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ARYL TRIFLUOROMETHYL ACETYLENES

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SUMMARY

A wide variety of aryl trifluoromethyl acetylenes may be prepared in high yield by allowing $CF_3C{\equiv}CZnCl$, generated from $CF_3C{\equiv}CH$, to react with aryl iodides and a catalytic amount of tetrakis(triphenylphosphine)-palladium.

INTRODUCTION

In connection with a study of polymer formation utilizing the trifluoropropynyl group we needed a number of aryl trifluoromethyl acetylenes with a variety of substituents on the aromatic ring. Application of the method reported for preparation of phenyl trifluoromethyl acetylene did not appear attractive [1]. This procedure consisted of free radical addition of $BrCCCl_3$ to styrene, conversion of the CCl_3 group to a CF_3 group by halogen exchange and finally dehydrobromination with powdered KOH at over 200°. More recently a modified Wittig reaction was used to prepare several aryl trifluoromethyl acetylenes [2], but this approach also required a potentially troublesome pyrolysis step. In our quest for an improved general method for introducing the trifluoropropynyl moiety into aromatic rings we were attracted by the observation of Negishi et al. [3] who noted that simple alkynyl zinc reagents could be coupled with aromatic iodides in a Pd^0-mediated process. Since Finnegan and Norris [4] have described how readily

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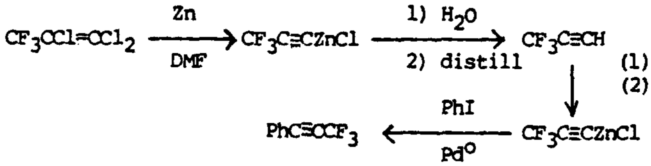
available $CF_3CCl=CCl_2$ can be converted conveniently into $CF_3C\equiv CZnCl$, we decided to combine these methodologies. This strategy proved successful and provides a general route to aryl trifluoromethyl acetylenes.

RESULTS AND DISCUSSION

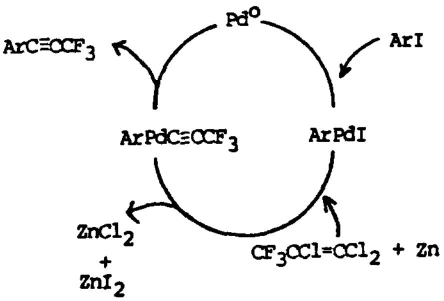
1,1,1-Trichloro-3,3-trifluoropropene was treated with Zn in DMF as described by Finnegan and Norris [4]. Although the Zn reagent thus formed could be coupled with PhI in THF containing a catalytic amount of tetrakis(triphenylphosphine)palladium, the yield of $PhC\equiv CCF_3$ was not high (40%). Improved yields were obtained by regenerating the Zn reagent as indicated in eqn. 1.



(eq. 1)

Table 1 summarizes the results of applying this scheme to a series of aryl iodides. Products were isolated by distillation or chromatography and were characterized by ^1H and ^{19}F nmr spectroscopy. All new compounds gave satisfactory elemental analyses.

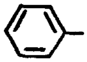
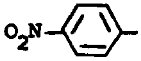
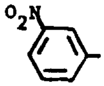
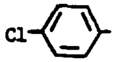
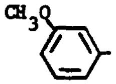
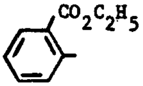
The overall reaction may be described by the catalytic cycle shown in scheme I.



Scheme I. Synthesis of $ArC\equiv CCF_3$.

TABLE I

Preparation of $ArC{\equiv}CCF_3$

			NMR[b]		
Ar	Yield	mp(bp)°C	^1H	^{19}F	Ref.
	86%	(165°)	7.3-8.0 (m)	50(s)	[2]
	85%	72-73°	7.8(d) 8.3(d)	51(s)	[2]
	85%	(110°, 5mm)	7.2-8.6(m)	51(s)	a
	90%	(65°, 5mm)	7.3-7.8(m)	50(s)	[2]
	92%	(91°, 5mm)	3.8(s) 7.2-7.0(m)	49(s)	a
	86%	(119°, 5mm)	1.35(t) 4.3(q) 7.3-8.2(m)	51(s)	a

[a] This work.
[b] $CDCl_3$ solvent. ^{19}F shifts upfield relative to $CFCl_3$.

Oxidative insertion of the Pd° into ArI gives rise to the intermediate ArPdI. This in turn is transformed via nucleophilic displacement of iodide by $CF_3C{\equiv}CZnCl$ into $ArPdC{\equiv}CCF_3$. Reductive elimination from this intermediate furnishes $ArC{\equiv}CCF_3$ and regenerates Pd°. From the range of substrates in Table I it is clear that this method of introducing the trifluoropropynyl group is widely applicable. This observation, coupled with the availability of starting materials and mild conditions, makes the elimination coupling sequence described in scheme I an attractive general route to aryl trifluoromethyl acetylenes.

EXPERIMENTAL

General Procedure

Zinc dust (9.6 g), $ZnCl_2$ (0.91 g) and 50 ml of dried, freshly distilled N,N-dimethyl formamide (DMF) were placed in a 250 ml round-bottom flask equipped with a mechanical stirrer, addition funnel and condenser. The mixture was heated under N_2 to 100° and a total of 13 g (0.067 moles) of 1,1,2- trichloro-3,3,3-trifluoropropene (SCN-PCR, Gainesville, FL) was added dropwise while maintaining the temperature at 100°. The reaction mixture was then cooled to 50° and 50 ml of distilled water was added slowly (careful-evolution of $CF_3C{\equiv}CH$). The gaseous $CF_3C{\equiv}CH$ generated was passed through the reflux condenser and a $CaCl_2$ drying tube and condensed into a flask containing dried and freshly distilled tetrahydrofuran (THF) maintained at -78°. To this solution under N_2 was added 0.050 moles of n-butyl lithium in hexane. The resulting mixture was stirred for 2 h at -78° and then the temperature was raised to -35°. $ZnCl_2$ (0.050 moles) was added and the temperature was raised to 0°. The aryl iodide (0.050 moles) dissolved in 20 ml of THF was then introduced. This addition was followed immediately by 1 g of $Pd(Ph_3P)_4$ (Aldrich, Milwaukee, Wi) in 20 ml of THF. Fifteen minutes after this addition the reaction mixture was allowed to warm to room temperature and then was stirred under N_2 at room temperature for 4 h. The reaction was quenched by pouring the mixture into 50 ml of 2N HCl. Petroleum ether was then added and the layers separated. The aqueous solution was extracted with petroleum ether and the combined organic solutions were washed with aqueous $NaHCO_3$ solution and dried over $MgSO_4$. The dried organic solution was passed through a short alumina column to remove traces of Pd-containing compounds and concentrated under reduced pressure. The residue was purified by distillation or chromatography over silica gel. Results are recorded in Table I.

REFERENCES

1 L.M. Yagupol'skii and Y.A. Fialkov, Zh. Obshch. Kim., 30, (1960) 1291.

Y.A. Fialkov and L.M. Yagupol'skii, Zh. Obshch. Khim., 36 (1966) 739.

2 Y. Kobayashi, T. Yamashita, K. Takahashi, H. Kuroda and I. Kumadaki, Tetrahedron Lett., 23, (1982) 243.

3 A.O. King, E. Negishi, F.J. Villani and A. Silverra, J. Org. Chem., 43, (1978) 358.

4 W.G. Finnegan and W.P. Norris, J. Org. Chem., 28, (1963) 1139.