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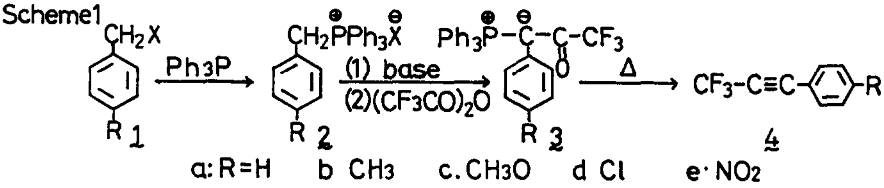
SYNTHESIS OF ARYLTRIFLUOROMETHYLACETYLENES

Yoshiro Kobayashi*, Toshinori Yamashita, Katsuhiro Takahashi,
Hisashi Kuroda, and Itsumaro Kumadaki

Tokyo College of Pharmacy, Horinouchi, Hachioji, Tokyo, 192-03, Japan.

Abstract. Aryltrifluoromethylacetylenes were synthesized by an intramolecular Wittig reaction of trifluoroacetylarylidenephosphoranes, which were synthesized from arylmethyl halides.

In the course of our studies on organic fluorine compounds, hexafluorobutyne-2 was found to be a good dipolarophile and dienophile, and a very useful species for the synthesis of various trifluoromethylated compounds[1]. For the extention of these studies, we needed mono(trifluoromethyl)acetylene compounds, but simple methods for the synthesis of these compounds had not been reported To solve this problem, we examined pyrolysis of α-trifluoroacetylbenzylidenephosphorane[2], and succeeded in the convenient synthesis of the titled compounds from substituted benzyl halides (Scheme 1).



Substituted benzyl halides (1) reacted with triphenylphosphine under usual conditions[3] to give phosphonium compounds (2), which were trifluoroacetylated with trifluoroacetic anhydride in the presence of a suitable base to α-trifluoroacetylbenzylidenephosphoranes (3). The reaction conditions and properties of 3 are shown in Table 1.

Table 1. Reaction Conditions and Properties of Compounds (3)

Subst.	Base	Solv.	Temp.	Time	Yield	mp(°C)	^{1}H-NMR(δ)	^{19}F-NMR(δ)^4	Mass
2a	BuLi	THF	R.T.	1 h	69%	223-5	7.0(5H) 7.3-7.7(15H)	4.0	448 379
2b	BuLi	THF	R.T.	1.5h	39%	206-7	2.2(3H),6.9(4H), 7.3-7.8(15H)	4.0	462
2c	BuLi	THF	R.T.	1 h	17%	241-3	3.7(3H),6.4-7.1 (4H),7.4-7.7(15H)	4.2	478
2d	LDA	THF	R.T.	2 h	17%	200	7.0(4H) 7.3-7.8(15H)	4.0	482
2e	NaOH	C_6H_6	R.T.	2 h	71%	219	7.3-7.8(m)	4.3	493

The phosphorane compounds (**3**) were thermolyzed under vacuum to give phenyltrifluoromethylacetylene derivatives (**4**) in moderate to good yields. The reaction conditions and properties of **4** are shown in Table 2.

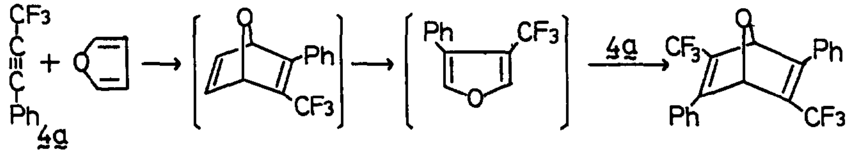
Table 2. Reaction Conditions and Properties of the Acetylene Compounds (4)

Subst.	Pressure	Temp.(°C)	Yield	bp(mp)(°C)	ir(cm^{-1})	^{1}H-NMR	^{19}F-NMR[4]	Mass
3a	10 mmHg	280	85%	165	2240	7.3-7.7	-14.3	170
3b	10 mmHg	280	54%	70[5]	2240	2.4 7.1-7.7	-14.0	184
3c	10 mmHg	410	54%	172[5]	2240	3.8 7.4	-14.7	200
3d	10 mmHg	280	40%	63-70[5]	2240	7.3-7.5	-14.0	204
3e	10 mmHg	280	85%	(72-3)	2260	7.8(d) 8.3(d)	-13.7	215

This process is a simple method of the synthesis of aryltrifluoromethylacetylenes of wide applicability.

Phenyltrifluoromethylacetylene was found to be much less reactive than hexafluorobutyne-2 in the Diels-Alder reaction. It did not react with furan at room temperature, and at elevated temperature it gave a complex mixture of products. The formation of the oxanorbornadiene, which seemed to be formed by successive Diels-Alder and retro-Diels-Alder reactions (Scheme 2), was estimated by g.l.c.-mass spectrometry More detailed studies on the reactivities of these acetylene compounds are in progress.

Scheme 2



References and Notes

1. Y. Kobayashi, I. Kumadaki, and S. Fujino, Heterocycles, 1977, 7, 871.
2. For an intramoleculai Wittig reaction, see S. T. D. Gough, and S. Trippett, J. Chem. Soc., 1962, 2333.
3. e.g. K. Friedrich, and H. G. Henning, Chem. Ber., 1959, 92, 2756.
4. Benzotrifluoride was used as an external standard, which is 64 ppm higher than $CFCl_3$. Higher field is shown by plus.
5. Bath temperature in bulb-to-bulb distillation.

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