1.71–1.84 (m, 2 H), 2.32 (s, 3 H), 3.01–3.09 (m, 2 H), 7.09 (d, J = 8.1 Hz, 2 H), 7.26 (d, J = 8.1 Hz, 2 H); ^{13}C NMR (CDCl$_3$) δ 16.84 (q, J = 125 Hz), 17.52 (q, J = 125 Hz), 20.98 (q, J = 111 Hz), 22.79 (q, J = 125 Hz), 28.97 (t, J = 134 Hz), 37.17 (d, J = 125 Hz), 38.89 (t, J = 127 Hz), 129.65 (d, J = 159 Hz), 129.82 (d, J = 160 Hz), 132.7 (s), 136.0 (s).

Acknowledgment. We thank the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their generous support of this research.

Supplementary Material Available: The competition data for the reactions of 1 with tetramethylethylene, 2 with 2,5-dimethyl-2,4-hexadiene, and 3 with limonene and the derivation of the equations for the observed enthalpy and entropy of activation (4 pages). Ordering information is given on any current masthead page.

Gas-Phase Reaction between Oxygen (^{3}P) Atoms and Hexafluoro-2-butyne

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The gas-phase addition of oxygen (^{3}P) atoms from the mercury-sensitized photodecomposition of nitrous oxide to hexafluoro-2-butyne has been studied at 298 K. Tetrakis(trifluoromethyl)furan (4) is the major final product that arises from the reaction of the initial triplet ketocarbene adduct with a second molecule of hexafluoro-2-butyne.

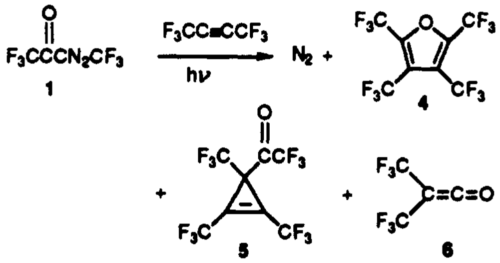
Introduction

A great deal of effort has been devoted in recent years to elucidating the mechanism of the photochemical Wolff rearrangement. Of fundamental theoretical interest has been the involvement of transient ketocarbene and antiaromatic 4π-electron oxirene species. One aspect of recent experimental investigations has been to carry out the photolysis of precursor diazo ketones with substituents potentially capable of stabilizing the elusive oxirene intermediates.[1,2] Since perfluoroalkyl substituents have been shown[3-5] to have the capability of providing remarkable stabilization of certain highly strained compounds, we have investigated and reported the photolysis of several perfluorinated α-diazo ketones in the gas phase[6] and inert matrices.[7,8]

Concurrently, theoretical studies of the various species on the unsubstituted formylmethylene–oxirene surface have provided insight into the nature and relative energies of various structures that might be involved in the Wolff rearrangement of the parent system.[9,10]

The addition of ground-state oxygen atoms to substituted acetylenes provides another entry point to one of the possible intermediates in the diazo ketone photolysis. There are many reports of the addition of ground state O(^{3}P) atoms to alkenes[11-15] and a few reports of the addition to alkynes.[16-20] Most of these reactions appear to proceed via initial formation of a triplet diradical. Thus, the investigation of the reaction between O(^{3}P) atoms and selected alkynes may facilitate the interpretation of results from mechanistic studies of the Wolff rearrangement.[21]

Scheme I



This paper presents the first report of the gas-phase reaction of O(^{3}P) atoms with a perfluorinated alkyne, hexafluoro-2-butyne. This study was undertaken to supplement our previously reported investigation of the gas-phase photolysis of hexafluoro-3-diazo-2-butanone (1), octafluoro-2-diazo-3-pentanone (2), and octafluoro-3-dia-

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zo-2-pentanone (**3**) in the presence of a large excess of the chemical trapping agent hexafluoro-2-butyne.[6]

$F_3C\overset{O}{\overset{\|}{C}}CN_2CF_3$

1

$F_3CCN_2\overset{O}{\overset{\|}{C}}CF_2CF_3$

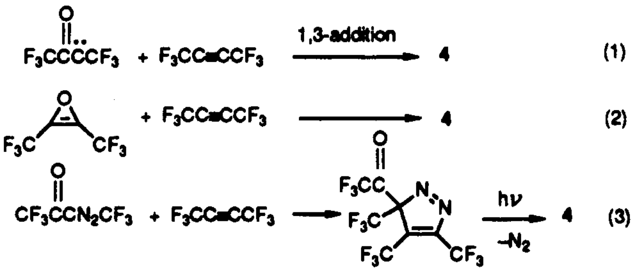
2

$F_3C\overset{O}{\overset{\|}{C}}CN_2CF_2CF_3$

3

The gas-phase photolysis of perfluorinated diazo ketones **1**–**3** in the presence of hexafluoro-2-butyne yielded furans as the major trapped products. Thus, photolysis of **1** with a 400-fold excess of hexafluoro-2-butyne yielded nitrogen and furan **4**, along with small amounts of cyclopropenyl ketone **5**, bis(trifluoromethyl)ketene **6**, and a trace of polymer, as shown in Scheme I.

Photolysis of either of the isomeric diazopentanones **2** or **3** in the presence of hexafluoro-2-butyne produced the corresponding ketene and cyclopropenyl ketone and furan adducts, suggesting the transient involvement of an oxirene species to provide a facile pathway for equilibration of the isomeric ketocarbene intermediates. An unanswered question, however, fell outside of the scope of this study. We were unable to differentiate between several reasonable transient species as the precursors that react with hexafluoro-2-butyne to yield cyclopropenyl ketone and furan adducts. In principle, furan **4**, the major product formed in the photolysis of **1**, could be rationalized via addition of hexafluoro-2-butyne to a singlet or a triplet ketocarbene, or to an oxirene, or loss of nitrogen from an intermediate pyrazolene (eqs 1–3).



The present study was designed to determine whether ground-state oxygen atoms would add to hexafluoro-2-butyne, and if so, whether furan **4**, cyclopropenyl ketone **5**, or ketene **6** would be formed in this reaction. A comparison of products from this reaction (which should afford a triplet ketocarbene adduct) with those from the photolysis of diazo ketone **1** should shed additional light on the nature of the intermediate species present in the Wolff rearrangement of perfluorinated diazo ketones.

Results and Discussion

Ground-state $O(^3P)$ atoms were generated by the mercury photosensitized decomposition of nitrous oxide at 298 K.[22] Thus, N_2 production served as an internal measure of the production of oxygen atoms.

$$Hg(^1S_0) + h\nu\ (253.7\ \text{nm}) \rightarrow Hg^*(^3P_1) \qquad (4)$$

$$Hg^*(^3P_1) + N_2O \rightarrow Hg(^1S_0) + O(^3P) + N_2 \qquad (5)$$

The sensitized photolysis of N_2O in the presence of hexafluoro-2-butyne was carried out under conditions of low conversion, giving N_2, tetrakis(trifluoromethyl)furan (**4**), a white polymer, trace amounts of CO, and other products as described in the following text. Reactant concentrations, photolysis times, and the yields of oxygen atoms and CO are shown in Table I.

Table I. Photolysis Conditions

run	P (N_2O) (Torr)	P (C_4F_6) (Torr)	phot time (h)	*P* (O atoms)[a] (Torr)	% CO[b]
1	2	50	15.25	0.7	nd[c]
2	4	48	16.25	0.8	0
3	4	52	16.25	0.5	<1
4	54	54	3.0	2.2	<3
5	84	202	13.5	2.5	0
6	417	100	3.25	1.7	<2
7	0	165	4.0	0	0

[a] Yield of $O(^3P)$ atoms produced, in units of pressure, as calculated from N_2 yield. [b] Mole fraction of CO in noncondensible gases. [c] Not determined.

In contrast to the addition of oxygen atoms to nonfluorinated alkynes, where the major products arise from fragmentation of ketene intermediates,[21] the major product here corresponds to the trapping of the initially formed triplet ketocarbene adduct by hexafluoro-2-butyne. Regardless of the nitrous oxide/hexafluoro-2-butyne ratio, the only identifiable trapped product was **4**. Since the condensible products were analyzed directly by GC/MS, quantitative yields of **4** cannot be estimated. Nevertheless, it was observed that the highest yield of **4** was obtained in runs 1 and 2, despite the fact that more oxygen atoms were produced in runs 4–6. The greatest amount of polymer was formed in run 5, where the pressures of the alkyne and the yield of oxygen atoms were highest. Thus, polymer formation appears to be competing effectively with furan formation at higher alkyne pressures. In several runs, trace amounts of CO (mole fractions varying from 0 to 3% of the noncondensible gases) were formed. In runs 1 and 2, a high molecular weight compound was also observed by GC/MS (peaks at 506, 487, 418, 349, and 69). We were unable to further characterize this compound.

Several other products were also observed by GC/MS that did not have mass spectra consistent with C_4F_6 + C_4F_6O adducts. Since it seemed likely that these were due to the photolysis of either hexafluoro-2-butyne or trace contaminants in the hexafluoro-2-butyne, the mercury-sensitized photolysis of 150 Torr hexafluoro-2-butyne was carried out in the absence of nitrous oxide (run 7, Table I). These same products were observed, along with a trace amount of white polymer.

Neither ketene **6** nor cyclopropenyl ketone **5** was observed, nor was the perfluoropropylene that might result from decomposition of ketene **6**.

Theoretical and experimental investigations of the addition of $O(^3P)$ to alkynes have demonstrated that the reaction usually proceeds by formation of an initial adduct, which, on the basis of spin conservation, must be a triplet diradical. Because of its importance in flame chemistry, the reaction of oxygen atoms with acetylene has been particularly well studied. The initially formed diradical intermediate (HCCHO) and its isomerized product (CH_2CO) undergo unimolecular decomposition via two channels to give (a) CH_2 + CO or (b) HCCO + H.[17] Ab initio MO calculations have been used to characterize the two lowest triplet potential energy surfaces for the addition of $O(^3P)$ to acetylene.[23]

There are, however, fewer reports of the addition of oxygen atoms to substituted alkynes, and, while oxygen atom addition to perfluorinated alkenes[12] and (trifluoromethyl)acetylene[24] have been reported, no helpful precedents reporting the reactions of nonterminal alkynes with substituents similar to perfluoroalkyl groups are available. Perhaps the closest parallel is the addition of

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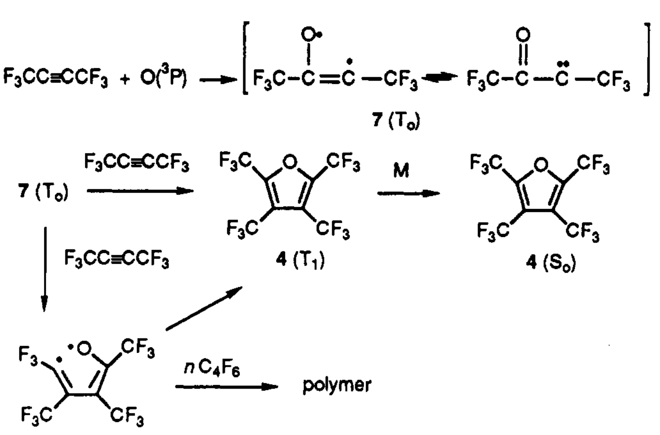
Scheme II



oxygen atoms to 2-butyne. We have previously described the gas-phase reaction of O(^{3}P) atoms from the mercury-sensitized photolysis of 100 Torr N_2O with 10 Torr 2-butyne.[21] Major products formed were N_2, CO, methyl vinyl ketone, propylene, and polymer. These results are consistent with other studies on ground-state oxygen atom addition to 2-butyne where CO, propylene, and methyl vinyl ketone were observed.[25,26] A vibrationally excited triplet ketocarbene was proposed as the initial intermediate in this reaction. It was suggested[21] that methyl vinyl ketone and dimethylketene are formed by hydrogen migration and Wolff rearrangement, respectively, from the ketocarbene, and propylene is a product of fragmentation of the initially formed hot ketene. Stabilized ketene may also undergo secondary photolysis to give CO and propylene.

Similarly, the formation of furan 4 in this reaction is most readily explained by the trapping of triplet 7 by hexafluoro-2-butyne to give triplet furan directly or a 1,5-biradical that subsequently undergoes ring closure to give triplet furan (Scheme II).

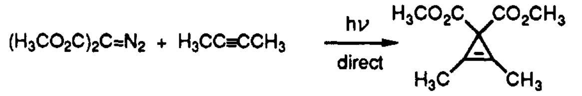
The absence of both cyclopropenyl ketone 5 and ketene 6 in the products suggests that the singlet surface is likely not accessed during the oxygen atom addition reaction. Thus, 7 must be in the ground T_0 state.

By contrast, the minor products 5 and 6 formed in the gas-phase photolysis of diazobutanone 1 in the presence of hexafluoro-2-butyne are likely singlet derived. The formation of 4 as the major product is consistent with the suggestion that intersystem crossing from a S_1 to T_0 ketocarbene is important in the gas-phase photochemical reaction of 1.[6]

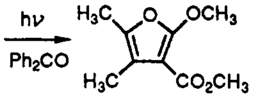
The interpretation of the present results as discussed previously is in agreement with earlier observations[7,27] reported from this laboratory on the IR spectroscopic detection of bis(trifluoromethyl)oxirene in the argon matrix photolysis of 1 at 10 K and the ESR spectroscopic detection of the *s-Z* and *s-E* conformers of 7 in the polycrystalline phase photolysis at 30 K. Thus, the low-temperature photolysis of 1 yields singlet excited (trifluoroacetyl)(trifluoromethyl)methylene, which can undergo cyclization to yield oxirene, Wolff rearrangement to yield the ketene, or intersystem crossing to the lowest triplet state, 7.

In summary, a plausible explanation for the formation of the two adducts in the photolysis of 1 (and the corresponding products from the photolysis of 2 and 3) is that ketone 5 results from trapping of a singlet ketocarbene by hexafluoro-2-butyne, and the present study, while providing no proof, suggests that furan 4 may arise from the trapping of the triplet-state ketocarbene by hexafluoro-2-butyne.

This explanation is also consistent with a report on the reaction of dicarbomethoxycarbene with 2-butyne, where direct photolysis of methyl diazomalonate led to cyclopropene products and sensitization with benzophenone gave predominantly furans[28] (eqs 6 and 7).

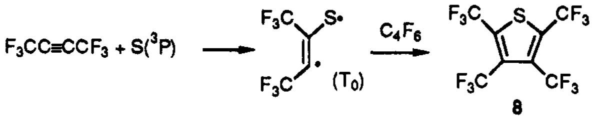


(6)



(7)

The reactivity of O(^{3}P) atoms with hexafluoro-2-butyne as established here is closely analogous to that of S(^{3}P) atoms as we have shown before.[29] The gas-phase reaction of COS in the presence of hexafluoro-2-butyne yields, as the only detectable products at low conversion, CO and the sulfur analogue of 7, tetrakis(perfluoromethyl)thiophene (8), via the initial reaction of S(^{3}P) with hexafluoro-2-butyne to form a T_0 biradical.



8

(8)

It is interesting to note that the yield of thiophene products was much greater from the reaction of S(^{3}P) atoms with hexafluoro-2-butyne than with acetylene, propyne, or 2-butyne.[30]

The present results, then, lend further support to the involvement of triplet ground-state (trifluoroacetyl)(trifluoromethyl)methylene (7) in the gas-phase photolysis of diazo ketone 1. Recent MC-SCF calculations of the formylmethylene–oxirene surface show that the ground state of formylmethylene is triplet and that triplet and singlet ketocarbenes might exist as planar diradicals with an energetically accessible crossing point. The same calculations show triplet oxirene to be a π–π diradical, lying 47 kcal mol^{-1} above the ground state of formylmethylene.[10] The steric and electronic effects of perfluoroalkyl substituents would be expected to substantially complicate extrapolations from this simple model; nevertheless, it appears clear that the ground state of perfluoroalkyl ketocarbenes is most probably the triplet.

Experimental Section

A standard high-vacuum apparatus[6] coupled to a gas–liquid chromatograph was employed to manipulate gases and isolate products for spectroscopic analysis. Photolyses were carried out in a cylindrical 5 × 15 cm quartz cell connected through stainless steel high-temperature Hoke valves to the grease-free vacuum system. The mercury resonance line at 2537 Å was obtained from a Hanovia low-pressure lamp equipped with a 7910 Vycor filter. Mass spectra were obtained on an AEI MS 12 instrument coupled to a 10% tricresyl phosphate (6 mm × 4 m, 25 °C) gas–liquid chromatography column.

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Materials. Hexafluoro-2-butyne (PCR Research Chemicals) was purified by repeated distillation at −107 °C. Nitrous oxide (Linde Gas) was purified by distillation at −130 °C. Both were thoroughly degassed prior to introduction into the photolysis cell.

Typical Photolysis Procedures. Nitrous oxide and hexafluoro-2-butyne were placed in the photolysis cell with a drop of mercury and photolyzed under the conditions listed in Table I. The yield of nitrogen was used to monitor the extent of the photolysis. After each run, the −195 °C noncondensible gases were measured in a gas buret and analyzed by gas-liquid chromatography on a molecular sieve column (6 mm × 2 m, 25 °C). The reaction mixture was then distilled through two −107 °C traps to separate the products from nitrous oxide and hexafluoro-2-butyne. The condensate, which contained the products, was then analyzed by GC/MS, using the same tricresyl phosphate column.

Products were identified by comparison with authentic samples. Complete spectral data for **4** have been reported.[6]

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Photocyclization of Cyclononene and Cycloundecene[1]

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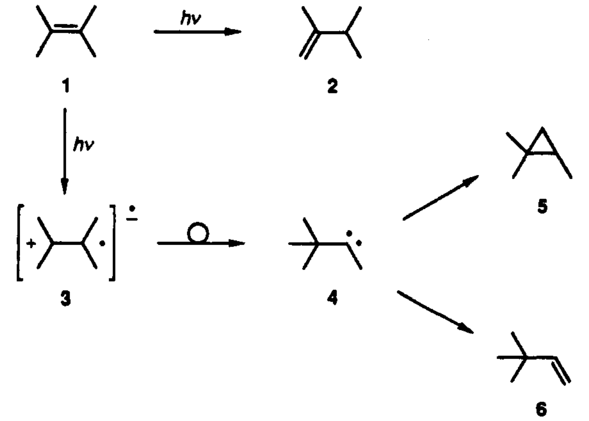
Irradiation of cyclononene (**7b**) and cycloundecene (**7d**) in pentane afforded *cis*-bicyclo[4.3.0]nonane (**10b**) and *cis*-bicyclo[6.3.0]undecane (**10d**), respectively. Small amounts of the fragmentation products 1-undecene (**14d**) and 1-undecyne (**15d**) were also obtained from cycloundecene (**7d**). The photobehavior of the series of medium- and large-ring alkenes **7a–e** is compared. Aside from $E \rightleftharpoons Z$ isomerization, the principal pathway in each case involves rearrangement of the π,R(3s) excited state to the cycloalkylidene intermediate **8**, which undergoes predominant, if not exclusive, 1,5-transannular insertion to afford the corresponding *cis*-bicyclo[*n*.3.0]alkane (**10**). The cycloalkylidenes **8** formed in this way exhibit behavior somewhat different from those generated by other methods. The possible contributory role of carbene intermediates derived from π,R(3s) excited states in $E \rightleftharpoons Z$ photoisomerization of acyclic alkenes is also discussed.

The deceptively simple chromophore of the isolated carbon–carbon double bond displays a surprisingly rich array of photobehavior.[2] Most well-known is $E \rightleftharpoons Z$ photoisomerization, involving the π,π^* excited state. However, alkenes also undergo competing 1,3-sigmatropic hydrogen migration and rearrangement via carbene intermediates on irradiation in nonnucleophilic media. Thus, for example, irradiation of 2,3-dimethyl-2-butene (**1**) in pentane affords a mixture of the double-bond migration product **2**, formed via a 1,3-sigmatropic hydrogen shift,[3] and the cyclopropane **5** and rearranged alkene **6**, formed via the carbene intermediate **4**.[4] Carbene formation apparently involves rearrangement of the π,R(3s) Rydberg excited state **3**, which has radical-cation character due to promotion of one of the π electrons to a large molecular orbital having approximately the same size and shape as the 3s atomic orbital of carbon.[4,5]



These two types of photobehavior are also exhibited by cyclic analogues.[2] However, the photobehavior of unsubstituted cycloalkenes is somewhat simplified by the fact that double-bond migration is an identity process—affording a product indistinguishable from the starting material and, in a sense, isolating the Rydberg-type photobehavior.

The π,R(3s) excited state of a cycloalkene such as cyclooctene (**7a**) can in principle undergo rearrangement to either a cycloalkylidene **8a** or a ring-contracted cycloalkylmethylene intermediate **9a**, depending on whether a hydrogen atom or alkyl group migrates. Thus, a mixture of products **10a–12**, arising from the two carbene intermediates **8a** and **9a**, was formed on irradiation of **7a** in pentane.[1b] By contrast, however, the higher homologues cyclodecene (**7c**) and cyclododecene (**7e**) afforded only

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[†] Universität Leipzig.

[‡] University of North Carolina.

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