

SHORT
COMMUNICATIONS

Synthesis of 2,2-Dibromovinyl Trifluoromethyl Ketone by Acylation of 1,1-Dichloroethene in the Presence of Aluminum Bromide

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It is known [1, 2] that aluminum bromide promotes halogen exchange reactions between alkyl chlorides and iodides or bromides, whose mechanism remains so far unclear. Replacement of chlorine by bromine in tetrachloromethane also occurs in the presence of aluminum bromide [3]. A procedure was developed [4] for substitution of sterically shielded chlorine atoms by bromine in reactions of chloro derivatives of bicyclic systems with dibromomethane and tri-bromomethane using aluminum bromide generated *in situ* from aluminum and bromine.

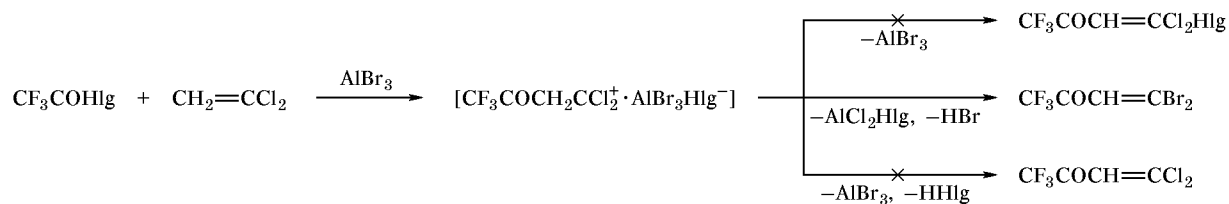
We were the first to effect halogen exchange in the synthesis of functionally substituted haloalkanes, namely in the reaction of trifluoroacetyl halides with 1,1-dichloroethene in the presence of aluminum bromide. Previously unknown 2,2-dibromovinyl trifluoromethyl ketone was obtained in a preparative yield by reactions of trifluoroacetyl chloride and trifluoroacetyl bromide with 1,1-dichloroethene in the presence of aluminum bromide (Scheme 1). Neither 2,2-dichlorovinyl trifluoromethyl ketone [5] nor trifluoromethyl trihaloethyl ketones were formed (which could be expected in keeping with the mechanism

of electrophilic addition to ethenes, catalyzed by Lewis acids [6]).

Previously [5], by the reaction of trifluoroacetyl chloride with 1,1-dichloroethene in the presence of aluminum chloride under analogous conditions we isolated 2,2-dichlorovinyl trifluoromethyl ketone. Here, we also observed no formation of a saturated product, trichloroethyl trifluoromethyl ketone. By contrast, reactions of alkanoyl and aroyl chlorides with 1,1-dichloroethene in the presence of aluminum chloride lead to formation of the corresponding tri-chloroethyl ketones which can be isolated. The latter can be converted into 2,2-dichlorovinyl ketones only by thermolysis, treatment with bases, or steam distillation [6].

Therefore, the mechanism of formation of dibromovinyl ketone via replacement of chlorine by bromine at the C_{sp^3} atom in the initially formed trihaloethyl trifluoromethyl ketone and subsequent dehydrohalogenation seems to be improbable. The halogen exchange process is likely to occur in the transition state. In order to elucidate the mechanism of halogen exchange we are now studying chlorine replacement

Scheme 1.



Hlg = Cl, Br.

by bromine in 2,2-dichlorovinyl trifluoromethyl ketone and other chlorovinyl ketones by the action of aluminum bromide, reactions of acyl halides with 1,1-dichloroethene in the presence of AlBr_3 , etc.

Taking into account a sufficiently high yield of 2,2-dibromovinyl trifluoromethyl ketone, optimization of the reaction conditions and extension of the series of acyl halides could make the above halogen exchange reaction a convenient method for preparation of previously inaccessible dibromovinyl ketones. Such compounds are promising as reactive intermediate products in the synthesis of polyfunctional and heterocyclic compounds (including those possessing a trifluoromethyl group), biologically active compounds, dyes, insectoacaricides, etc.

2,2-Dibromovinyl trifluoromethyl ketone. Trifluoroacetyl chloride or bromide, 0.11 mol, was added at -50 to -60°C through a bubbling tube to a suspension of 44 g (0.165 mol) of AlBr_3 and 0.5 g of anhydrous FeCl_3 in 150 ml of dry ethyl bromide or methylene bromide, and 11.5 g (0.11 mol) of 1,1-dichloroethene was then added dropwise. The mixture was stirred for 3 h at -50 to -60°C , allowed to warm up to room temperature, kept for 15 min at 25 – 30°C , and decomposed with ice. The product was extracted into chloroform, and the extract was dried over CaCl_2 and distilled. Yield of 2,2-dibromovinyl trifluoromethyl ketone 16.9 g (55%) and 21.7 g (70%), respec-

tively. bp 73 – 76°C (52 mm). IR spectrum (Specord 75IR, film), ν , cm^{-1} : 3060 ($=\text{C}-\text{H}$), 1720 ($\text{C}=\text{O}$), 1550 ($\text{C}=\text{C}$). NMR spectra (Bruker DPX-400, CDCl_3 , HMDS): δ 7.63 ppm ($=\text{CH}$); δ_{F} -79.83 ppm (CF_3). Found, %: C 16.78; H 0.24; Br 56.47. $\text{C}_4\text{H}_1\text{Br}_2\text{F}_3\text{O}$. Calculated, %: C 17.05; H 0.36; Br 56.70.

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