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SHORT COMMUNICATION

A New Synthesis for Fluoroacetylenes. Potassium Fluoride as a Dehydroiodination Agent.

J. J. MIELCAREK, J. G. MORSE*, AND K. W. MORSE

Department of Chemistry and Biochemistry, Utah State University, UMC 03,
Logan, Utah 84322 (U.S.A.)

In the course of our study of the photoreactions of tetrafluorodiphosphine [1-3] a need developed for a number of acetylene derivatives having substituents varying in steric and electronic character. Of particular interest were partially fluorinated acetylene derivatives, few of which are commercially available. While published procedures are available for the preparation of $CF_3C{\equiv}CH$ [4,5] and $CF_3C{\equiv}CCH_3$ [6], it appeared that some simplification of these procedures, especially in the latter case, was possible.

Haszeldine and Leedham [6] prepared 1,1,1-trifluoro-2-butyne by means of the following sequence:

$$(1)\quad CF_3I + HC{\equiv}CCH_3 \xrightarrow{h\nu} CF_3CH{=}CICH_3$$

$$(2)\quad CF_3CH{=}CICH_3 + Br_2 \longrightarrow CF_3CHBrCBr_2CH_3$$

$$(3)\quad CF_3CHBrCBr_2CH_3 + KOH \longrightarrow CF_3CBr{=}CBrCH_3 + KBr + H_2O$$

$$(4)\quad CF_3CBr{=}CBrCH_3 + Zn \longrightarrow CF_3C{\equiv}CCH_3 + CF_3CH_2C{\equiv}CH + ZnBr_2.$$

The total yield of the two acetylene products based on CF_3I was about 50%. It appeared that dehydroiodination of the product of (1) should give the desired product directly if an appropriate agent could be found. Potassium fluoride has been shown to be a good base in organic solvents in the presence of an 18-crown-6 polyether [7] such as 2,3,11,12-dicyclohexyl-1,4,7,10,13,16-hexaoxacyclooctadecane. Chelation of the K^+ ion by the 18-crown-6 enhances solubility and presents an essentially "bare" F^- ion as a reactive base in organic solvents. Accordingly the following reaction was tried.

$$(5)\quad CF_3CH{=}CICH_3 + 2\ KF \xrightarrow[\text{dioxane, 3-4 h}]{\text{18-crown-6}} CF_3C{\equiv}CCH_3 + KI + KHF_2.$$

1,1,1-trifluoro-2-butyne was obtained in 45% yield while 3,3,3-trifluoro-1-butyne was obtained in 10% yield. Given a yield from reaction (1) in excess of 90%, the total yield of product based on CF_3I is about 50%, quite comparable with that obtained in the four step procedure (1-4).

We attempted in a similar way the dehydroiodination of $CF_3CH{=}CHI$. This had been accomplished by Haszeldine [4] using anhydrous KOH in the absence of solvent:

$$(6)\quad CF_3I + HC{\equiv}CH \longrightarrow CF_3CH{=}CHI$$

$$(7)\quad CF_3CH{=}CHI + KOH \xrightarrow[6h]{120^\circ} CF_3C{\equiv}CH + KI + H_2O$$

The yield of reaction (6) was about 70% as was that from (7) for an overall yield of about 50%. The reaction with KF and dicyclohexyl-18-crown-6 in dioxane was carried out much as before:

$$(8)\quad CF_3CH{=}CHI + 2\ KF \xrightarrow[\text{dioxane, 3.5 h}]{\text{18-crown-6}} CF_3C{\equiv}CH + KI + KHF_2$$

The yield obtained was about 20% for this step alone. In toluene, a higher boiling solvent, about the same yield was obtained, though in a substantially longer time (ca. 19 h). Dehydroiodination by KOH would seem to be preferred of these two methods by virtue of its higher yield, though admittedly in our hands the yields were quite comparable for the one run attempted with KOH.

As a synthetic procedure leading to $CF_3C{\equiv}CH$ this procedure is inferior to the reaction of SF_4 with propynoic acid, $HO_2CC{\equiv}CH$, from which yields the order of 60-80% are reported [5]. Presumably the fluorination of 2-butynoic acid, $CH_3C{\equiv}CCO_2H$, by SF_4 would yield comparable results, though it was not reported [5], but $CH_3C{\equiv}CCO_2H$ is not readily accessible commercially. In this instance the method reported here may be competitive. In both instances these observations do suggest the utility of KF in 18-crown-6 as a dehydrohalogenating agent using rather mild conditions where KOH may not be tolerable or effective. It is noteworthy that KF in 18-crown-6 is reported [7] to extract HBr from secondary aliphatic bromides very efficiently while producing primarily the substitution product, a primary fluoride, from primary aliphatic bromides. While we observed no fluorination product from $CF_3CH{=}CHI$, the efficiency of dehydrohalogenation was markedly less than from $CF_3CH{=}CICH_3$, paralleling the saturated compounds.

EXPERIMENTAL

These reactions are conveniently carried out in a standard high vacuum system. $CF_3CH{=}CHI$ and $CF_3CH{=}CICH_3$ were prepared by literature methods [4,6]. Anhydrous KF was oven dried at 120° before use. Dicyclohexyl-18-crown-6 was obtained from PCR, Inc. Dioxane and toluene were dried over molecular sieves and transferred under vacuum.

Preparation of $CF_3C{\equiv}CCH_3$

To 7.56 g (0.130 mol) of anhydrous KF in a 100 mL vessel were added 6.96 g (17.9 mMol) of dicyclohexyl-18-crown-6. Onto this were condensed 25 mL of anhydrous dioxane and 1.95 g (8.25 mMol) of $CF_3CH{=}CICH_3$. The mixture was brought to reflux under a stream of dry N_2 and refluxed for 3-4 h. Fractionation of the product mixture through traps held at -78° and -112° to a -196° trap gave 0.78 mMol of $CF_3CH_2C{\equiv}CH$ (10%) at -196° and 3.73 mMol (45.2%) of $CF_3C{\equiv}CCH_3$ in the -112° trap. A small amount of starting material was retained at -78°. Products were identified by their infrared spectra.

Preparation of $CF_3C{\equiv}CH$

Onto 7.0 g (0.12 Mol) of anhydrous KF and 1.0 g (2.6 mMol) of dicyclohexyl-18-crown-6 in a 100 mL flask were condensed 20 mL anhydrous dioxane (or toluene) and 1.53 g (6.78 mMol) of $CF_3CH{=}CHI$. The mixture was brought to reflux for 3.5 h (10 h) under a stream of dry nitrogen. The volatile $CF_3C{\equiv}CH$ product was collected in a series of traps held at -196° then purified by passage through a trap held at -130° to one at -196° was identified by its infrared spectrum. Collected were 1.38 mMol for 20% yield (19% in toluene).

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REFERENCES

1 J. G. Morse and K. W. Morse, Inorg. Chem., 14 (1975) 565.

2 W. K. Glanville, K. W. Morse and J. G. Morse, J. Fluorine Chem., 7 (1976) 153.

3 J. J. Mielcarek, K. W. Morse, and J. G. Morse, 175th National Meeting, Am. Chem. Soc. (1977).

4 R. N. Haszeldine, J. Chem. Soc., (1951) 588.

5 W. R. Hasek, W. C. Smith and V. A. Engelhardt, J. Am. Chem. Soc., 82 (1960) 543.

6 R. N. Haszeldine and K. Leedham, J. Chem. Soc., (1954) 1261.

7 C. L. Liotta and H. P. Harris, J. Am. Chem. Soc., 96 (1974) 2250.