix Deposition

The entire system was evacuated to at least 1 x 10^{-5} Torr prior to each deposition. The Cs-I window was then cooled to 23 K. Approximately 500 ± Torr of Ar or N_2 (Matheson, 99.9995% Minimum purity) was released into the matrix manifold. The diazo compound was attached to the vacuum line via the deposition port on the matrix shroud and through a vacuum hose attached to the matrix manifold containing the inert gas. The flow valve was set so that rate of deposition through the cold trap containing the diazo compound and on to the cold window was ~ 2 Torr of Ar or N_2 per minute, with a total deposition of 100 Torr of Ar or N_2. The cold trap containing the diazo compound was warmed to -70° C, unless otherwise noted, and maintained at this temperature during the deposition period. Before photolysis, the window was cooled to at least 12 K. This prevents localized warming of the matrix due to the exothermic loss of nitrogen which might lead to migration and subsequent intermolecular reactions. IR spectra were taken at various intervals during the photolysis in order to monitor the growth and loss of the various bands. Variations of this procedure are reported in the individual experimental section for each compound.

Photolysis of 2-Furyldiazomethane



Results are reported for the isolation of this compound in a nitrogen matrix. Photolysis of the diazo compound was done at λ of 360 nm. The total photolysis time was 58 hours. Results of the IR spectra taken before and after photolysis are reported as well as the difference spectrum.

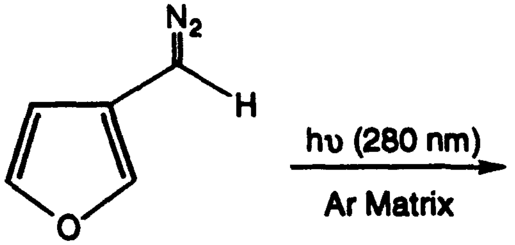
Peaks identified as decreasing with photolysis: 2079 (s, N_2), 1593 (m), 1522 (w), 1423 (w), 1191 (w), 1013 (w), 1007 (w), 930 (w), 885 (w), 777 (w), 722 (m), 718 (w).

Peaks identified as growing in with photolysis: 3312 (m, ≡C-H) , 1710 (w, C=O), 1697 (s), 1123 (w), 651 (w).

Peaks that remained unchanged with photolysis: 3726 (s, H_2O), 2349 (w, CO_2), 1597 (m, H_2O), 938 (w)

Product collected from matrix while warming to room temperature: 1H NMR (500 MHz, $CDCl_3$) δ (Coupling constants were not determined) Cis-2-penten-4-ynal; 10.15 (d, 1H, aldehyde H), 3.54 (s, 1H, acetylene H). Trans-2-penten-4-ynal; 9.59 (d, 1H, aldehyde H), 3.69 (s, 1H, acetylene H). Peaks not assigned; 6.62 (d), 6.54 (d), 6.36 (m). (cis : trans ratio ~3:1).

Photolysis of 3-Furyldiazomethane



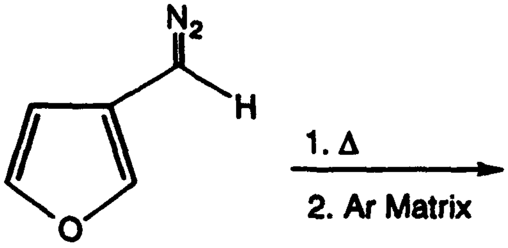
Results are reported for the isolation of this compound in an argon matrix. Photolysis of the diazo compound was done at a λ of 280 nm. The total photolysis time was 24 hours. Results of the IR spectra taken before and after photolysis are reported as well as the difference spectrum.

Peaks identified as decreasing with photolysis: 2069 (s, N_2), 1421 (w), 1173 (w), 1065 (w), 1028 (w), 874 (w), 756 (m), 589 (w).

Peaks identified as growing in with photolysis: 1750 (m) , 1689 (s), 1647 (w), 1516 (w), 1495 (w), 1146 (w), 1139 (m), 705 (w).

Peaks that remained unchanged with photolysis: 3754 (m, H_2O), 2345 (m, CO_2), 1624 (m, H_2O), 1361 (m), 1216 (m), 938 (m), 613 (w, CO_2).

Flash Vacuum Pyrolysis of 3-Furyldiazomethane



Pyrolyses were accomplished by inserting a hot tube (diameter of 1 cm and a length of 17 cm) between the cold trap containing the diazo compound and the deposition port of the matrix shroud. Temperatures of the hot tube were measured using a thermocouple. Temperature of the cold trap was raised to -55° C due to the small amount of diazo compound remaining in the trap. Three different temperatures were used for the pyrolysis; 250°, 300°, and 350° C. As the temperature was raised a uniform change was noted for both the peaks growing in and for the peaks decreasing. Results are reported based on the comparison of the three spectra.

Peaks identified as decreasing with thermolysis (Intensities based on spectra taken at 250° C): 2070 (s, N_2), 1420 (w), 1364 (w), 1214 (w), 1172 (m), 1065 (w), 1028 (w), 875 (m), 756 (s), 589 (m).

Peaks identified as growing in with thermolysis (Intensities based on spectra taken at 350° C): 1746 (m) , 1688 (s), 1650 (w), 1515 (w), 1495 (m), 1154 (w), 703 (w).

5.5 References for Chapter 5

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Spectra Relevant to Chapter 5

Figure 5.1 IR Spectrum of 2-Furyldiazomethane Before Photolysis (N_2, 12 K).

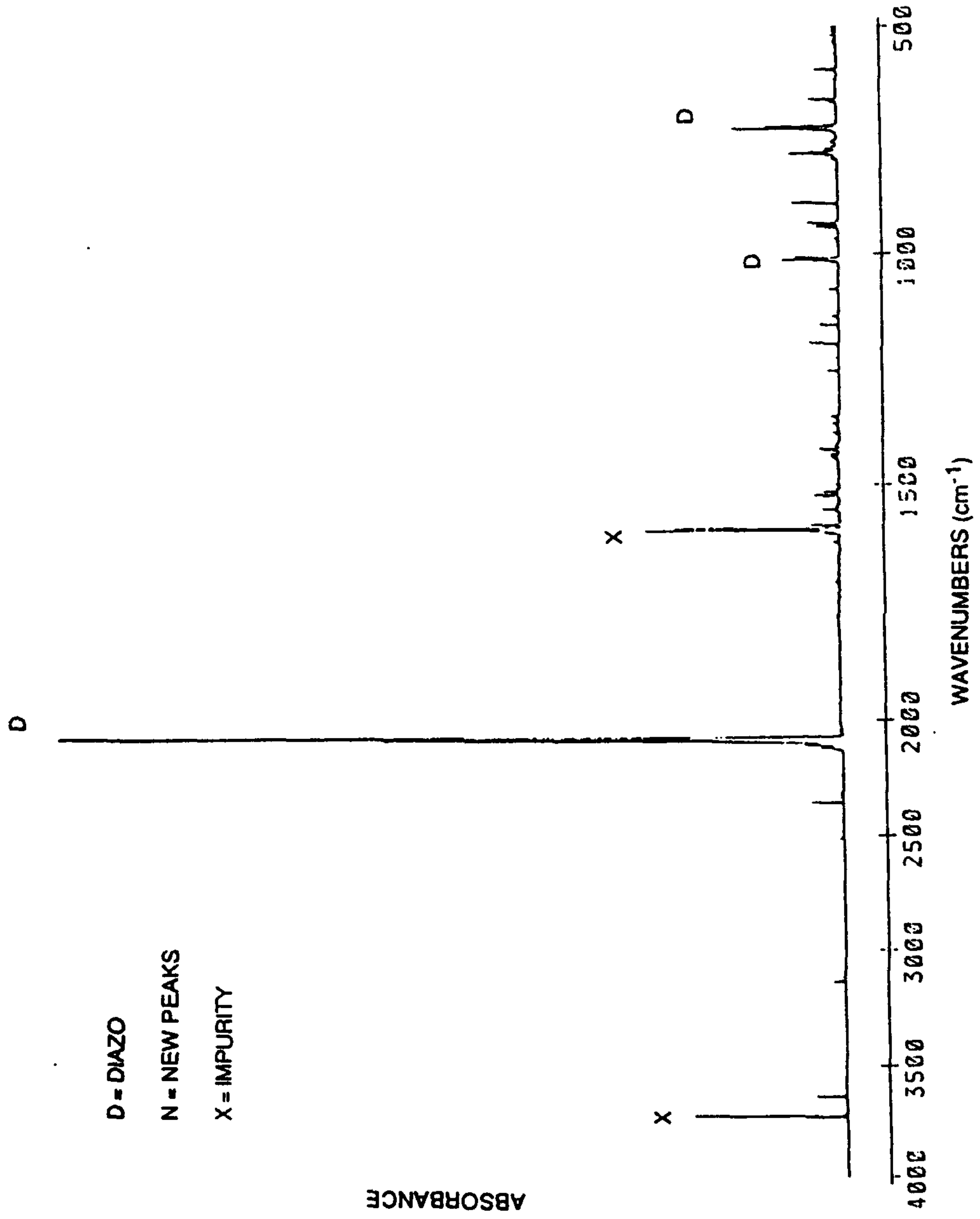

Figure 5.2 IR Spectrum of 2-Furyldiazomethane After Photolysis (N_2, 12 K).

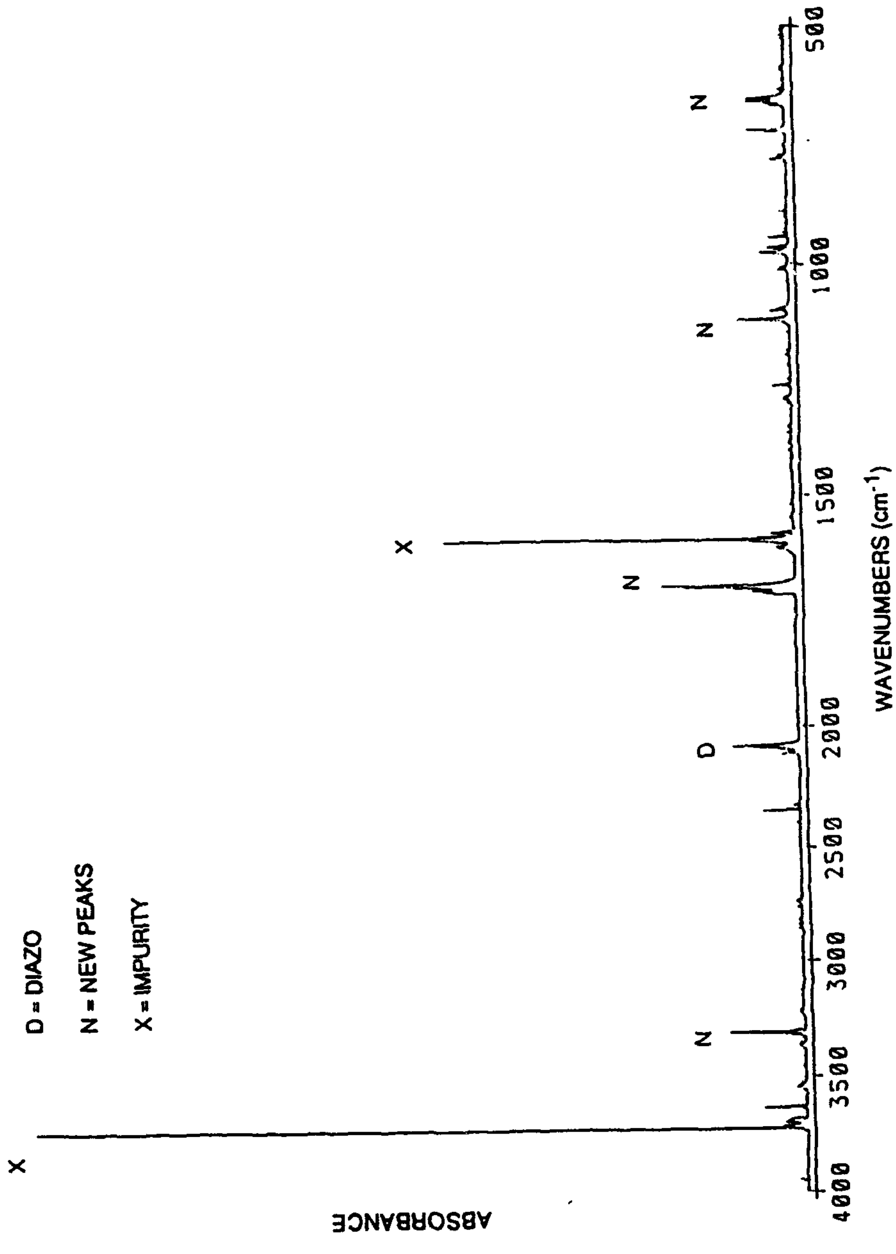

Figure 5.3 IR Spectrum of 2-Furyldiazomethane, Product After Photolysis - Product Before Photolysis (N_2, 12 K).

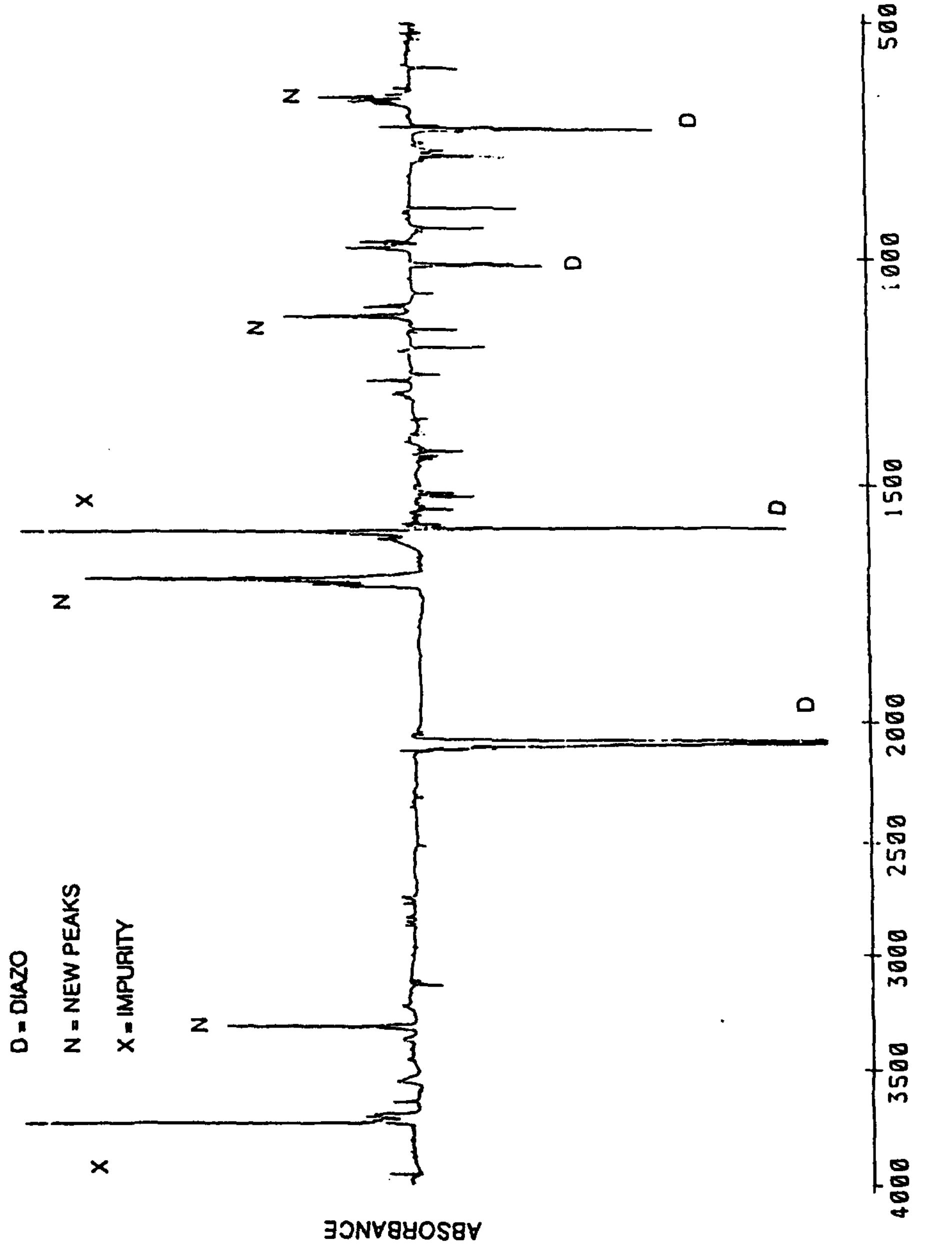

Figure 5.4 ^1H NMR of Product Collected from Matrix After Photolysis ($CDCl_3$, 500 MHz)

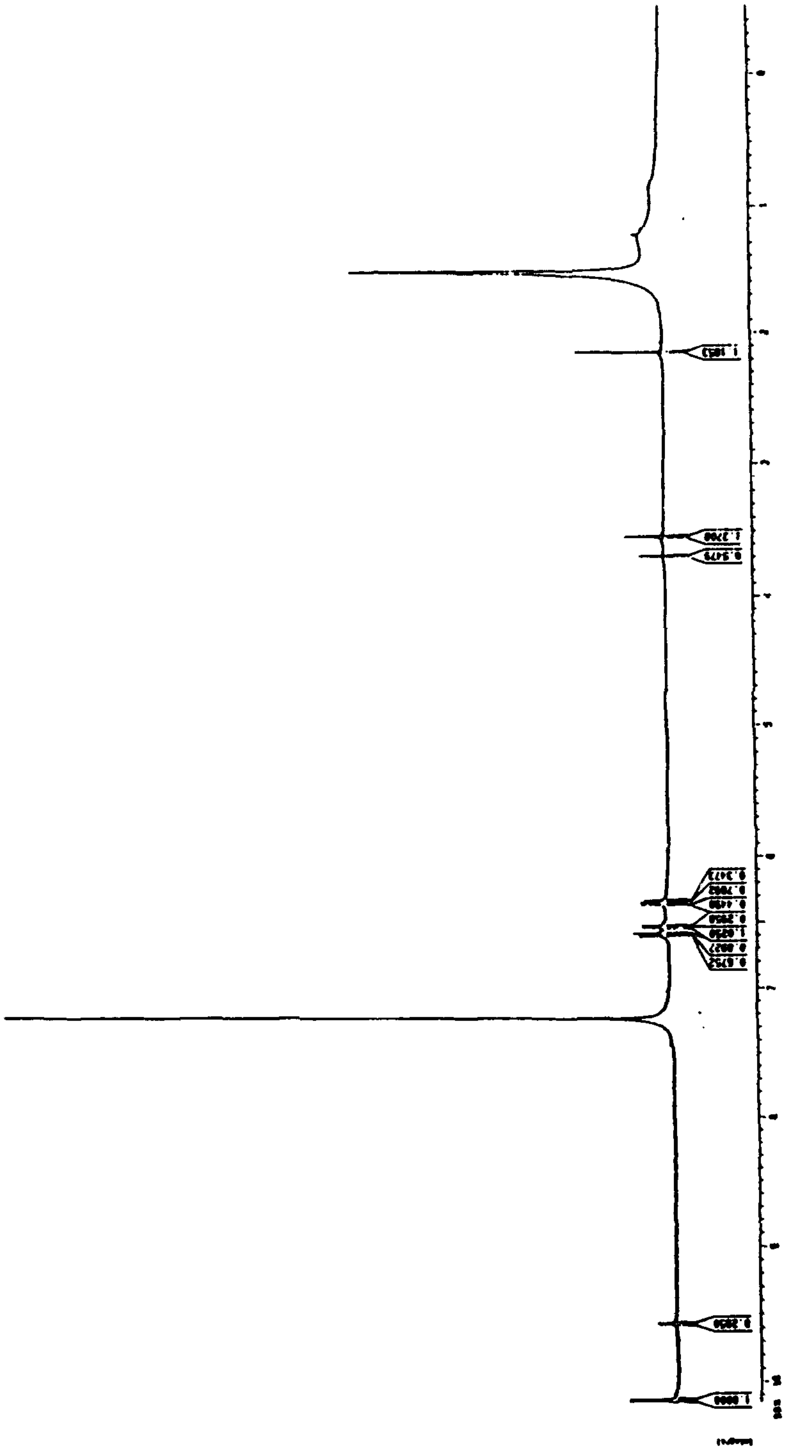

Figure 5.5 IR Spectrum of 3-Furyldiazomethane Before Photolysis (Ar, 12 K).

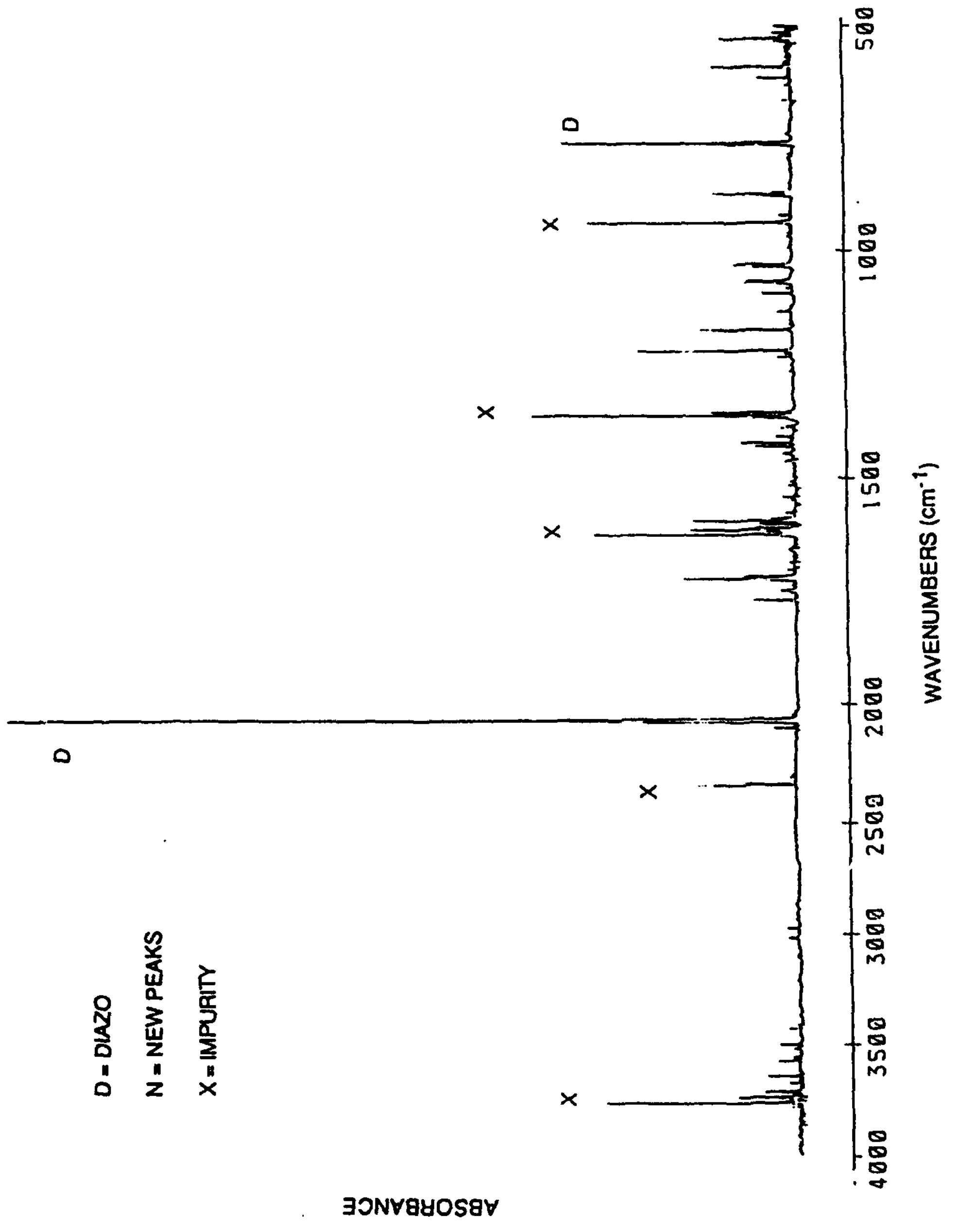

Figure 5.6 IR Spectrum of 3-Furyldiazomethane After Photolysis (Ar, 12 K).

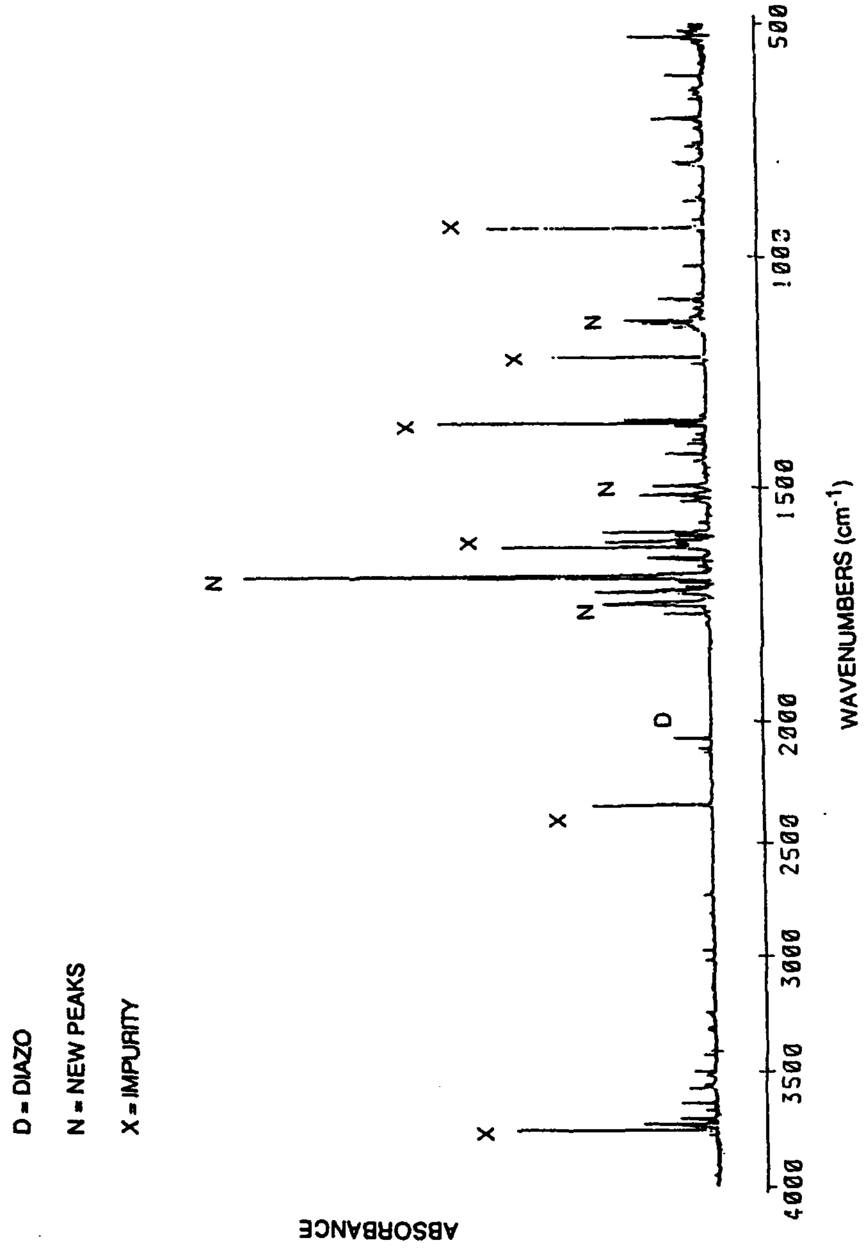

Figure 5.7 IR Spectrum of 3-Furyldiazomethane, Product After Photolysis - Product Before Photolysis (Ar, 12 K).

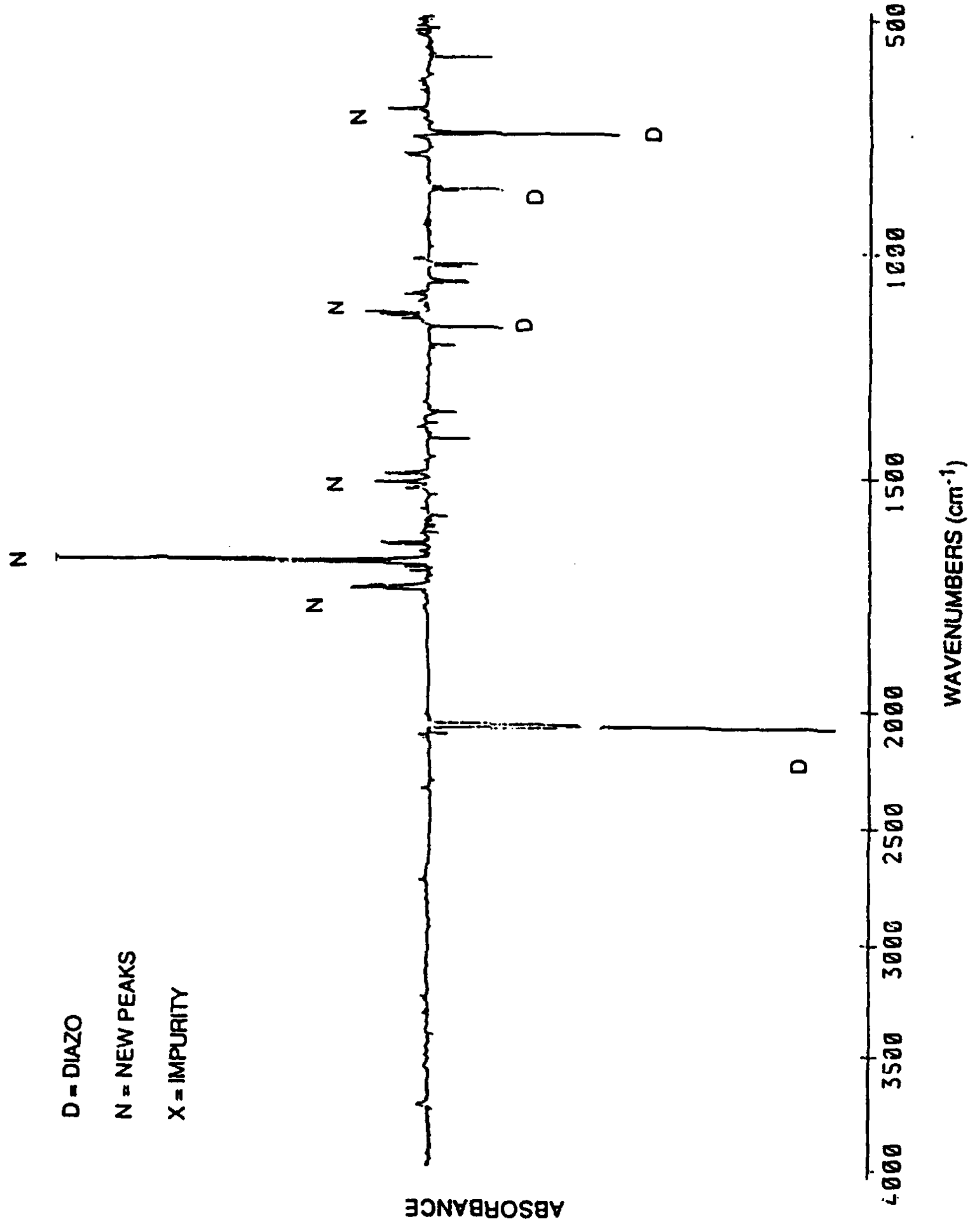

Figure 5.8 IR Spectrum of 3-Furyldiazomethane Thermolysis 250° C (Ar, 12 K).

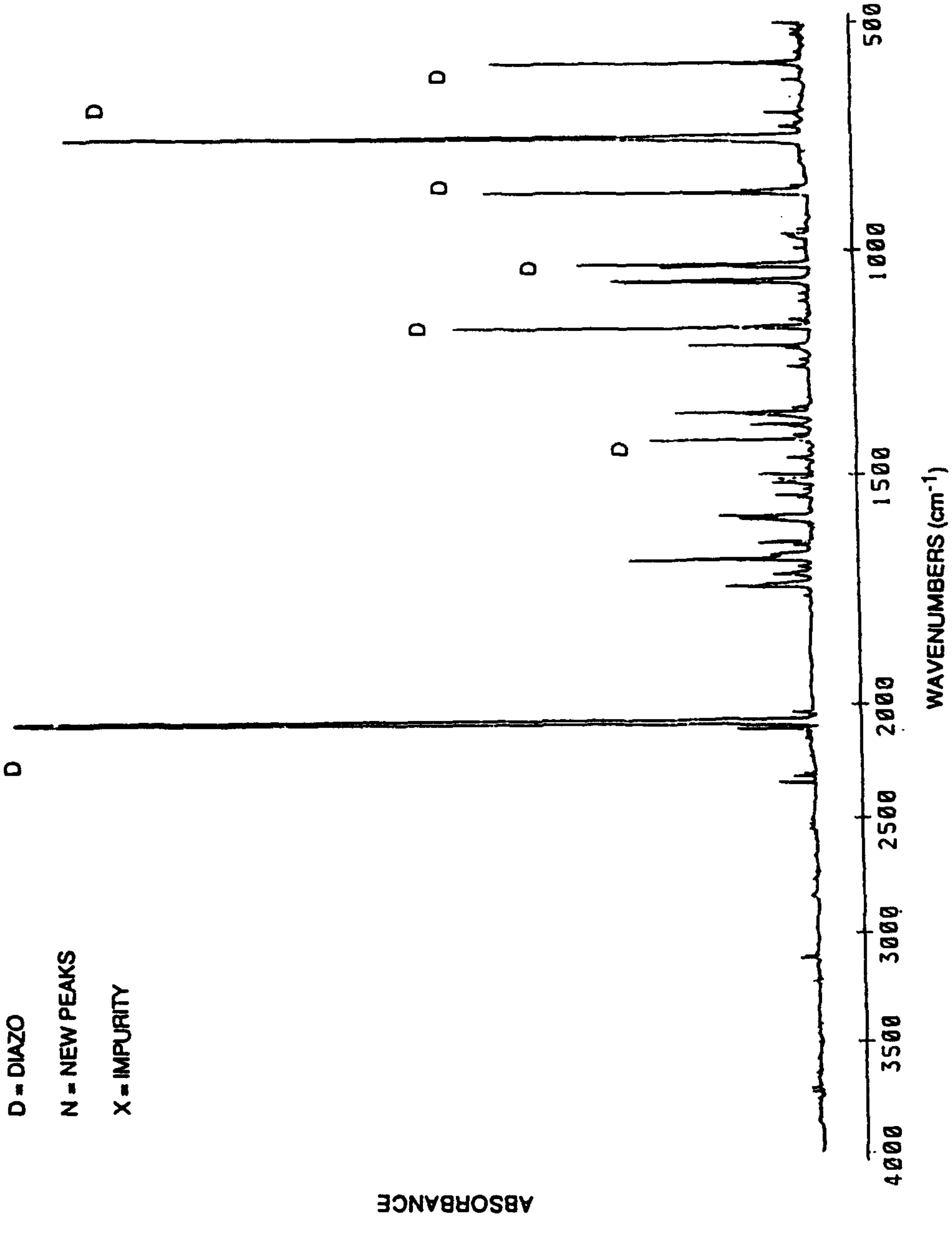

Figure 5.9 IR Spectrum of 3-Furyldiazomethane Thermolysis 300° C (Ar, 12 K).

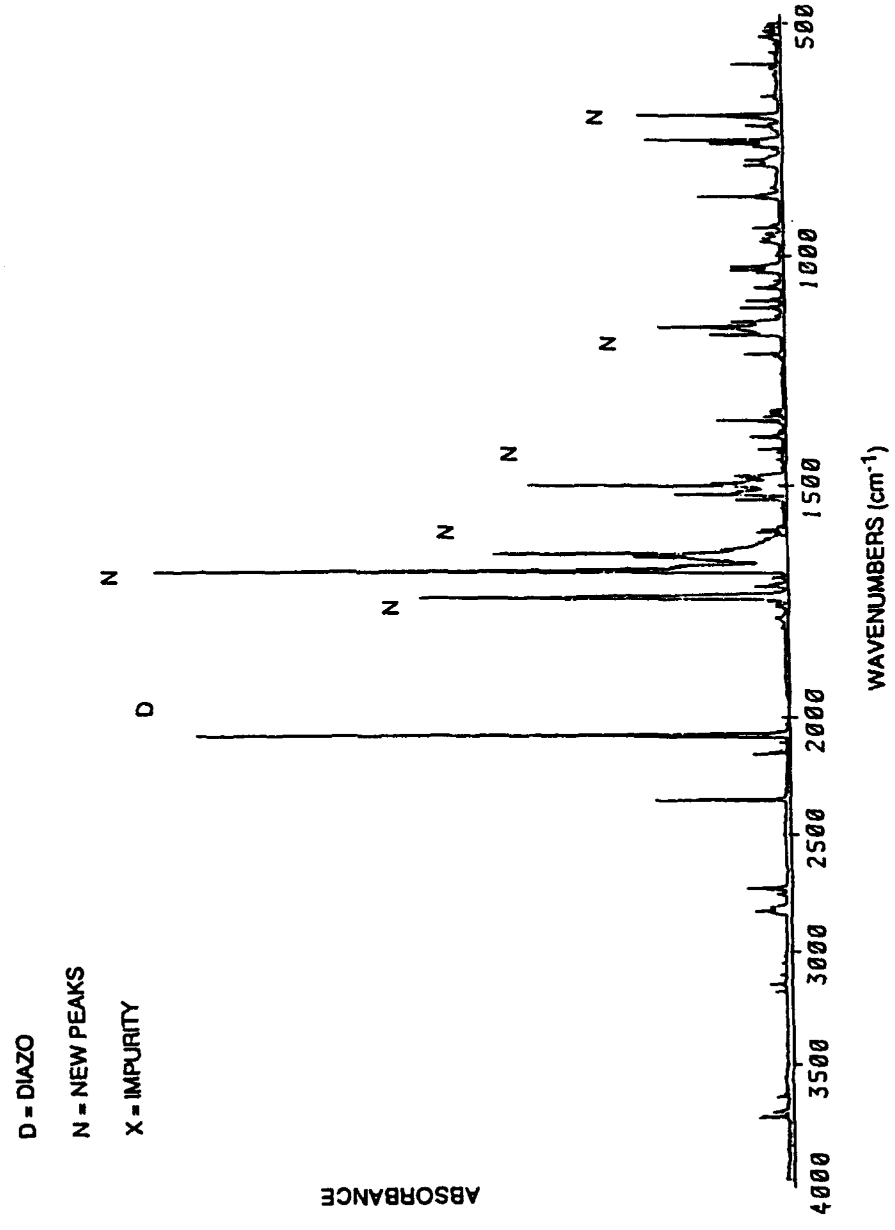

Figure 5.10 IR Spectrum of 3-Furyldiazomethane Thermolysis 350° C (Ar, 12 K).