where (I) is derived from the primary form of the allylbenzene carbanion. It was assumed that the acid derived from the secondary form of the allylbenzene carbanion would have extinction coefficients of approximately zero at 294 mμ, 20 at 283 mμ and $\epsilon^{\text{mixture}}_{\text{molar}}$ was accordingly corrected. The results are tabulated in Table III.

Summary

1. Sodium allylbenzene has been prepared and allowed to react with a series of α-haloacetic acids to give mixtures of substituted γ-benzalbutyric and hydrocinnamic acids.

2. The observed results have been discussed with regard to the possible influences which may alter the course of the reaction.

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

Perfluoro-2-butyne and its Hydrogenation Products

BY ALBERT L. HENNE AND WILLIAM G. FINNEGAN

Preceding articles have reported fluorinated compounds with a CF_3 group adjacent to another function, double bond, acid, alcohol or halide. A compound, $CF_3C{\equiv}CCF_3$, with a triple bond flanked by two CF_3 groups has now been prepared[1] and examined. In line with our expectations, the triple bond is so sluggish that it does not appreciably accept halogens at room temperature; it is however very sensitive to alkaline oxidation, and breaks quantitatively to give two moles of trifluoroacetic acid. In addition, it easily accepts one mole of hydrogen on Raney nickel to yield $CF_3CH{=}CHCF_3$, presumed to be the *cis*-isomer; it takes up two molecules of hydrogen with equal facility to form $CF_3CH_2CH_2CF_3$.

Preparation of $CF_3C{\equiv}CCF_3$.—A three-liter flask heated on an electric nest is equipped with a sealed stirrer and a reflux condenser of the "down draft and overflow return" type the outlet of which leads to a Dry Ice-cooled receiver. This type of condenser permits high rates of reflux without flooding; it receives vapors at its top and syphons the condensate from its bottom back to the boiler. The flask is loaded with six moles (420 g.) of zinc dust, six moles (1380 g.) of dried and distilled $CF_3CCl{=}CClCF_3$[2] and 900 ml. of absolute alcohol. Constant stirring and refluxing is maintained for ten days, with a liquid temperature of about 40°. At the end of this period, distillation is performed until the liquid in the flask reaches 78°; the distillate is combined with the reaction product which had been collected in the chilled receiver during the ten-day period. Rectification of this combined material yields 477 g. (49.1% conversion, 54.4% net yield) of $CF_3C{\equiv}CCF_3$, b. p. −24.7° to −24.5°; 5 g. of an intermediate fraction, b. p. −20° to +24°; 14 g. of impure $CF_3CH_2CH_2CF_3$, b. p. 25° to 27°; 322 g. of impure $CF_3CCl{=}CHCF_3$ (mixed *cis* and *trans*), b. p. 31 to 37°; 31.5 g. of an intermediate cut; and 140 g. of recovered $CF_3CCl{=}CClCF_3$, b. p. 65 to 67°. The material balance is thus 90%. Refractionation of the (−20 to +24°) intermediate yielded 4 g. of a compound boiling within one degree of 6°; this will be referred to as "the 6° cut." Wojcik[1] mentions a (0 to +5°) cut, and states that it is "a C_4F_6 isomer."

The main reaction product was quantitatively oxidized in a sealed vessel by the procedure previously reported[3] to give 1.74 moles of trifluoroacetic acid per mole of $CF_3C{\equiv}CCF_3$, identified as its amide. The next most important product, $CF_3CCl{=}CHCF_3$, was found identical with a by-product obtained in the preparation of $CF_3CCl{=}CClCF_3$ and previously reported[2] as "presumably $CF_3CCl{=}CFCF_3$" on account of its ability to yield two moles of trifluoroacetic acid when oxidized. Recalculation of the atomic refraction AR_F for fluorine on this new basis gave the excellent value of 1.07.

Hydrogenation of $CF_3C{\equiv}CCF_3$.—In a one-liter pressure vessel, 3.43 moles (556 g.) of $CF_3C{\equiv}CCF_3$ was hydrogenated by means of 3.5 moles of hydrogen at an initial pressure of 100 atm. and with 5 g. of Raney nickel and 10 ml. of absolute alcohol as catalyst. Reduction started at room temperature and proceeded rapidly with a large evolution of heat. A leak caused some material loss. The reduced material was distilled from the pressure vessel (heated to 50°) directly into a receiver cooled with Dry Ice. Rectification of this distillate gave 100 g. of recovered $CF_3C{\equiv}CCF_3$, and 368 g. of material boiling from 0 to +33°. The latter material was refractionated to give 119 g. of $CF_3CH_2CH_2CF_3$ and 191 g. of $CF_3CH{=}CHCF_3$. The material balance in the reduction step was only 83% on account of the leakage; the distillation steps had a material balance of 90%.

Identification.—The saturated derivative $CF_3CH_2CH_2CF_3$ was analyzed for fluorine: 68.6% calcd., 68.2% found. The identity of the olefin and that of the alkyne are derived from the facts that both yielded two molecules of CF_3CO_2H on oxidation, and were transformed into the analyzed

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(1) Others have also obtained this derivative recently: W. T. Miller, Cornell, and E. T. McBee, Purdue, private communications; Wojcik, American Chemical Society fall meeting, New York, N. Y., 1947.

(2) Henne and Trott, THIS JOURNAL, 69, 1820 (1947).

(3) Henne and Zimmerschied, *ibid.*, 69, 281 (1947).

paraffin by acceptancy of one mole and two moles of hydrogen, respectively; this was done quantitatively in independent, conventional experiments, using Raney nickel, and differing only by the amount of hydrogen supplied. The Bayer (potassium permanganate) test was positive while the bromine in carbon tetrachloride negative for both the alkyne and the alkene.

Physical Tests.—All three compounds are soluble in light paraffins, toluene, carbon tetrachloride, acetone, alcohol and ether as far down as −25°; they are also soluble in acetic acid above its freezing point. At −78° the alkyne was insoluble in all those solvents which were still liquid, while the olefin and the paraffin were not observed. In concentrated sulfuric acid, all three were insoluble at room temperature.

A dielectric constant measurement on the alkyne at −30°, by the heterodyne beat procedure showed a value comparable to that of a saturated straight-chain paraffin, indicative of a substantially zero dipole moment. The olefin, however, had a dielectric constant of approximately 20.8 at +20°, as compared to 4.3 for ether and 80.0 for water. This indicates a substantial dipole moment and the *cis*-configuration was therefore assigned to this compound.

The alkyne boils remarkably low; a contrast between hydrocarbons and their perfluorinated derivatives emphasizes the fact that the fluorinated derivatives are less associated, probably not at all.

Contrasting boiling points.

$CH_3CH_2CH_2CH_3$	− 0.4°	− 1.4°	$CF_3CF_2CF_2CF_3$
$CH_3CH{=}CHCH_3$	+ 1.0°	+ 0.4°	$CF_3CF{=}CFCF_3$
$CH_3C{\equiv}CCH_3$	+27.2°	−24.6°	$CF_3C{\equiv}CCF_3$

Addition of hydrogen to the triple bond affects the molecular weight negligibly but permits hydrogen bonding[4] in the resulting product, and the boiling point rises consequently by nearly 50°.

$CF_3C{\equiv}C{-}CF_3$	−24.6°	+24.6°	$CF_3CH_2CH_2CF_3$

The importance of hydrogen bonding is also shown by the fact that both $CF_3CH{=}CHCF_3$ and $CF_3CH{=}CClCF_3$ boil at nearly the same temperature (33° and 34°, respectively) in spite of their different masses, a case similar to that of CHF_3 and $CClF_3$ (−82° and −81°). An additional example is the contrast between CF_3-$CH{=}CClCF_3$ and $CF_3CF{=}CFCF_3$, boiling about +35° and 0°, respectively, in spite of their almost identical molecular masses.

Physical Properties.—Conventional physical measurements[5] were made after repurification, with the accuracy claimed by the decimals shown in the table:

Compound	$CF_3C{\equiv}CCF_3$	$CF_3CH{=}CHCF_3$	$CF_3CH_2CH_2CF_3$	$CF_3CH{=}CClCF_3$
B. p., °C., 760 mm.	− 24.6	+33.2	+24.6	+ 34.4
F. p., °C.	−117.4	−90.5	−53.7	−106.1
d_4		1.4128 at 0°	1.3702 at 0°	1.4909 at 20.0°
n_D		1.2825 at 2.2°	1.2732 at 3.0°	1.2996 at 20.0°
AR_F		1.16	1.12	1.07

The atomic refraction for fluorine, AR_F, was computed in the conventional way by subtracting from the experimental molecular refraction the customary increments for C, H, Cl and double bond.

Infrared Spectrum.—Infrared adsorption spectra were taken on the alkyne, *cis*-alkene and the 6° by-product in order to obtain information as to the structure of the 6° by-product. Inasmuch as the alkyne is symmetrical, it would show only C–F bond absorption in the infrared, and any other absorption would be attributable to the 6° material present as an impurity. The alkyne and 6° cut absorption curves are indeed essentially the same.

Strong C–F bond absorption was noted from 7 to 10 microns with the C—F bond overtone at 4.2 microns for all three compounds. A major C—H bond stretching band was obtained at 3.35 microns with the alkene and a smaller one at the same place with the 6° cut. This latter is probably due to $CF_3{-}CH{=}CH{-}CF_3$ (*trans*) or $CF_3{-}CH_2{-}CH_2{-}CF_3$ as impurities in the 6° cut, as this absorption is not present in the alkyne absorption curve. A strong absorption from 6.4 to 7.1 microns in the alkene, absent in the alkyne and 6° cut curves, could be attributed to hydrogen bonding. A very strong absorption at 5.95 microns in the alkene curve is attributed to C=C; this absorption is absent in the alkyne curve and is present to a smaller degree in the 6° cut curve. Thus the 6° by-product is contaminated with olefinic material similar in nature to the *cis*-alkene; this is probably the *trans*-alkene.

The alkyne and 6° cut curves show five bands from 6 to 7 microns with the strongest at 6.4 microns; these bands are absent in the alkene curve and could thus be attributed to components of an allenic type of structure. Two absorption peaks at 4.7 and 4.85 microns, respectively, appear in the alkyne and 6° cut curves, but only the 4.7 micron peak appears in the olefin. The 4.7 micron peak is attributed to partial allenic character of the following types: $CF_3\overset{\cdots}{-}C\overset{\cdots}{\equiv}C\overset{\cdots}{-}CF_3$, $CF_3\overset{\cdots}{-}CF\overset{\cdots}{-}C{=}CF_2$, and $CF_3\overset{\cdots}{-}CH\overset{\cdots}{-}CH\overset{\cdots}{-}CF_3$.

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[4] The term "hydrogen bonding" is used in extension of the conventional cases, on the basis that fluorinated compounds containing hydrogen invariably boil higher than the perfluoro compounds: $CH_2F_2 > CF_4$; $CHF_2CO_2H > CF_3CO_2H$; $CHF_2COCl > CFCOCl$; etc. . . . The hydrogen is attached to an electronegative group (CF_2) instead of electronegative atom (O).

[5] Weissberger, "Techniques of Organic Chemistry," Interscience Publishers, New York, N. Y., Vol. I, New York, N. Y., 1945. For freezing point, Mair, Glasgow and Rossini, *J. Research Natl. Bur. Standards*, **26**, 591 (1941).

The peak at 4.85 microns could be attributed to absorption of the C=C=C structure.

Because of the symmetry of the alkyne and similarities between the absorption curves of the alkyne and 6° by-product curves, and because of the almost complete dissimilarity between these and the alkene absorption curves, the following conclusions are drawn.

(1) The impurity of the alkyne is essentially the 6° by-product material.

(2) The 6° by-product material is probably the perfluorinated methylallene, $CF_3—CF=C=CF_2$, obtained by rearrangement of the alkyne by zinc chloride during its synthesis.

Summary

The preparation and physical properties of $CF_3C \equiv CCF_3$, $CF_3CH=CHCF_3$, $CF_3CH_2CH_2CF_3$ and $CF_3CH=CHClCF_3$ are reported.

COLUMBUS, OHIO RECEIVED MAY 6, 1948

[CONTRIBUTION FROM ST. OLAF COLLEGE]

Preparation and Reactions of α,β-Dichlorovinyltrichlorosilane

BY C. L. AGRE

Recently several publications[1] have disclosed the addition of trichlorosilane and related silanes to ethylenic and acetylenic hydrocarbons under the activation of peroxide, ultraviolet light, or elevated temperature below the decomposition point of the reactants. The results, in general, are illustrated by the addition of trichlorosilane to propylene and to acetylene to yield, respectively, *n*-propyltrichlorosilane and 1,2-bis-(trichlorosilyl)-ethane. The yields of the products varied appreciably and were dependent both on the experimental conditions and on the nature of the reactants. Silicon tetrahalides were reported not to add to the unsaturated materials.

The present investigation, based in part on work done several years ago, is somewhat parallel to the above efforts but differs primarily in that the reaction was carried out at a temperature appreciably above the decomposition temperature of the unsaturated compound charged to the apparatus. Preliminary experiments showed that trichloroethylene and trichlorosilane, in the presence of a peroxide catalyst, gave very little addition product under the experimental conditions employed. It was thought worthwhile, however, to pass the mixture through a hot tube at atmospheric pressure to determine the effect of the greatly elevated temperature. The reaction thus would be run under conditions amenable to commercial practice should interesting products be obtained. It was observed that at a temperature of about 500° a mixture of trichloroethylene and trichlorosilane evolved hydrogen chloride and gave a good yield of a product identified as α,β-dichlorovinyltrichlorosilane. The reaction can be explained simply according to the equations

$$Cl_2C=CHCl + HSiCl_3 \longrightarrow Cl_2HCCHClSiCl_3 \qquad (1)$$

$$Cl_2HCCHClSiCl_3 \longrightarrow HCl + ClHC=CClSiCl_3 \text{ I} \qquad (2)$$

It is more likely, however, that hydrogen chloride first is eliminated from the trichloroethylene to give dichloroacetylene. In the absence of trichlorosilane, and to a very limited extent in its presence, the dichloroacetylene almost instantaneously polymerizes to give hexachlorobenzene in a manner parallel to the formation of benzene from acetylene. However, the dichloroacetylene preferentially adds to trichlorosilane to give the observed product I.

$$Cl_2C=CHCl \longrightarrow HCl + ClC \equiv CCl \qquad (3)$$

$$ClC \equiv CCl + HSiCl_3 \longrightarrow ClHC=CClSiCl_3 \text{ I} \qquad (4)$$

In similar manner, I is obtained in low yield from *s*-tetrachloroethane and trichlorosilane. The first step apparently is the elimination of hydrogen chloride[2] to form trichloroethylene, which then reacts as indicated above.

It is reported[3] that a halogen atom in a position beta (as contrasted to alpha and gamma) to $-SiCl_3$ has unusual activity and upon titration reacts as illustrated in the example

$$ClCH_2CH_2SiCl_3 + 4NaOH \longrightarrow CH_2=CH_2 + Si(OH)_4 + 4NaCl \qquad (5)$$

It was obviously of interest to determine if the beta-chlorine atom in I would have similar activity. Titration of I with standard base showed the presence of three active chlorine atoms, which are the three chlorine atoms attached to silicon. The presence of the ethylenic bond in the side chain has, in the customary manner, deactivated the adjoining chlorine atoms to the extent that the beta-chlorine atom does not have the unusual activity observed in the saturated analog, β-chloroethyltrichlorosilane.

The silane I reacts with ethylmagnesium bromide in the expected manner to give α,β-dichlorovinyltriethylsilane (II)

$$ClHC=CClSiCl_3 + 3C_2H_5MgBr \longrightarrow ClHC=CClSi(C_2H_5)_3 \text{ II} \qquad (6)$$

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[1] (a) Sommer, Pietrusza and Whitmore, THIS JOURNAL, **69**, 188 (1947); (b) Burkhard and Krieble, *ibid.*, **69**, 2687 (1947); (c) Barry, *ibid.*, **69**, 2916 (1947); (d) Miller and Schreiber, U. S. Patent 2,379,821 (1945); (e) Pietrusza, Sommer and Whitmore, THIS JOURNAL, **70**, 484 (1948).

[2] British Patent 575,530; *Chem. Abst.*, **41**, 6891 (1947).

[3] (a) Sommer and Whitmore, THIS JOURNAL, **68**, 485 (1946); (b) Sommer, Dorfman, Goldberg and Whitmore, *ibid.*, **68**, 488 (1946).