



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

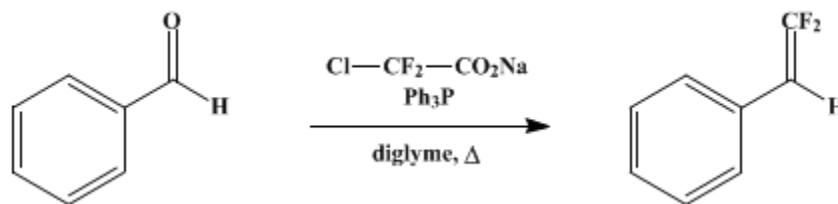
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 5, p.390 (1973); Vol. 47, p.49 (1967).*

## $\beta,\beta$ -DIFLUOROSTYRENE

[1,1-Difluoro-2-phenylethylene]



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### 1. Procedure

In a 250-ml. two-necked flask fitted with a reflux condenser, a drying tube, a magnetic stirrer, and a heated dropping funnel with a pressure-equalizing side arm (Note 1) are placed 23.1 g. (0.088 mole) of triphenylphosphine, 8.5 g. (0.081 mole) of benzaldehyde, and 10 ml. of anhydrous 2,2'-dimethoxydiethyl ether (diglyme) (Note 2). A solution of 18.3 g. (0.12 mole) of dry sodium chlorodifluoroacetate (Note 3) is prepared by stirring the finely divided salt in 50 ml. of anhydrous diglyme at 70° for about 5 minutes. This warm solution is placed in the dropping funnel which is heated to 60°. The system is purged with dry nitrogen. The solution in the flask is stirred and heated in an oil bath held at 160°, while the contents of the dropping funnel are added dropwise over a period of 1.5–2 hours (Note 4). The diglyme and product are flash-distilled at 1 mm and a bath temperature of 100° into a receiver cooled with dry ice. The distillate is fractionated through a spinning-band column (18 in.  $\times$  6 mm. I.D.); the yield of product collected at a head temperature of 52–54° (40 mm.) is 7.6–8.9 g. (67–79%) (Note 5),  $n_D^{20}$  1.4939 (Note 6).

### 2. Notes

- All glassware is oven-dried. The dropping funnel is wrapped with heating tape, and a thermometer is inserted between the funnel and the tape.
- Triphenylphosphine is available from M and T Chemicals, Inc. Benzaldehyde is distilled immediately before use. Diglyme is refluxed for 4 hours over calcium hydride and distilled under reduced pressure.
- Sodium chlorodifluoroacetate is prepared from chlorodifluoroacetic acid (K & K Laboratories) as follows: To a cooled, stirred solution of 60.7 g. (1.52 moles) of sodium hydroxide in 700 ml. of methanol is slowly added a solution of 198 g. (1.52 moles) of chlorodifluoroacetic acid in 300 ml. of methanol, the temperature being kept below 40°. The methanol is removed under reduced pressure at 40°. The salt, which is pulverized and dried overnight at room temperature at 1 mm., is obtained in essentially quantitative yield. The salt is again dried in the same way immediately before use.
- During the development of this procedure, evolution of carbon dioxide was monitored with a wet-test meter. At the bath temperature given (160°), sodium chlorodifluoroacetate eliminates carbon dioxide as rapidly as it is added over a period of 1.5–2 hours. If the bath temperature is allowed to drop, there is danger of buildup of sodium chlorodifluoroacetate followed by violent exothermic decomposition. Addition of the sodium chlorodifluoroacetate solution should not be started until the flask contents are equilibrated with the oil bath. It is quite feasible to run the reaction at a bath temperature of 90–95° by adding all reagents to the flask initially; a quantitative evolution of carbon dioxide occurs over a period of about 18 hours. The reaction can also be carried out in refluxing 1,2-dimethoxyethane (Arapahoe Chemicals, Inc.) over a period of about 50 hours (yield 40–55%), or in triethylene glycol dimethyl ether (Ansul Chemical Company) at a bath temperature of 160° over a period of 2 hours (yield 64%).
- The distilled product gave a single symmetrical peak on gas chromatography under the following conditions: 25% LAC on Chromosorb W, 6 ft.  $\times$  1/4 in., 110°, helium flow 41 ml./min., elution time 14.2

minutes. The checkers used LB 5-50 on Fluoropak 80 and obtained a single peak. Gas chromatography of the flash distillate before fractionation showed an actual yield of 10.6 g. (95%). The product fumes in moist air, and some etching of glass containers was noted. This is presumably due to elimination of [hydrogen fluoride](#). Samples in open glass containers deposit a small amount of solid on standing; the solid is probably a product of the glass-hydrogen fluoride reaction.

6. Care must be taken to clean and dry the refractometer prisms before and after use in order to prevent etching of the prisms.

### 3. Discussion

The literature preparation<sup>3</sup> of [β,β-difluorostyrene](#) consists of seven steps from [sodium difluoroacetate](#), the last step involving pyrolysis at 600°; the overall yield was 5%.

### 4. Merits of the Preparation

The method described is a general synthesis for compounds containing the -CH=CF<sub>2</sub> moiety. There is no other simple general route to such compounds. Aromatic, aliphatic, and heterocyclic aldehydes to which this procedure has been applied are: [p-fluorobenzaldehyde](#) (65%), [p-methoxybenzaldehyde](#) (60%), [heptanal](#) (43–51%), and [furfural](#) (75%).<sup>4</sup> The method is also applicable to ketones<sup>5</sup> and to α-perfluoroketones.<sup>6</sup> Substitution of [lithium chlorodifluoroacetate](#) for the sodium salt has been advocated.<sup>7</sup>

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 949](#)

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### References and Notes

1. Deceased.
2. Stanford Research Institute, Menlo Park, California.
3. M. Prober, *J. Am. Chem. Soc.*, **75**, 968 (1953).
4. S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, *J. Org. Chem.*, **30**, 1027 (1965).
5. S. A. Fuqua, W. G. Duncan, and R. M. Silverstein, *J. Org. Chem.*, **30**, 2543 (1965).
6. F. E. Herkes and D. J. Burton, *J. Org. Chem.*, **32**, 1311 (1967).
7. R. C. Slagel, *Chem. Ind. (London)*, 848 (1968).

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### Appendix

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

2,2'-dimethoxydiethyl ether (diglyme)

[methanol](#) (67-56-1)

[sodium hydroxide](#) (1310-73-2)

[nitrogen](#) (7727-37-9)

[carbon dioxide](#) (124-38-9)

[hydrogen fluoride](#) (7664-39-3)

benzaldehyde (100-52-7)

Furfural (98-01-1)

1,1-Difluoro-2-phenylethylene,  
 $\beta,\beta$ -Difluorostyrene (405-42-5)

sodium chlorodifluoroacetate (1895-39-2)

chlorodifluoroacetic acid (76-04-0)

sodium difluoroacetate

lithium chlorodifluoroacetate

Heptanal (111-71-7)

calcium hydride (7789-78-8)

1,2-dimethoxyethane (110-71-4)

helium (7440-59-7)

triphenylphosphine (603-35-0)

triethylene glycol dimethyl ether (112-49-2)

p-methoxybenzaldehyde (123-11-5)

p-fluorobenzaldehyde (459-57-4)