FLUORINATED STYRENES

COMMUNICATION 6. α-DIFLUOROMETHYLSTYRENES AND α-TRIFLUOROMETHYLSTYRENES

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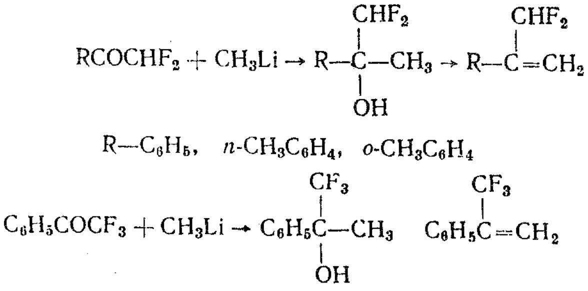
α-Trifluoromethylstyrene and α-difluoromethylstyrene have been mentioned in a patent [1] as monomers which give stable polymers and copolymers suitable for the production of technical fiber. More recently a synthesis of α-trifluoromethylstyrene through phenylmagnesium bromide has been published and the constants of this compound have been reported [2].

The problem of the synthesis of styrenes of this class for the investigation of their polymerization was presented to us [3]. Thus, α-difluoromethylstyrene, α-difluoromethyl-p-methylstyrene, α-difluoromethyl-o-methylstyrene, α-trifluoromethylstyrene, and α-trifluoromethyl-p-fluorostyrene were synthesized. The synthesis of these compounds was carried out by the following route:



$$RCOCHF_2 + CH_3Li \rightarrow R-\underset{OH}{\overset{CHF_2}{C}}-CH_3 \rightarrow R-\overset{CHF_2}{C}=CH_2$$

$$R-C_6H_5,\quad n\text{-}CH_3C_6H_4,\quad o\text{-}CH_3C_6H_4$$

$$C_6H_5COCF_3 + CH_3Li \rightarrow C_6H_5\underset{OH}{\overset{CF_3}{C}}-CH_3 \qquad C_6H_5\overset{CF_3}{C}=CH_2$$

Furthermore, starting from phenylmagnesium bromide and p-fluorophenylmagnesium bromide with trifluoroacetone (through the carbinol stage) α-trifluoromethylstyrene and α-trifluoromethyl-p-fluorostyrene were prepared. The most convenient method was the use of methyllithium and the readily available ω-difluoroacetophenones or ω-trifluoroacetophenones prepared from RLi and fluorinated acids [4] or diethylamides of the acids [5]. Condensations of methyllithium with fluorinated acetophenones were carried out at a temperature of −20 to −25° in ether medium and the tertiary carbinols were obtained in 80-95% yield. Dehydration of the carbinols took place readily under the action of phosphorus pentoxide to yield 65-85% of the styrene. We further introduced a very simple method for the synthesis of p-chlorostyrene.

EXPERIMENTAL

The organolithium compounds were prepared by the usual methods under nitrogen or argon. The fluorinated compounds were analyzed either by combustion of a weighed sample with sodium peroxide with subsequent titration with thorium nitrate to determine the fluorine content or by elementary analysis by the method of Zimin et al. [6].

Preparation of o-methyl-ω,ω-difluoroacetophenone. In an apparatus for low temperature condensations under argon 250 ml of an ether solution of o-tolyllithium (24.5 g; 0.25 M) was cooled to −75°, and 33.7 g of freshly distilled diethylamide of difluoroacetic acid was added at this temperature during the course of 40 minutes, with vigorous stirring, then the mixture was stirred for 1 hr more. It was then decomposed by pouring into ice water acidified with hydrochloric acid. Yield 28 g (65.7%) of o-methyl-ω,ω-difluoroacetophenone with b. p. 61-63° (4 mm); $n^{20}D$ 1.4995. Found: F 23.01, 22.80%. $C_9H_8F_2O$. Calculated: F 22.35%.

Preparation of p-methyl-ω,ω-difluoroacetophenone. In an apparatus for low temperature condensations under argon 250 ml of an ether solution of p-tolyllithium (24.5 g; 0.25 M) was cooled to −75°, and 33.7 g of freshly distilled diethylamide of difluoroacetic acid was added at this temperature during the course of 40 minutes, with good stirring, then the mixture was stirred for 1 hr more. The mixture was then decomposed by pouring it into ice water acidified with hydrochloric acid. After the usual treatment and distillation of the ether, crystals were obtained; they were filtered by suction, and washed with hexane and pentane. After recrystallization from absolute methyl alcohol, 22 g (51.7%) of p-methyl-ω,ω-difluoroacetophenone was obtained with m. p. 48-51°. Found: F 23.10, 22.95%. Calculated: F 22.94%.

Preparation of difluoromethylmethyl-o-tolylcarbinol. In an apparatus for low temperature condensations under argon 120 ml of an ether solution of methyllithium (1.97 g; 0.09 M) was cooled to −25°. At this temperature 15.7 g (0.09 M) of difluoromethyl-o-tolyl ketone in 50 ml of absolute ether was added at such a rate that the temperature did not rise above −20°. At the end of the addition the reaction mixture was stirred for 30 minutes and treated in the usual manner. Yield 12 g of difluoromethylmethyl-o-tolylcarbinol; b. p. 88.5-89° (3 mm); n^{20}D 1.5039.

Preparation of α-difluoromethyl-o-methylstyrene. In a flask with a reflux condenser were placed under nitrogen 10 g of difluoromethylmethyl-o-tolylcarbinol (0.053 M), 3.96 g of phosphorus pentoxide (0.026 M), 0.3 g of copper powder, and 100 ml of dry benzene. The reaction mixture was heated for 4.5 hr at the boiling point of benzene. Yield 3.5 g of α-difluoromethyl-o-methylstyrene (42%); b. p. 98° (50 mm); $n^{20.5}$D 1.4910. Found: C 71.47, 71.48; H 5.99, 6.00; F 22.50, 22.49%. Calculated: C 71.42; H 5.95; F 22.63%.

Preparation of difluoromethylmethyl-p-tolylcarbinol. In a special apparatus for work at low temperatures under argon was placed 130 ml of an ether solution of methyllithium (2.2 g; 0.1 M) and the mixture was cooled to −20°. At this temperature and with good stirring 17.0 g (0.1 M) of difluoromethyl o-tolyl ketone in 50 ml of absolute ether was added. The temperature during the time of reaction was maintained at −20 to −22°. Stirring was continued for 2 hr more. After the usual treatment, 10 g of difluoromethyl-p-tolylcarbinol (53.6%) was obtained; b. p. 92° (3 mm); n^{20}D 1.5009.

Preparation of α-difluoromethyl-p-methylstyrene. In a flask with a reflux condenser were placed, under nitrogen, 8.5 g of difluoromethylmethyl-p-tolylcarbinol (0.045 M), 3.19 g of phosphorus pentoxide (0.0225 M), 0.3 g of copper powder, and 100 ml of dry benzene. The reaction mixture was heated for 4.5 hr at the boiling point of benzene. Yield 4.1 g of α-difluoromethyl-p-methylstyrene (54%); b. p. 103° (50 mm); n^{20}D 1.4898. Found: C 72.18, 71.98; H 5.60, 5.56; F 22.0, 22.02%. $C_{10}H_{10}F_2$. Calculated: C 71.43; H 5.93; F 22.62%.

Preparation of α-trifluoromethyl-α-methylbenzyl alcohol. From methyllithium and trifluoroacetophenone. The reaction was carried out in an apparatus for condensations at low temperatures under nitrogen. In the apparatus was placed 255 ml of an ether solution of methyllithium containing 4.4 g of methyllithium (0.2 M), which then was cooled to −30°. At this temperature, with vigorous stirring, the addition of 34.8 g (0.2 M) of trifluoroacetophenone [7] in 50 ml of absolute ether was started at such a rate that the temperature did not rise above −20°; the addition required 2 hr. Then stirring was continued for another 2 hr at −20°, and the mixture was decomposed by pouring it into ice with dilute hydrochloric acid. After the usual treatment 32.5 g of α-trifluoromethyl-α-methylbenzyl alcohol was obtained; b. p. 91-91.5° (21 mm); 71-72° (10 mm); yield 79%; n^{20}D 1.4658. According to literature data [2]: b. p. 62-66° (4.5 mm); n^{20}D 1.4656.

From phenylmagnesium bromide and trifluoroacetone. An ether solution of phenylmagnesium bromide was prepared from 7.3 g of magnesium and 47.1 g of bromobenzene in 200 ml of absolute ether. This solution was cooled under nitrogen to −10°, and with vigorous stirring over a period of 1 hr 40 g of trifluoroacetone in 50 ml of absolute ether previously cooled to −30° was added. The dropping funnel for the addition of this solution was cooled to −10°. At the end of the addition stirring was continued for 2 hr, with gradual raising of the temperature to that of the room, and the mixture was then left to stand until the next day. The reaction mixture was decomposed by pouring into ice with the addition of dilute hydrochloric acid. Yield 46 g of α-trifluoromethyl-α-methylbenzyl alcohol (70%).

Preparation of α-trifluoromethylstyrene. The dehydration of 40 g of α-trifluoromethyl-α-methylbenzyl alcohol was carried out by heating with 36 g of phosphorus pentoxide on an oil bath in a current of nitrogen and distilling the products of the reaction off at a bath temperature of 160-165° (at the end of the distillation up to 185°). The material obtained was diluted with ether and washed with 5% sodium hydroxide solution and with a saturated solution of calcium chloride, and dried after the usual treatment. Yield 30 g of α-trifluoromethylstyrene (82%); b. p. 80.5° (77 mm); n^{20}D 1.4620; d^{20}_4 1.172; found MR 41.29; calculated MR 41.97. According to literature data [2]: n^{21}D 1.4603; d^{21}_4 1.167.

Preparation of α-difluoromethyl-α-methylbenzyl alcohol. The reaction was carried out in an apparatus for condensations at low temperatures under nitrogen. In the apparatus was placed an ether solution of methyllithium containing 4 g of methyllithium (prepared from methyl chloride). The mixture was cooled to −30° and at this temperature 22.7 g of ω,ω-difluoroacetophenone [8] (0.15 M) in 50 ml of ether was added dropwise, with stirring. The temperature of the reaction mixture was not allowed to rise above −25° and the addition took 2.5 hr. Then the mixture was stirred for 1.5 hr more at a temperature of about −20° and decomposed by pouring it into water and ice acidified with dilute hydrochloric acid. Yield 23.2 g of α-difluoromethyl-α-methylphenylcarbinol (92.5%); b. p. 81° (7 mm); $n^{20}D$ 1.4929. Found: F 21.84, 21.65%. $C_9H_{10}OF_2$. Calculated: F 22.09%.

Preparation of α-difluoromethylstyrene. A solution of 10.5 g of α-difluoromethyl-α-methylbenzyl alcohol (0.06 M) in 100 ml of benzene was prepared and 4.2 g of phosphorus pentoxide (0.03 M) in 20 ml of benzene was added. The mixture was refluxed with moderate boiling under nitrogen for 5 hr on a glycerol bath. Then the solution was poured off, dried with sodium sulfate with a little added copper poweder, the benzene was distilled off, and the residue was distilled. Yield 6.2 g (60.5%) of α-difluoromethylstyrene; b. p. 90.0-90.5° (40 mm); $n^{20}D$ 1.4980. Found: F 24.35, 24.45%. $C_9H_8F_2$. Calculated: F 22.09%.

Preparation of α-trifluoromethyl-α-methyl-p-fluorobenzyl alcohol. p-Fluorophenylmagnesium bromide was prepared in the usual way from 26.3 g (0.15 M) of p-fluorobromobenzene in 200 ml of absolute ether and 3.7 g (0.15 M) of magnesium. It was cooled to −10° and over the course of 45 minutes 18.4 g (10% excess) of trifluoroacetone in 40 ml of absolute ether (cooled to −50°) was added dropwise with vigorous stirring, the stirring was continued for 3 hr more at a temperature of about 0°, and the mixture was left at room temperature overnight. After the usual treatment and distillation in vacuum, 20.5 g (65%) of α-trifluoromethyl-α-methyl-p-fluorobenzyl alcohol was obtained; b. p. 83-84° (17 mm). Found: F 36.82, 36.64%. $C_9H_8OF_4$. Calculated: F 36.97%.

Preparation of α-trifluoromethyl-p-fluorostyrene. Dehydration of α-trifluoromethyl-α-methyl-p-fluorobenzyl alcohol (16.5 g) was carried out by treating with 15 g of phosphorus pentoxide and gradually heating the mixture on an oil bath under nitrogen. Distillation began at a bath temperature of 170-180° and continued at this temperature for 1 hr. The mixture was further heated for 30 minutes at 190-200°. A total of 14 g of crude product was obtained. After distillation, 11.5 g (76%) of α-trifluoromethyl-p-fluorostyrene with b. p. 53° (20 mm) and 1.5 g of the starting carbinol were isolated. Found: F 39.76, 39.80%. $C_9H_6F_4$. Calculated: F 40.0%.

Preparation of p-chlorophenylmethylcarbinol. In an apparatus filled with argon was placed 270 ml of 0.64 N ether solution of n-butyllithium and at a temperature of 20°, 30.7 g of p-chlorobromobenzene in 50 ml of absolute ether was added, with vigorous stirring, over a period of 20 minutes, then stirring was continued for 10 minutes more, and an excess (10 g) of acetaldehyde in 10 ml of absolute ether was added at a temperature not higher than 25°. The mixture was decomposed by pouring into ice with hydrochloric acid; after the usual treatment p-chlorophenylcarbinol [9] (80-85%) was obtained; b. p. 118-121° (12 mm).

Preparation of p-chlorostyrene. Dehydration of 31.5 g of p-chlorophenylmethylcarbinol with 3 g of potassium acid sulfate was carried out under the usual conditions [8]. After treatment about 20 g of p-chlorostyrene was obtained with b. p. 75-76° (19 mm); $n^{9}D$ 1.5665; $n^{20}D$ 1.5646; yield 60-65%. According to the data in the literature [10]: b. p. 39° (2 mm); $n^{20}D$ 1.5648.

SUMMARY

1. Methods have been developed for the synthesis of α-difluoromethylstyrenes and α-trifluoromethylstyrenes.

2. α-Difluoromethylstyrene, α-difluoromethyl-o-methylstyrene, α-difluoromethyl-p-methylstyrene, and α-trifluoromethyl-p-fluorostyrene have been described for the first time.

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