orated. The residue gave 37 g. (69%) of the silane boiling at 120° (760 mm.).[7]

Phenylsilane with Alloy.—A mixture of 10 g. (0.092 mole) of the silane and 8 cc. of alloy in 250 cc. of anhydrous ether was stirred under nitrogen for 12 hours at room temperature. The solution became red after 4 hours and deep black after an additional 2 hours of stirring. To the mixture was added 43 g. (0.27 mole) of bromobenzene. The solution refluxed vigorously and was decolorized. The ether solution was filtered through a filter stick and evaporated to give a white solid, m.p. 170–228°. Recrystallized from xylene, it melted at 200–228°. The material was shaken with anhydrous ether and filtered. The solid obtained melted at 227–228° and did not depress the melting point of authentic tetraphenylsilane. The yield was 2.1 g. (7%).

Triethylsilane with Alloy.—To 10 cc. of 1:5 sodium-potassium alloy in 250 cc. of anhydrous ether under nitrogen was added 8.5 g. of triethylsilane. The mixture was stirred 30 hours at room temperature without visible reaction. To this mixture was added 30 g. of triphenylchlorosilane in 200 cc. of ether. There was slight reaction as evidenced by slow reflux. The mixture was stirred 2 hours then filtered from the alloy through a filter stick. The residue in the flask was stirred with 100-cc. portions of ether and filtered twice. The combined filtrates were evaporated. Distillation of the residue gave 7.5 g. (88% recovery) of triethylsilane, b.p. 107°. The residue was slightly impure triphenylchlorosilane, 16 g., m.p. 85–92°. The flask residue from filtration was treated with *i*-amyl alcohol to destroy the alloy and ethanol was added. The mixture was then filtered to give 7.3 g. of hexaphenyldisilane, m.p. 340–352°.

Acknowledgment.—The authors gratefully acknowledge the Research Corporation whose financial assistance made this work possible.

LAFAYETTE, INDIANA RECEIVED AUGUST 9, 1951

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[7] A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, THIS JOURNAL, **69**, 2692 (1947).

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

Trifluoropropyne. II. The Triple Bond and the Acetylenic Hydrogen

BY ALBERT L. HENNE AND MAXWELL NAGER[1]

Addition of hydrogen bromide to $CF_3C{\equiv}CH$ yields $CF_3CH{=}CHBr$, illustrating the direction of addition in an electrophilic reaction. Addition of ethanol with base catalysis yields $CF_3CH{=}CHOC_2H_5$. In the presence of mercuric salts, addition of water yields a mixture of CF_3COCH_3 and CF_3CH_2CHO. Polymerization occurs with cuprous salts. Ethane is displaced from C_2H_5MgBr by $CF_3C{\equiv}CH$, and the resulting $CF_3C{\equiv}CMgBr$ condenses normally with acetone to yield $CF_3C{\equiv}CC(CH_3)_2OH$. The acidity of the acetylenic hydrogen (${\equiv}C{-}H$) is discussed.

The influence of a trifluoromethyl group on an adjacent double bond has been reported in directed additions to $CF_3CH{=}CH_2$ by electrophilic,[2] nucleophilic[3] and free radical mechanisms.[4] The influence on a triple bond has been investigated only in nucleophilic additions to $CF_3C{\equiv}CCF_3$,[5,6] and found to occur easily and in stepwise manner. To learn how the CF_3-group affects the direction of addition of the triple bond and the acidity of an acetylenic hydrogen, trifluoropropyne, $CF_3C{\equiv}CH$, was synthesized[7] and is here examined.

Three asymmetrical reagents have been added to the triple bond of $CF_3C{\equiv}CH$, namely hydrogen bromide, ethanol and water. Addition of hydrogen bromide occurred easily and without need of any catalyst, to give only one product, $CF_3CH{=}CHBr$. The direction of addition is thus the same as in $CF_3CH{=}CH_2$ and is attributed to the polarization of the triple bond induced by the CF_3– group; the ease of addition was, however, much greater and since addition stopped with the first molecule of hydrogen bromide, the difference in the deactivations of the double and triple bond is clearly contrasted. A further example is the stepwise hydrogenation of $CF_3C{\equiv}CC(CH_3)_2OH$ shown in the experimental section.

Addition of alcohol in the presence of a base was very exothermic and, under the conditions used, stopped with the formation of the vinyl ether, $CF_3CH{=}CHOC_2H_5$; the direction of addition therefore was again that expected from the electronegativity of the CF_3– group, and the ease of stopping the addition after the first step paralleled the results reported for $CF_3C{\equiv}CCF_3$. By limited hydrogenation, the vinyl ether, $CF_3CH{=}CHOC_2H_5$ underwent splitting rather than addition and CF_3CH_2CHO was isolated, which proved its structure. This split is in accord with the previous observations of Baker and co-workers,[8] that vinyl ethers activated by an electronegative group (*i.e.*, carbonyl, quaternary ammonium) undergo hydrogenolysis easily.

Addition of water could not be brought about without the use of mercuric salts as catalyst, but in their presence a mixture of CF_3CH_2CHO and CF_3COCH_3 was obtained, in which the ketone predominated. We believe this orientation to be due to the formation of an intermediate mercurated complex in which the directing effect of the CF_3-group is overshadowed. Listing the hydration of α,β-acetylenic acids and esters, Johnson[9] states that all give β-keto derivatives, but his list does not include mercuric salt catalyzed hydrations. Hennion[10] states that all terminal alkynes yield 2-ketones, but found both possible ketones in the mercuric salt hydration of 2-heptyne and concluded that "the direction of electromeric polarization in alkyl and dialkyl acetylenes is not seriously affected by hyperconjugation or other factors ascribable to simple alkyl groups." Evidence for the exist-

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[1] Shell Oil Co., Houston, Texas.

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

[3] A. L. Henne, M. A. Shook and R. L. Pelley, *ibid.*, **72**, 4756 (1950).

[4] A. L. Henne and M. Nager, *ibid.*, **73**, 5527 (1951).

[5] A. L. Henne, J. V. Schmitz and W. G. Finnigan, *ibid.*, **72**, 4195 (1950).

[6] D. W. Chaney, U. S. Patent 2,522,566 (1950); *C. A.*, **45**, 2015 (1951).

[7] A. L. Henne and M. Nager, THIS JOURNAL, **73**, 1042 (1951).

[8] R. H. Baker, *et al.*, *ibid.*, **66**, 343 (1944); **68**, 2009 (1946); **70**, 1490 (1948).

[9] A. W. Johnson, "The Chemistry of the Acetylene Compounds, Vol. II, The Acetylenic Acids," Arnold and Co., London, 1950.

[10] G. F. Hennion and C. J. Pillar, THIS JOURNAL, **72**, 5317 (1950).

ence of an intermediate complex is offered by Lucas[11] from kinetics studies, with the conclusion that the intermediate complex consists of one molecule of acetylene and two molecules of mercuric bisulfate. We are essentially in agreement with Lucas and Hennion. Apparently, a complex is formed between trifluoropropyne and the mercuric salt, in which the induction of the CF_3-group which should cause the formation of an aldehyde is mostly overcome, so that only 15% of the total carbonyl compounds is the anticipated CF_3CH_2CHO while the remainder is CF_3COCH_3.

A single experiment was performed to ascertain whether $CF_3C\equiv CH$ could be polymerized by means of the catalyst commonly used for acetylene. After standing a week in an aqueous solution of cuprous and ammonium salts properly aged, a small amount of polymeric material was observed. Polymerization thus appears feasible, and was not examined further.

It is known that $CF_3C\equiv CH$ forms silver,[7,12] copper and mercury[12] salts. An attempt to prepare the sodium salt by use of sodamide in liquid ammonia failed and yielded only tar.

Trifluoropropyne displaced ethane from ethylmagnesium bromide and formed the expected $CF_3C\equiv CMgBr$ which reacted normally with acetone to form a tertiary carbinol, $CF_3C\equiv CC(CH_3)_2OH$. The structure of this carbinol was proven by hydrogenation to $CF_3CH_2CH_2C(CH_3)_2OH$, which in turn was synthesized independently from $CF_3CH_2CH_2MgCl$ and acetone.

When trifluoropropyne was bubbled through a solution of 1-hexynylmagnesium bromide in ether at room temperature, very little propyne was absorbed and a subsequent condensation with acetone yielded only the unfluorinated nonanol, $CH_3(CH_2)_3C\equiv CC(CH_3)_2OH$. When the order of addition was reversed, by feeding hexyne into an ether solution of $CF_3C\equiv CMgBr$, trifluoropropyne was evolved and the subsequent treatment with acetone again yielded the unfluorinated nonanol. These reactions may be represented by the equilibrium $CF_3C\equiv CMgBr + CH_3(CH_2)_3C\equiv CH \rightleftarrows CF_3C\equiv CH + CH_3(CH_2)_3C\equiv CMgBr$, which will be displaced toward the right if the low boiling trifluoropropyne (b.p. −48°) is allowed to escape, even if the acidities of the fluorinated and unfluorinated alkynes are of the same order of magnitude. The second experiment was then repeated at −78°, in an attempt to prevent the evolution of the low boiling $CF_3C\equiv CH$ from the reaction mixture, but $CF_3C\equiv CMgX$ froze out of solution, and the observed lack of interchange became therefore meaningless. Basing our estimation on the work of McEwen[13] and of Conant and Wheland,[14] who obtained complete displacement when the pK_a of two acids differed by two units, our opinion is that, if there is any difference in ionization coefficient between a fluorinated and an unfluorinated alkyne, this difference is less than 10^2. This is in marked contrast with the difference of 10^5 between fluorinated and unfluorinated acetic acids[15] and the difference of 10^4 between ethanol and trifluoroethanol.[16] The results are however, in agreement with the inability[17] to demonstrate experimentally an enhanced α-hydrogen character in $CF_3CH_2CH_3$ and in $CF_3CH_2CF_3$.

R. N. Haszeldine and K. Leedham, Chemical Laboratory, Cambridge, England, have investigated the addition of water, ethanol, hydrogen bromide (ionic and free radical), hydrogen chloride and hydrogen fluoride across $CF_3C\equiv CH$ and $C_2F_5C\equiv CH$, and report results similar to ours (personal communication from R. N. H.).

Experimental

Trifluoropropyne.—Trifluoropropyne was prepared as previously shown[7] and dried by passage through a calcium chloride tower before use.

Addition of Hydrogen Bromide.—A 12 × 1 inch ampule prepared from Carius tubing was cooled with Dry Ice. Into it were distilled 10 g. (0.104 mole) of trifluoropropyne and 15 g. (0.19 mole) of anhydrous hydrogen bromide. The ampule was sealed, allowed to warm up to room temperature and shaken in the dark for 24 hours. The ampule was opened in Dry Ice, then allowed to warm to room temperature to remove the excess of HBr. Distillation of the residue yielded 15 g. (0.86 mole, 83%) of $CF_3CH=CHBr$, b.p. 39–39.5°, $n^{23}D$ 1.3580 (calcd., Br, 45.68; found, Br, 46.03) and 3 g. of high boiling residue. The physical constants for the isomeric $CF_3CBr=CH_2$ have been given previously,[7] b.p. 33–33.5°, $n^{25}D$ 1.3503. In subsequent experiments, it was observed that small amounts of adduct could be obtained by merely mixing the two reactants at −78° and allowing the mixture to warm up to room temperature.

Addition of Ethyl Alcohol.—A solution of 2 g. of sodium in 100 ml. of absolute ethyl alcohol was placed in a three-necked flask fitted with a stirrer, a reflux condenser and a gas inlet tube. Ten grams (0.104 mole) of trifluoropropyne was bubbled in at a rapid rate. The alkyne was absorbed immediately with evolution of sufficient heat to cause the alcohol to reflux vigorously. As soon as all the trifluoropropyne had been added, the reaction was quenched with a large volume of ice-water. The oil which separated to the bottom was dried over anhydrous sodium sulfate and distilled to yield 13 g. (0.192 mole, 89%) of $CF_3CH=CHOC_2H_5$, b.p. 102.5–103°, $n^{21}D$ 1.3494 (Calcd.: C, 42.86; H, 5.04. Found: C, 42.76; H, 5.41). The vinyl ether decolorized aqueous permanganate instantly.

Hydrogenolysis of $CF_3CH=CHOC_2H_5$.—Treatment with Raney nickel in absolute methanol and hydrogen under two atmospheres, in a Parr low pressure hydrogenation apparatus, resulted in a steady uptake of hydrogen above the theoretical amount required for saturation of the double bond. The hydrogenation was stopped short of completion and the reaction mixture poured into water. The Raney nickel was filtered off and 2 g. of the original vinyl ether was recovered. No other water-insoluble matter was obtained. Treatment of the aqueous solution with a saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* HCl yielded a voluminous precipitate which after recrystallization from aqueous alcohol gave yellow needles, m.p. 150–151°; a mixed melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of CF_3CH_2CHO showed no depression.

Addition of Water.—In a Carius type ampule were placed 0.5 g. of $HgSO_4$, 20 ml. of 75% methanol and 5 drops of concentrated H_2SO_4. The ampule was cooled in Dry Ice and 1.5 g. of trifluoropropyne was distilled in. The ampule was sealed and shaken at room temperature for 24 hours, then opened at −78° and allowed to warm up to room temperature. A small amount of $CF_3C\equiv CH$ distilled out and the remainder of the material was diluted with 25 ml. of methyl alcohol and distilled until the distillate no longer gave a positive test with 2,4-dinitrophenylhydrazine. The

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[11] H. J. Lucas, E. R. Kennedy and R. H. Frieman, THIS JOURNAL, 59, 722 (1937).

[12] R. N. Haszeldine, *J. Chem. Soc.*, 588 (1951).

[13] W. K. McEwen, THIS JOURNAL, 58, 1124 (1936).

[14] J. B. Conant and G. W. Wheland, *ibid.*, 54, 1212 (1932).

[15] A. L. Henne and C. J. Fox, *ibid.*, 73, 2323 (1951).

[16] A. L. Henne and R. L. Pelley, *ibid.*, 74, Feb. (1952); also R. L. Pelley, Ph.D. Dissertation, The Ohio State University, 1951.

[17] J. V. Schmitz, Ph.D. Dissertation, The Ohio State University (1949).

residue also gave a negative test. The distillate was diluted to 50 ml. with methyl alcohol. A 5-ml. aliquot was treated with a saturated solution of 2,4-dinitrophenylhydrazine in 2 *N* HCl until no further precipitation occurred. This yielded 0.113 g. of mixed 2,4-dinitrophenylhydrazones, m.p. 116–120°.

A 25-ml. aliquot was treated with an aqueous alcoholic solution of dimedon (dimethyldihydroresorcinol) to yield 0.111 g. of a dimedon derivative which on recrystallization from aqueous alcohol melted at 113–114°; a mixed melting point with an authentic sample of the dimedon derivative of CF_3CH_2CHO showed no depression. This yield corresponds to 16% aldehyde in the mixture; the procedure is not strictly quantitative but it does serve to establish an order of magnitude.

Recrystallization of the mixture of 2,4-dinitrophenylhydrazones from aqueous alcohol failed to give a clean separation. Analysis for nitrogen yielded a value of 19.32%. The calculated value for the 2,4-dinitrophenylhydrazone of either CF_3CH_2CHO or CF_3COCH_3 is 19.18%.

A portion of the mixture of 2,4-dinitrophenylhydrazones was dissolved in absolute benzene and chromatographed on alumina. The dark red band was eluted with 1% alcohol–benzene, followed by 50% alcohol–benzene. Several fractions were collected and an appreciable amount of the material was observed to be irreversibly adsorbed on the column. Evaporation of the solvent yielded only trace amounts of material from all but one fraction. This fraction consisted of fine yellow needles which melted at 138–139°. A mixed melting point with an authentic sample of the 2,4-dinitrophenylhydrazone of CF_3COCH_3 showed no depression.

An attempt to bring about the hydration of $CF_3C\equiv CH$ under identical conditions but in the absence of mercuric sulfate resulted in the recovery of the propyne and a negative test with 2,4-dinitrophenylhydrazine. A modified attempt to hydrate $CF_3C\equiv CH$ in the absence of mercuric salts also failed: 1 g. of $CF_3C\equiv CH$ was distilled into a small ampule containing 5 g. of concentrated sulfuric acid. The ampule was sealed and shaken at room temperature for 24 hours. The ampule was opened and the unreacted propyne allowed to distil out. The remainder of the material was poured into crushed ice. The aqueous solution failed to give a positive test for carbonyl compounds.

Polymerization.—The polymerization of trifluoropropyne was carried out essentially after the technique of Nieuwland, Calcott, Downing and Carter.[18] The catalyst was prepared by mixing 100 g. of $CuCl_2$, 3 g. of HCl, 42.5 g. of H_2O and 30 g. of NH_4Cl in a 500-ml. flask and sealing the flask tightly with a rubber stopper. The flask was placed on a steam-bath for 24 hours after which time no green cupric color could be observed. The catalyst was cooled to room temperature and $CF_3C\equiv CH$ was bubbled in until no further absorption took place. In all, about 2 g. was absorbed. The flask was once again sealed and the reaction mixture was allowed to age at room temperature for one week. At the end of this period, the flask was connected by a glass bend to a condenser and heated so as to effect a steam distillation. A few drops of a greenish fluorinated oil was observed in the distillate.

Preparation of $CF_3C\equiv C(CH_3)_2OH$.—A solution of C_2H_5MgBr in 200 ml. of dry ether was prepared from 8.5 g. (0.35 mole) of magnesium turnings and 21.2 g. (0.195 mole) of C_2H_5Br. A Dry Ice tail trap and a bubbler were attached to the reflux condenser, and 19 g. (0.197 mole) of $CF_3C\equiv CH$ was bubbled into the Grignard solution. When the evolution of ethane had ceased, the small amount of low-boiling material in the Dry Ice trap was recycled until no further absorption of the propyne took place. Two grams (0.017 mole) of unabsorbed $CF_3C\equiv CH$ was recovered in this manner. Acetone, 17.3 g. (0.3 mole), was added dropwise to the Grignard reagent. The salt was hydrolyzed with saturated aqueous ammonium chloride and the ether solution decanted and combined with the ether washings of the solid mass. The ether was removed and distillation yielded 20.5 g. (0.135 mole, 75% based on the amount of $CF_3C\equiv CH$ consumed) of $CF_3C\equiv CC(CH_3)_2OH$, b.p. 110–111°, $n^{20}D$ 1.3629 (Calcd.: C, 47.4; H, 4.64. Found: C, 47.9; H, 5.45) and 4 g. of tarry residue.

In a similar manner, $CH_3(CH_2)_3C\equiv C(CH_3)_2OH$ was prepared from $CH_3(CH_2)_3C\equiv CH$ in 80% yield.

Hydrogenation of $CF_3C\equiv CC(CH_3)_2OH$.—The hydrogenation of 15.2 g. (0.1 mole) of $CF_3C\equiv C(CH_3)_2OH$ was carried out with 0.5 g. of Raney nickel and 30 ml. of absolute ethanol in a Parr low pressure hydrogenation apparatus. The uptake of the first mole of hydrogen was extremely rapid and exothermic. The second mole of hydrogen was taken up easily but at a markedly slower rate. The Raney nickel was filtered off and the filtrate poured into several times its volume of water. The oil which separated was dried and distilled to yield 14.5 g. (0.095 mole, 95%) of $CF_3CH_2CH_2C(CH_3)_2OH$, b.p. 129°, $n^{20}D$ 1.3645.

Preparation of $CF_3CH_2CH_2C(CH_3)_2OH$.—A solution of 53 g. (0.4 mole) of $CF_3CH_2CH_2Cl$ in 200 ml. of dry ether was added dropwise to a well-stirred mixture of 36.5 g. (1.5 moles) of magnesium turnings in 300 ml. of dry ether. When the addition was complete, 29 g. (0.5 mole) of acetone was slowly added to the Grignard solution. The salt was hydrolyzed with saturated aqueous ammonium chloride and the ether solution decanted and combined with the washings of the solid mass. The ether was stripped off and distillation yielded 58 g. (0.37 mole, 93%) of $CF_3CH_2CH_2C(CH_3)_2OH$, b.p. 129–129.5°, $n^{20}D$ 1.3645.

Grignard Interchange Experiments.—(a) A 0.2 molar solution of $CH_3(CH_2)_3C\equiv CMgBr$ was prepared in ether and 17 g. (0.18 mole) of $CF_3C\equiv CH$ was bubbled in. Fourteen grams of $CF_3C\equiv CH$ was recovered from the tail Dry Ice trap attached to the reaction flask. When the solution failed to absorb more $CF_3C\equiv CH$, 11.8 g. (0.2 mole) of acetone was added slowly. The hydrolysis of the Grignard salt was carried out with saturated aqueous ammonium chloride. Removal of the ether and distillation yielded 19 g. (76%) of $CH_3(CH_2)_3C\equiv CC(CH_3)_2OH$, b.p. 89–91° (31 mm.), $n^{20}D$ 1.3920. (b) A 0.18 molar solution of trifluoropropynylmagnesium bromide in ether was prepared and 16.4 g. (0.2 mole) of 1-hexyne was added dropwise. During the addition, 15 g. of $CF_3C\equiv CH$ was evolved and collected. When the addition of the hexyne was completed, 11.6 g. (0.2 mole) of acetone was added. The hydrolysis of the salt was carried out with saturated aqueous ammonium chloride. Removal of the ether and distillation yielded 16 g. (0.112 mole, 56%) of $CH_3(CH_2)_3C\equiv CC(CH_3)_2OH$. (c) When the preceding experiment was carried out at −78°, a grayish-white solid suspension was observed in the reaction flask before the addition of the 1-hexyne. After the addition of acetone the flask was allowed to warm to room temperature and no $CF_3C\equiv CH$ was evolved. Hydrolysis and removal of the ether yielded on distillation 17 g. (0.112 mole, 70%) of $CF\cdot C\equiv CC(CH_3)_2OH$, b.p. 110−111°, $n^{20}D$ 1.3629.

Columbus, Ohio Received August 9, 1951

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[18] J. A. Nieuwland, W. S. Calcott, F. B. Downing and A. S. Carter, This Journal, 53, 4197 (1931).