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Synthesis of Trifluoromethylalkenes and Alkynes. - Trifluoromethyl Captodative Olefins

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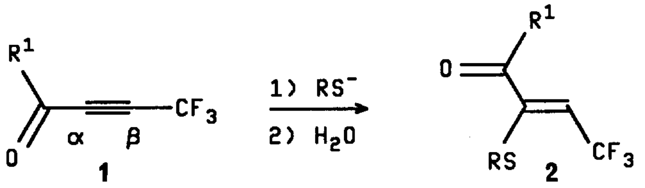
Key words : ethylthiotrifluoromethylaldehyde ; trifluoromethylalkynes ; captodative olefins ; decarbonylation ; nucleophilic substitution.

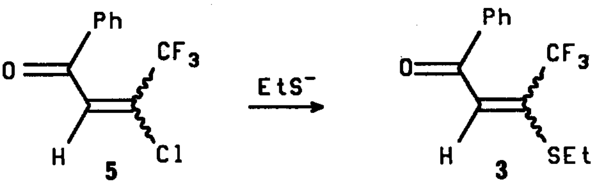
Abstract : β-ethylthio-β-trifluoromethylketones 3 *and aldehydes* 4 *are easily prepared from β-chloroolefines* 5 *and* 6. *Trifluoromethylalkynes* 7 *and captodative alkenes* 8 *are obtained by reaction of KOH on aldehydes* 6 *or* 4.

Michael addition of thiolate on α,β-acetylenic carbonyl systems is the most common reaction to introduce a nucleophile in the β position. But recently Bumgardner[1] shown that the reaction of carbonyl(trifluoromethyl)-acetylene 1 (R^1=Ph, H) with thiolate leads to the anti-Michael adduct 2. This result was rationalized by molecular orbital calculations.

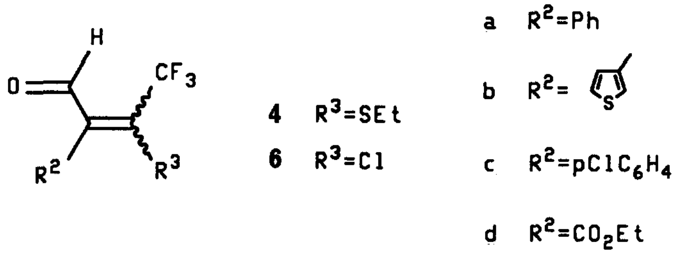


In this communication, we present a synthetic reaction for the preparation of "Michael compounds" 3 and 4 (which cannot be obtained by Michael addition on 1) and the use of compounds 6 and 4 to prepare trifluoromethylalkynes or alkenes.

The Vilsmeier reaction on 4,4,4-trifluoro-1-phenyl-1,3-butanedione produced 5[2] as the major regioisomer. 5 reacted with thiolate to give exclusively the "Michael" sulfur com-



pound **3**[3]. The same reaction was performed from **6a,b,c,d**[4] and β-ethylthioacroleins **4a,b,c,** were obtained in a good yield[5].

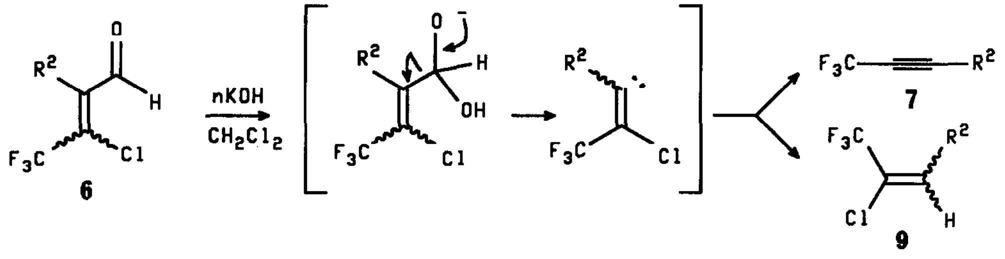


4 R^3=SEt
6 R^3=Cl

a R^2=Ph
b R^2=
c R^2=$pClC_6H_4$
d R^2=CO_2Et

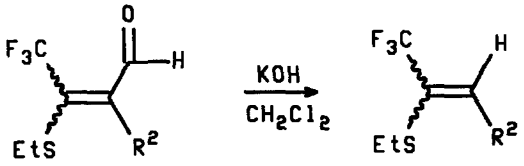
1-Aryl-3,3,3-trifluoropropynes 7 (R^2=Ar) have been attracting much attention from polymer chemists and synthetic chemists as well as pharmaceutical scientists[6]. Recently, two synthetic methods were reported, one from the palladium-mediated coupling reaction of 3,3,3-trifluoropropyne with iodoarenes[6c] and the other involves conversion of aldehyde with 1,1,1-trichloro-2,2,2-trifluoroethane and dehydrochlorination with sodium *t*-butoxide[6d]. In using a modified Bodendorf reaction, it is easy to synthesize 1-aryl-3,3,3-trifluoropropynes **7** (R^2=Ar) from β-chloroacroleins **6** and captodative olefines **8** from ethylthioacroleins **4a,b,c.** Bodendorf and Mayer[7] have shown that acetylenic compounds can be obtained by reaction of aqueous sodium hydroxyde on 3-chloro-3-arylacroleins.

In using Bodendorf's conditions (KOH/H_2O) trifluoromethylalkene **6a** produced, in a moderate yield (54.5 %), a mixture of alkyne **7a** (80 %) and alkene **9a** (20 %)[8].



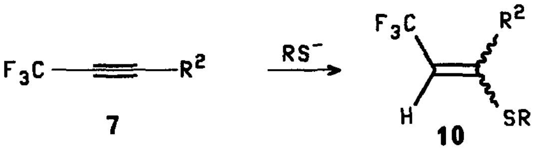
In other conditions (powdered KOH/CH_2Cl_2) only trifluoromethylalkynes **7a,b** were obtained in a good yield (∿75 %)[9]. From **6c** a mixture (yield 97 %) of alkyne **7c** (88 %) and alkene **9c** (12 %) is isolated[10]. The obtention of alkenes **9** is a proof of the formation of a carbanion intermediate. The presence of alkene **9c** must result from a better stabilization of the carbanion by the *para*chlorosubstituent. This hypothesis is supported by the formation of the alkene **9d** from **6d**[11]. In this compound, the carboxylate increases the stability of the carbanion and favours the formation of the olefin **9d.**

According to the captodative Viehe's concept, a lot of radicophilic olefines are described[12]. Generally, the electrodonating group is an alkylthiosubstituent, but the electrowithdrawing group is, in most cases, a conjugated system. In using the previous reaction, it is easy to obtain from **4**, captodative olefines **8** with a trifluoromethylsubstituent as an inductive acceptor and an alkylthiosubstituent as an electron donor group. From **8a,b**, the Z stereoisomer is widely predominant (> 90 %) and the E-Z ratio is independant from the diastereoisomeric mixture of the starting material[13].



4 a,b,c **8 a,b,c**

As recently shown by Bumgardner[14], it is not possible to obtain **8** by thiolate addition on alkyne **7** ; the regiosiomers **10** are formed.



7 **10**

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References and Notes

Chemical shifts are given in ppm (δ H ; ϕ F) relative to the TMS and CFCl$_3$. Coupling constants for J$_{ab}$ are Hz (yield).

1 C.L. Bumgardner, J.E. Bunch and M.H. Whangbo, *J. Org. Chem.*, 1986, 51, 4082.
Kinetic control leads only to the anti-Michael adducts **2**.
A mixture of Michael (39 %) and anti-Michael (43 %) addition was obtained by Bumgardner, under thermodynamically conditions.

2 **5** was recently obtained by an other reaction described by T. Okano, T. Uekawa and S. Eguchi, *Bull. Chem. Soc. Jpn.*, 1989, 62, 2575. **5** was synthesized according to R.E. Mewshaw, *Tetrahedron Lett.*, 1989, 30, 3753. A mixture of 5 (70 %, Z/E = 96/4) and regioisomers Ph-CCl=CH-CO-CF$_3$ (30 %) is obtained (78 %).

3 **3** (77 %). MS m/z = 260 (M$^{+\cdot}$), 105 (100 %). Z (88 %) : δ = 1.2 (t, 3H, J=7), 3.0 (q, 2H, J=7), 7.2-8.2 (m, 6H) ; ϕ = -63.3 (s, 3F). E (12 %) : δ = 1.3 (t, 3H, J=7), 2.9 (q, 2H, J=7), 7.2-8.2 (m, 6H) ; ϕ = -70.0 (s, 3F).

4 **6a,d** are described by G. Alvernhe, B. Langlois, A. Laurent, I. Le Dréan, A. Selmi and M. Weissenfels, *Tetrahedron Lett.*, 1991, 32, 643. 6b (70 %). E (68 %) : δ = 6.9-7.7 (m, 3H), 10.3 (q, 1H, J=2.5) ;

ϕ = -57.8 (d, 3F, J=2.5). Z (32 %) : δ = 6.9-7.7 (m, 3H), 10.5 (s, 1H) ; ϕ = -62.2 (s, 3F).
6c (78 %). Z (59 %) : δ = 6.9-7.6 (m, 4H), 10.4 (s, 1H) ; ϕ = -62.3 (s, 3F). E (41 %) : δ = 6.9-7.6 (m, 4H), 10.2 (q, 1H, J=2) ; ϕ = 58.3 (d, 3F, J=2).

5 **4a** (90 %). Z (68 %) : δ = 1.2 (t, 3H, J=8), 2.9 (q, 2H, J=8), 6.9-7.5 (m, 5H), 10.4 (s, 1H) ; ϕ = -58.7 (s, 3F). E (32 %) : δ = 1.2 (t, 3H, J=8), 2.4 (q, 2H, J=8), 6.9-7.5 (m, 5H), 10.1 (q, 1H, J=2) ; ϕ = -54.7 (d, 3F, J=2).
4b (88 %). Z (68 %) : δ = 1.3 (t, 3H, J=8), 2.9 (q, 2H, J=8), 6.9-7.5 (m, 3H), 10.5 (s, 1H) ; ϕ = -59.0 (s, 3F). E (32 %) : δ = 1.1 (t, 3H, J=8), 2.4 (q, 2H, J=8), 6.9-7.5 (m, 3H), 10.2 (q, 1H, J=2) ; ϕ = -55.3 (d, 3F, J=2).
4c (61 %). Z (84 %) : δ = 1.3 (t, 3H, J=7), 2.9 (q, 2H, J=7), 6.8-7.6 (m, 4H), 10.5 (s, 1H) ; ϕ = -58.8 (s, 3F). E (16 %) : δ = 1.1 (t, 3H, J=7), 2.5 (q, 2H, J=7), 6.8-7.6 (m, 4H), 10.2 (q, 1H, J=3) ; ϕ = -54.7 (d, 3F, J=3).

6 a) H.C. Clark, G. Fergerson, A.B. Goel, E.G. Garizen, H. Ruegger, P.H. Siwo and C.S. Wong, *J. Am. Chem. Soc.*, 1986, 108, 6961.
b) Y. Kobayashi, T. Yamashita, K. Takahoshi, H. Kuroda and I. Kumadaki, *Tetrahedron Lett.*, 1982, 23, 343.
c) J.E. Bunch and C.L. Bumgardner, *J. Fluor. Chem.*, 1987, 36, 313.
d) T. Hiyama, K. Sato and M. Fujita, *Bull. Chem. Soc. Jpn.*, 1989, 62, 1352.

7 K. Bodendorf and R. Mayer, *Chem. Ber.*, 1965, 98, 3554.

8 The same mixture of **7a** and **9a** is obtained from **6a** E/Z = 40/60 and **6a** Z.
7a is described in ref. 6c).
9a E : IR (C=C) = 1630 cm^{-1}. δ = 7.1-7.7 (m, 5H) ; ϕ = -62.0 (s, 3F). MS m/z = 206 ($M^{+\cdot}$).

9 As a typical procedure : 6.5 mmol KOH, 12 ml CH_2Cl_2, 2 mmol aldehyde. The solution was stirred for 12 h at RT. Classical work up.
7a (74 %) ; **7b** (75 %). IR (C≡C) = 2330 cm^{-1}. δ = 7.1-7.9 (m, 3H) ; ϕ = -50.7 (s, 3F).

10 **7c** (88 %) is described in ref. 6d).
9c (12 %), E/Z = 1. MS m/z = 240 ($M^{+\cdot}$, 100 %). δ = 7.1-7.6 (m, 4H). E : ϕ = -62.0 (s, 3F) ; Z : ϕ = -69.3 (s, 3F).

11 **9d** (46 %). MS m/z = 157 (100 %). E (72 %) : δ = 1.3 (t, 3H, J=8), 4.3 (q, 2H, J=8), 6.5 (s, 1H) ; ϕ = -65.7 (s, 3F). Z (28 %) : δ = 1.3 (t, 3H, J=8), 4.3 (q, 2H, J=8), 6.7 (s, 1H) ; ϕ = -71.0 (s, 3F).

12 H.G. Viehe, R. Merenyi, L. Stella and Z. Janousek, *Angew. Chem. Int. Ed. Engl.*, 1979, 18, 917.

13 **8a** (74 %). MS m/z = 232 ($M^{+\cdot}$, 100 %). Z (89 %) : δ = 1.1 (t, 3H, J=8), 2.7 (q, 2H, J=8), 7.2-8.0 (m, 6H) ; ϕ = -65.3 (s, 3F). E (11 %) : δ = 1.1 (t, 3H, J=8), 3.4 (q, 2H, J=8), 7.2-8.0 (m, 6H) ; ϕ = -58.6 (s, 3F).
8b (43 %). MS m/Z = 238 ($M^{+\cdot}$, 100 %). Z (95 %) : δ = 1.2 (t, 3H, J=8), 2.8 (q, 2H, J=8), 7.1-8.0 (m, 4H) ; ϕ = -65.3 (s, 3F). E (5 %) : ϕ = -59.3 (s, 3F).
8c (74 %). MS m/z = 266 ($M^{+\cdot}$, 100 %). Z (95 %) : δ = 1.1 (t, 3H, J=8), 2.7 (q, 2H, J=8), 7.0-7.8 (m, 5H) ; ϕ = -64.9 (s, 3F). E (5 %) : ϕ = -66.2 (s, 3F). Relative configurations of **8c** are not yet determined.

14 C.L. Bumgardner, J.E. Bunch and M.H. Whangbo, *Tetrahedron Lett.*, 1986, 27, 1883.

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