[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF FLORIDA]

Fluoroolefins. VI.[1] The Synthesis of Some α-Trifluoromethylstyrenes

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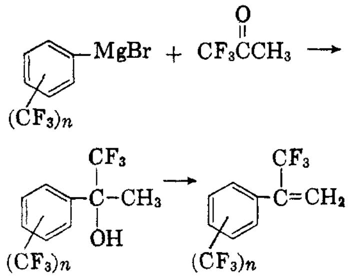
Three new α-trifluoromethylstyrenes were prepared in a two-step synthesis involving the dehydration of the carbinols made from trifluoroacetone and Grignard reagents. The effect of hydrogen bonding in the carbinols is discussed.

According to the patent literature[2] α-difluoromethyl- and α-trifluoromethylstyrene have been made from the corresponding phenylpropanols. However, neither physical constants nor yields were given. Furthermore, the use of mild dehydrating agents such as oxalic acid, zinc chloride, *etc.*, indicated an ease of dehydration not normally associated with carbinols containing the trifluoromethyl group.[3] It thus seemed of some interest to prepare some α-trifluoromethylstyrenes and to observe any unusual behavior exhibited.

In the present study phenyl-, 3-trifluoromethylphenyl-, and 3,5-bis(trifluoromethyl)phenylmagnesium bromide were allowed to react with trifluoroacetone to give a carbinol which was dehydrated to the desired olefin. This method has previously been employed[4-6] to give styrenes containing substituents on the benzene ring. McBee and Sanford synthesized some bis-trifluoromethyl- and trifluoromethylchlorostyrenes. Renoll prepared *m*-trifluoromethylstyrene by dehydrating *m*-trifluoromethylphenylmethylcarbinol, and Bachman and Lewis prepared some styrenes and α-methylstyrenes substituted by fluorine and trifluoromethyl groups on the ring by a similar method.



It was found that decreased yields of carbinol resulted when the highly substituted Grignard reagent was used. Furthermore, the dehydration of the resulting carbinols required heating with phosphoric oxide at atmospheric pressure at temperatures above 150°. The 3,5-bistrifluoromethylcarbinol was particularly difficult to convert to the styrene and low yields were obtained.

The compounds were characterized by physical properties, infrared spectra, and elemental analysis.

It is of interest to note that the boiling points of the three intermediate carbinols are not in line for materials of increasing molecular weight in a homologous series. This may be readily seen in Table I. Evidence has been presented[7] to show that an unassociated hydroxyl group exhibits an absorption band at approximately 2.75μ, while an associated hydroxyl absorbs near 3.00μ. As is readily seen in the above table, the absorption peak at 2.79μ increases in strength as the aromatic ring becomes increasingly electronegative due to the presence of trifluoromethyl groups. On the other hand, the absorption band at 2.89μ constantly decreases in intensity. If the 2.79μ and 2.89μ bands are assigned to unassociated and associated hydroxyl groups, respectively, it becomes apparent that the degree of association is being constantly decreased as the ring becomes more electronegative.

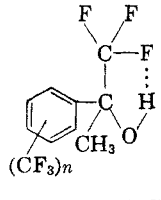
TABLE I

BOILING POINTS AND INFRARED ABSORPTION OF CARBINOLS

Carbinol	Boiling Point/°C.	Infrared Absorption[a] 2.79μ	Infrared Absorption[a] 2.89μ
$C_6H_5C(CF_3)(OH)CH_3$	62–66/4.5 mm	...	s
$3\text{-}(CF_3)C_6H_4C(CF_3)(OH)CH_3$	87.5–88.0/4 mm	w	m-s
$3,5\text{-}(CF_3)_2C_6H_3C(CF_3)(OH)CH$	59.0–60.0/3 mm	m	m

[a] s = strong. w = weak. m-s = medium strong. m = medium.

Two types of association are possible in this case. The first is of the intramolecular type:



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(1) Paper V: Paul Tarrant, John Attaway, and A. M. Lovelace, *J. Am. Chem. Soc.*, **76**, 2343 (1954).

(2) J. B. Dickey and T. E. Stanin, U.S. Patent **2,475,423** (July 5, 1949).

(3) K. A. Campbell, J. O. Knoblock, and B. K. Campbell, *J. Am. Chem. Soc.*, **72**, 4380 (1950).

(4) M. W. Renoll, *J. Am. Chem. Soc.*, **68**, 1159 (1946); U.S. Patent **2,580,504** (January 1, 1952).

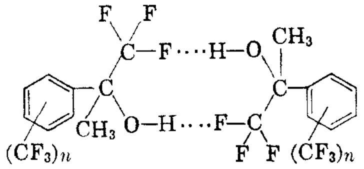
(5) G. B. Bachman and L. L. Lewis, *J. Am. Chem. Soc.*, **69**, 2022 (1947); U.S. Patent **2,414,330** (January 14, 1947).

(6) E. T. McBee and R. A. Sanford, *J. Am. Chem. Soc.*, **72**, 4053 (1950).

(7) Ferguson A. Smith and E. C. Creitz, *J. Research Nat. Bur. Standards*, **46**, (2), 145 (1951).

J. J. Fox and A. E. Martin, *Trans. Faraday Soc.*, **36**, 897 (1940).

Association of this type would decrease the boiling point of the material as the degree of association increased. The second possible type of association is of the intermolecular type:



Association of this type would increase the boiling point by increasing the effective molecular weight of the carbinol. As the degree of association decreased the boiling point would decrease. Since this is the observed result, it becomes apparent that this is the actual type of association occurring in the above carbinols.

EXPERIMENTAL

Formation of the carbinols. A one-liter, three-neck flask equipped with a stirrer, pressure equalized addition funnel, and ice water reflux condenser topped with a drying tube was charged with 0.5 mole (12.2 g.) of magnesium turnings and flame-dried under an atmosphere of dry nitrogen. The nitrogen was supplied from a cylinder, dried by passing through concentrated sulfuric acid and a tube containing Drierite, and admitted to the system through the top of the addition funnel. Dry ether (400 ml.) was added to cover the magnesium and a small portion of bromobenzene added to initiate the reaction. Cooling was often required to control the reaction once it had commenced. After the initial reaction had subsided, the remainder of 0.5 mole (78.5 g.) of bromobenzene was added at such a rate as to cause gentle boiling of the solvent. An hour was allowed after completion of the addition to ensure complete reaction. The Grignard reagent was then treated with 0.6 mole (67 g.) of trifluoroacetone *via* a gas inlet which replaced the addition funnel and the mixture left overnight. Hydrolysis was accomplished by pouring the ether solution onto 100 ml. of hydrochloric acid and 1 kg. of cracked ice. The ether layer was separated and the water extracted several times with small portions of ether. The combined extracts were dried and fractionated to give 71 g. (74.7%) of $C_6H_5C(CF_3)$ $(OH)CH_3$, b.p. 62–6°/4.5 mm, n_D^{22} 1.4656, d_4^{22}1.2511.

Anal. Calcd. for $C_6H_5C(CF_3)(OH)CH_3$: C, 56.8; H, 4.78; MR_D, 41.70. Found: C, 57.01; H, 4.87; MR_D, 42.07.

The Grignard reagent prepared from *m*-bromobenzotrifluoride (73 g., 0.325 mole) reacted with trifluoroacetone (36.4 g., 0.325 mole) to give a 70% yield of *m*-$CF_3C_6H_4C(CF_3)(OH)CH_3$. The constants for this compound are b.p. 87.5–88.0° at 4 mm., n_D^{24} 1.4148, d_4^{24} 1.4267.

Anal. Calcd. for $C_{10}H_8F_6O$: C, 46.6; H, 3.13. Found: C, 46.7; H, 3.04.

This Grignard reagent was also reacted with formaldehyde and gave a 33% yield of *m-trifluoromethylbenzyl alcohol*, b.p. 68° at 2 mm., n_D^{21} 1.4606, d_4^{21} 1.2949.

Anal. Calcd. for $C_8H_7F_3O$: C, 54.6; H, 4.01. Found: C, 54.5; H, 3.89.

The Grignard reagent from 3,5-bis(trifluoromethyl)-bromobenzene (189 g., 0.645 mole) reacted with trifluoroacetone (78.5 g., 0.7 mole) to give 3,5-$(CF_3)_2C_6H_3C(CF_3)$ $(OH)CH_3$ in 40.2% yield. A center fraction of the distilled product had the following physical constants: b.p. 59–60° at 3 mm., n_D^{22} 1.3966, d_4^{22} 1.5118.

Anal. Calcd. for $C_{11}H_7F_9O$: C, 40.6; H, 2.17. Found: C, 40.4; H, 2.51.

Preparation of the α-trifluoromethylstyrenes. (*a*) A 500-ml. flask fitted with a stirrer, addition funnel, and short fractionation column topped with a variable take-off distilling head was charged with 15.0 g. of phosphoric oxide and cooled in ice water. One tenth mole (19 g.) of α-methyl-α-trifluoromethylbenzyl alcohol was added and the mixture stirred until an even paste formed. The ice bath was then replaced by a heating mantle and the mixture slowly heated until the desired product distilled at 148–157°. Fractionation of this crude distillate gave 11.6 g. (66.9%) of $C_6H_5C(CF_3){=}CH_2$, b.p. 148.0–151.0°. A center fraction of 9.1 g. had the physical constants: b.p. 148.0–148.5°C., n_D^{21} 1.4603, d_4^{21} 1.167.

Anal. Calcd. for $C_9H_7F_3$: C, 62.7; H, 4.09; MR_D, 41.39. Found: C, 62.57; H, 4.16; MR_D, 40.42.

(*b*) Preparation of 3-trifluoromethyl-α-trifluoromethylstyrene: The above procedure was repeated using 0.2 mole (28.4 g.) of phosphoric oxide and 0.194 mole (50 g.) of 3-trifluoromethyl-α-methyl-α-trifluoromethylbenzyl alcohol to give crude material boiling up to 151°. Fractionation gave 23 g. (47.7%) of 3-$(CF_3)C_6H_4C(CF_3){=}CH_2$, b.p. 151–159° with a center cut taken at 157–158°, n_D^{22} 1.4151, d_3^{22} 1.346.

Anal. Calcd. for $C_{10}H_6F_6$: C, 50.01; H, 2.52; MR_D, 46.00. Found: C, 49.89; H, 2.89; MR_D, 44.68.

(*c*) Preparation of 3,5-bis(trifluoromethyl)-α-trifluoromethylstyrene: The procedure above was repeated in the following two sections to give the results described below.

(1) The flask was charged with 0.2 mole (28.4 g.) of phosphoric oxide and 0.237 mole (77 g.) of 3,5-bis(trifluoromethyl)-α-methyl-α-trifluoromethylbenzyl alcohol added as described. The mixture was heated until material distilled between 170–180°. Redistillation gave 47 g. of recovered carbinol and 18.5 g. of lower boiling material whose infrared spectrum indicated it to be the desired styrene. The conversion was 9.3%.

(2) The procedure was repeated using 0.1 mole (14.2 g.) of phosphoric oxide and 0.144 mole (47 g.) of 3,5-bis(trifluoromethyl)-α-methyl-α-trifluoromethylbenzyl alcohol to give the crude distillate from which 9.5 g. of product boiling from 158° to 178° was obtained.

The olefin fractions from the two runs were combined and refractionated to give 14.8 g. of 3,5-bis(trifluoromethyl)-α-trifluoromethyl styrene, b.p. 59.5–60.0°/14 mm., n_D^{22} 1.3921, d_4^{22} 1.456.

Anal. Calcd. for $C_{11}H_5F_9$: C, 42.8; H, 1.63; MR_D, 51.63. Found: C, 42.41; H, 1.92; MR_D, 40.43.

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