A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

## Working with Hazardous Chemicals

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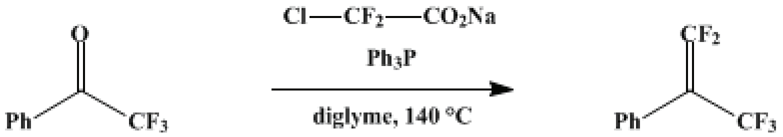
*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

DOI:10.15227/orgsyn.048.0116

*Organic Syntheses, Coll. Vol. 5, p.949 (1973); Vol. 48, p.116 (1968).*

# 2-PHENYLPERFLUOROPROPENE

## [Styrene, β,β-difluoro-α-(trifluoromethyl)-]



Submitted by Frank E. Herkes and Donald J. Burton[1].
Checked by W. C. Ripka and R. E. Benson.

## 1. Procedure

*Caution! This compound is an analog of the toxic olefin, perfluoroisobutylene. Since its toxicity is unknown, proper care should be exercised in its handling.*

A 1-l., three-necked, round-bottomed flask is equipped with a mechanical stirrer, a nitrogen-inlet tube, and a reflux condenser connected to a dry ice-trichloroethylene trap (Note 1) that is followed by a water trap to measure carbon dioxide evolution (Note 2). The flask is charged with 65.6 g. (0.250 mole) of triphenylphosphine (Note 3) and 43.5 g. (0.250 mole) of α,α,α-trifluoroacetophenone (Note 4) in 200 ml. of dry diglyme (Note 5). The solution is heated to a bath temperature of 140° under a nitrogen atmosphere, and the nitrogen-inlet tube is replaced by a pressure-equalizing dropping funnel (Note 6) containing a solution of 76.2 g. (0.500 mole) of sodium chlorodifluoroacetate (Note 7) in 150 ml. of dry diglyme. The solution of sodium chlorodifluoroacetate is added dropwise over a period of 1 hour (Note 8), and the reaction mixture is heated for an additional hour at 130–140° to ensure complete decarboxylation of the salt (Note 9). The colors of the reaction mixture are characteristic of ylid reactions, changing from a creamy white to a creamy orange and finally to a deep brown.

The reaction mixture is then cooled to room temperature under nitrogen. The cool mixture is steam distilled until 2 l. of distillate has been collected. The lower, organic layer is separated from the distillate, washed with cold water (Note 10) to remove diglyme, and dried over anhydrous calcium sulfate. Fractional distillation gives 26–31 g. (50–60%) of 2-phenylperfluoropropene, b.p. 58–59° (54 mm.), $n^{20}$D 1.4225 (Note 11) and (Note 12).

## 2. Notes

1. In addition to carbon dioxide, small amounts of fluoroformyl fluoride and chloride are formed and swept out with the carbon dioxide.
2. The rate of decarboxylation can be followed qualitatively by collecting the liberated carbon dioxide over water, *e.g.*, by the use of a wet test meter.
3. Eastman Organic Chemicals white label triphenylphosphine was used directly.
4. Available from Pierce Chemical Co., Rockford, Illinois. The ketone can also be prepared conveniently from phenylmagnesium bromide and trifluoroacetic acid by the method of Dishart and Levine.[2]
5. Diglyme (Ansul Ether 141) was predried over calcium hydride and distilled under reduced pressure from lithium aluminum hydride; b.p. 62–63° (15 mm.).[3] The yield of olefin is dependent on the dryness of the solvent. The formation of 2-phenyl-2H-perfluoropropane is favored by the presence of water in the solvent.
6. A dropping funnel of the type described by Benson and McKusick[4] is satisfactory.
7. Sodium chlorodifluoroacetate is prepared in quantitative yield by careful neutralization of 130.5 g. (1.00 mole) of chlorodifluoroacetic acid (available from Allied Chemical Corp.) in 300 ml. of ether with 53.0 g. (0.500 mole) of anhydrous sodium carbonate, removal of the solvent and water under reduced pressure, and drying over phosphorus pentoxide in a vacuum desiccator. Studies have shown that the

best yield of olefin is obtained when a 100% excess of salt is used.
8. The salt is added at a rate sufficient to cause a constant evolution of carbon dioxide. The reaction is slightly exothermic (*ca.* 10° temperature rise).
9. A total of 9460 ml. (72% STP) of carbon dioxide was collected.
10. Eight washings with 50-ml. portions of water were found to remove all the diglyme.
11. The submitters used an 18-in. spinning-band column. The product was shown to be >99.9% pure by gas-liquid chromatography on Carbowax 20M.
12. The checkers used a 40-cm. spinning-band column. The product, $n^{25}D$ 1.4237, was shown to be 98.9% pure by gas-liquid chromatography on a 6-ft. 20% fluorosilicone column. The retention time was 3.75 minutes with a flow rate of helium of 100 ml. per minute, and a column temperature of 125° with the injection port at 170°. The $^{19}F$ n.m.r. spectrum (56.4 MHz) consists of four lines of equal intensity centered at +3396 Hz from trichlorofluoromethane (internal) and two sets of two overlapping quartets centered at +4369 Hz and +4461 Hz, respectively. The integrated intensities of the three sets of fluorine resonances are 3:1:1.

## 3. Discussion

This procedure is a modification of the method previously reported by the submitters.[5] 2-Phenylperfluoropropene has been reported as a by-product of the thermal decomposition of 7,7-bis (trifluoromethyl)-1,3,5-cycloheptatriene; however, no experimental procedure was given.[6]

## 4. Merits of the Preparation

The procedure illustrates a fairly general method for the preparation of β-substituted perfluoroolefins. The method has been applied to the synthesis of 2-cyclohexyl- (70%), 2-benzyl- (61%), and 2-(*p*-fluorophenyl)perfluoropropenes (67%), and it is probably applicable to any α-trifluoromethyl ketone. Olefins containing a perfluoroalkyl group other than trifluoromethyl can be prepared by the same procedure by the substitution of lithium chlorodifluoroacetate for sodium chlorodifluoroacetate.[7] Other routes to β-substituted perfluoroolefins are not general or convenient. Routes to perfluoroolefins generally yield the α-substituted olefin rather than the β-substituted olefin.

This method can also be utilized as a general method for the preparation of olefins with terminal difluoromethylene groups from aldehydes.[8] Also, by the substitution of tributylphosphine for triphenylphosphine in this procedure, ketones other than those containing an α-perfluoroalkyl group can be converted to terminal difluoromethylene compounds.[9]

## References and Notes

1. Department of Chemistry, University of Iowa, Iowa City, Iowa 52240.
2. K. T. Dishart and R. Levine, *J. Am. Chem. Soc.*, **78**, 2268 (1956).
3. G. Zweifel and H. C. Brown, *Org. Reactions*, **13**, 28 (1963).
4. R. E. Benson and B. C. McKusick, *Org. Syntheses*, Coll. Vol. **4**, 747 (1963).
5. D. J. Burton and F. E. Herkes, *Tetrahedron Lett.*, 1883 (1965).
6. D. M. Gale, W. J. Middleton, and C. G. Krespan, *J. Am. Chem. Soc.*, **87**, 657 (1965).
7. D. J. Burton and F. E. Herkes, *Tetrahedron Lett.*, 4509 (1965).
8. S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, *J. Org. Chem.*, **30**, 1027 (1965); this volume, p. 390.
9. S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, *J. Org. Chem.*, **30**, 2543 (1965).

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## Appendix
## Chemical Abstracts Nomenclature (Collective Index Number);
## (Registry Number)

fluoroformyl fluoride and chloride

Diglyme (Ansul Ether 141)

ether (60-29-7)

sodium carbonate (497-19-8)

nitrogen (7727-37-9)

carbon dioxide (124-38-9)

calcium sulfate (7778-18-9)

Phenylmagnesium bromide (100-58-3)

lithium aluminum hydride (16853-85-3)

sodium chlorodifluoroacetate (1895-39-2)

chlorodifluoroacetic acid (76-04-0)

lithium chlorodifluoroacetate

calcium hydride (7789-78-8)

diglyme (111-96-6)

trifluoroacetic acid (76-05-1)

helium (7440-59-7)

triphenylphosphine (603-35-0)

2-Phenylperfluoropropene,
Styrene, β,β-difluoro-α-(trifluoromethyl)- (1979-51-7)

perfluoroisobutylene (382-21-8)

α,α,α-trifluoroacetophenone (434-45-7)

2-phenyl-2H-perfluoropropane

7,7-bis(trifluoromethyl)-1,3,5-cycloheptatriene

tributylphosphine (998-40-3)

phosphorus pentoxide (1314-56-3)

2-cyclohexyl-perfluoropropene

2-(p-fluorophenyl)perfluoropropene

2-benzyl-perfluoropropene