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The Gas-Phase Photolysis of Perfluoro α-Diazo Ketones: Furan Formation and the Involvement of Transient Oxirenes

P. G. Mahaffy and D. Visser

Department of Chemistry, The King's College, Edmonton, Alberta, Canada, T5H 2M1

M. Torres, J. L. Bourdelande, and O. P. Strausz*

Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada, T6G 2G2

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The gas-phase photolyses of hexafluoro-3-diazo-2-butanone (**1**), octafluoro-2-diazo-3-pentanone (**2**), and octafluoro-3-diazo-2-pentanone (**3**) have been studied. Chemical trapping experiments with hexafluoro-2-butyne provide evidence that isomeric ketocarbene intermediates equilibrate, presumably via transient 4-π-electron oxirenes. **1** yields tetrakis(trifluoromethyl)furan (**8**) as a major product, with a trace of 1,2,3-tris(trifluoromethyl)-3-(trifluoroacetyl)cyclopropene (**9**) and bis(trifluoromethyl)ketene (**10**). Photolysis of either **2** or **3** yields the same four trapped products: 2-(pentafluoroethyl)-3,4,5-tris(trifluoromethyl)furan (**12**), 3-(pentafluoroethyl)-2,4,5-tris(trifluoromethyl)furan (**14**), 1,2,3-tris(trifluoromethyl)-3-(pentafluoropropionyl)cyclopropene (**13**), and 1,2-bis(trifluoromethyl)-3-(pentafluoroethyl)-3-(trifluoroacetyl)cyclopropene (**15**), in approximately the same ratio, along with the Wolff rearrangement product, (pentafluoroethyl)(trifluoromethyl)ketene (**16**).

Introduction

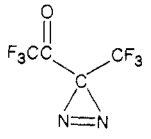
The theoretical interest in the nature of antiaromatic species has resulted in a large number of recent attempts to demonstrate the intermediacy of oxirene and related 4-π-electron heterocyclic thiirene and 2-azirene species in a wide variety of thermal and photochemical reactions. Our efforts have focused on reactions involving oxirene and thiirene intermediates. The earliest solid experimental evidence for the intermediacy of oxirenes came from studies of the decomposition of α-diazo ketones (the Wolff rearrangement). Labeling experiments demonstrated that in the photodecomposition of many α-diazo ketones, oxygen migration occurs from intermediate ketocarbenes, presumably via transient 4-π-electron oxirenes.[1]

This early work has led to intense experimental and theoretical investigations of the Wolff rearrangement over the last two decades.[2,3] The oxidation of alkynes, β-elimination and retrocycloaddition reactions, and reactions involving extrusion from larger heterocycles have all been suggested as viable routes to the formation of oxirenes. The theoretical and experimental evidence for the existence of oxirenes as actual intermediates has recently been reviewed.[4]

Perfluoroalkyl substituents have been shown to provide remarkable stabilization of a number of highly strained compounds.[5] In this laboratory the low-temperature matrix isolation and IR characterization of several substituted thiirenes has demonstrated that electron-withdrawing substituents enhance the stability of the thiirene ring.[6] Consequently, investigations of the low-temperature matrix photolysis of several perfluoro α-diazo ketones have been carried out with the intent of directly observing the resulting transient intermediates by electron-spin resonance and Fourier transform infrared spectroscopy.

We previously reported the low-temperature matrix photolysis of hexafluoro-3-diazo-2-butanone (**1**), octafluoro-2-diazo-3-pentanone (**2**), and octafluoro-3-diazo-2-pentanone (**3**). Irradiation of **1** at $\lambda > 300$ nm produced species whose ESR signals were consistent with the s-*Z* and s-*E* conformers of the ketocarbene $CF_3\ddot{C}COCF_3$ (**4**).[7]

We also reported the FTIR spectra for the species obtained in the $\lambda > 335$ nm and $\lambda = 270$ nm irradiation of argon matrix isolated **1**–**3**.[8] Initially we assigned the observed spectra in the $\lambda > 335$ nm to intermediate ketocarbenes. Subsequent studies by Lemal et al.[9] demonstrated that the species responsible for the IR spectrum in the $\lambda > 320$ nm matrix photolysis of **1** was actually a stable compound, identified as perfluoro-3-acetyl-3-methyldiazirene (**5**) arising from a diazo ketone–keto-diazirene rearrangement. The species formed in the $\lambda =$ 270 nm irradiation were assigned to oxirenes and constitute the first direct evidence for the formation of an oxirene. We also reported[3] ^{13}C scrambling and hence oxirene involvement in the dimethylketene formed upon photolysis of argon matrix isolated diazobutanone (^{13}CO). Recently, Bodot and co-workers[10] have added to these findings by the isolation of dimethyloxirene in the argon-matrix photolysis of diazobutanone.



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Further studies on the low-temperature matrix photolysis of **2** and **3** have recently been carried out in our laboratory.[11] We have shown that the photolysis of either **2** or **3** in the polycrystalline phase at 10 K with $\lambda > 335$ nm resulted in the formation of species with ESR signals

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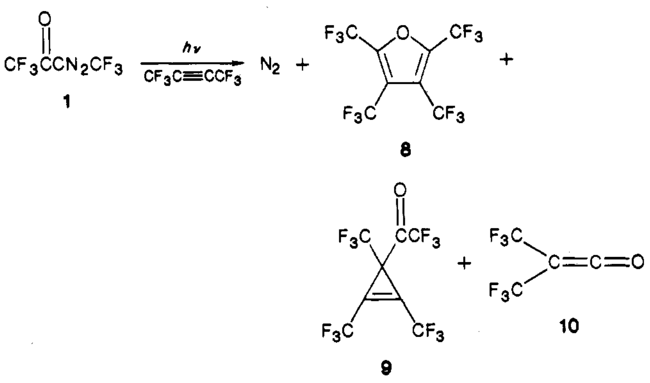
Scheme I



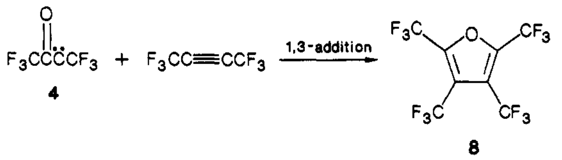
consistent with the corresponding ketocarbenes **6** and **7**, respectively. Concurrent FTIR studies of the photolysis of argon matrix isolated **1**–**3** have confirmed the finding by Lemal et al. that diazirene **5** is formed in the $\lambda > 335$ nm photolysis of **1** and shown that analogous diazirenes are formed in the photolysis of **2** and **3**.

This paper reports the results of gas-phase photolysis of **1**–**3** in the presence of a large excess of the trapping agent, hexafluoro-2-butyne. The chemical trapping studies were designed to shed further light on the intermediacy of oxirene species in the photochemical Wolff rearrangement.

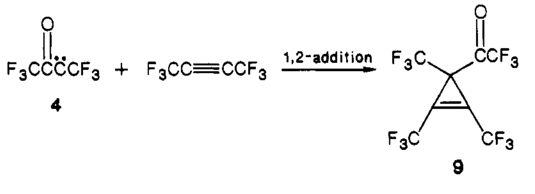
Results and Discussion

Gas-phase photolysis of **1** with $\lambda > 335$ nm in the presence of a large excess of hexafluoro-2-butyne yields nitrogen and only one major trapped product, tetrakis(trifluoromethyl)furan (**8**) along with a trace of cyclopropenyl ketone **9**, bis(trifluoromethyl)ketene (**10**), and polymer (Scheme I).

Photoproducts **8**–**10** can be rationalized via a ketocarbene intermediate, **4**, which undergoes 1,3-addition to hexafluoro-2-butyne to give furan **8**, 1,2-addition to hexafluoro-2-butyne to give cyclopropenyl ketone **9**, and Wolff rearrangement to give ketene **10** (eq 1-3).



(1)



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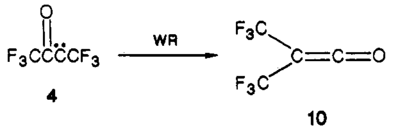
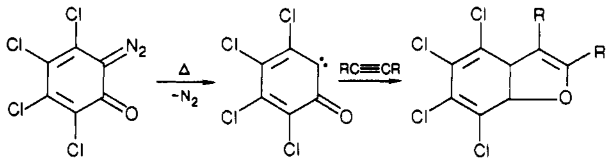


(3)

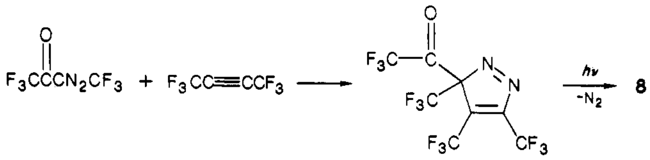
Furan formation as the major product in the addition of a ketocarbene to an acetylene is unusual. Furans have been reported in the photochemical reaction of triplet dicarbomethoxycarbene with 2-butyne[12] and the $CuSO_4$-catalyzed addition of carboethoxycarbene to phenylacetylene.[13] In the latter case it has also been suggested that furan formation may not result from 1,3-addition but rather from isomerization of the initially formed cyclopropenyl ketone.[14] Benzofurans have been reported in the thermal uncatalyzed addition of ketocarbene **11** to acetylenes[15] (eq 4). The gas-phase photolysis of several



(4)

1,2,3-thiadiazoles in the presence of hexafluoro-2-butyne led to the formation of thiophene products, most likely from the addition of thiirene intermediates to the alkyne, as discussed later.[16] $S(^1D_2)$ atoms formed in the photolysis of COS have also been trapped by hexafluoro-2-butyne to give tetrakis(trifluoromethyl)thiophene via the corresponding thiirene intermediate.[17]

In principle, furan **8** could also be formed by loss of nitrogen from an intermediate pyrazolene (eq 5) or by



(5)

addition of hexafluoro-2-butyne to an oxirene intermediate. The symmetry of substituents in precursor **1** and furan **8** does not allow us to infer the nature of the intermediates involved and therefore prevents further elucidation of the mechanism or detection of the transient formation of an oxirene from product studies alone.

α-Diazopentanones **2** and **3** were therefore photolyzed under the same conditions. If photolysis of the isomeric diazopentanones each proceeds via single ketocarbene intermediates, isomeric furans and cyclopropenyl ketones would be expected. Thus, diazo ketone **2** would be expected to give furan **12** and cyclopropenyl ketone **13** and diazo ketone **3**, furan **14** and cyclopropenyl ketone **15**, unless ketocarbenes **6** and **7** can be readily interconverted.

Photolysis ($\lambda > 335$ nm) of either **2** or **3** in the presence of a 400-fold excess of hexafluoro-2-butyne yielded ketene **16** and the two isomeric furans (**12** and **14**) and cyclopropenyl ketones (**13** and **15**) shown in Scheme II in essentially the same 3:4 ratio (**12** to **14** and **13** to **15**, determined by GC, average of 12 runs), regardless of which isomeric pentanone was the starting material. Ketene **16** is the expected photoproduct in the Wolff rearrangement. Furans **12** and **14** were major photoproducts, with furan **14** being consistently formed in slightly greater yield than furan **12**, while cyclopropenyl ketones **13** and **15** constituted minor products. Structures for these four compounds were assigned on the basis of GC/MS, GC/FTIR, and ^{19}F NMR data. Spectral data for furans **12** and **14** are consistent with data for furan **8**, which has previously been reported,[18] and are given in Table I. Because cyclopropenyl ketones **13** and **15** constituted minor products,

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Scheme II

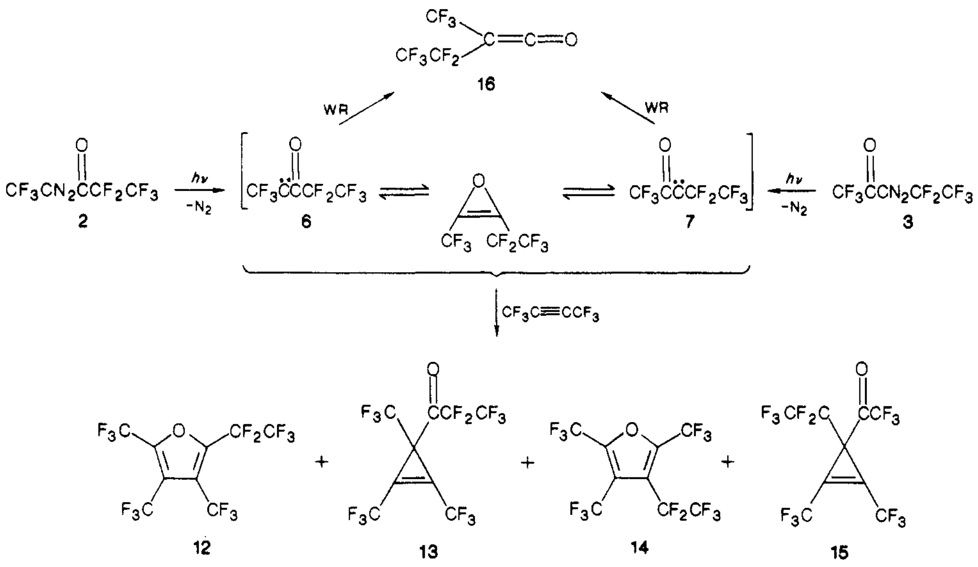
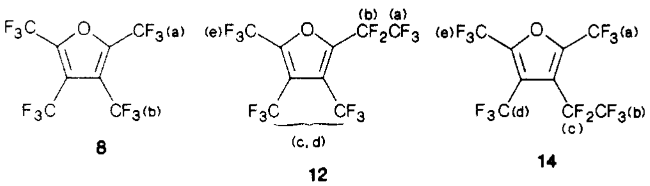


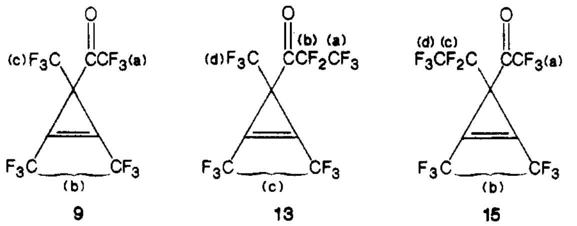
Table I. Spectral Data for Furans 8, 12, and 14



	8	**12**	**14**
MS, *m/e*	340 (M$^+$), 321 (base), 290, 271, 243, 221, 193, 155, 69	390 (M$^+$), 371, 322, 321 (base), 271, 69	390 (M$^+$), 371, 322, 321 (base), 271, 69
IR,[a] cm^{-1}	1640, 1458, 1290, 1265–1140, 985, 815, 758, 748, 715, 661	1635, 1435, 1335, 1280–1155, 1080, 1000, 950, 855, 800	1635, 1435, 1320, 1280–1155, 1060, 1000, 950, 860, 800
^{19}F NMR[b]	–56.2 (a), –62.2 (b) [rel area, 1:1]	–84.1 (a), 107.8 (b), –62.0, –61.9 (c,d), –56.7 (e) [rel areas, 3:2:6:3]	–56.7, –57.5 (a,e), –83.7 (b), –113 (e), –62.2 (d) [rel areas, 6:3:2:3]

[a] The IR spectrum of **8** was recorded in an argon matrix at 10 K. Spectra for **12** and **14** were recorded in the gas phase. [b] ^{19}F NMR spectra were measured in $CDCl_3$. Chemical shifts are reported in ppm with reference to $CFCl_3$, with positive shifts to high frequency of the reference.

Table II. Spectra Data for Cyclopropenyl Ketones 9,[a] 13, and 15



	9	**13**	**15**
MS, *m/e*	340 (M$^+$), 243 (base)	371, 321, 271, 243 (base), 193, 155, 119, 69	371, 321, 293, 243, 205, 193, 155, 69 (base)
IR, cm^{-1}	1927 ($\nu_{C=C}$), 1770 ($\nu_{C=O}$)	1920, 1775, 1355, 1300–1140, 1030, 1000, 950, 890, 810	1755, 1350, 1300–1140, 1040, 1000, 950, 880, 800
^{19}F NMR[b]	–74.79 (a), –60.73 (b), –67.23 (c) [rel areas, 1:2:1]	–86.5 (a), –121.4 (b), –67.5 (c), –68.8 (d) [rel areas, 3:2:6:3]	–76.5 (a), –62.2 (b), –114.4 (c), –83.9 (d) [rel areas 3:6:2:3]

[a] From Lemal et al. for comparison. See ref 18. [b] ^{19}F NMR spectra for **13** and **15** were measured in $CDCl_3$. Chemical shifts are reported in ppm with reference to $CFCl_3$, with positive shifts to high frequency of the reference.

their isolation and characterization was more difficult. Spectral data obtained for **13** and **15**, however, are fully consistent with previously reported data[18a,19] for ketone **9** and are given in Table II.

Formation of trapped products **12**, **14** and **13** and **15** in essentially the same ratio from either **2** or **3** implies either a facile pathway for equilibrium of the two isomeric ketocarbene intermediates or a common intermediate for the two photoreactions. Although these results do not provide direct information on the actual nature of the transient

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(19) Reference 18a. Note that the assignment of ^{19}F NMR signals to the nonvinyl CF_3 groups in cyclopropenyl ketone **7** was inadvertently switched by the authors.

Table III. Spectral Data of Diazo Ketones 1–3

	$CF_3COCN_2CF_3$ (1)	$CF_3CF_2COCN_2CF_3$ (2)	$CF_3COCN_2CF_2CF_3$ (3)
mass spectra, *m/e*	206, 178, 137, 109, 69	256, 159, 137, 119, 109, 81, 69	256, 209, 187, 159, 109, 93, 69
IR (CCl_4), cm^{-1}	2120 (ν_{CN_2}), 1710 ($\nu_{C=O}$)	2140 (ν_{CN_2}), 1710 ($\nu_{C=O}$)	2140 (ν_{CN_2}), 1740 ($\nu_{C=O}$)
^{19}F NMR[a]			
298 K ($CDCl_3$)	−55.0 (br m), −58.9 (br s), −75.2 (q + s) [coalescence]	−59.2 (br m, 3 F), −82.6 (s, 3 F), −120.6 (br m, 2 F)	−75.0 (s, 3 F), −85.0 (s, 3 F), −112.6 (br s, 2 F)
213 K (CD_2Cl_2)	s-*E* −58.8 (s, 3 F), −75.0 (s, 3 F)	−58.8 (s, 3 F), −82.6 (br m, 3 F), −121.1 (br m, 2 F)	−74.1 (s, 3 F), −85.2 (t, 3 F), −114.3 (q, 2 F)
	s-*Z* −54.5 (q, 3 F), −75.0 (q, 3 F)	−53.6 (t, 3 F), −81.8 (br m, 3 F), −121.8 (q, 2 F)	−74.0 (br m, 3 F), −86.5 (br m, 3 F), −109.7 (br m, 2 F)
400 K (DMF-d_6)	−57.4 (q, 3 F), −74.0 (q, 3 F)		

[a] Chemical shifts are reported in ppm with reference to $CFCl_3$, with positive shifts in high frequencies of the reference: br, broad; s, singlet; m, multiplet; q, quartet; t, triplet.

species involved, the most plausible pathway for interconversion of the ketocarbenes, consistent with our results and previous studies is via transient formation of an oxirene. Oxirene formation is known to take place on a singlet surface. Whether the intermediate species responsible for the formation of trapped products is the ketocarbene or the oxirene, we are unable to determine. Our results do, however, demonstrate that oxygen migration occurs to equilibrate the isomeric ketocarbenes **6** and **7** prior to their chemical trapping with hexafluoro-2-butyne to form isomeric furan and cyclopropenyl ketone products. Currently, ongoing studies are aimed at determining whether products are derived directly from oxirenes or from singlet or triplet carbenes. A useful analogy in distinguishing between singlet and triplet carbenes may be found in the reaction of dicarbomethoxymethylene with 2-butyne, where direct photolysis led to cyclopropene products and sensitization with benzophenone gave predominantly furans.[12]

In this study we did not obtain evidence of diazirene formation. It is possible that diazirenes were formed and not isolated, but if so, they did not interfere with ketocarbene formation and trapping.

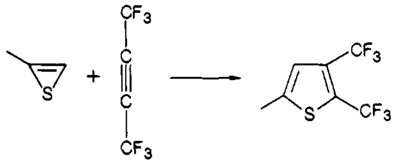
Since the previously reported[8] matrix photolysis of **1**–**3** showed a wavelength dependence, we also carried out the gas-phase photolysis of these three α-diazo ketones with hexafluoro-2-butyne as a trapping agent at $\lambda = 254$ nm. No significant changes in product distribution were observed with any of the three precursor ketones.

In the photolysis of α-diazo ketones **2** and **3**, the yield of cyclopropenyl ketone products **13** and **15** relative to furan products **12** and **14** did not vary significantly as a function of photolysis duration. The relative yield of **13** to **15** and **12** to **14** was also constant within experimental error. We therefore thought it is likely that **12** and **14** and **13** and **15** are trapped products arising from the reaction of the primary transient species formed in the photolysis of diazo ketones with the hexafluoro-2-butyne. It has been reported,[20,21] however, that tetrakis(trifluoromethyl)furan (**8**) can be photochemically converted to its cyclopropenyl ketone isomer, **9**, although the reported conditions (high-pressure Hg lamp and "transfer conditions"[21]) were very different from those used in this study.

To assess whether this photorearrangement might be occurring under our experimental conditions, we isolated the mixture of furans **12** and **14** from the photolysis of α-diazopentanone **2**. The mixture of furans was then subjected to extended photolysis at 254 nm, after which products were analyzed by gas chromatography/mass spectrometry. No cyclopropenyl ketone products were observed, and the ratio of furan **12** to furan **14** remained constant. We therefore conclude that cyclopropenyl ketone formation does not result from secondary photolysis of the furans and that furans **12** and **14** do not isomerize under our experimental conditions even at $\lambda = 254$ nm. At the longer wavelength $\lambda > 335$ nm the furans do not absorb light.

Furthermore, the fact that furans **12** and **14** do not photoisomerize under our reaction conditions eliminates one possible mechanism for the formation of two isomeric furans from each precursor diazo ketone **2** and **3**. This observation lends further support to our conclusion that ketocarbenes **6** and **7** can be readily interconverted and supports the invoking of the transient involvement of an oxirene.

In the previously mentioned gas-phase photolysis of 1,2,3-thiadiazole, 4-methyl-1,2,3-thiadiazole, and 5-methyl-1,2,3-thiadiazole in the presence of hexafluoro-2-butyne, evidence was presented which suggests that the thiophene products result from the trapping of thiirene intermediates by the alkyne. Furthermore, in the case of methylthiirene, products were rationalized as resulting from addition of the alkyne to methylthiirene across the less hindered C–S side of the ring[14] (eq 6).



(6)

Oxirenes and thiirenes, however, may not be directly comparable. Thiirene has been computed to lie ~15 kcal mol^{-1} below its ring-opened isomer.[22] However, oxirene is more antiaromatic. Ab initio type molecular orbital calculations at increasing level of sophistication predict oxirene to lie at progressively lower energies relative to its ring-opened isomer, the lowest singlet-state formylmethylene. The values taken in order of increasing level of sophistication are +0.9,[23] −2.7,[24] and −5.5[25] kcal/mol. Perfluoroalkyl substitution should make the oxirene ring even more stable than its ring-opened isomer. In light of this information, it may be assumed that it is the oxirene structure that adds to the acetylene to form the furan. However, this assignment remains tentative. Besides strong electronic effects, perfluoroalkyl substitution will have significant steric effects altering the energetics of the

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available reaction channels and the relative stability of the reaction products, thus possible causing the slight difference in the relative yield of the two isomeric furans.

Further work is in progress.

Experimental Section

^{19}F NMR spectra were recorded on a Bruker WH-400 NMR spectrometer. Mass spectra were recorded on an AEI MS 12 instrument, coupled to a 10% tricresylphosphate (6 mm × 4 m, 25 °C) gas-liquid chromatography column, and exact mass measurements were obtained on an AEI MS 50 spectrometer. Infrared spectra were recorded on a Nicolet 7199 fourier transform instrument, coupled to the same GLC column. Spectral data are summarized in Tables I, II, and III.

In the $\lambda > 335$ nm photolysis a medium-pressure mercury lamp (Hanovia #30620) with a window glass filter was used. In $\lambda = 254$ nm photolysis the source of radiation was a Hanovia low-pressure mercury resonance lamp with a 7910 Vycor filter.

A standard high-vacuum apparatus coupled to a gas-liquid chromatograph was employed to manipulate gases and isolate products for spectroscopic analysis.

Materials. Diazo ketones **1-3** were prepared according to the procedure reported for **1**.[26] Purification was carried out by preparative GC on a 10 ft × 1/4 in. i.d. SE-30 column at room temperature, and the spectral data are summarized in Table III. Exact $M^{\cdot+}$ mass spectral measurements for **2** and **3** were 255.98812 and 255.98818, respectively; the calculated value for $C_5F_8N_2O$ was 255.98828. The known s-*Z*/s-*E* conformational equilibrium of diazo ketones could be resolved for **1**, **2**, and **3** by low-temperature ^{19}F NMR as described in Table III and yielded an s-*Z*/s-*E* ratio of 1:4, 1:8, and 1:12, respectively.

Typical Photolysis Procedures. Precursor ketones with a sample pressure of 1.00-1.25 torr were placed in a 5 cm × 15 cm quartz cell with a 400-fold excess of hexafluoro-2-butyne. Photolysis times were varied from a few minutes to 16 h. Typical photolysis times were 2-3 at $\lambda = 254$ nm and 14 h at 335 nm. Determination of nitrogen and CO was used to monitor the extent of the photolysis and the absence of secondary photolysis of the ketene. Therefore, after each run the −195 °C noncondensible gases were measured in a gas buret followed by gas-liquid chromatographic analysis on a molecular sieve column (6 mm × 2 m, 25 °C). The reaction mixture was then distilled through two −98 °C traps. The condensate, which contained the products of interest, was analyzed by gas-liquid chromatography on the same tricresyl phosphate column and subjected to further spectroscopic analysis. The distillate, which contained the unreacted hexafluoro-2-butyne, was analyzed by gas-liquid chromatography using a medium activity silica gel column (6 mm × 3 m, 25 °C).

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Electron Delocalization in Pyrimidine Dimers and the Implications for Enzyme-Catalyzed Dimer Cycloreversion

Rosemarie F. Hartman, John R. Van Camp, and Seth D. Rose*

Department of Chemistry, Arizona State University, Tempe, Arizona 85287

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Pyrimidine dimers are cyclobutane derivatives produced by the photochemical cycloaddition reaction of two pyrimidines at their 5,6-double bonds. They are split by the photolyases, light-utilizing enzymes that may operate by a photoinduced, electron-transfer reaction that produces dimer radical anions. To assess the extent of charge delocalization in anionic species derived from dimers, we have measured base-catalyzed, cyclobutyl hydrogen exchange rates for a dimer in borate-buffered D_2O from pD 9.16 to 9.65. The kinetics were followed by NMR spectroscopy, and the rate constant for deuteroxide-catalyzed exchange, k_{OD}, was found to be 2.4×10^4 M^{-1} min^{-1}. The high rate of exchange supports the view that there is a carbanionic intermediate that is resonance-stabilized by electron delocalization from the cyclobutyl ring into the adjacent π system of the dimer. Simple Hückel molecular orbital theory has been applied to the π system of the dimer. The LCAO wave functions and approximate orbital energies have been derived. The Woodward-Hoffmann orbital symmetry conservation rules specify that the cycloreversion of the radical anion of cyclobutane is symmetry forbidden in the ground state. For the pyrimidine dimer radical anion, calculations showed that two cycloreversion mechanisms, a nonsynchronous concerted pathway and a totally nonconcerted pathway, proceed via transition states that are stabilized by a significant decrease in the energy of the orbital bearing the unpaired electron. A clearer view of why dimer radical anions are more prone to splitting than the neutral dimer has emerged from this study.

Pyrimidine dimers arise in DNA exposed to UV light as a consequence of a $(\pi^2_s + \pi^2_s)$ photocycloaddition reaction between two stacked pyrimidines in the double helix.[1] The dimers, which are cyclobutane derivatives, exert deleterious effects in living systems,[2] many of which possess the ability to repair DNA photodamage of this type. Repair in a wide variety of living systems is accomplished, remarkably, by enzyme-catalyzed splitting of the cyclobutane ring of the dimer to regenerate pyrimidines.[3]

The light-requiring enzymes responsible for dimer splitting are the DNA photolyases.[4] These exceptional enzymes utilize light in the visible and near-UV range of the spectrum to accomplish pyrimidine dimer photocycloreversion.[5] The nature of the interaction of enzyme

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