[Contribution from the Department of Chemistry of the University of Florida]

Fluoroolefins. VII. The Synthesis of 2-Trifluoromethyl-1,3-butadiene[1]

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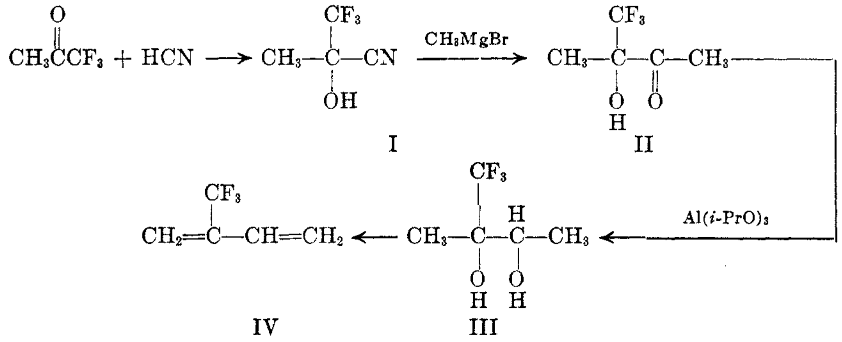
The synthesis of 2-trifluoromethylbutadiene by two new methods is described. The better method involves the reaction of trifluoroacetone with malonic acid and the reduction of the resulting β-trifluoromethylcrotonic acid to the carbinol and its dehydration.

Previous work in our laboratory has shown that 2-trifluoromethylbutadiene cannot be prepared in a simple manner from acetylene and trifluoroacetone because of the ready formation of 2,5-bis-(trifluoromethyl)-3-hexyne-2,5-diol.[2]

Henne and Hinkamp[3] prepared trifluoromethylbutadiene by a procedure involving the reaction of trifluoroacetone with ethylmagnesium bromide, dehydration to the olefin, reaction with *N*-bromosuccinimide, and, finally, dehydrobromination to the desired compound. The over-all yield of the diene was low.

An investigation of the synthesis of trifluorobutadiene in our laboratory followed a different route and two synthetic methods were developed. The first of these involved the following steps:



$$CH_3\overset{O}{\overset{\|}{C}}CF_3 + HCN \longrightarrow \underset{\text{I}}{CH_3-\overset{CF_3}{\overset{|}{\underset{OH}{\underset{|}{C}}}}-CN} \xrightarrow{CH_3MgBr} \underset{\text{II}}{CH_3-\overset{CF_3}{\overset{|}{\underset{\underset{H}{O}}{\underset{|}{C}}}}-\underset{O}{\underset{\|}{C}}-CH_3}$$

$$\xrightarrow{Al(i\text{-}PrO)_3} \underset{\text{III}}{CH_3-\overset{CF_3}{\overset{|}{\underset{\underset{H}{O}}{\underset{|}{C}}}}-\overset{H}{\underset{\underset{H}{O}}{\underset{|}{C}}}-CH_3} \longrightarrow \underset{\text{IV}}{CH_2{=}\overset{CF_3}{\overset{|}{C}}-CH{=}CH_2}$$

The addition of hydrogen cyanide was carried out under the conditions described by Darrall *et al.*[4] and a 70% yield of I was obtained. The Grignard reaction was carried out without difficulty and gave a 70% yield of 2-trifluoromethyl-2-hydroxy-3-butanone (II). Reduction of II by aluminum isopropoxide afforded only a 24% yield of the glycol (III). However, the use of lithium aluminum hydride gave III in 66% yield. Sodium borohydride reduction of II was even less successful than aluminum isopropoxide reduction. The dehydration step was accomplished by heating III with phosphoric oxide; the yield of diene was 37% but this value could undoubtedly be improved on a larger scale because handling losses were large. No carbonyl compounds were isolated after dehydration of the glycol indicating that a pinacol-pinacolone type rearrangement had not occurred.

It will be noted that good yields of products were obtained in all reactions except the dehydration step. Difficulty in dehydrating carbinols with a hydroxyl and a trifluoromethyl group on the same carbon atom has been noted previously.[5] It was anticipated that a better method for the synthesis of the desired diene could be developed by carrying out the dehydration step involving the trifluoromethyl carbinol as early as possible. Consequently, a study was made of the dehydration of trifluoroacetone cyanohydrin (I). Efforts to duplicate the results shown in the patent literature with thionyl chloride as the dehydrating agent[6] were unsuccessful. However, pyrolysis of the acetate of the cyanohydrin was realized, although the yields of 2-trifluoromethylacrylonitrile were not so high as those reported by Buxton, Stacey, and Tatlow.[7] The acetate was not pyrolyzed appreciably at temperatures below 450° while much carbonization occurred above 550°. Several experiments were carried out at 500 ± 5° but reproducibility of results was difficult to obtain.

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[1] Paper VI. *J. Am. Chem. Soc.*, **76**, 2343 (1954). This research was supported by Contract DA44-109 qm-1469 between the Office of the Quartermaster General and the University of Florida with Dr. J. C. Montermoso as the Project Officer. From the Ph.D. dissertation of R. E. Taylor, January 1955.

[2] P. Tarrant and D. A. Warner, *J. Am. Chem. Soc.*, **76**, 1624 (1954).

[3] A. L. Henne and P. E. Hinkamp, *J. Am. Chem. Soc.*, **76**, 5147 (1954).

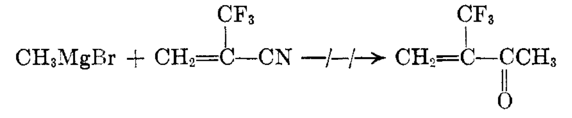
[4] R. A. Darrall, F. Smith, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 2329 (1951).

[5] K. N. Campbell, J. O. Knobloch, and B. K. Campbell, *J. Am. Chem. Soc.*, **72**, 4380 (1950).

[6] J. B. Dickey, U. S. Patent **2,472,812** (1949).

[7] M. W. Buxton, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 366 (1954).

The reaction between 2-trifluoromethylacrylonitrile and methylmagnesium bromide did not give the desired ketone (V).



$$CH_3MgBr + CH_2{=}\overset{CF_3}{\overset{|}{C}}{-}CN \not\longrightarrow CH_2{=}\overset{CF_3}{\overset{|}{C}}{-}\underset{\underset{O}{\|}}{C}CH_3$$

V

Instead, a constant boiling fraction was obtained which contained 9% nitrogen. Infrared analysis indicated the presence of the nitrile group. Apparently addition occurred largely to the carbon-carbon double bond, although analytical data do not fit the requirements for $CH_3CH_2CH(CF_3)CN$. Examples of 1,4- addition of RMgX to α-substituted, α,β-unsaturated nitriles have been reported.[8]

The second method developed for the preparation of 2-trifluoromethylbutadiene made use of the activating effect of the carboxylic acid group to overcome the influence of the trifluoromethyl group in the dehydration step. Trifluoroacetone was condensed with malonic acid to give β-hydroxy-β-trifluoromethylbutyric acid according to the method of Walborsky *et al.*[9] The acid was dehydrated to β-trifluoromethylcrotonic acid by refluxing with sulfuric acid. The unsaturated acid was reduced to $CH_3C(CF_3){=}CHCH_2OH$ (VI), by lithium aluminum hydride in 38% yield. The conversion of the crotonic acid to VI with lithium aluminum hydride *via* the acid chloride gave a 49% yield of the carbinol. Dehydration of VI gave 2-trifluoromethylbutadiene in 60% yield.

It will be seen that the dehydration of VI to IV occurred 1,4- and improved yields are attributed to the less difficult operation of removing the hydroxyl group from a carbon atom which did not bear a trifluoromethyl group.

The infrared spectra of 2-trifluoromethylbutadiene prepared by the two methods were identical.

EXPERIMENTAL

3-Trifluoromethyl-3-hydroxy butanone (II). A 2-l. flask equipped with a stirrer, addition funnel, gas inlet tube, and ice water cooled condenser was charged with magnesium (48.6 g.) and flame dried under nitrogen. Ether and methyl bromide were added to form the Grignard reagent. Trifluoroacetone cyanohydrin[4] (139 g., 1.0 mol.) was added slowly and the mixture allowed to stand overnight. Hydrolysis was accomplished with 10% sulfuric acid. The organic layer and ether extracts were dried and distilled to give 110 g. (70.5% yield) of II boiling over a 4° range. A center fraction had the following properties: b.p. 118.0°, n_D^{25} 1.3581, d_4^{25} 1.2701.

Anal. Calcd. for $C_5H_7F_3O$: C, 38.47; H, 4.52; MR_D 26.53. Found: C, 38.3; H, 5.00; MR_D 26.99.

2-Trifluoromethyl-2,3-butanediol (III). (a) Reduction with aluminum isopropoxide. A solution of aluminum isopropoxide (140 g., 0.68 mol.) in 2-propanol was reacted in the usual manner with II (83 g., 0.55 mol.). After hydrolysis with 6*N* sulfuric acid and distillation, 21 g. of (24%) III, b.p. 58° at 5.5 mm., n_D^{25} 1.3866, d_4^{25} 1.3282, was obtained.

Anal. Calcd. for $C_5H_9F_3O_2$: C, 38.0; H, 5.74; MR_D 28.04. Found: C, 38.16; H, 5.84; MR_D 28.00.

(b) Reduction with lithium aluminum hydride. A slurry of the hydride (16 g., 0.42 mol.) in ether was treated with II (39 g., 0.25 mol.). Fractionation of the organic material gave 26 g. (66%) of III, b.p. 41–43° at 2 mm.

(c) Reduction by a water solution of sodium borohydride yielded 16% (5 g.) of III while III was obtained (66 g., 55%) under anhydrous conditions.

β-Hydroxy-β-trifluoromethylcrotonic acid. A solution of malonic acid (240 g., 2.3 mol.) in 370 ml. of pyridine was prepared in a 2-l. flask equipped with a gas-inlet tube, stirrer, and ice water reflux condenser. The flask was cooled in ice. Trifluoroacetone (224 g., 2.0 mol.) was distilled into the solution which became pasty. The mixture was heated slowly to 90° and maintained at that temperature for 14 hr. The solution was heated to 130° until the evolution of carbon dioxide stopped. After removal of pyridine, 212 g. (62%) of β-hydroxy-β-trifluoromethylbutyric acid, b.p. 100–115° at 8 mm., was obtained.

β-Trifluoromethylcrotonic acid. The acid from above (212 g., 1.23 mol.) was refluxed with 50% sulfuric acid. The unsaturated acid was removed as it formed *via* a water separator. After 14 hr. no further acid was isolated. The crude acid was dried over sodium sulfate to give 134 g. (71%) of β-trifluoromethylcrotonic acid, b.p. 160–166°. Walborsky[9] used phosphoric acid for this dehydration.

β-Trifluoromethylcrotonyl chloride. Freshly distilled thionyl chloride (11.9 g.) was refluxed with β-trifluoromethylcrotonic acid (15.4 g., 0.1 mol.) in an appropriate flask until no further hydrogen chloride was evolved. The residue was distilled to give 12 g. (69.8%) of trifluoromethylcrotonyl chloride, b.p. 99.5–100.5°, n_D^{23} 1.3916, d_4^{23} 1.3037.

Anal. Calcd. for $C_5H_4ClF_3O$: Cl, 20.6; MR_D 31.47. Found: Cl, 20.2; MR_D 29.71.

β-Trifluoromethylcrotyl alcohol. (a) Reduction of trifluoromethylcrotonic acid. A slurry of lithium aluminum hydride (17 g., 0.447 mol.) in 1 l. of dry ether was prepared in a 5-l. flask equipped as previously described, cooled in an ice bath, and treated with 3-trifluoromethylcrotonic acid (78 g., 0.5 mol.) at such a rate as to produce an internal temperature of 5–10°. After 1 hr., 150 ml. of water was added followed by 1.5 l. of 10% sulfuric acid. The ether was separated, the water extracted with ether, and the extracts were dried thoroughly over sodium sulfate. Fractionation gave 24.0 g. (38.4%) of β-trifluoromethylcrotyl alcohol, b.p. 144–145°, n_D^{22} 1.3761, d_4^{22} 1.2021.

Anal. Calcd. for $C_5H_7F_3O$: C, 42.8; H, 5.04; MR_D 26.36. Found: C, 42.61; H, 5.44; MR_D 26.75.

(b) Reduction of β-trifluoromethylcrotyl chloride. The procedure was the same as described above for the 3-trifluoromethylcrotonic acid. The use of lithium aluminum hydride (22 g., 0.58 mol.) and 3-trifluoromethylcrotonyl chloride (82 g., 0.477 mol.) gave 47 g. (70.0%) of β-trifluoromethylcrotyl alcohol, b.p. 141–146°, n_D^{22} 1.3762, d_4^{22} 1.202.

2-Trifluoromethylbutadiene. (a) By dehydration of 2-trifluoromethyl-2,3-butanediol. A 500-ml. three-neck flask equipped with a 6-in. column and ice-water cooled variable take-off head, stirrer, and addition funnel was charged with phosphoric oxide (14.2 g., 0.1 mol.). One-tenth mol. (15.8 g.) of 2-trifluoromethylbutanediol-2,3 was added dropwise and slowly heated. A relatively high temperature (200–250°) was required before decomposition to the intermediate began. Thirteen g. of crude product was obtained up to a head temperature of 76°. Fractionation of the crude material gave 4.5 g. (36.9%) of very volatile 2-trifluoromethylbutadiene-1,3, b.p. 35.0–35.5°, n_D^{22} 1.3431, d_4^{22} 1.037. The literature values are b.p. 34–35°, n_D^{20} 1.3485, d_D^{20} 1.064.

Anal. Calcd. for $C_5H_5F_3$: C, 49.3; H, 4.13; MR_D 24.36. Found: C, 49.51; H, 4.34; MR_D 24.87.

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(8) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, pp. 782–3, Prentice-Hall, Inc., 1954.

(9) H. M. Walborsky, M. Baum, and D. F. Loncrini, *J. Am. Chem. Soc.*, **77**, 3637 (1955).

(b) By dehydration of 3-trifluoromethyl-2-buten-1-ol. 2-Trifluoromethyl-2-buten-1-ol (45 g., 0.32 mol.) was added slowly with external cooling to phosphoric oxide (42.6 g., 0.3 mol.) in a 500-ml. flask equipped as above in part (a) above and stirred without heating until a uniform paste was formed. Heat was then applied and 23 g. of crude product obtained. Fractionation gave 22 g. (60.3%) of 2-trifluoromethylbutadiene-1,3, b.p. 36°, n_D^{22} 1.3434. Infrared spectra of this sample were identical with that of the sample prepared by the dehydration of 2-trifluoromethylbutadiol-2,3.

α-Trifluoromethylacrylonitrile. The equipment used for pyrolysis of trifluoroacetone cyanohydrin acetate consisted of the following: A flowmeter for measuring the volume of nitrogen and a dropping funnel for the acetate were connected to one end of a 1 × 12 in. Pyrex tube packed with borosilicate beads. The Pyrex tube was heated by a combustion furnace to 500 ± 5° and the internal temperature automatically controlled by a thermocouple and pyrometer. Pyrolyzed material was led directly from the furnace into an ice-water cooled receiver equipped with a reflux condenser. A tube connected the top of the reflux condenser to two cold traps in Dry Ice and acetone.

A typical reaction was carried out as follows: Acetate (45 g.) was added in 57 min. Nitrogen was added at the rate of 10 l. per hour. The crude product (37.5 g.) was fractionated to give 14.0 g. (46.6%) of 2-trifluoromethylacrylonitrile, b.p. 73–85°.

Trifluoromethylacrylonitrile has the following physical properties: b.p. 78–79°, $n_D^{26.4}$ 1.3261, $d_D^{26.4}$ 1.1753.

Anal. Calcd. for $C_4H_2F_3N$: MR_D 20.79. Found: MR_D 19.96. Lit.,[4] b.p. 75.9–76.2°, n_D^{20} 1.3239.

Reaction of methylmagnesium bromide with α-trifluoromethylacrylonitrile. Two mol. of methylmagnesium bromide was prepared in a 2-l., three-neck flask from 2.00 mol. (48.6 g.) of magnesium and enough methyl bromide to react completely with it in 1 l. of dry ether. To this cold solution was added trifluoromethylacrylonitrile (212 g., 1.75 mol.) dissolved in 200 ml. of dry ether. After refluxing for 4 hr., during which time a wax-like precipitate formed, 10% sulfuric acid was added and the precipitate dissolved. The ether solution was separated and the water layer extracted with additional ether. After drying and removal of the ether, fractionation gave 15 g. of material with the following properties: b.p. 127–127.5°, n_4^{27} 1.4108, d_4^{27} 0.9350.

Anal. Found: C, 49.7; H, 5.99; N, 9.13.

GAINESVILLE, FLA.

[CONTRIBUTION NO. 158 FROM THE CENTRAL RESEARCH LABORATORIES OF MINNESOTA MINING AND MANUFACTURING CO.[1]]

The Chemistry of Xylylenes. IV. The Stabilization of Benzyl Radicals in Solution

L. A. ERREDE AND J. P. CASSIDY[2]

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Solutions of benzyl radicals, in concentrations as high as 10^{-4} molar, were prepared by fast flow pyrolysis of toluene at low pressure and subsequent condensation of the pyrolyzate into a solvent kept at −78°. Solvated radicals were still present 1.5 hr. after termination of pyrolysis. Surprisingly, an equal amount of *p*-xylylene was also accumulated during the reaction. Apparently this was formed by dehydrogenation of *p*-xylene produced *via* methylation of toluene. The unusual stability of solvated benzyl radicals at −78° may be a manifestation of complex formation with toluene thereby decreasing their rate of coupling.

It has been reported by one of us[3] that solutions of extremely reactive compounds such as *p*-xylylene can be prepared by instantaneous condensation of its low pressure stream into a suitable solvent kept at low temperature. This technique was also applied successfully to the preparation of solutions of benzyl radicals, albeit in low concentration. Thus, 500 g. toluene, metered at the rate of 0.03 mol./min., was pyrolyzed at 1000°, 4 mm. pressure, and 0.004 sec. residence time, and the pyrolyzate was condensed at −78° into 4.5 l. toluene. Iodometric titration of an aliquot sample indicated that about 1.5 × 10^{-3} equivalents of active species had accumulated in the final solution. The concentration of titratable species decreased steadily at −78° from 3 × 10^{-4} molar to 3 × 10^{-5} molar over a period of 90 min. and thereafter decreased very slowly to 1 × 10^{-5} molar over a period of 28 hr.

Apparently this was a mixture of two active compounds. The more stable species, despite the fact that it decolorized test solutions of diphenylpicrylhydrazyl, was not a free radical since negative results were obtained when an aliquot of this solution, that had been aged for 20 hr.; was analyzed in an electron spin spectrometer.[4]

Gas chromatography and infrared analysis indicated that the pyrolysis feed stock (b.p. 110–111°) used in these experiments was 99.8% toluene, 0.1% benzene, and 0.1% aliphatic hydrocarbon. The presence of xylenes was not detected in even a trace amount. The composition of the condensate obtained as a result of its pyrolysis at 970° and 0.02 sec. residence time was 97.2% toluene, 1.1% dibenzyl, 0.7% benzene, 0.4% ethylbenzene, 0.4%

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(1) A portion of this work was carried out in the laboratories of the M. W. Kellogg Co. The data were acquired by the Minnesota Mining and Manufacturing Co. with the purchase of the Chemical Manufacturing Division of the M. W. Kellogg Co. in March 1957.

(2) Present address: The M. W. Kellogg Co., Jersey City, N. J.

(3) L. A. Errede and B. F. Landrum, *J. Am. Chem. Soc.*, 79, 4952 (1957).

(4) The authors are indebted to Professor John Wertz of the University of Minnesota for use of the electron spin spectrometer.