

Preliminary note

Polyfluorinated olefins from reaction of perfluoroalkyl iodides with allyl chloride

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Abstract

During experiments on addition of perfluoroalkyl iodides to allyl chloride an unexpected reaction has been observed leading to polyfluorinated olefins $R_F-CH_2-CH=CH_2$ in addition to the expected adduct $R_F-CH_2-CHI-CH_2Cl$. Preliminary experimental results show that the relative amounts of these two products depend particularly on the molar ratio of reagents and on temperature. A mechanism for the formation of the polyfluorinated olefin is suggested. © 1997 Elsevier Science S.A.

Keywords: Polyfluorinated olefins; Perfluoroalkyl iodides; Allyl chloride

Terminal perfluoro-olefins $R_F-CF_2-CF=CF_2$ were recently synthesized by thermal reaction of perfluoroalkyl iodides with perfluoroallyl chloride [1]. The formation of the analogous polyfluorinated olefins $R_F-CH_2-CH=CH_2$ from perfluoroalkyl iodides and allyl halides have not been previously reported in the literature, although these reagents are reported to give the corresponding adduct [2–4], from which the polyfluorinated olefins can be obtained by a subsequent treatment [5]. These olefins were also prepared by reaction of perfluoro-olefins with allyl halides [6].

During some of our experiments on the addition of perfluoroalkyl iodides to allyl halides the formation of these olefins was observed under the same conditions as normally give the corresponding adduct. Thus, as a representative example, by reacting 44.6 g (0.10 moles) of $C_6F_{13}I$ and 15.7 g (0.20 moles) of allyl chloride in the presence of 2 g (0.012 moles) of azobisisobutyronitrile in a stainless autoclave at 80 °C for 3 h, 60.1 g of a reaction mixture were obtained, in which the polyfluorinated olefin $C_6F_{13}CH_2CH=CH_2$ was present together with the corresponding adduct $C_6F_{13}CH_2CHICH_2Cl$. The experiment was repeated at different molar ratios of the reagents.

Some other similar experiments were also carried out with perfluoro-octyl iodide at various temperatures.

The formation of the polyfluorinated olefin in particular depended either on the molar ratio of perfluoroalkyl iodide to allyl chloride or on temperature. In Tables 1 and 2 experimental data are reported which confirm these correlations.

The same polyfluorinated olefins $R_FCH_2CH=CH_2$ ($R_F=C_6F_{13}-$, $C_8F_{17}-$) were also obtained in the subsequent

Table 1

Dependence of olefin formation on the molar ratio of reagents in the reaction of $C_6F_{13}I$ with allyl chloride

Molar ratio iodide/allyl chloride	2	1	0.5	0.3
Reaction time (h)	3	3	3	3
Reaction temperature (°C)	80	80	80	80
Mean value of the ratio olefin/adduct	no olefin	0.09	0.33	0.56

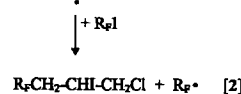
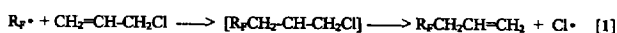
Table 2

Dependence of olefin formation on temperature in the reaction of $C_8F_{17}I$ with allyl chloride

Molar ratio iodide/allyl chloride	0.5	0.5	0.5	0.5
Reaction time (h)	3	3	3	3
Reaction temperature (°C)	50	60	70	80
GLC areas ratio olefin/adduct	0.06	0.12	0.27	0.46

reduction of the corresponding adducts with zinc and gaseous HCl, as reported in Ref. [5].

The simultaneous presence of the polyfluorinated olefin and the corresponding adduct in the reaction mixture could be explained by the following mechanism, in accordance with that reported in Ref. [1] (where, however, the adduct is not present):



This hypothesis agrees with what is observed experimentally: in fact, when the allyl chloride amount is increased, path **1** is favoured over path **2**, because of a low availability of the R_FI molecules; then the formation of chlorine radicals is favoured with respect to chain transfer and in this manner the olefin production increases.

Also, temperature seems to exert a positive influence over the formation of chlorine radicals with a consequent increase of the olefin production.

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