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SYNTHESIS OF ACETYLENIC KETONES FROM THIOL ESTERS AND 1-ALKYNYLTRIMETHYLSILANES

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Summary: In the presence of silver tetrafluoroborate, S-ethyl carbothioates reacted with 1-alkynyltrimethylsilanes to give the corresponding acetylenic ketones in good yields.

Acetylenic ketones are useful precursors of α,β-unsaturated ketones, chiral propargyl alcohols, and allylic alcohols, which occur in a variety of natural products, and many methods$^{1,2)}$ have been developed for their synthesis. However, these methods are occasionally inadequate in the presence of sensitive functionalities, because of the frequent need of strong reaction conditions or of reactive acid halides as one of the starting materials.

Trimethylsilylacetylenes have been used for the synthesis of acetylenic ketones in combination with acyl halides and aluminum chloride$^{2)}$ and alkyl carbothioates or their derivatives have also been used for the synthesis of saturated ketones.$^{3)}$ In connection with these works, we report here a mild and efficient synthesis of acetylenic ketones from thiol esters$^{4)}$ as acyl transfer reagents and trimethylsilylacetylenes under the presence of a soft acid-hard base salt as a catalyst which activates both the reactants simultaneously (equation 1). However, it is mechanistically not clear at present whether the silylacetylenes participate in this reaction simply as the source of acetylide ions.

$$R^1COSEt \quad + \quad R^2C{\equiv}CSiMe \quad \xrightarrow[CH_2Cl_2,rt]{AgBF_4} \quad R^1COC{\equiv}CR^2 \qquad \text{(eq. 1)}$$

Among the catalysts examined, $AgBF_4$ proved to be the most effective one and the reaction indicated above took place very smoothly in dichloromethane at room temperature to give acetylenic ketones within 30 minutes. The results obtained are summarized in Table 1. Other catalysts, such as AgF and $CuCl_2$, for example, gave no product and $SnCl_4$ gave a yield less than 10% under the same conditions. The reaction in benzene gave only moderate yields and in DMF or THF no acetylenic ketones were obtained. It is noteworthy that in this reaction, esters of ethanethiol gave the most satisfactory results in yield and rate, while the esters of 2-methyl-2-propanethiol$^{5)}$ or of 2-pyridinethiol$^{6)}$ resulted in low yield (3% or 33%, respectively) even with prolonged reaction time at an elevated temperature.

The typical reaction procedure is as follows: S-Ethyl 2-methylthiopropionate (79 mg, 0.6 mmol) was added to a suspension of anhydrous $AgBF_4$ (214.2 mg, 1.1 mmol) in dichloromethane (0.5 ml) under nitrogen. After stirring for 10 minutes, 1-octynyltrimethylsilane (117.8 μl, 0.5 mmol) was added rapidly and the resulting mixture was stirred for an additional 20 min at room temperature. The solution was diluted with ether and filtered through Celite. After the usual work-up, 2-methyl-4-undecyn-3-one (74.6 mg, 83%) was isolated by column chromatography on silica gel.

Table 1. Reactions of Thiol Esters with Trimethylsilylacetylenes Catalyzed by $AgBF_4$[a)]

Thiol Ester R^1 in R^1COSEt	Silylacetylene R^2 in $R^2C{\equiv}CSiMe_3$	Time (min)	Acetylenic Ketone Yield(%)[b)]
$CH_3CH_2CH_2$	$n\text{-}C_6H_{13}$	10	96
$CH_3CH_2CH_2$	C_6H_5	10	88
$(CH_3)_2CH$	$n\text{-}C_6H_{13}$	20	97(83)
$(CH_3)_2CH$	C_6H_5	10	97
$CH_3CH_2CH_2(CH_3)CH$	$n\text{-}C_6H_{13}$	30	91
$CH_3CH_2CH_2(CH_3)CH$	$(CH_3)_2CHCH_2CH_2$	30	80
$c\text{-}C_6H_{11}$	$n\text{-}C_6H_{13}$	10	92[c)]
C_6H_5	$(CH_3)_2CHCH_2CH_2$	20	(55)
C_6H_5	C_6H_5	10	(62)
$(CH_3)_3C$	C_6H_5	20	(62)
$C_6H_5CH{=}CH$	$n\text{-}C_6H_{13}$	30	(82)

a)Reactions were carried out in dichloromethane at room temperature with a reactant ratio; silylacetylene / thiol ester / $AgBF_4$ = 1.0 / 1.2 / 2.2.

b) Yields were determined by GLPC by comparing with the appropriate internal standards. Isolated yields were given in parentheses. All the products were identified by ^{1}H-NMR by comparing with authentic specimens.

c) Silylacetylene / thiol ester / $AgBF_4$ = 1/ 1.5 / 3

References and Notes

1) For example: D.Nightingale and F.Wadsworth, J. Am. Chem. Soc., 67, 416 (1945); R.B.Davis and D.H.Scheiber, ibid, 78, 1675 (1956); J.F.Normant and M.Bourgain, Tetrahedron Lett., 2659 (1970); H.Newman, J. Org. Chem., 38, 2254 (1973); J.C.Chabala and J.E.Vincent, Tetrahedron Lett., 937 (1978); G.Cahiez, D.Bernard, J.F.Normant, Synthesis, 130 (1977); Y.Tohda, K.Sonogashira, N.Hagihara, ibid., 777 (1977); M.W.Logue and K.Teng, J. Org. Chem., 47, 2549 (1982).

2) L.Birkofer, A.Ritter, and H.Uhlenbrauck, Chem. Ber., 96, 3280 (1963).

3) K.Takai, K.Oshima, and H.Nozaki, Bull. Chem. Soc. Jpn., 54, 1281 (1981); R.J.Anderson, C.A.Henrick, and L.D.Rosenblum, J. Am. Chem. Soc., 96, 3654 (1974); T.Mukaiyama, M.Araki, and H.Takei, ibid., 95, 4763 (1973).

4) Very mild and efficient preparations of thiol esters have recently been developed: H.J.Gais, Angew. Chem. Int. Ed. Engl., 16, 244 (1977); Y.Kawanami, Y.Dainobu, J.Inanaga, T.Katsuki, and M.Yamaguchi, Bull. Chem. Soc. Jpn., 54, 943 (1981).

5) Used as the substrates for thiophilic metal-catalyzed alcoholysis: S.Masamune, Y.Hayase, W.Schilling, W.K.Chan, and G.S.Bates, J. Am. Chem. Soc., 99, 6756 (1977).

6) Used as the substrates for alcoholysis [E.J.Corey and K.C.Nicolaou, J. Am. Chem. Soc., 96, 5614 (1974); H.Gerlach and A.Thalmann, Helv. Chim. Acta., 57, 2661 (1974)] and for aminolysis [T.Mukaiyama, R.Matsueda, and H.Murayama, Bull. Chem. Soc. Jpn., 43, 1271 (1970)].

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