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ETHYLENIC ACYL CYANIDES I.: CONJUGATE ADDITION OF ALLYL AND ALLENYLSILANES TO ETHYLENIC ACYL CYANIDES.

Abdelkebir JELLAL and Maurice SANTELLI*

(Centre de St-Jérôme, Rue H. Poincaré, 13397 - MARSEILLE Cedex 4 France)

Summary : *δ,ε-Ethylenic (or acetylenic) acyl cyanides, or δ,ε-ethylenic (or acetylenic) acids and their methyl esters, can be obtained by a conjugate addition of allyl (or allenyl) silanes to α,β-ethylenic acyl cyanides.*

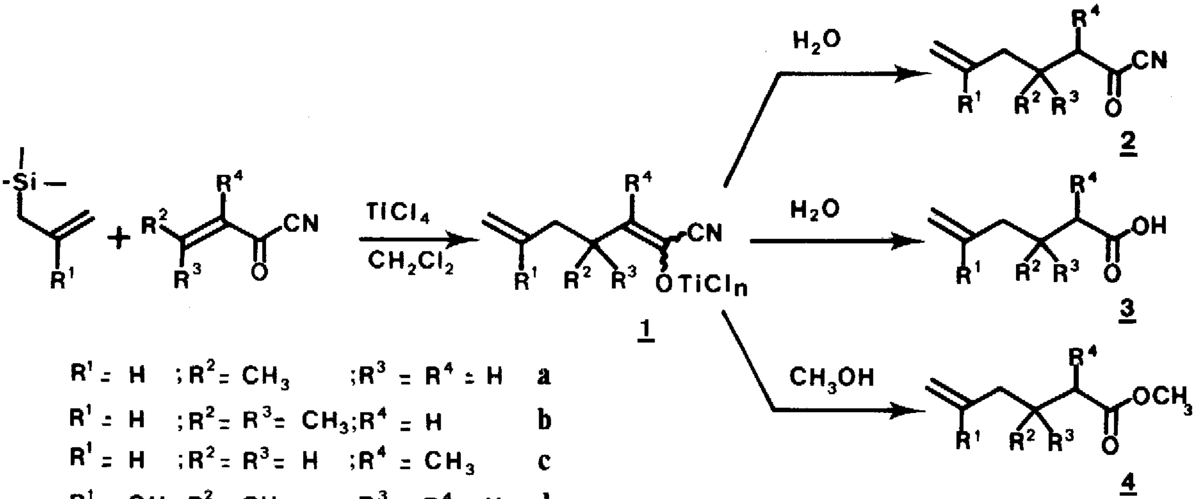
Recently there has been a great deal of interest in the addition of allylsilanes to carbonyl compounds (1). In particular, it has been reported that allyl transfer reactions take place very smoothly from allylsilanes to α,β-enones to give δ,ε-enones (2). But all attempts to alkylate α,β-ethylenic esters were unsuccessful (2b)(3).

We have found that allyl transfer on α,β-ethylenic acyl cyanides (4) occurs *quantitatively*. From the intermediate enolate **1**, three derivatives can be isolated according to the following procedures (7) :

* hydrolysis and rapid extraction with pentane lead to acyl cyanides **2** (8).

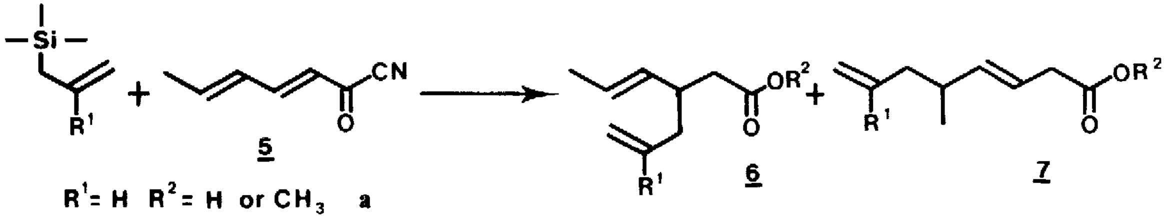
* hydrolysis and stirring with water lead to δ,ε-ethylenic acids **3** .

* methanolysis and standing before work-up give δ,ε-ethylenic methyl esters **4** .



R^1 = H ;R^2 = CH_3 ;R^3 = R^4 = H **a**
R^1 = H ;R^2 = R^3 = CH_3;R^4 = H **b**
R^1 = H ;R^2 = R^3 = H ;R^4 = CH_3 **c**
R^1 = CH_3;R^2 = CH_3 ;R^3 = R^4 = H **d**
R^1 = CH_3;R^2 = R^3 = CH_3;R^4 = H **e**

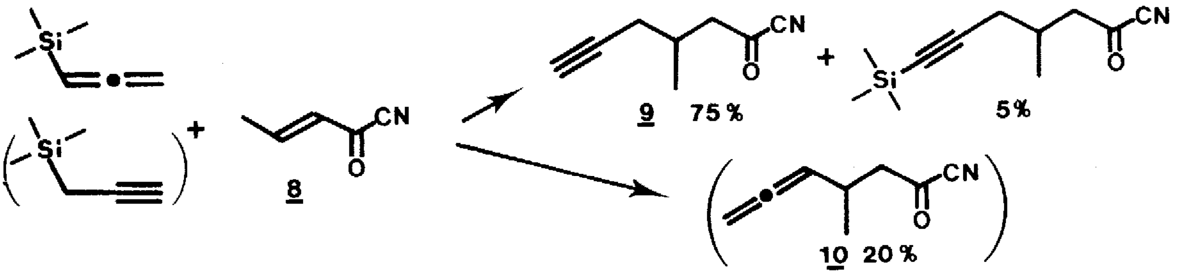
In the case of the dienic acyl cyanide **5**, we observe both 1,4 and 1,6 addition of allylsilanes (overall yield 70 %; **6a** :44 %, **7a** : 56 %; **6b** : 60 %, **7b** 40 %).


5 6 7

R^1= H R^2= H or CH_3 a

R^1= CH_3 R^2= H or CH_3 b

In a similar manner, treatment of the acyl cyanide **8** with allenylsilane (containing 20 % of propargylsilane)(9) gives upon work-up the δ,ε-acetylenic acyl cyanide **9** (partly silylated) and 20 % of the γ-allenyl ketone **10** (overall yield : 75 - 80 %).

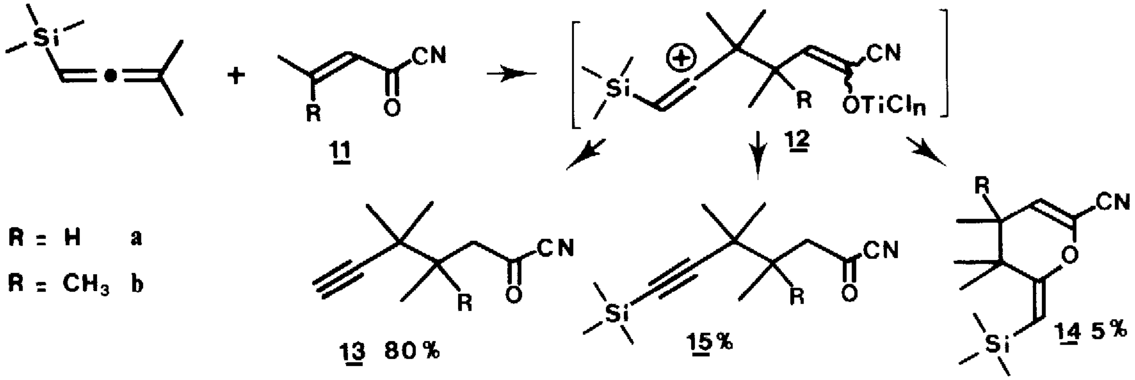

8

9 75%

5%

10 20%

Condensation of dimethylallenylsilane (9) and acyl cyanide **11** leads with excellent yields to δ,ε-acetylenic acyl cyanide **13b** in which the formed bond is between two tertiary carbon atoms. This is rarely encountered because of the F-strain (10), and underlines the efficiency of ethylenic acyl cyanides as electrophilic acceptors (overall yield : 80-85 %).


11

12

R = H a

R = CH_3 b

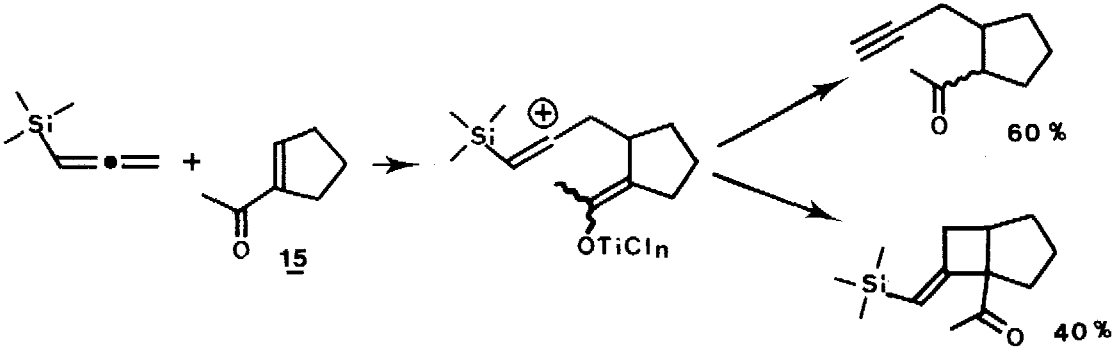
13 80%

15%

14 5%

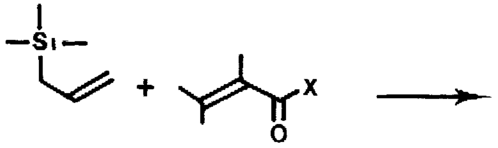
Minor products **14** (11) result from intramolecular O-alkylation of the titanium enolate by the vinyl cation.

In contrast, titanium enolate obtained by conjugate addition of allenylsilane to α-enone <u>15</u> gives a minor product corresponding to intramolecular C-alkylation (overall yield 30 %, 65 % starting material recovery).



The difference of reactivity between enolates of ketones and cyanoketones is in agreement with the harder character of oxygen in the last case (12).

In conclusion, if we compare the behaviour of α-enones (2), ethylenic acyl cyanides, ethylenic acyl chlorides (13) and ethylenic esters (2a) toward allylsilanes, we find that the reactivity of ethylenic acyl cyanides is close to that of α-enones and even better.



X = alkyl : conjugate addition
X = CN : easier conjugate addition
X = Cl : chlorine substitution
X = OCH_3 : no reaction

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3 This is presumably a reflection of the more negative reduction potential of esters *vs.* ketones, see :
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4 The acyl cyanides were prepared according to the procedures reported previously (5) : a mixture of 1,0 mol. of acyl chloride and 1,0 mol. of

cuprous cyanide in acetonitrile (400 ml), is heated under reflux during 20 mn. It has now been found that deleterious side reactions can be minimized by rapidly distilling out the excess acetonitrile and crude products under vacuum. This crude distillate was then carefully refractionated to yield 80 % acyl cyanide. For others synthetic methods see (6).

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7 Titanium chloride (10 mmol.) and anhydrous CH_2Cl_2 under nitrogen were cooled (-20 °C) and acyl cyanide (10 mmol.) in anhydrous CH_2Cl_2 was added. The reaction mixture was cooled (-78 °C) and silane derivative (15 mmol.) was added. The solution was allowed to stir at -78 °C for 3 h and at -30 °C during 4h. Work-up : to isolate **2** : the reaction mixture was poured into ice-water, followed by rapidly extractive work-up with pentane. To isolate **3** : the reaction mixture was stirred with water during 1 h followed by extractive work-up with diethyl ether. To isolate **4** : the reaction mixture was diluted with 30 ml of anhydrous methanol after which it was allowed to stand at room temp. for about 24 h. Hydrolysis and extractive work-up gave ester **4** .

8(a) All products have been characterized by usual spectroscopic techniques. Analytical values were in good agreement with calculated values : C ±0,3 %, H ±0,5 %, N ±0,5 %.

(b) **2** : IR (neat) : 2230, 1725 cm^{-1}.

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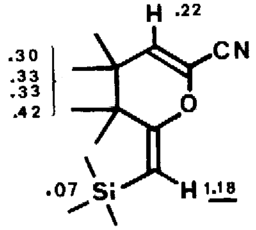
11 Stereochemistry of the double bond of **14b** was established using shift reagent Eufod.

(146 mg Eufod, 50 mg **14b** , 1.18 ml $CDCl_3$)



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