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PREPARATION OF O-(POLYFLUOROALKYL) ALKYLCHLOROPHOSPHONATES

AND O-(POLYFLUOROALKYL) ARYL CHLOROPHOSPHATES BY

CATALYTIC PHOSPHORYLATION OF POLYFLUOROALKANOLS

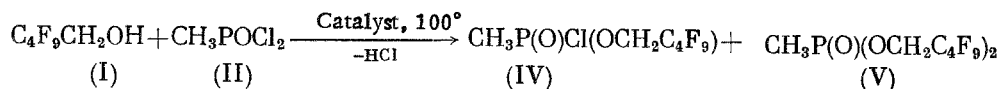
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UDC 542.97:547.1'118

The full polyfluoroalkyl esters of alkylphosphonic and aryl phosphoric acids can be obtained by the catalytic phosphorylation of polyfluoroalkanols with the dichlorides of these acids [1, 2]. At the same time, the corresponding ester-acid chlorides are difficultly available; information exists only on the O-(fluoroalkyl) alkylchlorophosphonates, which are formed by treating the mixed alkyl fluoroalkyl esters of alkylphosphonic acids with PCl_5 [3]. Taking into account the fact that the ester-acid chlorides of phosphorus acids, which contain polyfluoroalkyl groups, can be used as phosphorylating agents to synthesize the unsymmetrical esters of these acids, we examined on the example of 1,1-dihydroperfluoroamyl alcohol (I) the possibility of using the catalytic phosphorylation method to obtain such ester-acid chlorides directly from polyfluorinated alcohols and the dichlorides of phosphorus acids.

As study objects we selected the readily available methylphosphonic dichloride (II) and phenyl dichlorophosphate (III). In order to hinder the formation of the full esters, a double excess of the phosphorylating agent was used. As catalysts we used the salts of the Group II metals of the periodic system, which proved to be best for the catalytic phosphorylation of polyfluoroalkanols [1, 2].

In the case of acid chloride (II) it proved that the magnesium and calcium salts, which are readily soluble in the reaction mixture, have approximately the same efficiency. Thus, when (I) is heated with excess (II) at 100°C in the presence of 1-4 mole% of either MgSO_4 or CaCl_2 we isolated O-(1,1-dihydroperfluoroamyl) methylchlorophosphonate in 59-65% yield (see [4]), together with 10-17% of O,O-di(1,1-dihydroperfluoroamyl) methylphosphonate (V). As regards BaCl_2 , which is practically insoluble in the reaction mixture, then its catalytic activity proved to be exceedingly low and reaction is not complete even after 15 h at 100° , while the yield of (IV) is only 29%.



In a similar manner, when (I) is heated with excess (III) in the presence of CaCl_2 at 120° the main product is O-(1,1-dihydroperfluoroamyl) phenyl chlorophosphate (VI). Besides (VI), we also isolated O,O-di(1,1-dihydroperfluoroamyl) phenyl phosphate (VII) from the reaction mixture.

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 3, pp. 656-658, March, 1979. Original article submitted July 3, 1978.

CONCLUSIONS

A new method was developed for the synthesis of O-(polyfluoroalkyl) alkylchlorophosphonates and O-(polyfluoroalkyl) aryl chlorophosphates, which consists in phosphorylating polyfluoroalkanols with an excess of the dichlorides of the corresponding phosphorus acids in the presence of salts of the Group II metals.

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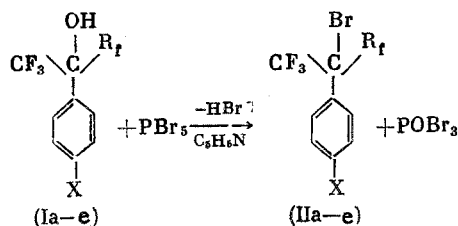
EPR SPECTRA OF 2-ARYLPOLYFLUOROISOPROPYL RADICALS

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UDC 543.422.27:541.515:547.539.162

We established that 2-bromo-2-arylpolyfluoropropanes when heated or subjected to photolysis in the presence of di-tert-butyl peroxide form substituted benzyl radicals, which we studied by the EPR method.

The starting compounds were synthesized from the corresponding alcohols, which were obtained as described in [1, 2] (Table 1).



$\text{R}_f = \text{CF}_3$, $\text{X} = \text{H}$ (a); $\text{R}_f = \text{CF}_3$, $\text{X} = \text{F}$ (b); $\text{R}_f = \text{CF}_3$, $\text{X} = \text{MeO}$ (c);
 $\text{R}_f = \text{CF}_3$, $\text{X} = \text{CF}_3\text{CONH}$ (d); $\text{R}_f = \text{CF}_2\text{Cl}$, $\text{X} = \text{F}$ (e)

The reactions of (Ia), (Ib), and (Ie) were run in refluxing benzotrifluoride (BTF), while those of the more active (Ib) and (Id) were run in CH_2Cl_2 .

The hyperfine structure of the EPR spectra of the radicals (III), formed from the bromides (II) (Table 2), testifies to the fact that the distribution of the electron density in them is essentially the same as is characteristic for benzyl radicals. The hyperfine coupling (HFC) constants with the nuclei of the benzene rings are very close to those observed in the spectra of benzyl radicals that contain the corresponding substituents at the end [3].

As a result, the insertion of bulky fluoroalkyl groups as substituents on the benzene C atom evidently does not prevent the radical from retaining the planar structure that is characteristic for the unsubstituted benzyl radical, even if an o-F atom is present (radical (IIIIf)).

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, No. 3, pp. 659-661, March, 1979. Original article submitted July 6, 1978.