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

Trifluoromethylated Butadienes

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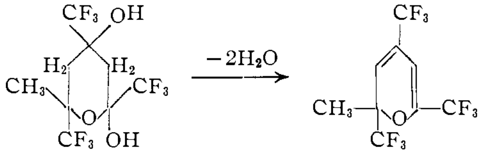
RECEIVED MARCH 6, 1954

The synthesis of $CF_3—CH=CH—CH=CH_2$, $CF_3—CH=CH—C(CH_3)=CH_2$ and $CH_2=C(CF_3)CH=CH_2$ is reported. The failure to obtain $CH_2=C(CF_3)C(CF_3)=CH_2$ is shown to be due to the preferential formation of cyclic compounds I and II.

True copolymerization of fluorinated monomers with unfluorinated dienes is difficult and limited in range. To overcome these difficulties, the monomeric fluorinated dienes $CF_3—CH=CH—CH=CH_2$, $CF_3—CH=CH—C(CH_3)=CH_2$ and $CH_2=C(CF_3)—CH=CH_2$ have been prepared. An attempt to synthesize $CH_2=C(CF_3)—C(CF_3)=CH_2$ by dehydration of the pinacol from CF_3COCH_3 failed to give the desired product, because pinacol formation was superseded by cyclic trimerization to I, the dehydration of which gave II.



I II

For the preparation of $CF_3—CH=CH—CH=CH_2$, the starting dione $CF_3\text{-}CO\text{-}CH_2\text{-}CO\text{-}CH_3$ was reduced to the diol $CF_3\text{-}CHOH\text{-}CH_2\text{-}CHOH\text{-}CH_3$ which easily lost one mole of water to form $CF_3—CHOH—CH=CH—CH_3$ but could not effectively be dehydrated further to the diene on polar reagents. However, pyrolysis of the diacetate of the diol gave a good yield of $CF_3—CH=CH—CH=CH_2$, b.p. 45–46°, maleic anhydride adduct, m.p. 95.5°.

For the preparation of $CF_3—CH=CH—C(CH_3)=CH_2$, the same dione was treated with two moles of methylmagnesium bromide to evolve one mole of methane first, then yield the keto tertiary alcohol $CF_3\text{-}CO\text{-}CH_2C(OH)Me_2$, which easily lost water to give $CF_3—CO—CH=CMe_2$. This ene-one was reduced with aluminum isopropoxide to $CF_3CHOHCH=CMe_2$, the acetate of which was pyrolyzed to the desired $CF_3—CH=CH—C(CH_3)=CH_2$, b.p. 75°, maleic anhydride adduct, m.p. 127–128°, with polymerization.

For the preparation of $CH_2=C(CF_3)CH=CH_2$, an attempted condensation of acetylene with CF_3COCH_3 gave a 1:2 reaction product instead of the desired 1:1 condensate $CF_3—C(OH)(CH_3)C\equiv CH$, and the same observation was made with acetone and acetylene which could not be made to yield anything but $Me_2C(OH)C\equiv CC(OH)Me_2$. When CF_3COCH_3 was treated with ethylmagnesium bromide, one-third of the ketone underwent reduction to $CF_3CHOHCH_3$, but the main part condensed with the Grignard reagent to yield $CH_3C(OH)(CF_3)C_2H_5$. Dehydration of this carbinol gave a mixture of olefins $CH_2=C(CF_3)C_2H_5$ and $CH_3—C(CF_3)=CH—CH_3$ which was not separated, but was allylically brominated with N-bromosuccinimide to a mixture of allyl bromides $CH_2=C(CF_3)—CHBr—CH_3 \rightleftarrows CH_2Br—C(CF_3)=CH—CH_3 \rightleftarrows CH_3—C(CF_3)=CHCH_2Br \rightleftarrows CH_3—C(CF_3)Br—CH=CH_2$. When treated with triethylamine, this mixture yielded the desired $CH_2=C(CF_3)\text{-}CH=CH_2$, b.p. 34–35°, maleic anhydride adduct, m.p. 107–107.5°.

The failure of the $CH_2=C(CF_3)C(CF_3)=CH_2$ synthesis is explained as follows. When CF_3COCH_3 was dropped on sodium at 0°, a solid was formed which was first thought to be the sodium pinacolate. After hydrolysis, a crystalline product, m.p. 93 to 100°, was obtained from hot benzene, the analysis and molecular weight determination of which proved it to be a trimer of the starting ketone. This trimer did not give a phenylhydrazone, and its infrared spectrum showed the presence of OH, F but no C=O or C=C; this led to the consideration of a cyclic formulation $CH_2\text{-}C(CF_3)(OH)\text{-}CH_2\text{-}C(CF_3)(OH)\text{-}CH_2\text{-}C(CF_3)(OH)$ the dehydration of which would have given nonafluoromesitylene $C(CF_3)=CH—C(CF_3)=CH—C(CF_3)=CH$. However, a Zerewitinov determination indicated that the trimer had only two instead of three "active" hydrogens, and its dehydration over P_2O_5 or H_2SO_4 gave a diene, b.p. 119°, molecular weight 300, which absorbed two moles of hydrogen, and had an analysis calling for one oxygen atom, but did not have a C=O nor an OH group. Formulas I and II consequently were adopted. Formula II was confirmed by the brilliant magenta color caused by aluminum chloride in chloroform, as one electron pair of the ring oxygen can coördinate to form an ionized complex with resonating cation.

Experimental

$CF_3CHOHCH_2CHOHCH_3$.—Three batches of $CF_3COCH_2COCH_3$ (40 g. each) were reduced with Raney nickel in a glass-lined steel bomb at pressures of about 150 atm. and a temperature of 100°. An aggregate amount of 103 g. (85% yield) of diol was obtained, b.p. 78° at 3 mm., b.p. 190–192° at 747 mm., $n^{20}D$ 1.3798, d^{20}_4 1.294, MR obsd. 28.22, AR_F 1.06; % F 35.7, calcd. 36.0. The only other product encountered was the half-reduced ketol assumed to be $CF_3COCH_2CHOHCH_3$, b.p. 58° at 3 mm., b.p. 170–171° at 747 mm., $n^{20}D$ 1.3719, d^{20}_4 1.3031, which was returned to the next hydrogenation run. The pH of the diol was measured continuously during neutralization, and the following values read off the curve were translated into K_A values: at one-fourth neutralization pH 11.18, $K_A = 6.6 \times 10^{-12}$; at one-half neutralization, pH 11.45, $K_A = 3.6 \times 10^{-12}$. This order of magnitude characterizes alcohols flanked by one CF_3 group: for example, $CF_3CHOHCH_3$ has $K_A = 6 \times 10^{-12}$.

Dehydration to $CF_3CH=CH—CH=CH_2$.—Acetic anhydride in 10% excess and one drop of sulfuric acid added cautiously to the diol gave, in 88% yield, a diacetate, b.p. 188–190°, $n^{20}D$ 1.3809; but for pyrolysis the diacetate need not be isolated from acetic acid and the excess of acetic anhydride. Pyrolysis was carried out in a Pyrex tube heated to 470°, filled with short sections of Pyrex tubing, swept by a slow stream of nitrogen, and at the rate of 15 g. of diol an hour. The pyrolyzed material boiling above 46° was recycled twice. A 75% yield of $CF_3CH=CH-CH=CH_2$ was thus obtained, b.p. 45.2–45.9°, n^{20}_D 1.3571, d^{20}_4 1.027. *Anal.* Found: C, 49.6; H, 4.1. Calcd.: C, 49.1; H, 4.1. The recrystallized maleic anhydride adduct was obtained in 38% yield, m.p. 93.5 to 94.5°; % F 24.6, calcd. 25.8.

In another test, the diol was transformed in 75% yield to its di-trifluoroacetate b.p. 158–160°, n^{20}_D 1.3350, but this was abandoned when pyrolysis yielded only a 40% yield of diene, with much decomposition.

$CF_3COOH=CMe_2$.—Two moles of methylmagnesium bromide was added to one mole of $CF_3COCH_2COCH_3$. One mole of methane was evolved first, then condensation occurred normally. After hydrolysis, distillation caused a spontaneous dehydration, and a two-phased mixture distilled over around 85°. After decantation and drying, the distillate gave a 33% yield of crude $CF_3COCH=CMe_2$, b.p. 108°, n^{20}_D 1.3802; % F 36.6, calcd. 37.6. From the distillation residue, a 26% yield of crude $CF_3COCH_2C(OH)Me_2$, b.p. 30° at 2 mm., was recovered, which was easily dehydrated to bring the final yield of olefinic ketone to 55%.

Reduction to $CF_3CHOHCH=CMe_2$.—By conventional aluminum isopropoxide reduction, the olefinic ketone was reduced in 60% yield to crude $CF_3CHOHCH=CMe_2$, b.p. 139–140, n^{20}_D 1.3823. *Anal.* Found: C, 46.4; H, 6.0. Calcd.: C, 46.8; H, 5.8.

Dehydration to $CF_3CH=CH-C(CH_3)=CH_2$.—The olefinic alcohol was acetylated, and the crude acetate, b.p. about 122°, was pyrolyzed as above to give in 58% yield $CF_3CH=CH-C(CH_3)=CH_2$, b.p. 74–75°, n^{20}_D 1.3780, d^{20}_4 1.052. *Anal.* Found: C, 53.0; H, 5.5. Calcd.: C, 52.9; H, 5.2. Polymerization occurred promptly on standing. The maleic anhydride adduct was obtained in 17% yield, m.p. 127–128°, % F 23.9, calcd. 24.3, and decomposed to a polymer on standing.

$CF_3C(OH)(CH_3)C_2H_5$.—One mole of ethylmagnesium bromide and 0.9 mole of CF_3COCH_3 gave 32 g. (31% yield) of $CF_3CHOHCH_3$, b.p. 78°, by reduction and 65 g. (51% yield) of crude $CF_3C(OH)(CH_3)C_2H_5$, b.p. 96–97°, by condensation. Alternatively, the acetates, b.p. 87 and 112°, respectively, may be separated rather than the alcohols.

Dehydration to **Mixed Olefins**.—The crude acetate of the above tertiary alcohol (65 g.) was pyrolyzed to give 37.5 g. (66% yield) of mixed $CF_3C(CH_3)CH=CH_2$ and $CH_2=C(CF_3)C_2H_5$, b.p. 38–40°, n^{20}_D 1.3258.

$CH_2=C(CF_3)CH=CH_2$.—The above mixture of olefins (33 g.) was allylically brominated by refluxing it with N-bromosuccinimide (48 g.) in dry carbon tetrachloride under a sun-lamp for eight hours. The crystals of succinimide were filtered off, and the filtrate distilled, to remove 4.5 g. of recovered olefins first, then the solvent. The distillation residue above 78° was added to 100 ml. of triethylamine, and this caused an immediate precipitation. The dehydrobromination was completed by heating gently so as to permit distillation of $CH_2=C(CF_3)CH=CH_2$, in 20% yield, b.p. 34–35°, n^{20}_D 1.3485, d^{20}_4 1.064. *Anal.* Found: C, 48.8; H, 4.3. Calcd. C, 49.3; H, 4.1. Maleic anhydride adduct, m.p. 107–107.5° F, 25.7; calcd. 26.0, obtained in 76% yield.

Sodium and CF_3COCH_3.—Sodium (11.5 g.) was cut into small cubes and placed in a flask cooled with an ice-bath, and fitted with a stirrer and an ice-water reflux condenser. Trifluoroacetone (48 g.) was added dropwise, with constant stirring. A crystalline slurry was formed, which made further stirring impractical. Twelve hours later, the remaining pieces of sodium were picked out and destroyed in ethanol. Titration of the resulting alcoholate accounted for four-fifths of the original amount of sodium and this ruled out the formation of sodium pinacolate by reaction of the sodium with the trifluoroacetone.

The crystalline mass was broken up and very cautiously added to 100 ml. of vigorously stirred 20% hydrochloric acid. The solid was filtered off and placed in 100 ml. of benzene. The aqueous filtrate was extracted with benzene, and both portions were combined. Crystallization from this benzenic solution gave 38 g. (81% yield) of product, m.p. 93–100°, b.p. 200–210°. Fractional recrystallization yielded small amounts of crystals, m.p. 92–93°, and a main product m.p. 107.5–108.5°; % F 50.0, calcd. 50.4 for $(C_3F_3H_3O)_n$; mol. weight 338, calcd. 336 for a trimer. After 24 hours of reflux with 6 *N* sulfuric acid, the crystals were recovered intact. Neither the crystals nor the sulfuric acid solution gave a positive carbonyl test. A Zerewitinov titration showed the presence of two active hydrogen atoms. Acetylation showed two alcohol groups, with the diacetate boiling about 175–180°. On this evidence, formula I was proposed for the reaction product of sodium on trifluoroacetone; it represents a ketolization with cyclic ketal formation instead of a pinacol formation.

The crystalline material I (80 g.) was then mixed with P_2O_5 (97 g.) and heated to 160°. This caused a slow distillation. The remaining phosphoric acid was treated with water, and heated to distil more dehydration product. Rectification of the combined distillation gave a wet fraction (1.8 g.) b.p. 118–119°; a main fraction II (23 g.), m.p. −27.3 to −26.3°, b.p. 119–120°, n^{20}_D 1.3410, d^{20}_4 1.468 (*Anal.* Found: F, 56.9; H, 1.07; C, 35.1. Calcd. for $C_9F_9H_5O$: F, 57.0; H, 1.7; C, 36.1); a fraction (7.3 g.), b.p. 120–153°; and material (4 g.), b.p. 153–154°. A molecular weight determination of the main fraction gave 291 by cryoscopy, and 295 by vapor density, calcd. 300. A similar dehydration of 10 g. of I in 50 g. of concentrated sulfuric acid at 150° for 12 hours gave a much better conversion to 7.3 g. of material, b.p. 119–120°, n^{20}_D 1.3410, % F 56.4.

Qualitative tests showed no reaction with sodium; bromine was slowly absorbed from a carbon tetrachloride solution; an oxygen test with Ferrox paper was negative; neutral permanganate acted only slowly; aluminum chloride in chloroform gave a bright magenta color, even in trace amounts; micro-hydrogenation on platinum at room temperature absorbed two moles of hydrogen; a mass spectrogram confirmed the presence of $C_9H_5F_9O$ as the parent molecule; an infrared spectrum showed unsaturation and ruled out any carbonyl function.

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