Preparation of 1-Choro-1-fluoroethylenes *via* Chlorofluorocarbene

Hiroki YAMANAKA, Teiichi ANDO and Wataru FUNASAKA

Department of Industrial Chemistry, Faculty of Engineering, Kyoto University, Sakyo-ku, Kyoto

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It has already been reported that chlorofluorocarbene reacts with triphenylphosphine to yield chlorofluoromethylenetriphenylphosphorane, and that the ylid reacts with benzophenone to give 1-chloro-1-fluoro - 2, 2 - diphenylethylene.[1] This paper will deal with the synthesis of some other 1-chloro-1-fluoroethylenes by a modification of this method.

Chlorofluorocarbene was generated by the addition of methanol to a mixture of sodium hydride and methyl dichlorofluoroacetate.[2] After it had been allowed to react with triphenylphosphine, the reaction mixture was treated, without the isolation of the ylid, with a carbonyl compound. The reaction scheme is shown below, and the results are summarized in Table 1.

$$CFCl_2COOCH_3 + CH_3OH/NaH \rightarrow :CFCl$$

$$:CFCl + Ph_3P \rightarrow Ph_3P{=}CFCl$$

$$Ph_3P{=}CFCl + RCOR' \rightarrow RR'C{=}CFCl + Ph_3PO$$

The main product obtained from an aldehyde or an unsymmetrical ketone gave a gas chromatogram composed of two peaks, indicating the formation of two geometrical isomers. Unfortunately, however, the retention times of the isomers under the conditions employed were too close to each other to make the gas chromatographic separation of the

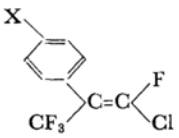
1) A. J. Speziale and K. W. Ratts, *J. Am. Chem. Soc.*, **84**, 854 (1962).
2) T. Ando, H. Yamanaka, S. Terabe, A. Horike and W. Funasaka, *Tetrahedron Letters*, **1967**, 1123.

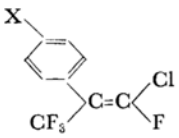
TABLE 1. REACTION OF CHLOROFLUOROMETHYLENETRIPHENYLPHOSPHORANE WITH CARBONYL COMPOUNDS

Carbonyl compound	Product	Yield %	Bp °C/mmHg	n_D^t (t, °C)	$\nu_{C=C}$ cm^{-1}	C, %		H, %	
						Calcd	Found	Calcd	Found
cyclo-$(CH_2)_5CO$	cyclo-$(CH_2)_5C{=}CFCl$	25	68—70/80	1.4627(21)	1688	56.58	56.69	6.78	6.82
PhCOMe	$PhC(Me){=}CFCl$	8	75—80/25	—	1665	63.36	63.47	4.73	4.80
PhCHO	$PhCH{=}CFCl$[4]	40	79—80/26	1.5293(22)[a] 1.5330(22)[b]	1665[a] 1666[b]	61.36	61.61	3.86	4.06
p-ClC_6H_4CHO	*p*-$ClC_6H_4CH{=}CFCl$[4]	63	93—96/12	1.5606(19)	1663	50.30	50.50	2.67	2.72
p-$MeOC_6H_4CHO$	*p*-$MeOC_6H_4CH{=}CFCl$[4]	40	97—104/7	1.5533(23)	1663	57.92	57.89	4.32	4.54
o-$MeOC_6H_4CHO$	*o*-$MeOC_6H_4CH{=}CFCl$	50	92—93/6	1.5404(22)	1660	57.92	58.02	4.32	4.25
$PhCOCF_3$	$PhC(CF_3){=}CFCl$	40	60—61/25	1.4603(21)[a] 1.4549(21)[b]	1660[a] 1668[b]	48.13	48.23	2.24	2.26
p-$FC_6H_4COCF_3$	*p*-$FC_6H_4C(CF_3){=}CFCl$	45	44—45/35	1.4473(22)	1660	44.56	44.85	1.66	1.71
p-$ClC_6H_4COCF_3$	*p*-$ClC_6H_4C(CF_3){=}CFCl$	41	85—86/14	1.4788(24)	1663	41.73	41.67	1.56	1.79
p-$MeC_6H_4COCF_3$	*p*-$MeC_6H_4C(CF_3){=}CFCl$	38	65—70/16	1.4628(21)	1665	50.34	50.67	2.96	3.23
p-$MeOC_6H_4COCF_3$	*p*-$MeOC_6H_4C(CF_3){=}CFCl$	36	98—100/11	—	1665	47.17	47.05	2.77	2.74

a) For the *anti*-isomer. b) For the *syn*-isomer.

TABLE 2. PARAMETERS OF THE ^{19}F NMR SPECTRA OF 1-CHLORO-1,3,3,3-TETRAFLUORO-2-ARYLPROPENES[a)]

anti-form: 

syn-form: 

X	Configration	Chemical shift, ppm[b)] δ_{-CF_3}	Chemical shift, ppm[b)] $\delta_{=CF}$	Coupling constant between $-CF_3$ and $=CF$, cps
H	anti	20.33	17.52	13.0
	syn	20.42	15.03	23.1
Me	anti	18.48	15.32	13.0
	syn	18.53	13.45	25.4
MeO	anti	19.47	16.15	12.5
	syn	19.45	14.25	25.4
Cl	anti	18.82	17.04	13.5
	syn	18.93	15.13	24.0
F	anti	19.05	16.97	13.0
	syn	19.09	14.94	25.4

a) Measured on a JNM C-60 NMR spectrometer at 56.446 Mc (20—40% in CCl_4).
b) Downfield from external trifluoroacetic acid.

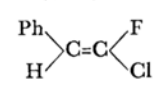
TABLE 3. COMPETITION REACTION

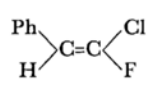
Carbonyl compounds	Products and their ratio
PhCHO + PhCOMe	PhCH=CFCl (100) + PhC(Me)CFCl (0)
PhCHO + $PhCOCF_3$	PhCH=CFCl (54) + $PhC(CF_3)$=CFCl (46)
PhCHO + *p*-ClC_6H_4CHO	PhCH=CFCl (37) + *p*-ClC_6H_4CH=CFCl (63)
PhCHO + *p*-$MeOC_6H_4CHO$	PhCH=CFCl (74) + *p*-$MeOC_6H_4CH$=CFCl (26)
$PhCOCF_3$ + PhCOMe	$PhC(CF_3)$=CFCl (100) + PhC(Me)=CFCl (0)

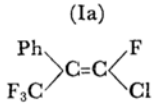
isomers feasible,[3)] except in the following two cases.

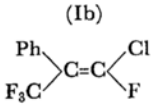
The product obtained from benzaldehyde (β-chloro-β-fluorostyrene) was successfully separated, by preparative gas chromatography (TCP 10%, 80°C, He 30 ml/min) into two isomers, the *anti*- (Ia) and the *syn*-form (Ib). The structures of the isomers were determined by their proton NMR spectra,[4)] and the ratio of Ia to Ib (57 : 43) was determined by gas chromatography before distillation. The *anti*-isomer had a longer retention time than the *syn*-isomer.

Similarly, the product from α, α, α-trifluoroacetophenone (1 - chloro - 1, 3, 3, 3 - tetrafluoro-2-phenylpropene) could also be separated into *anti*-(IIa) and *syn*- (IIb) isomers (PEG 6000 10%, 120°C, He 30 ml/min). The ratio of IIa to IIb was 52 : 48, the *anti*-isomer again possessing a longer retention time.


(Ia)


(Ib)


(IIa)


(IIb)

The structural assignments of the ethylenes derived from aryl trifluoromethyl ketones, including IIa and IIb, were made by means of their fluorine NMR spectra, based on the fact that the coupling constant between $-CF_3$ and $=CF$ in the $-C(CF_3)=CF-$ system is larger when they are cis to each other than when they are trans.[5)] The NMR data are shown in Table 2.

Table 3 shows the results of the competition reactions which were carried out in order to examine the relative reactivities of carbonyl compounds toward chlorofluoromethylenetriphenylphosphorane. As is evident from the table, the ylid reacts with aldehydes or with ketones having electron-withdrawing groups more rapidly than with ketones having electron-releasing groups. Analogous results have been obtained with dichloromethylenetriphenylphosphorane.[1)]

3) As judged from the areas of the NMR signals and/or the half-height widths of the gas chromatographic peaks, the ratio of the isomers formed was estimated to be approximately 50 : 50 in all of these cases.
4) T. Ando, F. Namigata, M. Kataoka, K. Yachida and W. Funasaka, This Bulletin, **40**, 1275 (1967).
5) J. W. Emsley, J. Feeney and L. H. Sutcliffe, "High Resolution NMR Spectroscopy," Vol. 2, Pergamon Press, London (1966), p. 909.

As compared with the other methods for preparing 1-chloro-1-fluoroethylenes,[6] the method described in this paper seems to have the advantages of being simpler and of wider applicability, although the yields are not always satisfactory.

Experimental

General Procedure for Preparing 1-Chloro-1-fluoroethylenes. A mixture of 0.2 mol of triphenylphosphine, 0.25 mol of sodium hydride, 0.25 mol of methyl dichlorofluoroacetate,[4] and 100 m*l* of dry petroleum ether (bp 60—70°C) was placed in a 200-m*l*, four-necked flask equipped with a stirrer, a thermometer, a gas inlet tube for introducing nitrogen, and a reflux condenser. To the mixture was added, under an atmosphere of nitrogen, 0.25 mol of methanol at 25—30°C (3—5 hr), and then 0.25 mol of a carbonyl compound at the same temperature (0.5 hr). After the reaction mixture had been allowed to stand at 60—80°C for 10 hr, it was cooled to room temperature and poured into 100 m*l* of water. The organic layer was separated from the aqueous layer, the aqueous layer was extracted twice with 50 m*l* portions of ether, and the combined organic layer was dried over anhydrous sodium sulfate. The distillation of the organic layer gave the desived ethylene (8—63%), the unchanged carbonyl compound (10—25%), and an unidentified product whose bp was a little higher than that of the ethylene. The ethylenes were identified by elemental analysis as well as by IR and /or NMR spectroscopy.

Competition Reaction. A mixture of two different carbonyl compounds (each 0.017 mol) was gradually added, at 25°C (0.5 hr), to a reaction mixture containing chlorofluoromethylenetriphenylphosphorane, which had been obtained, in the way described above, from 0.017 mol of triphenylphosphine, 0.02 mol of sodium hydride, 0.02 mol of methyl dichlorofluoroacetate, 0.02 mol of methanol, and 20 m*l* of benzene. The reaction mixture was kept at 60—80°C for 10 hr, and then cooled to room temperature. The ratio of the olefinic products was determined, without distillation, by gas chromatography with TCP, Apiezon Grease L, PEG 4000, or Silicone Grease as the liquid phase. All the olefins were assumed to have the same molar response under the conditions employed.

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6) See Ref. 4, and the references cited therein.