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Synthesis of 2-phenylperfluoropropene and 1,1,1,3,3,3-hexafluoro-2-phenylpropane

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Abstract

We describe the optimisation of reaction conditions for the synthesis of 2-phenylperfluoropropene and its HF addition product 1,1,1,3,3,3-hexafluoro-2-phenylpropane from 1,1,1-trifluoroacetophenone by the reaction with sodium chlorodifluoroacetate and triphenylphosphine in dimethylformamide. The formation of olefin and the addition product has been studied over a range of temperature (50–150 °C) as a function of time. © 1997 Elsevier Science S.A.

Keywords: Wittig reagent; 2-Phenylperfluoropropene; 1,1,1,3,3,3-Hexafluoro-2-phenylpropane; 1,1,1-Trifluoroacetophenone

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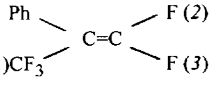
1. Introduction

In our on-going studies on organofluorine compounds [1] we required 1,1-difluoroalkenes. A number of procedures available for their synthesis are based on ylide [2–4] or alternative methodologies [5–7]. Reports also exist about the fact that the electron deficient terminal difluoro-olefins can add a molecule of hydrogen fluoride [8]. However, information is lacking with regards to optimum conditions under which the olefins and their hydrogen fluoride addition products are formed separately. Herein we wish to report the synthesis of 2-phenylperfluoropropene (PPFP) (**2**) and 1,1,1,3,3,3-hexafluoro-2-phenylpropane (HFP) (**3**) from 1,1,1-trifluoroacetophenone (TFAP) (**1**) by varying the reaction conditions with respect to temperature and time under which one product forms predominantly, and their isolation in good yield. In addition, the kinetics of the reaction has been studied for ascertaining their mechanism of formation.

2. Preparation of 2-phenylperfluoropropene (2)

Trifluoroacetophenone (**1**) (12.79 g, 0.0734 mol) and triphenylphosphine (38.53 g, 0.1468 mol) were dissolved in 30 ml of dry DMF at 50 °C and placed in a 250 ml three-necked round bottom flask containing a stir bar and equipped with reflux condenser, dropping funnel and a dry nitrogen inlet. The homogeneous solution was heated to 50–55 °C (bath temperature). Sodium chlorodifluoroacetate (22.47 g, 0.147 mol) dissolved in 30 ml of dry DMF was added dropwise into the reaction mixture over 30 min without altering the bath temperature. The reaction mixture was further heated for an additional 2 h when, practically, the conversion of TFAP (**1**) into olefin (**2**) ceased. Heating was stopped and the reaction mixture was immediately quenched in an ice bath, which was then treated with dichloromethane followed by filtering off the insoluble triphenylphosphine oxide. DMF was then removed by repeatedly washing the dichloromethane extract with plenty of water. Dichloromethane was evaporated on water bath and the product 2-phenylperfluoropropene was isolated by distillation under reduced pressure, b.p. 58–60 °C (55 mm Hg), 10.5 g (69%); IR, 1736 cm^{-1} (5.76 μ, $C{=}CF_2$ stretching, lit. [8] 5.75 μ); ^1H-NMR (δ ppm) 7.40 (s, Ar), lit. [8] 7.30; ^{19}F-NMR (δ ppm)



δ_1 −59.2, δ_2 −76.1, δ_3 −77.7; J_{F-F} (Hz), J_{1-2} 11.3, J_{2-3} 11.3, J_{1-3} 22.6; Mass spectrum (EI) *m/z* 208 (M^+), 189 (M–F), 169 (189 − HF), 158 ($M-CF_2$), 139 ($M-CF_3$).

3. Preparation of 1,1,1,3,3,3-hexafluoro-2-phenylpropane (3)

A procedure similar to that described above was used wherein dropwise addition of the salt was carried out in 15

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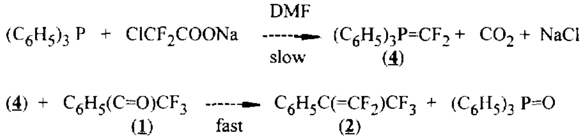
min intervals and the reaction temperature maintained at 125–135 °C. The reaction mixture assumed a dark brown colour indicating decomposition of the salt at higher temperature. The reaction was over after 4 h. The reaction mixture was processed as above to yield 1,1,1,3,3,3-hexafluoro-2-phenylpropane, b.p. 66 °C (55 mm Hg), 10.2 g (61%); IR, 1350, 1270, 1130, 730, 690 (CF_3 stretching); ^{1}H-NMR (δ ppm) 3.90 (m, CH), 7.10 (s, Ar), lit. [8] 3.90, 7.10; ^{19}F-NMR (δ ppm) -65.3 (d), J_{H-F} 8.5 Hz; Mass spectrum (EI) 228 (M^+), 209 (M–F), 189 (209 – HF), 159 (M–CF_3).

*Even though the toxicity data for **2** and **3** have not been well documented, but in view of the fact that some* 1,1*-difluoroalkenes are highly toxic* [9], *it is recommended that precautions taken in handling toxic organofluorine chemicals should also be followed in these cases.*

The above-mentioned procedure has been worked out from the studies on the formation of PPFP (**2**) and HFP (**3**) monitored by GLC (carbowax 20 MN 10% packed column operated in programmed temperature mode from 50–150 °C at the rate of 10 °C using FID detector) as a function of temperature and time of reaction. The results suggest that PPFP forms at lower temperature and the most favoured temperature for its formation is 50–75 °C when no addition product forms even after long reaction time. On the other hand HFP forms predominantly at higher temperature, and forms rather exclusively at > 125 °C. In the intermediate temperature ranging from 90–120 °C, the mixtures of **2** and **3** result whose ratio decreases as a function of time due to the slow addition of fluoride ion on the olefin leading to the formation of addition product.

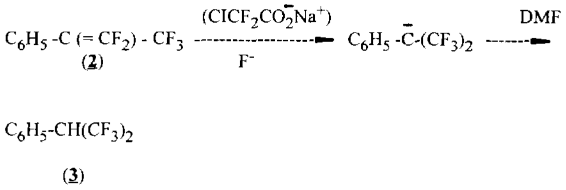
Furthermore, for determination of the order of the reaction, TFAP, TPP and the salt all were mixed in the ratio 1:2:2 at 50–55 °C and heated in DMF. The second-order kinetics for the formation of olefin has been realised by plotting [1/time] vs. [conc. of TFAP/conc. of TFAP consumed]. Based on these results it is presumed that the formation of Wittig (**4**) from TPP and the salt is slow and rate determining. Once it is generated in situ it readily attacks on the carbonyl moiety to yield the olefin as shown in Scheme 1.



$$(C_6H_5)_3P + ClCF_2COONa \xrightarrow[\text{slow}]{\text{DMF}} \underset{(\mathbf{4})}{(C_6H_5)_3P{=}CF_2} + CO_2 + NaCl$$

$$(\mathbf{4}) + \underset{(\mathbf{1})}{C_6H_5(C{=}O)CF_3} \xrightarrow[\text{fast}]{} \underset{(\mathbf{2})}{C_6H_5C({=}CF_2)CF_3} + (C_6H_5)_3P{=}O$$

Scheme 1. Formation of PPFP from TPP and salt through in-situ Wittig reagent.



$$\underset{(\mathbf{2})}{C_6H_5\text{-}C({=}CF_2)\text{-}CF_3} \xrightarrow[F^-]{(ClCF_2CO_2^-Na^+)} C_6H_5\text{-}\overset{-}{C}\text{-}(CF_3)_2 \xrightarrow{\text{DMF}} \underset{(\mathbf{3})}{C_6H_5\text{-}CH(CF_3)_2}$$

Scheme 2. Formation of HFP from PPFP.

In order to account for the formation of **3** a reaction was carried out with TFAP, TPP and the salt in the molar ratio 1:1:2 at 70–75 °C for a longer period of time, allowing for maximum conversion of ketone into olefin. At this stage increasing the temperature beyond 90 °C and up to 150 °C most of the olefin was consumed into the HF addition product. Since the entire Wittig reagent (**4**) has been consumed in the production of PPFP (Scheme 1), it shows unambiguously that it is the salt not **4** which is decomposed at high temperature to liberate fluoride ion. This point is further substantiated from the observation that when some salt is added into the reaction mixture in the later stage when the conversion of PPFP to HFP was practically stopped the rate of formation of HFP from unreacted PPFP was found to be drastically enhanced.

A plausible mechanism for the formation of the addition product (**3**) involves the generation of a carbanion by the attack of the fluoride ion generated from the decomposition of the sodium chlorodifluoroacetate at a temperature > 80 °C on the olefin PPFP which may extract a proton from the solvent to yield HFP in good yield (Scheme 2).

It may be concluded that optimum conditions have been generated for the synthesis of 2-phenylperfluoropropene and 1,1,1,3.3.3,3-hexafluoro 2-phenylpropane from 1,1,1-trifluoroacetophenone based on difluoromethylene triphenylphosphorane Wittig, from which it is easy to pick up the condition of interest under which one product forms predominantly.

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