[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF FLORIDA]

Fluoroölefins. IV. The Addition of the Grignard Reagent to Fluoroölefins[1]

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Aliphatic and aromatic Grignard reagents have been found to react with various fluoroölefins. Addition apparently takes place across the double bond in a manner consistent with the behavior of fluoroölefins with other bases; the resulting adduct loses MgX_2 to give a new fluoroölefin containing a longer carbon chain. Phenylmagnesium bromide and *unsat.*-dichlorodifluoroethylene gave a 64% yield of α-fluoro-β-dichlorostyrene; α,β-difluoro-β-chlorostyrene resulted from chlorotrifluoroethylene. The effect of structure of the Grignard reagent on the yields of olefins is discussed.

In the search for a simple method for introducing functional groups into organic compounds containing fluorine, attention was turned to the reaction of the Grignard reagent with fluoroölefins. Since the Grignard reagent may act as a base and certain bases add to fluoroölefins, it was supposed that a new Grignard reagent should arise from the addition of the reagent to compounds such as chlorotrifluoroethylene or 1,1-dichloro-2,2-difluoroethylene. The addition product, if stable, should undergo the normal reactions of the Grignard reagent, leading to acids, alcohols, ketones, etc., which contain fluorine atoms.

Since 1,1-dichloro-2,2-difluorobutane has been prepared and characterized previously,[2] its synthesis by the reaction of ethylmagnesium bromide with 1,1-dichloro-2,2-difluoroethylene was chosen to test the procedure. The expected reactions were

$$C_2H_5MgBr + CF_2{=}CCl_2 \longrightarrow C_2H_5CF_2CCl_2MgBr \xrightarrow{H_2O} C_2H_5CF_2CHCl_2 + Mg(OH)Br$$

However, a butene corresponding to the formula $C_4H_5Cl_2F$ was obtained instead of the saturated compound anticipated. This compound was assigned the structure $CH_3CH_2CF{=}CCl_2$. In a second experiment, phenylmagnesium bromide was treated with chlorotrifluoroethylene and a 16.6% yield of the known[3] 2-chloro-1,2-difluoro-1-phenylethylene was obtained.

The formation of the styrene derivative may be accounted for by the mechanism

$$C_6H_5MgBr + CF_2{=}CFCl \longrightarrow [C_6H_5CF_2CFClMgBr] \longrightarrow C_6H_5CF{=}CFCl + MgFBr$$

The point of attack on the double bond by the phenyl group is consistent with the behavior of alcohols and phenols, which in the presence of bases add the alkoxy or phenoxy group to the carbon atom of the double bond of a fluoroölefin holding the greater number of fluorine atoms. It has previously been postulated[4] that base-catalyzed additions to fluoroölefins proceed as

$$RZ^- + CF_2{=}CX_2 \longrightarrow [RZCF_2CX_2]^- \xrightarrow{RZH} RZF_2CHX_2 + RZ^-$$

In the case of the reaction with the Grignard reagent, the intermediate loses a halogen atom from the carbon atom adjacent to that associated with the magnesium to give an olefin.

In cases where fluoropropenes are used in the reaction, it is thus possible to obtain two products depending upon which adjacent halogen is eliminated. For example, phenylmagnesium bromide reacted with 3-chloropentafluoropropene to give both $C_6H_5CF{=}CFCF_2Cl$ and $C_6H_5CF_2CF{=}CF_2$. It is interesting to note that the former was obtained in almost four times the quantity of the latter. Undoubtedly the basis for the formation of $C_6H_5CF{=}CFCF_2Cl$ is the added stability gained from the conjugation of the lateral double bond with the benzene ring. It might be expected that in the absence of this additional stabilization effect the heavier halide ion would be lost. This was found to be the case in the reaction of methylmagnesium bromide and 3-bromopentafluoropropene where a 24% conversion to $CH_3CF_2CF{=}CF_2$ was obtained, while the alternate reaction product, $CH_3CF{=}CFCF_2Br$, was obtained, if at all, in amounts too small for characterization.

It follows from the discussion above that a well defined carbanion is necessary for the initiation of the reaction of the Grignard reagent with the fluoroolefin. Thus, in general, aliphatic Grignard reagents should be less effective than the aromatic since the resonance stability of the phenyl anion, for example, involves lower energy forms than are possible wlth the ethyl anion. The conversions obtained using the two Grignard reagents bear out this supposition; by using 1,1-dichloro-2,2-difluoroethylene, a 64% conversion to 1,1-dichloro-2-fluoro-2-phenylethylene was obtained with phenylmagnesium bromide, while only a 10% conversion to 1,1-dichloro-2-fluorobutene-1 resulted with ethylmagnesium bromide under the same conditions.

There is a variation in yields of resulting fluoroolefins among the aliphatic Grignard reagents proportional to the expected degree of ionization; as the electron release of the alkyl residue is increased the conversion rapidly diminishes. Thus, while ethylmagnesium bromide and 1,1-dichloro-2,2-difluoroethylene gave a 10% conversion to 1,1-dichloro-2-fluorobutene-1, isopropylmagnesium bromide and the same olefin gave evidence of reaction only in trace amounts. On the other hand, methylmagnesium bromide with 3-iodopentafluoropropene gave a 24% conversion to 1,1,2,3,3-pentafluorobutene-1.

A comparison of yields of products obtained when aromatic Grignard reagents react with 1,1-dichloro-1,1-difluoroethylene shows that a strongly electro-

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[2] A. L. Henne and J. B. Hinkamp, THIS JOURNAL, **67**, 1194 (1945).

[3] S. G. Cohen, H. T. Wolosinski and P. J. Scheuer, *ibid.*, **72**, 3952 (1950).

[4] M. D. Hurwitz and W. T. Miller, Jr., Abstracts of Papers, 114th Meeting of the American Chemical Society, 1948, p. 4L.

negative group on the aromatic nucleus retards the reaction. Although both phenyl- and mixed *o*- and *p*-methoxyphenylmagnesium gave 64% yields of the corresponding styrene derivatives, *m*-trifluoromethylphenylmagnesium bromide gave only 8% of a fluoroölefin. Undoubtedly, the reduction of electron density about the carbon atom at the site of attachment to the MgBr group caused by the trifluoromethyl group greatly reduces the tendency of the anion to attack the double bond.

Several fluoroethylenes were found to be essentially unreactive toward phenylmagnesium bromide under conditions which gave good yields of product from 1,1-dichloro-2,2-difluoroethylene. For example, a very small amount of high boiling liquid was isolated when 1-chloro-1-fluoroethylene was used and 63% of benzene was recovered; 2-chloro-1,1-difluoroethylene gave none of the expected product and 87% of benzene. 1,1-Difluoroethylene gave a complex mixture of products.

Several attempts were made to increase the yields of fluoroölefins by this reaction. Although it has been reported[5] that certain Grignard reactions gave better yields when carried out in a solution of anisole or phenetole, these solvents were ineffective in increasing the yields of fluoroölefins. It was anticipated that the relative low boiling points of the fluoroethylenes were responsible for low yields in certain cases. To test this idea, a reaction was attempted with dichlorodifluoroethylene and ethylmagnesium bromide at elevated pressure in a stainless steel autoclave. However, when the temperature reached 55°, a violent explosion occurred.

Experimental

1,1-Dichloro-2-fluorobutene-1.—One mole of ethylmagnesium bromide was prepared in 350 ml. of ether under an atmosphere of nitrogen and filtered through a plug of Pyrex wool into a nitrogen-flushed, 500-ml. three-neck flask equipped with a stirrer, ice-water cooled reflux condenser and gas inlet tube. One mole (133 g.) of 1,1-dichloro-2,2-difluoroethylene was added in two hours to the ice-cold, stirred solution. Stirring was continued for one day at 0–5°, and for one day at room temperature. At the end of this time the mixture was poured into ice and 100 ml. of concd. hydrochloric acid, and separated. The water layer was saturated with sodium chloride and extracted with fresh ether. After drying the combined ether extracts over calcium chloride and removal of the solvent, 14 g. of a compound with the following properties was obtained: b.p. 96.5–98.0°, $n^{25}\mathrm{D}$ 1.4219, d^{25}_4 1.217. *Anal.* Calcd. for $C_4H_5Cl_2F$: Cl, 49.59; MR_D, 29.84. Found: Cl, 49.92; MR_D, 29.85. This compound has been assigned the structure $C_2H_5CF{=}CCl_2$ on the basis of the mechanism outlined above. Furthermore, a migration of chlorine or hydrogen atoms would be required for the formation of any isomeric olefin in the reaction and this possibility seems highly unlikely.

1,1,2,3,3-Pentafluorobutene-1.—One-fourth mole of methylmagnesium bromide was prepared in dibutyl ether and filtered as before. 3-Iodopentafluoropropene[6] was added dropwise. After stirring for two days at 20–25° the liquid was decanted and distilled. Refractionation of the volatile portion gave 8 g. (24%) of $CH_3CF_2CF{=}CF_2$, b.p. 24–26°, $n^{11}\mathrm{D}$ 1.3571, d^{11}_4 1.57. *Anal.* Calcd. for $C_4H_3F_5$: C, 32.87; H, 2.06; MR_D, 19.7. Found: C, 31.47; H, 2.44; MR_D, 20.4.

1-Chloro-1,2-difluoro-2-phenylethylene.—One-half mole of phenylmagnesium bromide was prepared in 300 ml. of ether, filtered and treated with 0.48 mole of chlorotrifluoroethylene. After remaining in contact for four days, either packed in Dry Ice and allowed to warm up slowly, or by repeatedly recycling the olefin, the mixture was treated with iced 10% sulfuric acid, worked up as described for 1,1-dichloro-2-fluorobutene-1 and distilled. 1-Chloro-1,2-difluoro-2-phenylethylene, b.p. 97–98° (59 mm.), $n^{25}\mathrm{D}$ 1.5237 d^{25}_4 1.282, was obtained in a yield of 16.6% (29 g.). Cohen, *et al.*,[3] reported $n^{20}\mathrm{D}$ 1.524. *Anal.* Calcd. for $C_8H_5ClF_2$: Cl, 20.32; MR_D, 41.77.[7] Found: Cl, 21.09; MR_D, 40.07.

1,1-Dichloro-2-fluoro-2-phenylethylene.—One-half mole of phenylmagnesium bromide under an atmosphere of nitrogen was stirred for 18 hours with 0.47 mole (62 g.) of 1,1-dichloro-2,2-difluoroethylene. The mixture was poured into iced 10% sulfuric acid and processed as described above. A 63% yield (58 g.) of 1,1-dichloro-2-fluoro-2-phenylethylene was obtained with these properties: b.p. 89.0–89.9° at 10.5 mm., $n^{26}\mathrm{D}$ 1.5596, d^{26}_4 1.330. *Anal.* Calcd. for $C_8H_5Cl_2F$: Cl, 37.12; MR_D, 46.72. Found: Cl, 37.62; MR_D, 46.40.

3-Chloro-1,2,3,3-tetrafluoro-1-phenylpropene-1.—To 0.5 mole of phenylmagnesium bromide stirred under nitrogen in an ice–salt-bath was added 0.48 mole (80 g.) of 3-chloropentafluoropropene in four portions. After standing for 18 hours at room temperature the reaction mixture was hydrolyzed, worked up and distilled as before. A compound, b.p. 90–91° at 22 mm., $n^{25}\mathrm{D}$ 1.4842, d^{25}_4 1.365, was obtained in 32.4% yield (35 g.). *Anal.* Calcd. for $C_9H_5ClF_4$: Cl, 15.79; MR_D, 46.15. Found: Cl, 15.47; MR_D, 47.01. On the basis of the known reactions of compounds such as $CF_2{=}CFCF_2Br$ and $CF_2{=}CFCF_2I$ the intermediate formed is assumed to be $C_6H_5CF_2CF(MgBr)CF_2Cl$. This intermediate could presumably give $C_6H_5CF{=}CFCF_2Cl$ or $C_6H_5CF_2CF{=}CFCl$ by loss of MgBrF. The structure of the olefin was shown to be $C_6H_5CF{=}CFCF_2Cl$ by oxidation to benzoic acid.

In addition to the compound isolated above, 9 g. of material, b.p. 77.0–78.5° at 65 mm., $n^{28}\mathrm{D}$ 1.4379, d^{26}_4, was obtained. The molar refraction of this material is reasonably close to the value expected for $C_6H_5CF_2CF{=}CF_2$.

1,1-Dichloro-2-fluoro-2-(2- and 4-methoxyphenyl)-ethylene.—The Grignard reagent was made from bromoanisole, obtained by brominating anisole, and treated with the theoretical amount (0.5 mole) of 1,1-dichloro-2,2-difluoroethylene as described. Distillation gave 66 g. (64.5%) of 1,1-dichloro-2-fluoro-2-(methoxyphenyl)-ethylene, b.p. 93.0–94.0° at 0.5 to 0.7 mm., $n^{24}\mathrm{D}$ 1.5744, d^{24}_4 1.345. *Anal.* Calcd, for $C_9H_7Cl_2FO$: Cl, 31.79; MR_D, 53.87. Found: Cl, 31.89; MR_D, 54.25.

1,1-Dichloro-2-fluoro-2-(3-trifluoromethylphenyl)-ethylene.—One-half mole of 3-trifluoromethylphenylmagnesium bromide was treated with 0.48 mole (64 g.) of 1,1-dichloro-2,2-difluoroethylene and processed as described. Distillation gave 10 g. of 1,1-dichloro-2-fluoro-2-(3-trifluoromethylphenyl)-ethylene, b.p. 82.0–83.5° at 7.7 mm., $n^{30}\mathrm{D}$ 1.4898, d^{30}_4 1.442. *Anal.* Calcd. for $C_9H_4Cl_2F_4$: Cl, 27.37; MR_D, 51.02. Found: Cl, 27.40; MR_D, 51.92.

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(5) R. N. Lewis and J. R. Wright, THIS JOURNAL, **74**, 1253 (1952).

(6) A. H. Fainberg and W. T. Miller, Jr., "Preferential Replacement Reactions of Highly Fluorinated Alkyl Halides. Preparation of Certain Fluorinated Allyl Iodides," paper presented at the 119th Meeting of the Division of Organic Chemistry of the American Chemical Society, Boston, Mass., April 2-5, 1951.

(7) The molar refractions were calculated using the generally accepted values for the various atoms. Exaltations of the styrene derivatives were given a value of 2.00.