ALKYLATING PROPERTIES OF ALKYLFLUOROALKENYL ETHERS

COMMUNICATION 3. COMPLEXES OF ETHERS OF PERFLUOROPROPENOL AND 2,4-BIS(TRIFLUOROMETHYL)-1,1,5,5,5-PENTENE-3-OL WITH TERTIARY AMINES*


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We showed earlier that alkylperfluoroisobutenyl ethers (I) behave like esters of strong acids in reactions with trialkylamine, manifesting alkylating properties and forming salts (II), containing the tetraalkylammonium cation and a mesomeric carbanion of perfluoroisobutenolate [2]

\[
\begin{align*}
\text{(I)} & \quad \text{(II)} \\
\{\text{CF}_3\}_n \text{CF}_2 = \text{O} \rightarrow \text{R} & \quad \left[\{\text{CF}_3\}_n \text{CF}_2 = \text{O} \right] \rightarrow \text{R} = \text{NR}_3, \\
\text{R, R} & = \text{CH}_3, \text{C}_2\text{H}_5.
\end{align*}
\]

We were interested in studying the behavior of other alkylfluoroalkenyl ethers under the action of tertiary amines.

It was found that replacement of the trifluoromethyl group by a fluorine atom has practically no effect on the alkylating properties of the ether (I). Methyl perfluoropropenyl ether (III) reacts readily with trimethylamines, forming the adduct (IV). The structure of this adduct is confirmed by its chemical reactions. In the interaction with dry hydrogen chloride it was converted to \(\alpha\)-hydrotetrafluoropropionyl fluoride (V) and tetramethylammonium chloride (the latter was isolated in the form of the corresponding picrate). Methylolation of the adduct with metal iodide leads to \(\alpha\)-methyltetrafluoropropionyl fluoride (VI), identified in the form of the methyl ester (VII)

\[
\begin{align*}
\text{(V)} & \quad \text{(IV)} \\
\text{CF}_3\text{CFHCOF} + (\text{CH}_3)_3 \text{NCl} & \quad \left[\text{CF}_3\text{CF}_2 = \text{O} \right] \rightarrow \text{N} (\text{CH}_3)_3, \\
\text{CF}_3\text{CF}_2 = \text{O} - \text{CH}_2 & \quad \left[\text{CF}_3\text{CF}_2 = \text{O} \right] \rightarrow \text{N} (\text{CH}_3)_3.
\end{align*}
\]

It was shown by preliminary experiments that the alkylating properties of the ether (I) with respect to tertiary amines are also preserved when the second trifluoromethyl group is replaced by a fluorine atom, as well as when one trifluoromethyl group is replaced by a methyl group or the "vinyl" fluorine atom is replaced

*Previous communication, see [1].

by a hydrogen atom. Methyl trifluorovinyl (VIII), methyl 2-methyltetrafluoropropenyl (IX),* and methyl 1-hydro-2- (trifluoromethyl)trifluoropropenyl (X) ethers react with trimethylamine to form solid adducts, containing the tetramethylammonium cation (the structure of the anionic portion of these adducts was not established)

\[
\begin{align*}
\text{CF}_3&=\text{CFOCH}_3 \\
\text{CH}_3 (\text{IX})
\end{align*}
\]

\[
\begin{align*}
\text{CF}_3&=\text{CCH(OCH}_3) \\
\text{CH}_3 (\text{X})
\end{align*}
\]

However, these ethers react with trimethylamine more slowly than methyl perfluoroisobutenyl ether (I, R = CH\text{\textsubscript{3}}) or methyl perfluoropropenyl ether (III).

The methyl ether of 2,4-bis (trifluoromethyl)-1,1,5,5,5-hexafluoro-2-pentene-3-ol (XIa) reacts readily with trimethylamine to form the adduct (XIIa)

\[
\begin{align*}
\text{(C}_2\text{F}_3)\text{C} &= \text{C} \equiv \text{CH (C}_2\text{F}_3) \equiv \text{CH (C}_2\text{F}_3) + \text{NR}_3^+ \\
\text{(XIa)}
\end{align*}
\]

\[
\begin{align*}
\text{R} &= \text{CH}_3 \\
\text{a} \\
\text{b} \\
\text{c}
\end{align*}
\]

This adduct contains a mesomeric carbanion, which, in contrast to the anions of the adducts (II) and (IV), has a (C\text{\textsubscript{2}}F\text{\textsubscript{3}})\text{CH} group in place of the "vinyl" fluorine atom. Evidently such replacement does not lead to any significant decrease in the stability of the mesomeric carbanion. Analogous adducts (XII b, c) were obtained from the methyl ether (XIa) and triethylamine, as well as from the benzyl ether of 2,4-bis(trifluoromethyl)-1,1,5,5,5-hexafluoro-2-pentene-3-ol (XIb) † and triethylamine. The structure of the adducts (XII) was confirmed by the NMR spectra, as well as by their chemical conversions - methylation to 2-methyl-2,4-bis(trifluoromethyl)-1,1,5,5,5-hexafluoro-3-pentanone (XIII) and by conversion to the corresponding quaternary ammonium picrate

\[
\begin{align*}
\text{(XIIa)} & \text{CH}_3 \bigg[ \text{C} \equiv \text{C} \equiv \text{CH (C}_2\text{F}_3) \bigg] \text{C} \equiv \text{CH (C}_2\text{F}_3) + \text{NR}_3^+ \\
\text{(XIII)}
\end{align*}
\]

\[
\begin{align*}
\text{R} &= \text{CH}_3, \text{C}_6\text{H}_5\text{CH}_2
\end{align*}
\]

It is interesting that the mesomeric carbanion contained in the adducts (XII) can also theoretically be generated by another method, on account of the stripping of a proton from the corresponding CH-acid. ‡ Actually, under the action of triethylamine on 2,4-bis(trifluoromethyl)-1,1,5,5,5-hexafluoro-3-pentanone (XIV), the adduct (XV) is formed

\[
\begin{align*}
\text{(CF}_3\text{CH} \equiv \text{C} \equiv \text{CH (CF}_3) \equiv \text{CH (CF}_3) + \text{N (C}_2\text{H}_5) & \bigg[ \text{C} \equiv \text{C} \equiv \text{CH (CF}_3) \bigg] \text{C} \equiv \text{CH (CF}_3) + \text{NR}_3^+ \\
\text{(XIV)}
\end{align*}
\]

The NMR-\text{F}^{19} spectrum of this adduct, characterizing the structure of its anionic portion, practically does not differ from the spectra of the adducts (XII).

Thus, it was found that ethers with the general formula (A) with various degrees of substitution by fluorine atoms or trifluoromethyl groups manifest alkylating properties with respect to trialkylamines.

*The ethers (IX) and (X) were produced by the interaction of the corresponding fluoroolefins with sodium methylate.

†The ether (XIb) was produced by addition of benzyl alcohol to tetrakis(trifluoromethyl)allene.

‡For a survey of methods of generation and properties of fluorine-containing mesomeric carbanions, see [3].