# THE REACTION OF METHOXIDE ION WITH PERFLUOROCYCLOPENTENE

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### ABSTRACT

The reaction of methoxide ion with perfluorocyclopentene gave two major components. These have been identified as 1-fluoro-2-methoxyhexafluorocyclopentene (IIf) and 1,2-dimethoxyhexafluorocyclopentene (IIe).

A third component (3-methoxy-2,4,4,5,5-pentafluoro-2-cyclopenten-1-one (VII)) was isolated and a structure is proposed based on n.m.r. evidence.

A list of carbon-carbon double bond stretch frequencies is given for a number of 1,2disubstituted perfluorocyclopentenes which follow the electronegativities of the atoms adjacent to the double bond.

## INTRODUCTION

While the four- (1) and five-membered (2) 1,2-dichlorofluorocycloalkenes (Ia, Ib) gave the mono- (IIa, IIb) and tri-substituted (IIIa, IIIb) unsaturated ethers on treatment with methoxide ion, perfluorocyclobutene (3) (Ic) yielded unexpectedly the 1,2-dimethoxy (IId)and the mono derivative (IIc). For the latter procedure no trimethoxy compound was detected. Recently, a low yield of the dimethoxy derivative (4) (IVa) was obtained by



treating 1,2-dichlorohexafluorocyclopentene-1 (Ib) with methoxide ion. This was found to be an extremely reactive intermediate because of the vinyl fluoride structure and it was easily converted to the more stable trimethoxy compound (IIIb).

### DISCUSSION

To determine whether perfluorocyclobutene (Ic) behaved anomalously with methoxide ion in comparison with the 1,2-dichlorofluorocycloalkenes, the reaction was studied with perfluorocyclopentene (Id) as the substrate. By the consecutive addition of two equivalents of methoxide ion to one equivalent of olefin at low temperature, a mono- and a di-alkoxide derivative were found to be the major components. These were (IIf) and (IIe), respectively, determined by analysis and infrared spectroscopy.

Thus both the perfluoro and 1,2-dichloro alicyclic olefins undergo a similar  $S_N^2$  for the first step by what is believed to be an addition-elimination mechanism (1, 5). The second methoxide ion must go via another addition-elimination with the perfluorocyclic olefin, while it is known that the 1,2-dichloro derivative undergoes an  $S_N^2$ ' (6) as the second step. The difference is that a vinyl fluoride is much more reactive towards nucleophilic dis-

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placement than a vinyl chloride (5). Another factor is steric hindrance. Chlorine is much more bulky than fluorine, and this also contributes to the difference in mechanism.

From the experimental data it is obvious that the 1,2-dialkoxy derivative is stable towards further nucleophilic displacement under these conditions because the theoretical amount of base is not completely consumed.

From the second fraction a minor component ( $\cong 4\%$ ) was obtained by a vapor-phase chromatographic (v.p.c.) Autoprep.\* While analysis was inconclusive, both the infrared and n.m.r. spectra<sup>†</sup> were obtained and a structure was rationalized.

From the physical data three structures were possible, V, VI, or VII. The infrared



spectrum showed 3 H—C stretch bands at 3.35, 3.42, and 3.55  $\mu$ ; a C—O—C stretch at 8.82–8.93  $\mu$ ; a C=O at 5.68  $\mu$ ; and a C=C stretch at 5.98  $\mu$ . This information can fit any of the above structures; however, the fluorine n.m.r. of this component led to a more concrete decision. The spectrum showed a doublet (splitting  $\approx 13.8$  c.p.s.) at 121.0  $\phi$ , a doublet (splitting  $\cong$  5.4 c.p.s.) at 127.2  $\phi$ , and a complex band at 140.6  $\phi$ . Intensity ratio was 2:2:1. Therefore, VI was ruled out. A decision between V and VII was difficult, but it was significant that the average of the two F to F<sub>2</sub> couplings was about the same as that for compound VIII.<sup>‡</sup> On this basis structure VII was favored. It should be noted that very little coupling occurred between the two F<sub>2</sub>'s and that the single F coupled appreciably to the OCH<sub>3</sub>.

It is proposed that during the reaction, work-up, or distillation the allylic fluorines were hydrolyzed to a carbonyl group by the presence of water, which was not rigorously excluded. Alternately, structure VII could have come from the hydrolysis of the trisubstituted unsaturated ether (IIIc). This is the same type of product observed with the reaction of methoxide ion with the 1,2-dichlorofluorocycloalkenes (Ia, Ib). This would mean that two separate reaction paths are operating at the same time, with the latter resulting in the minor product. More studies are contemplated on this point in subsequent work.

Finally, a list of double bond absorptions for symmetrical and unsymmetrical 1,2disubstituted hexafluorocyclopentene-1 is given. It is apparent from Table I that the 1,2-dimethoxy derivative is intermediate in relation to the 1,2-dichloro and 1,2-diffuoro double bond position. The frequency of the double bond absorption follows the electronegativity (7) of the adjacent atoms, i.e., the order of increasing frequency is F > O > Cl. The magnitude of  $\Delta v$  is also in this order. It is interesting to note that the 1,2-dichloro compound has approximately the same carbon-carbon double bond stretch as found in cyclopentene (10), so that the double bond order is not reduced to any degree by resonance effects involving chlorine.

\*An Acrograph Autoprep was used with the following conditions: nonlinear program 70–135°, oven setting 40, on column injection,  $\frac{1}{4}$  cc sample, 20  $\times \frac{3}{6}$  in. SE 30 Silicon on 45/60 Chromosorb P column, flow rate 200 cc/min, retention time 6.84 min.

A Varian HR 60 operating at 56.4 mc run as a 10% solution using CFCl<sub>3</sub> as an internal standard.

The fluorine n.m.r. spectrum of this salt will be reported in another paper.

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TABLE I		
Compound	Infrared	Reference
$(CF_2)_3$		
C! - C = C - Cl	$6.19 \ \mu^*$	
$(CF_2)_3$		
Cl—C=C-OCH <sub>3</sub>	$6.00 \mu$	4
$(CF_2)_3$		
Cl - C = C - F	5.85 μ	8
$(CF_2)_3$		
F—C=CF	$5.70 \mu$	9
$(CF_2)_3$		
CH₃O—C=C—F	$5.80 \mu$	—
$(CF_2)_3$		
CH <sub>3</sub> O-C-C-OCH <sub>3</sub>	5.90 <b>µ</b>	

\*A value of 6.13 was reported by C. O. Parker. J. Am. Chem. Soc. 81, 2183 (1950). However, a value of 6.19  $\mu$  was consistently obtained on a Perkin-Elmer Model 317 spectrophotometer. All spectra were run as films (neat).

# EXPERIMENTAL

Reaction of Methoxide Ion and Perfluorocyclopentene

To 100 ml of methanol was added 4.6 g (0.2 mole) sodium with stirring. When all of the sodium reacted, the solution was cooled with dry ice. Then 42.4 g (0.2 mole) of olefin was added over a 10 min period. After stirring for 1 h at approximately  $-40^\circ$ , another equivalent of methoxide ion, 4.6 g (0.2 mole) sodium in 50 ml of methanol, was added. The solution was then allowed to stir for 5 h. The solution was then poured into water (\approx 400 ml) and the organic layer (lower) was isolated and washed twice with 50 ml water and dried over magnesium sulfate. The crude weight was 40.5 g, excluding volatile starting material.

Distillation, at atmospheric pressure, of the crude in a microapparatus gave two fractions: (1) 99-102° (2) 144-151°. Neither fraction was found to be homogeneous by an F&M Model 500 VPC equipped with an automatic integrator. On a 10 ft 10% Silicon Gum Rubber on Chromosorb P column run as an isotherm at 125°, a total of three peaks was obtained in both fractions with the following retention times in minutes, IIf, 2.04; VII, 2.48; IIe, 2.70. The combined integrated peak areas of both fractions were 34.36, 4.14. 61.50%, respectively.

The two major components were easily separated by redistillation of their respective fractions. From fraction one, IIf was obtained in analytical purity. It was identified as 1-methoxyheptafluorocyclopentene-1 by analysis and infrared spectroscopy. Its boiling point was  $100-101^{\circ}$  (uncorrected).  $\eta_{D}^{27} = 1.3223$ . The infrared spectrum gave the following bands: three C—H stretches at 3.30, 3.36, and 3.48  $\mu$ ; C=C stretch at 5.80  $\mu$ ; C—O—C stretch, broad 8.70-8.80  $\mu$  with other bands at 6.83, 7.30, 7.50, 7.71, 8.29, 9.63, 10.15, 10.74, and 11.44 µ.

Anal. Calcd. for C<sub>6</sub>H<sub>3</sub>F<sub>7</sub>O: C, 32.15; H, 1.34. Found: C, 31.76; H, 1.75.

Component IIe was similarly identified by redistillation of the second fraction. Its boiling point was 148-149° (uncorrected).  $\eta_D^{27} = 1.3658$ . The infrared spectrum gave the following bands: three C--H Stretches at 3.30, 3.35, and  $3.49 \mu$ ; C=C stretch  $5.90 \mu$ ; C-O-C stretch, broad  $8.80-8.90 \mu$  with other bands at 6.80, 7.40, 7.51, 7.73, 8.27, 8.34, 9.50, 10.00, 10.65, and  $11.52 \mu$ . Anal. Calcd. for C<sub>1</sub>H<sub>6</sub>F<sub>6</sub>O<sub>2</sub>: C, 35.60; H, 2.56. Found: C, 35.70; H, 2.73.

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