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REACTIVITY OF THE PERHALOALKANES CF_2BrX (X:Cl,Br) WITH NUCLEOPHILES. PART 5[1]. CONDENSATION WITH POTASSIUM 2-ALLYL PHENOXIDE ; EVIDENCE FOR DIFLUOROCARBENE FORMATION

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SUMMARY

CF_2Br_2 reacts spontaneously with potassium 2-allyl phenoxide, as opposed to the case of phenoxides where an initiation is necessary [2,3]. The products of the reaction are identified. A double insertion of the difluoromethylene is observed, which is a proof of the mechanism postulated with potassium phenoxides.

INTRODUCTION

Recently we showed that condensation of the perhaloalkanes CF_2BrX (X:Cl,Br) with different phenoxides and thiophenoxides gives O or S alkylated products ($ArOCF_2X$ and $ArSCF_2X$, X=H,Br). An ionic chain mechanism was postulated involving the difluorocarbene [2,3]. SUDA [4] and BURTON [5] have also postulated a carbenic process for condensation of thiolates with CF_2BrX. A similar mechanism is involved with carbanions [1,6].

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The general mechanism can be written as follows :

$$
\begin{aligned}
Nu^- + BrCF_2X &\longrightarrow NuBr + CF_2X^- \\
CF_2X^- &\longrightarrow :CF_2 + X^- \\
Nu^- + :CF_2 &\longrightarrow NuCF_2^- \\
NuCF_2^- + BrCF_2X &\longrightarrow NuCF_2Br + CF_2X^- \\
NuCF_2^- + \text{"H"}_{\text{solvent}} &\longrightarrow NuCF_2H
\end{aligned}
$$

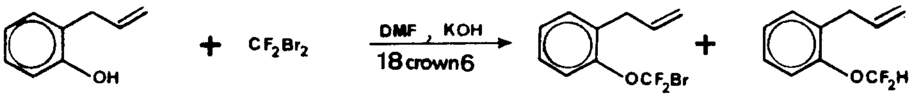
The formation of hydrogenated by products, the fact that only bromoderivatives are obtained from CF_2BrCl, and the initiation by RS^- in the case of phenoxides are in favor of this mechanism. Although all the attempts to trap the carbene by an olefin failed, we present here evidence for difluorocarbene formation in the case of the condensation of CF_2Br_2 with potassium 2-allyl phenoxide.

We were interested in the reactivity of this phenoxide in the hope that the double bond, near the reactive center ($-O^-$), could trap $:CF_2$. This attempt failed ; however some interesting features appear.

RESULTS

In contrast to the case of usual phenoxides recently studied [3], 2-allyl phenoxide has been prepared in situ in dry DMF from solid KOH and 18 crown 6. This phenoxide is prepared in situ because of its instability and cannot be isolated. In these conditions, the reaction of 2-allyl phenoxide is spontaneous when usual phenoxides [3] require initiation by RS^-. Furthermore, the nature of the products obtained is dependent on the reaction time.

a) When the mixture is hydrolysed and analyzed after four hours, the expected products $ArOCF_2Br$ and $ArOCF_2H$ only are observed.

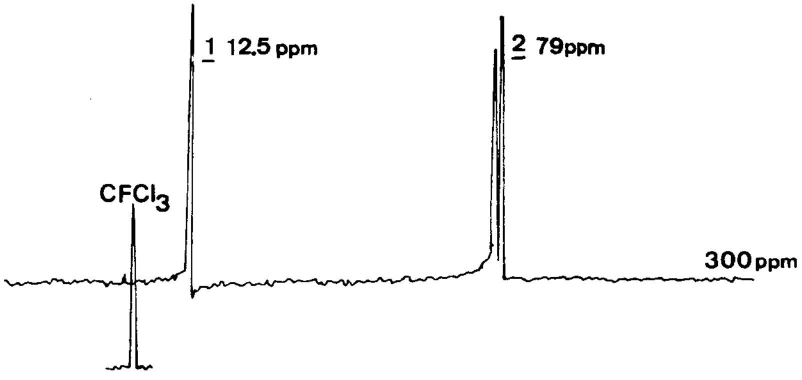


1 45%

2 55%

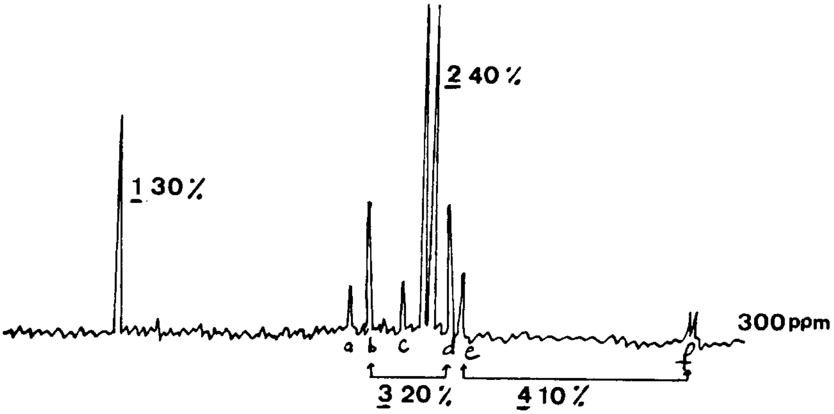
total yield = 20 %

^{19}F n.m.r. spectrum of the mixture after four hours :



b) However if the mixture is hydrolysed and analyzed after twelve hours, new signals appear in the ^{19}F n.m.r.

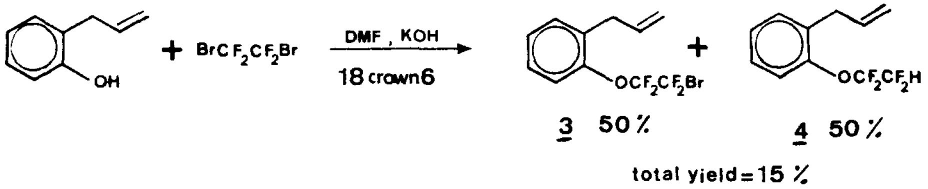
^{19}F n.m.r. spectrum of the mixture after twelve hours :



a= singlet ; b=triplet (J=5,6 Hz) ; c= singlet ; d=triplet (J=5,6 Hz) e=triplet (J=5,6 Hz) ; f=doublet x triplet (J=42 Hz, J=5,6 Hz).

a and c have not been identified. The other signals have been attributed to compounds 3 and 4 by comparison with authentic samples prepared from 2-allyl phenoxide and $BrCF_2CF_2Br$. This type of condensation is described in the preceding paper of this journal.

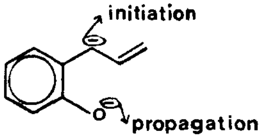
Mass spectrum of the mixture has been also recorded and is in agreement with the existence of compounds 1, 2, 3 and 4.



DISCUSSION

a) spontaneous reaction

The spontaneity of the reaction of 2-allyl phenol in the mixture (KOH/18 crown 6 - DMF) could be attributed to the formation of a small amount of di-anionic compound, resulting from the removal of the acidic allylic hydrogen in a strongly basic mixture. It is known that the reaction of carbanions with CF_2Br_2 is spontaneous [1,6] :



This 'auto-initiation' is also observed in the condensation of the same phenoxide with $BrCF_2CF_2Br$.

The fact that no bromo allyl compound has been seen in the reaction mixture is not in contradiction with this step of initiation because it can be formed in a too small quantity to be detected.

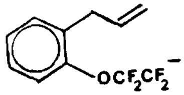
In the same manner with 2-benzyl phenoxide which has also an acidic hydrogen, no initiation is necessary. However, in this case, no double insertion of the difluoromethylene is observed.

b) Formation of compounds 3 and 4

We have verified that 1 and 2, in DMF with CF_2Br_2 and KOH/18 crown 6 do not react to give compounds 3 and 4. So there are two possible explanations for the formation of compounds 3 and 4.

First, it is possible that, in this case, the difluorocarbene : CF_2 duplica to give tetrafluoroethylene which then reacts with the phenoxide to form the tetrafluorinated compounds 3 and 4.

On the other hand, it is also possible that the intermediate $ArOCF_2^-$, substituted in the 2 position by an allyl group, has a lifetime longer than that of the other phenoxides recently studied [3]. If this is the case, the intermediate could trap a second carbene to give the anion :



which reacts further with CF_2Br_2 (or trap a hydrogen).

In any case, the formation of compounds 3 and 4 is evidence of difluorocarbene formation and is a proof of the carbenic mechanism in the condensation of CF_2Br_2 with phenoxides.

EXPERIMENTAL

Experimental details are described in the preceding paper of this journal.

2-allyl phenoxide + CF_2Br_2

2.6 g (0.02 mole) of 2-allyl phenol are dissolved in 40 ml of dry DMF under an argon atmosphere. 1.2 g (0.02 mole) of KOH and 200 mg of 18 crown 6 are added. The mixture is stirred for twenty minutes at room temperature. Then 8.4 g (0.04 mole) of CF_2Br_2 are added dropwise. After stirring for four hours, 150 ml of 17 % HCl are added. The aqueous phase is extracted with ether. After drying with Na_2CO_3, ether is evaporated and the residue is purified by a 'bulb to bulb' distillation at 0.01 mmHg. The pure liquid compounds are obtained by distillation using a spinning band column : 0.55 g (11 %) of 2 and 0.40 g (9 %) of 1.

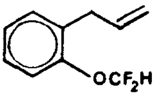
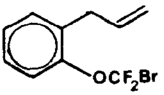
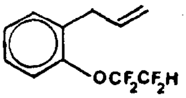
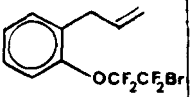
If the mixture is stirred for twelve hours, compounds 3 and 4 appear.

2-allyl phenoxide + $BrCF_2CF_2Br$

6.7 g (0.05 mole) of 2-allyl phenol are dissolved in 100 ml of dry DMF under an argon atmosphere. 2.8 g (0.05 mole) of KOH and 300 mg of 18 crown 6 are added. The mixture is stirred for half an hour at room temperature. Then 26 g (0.1 mole) of $BrCF_2CF_2Br$ are added dropwise. After stirring for four hours, 250 ml of 17 % HCl are added. The aqueous phase is extracted with ether. After drying with Na_2CO_3, ether is evaporated and the residue is purified by a 'bulb to bulb' distillation at 0.01 mmHg. The pure liquid compounds are obtained by distillation using a spinning band column : 0.88 g (7.5 %) of 4 and 1.14 g (7.5 %) of 3.

The characteristics of compounds 1, 2, 3 and 4 are summarized in the following table.

Characteristics of compounds

Compounds	b.p. °C/mmHg	H NMR[a]	F NMR[b]	mass spectra
 2 nc	80/40	m(2H)=3.4 m(2H)=5 m(1H)=6 m(4H)=7 t(1H)=6.4	d(CF_2H)=79 J_{FH}=72 Hz	M^+(184)
 1 nc	90/40	m(2H)=3.4 m(2H)=5 m(1H)=6 m(4H)=7	s(OCF_2Br)=12.5	M^+(262-264)
 4 nc	82/30	m(2H)=3.4 m(2H)=5 m(2H)=6 m(4H)=7	t(OCF_2)=87 dxt(CF_2H)=133 J_{HF}=42 Hz J_{FF}=5.6 Hz	M^+(234)
 3 nc	92/30	m(2H)=3.5 m(2H)=5 m(1H)=6 m(4H)=7	t(CF_2Br)=66.5 t(OCF_2)=83.2 J_{FF}=5.6 Hz	M^+(312-314)

[a] in $CDCl_3$ with TMS as internal reference.

[b] in $CDCl_3$ with $CFCl_3$ as internal reference.

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