[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT AT THE OHIO STATE UNIVERSITY]

Influence of a CF_3 Group on an Adjacent Double Bond

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The powerful electronegative effect of the CF_3 group subjects an adjacent double bond to "electron drain" and to induced polarization. In $CF_3CH{=}CH_2$, the central CH becomes more negative than the end CH_2, and the double bond is electron-poor, in contrast to $CH_3CH{=}CH_2$ in which the double bond is electron-rich and the central CH more positive than the end CH_2. As a consequence, addition of a molecule of hydroacid to $CF_3CH{=}CH_2$ was found difficult but proceeded in a direction such as to yield $CF_3CH_2CH_2X$ exclusively. Water could not be added in an acid medium, and poly-acrylates were formed in concentrated sulfuric acid. Neither carbon tetrachloride nor chloroform could be added in the presence of aluminum chloride.

Addition of water or alcohol in the presence of a base was defeated by predominant solvolysis of the allylic CF_3, to form derivatives of acrylic acid.

Addition of hydrogen in the presence of a metallic catalyst was sluggish, but proceeded readily to completion. Reactions of the free radical type, such as addition of CCl_4 or $CHCl_3$ and polymerization in the presence of a peroxide did not succeed.

The directing influence is in agreement with the fact that $CH_3CF_2CH{=}CH_2$ accepts hydrogen chloride in the presence of aluminum chloride to yield $CH_3CF_2CH_2CH_2Cl$ exclusively.[1] The retarding influence agrees with our own unpublished observations that $CF_2{=}CH_2$ accepts hydrogen fluoride with great avidity, while $CF_2{=}CHCF_3$ and $CF_2{=}C(CH_3)CF_3$ will do so at high temperature only and need the help of a Lewis acid such as antimony fluoride.

Experimental

$CF_3CH{=}CH_2$ was prepared by the previously reported[2] sequence: $CCl_2{=}CHCH_3$ to $CF_3CH_2CH_3$ to $CF_3CH_2CH_2Cl$ to $CF_3CH{=}CH_2$ in improved yields. Later, with $CCl_3CH_2CH_2Cl$ available commercially from CCl_4 addition to ethylene in the presence of a peroxide, a conventional antimony trifluoride treatment gave in one step $CF_3CH_2CH_2Cl$ together with its decomposition product, $CF_3CH{=}CH_2$; optimum conditions were not searched for, in view of the cheapness of the raw materials.

Addition of HCl.—$CF_3CH{=}CH_2$ did not accept hydrogen chloride until aluminum chloride was used as a catalyst, at high temperature; other conventional catalysts (BF_3, $FeCl_3$, $BiCl_3$ and $ZnCl_2$) failed. A 200-ml. steel bomb cooled to $-78°$ was charged with $CF_3CH{=}CH_2$ (38 g. or 0.39 mole) and $AlCl_3$ (2.5 g.), then was connected to a tank from which it received 69 g. (or 1.9 moles) of hydrogen chloride. It was rocked mechanically for 6 hours at room temperature, then for nine hours at 100°. After cooling, the gases were vented through an alkaline solution, and liquefied in a Dry-Ice trap, where unreacted $CF_3CH{=}CH_2$ (28 g. or 0.28 mole) was collected. The residue in the bomb was poured over cracked ice, steam distilled, dried and distilled; at 45–46°, the expected $CF_3CH_2CH_2Cl$, $n^{20}D$ 1.3379 was collected (12.5 g. or 0.09 mole); there was no trace of the isomer $CF_3CHClCH_3$,[3] which would have distilled at 30°.

Addition of HBr.—$CF_3CH{=}CH_2$ did not accept hydrogen bromide in the conventional procedures with acetic anhydride or nitroethane solvents. Addition succeeded at 100° in the presence of aluminum bromide with the operative conditions described for hydrogen chloride. $CF_3CH{=}CH_2$ (0.54 mole) gave 0.13 mole of unreacted material, then 0.19 mole of the expected[4] $CF_3CH_2CH_2Br$, b. p. 62–63°, $n^{20}D$ 1.3602, and the latter was free of its isomer[5] $CF_3CHBrCH_3$ which would have boiled at 49°. The balance of the material (0.32 mole) was lost in handling and in resin formation. The secondary bromide is known to be more stable than the primary bromide, and is thus unlikely to have resinified.

Addition of H_2.—Hydrogenation was performed on a commercial (Universal Oil Products) nickel catalyst supported on kieselguhr, in absolute alcohol, at 250–300 atmospheres and a temperature of 125°; after half of the computed hydrogen had been absorbed, the temperature was raised rapidly to 200° to complete the addition. Hydrogenation was quantitative, and the product did not decolorize a permanganate solution. With the catalyst used, the operating conditions correspond to those needed for hydrogenation of aniline.[6]

Summary

In $CF_3CH{=}CH_2$, the CF_3 group "drains" the double bond and polarizes it in a manner to make the central carbon the more negative; this makes the addition of HCl or HBr difficult, and directs it to form $CF_3CH_2CH_2Cl$ or $CF_3CH_2CH_2Br$ exclusively. Catalytic hydrogenation to $CF_3CH_2CH_3$ proceeds quantitatively under experimental conditions adequate for aniline reduction.

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[1] McBee, *Ind. Eng. Chem*, **39**, 418 (1947).

[2] Henne and Waalkes, THIS JOURNAL, **68**, 496 (1946).

[3] Henne and Whaley, *ibid.*, **64**, 1157 (1942).

[4] McBee, *Ind. Eng. Chem.*, **39**, 420 (1947).

[5] Swarts, *Bull. soc. chim. belg.*, **48**, 106 (1929)

[6] H. Adkins, "Reactions of Hydrogen" University of Wisconsin Press, Madison, Wisconsin, 1937, pp. 52–64.