

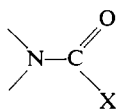
Solid-State Conformation of Amide Groups. Crystal Structures of *N*-Ethyl-*N*-*p*-nitrophenylcarbamoyl Chloride and of *N*-Phenylurethane

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Abstract: In this paper we report the crystal structure for two amide-like compounds, *N*-ethyl-*N*-*p*-nitrophenylcarbamoyl chloride and *N*-phenylurethane. The X-ray patterns were obtained using an automated Picker diffractometer. The first substance crystallizes in the space group $P2_1/c$ with unit cell constants $a = 7.063 \pm 0.004$, $b = 22.691 \pm 0.011$, $c = 7.032 \pm 0.005$ Å, $\beta = 110^\circ 37' \pm 5'$, $Z = 4$ ($D_x = 1.441$ g cm⁻³, $D_{\text{meas'd}} = 1.43$ g cm⁻³). The second compound crystallizes in the space group $Pbca$ with unit cell constants $a = 8.56 \pm 0.01$, $b = 9.67 \pm 0.01$, $c = 22.44 \pm 0.03$ Å ($D_x = 1.18 \pm 0.01$ g cm⁻³, $D_{\text{meas'd}} = 1.16$ g cm⁻³). For the carbamoyl chloride we collected intensities for 1394 nonzero independent reflections, while for the urethane we tabulated 1006 intensities. The carbamoyl chloride crystal structure was solved by Patterson methods, while the urethane structure was elucidated by direct methods. Both structures were refined by block-diagonalized-matrix-least-squares calculations. The carbamoyl chloride shows a nonplanar distortion of the amide group of 12° which is accomplished through a torsion about the amide bond. The amide bond length of 1.325 Å is normal. The urethane similarly exhibits a nonplanar amide group with a distortion of 9° . We find a somewhat elongated amide (1.352 Å) for this compound.

We recently reported the crystallographic study of a number of compounds containing the grouping



where the nitrogen is singly or doubly substituted and X is a carbon, a nitrogen, or an oxygen atom.² Our interest was primarily in the conformation of the amide group as a function of the number and nature of the substituents on nitrogen and on the nature of X. In the case of the structure of acetanilide³ (X = CH₃), the deviation from the planarity of the amide group is about 4° . In this compound, the nonplanar distortion is accomplished through a torsion about the C-N amide bond. This paper deals with the crystal structures both of *N*-ethyl-*N*-*p*-nitrophenylcarbamoyl chloride and of *N*-phenylurethane. It was interesting for us to determine whether the amide group in the urethane deviates from planarity. We expected that the deviation from planarity in carbamoyl chloride would be greater than that reported for acetanilide³ because of the presence of two substituents as well as the presence of a chlorine atom with its greater steric encumbrance.

Experimental Section

***N*-Ethyl-*N*-*p*-nitrophenylcarbamoyl Chloride.** This compound was prepared starting from *N*-ethyl-*p*-nitroaniline.⁴ Phosgene was passed through a two-phase mixture of toluene (50 ml) containing *N*-ethyl-*p*-nitroaniline (5 g, 30 mmol) and a water solution of sodium hydroxide (1.3 g of NaOH in 10 ml of H₂O) at 0° for

approximately 1 hr. The excess of phosgene was removed by flushing the system with nitrogen. The toluene layer was separated from the water phase. The aqueous phase was extracted with ether. The organic solvents were combined, washed with water, dried (Na₂SO₄), and evaporated. The solid (4.7 g, 68% yield) was filtered and washed with toluene to give a crystalline product (mp 118° ⁵).

Crystals of *N*-ethyl-*N*-*p*-nitrophenylcarbamoyl chloride have a prismatic shape. A single crystal was chosen with dimensions $0.25 \times 0.35 \times 0.2$ mm. Weissenberg photographs showed that the crystal was monoclinic with space group $P2_1/c$. The crystal was mounted on a Picker automated diffractometer with the *b* axis parallel to the spindle axis. The unit cell constants were determined from a least-squares fit of the angular positions of 12 independent reflections. They are reported in Table Ia. Data

Table I. Crystal Data

(a) <i>N</i> -Ethyl- <i>N</i> - <i>p</i> -nitrophenylcarbamoyl Chloride	
$a = 7.063 \pm 0.004$ Å	$V = 1056.4$ Å ³
$b = 22.691 \pm 0.011$ Å	$Z = 4$
$c = 7.032 \pm 0.005$ Å	$D_x^a = 1.441$ g cm ⁻³
	$D_o^a = 1.43$ g cm ⁻³
$\beta = 110^\circ 37' \pm 5'$	$\mu(\text{Mo K}\alpha) = 3.5$ cm ⁻¹
Space group $P2_1/c$	
(b) <i>N</i> -Phenylurethane	
$a = 8.56 \pm 0.01$ Å	$V = 1857.5$
$b = 9.67 \pm 0.01$ Å	$Z = 8$
$c = 22.44 \pm 0.03$ Å	$D_x = 1.18 \pm 0.01$ g cm ⁻³
Space group $Pbca$	$D_o = 1.16$ g cm ⁻³

^a D_x determined from X-ray; D_o measured from plot.

were taken to a 2θ value of 45° with Zr-filtered Mo K α radiation. We collected 1394 reflections, of which 1178 were observed. No absorption corrections were applied ($\mu = 3.5$).

***N*-Phenylurethane.** Crystals of *N*-phenylurethane were obtained in the form of needles. Weissenberg photographs indicate the space group $Pbca$ with eight units of C₉H₁₁NO₂ per unit cell. A single crystal was mounted on a Picker automated diffractometer and the unit cell constants were calculated from the setting of 12 reflections by least-squares procedures. They are reported in Ta-

(1) (a) Visiting professor at the Polytechnic Institute of Brooklyn, 1969–1970; (b) postdoctoral fellow on leave from the University of Naples; (c) postdoctoral fellow at the Polytechnic Institute of Brooklyn, 1970.

(2) (a) C. Pedone, E. Benedetti, A. Immirzi, and G. Allegra, *J. Amer. Chem. Soc.*, **92**, 3549 (1970); (b) P. Ganis, G. Avitabile, E. Benedetti, C. Pedone, and M. Goodman, *Proc. Nat. Acad. Sci. U. S.*, **67**, 426 (1970).

(3) C. J. Brown, *Acta Crystallogr.*, **21**, 442 (1966).

(4) W. Schweitzer, *Ber.*, **19**, 149 (1886).

(5) In British Patent 825,921; *Chem. Abstr.*, **54**, 15314f (1960); **55**, 16481c (1961); the same compound was synthesized under strictly anhydrous conditions using triethylamine.

Table II. Final Positional and Thermal Parameters for Nonhydrogen Atoms^a

(a) <i>N</i> -Ethyl- <i>N</i> - <i>p</i> -nitrophenylcarbamoyl Chloride									
	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
C1	0.4163 (3)	0.1077 (1)	0.6205 (3)	7.22 (12)	6.47 (11)	6.15 (10)	1.03 (9)	3.43 (9)	1.13 (9)
O1	0.7355 (8)	0.0449 (2)	0.6830 (8)	7.1 (3)	5.7 (3)	6.6 (3)	1.4 (2)	0.9 (2)	1.5 (2)
O2	0.0278 (8)	0.2749 (2)	-0.1901 (10)	6.6 (3)	5.3 (3)	11.1 (4)	1.7 (2)	3.4 (3)	3.1 (3)
O3	-0.1404 (10)	0.1955 (3)	-0.2972 (10)	7.7 (4)	7.5 (4)	9.7 (4)	1.2 (3)	-1.8 (3)	0.5 (3)
N1	0.6313 (8)	0.0950 (3)	0.3868 (9)	4.4 (3)	5.5 (3)	5.3 (3)	1.4 (2)	1.5 (2)	0.8 (2)
N2	0.0076 (9)	0.2223 (3)	-0.1902 (10)	6.3 (3)	4.8 (3)	6.6 (4)	1.2 (3)	2.8 (3)	1.1 (3)
C	0.6226 (11)	0.0763 (3)	0.5623 (11)	5.1 (4)	4.2 (3)	5.3 (4)	0.7 (3)	1.0 (3)	0.6 (3)
C1	0.4738 (10)	0.1266 (3)	0.2390 (10)	4.6 (3)	3.8 (3)	4.6 (3)	0.6 (2)	1.7 (3)	0.3 (2)
C2	0.2948 (10)	0.0990 (3)	0.1288 (10)	5.2 (3)	3.5 (3)	5.4 (3)	0.1 (3)	1.9 (3)	-0.1 (3)
C3	0.1428 (10)	0.1297 (3)	-0.0160 (10)	4.9 (3)	3.8 (3)	4.6 (3)	0.0 (3)	1.5 (3)	0.2 (3)
C4	0.1751 (10)	0.1879 (3)	-0.0438 (10)	5.0 (3)	4.3 (3)	3.8 (3)	1.1 (3)	1.2 (3)	0.6 (2)
C5	0.3541 (10)	0.2172 (3)	0.0588 (11)	5.3 (4)	3.7 (3)	5.6 (4)	-0.1 (3)	2.3 (3)	0.3 (3)
C6	0.5062 (10)	0.1856 (3)	0.2027 (11)	4.2 (3)	4.5 (3)	6.0 (4)	-0.1 (3)	2.0 (3)	0.1 (3)
C7	0.8230 (12)	0.0829 (4)	0.3405 (13)	4.9 (4)	7.2 (5)	7.4 (5)	0.3 (4)	1.2 (3)	0.0 (4)
C8	0.7817 (14)	0.0345 (4)	0.1943 (15)	7.5 (5)	8.3 (6)	8.8 (6)	0.9 (5)	2.7 (5)	-0.7 (5)

(b) <i>N</i> -Phenylurethane								
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>	
C1	0.0691 (6)	0.3081 (4)	0.1494 (2)	C7	0.5718 (9)	0.2857 (7)	0.0536 (4)	
C2	0.0057 (6)	0.4002 (5)	0.1902 (2)	C8	0.6935 (8)	0.3839 (9)	0.0454 (4)	
C3	-0.1148 (7)	0.3572 (6)	0.2275 (2)	C	0.3178 (6)	0.2751 (5)	0.0972 (2)	
C4	-0.1758 (7)	0.2231 (6)	0.2227 (2)	N	0.1954 (5)	0.3539 (4)	0.1146 (2)	
C5	-0.1122 (7)	0.1318 (6)	0.1800 (3)	O1	0.4278 (5)	0.3549 (4)	0.0717 (2)	
C6	0.0093 (6)	0.1730 (5)	0.1442 (2)	O2	0.3325 (5)	0.1525 (3)	0.1054 (2)	

^a Standard deviations are indicated in parentheses.

Table III

(a) Molecular Conformational Parameters of <i>N</i> -Ethyl- <i>N</i> - <i>p</i> -nitrophenylcarbamoyl Chloride ^a					
Distances, Å		Angles, deg		Torsion angles, deg	
C1-C	1.793 (8)	C1-C-O1	118.4 (4)	C2-C1-N1-C	-70.2
C-O1	1.180 (9)	C1-C-N1	112.9 (3)	C2-C1-N1-C7	110.7
C-N1	1.327 (10)	O1-C-N1	128.6 (3)	C1-N1-C-O1	171.3
N1-C7	1.524 (11)	C-N1-C1	124.3 (3)	C1-N1-C-C1	-12.4
N1-C1	1.424 (9)	C-N1-C7	118.2 (3)	C7-N1-C-O1	-9.6
C1-C2	1.381 (10)	C1-N1-C7	117.5 (3)	C7-N1-C-C1	166.7
C2-C3	1.382 (10)	N1-C7-C8	108.1 (4)	O2-N2-C4-C3	169.1
C3-C4	1.366 (9)	N1-C1-C6	118.7 (3)	O3-N2-C4-C3	-9.3
C4-C5	1.388 (11)	N1-C1-C2	120.8 (3)	C1-N1-C7-C8	-76.8
C5-C6	1.391 (10)	C6-C1-C2	120.5 (3)	C-N1-C7-C8	104.1
C6-C1	1.396 (10)	C1-C2-C3	120.6 (3)		
C4-N2	1.490 (10)	C2-C3-C4	117.8 (3)		
N2-O2	1.203 (8)	C3-C4-C5	123.8 (3)		
N2-O3	1.217 (10)	C4-C5-C6	117.6 (3)		
C7-C8	1.463 (14)	C5-C6-C1	119.5 (3)		
		C3-C4-N2	118.2 (3)		
		C5-C4-N2	118.0 (3)		
		O2-N2-C4	117.0 (3)		
		O3-N2-C4	118.1 (3)		
		O2-N2-O3	125.0 (4)		

(b) Some Molecular Parameters of <i>N</i> -Phenylurethane ^a					
Bond lengths, Å		Bond angles, deg		Torsion angles, deg	
C1-N	1.405 (6)	C1-N-H	119 (3)	C1-N-C-O1	189
N-C	1.352 (6)	C-N-H	115 (3)	C6-C1-N-C	-34
C-O1	1.344 (6)	C1-N-C	125.4 (2)		
C-O2	1.206 (6)	N-C-O1	110.0 (2)		
N-H	0.98 (6)	N-C-O2	126.2 (2)		
		O1-C-O2	123.8 (2)		

^a Standard deviations are indicated in parentheses.

ble Ib. Intensities for 1006 nonzero independent reflections were measured using Zr-filtered Mo K α radiation.

Determination of the Structures and Refinement

The structure factors for the carbamoyl chloride were phased by the heavy-atom method. The first Fourier located all the 15 nonhydrogen atoms of the asymmetric unit. The atomic positions and isotropic thermal parameters were refined by six cycles of block-matrix least-

squares calculations⁶ to an *R* value of 0.12. Six cycles including anisotropic thermal parameters and the geometrically located hydrogen atoms reduced the *R* value to 0.086. The hydrogen coordinates were not refined; their isotropic thermal parameter has been assumed to equal 4.5 Å². The function minimized was $\Sigma(wF_o - KF_c)^2$.^{2b} The form of Cruickshank's weighting func-

(6) A. Immirzi, *Ric. Sci.*, **37**, 743, 846, 850 (1967).

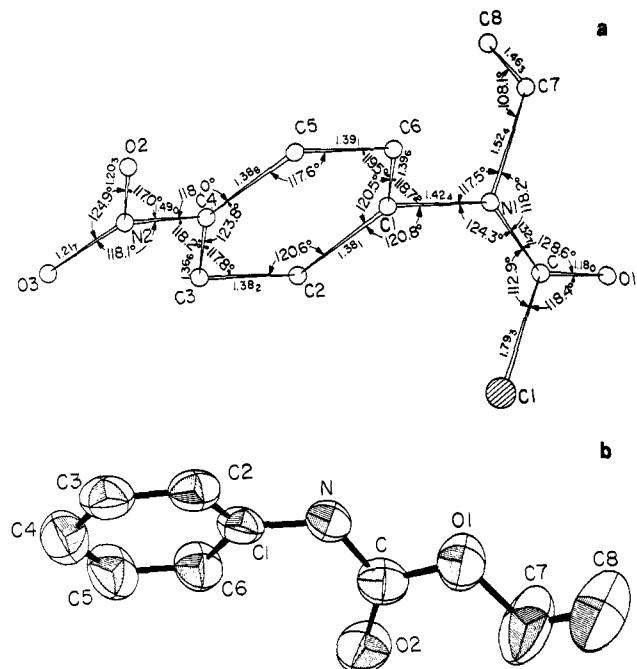


Figure 1. (a) Some conformational parameters of the molecule of *N*-ethyl-*N*-*p*-nitrophenylcarbamoyl chloride. (b) Molecular structure of *N*-phenylurethane. The ellipsoids indicate the anisotropic thermal vibrations of the atoms. C7 and C8 show relatively high thermal vibrations.

tion was $w = 0.1111 + 0.01243F_{\text{omin}} + 1.9888 \times 10^{-4}F_{\text{omax}}$. The atomic scattering factors were taken from Moore.⁷ The final positional and thermal parameters are listed in Table IIa.⁸

The *N*-phenylurethane structure was solved by direct methods using a procedure described by Allegra⁹ and refined by a block-diagonalized-matrix least-squares program.⁷ The final *R* value is 0.09 with anisotropic thermal factors. The positions of the hydrogen atoms were determined by difference Fourier, with the exception of those of the ethyl group. They were included in the structure calculations and refined isotropically. The ethyl hydrogens were not detectable because of the high thermal vibrations of the carbon atoms of the ethyl group ($B = >12 \text{ \AA}^2$) (see Figure 1b). In Table IIb the positional parameters of the nonhydrogen atoms are reported.

Description of the Structures

The most important conformational parameters for the two compounds with the corresponding standard deviations are listed in Table IIIa (see also Figure 1a) and Table IIIb.

For the carbamoyl chloride, the atoms Cl, N1, C, and C7, and the atoms N1, C, O1, and C1 lay almost in planes which form an angle of -12° . Unlike the case of *N,N'*-diethyl-*N,N'*-diphenylurea,^{2b} the nonplanar distortion of the amide group seems to be due only to a torsion about the amide bond C-N1 of $12 \pm 1^\circ$. We have found a similar distortion in *N*-phenylurethane, in

(7) F. H. Moore, *Acta Crystallogr.*, **16**, 1169 (1963).

(8) A list of the observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit \$3.00 for photocopy or \$2.00 for microfiche.

(9) G. Allegra, *Acta Crystallogr.*, **19**, 949 (1965).

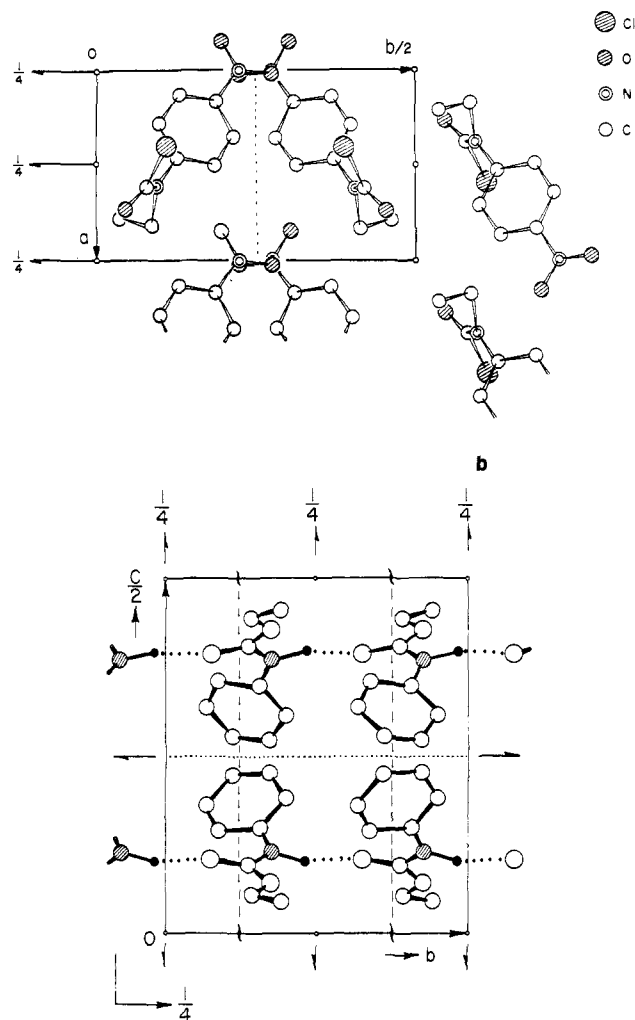


Figure 2. (a) Projection of the structure of *N*-ethyl-*N*-*p*-nitrophenylcarbamoyl chloride on 001. (b) Projection of the structure of *N*-phenylurethane on 100. The molecules form rows through hydrogen bonds (dotted lines).

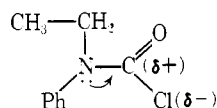
which the torsion angle C1-N-C-O2 about the amide bond is 189° . The resulting nonplanar distortion of the peptide group (9°) is appreciably higher than the distortion observed in several acyclic polypeptide units studied so far (5° or less).¹⁰ As expected for this conformation, the amide bond C-N ($1.352 \pm 0.006 \text{ \AA}$) is longer than usual for an amide group in a planar system (1.32 \AA).¹¹ It is interesting that the same deviation from planarity for an amide has been found in the case of the optically active alanine diketopiperazine.¹² In that case, we attributed the deviation to crystal packing forces. No such explanation seems appropriate for the acyclic *N*-phenylurethane. It is also not possible to invoke π -electronic interactions between the aromatic ring and the amide group to explain the deviation, since the phenyl and amide groups are not coplanar (see Table IIb).

(10) A. V. Lakshminarayarian, "Conformation of Biological Macromolecules," Vol. 1, Plenum Press, New York, N. Y., in press.

(11) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 281.

(12) E. Benedetti, P. Corradini, M. Goodman, and C. Pedone, *Proc. Nat. Acad. Sci. U. S.*, **62**, 650 (1969).

In Table IIIb some relevant geometric parameters of the molecule are given with the corresponding standard deviations. In the carbamoyl chloride, the amide bond does not seem to be lengthened (1.325 Å). The non-planar distortion of the amide group is slightly, but significantly, higher in this molecule than in the cases reported for acetanilide³ and found for the urethane. This can be explained by the stronger steric interactions between the two substituents of the nitrogen atom on one side and the oxygen and chlorine atoms on the other side. In addition, we must consider the inductive effect of the chlorine atom which we expected to affect the electron density in the amide bond. The fact that the C–N bond length is normal leads us to believe that the withdrawal of electrons by the chlorine is compensated by the donation of electrons to the C–N bond by the nitrogen.



In order to understand this effect it would be useful to compare it with the structure of a molecule, such as *N*-phenylcarbamoyl chloride.

In the carbamoyl chloride, the benzene ring forms an angle of 70° with the plane C7–N1–C. The nitro group is also out of the benzene plane (11°), as found in other

nitrophenyl derivatives.¹³ The conformation of the ethyl group is very similar to that found in *N,N'*-diethyl-*N,N'*-diphenylurea^{2b} and in 4-diethylcarbamoyl-1-cyclohexene-5-carboxylic acid.^{2a} All the other conformational parameters are quite normal.

In Figure 2a a projection of the structure on 010 is reported. Inspection of the intermolecular distances below 3.6 Å shows that there are no significant contacts between molecules.

Figure 2b shows the projection of the structure for the urethane on the 100 plane. The molecules form rows through hydrogen bonds between N–H and O=C groups (2.90 Å). The angle N–H···O is about 161°. All the intermolecular contact distances are longer than the sum of the van der Waals radii. Thus, hydrogen-bonding forces are not involved in the distortion from planarity of this amide-like grouping.

Levitt and Lifson¹⁴ have proposed that deviations for peptide bonds in proteins of up to 10° is reasonable. Our results support this view and may indicate that deviations from planarity of peptide bonds in proteins is more general than heretofore recognized.

Acknowledgment. We gratefully acknowledge the support of this research by the National Institutes of Health through Grant No. GM 08974.

(13) S. C. Abrahams, *Acta Crystallogr.*, **3**, 194 (1950).

(14) M. Levitt and S. Lifson, *J. Mol. Biol.*, **46**, 269 (1969).

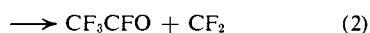
Reaction of Oxygen Atoms with 1,3-Perfluorobutadiene

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Contribution from the Department of Chemistry and Center for Air Environment Studies, The Pennsylvania State University, University Park, Pennsylvania 16802. Received August 26, 1970

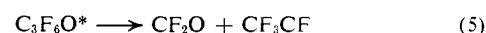
Abstract: The reaction of O(³P), produced from the mercury-photosensitized decomposition of N₂O, with 1,3-C₄F₆ was studied at 32 ± 6° in the absence and presence of O₂. The gaseous products of the reaction are CF₂O, *c*-C₃F₄, CF₂CFCFO (C₃F₄O), OCF₂CFCFCF₂ (C₄F₆O), OCF₂CFCFO (C₃F₄O₂), two C₇F₁₀ isomers, and C₂F₄. The quantum yields of the first five products are invariant to changes in reactant pressures or absorbed intensities. In the absence of O₂ they are 0.90, 0.68, 0.103, 0.025, and 0.022, respectively. They become 0.96, 0.64, 0.103, 0.20, and 0.21 in the presence of O₂. The quantum yields of the two C₇F₁₀ isomers are independent of the absorbed intensity and unaffected by the presence of O₂ but rise slightly with increases in the 1,3-C₄F₆ pressure. A mechanism is presented which explains all but the formation of C₃F₄O₂ in the absence of O₂. The initial steps are O(³P) + 1,3-C₄F₆ → CF₂O + *c*-C₃F₄; O(³P) + 1,3-C₄F₆ → C₃F₄O + CF₂; O(³P) + 1,3-C₄F₆ → C₄F₆O*, where the relative rates of the processes are 0.66, 0.10, and 0.24, respectively. By competitive studies with hydrocarbons, the overall rate constant for the O(³P) + 1,3-C₄F₆ reaction was found to be 2.9 × 10⁸ M⁻¹ sec⁻¹.

The reaction of ground-state oxygen atoms, O(³P), with C₂F₄ and C₃F₆ has been extensively studied and the mechanism is similar for both molecules.¹ Because of the asymmetry, the mechanism is slightly more complex with C₃F₆, and the first steps are



Presumably both CF₂ and CF₃CF as well as the excited

molecule C₃F₆O* are triplets. In the absence of molecular oxygen, C₂F₄ is probably produced (though not detected because of experimental difficulties) from the rearrangement of CF₃CF and dimerization of CF₂. The C₃F₆O* molecule does not produce propylene oxide but undergoes the reactions



In the presence of molecular oxygen the quantum yields of CF₂O and CF₃CFO are markedly enhanced

(1) J. Heicklen, *Advan. Photochem.*, **7**, 57 (1969).