1,1-Difluorobutadiene polymerized on standing to a rubber-like material. Maleic anhydride did not form an adduct with 1,1-difluorobutadiene.

Experimental

Fluorination of 3-Bromo-1,1,1,4-tetrachlorobutane.—Powdered antimony trifluoride (3 moles) was placed in a flask equipped with stirrer and reflux condenser. A stream of chlorine was introduced near the bottom of the flask until 90 g. (1.3 moles) had been absorbed. The flask was then carefully cooled in an ice-bath to give a thin film of $SbF_3 \cdot SbF_3Cl_2$ which could be broken up and dispersed throughout the organic compound to be fluorinated. After the addition of $CCl_3CH_2CHBrCH_2Cl$ (550 g., 2 moles), vigorous stirring was begun and the mixture allowed to warm to 40–50° where it was maintained for three hours.

The reaction mixture was made slightly basic with potassium carbonate and steam distilled to give 356 g. of organic product. Fractionation through a 40-cm. column packed with protruded packing gave 16.5 g. (4.5% conversion) of $CF_2ClCH_2CHFCH_2Cl$, b.p. 38–50° (27 mm.), 274 g. (51% conversion) of $CF_2ClCH_2CHBrCH_2Cl$, b.p. 52–57° (11 mm.), and 32 g. (6.2% conversion of $CFCl_2CH_2CHBrCH_2Cl$, b.p. 75–85° (11 mm.).

By carrying out the reaction with antimony fluoride (1 mole), chlorine (0.6 mole) and $CCl_3CH_2CHBrCH_2Cl$ (0.5 mole) at a maximum temperature of 62°, a larger amount (20%) of $CF_2ClCH_2CHFCH_2Cl$ was obtained with a decrease (17%) in the amount of $CF_2ClCH_2CHBrCH_2Cl$ formed.

Several experiments were carried out and the products combined and purified to give the compounds listed in Table I.

1,1-Dichloro-1-fluorobutene-3 and 1-Chloro-1,1-difluorobutene-3.—One mole of $CCl_2FCH_2CHBrCH_2Cl$ was added to a vigorously stirred slurry of zinc dust (1.3 moles) in methanol (380 ml.) maintained at the reflux temperature. The reaction was carried out in three hours. The mixture was steam distilled and the water-insoluble layer separated, dried and fractionated to give 58 g. of $CFCl_2CH_2CH{=}CH_2$, b.p. 84–92°.

By essentially the same procedure, $CF_2ClCH_2CHBrCH_2Cl$ (0.93 mole), zinc dust (1.54 moles) and isopropyl alcohol (110 ml.) gave a 79% yield of $CF_2ClCH_2CH{=}CH_2$, b.p. 47–53°.

1-Chloro-1-fluorobutadiene-1,3.—To a refluxing solution of $CFCl_2CH_2CH{=}CH_2$ (0.4 mole) in ethanol was added dropwise a solution of potassium hydroxide (0.63 mole) in 120 ml. of ethanol. The addition was carried out over a period of 1.5 hours and the mixture was refluxed an additional hour. The product was washed with water, dried and distilled to give 23 g. (53.5%) of 1-chloro-1-fluorobutadiene-1,3, b.p. 52–54.5°.

1,1-Difluorobutadiene.—A solution of potassium hydroxide (2.68 moles) in ethanol (450 g.) was slowly added to $CF_2ClCH_2CH{=}CH_2$ (1.66 moles) in a flask equipped with stirrer, addition funnel and reflux condenser connected to traps cooled in Dry Ice. The heat of the reaction was sufficient to maintain a gentle reflux. Reflux was maintained for one hour after the addition. The product in the cold trap was distilled through a vacuum jacketed column to give 50 g. of $CF_2{=}CHCH{=}CH_2$, b.p. 3.5–5.0°.

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The Association of Acetate with Ammonium and Guanidinium Ions

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It has recently been observed by Walker[1] that amidine salts of carboxylic acids are relatively insoluble. This observation led Walker to suggest that complex formation might occur (even in solution) between amidinium and carboxylate ions. A complex between these ions would be expected to be stabilized by the existence of several possible resonance forms.

If such complex formation were to occur in the particular case of guanidinium ion, it would be of great importance in the chemistry of proteins. All proteins contain guanidinium and carboxylate groups on their side chains, and complex formation between them could play a role in the maintenance of the native protein structure: it could account, for example, for the abnormally large intrinsic ionization constant observed for the carboxyl groups of serum albumin.[2]

Accordingly, the experiments described below were performed to test the extent to which guanidinium ions, as compared to ammonium and potassium ions, affect the activity of acetate ions in solution. The method used was intended to give only the order of magnitude of the interaction, and a more accurate study had been planned if evidence for appreciable interaction had been found. It was found, however, that complex formation between guanidium and acetate ion is only very weak, and probably weaker than that between ammonium and acetate ions. The association constant (K_a) is of the order of 0.5, *i.e.*, less than that for association between the ions of many strong electrolytes (*e.g.*, KNO_3).[3] It is much too weak to cause any appreciable association between guanidinium and carboxylate groups of protein molecules. The association constant would have to be ten times as great to account for the abnormal pK of the carboxyl groups of serum albumin.

Experimental

Reagent grade chemicals were used without further purification. Twenty-five ml. of a solution of 0.0104 M NaOAc and 0.0569 M HOAc was placed in a vessel containing a stirrer and Beckman glass and calomel electrodes, which were connected to a Beckman Model G pH meter. Approximately 3 M KCl was added from a buret in small increments, and the pH measured after each addition. The experiment was repeated using NH_4Cl and $C(NH_2)_3Cl$ in place of KCl, and all three determinations were repeated starting with 25 ml. of a solution of 0.0208 M NaOAc and 0.0561 M HOAc. A constant temperature of 25.0° was maintained. The results are shown in Fig. 1. Volumes were assumed additive in the calculation of concentrations.

In Fig. 2 is shown a plot of $p\mathrm{H} + 0.5\sqrt{\mu}$ for the points at lowest ionic strengths. Below $\mu = 0.05$ these points should fall roughly on a horizontal straight line and should extrapolate at $\mu = 0$ to a value of $pK + \log C^\circ_{\mathrm{OAc^-}}/C^\circ_{\mathrm{HOAc}}$, where $C^\circ_{\mathrm{OAc^-}}/C^\circ_{\mathrm{HOAc}}$ represents the ratio of added acetate and acetic acid concentrations, and pK is $-\log K_a$ for the ionization of acetic acid. Within the probable error of ±0.01 of the pH measurements, the three chlorides are indistinguishable. The best horizontal straight lines through the data give pK values of 4.765 and 4.758, respectively, in good agreement with the value of 4.756, obtained from accurate e.m.f. measurements.[4]

At higher concentrations of the added salts (Fig. 1) the pH in the experiments with ammonium and guanidinium ions falls below the curve obtained with KCl. If no complex formation at all is assumed to take place between po-

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[1] J. Walker, *J. Chem. Soc.*, 1996 (1949).

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[3] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 147.

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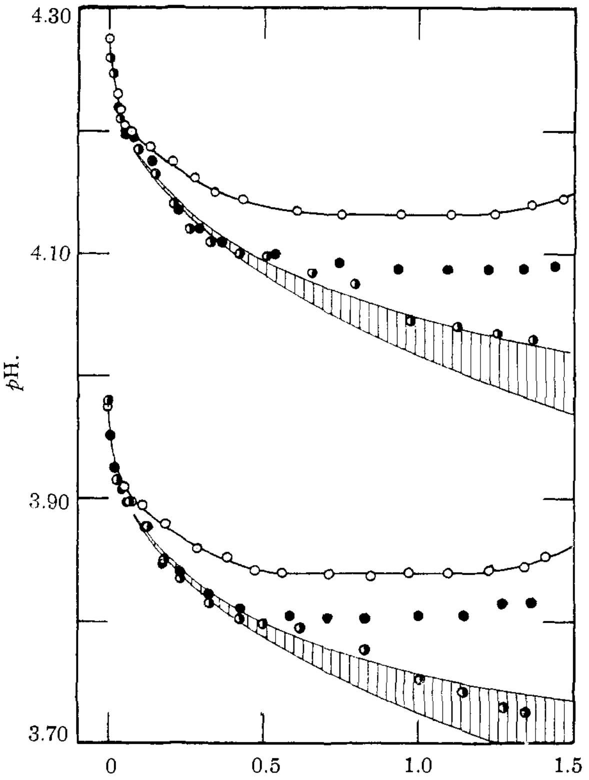

Fig. 1.—The effect of KCl, NH_4Cl and $C(NH_2)_3Cl$ on the pH of acetic acid–acetate mixtures. The upper curves represent the addition of KCl (○), NH_4Cl (◑), and $C(NH_2)_3$-Cl (●) to a solution initially containing 0.0561 M HOAc and 0.0208 M NaOAc. The lower curves represent the addition of the same salts to a solution of 0.0569 M HOAc and 0.0104 M NaOAc. The shaded areas show the possible location of these curves for an association constant of 0.5 between the cation and acetate ion. (Most of the experimental points for salt concentrations below 0.05 have been omitted in this figure.)

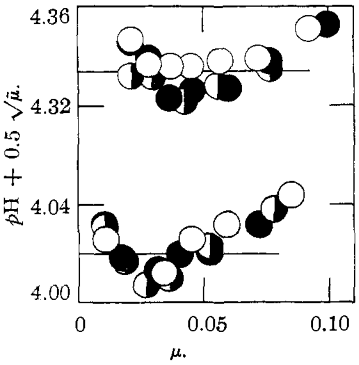

Fig. 2.—Extrapolation to zero ionic strength. The upper and lower curves have the same meaning as in Fig. 1. The experimental points are drawn with a radius of 0.005 pH unit, approximately one half the probable experimental error.

tassium and acetate ions, the pH at any concentration of KCl is given by equation 1

$$pH = pK - \log C^\circ_{OAc^-}/C^\circ_{HOAc} - \log y_{OAc^-}/y_{HOAc} + e \quad (1)$$

where y is used for activity coefficients (molarity scale) and e represents the sum of the errors due to changing liquid junction potentials and possible non-ideality of the glass electrode. The assumption of volume additivity does not introduce an error since only a ratio of concentrations is involved. In the experiments with ammonium and guanidinium ions the same equation applies, except that the concentration of acetate, C_{OAc^-}, is now lower than that calculated from the initial amount added, $C^\circ_{OAc^-}$, because of complex formation. If $\log y_{OAc^-}/y_{HOAc}$ and e are assumed at any given ionic strength to have the same value for each salt, then the pH difference between the curves for NH_4Cl and $C(NH_2)_3Cl$ and that for KCl is

$$\delta pH = -\log C^\circ_{OAc^-}/C_{OAc^-} \quad (2)$$

The concentration of undissociated cation acetate is $C^\circ_{OAc^-}\cdot((1 - C_{OAc^-})/C^\circ_{OAc^-})$. This quantity is much smaller than the concentration, C_s, of added salt, so that the association constant, in concentration units, becomes

$$K_C = \left(1 - \frac{C_{OAc^-}}{C^\circ_{OBc^-}}\right) \Big/ C_s \frac{C_{OAc^-}}{C^\circ_{OAc^-}} = (10^{-\delta pH} - 1)/C.$$

The values of K_c calculated from the data vary from 0.2 to 0.4. Correction for activity coefficients leads to a value of K_a near 0.5. The shaded area of Fig. 1 encompasses theoretical curves of pH *versus* salt concentration based on this value of K_a, and making use of several possible assumptions regarding activity coefficients. Below concentrations of 0.5 M the theoretical curve is insensitive to these assumptions and the points for both ammonium and guanidinium ions fall along the curve within the experimental error. Above 0.5 M the pH difference due to guanidinium ion is less than predicted, suggesting that the value of the association constant between guanidinium and acetate ions may actually be less than 0.5.

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Rearrangement of 2-Aminobicyclo[2.2.2]octene-5 with Nitrous Acid

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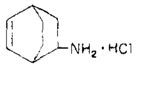
It is well known that the action of nitrous acid on aliphatic primary amines may give rise to a number of products, some possessing the original carbon skeleton and others with a rearranged structure. In view of the ease with which 2-aminobicyclo-[2.2.1]heptene-5 is converted to 3-hydroxynortricyclene[3] with nitrous acid, it seemed of interest to determine whether the homologous compound, 2-aminobicyclo[2.2.2]octene-5 (I) would form the unknown tricyclo[2.2.2.0^{2,6}]octan-3-ol (III) under similar conditions.



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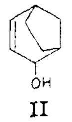

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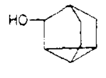
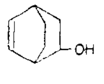


III



IV

Alcohols which might be anticipated as likely

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[1] National Heart Institute, National Institutes of Health, Bethesda, Maryland.

[2] Abstracted in part from a thesis submitted by D. R. Saunders in partial fulfillment of the requirements for the degree of Bachelor of Arts, Princeton University, May, 1953.

[3] W. Parham, W. T. Hunter and R. Hanson, THIS JOURNAL, 73, 5068 (1951).