contained no detectable free or neutralized carboxyl groups by the titration method and was designated A 15-CH_3.

The samples containing bound cations were prepared by neutralizing the carboxyls of the de-ashed ethyl celluloses. A weighed quantity of de-ashed ethyl cellulose of known (free) carboxyl content was dissolved in 70:30 benzene: alcohol to make a solution of 5-10% concentration. The calculated amount of standard sodium methylate or of standardized aqueous barium hydroxide was added to neutralize the free carboxyls, either completely or partially as desired, with Na^+ or Ba^{++}, respectively. For Ca^{++} and Mg^{++}, the solutions of the de-ashed ethyl celluloses were stirred with an excess of finely powdered calcium hydroxide or magnesium hydroxide and the excess was removed by centrifugation. The neutralized solutions were then poured into glass trays and the solvents allowed to evaporate. The stripped films were dried in the vacuum oven at 50-60° for 24 to 48 hours. In some cases the films were cut into small pieces and put through a Wiley Mill (20-40 mesh screens) along with small pieces of Dry Ice before drying in the oven. The samples containing bound cations were prepared by these procedures and designated A 15-Na, A 15-Mg, A 62-Ba, B 16-Ba, etc., with the numbers giving the microequivalents per gram of bound cations.

Viscosity Determinations.—For most of the work, solutions at the given concentrations were prepared by weight dilutions of a stock solution. The stock solution was prepared at the highest concentration desired which was usually 1 g./100 ml. of solution. The stock solution was either filtered or allowed to stand in a closed bottle for 24 hours to allow any sediment to settle to the bottom and then the top portion was siphoned into a clean bottle. The viscosities of these solutions were then measured in Ubbelohde viscometers applying kinetic energy corrections to the observed flow times.

The data given in Figs. 6 and 7 for ethyl cellulose F samples were determined in a Ubbelohde viscometer modified so that dilution of the stock solution could be performed within the viscometer. This viscometer was designed by Dr. R. L. Spaulding and its use has been described by Davis and Elliott.[11]

Osmotic Pressure Determinations.—The osmotic pressure measurements were made by the static elevation method in a Herzog and Spurlin[12] osmometer as modified by Fuoss.[13] Membranes of undried cellophane were employed.

Acknowledgment.—It is impossible to list all of those who have contributed to this problem. We would like particularly to mention Dr. R. L. Spaulding, who carried out much of the program; Dr. F. C. Foster and Mr. R. A. Mock, who carried out the osmotic work; and Mr. W. H. Markwood and Dr. J. H. Elliott, who took great interest in the viscosity determinations.

Summary

Free carboxyls present in ethyl cellulose molecules have no effect upon the viscosity of dilute solutions. Neutralization of these carboxyls with metal ions, however, caused an increase in the viscosity of solutions at finite concentrations. This increase was greatest in non-polar solvents and least in solvents containing appreciable water or alcohol. In the latter solvents the intrinsic viscosity was not affected. The viscosity increase was least for sodium, greatest for barium, and intermediate for calcium and magnesium. Bound barium decreased the slope of the reduced osmotic pressure–concentration curve but did not alter the intercept at infinite dilution for those solvents containing alcohol or water.

For polymers containing bound metal ions it is recommended that solvents containing water, alcohol, or acetic acid be used for the determination of viscosity or osmotic pressure and that the values at infinite dilution be obtained by the extrapolation of experimentally determined values. The best results are obtained by using solvents with a low slope of the reduced viscosity–concentration curve and a high slope for the reduced osmotic pressure–concentration plot.

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[11] W. E. Davis and J. H. Elliott, *J. Colloid Sci.*, **4**, 315 (1949).

[12] R. O. Herzog and H. M. Spurlin, *Z. physik. Chem.*, Bodenstein-Festband, p. 239 (1931).

[13] R. M. Fuoss and D. J. Mead, *J. Phys. Chem.*, **47**, 59 (1943).

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

Influence of a CF_3 Group on an Adjacent Double Bond. II

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In a preceding paper,[2] we have shown that $CF_3CH=CH_2$ accepts hydrogen chloride or bromide to yield $CF_3CH_2CH_2Cl$ or $CF_3CH_2CH_2Br$ exclusively, and that it does so only at high temperature, in the presence of a Lewis acid as catalyst. These results were taken as indication that the electronegative induction of the CF_3 group had polarized the double bond to make its central carbon more negative than its outer carbon, and had rendered it less responsive to an electrophilic attack. It seemed, therefore, fair to expect a nucleophilic attack to be favored, yet it is reported that sodium methoxide, primary amines and sodium malonic esters do not add to trifluorinated olefins of the $CF_3CH=CHR$ type,[3] and we could not add acetic acid to either $CF_3CH=CH_2$ or $CF_3CH=CHCF_3$ in the presence of sodium acetate.[4] These results looked illogical, in view of the fact that a triple bond flanked by CF_3 groups is very easily affected by a nucleophilic attack.[5] We had suggested that the experimental failures were due to a parasite reaction, predominant solvolysis of the CF_3

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[1] Socony Vacuum Fellows, 1948-1949 and 1949-1950, respectively.

[2] Henne and Kaye, THIS JOURNAL, **72**, 3369 (1950).

[3] Campbell and Knobloch, Abstracts of Papers, 116th Meeting, Am. Chem. Soc., Atlantic City, September, 1949, p. 6M.

[4] Henne and Pelley, unpublished.

[5] Henne, Schmitz and Finnegan, THIS JOURNAL, **72**, 4195 (1950).

group and not to inability to attack the double bond; we are now supporting this view by experimental evidence.

In the presence of a base, $CF_3CH{=}CH_2$ reacts with ethanol to give a mixture of the expected addition product, $CF_3CH_2CH_2OEt$, and substitution products including $EtOCF_2CH{=}CH_2$, ethyl acrylate and polymers. The substitution products predominate, but polymerize on long standing, and the addition product can then be isolated by mere distillation.

The formula of the addition product is demonstrably $CF_3CH_2CH_2OEt$. Its physical characteristics were found to be the same as those of a product prepared from $CF_3CH_2CH_2ONa$ and C_2H_5Br, in a Williamson type of reaction.[6] They were also found to differ markedly from those of the isomeric ether, $CF_3CH(CH_3)OEt$, prepared from ethyl bromide and the alcoholate of the secondary alcohol $CF_3CHOHCH_3$.

It is therefore proved that, in base as well as in acid catalyzed reactions, addition to a double bond flanked by a CF_3 group occurs in the direction determined by the inductive power of the CF_3 group.

The parasitic solvolysis of a CF_3 group is also observed, but to a much smaller extent, in the easier addition of acetic acid to the triple bond of $CF_3C{\equiv}CCF_3$, as trifluoroacetone replaces the normal product when the experimental conditions are not well adjusted.[5]

Experimental

Addition of Ethanol to $CF_3CH{=}CH_2$.—A 500-ml. autoclave charged with $CF_3CH{=}CH_2$ (57 g. or 0.5 mole), absolute alcohol (200 ml.) and sodium (9 g.) was heated in a steam-bath over a week-end. During that period, the pressure fell from 300 to 110 p. s. i., then to zero when the vessel was brought back to room temperature. Working up of the reaction products gave 12.5 g. (0.13 mole) of recovered $CF_3CH{=}CH_2$, and 40.6 g. (0.33 mole) of a liquid which was predominantly $EtOCF_2CH{=}CH_2$; this is a 75% yield of ether and an 82% material balance. On distillation, this liquid drifted from 59 to 65° and left 13 g. of polymerized material. The distillate fractions had refractive indices which drifted from 1.3365 to 1.3298 then back to 1.3338. After a month of storage, a jelly-like material settled out. After another month, a distillation cut of 16 g. which originally boiled about 62° and had an index of 1.3296 was decanted and redistilled at 751 mm. to give 3.2 g. of distillate ($n^{20}{}_D$ 1.3313) at 62-72.2°, then 5.0 g. ($n^{20}{}_D$ 1.3260) at 72.2-72.3°; polymerized material was left in the flask. The physical properties of synthetic[6] $CF_2CH_2CH_2OEt$ are: b. p. 72.2-72.3° at 746 mm., $n^{20}{}_D$ 1.3258, $d^{20}{}_4$ 1.0593. Agreement was thus quite good. The other distillation cuts proved to be similar mixtures of varying composition.

Synthesis of $CF_3CH(CH_3)OEt$.—Trifluoroacetone, CF_3COCH_3, was reduced with lithium aluminum hydride to the secondary alcohol in 82% yield. This alcohol (20 g. or 0.175 mole) was dissolved in dibutyl ether (20 g.), cautiously treated with metallic sodium (4 g. or 0.175 mole) over a period of thirty minutes, then refluxed until the sodium had completely disappeared. The cooled mixture was transferred to a steel vessel, ethyl bromide (19 g. or 0.174 mole) was added, and the vessel was sealed. After standing overnight, the reaction vessel was heated in a steam-bath for six hours. A maximum pressure of 30 p. s. i. was observed, which dropped to zero when the reaction mixture was cooled to room temperature. Rectification gave 4.5 g., b. p. 50-60°, $n^{20}{}_D$ 1.3390; 6.5 g., b. p. 60-63°, n 1.3245; 3.0 g., b. p. 63-64°, n 1.3225; and 1.5 g., b. p. 64-65°, n 1.3220. From the residue of butyl ether, 2.0 g. of trifluoroisopropyl alcohol was recovered, and from rinsings of the vessel, 1.5 g. of material b. p. 63-67°, n 1.3225 was isolated. Final rectification gave 3.0 g. of fore-run b. p. 45-62° containing some ethyl bromide; 5.5 g. of impure ether b. p. 62-63°, n 1.3270; 7.0 g. of good quality ether b. p. 63-64°, n 1.3219; and a residue of 0.5 g. The good quality ether had $d^{20}{}_4$ 1.062, its atomic refraction for fluorine was computed as AR_F = 1.1, and its fluorine content was 38.2 fd., 40.0 calcd., the usual agreement for this type of analysis.

Summary

A double bond flanked by a CF_3 group is polarized in a way to make the end carbon more positive than the center carbon, *i. e.*, $CF_3{}^{-\delta}CH{=}{}^{+\delta}CH_2$, and is sensitive to nucleophilic attack; addition can, however, be superseded by solvolysis of the CF_3 group. In a base-catalyzed reaction, $CF_3CH{=}CH_2$ and ethanol give mostly the solvolysis product $EtOCF_2CH{=}CH_2$, but the addition product has been isolated and proved to be exclusively $CF_3CH_2CH_2OEt$.

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(6) Henne and Smook, THIS JOURNAL, **72**, 4378 (1950).