# 1, 1-Diaryl- and 1-Aryl-2-chloro-2-fluoroethylenes

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In the course of other studies in this laboratory, it became necessary to prepare some 1, 1-diaryl- and 1-aryl-2-chloro-2-fluoroethylenes (IV and IX). In spite of their relatively simple structure, no compounds of these types have ever been reported in the literature, except 1, 1-diphenyl- and 1, 1-bis(*p*-chlorophenyl)-2-chloro-2-fluoroethylene.[1] Thus, the 1, 1-diphenyl derivative has been prepared by the reaction of benzophenone with chlorofluoromethylenetriphenylphosphorane[3] or by the action of chlorofluorocarbene upon diphenyldiazomethane,[4] while the 1, 1-bis(*p*-chlorophenyl) derivative has been obtained from 1, 1-bis(*p*-chlorophenyl)-2, 2-dichloro-2-fluoroethane by dehydrochlorination.[5]

This paper will describe the preparation of some of these ethylenes via the synthetic routes shown in Fig. 1.

The starting material, methyl dichlorofluoroacetate (I), was prepared in a good yield from methyl trichloroacetate by the action of antimony trifluoride in the presence of bromine.[6] It was treated with an excess of arylmagnesium bromide to give 1, 1-diaryl-2, 2-dichloro-2-fluoroethanol (II), which was then converted into the corresponding chloride III by refluxing with thionyl chloride in the presence of pyridine. The dechlorination of the product by zinc in ethanol led to one of the desired ethylenes IV.

It should be noted that the reaction of the ester I with *p*-chlorophenylmagnesium bromide resulted in a fairly good yield (58%) of the corresponding carbinol, in contrast to the observation of Bergmann *et al.*[5] that it gave mainly 4, 4′-dichlorobiphenyl.

The hydrolysis of the ester I by sodium hydroxide gave the sodium salt of dichlorofluoroacetic acid (V), from which $\alpha, \alpha$-dichloro-$\alpha$-fluoroacetophenone derivatives (VI) were then successfully prepared by treatment with an equimolar amount

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[1] A number of $\beta$-chloro-$\beta$-fluorostyrenes have been reported, but all of them have fluorine at $\alpha$; see Ref. 2.

[2] a) S. G. Cohen, H. T. Wolosinski and P. J. Sheuer, *J. Am. Chem. Soc.,* **72**, 3952 (1950). b) P. Tarrant and D. A. Warner, *ibid.,* **76**, 1624 (1954). c) S. Dixon, *J. Org. Chem.,* **21**, 400 (1956).

[3] A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.,* **84**, 854 (1962).

[4] H. Reimlinger, *Chem. Ber.,* **97**, 339 (1964).

[5] E. D. Bergmann, P. Moses, M. Neeman, S. Cohen, A. Kaluszyner and S. Reuter, *J. Am. Chem. Soc.,* **79**, 4174 (1957).

[6] E. Gryszkiewicz-Trochimowski, A. Sporzynski and J. Wnuk, *Rec. trav. chim.,* **66**, 419 (1947).

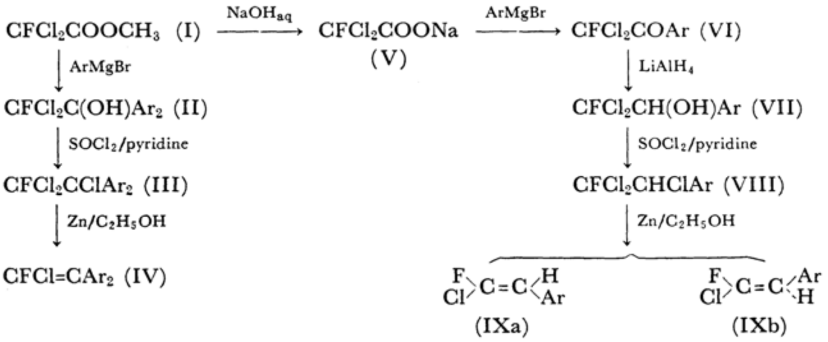

Fig. 1. Synthetic routes to *gem*-chlorofluoroethylenes.

TABLE 1. 1, 1-DIARYL-2-CHLORO-2-FLUOROETHYLENES AND THEIR PRECURSORS

(A) 1, 1-Diaryl-2, 2-dichloro-2-fluoroethanol (II)

| Aryl | Yield % | Bp °C/mmHg | Mp °C | $\nu_{O-H}$ cm$^{-1}$ | C, % |  | H, % |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Calcd | Found | Calcd | Found |
| Phenyl[5] | 84 | 150—158/5 | 35—36 | 3550 | 58.99 | 59.10 | 3.86 | 3.96 |
| *p*-Tolyl | 75 | 180—182/2 | 34—35 | 3600 | 61.38 | 61.29 | 4.79 | 4.68 |
| *p*-Chlorophenyl[5] | 58 | 182—200/2 | 79—81 | 3560 | 47.51 | 47.65 | 2.54 | 2.67 |
| *p*-Fluorophenyl | 52 | 154—156/4 | 50—51 | 3520 | 52.35 | 52.63 | 2.83 | 2.93 |
| *p*-Methoxyphenyl | 59 | — | 104—105 | 3450 | 76.68 | 76.63 | 4.35 | 4.29 |

(B) 1, 1-Diaryl-1, 2, 2-trichloro-2-fluoroethane (III)

| Aryl | Yield % | Bp °C/mmHg | Mp °C | C, % |  | H, % |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | Calcd | Found | Calcd | Found |
| Phenyl | 90 | 144—154/5 | 64—66 | 55.40 | 55.56 | 3.29 | 3.33 |
| *p*-Tolyl | 40 | — | 54 | 57.96 | 57.75 | 4.26 | 4.25 |
| *p*-Chlorophenyl | 61 | 200—202/3 | 138—140 | 45.15 | 44.98 | 2.15 | 2.21 |
| *p*-Fluorophenyl | 71 | 165—172/7 | <10 | 49.50 | 49.23 | 2.38 | 2.58 |
| *p*-Methoxyphenyl | 0 |  |  |  |  |  |  |

(C) 1, 1-Diaryl-2-chloro-2-fluoroethylene (IV)

| Aryl | Yield % | Bp °C/mmHg | Mp °C | $\nu_{C=C}$ cm$^{-1}$ | C, % |  | H, % |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Calcd | Found | Calcd | Found |
| Phenyl[3,4] | 78 | 120—124/5 | 36—36.5 | 1640 | 72.29 | 72.44 | 4.30 | 4.48 |
| *p*-Tolyl | 55 | — | 56—56.5 | 1630 | 73.73 | 73.47 | 5.38 | 5.54 |
| *p*-Chlorophenyl[5] | 56 | — | 50—51.5 | 1630 | 55.77 | 55.82 | 2.66 | 2.88 |
| *p*-Fluorophenyl | 47 | 138—144/11 | 25—26 | 1635 | 62.60 | 62.63 | 2.98 | 2.94 |

of arylmagnesium bromide. Only a small amount of the corresponding carbinol was formed under the reaction conditions.[7]

The Friedel-Crafts acylation with dichlorofluoroacetyl chloride was also attempted in preparing the ketones, but it resulted in low yields (less than 10%) of the desired products, probably due to the fluorine-chlorine exchange, as has been suggested by Bergmann *et al.*[9]

The ketone VI was easily reduced to the corresponding carbinol VII by lithium aluminum hydride. The conversion of the resulting carbinol to the corresponding chloride VIII, followed by

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[7] It is well known that $\alpha$-fluorinated carboxylic acids or their salts give the corresponding ketones upon reaction with Grignard reagents; see Ref. 8.

[8] a) K. T. Dishart and R. Levine, *J. Am. Chem. Soc.*, **78**, 2268 (1956). b) A. Sykes, J. C. Tatlow and C. K. Thomas, *J. Chem. Soc.*, **1956**, 835. c) W. Funasaka, T. Ando, T. Murase and H. Koike, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **65**, 1195 (1962).

[9] F. Bergmann and A. Kalmus, *J. Am. Chem. Soc.*, **76**, 4137 (1954).

Table 2. 1-Aryl-2-chloro-2-fluoroethylenes and their precursors

(A) Aryl dichlorofluoromethyl ketone (VI)

| Aryl | Yield % | Bp °C/mmHg | $n_D^t/t$, °C | $\nu_{C=O}$ $cm^{-1}$ | C, % |  | H, % |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Calcd | Found | Calcd | Found |
| Phenyl2a) | 50 | 90—98/6 | 1.5367/21 | 1712 | 46.41 | 46.25 | 2.43 | 2.65 |
| *p*-Tolyl | 53 | 90—93/3 | 1.5384/21 | 1705 | 48.90 | 49.04 | 3.19 | 3.38 |
| *p*-Chlorophenyl5) | 42 | 97—103/5 | 1.5548/21 | 1717 | 39.79 | 39.83 | 1.67 | 1.78 |
| *p*-Fluorophenyl | 42 | 84—86/10 | 1.5129/23 | 1702 | 42.70 | 42.42 | 1.79 | 1.92 |
| *p*-Methoxyphenyl | 63 | 110—112/2 | 1.5615/18 | 1699 | 45.60 | 45.70 | 2.98 | 3.05 |

(B) 1-Aryl-2, 2-dichloro-2-fluoroethanol (VII)

| Aryl | Yield % | Bp °C/mmHg | $n_D^t/t$, °C | $\nu_{O-H}$ $cm^{-1}$ | C, % |  | H, % |  |
|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  | Calcd | Found | Calcd | Found |
| Phenyl | 85 | 85—95/4 | 1.5389/13 | 3360 | 45.96 | 46.03 | 3.38 | 3.45 |
| *p*-Tolyl | 72 | 117—118/5 | 1.5276/26 | 3400 | 48.47 | 48.29 | 4.07 | 3.92 |
| *p*-Chlorophenyl5) | 79 | 110—126/4 | 1.5468/21 | 3440 | 39.46 | 39.72 | 2.48 | 2.53 |
| *p*-Fluorophenyl | 65 | 108—110/8 | 1.5120/18 | 3380 | 42.32 | 42.09 | 2.66 | 2.68 |
| *p*-Methoxyphenyl | 62 | 127—128/2 | 1.5615/18 | 3350 | 45.21 | 45.08 | 3.79 | 3.91 |

(C) 1-Aryl-1, 2, 2-trichloro-2-fluoroethane (VIII)

| Aryl | Yield % | Bp °C/mmHg | $n_D^t/t$, °C | C, % |  | H, % |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | Calcd | Found | Calcd | Found |
| Phenyl | 70 | 100—120/18 | 1.5349/21 | 42.24 | 42.29 | 2.66 | 2.75 |
| *p*-Tolyl | 60 | 97—104/4 | 1.5302/20 | 44.76 | 44.87 | 3.34 | 3.25 |
| *p*-Chlorophenyl | 55 | 107—109/4 | 1.5552/18 | 36.68 | 36.57 | 1.92 | 1.88 |
| *p*-Fluorophenyl | 69 | 88—95/10 | 1.5135/20 | 39.14 | 39.22 | 2.06 | 2.22 |
| *p*-Methoxyphenyl | 56 | 107—111/2 | 1.5410/23 | 41.97 | 42.15 | 3.13 | 2.99 |

(D) 1-Arlyl-2-chloro-2-fluoroethylene (IX)

| Aryl | Yield % | Bp °C/mmHg | $n_D^t/t$, °C | IXb/IXa | $\nu_{C=C}$ $cm^{-1}$ | C, % |  | H, % |  |
|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  | Calcd | Found | Calcd | Found |
| Phenyl | 68 | 62—72/14 | 1.5320/20 | 1.65 | 1667 | 61.36 | 61.29 | 3.86 | 4.00 |
| *p*-Tolyl | 66 | 87—88/13 | 1.5404/18 | 1.50 | 1663 | 63.36 | 63.44 | 4.73 | 4.84 |
| *p*-Chlorophenyl | 62 | 74—84/3 | 1.5605/18 | 1.46 | 1661 | 50.30 | 50.49 | 2.64 | 2.65 |
| *p*-Fluorophenyl | 76 | 60—64/12 | 1.5213/20 | 1.60 | 1665 | 55.04 | 54.95 | 2.89 | 3.01 |
| *p*-Methoxyphenyl | 57 | 87—97/3 | 1.5532/23 | 1.46 | 1663 | 57.92 | 58.01 | 4.32 | 4.20 |

Table 3. Parameters of $^1H$ NMR spectra of the ethylenic hydrogens of IXa and IXb*

| Aryl | IXa |  | IXb |  |
|---|---|---|---|---|
|  | δ, ppm** | $J_{HF}^{cis}$, cps | δ, ppm** | $J_{HF}^{trans}$, cps |
| Phenyl | 6.37 | 13.0 | 5.80 | 30.5 |
| *p*-Tolyl | 6.35 | 13.0 | 5.78 | 31.0 |
| *p*-Chlorophenyl | 6.34 | 12.3 | 5.78 | 30.0 |
| *p*-Fluorophenyl | 6.35 | 13.0 | 5.78 | 30.5 |
| *p*-Methoxyphenyl | 6.34 | 13.0 | 5.75 | 31.0 |

* Measured in $CDCl_3$ on a Varian A 60 spectrometer at 60 Mc.

** Downfield from TMS as internal reference.

the dechlorination of the product, afforded another type of ethylene IX. As expected, the product was a mixture of two geometrical isomers, IXa and IXb; analysis by v. p. c. showed the IXb/IXa ratio to be in the range of 1.46—1.65.

The physical properties of the ethylenes and their precursors are summarized in Tables 1 and 2, together with the yields obtained in their preparation.

The structures of IXa and IXb were determined by means of their $^1$H NMR spectra, based on the well-established fact that the coupling constant between H and F in the –CH=CF– system is larger when they are trans than when they are cis.(10) The coupling constants are listed in Table 3, together with the chemical shift of the ethylenic hydrogen.

Attempts were made to prepare each of the two geometrical isomers of 1-chloro-1-fluoro-2-phenylcyclopropane from IXa and IXb stereospecifically by the application of a modification of the procedure(11) of the Simmons-Smith reaction, but they resulted in failure. In view of the electrophilic nature of the reaction(12) and the electron-withdrawing effect of the two halogen atoms in the olefin molecule, this result does not seem surprising.

### Experimental

**Methyl Dichlorofluoroacetate (I).** A mixture of 305 g (1.70 mol) of methyl trichloroacetate, 202 g (1.13 mol) of antimony trifluoride, and 30 g of bromine was placed in a three-necked flask equipped with a distillation apparatus; the contents were then distilled with vigorous stirring at such a rate that the boiling point of the distillate did not exceed 120°C. After the distillate had been washed with aqueous sodium bicarbonate and with water, it was fractionally distilled to give 160 g (60%) of I (bp 117—118.5°C), together with 36 g (15%) of methyl chlorodifluoroacetate.

**1, 1-Diaryl-2, 2-dichloro-2-fluoroethanol (II).** To a Grignard solution prepared from 0.25 mol of an aryl bromide, 6.1 g (0.25 g-atom) of magnesium, and 250 m*l* of ether, a solution of 0.1 mol of I in 50 m*l* of ether was added gradually with stirring at −5 to 0°C. After the hydrolysis of the reaction mixture, the ether was distilled off from the organic layer. The residue was purified either by recrystallization from petroleum ether or by vacuum distillation, followed by recrystallization.

**1, 1-Diaryl-1, 2, 2-trichloro-2-fluoroethane (III).** A mixture of 0.07 mol of II, 12 g (0.1 mol) of thionyl chloride, and 8 g (0.1 mol) of pyridine was refluxed for 2hr. After being cooled, the reaction mixture was poured onto ice, and the product was extracted with ether. The ether was removed by distillation, and the residue was purified by vacuum distillation and/or recrystallization from petroleum ether.

**1, 1-Diaryl-2-chloro-2-fluoroethylene (IV).** A mixture of 0.016 mol of III, 1.5 g (0.023 g-atom) of zinc dust, and 20 m*l* of ethanol was refluxed for 3hr in the presence of a catalytic amount (50—100 mg) of zinc chloride, and then filtered. After the removal of the ethanol from the filtrate by distillation, the residue was distilled in vacuum and/or recrystallized from petroleum ether.

**Aryl Dichlorofluoromethyl Ketone (VI).** To a Grignard solution prepared from 0.3 mol of an aryl bromide, 7.5 g (0.3 g-atom) of magnesium, and 300 m*l* of ether, 0.25 mol of V was added gradually with stirring at −5 to 0°C. The product was isolated by the hydrolysis of the reaction mixture, followed by the vacuum distillation of the organic layer.

**1-Aryl-2, 2-dichloro-2-fluoroethanol (VII).** To a suspension of 2.5 g (0.065 mol) of lithium aluminum hydride in 120 m*l* of ether, a solution of 0.16 mol of VI in 80 m*l* of ether was added dropwise with stirring below 0°C. After the excess hydride had been decomposed with water and hydrochloric acid, the ethereal layer was distilled in vacuum.

**1-Aryl-1, 2, 2-trichloro-2-fluoroethane (VIII).** A mixture of 0.077 mol of VII, 12 g (0.1 mol) of thionyl chloride, and 8 g (0.1 mol) of pyridine was refluxed for 2hr, and then worked up as has been described above for III.

**1-Aryl-2-chloro-2-fluoroethylene (IX).** A mixture of 0.01 mol of VIII, 1.5 g (0.023 g-atom) of zinc dust, a catalytic amount of zinc chloride, and 20 m*l* of ethanol was refluxed for 3hr, and then filtered. The vacuum distillation of the filtrate gave a mixture of two isomers, IXa and IXb, the ratio of which was determined by v. p. c. (Apiezon-L 5%, 3 m) on the assumption that the molar responses of IXa and IXb were equal. Generally IXa had a shorter retention time than IXb.

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10) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York (1959), p. 86.

11) E. LeCoff, *J. Org. Chem.*, **29**, 2048 (1964).

12) E. P. Blanchard and H. E. Simmons, *J. Am. Chem. Soc.*, **86**, 1337 (1964).