

A ONE-STEP SYNTHESIS OF β -PHENYL SUBSTITUTED
PERFLUOROOLEFINS

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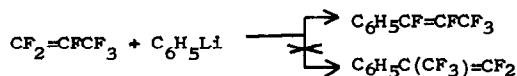
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Recently, Silverstein and co-workers have reported a novel synthesis of 1,1-difluoroolefins from aldehydes by heating an aldehyde, triphenylphosphine and sodium chlorodifluoroacetate in monoglyme or diglyme (1). Attempts to extend this reaction to cyclic and aromatic ketones under similar conditions were unsuccessful, although a modified procedure did yield some 1,1-difluoroolefin (2).

As part of a general program in the area of fluorocarbon chemistry, we have been interested in utilizing β -phenyl substituted perfluoroolefins for mechanism studies, and required a facile synthetic route to these olefins. Previous work by other authors have demonstrated that both free radical (3) and ionic reactions (4) yield the internal fluorinated olefin rather than the terminal fluorinated compound.



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Application of Silverstein's method appeared to give a convenient route to these olefins. The recent paper (2) by Silverstein and co-workers has prompted us to report some of our results in this area.

In contrast to the failure of ketones with alpha hydrogens to give difluoroolefins under the initial conditions utilized with aldehydes (1), we have found that various substituted α,α,α -trifluoroacetophenones gave excellent yields of β -phenyl substituted perfluoroolefins under these conditions. For example, α,α,α -trifluoroacetophenone, resulted in a 59% yield of 2-phenyl-pentafluoropropene. In an analogous manner, the reaction of p-methyl- α,α,α -trifluoroacetophenone, p-fluoro- α,α,α -trifluoroacetophenone and p-methoxy- α,α,α -trifluoroacetophenone were carried out and the results are summarized in Table I.

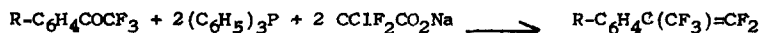


TABLE I

R	b.p. °C.	% Yield ^a	n _D ²⁰	-C=CF ₂ (μ)
p-H	51-52°/54 mm.	75.9	1.4216	5.75
p-CH ₃	153-154°/747 mm. ^b	81.9	1.4314	5.75
p-OCH ₃	74°/12 mm.	90.7	1.4459	5.75
p-F	62-63°/57 mm.	66.6	1.4107	5.74

a) The yield was determined by g.l.c. analysis on Silicon Rubber or Carbowax 20M columns.

b) Separated by g.l.c. on a Carbowax 20M column. The boiling point was determined by the Siwoloboff method and is uncorrected.

Since the substituted α,α,α -trifluoroacetophenones can be conveniently prepared from trifluoroacetic acid and the appropriate Grignard reagent (5), this reaction provides an attractive route to β -substituted perfluoropropenes.

The reaction with α,α,α -trifluoroacetophenone has been studied in some detail, and we have found that best results are obtained when the mole ratio of triphenylphosphine, sodium chlorodifluoroacetate, and ketone are 2:2:1 respectively. The results of the effect of concentration on the yield of olefin are shown in Table II.

TABLE II

$C_6H_5COCF_3$ mMoles	$(C_6H_5)_3P$ mMoles	$CClF_2CO_2Na$ mMoles	Time Hr.	$C_6H_5C(CF_3)=CF_2$ % Yield ^a
50	50	50	20	62.4
50	100	100	20	75.9
50	100	100	15	79.5
50	100	100	20	80.3 ^b
50	150	150	20	60.2

a) The yield (g.l.c.) of olefin was based on ketone.

b) This reaction was worked-up by extraction with n-hexane, followed by washing with water, removal of excess solvent and analyzed by g.l.c.

A typical procedure is as follows. A mixture of 52.5 g. (0.20 mole) of triphenylphosphine, 30.5 g. (0.20 mole) of sodium chlorodifluoroacetate, and 17.4 g. (0.10 mole) α,α,α -trifluoroacetophenone in 100 ml. dry diglyme were heated at a bath temperature of 100-105° for 20 hours under a nitrogen atmosphere. Car-

bon dioxide was evolved throughout the reaction, and after 20 hours 65-75% (STP) of the theoretical amount of the carbon dioxide had been evolved. The reaction mixture was cooled under a nitrogen atmosphere; steam distilled to give one liter of distillate, and the organic layer was separated. G.L.C. analysis on silicone rubber indicated 75.9% of 2-phenylpentafluoropropene based on starting ketone. Subsequent fractionation gave 12.3 g. (59%) of 2-phenylpentafluoropropene, b.p. 51-52° (54 mm.), n_D^{20} 1.4216, $\lambda_{\text{max}}^{\text{film}}$ 5.75 μ ($-\text{C}=\text{CF}_2$).

Elemental analysis, infrared and n.m.r. spectra were in agreement with the assigned structures.

It is tempting to speculate on the success of these reactions in contrast to the failure of cyclohexanone and acetophenone to give difluoroolefins under these conditions. Cyclohexanone is known to undergo a Knoevenagel reaction in the presence of fluoride ion (6). Under the conditions of the reaction, fluoride ion could have been generated either by decomposition of sodium chlorodifluoroacetate or the difluoromethylene ylide. The fluoride ion thus generated could have abstracted a proton to yield hydrogen fluoride which would decompose any ylide generated or could have brought about a condensation reaction of the ketone. In the case of the α,α,α -trifluoroacetophenone derivatives, no alpha proton abstraction could occur and the above side reactions could be avoided. Additional work on this possibility and further extension of this work to other fluorinated ketones is in progress and will be presented in future publications.

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