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# ETHYLENIC ACYL CYANIDES II†: CONJUGATE ADDITION OF ALKYNYLSILANES TO ETHYLENIC ACYL CYANIDES.

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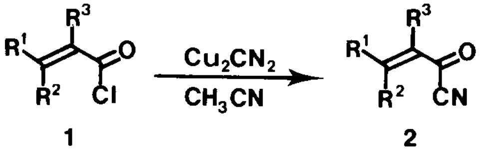
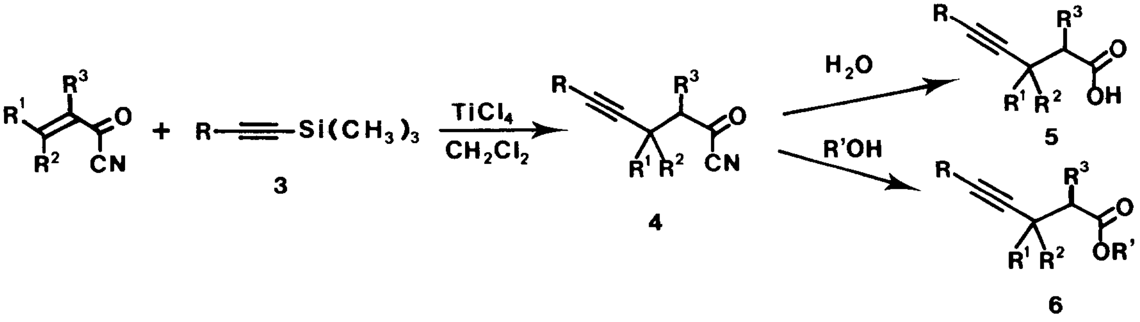
Summary : 3-Alkynylacyl cyanides or 3-alkynylacids and their esters can be obtained by a conjugate addition of alkynylsilanes to α,β-ethylenic acyl cyanides.

The conjugate addition reactions of alkyl, vinyl and aryl GRIGNARD reagents or organocopper species are part of standard synthetic repertoire (2). But alkynylcuprates cannot be used owing to the strength of the alkynyl copper (I) bond (3), and the conjugate addition of alkynyl unit to α,β-enones is achieved with alkynylalanes (4) or alkynylboranes (5). Extension to conjugate ethylenic esters has not been reported. For this purpose, we have studied a three steps indirect method from acyl chlorides: Condensation of acyl chlorides 1 and cuprous cyanide in acetonitrile led to ethylenic acyl cyanides 2 in excellent yield ( 90 % except for the obtention of acrylic cyanide and methactylic cyanide ( 50-60 %, benzonitrile was employed as the solvent ). Conjugate addition reaction of alkynylsilanes 3 to ethylenic acyl cyanides 2 in teh presence of $TiCl_4$ appears to be one of wide generality (6). Hydrolysis ( or methanolysis ) of 3-alkynyl acyl cyanides 4 gives γ,δ-acetylenic acids 5 ( or their methyl esters 6 ) :





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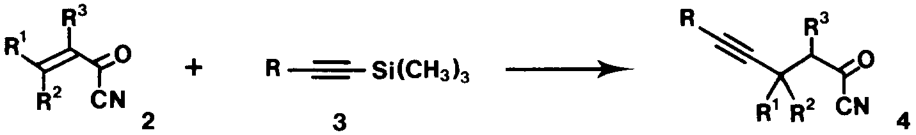
† Part I : see ref. 1.

The requisite alkynylsilane is easily prepared and we used only one equivalent. This constitutes a serious advantage in cases where the acetylenic moiety is a valuable intermediate.

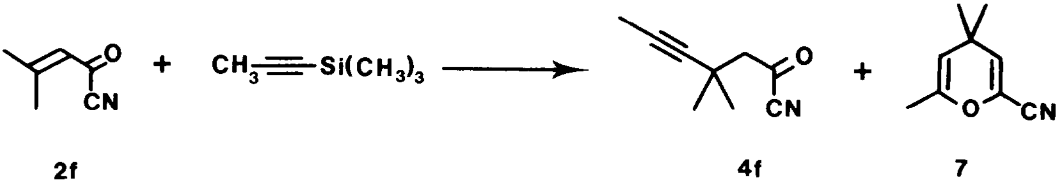
1° - R = Alkyl :

Acetylenic acyl cyanide is obtained as the only product ( no 1,2-addition products are detected ) (7) (yields are calculated on distilled products ) ( reaction temperature : -35 °C ).



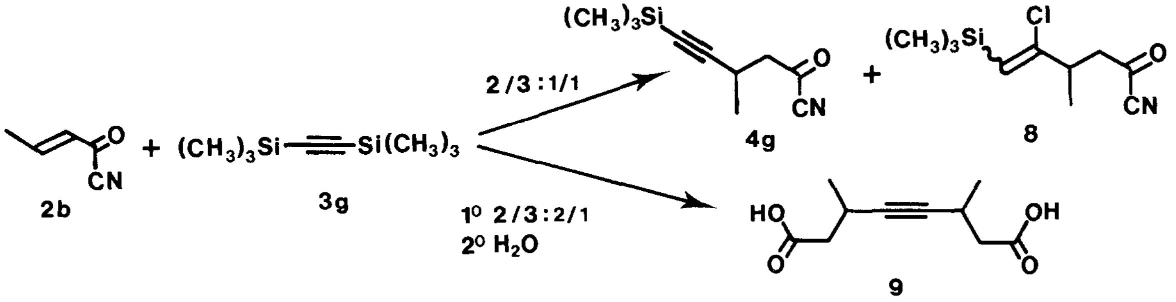
| | Yield | Reaction time |
|---|---|---|
| **a** $R = CH_3$, $R^1 = R^2 = R^3 = H$ | 55 % | 16 h |
| **b** $R = R^1 = CH_3$, $R^2 = R^3 = H$ | 65 % | 16 h |
| **c** $R = n\text{-}C_4H_9$, $R^1 = CH_3$, $R^2 = R^3 = H$ | 65 % | 16 h |
| **d** $R = CH_3$, $R^1 = C_6H_5$, $R^2 = R^3 = H$ | 80 % | 16 h |
| **e** $R = R^3 = CH_3$, $R^1 = R^2 = H$ | 55 % | 16 h |
| **f** $R = R^1 = R^2 = CH_3$, $R^3 = H$ | 70 % | 70 h |

In one the case ( entry f ), a by-product 7 resulting of the intramolecular addition of titanium enolate intermediate ( vide infra ) to the acetylenic bond (8) is isolated in low yield ( ≈ 10 % ). This cyclisation is presumably a consequence of a slower rate of addition :



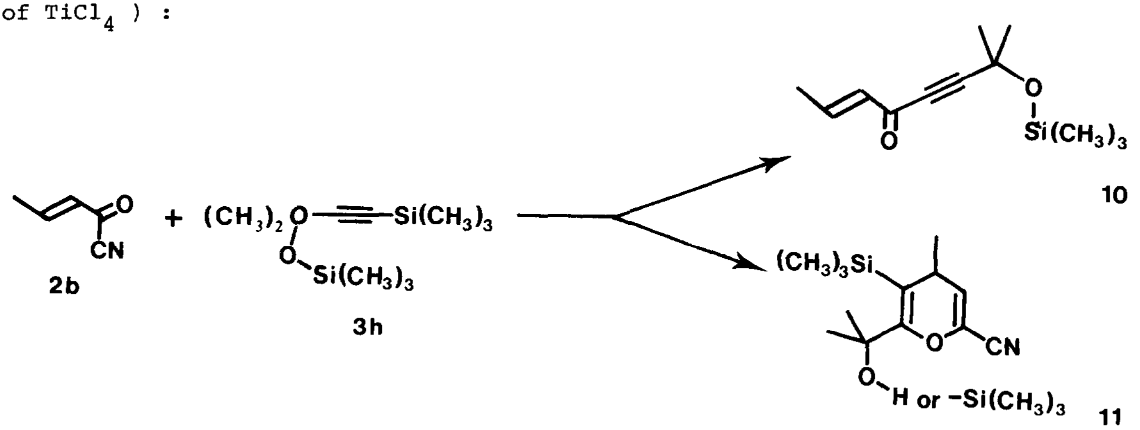
2° - R = Trimethylsilyl :

Silylated acetylenic acyl cyanide 4g is obtained in fair yield ( 65 % ) with one equivalent of each reactant ( in some runs, vinyl chloride derivatives 8 are minor products ( yield 0-10 %, E/Z = 2/1 ).
When we use 2 equivalents of acyl cyanide, 4-octynoic diacid 9 is isolated after hydrolysis on moderate yield ( 35-40 % ) ( diastereoisomeric mixture ):



3° - R = Trimethylsilyloxyalkyl :

The condensation of propargyl alcohol derivative 3h with acyl cyanide 2b leads to the 1,2-addition product 10 and to pyranne derivatives 11 ( 10/11 ≈ 70/30 ). To increase the yield, a large excess of alkynylsilane is used ( with one equivalent of each reactant, we observe a low overall yield ( 30 % ) and a moderate yield ( 55 % ) with 5 equivalents of 3h and 2 equivalents of $TiCl_4$ ) :

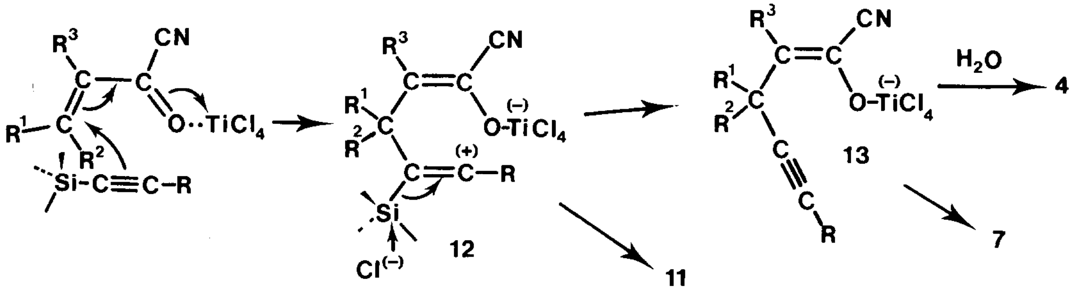


4° - Discussion :

The structural and regiochemical characteristics of the addition of alkynylsilanes to ethylenic acyl cyanides are best rationalised by a mechanism involving a nucleophilic conjugate attack of the acetylenic bond and the formation of vinyl cation 12. This pathway is supported by two observations :

* photoelectron data demonstrate that the acetylenic π ionisation potential is lowered by a silyl substitution (9).

* the C-Si bond in the vinyl cation 12 is oriented cis and is coplanar with the vacant orbital and thus can afford stabilisation by hyperconjugation (10) :



In one case, the intermediate vinyl cation 12 is trapped by the enolate oxygen before desilylation ( obtention of 11 ). After desilylation, nucleophilic addition of the enolate to the acetylenic bond of 13 leads to the minor product 7. Hydrolysis of the enolate 13 gives the acetylenic acyl cyanide 4. Analogous mechanisms have been proposed for the 1,4-addition reaction of allenyl silanes to enones (11) or ethylenic acyl cyanides (1).

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6 Titanium chloride ( 10 mmol ) and anhydrous $CH_2Cl_2$ ( 20 ml ) under $N_2$ were cooled ( -20 ° ) and acyl cyanide ( 10 mmol ) in anhydrous $CH_2Cl_2$ ( 10 ml ) was added. The reaction mixture was cooled ( -78 ° ) and alkynylsilane derivative ( 12 mmol ) was added. The solution was allowed to stir at -78 ° for 1 h and at -35 ° for 16 h. The reaction mixture was pourred into ice-water followed by rapidly extractive work-up with pentane.

7 All products have been characterised by usual spectroscopic techniques ( H.R.M.S., N.M.R. ( $^1H$ and $^{13}C$ ), I.R. ).

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