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ETHYLENIC ACYL CYANIDES IV† : INTRAMOLECULAR ENE CYCLISATION OF 5-METHYL-5-HEXENOYL CYANIDES TO 3-METHYL-2-CYCLOHEXENONES

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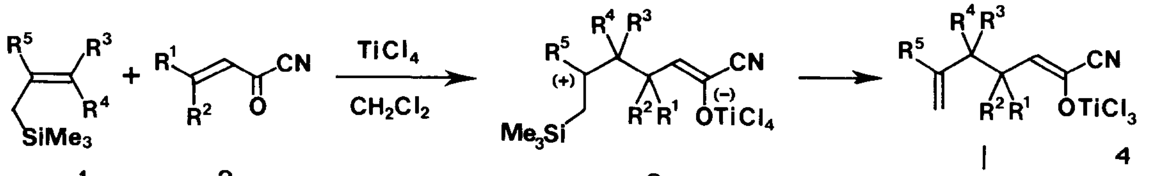
Summary : Condensation of methallyltrimethylsilanes with α,β-ethylenic acyl cyanides leads to 5-methyl-5-hexenoyl cyanides which after thermal cyclisation give 3-methyl-2-cyclohexenones and hydrogen cyanide.

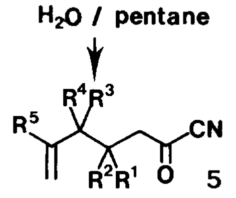
Compounds with CO groups activated by electronegative substituents *e.g.* CN, CO_2R, CX_3 give smoothly Diels-Alder or ene adducts (2). On the other hand much interest has recently focused on the intramolecular ene-reactions (3) with the carbonyl group serving as the enophile (4). We now show that 5-methyl-5-hexenoyl cyanides cyclise easily to give 3-methyl-2-cyclohexenones and hydrogen cyanide.

A - OBTENTION OF δ-ETHYLENIC ACYL CYANIDES :

These acyl cyanides are readily obtained by reaction of methallyltrimethylsilane or E-1,4-ditrimethylsilyl-2-butène (5) with α,β-ethylenic acyl cyanides according to the procedure recently described (6) :



1 2 3



with :

$R^1 = CH_3$, $R^3 = CH_2Si(CH_3)_3$, $R^2 = R^4 = R^5 = H$ **a**

$R^1 = R^5 = CH_3$, $R^2 = R^3 = R^4 = H$..............**b**

$R^1 = R^2 = R^5 = CH_3$, $R^3 = R^4 = H$ ....**c**

$R^1 = R^5 = CH_3$, $R^3 = CH_2Si(CH_3)_3$, $R^2 = R^4 = H$ **d**

$R^1 = R^2 = R^5 = CH_3$, $R^3 = CH_2Si(CH_3)_3$, $R^4 = H$ **e**

$R^1 = R^4 = R^5 = CH_3$, $R^3 = CH_2Si(CH_3)_3$, $R^2 = H$ **f**

$R^1 = R^2 = R^4 = R^5 = CH_3$, $R^3 = CH_2Si(CH_3)_3$....**g**

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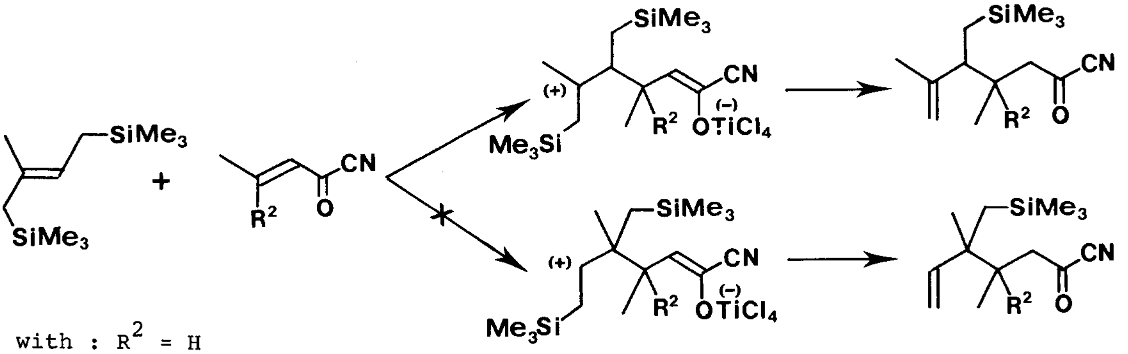
† Part III : see ref. 1.

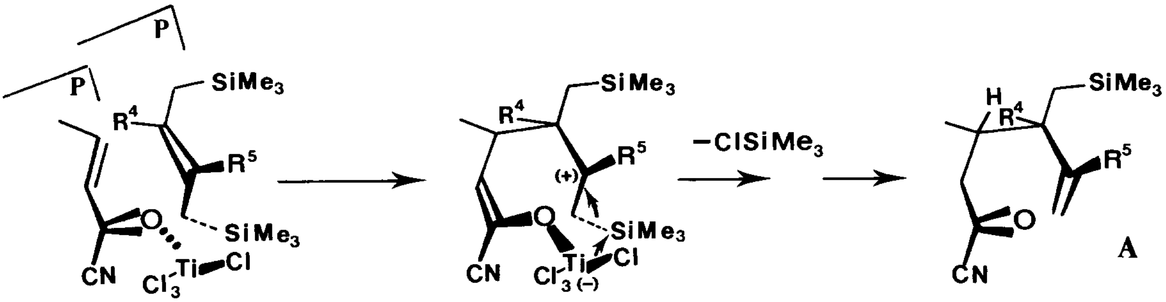
In cases d and e, the only products 5d and 5e obtained result from the formation of tertiary carbocations 3 instead of secondary carbocations:



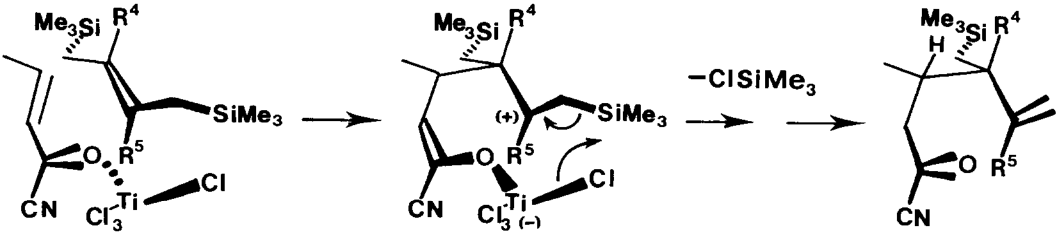
with : $R^2 = H$

$R^2 = CH_3$

In cases a, d and f, a diastereoisomeric mixture of acyl cyanides 5 is obtained. Model considerations and other observations in this area (7) show that the observed stereochemical results are consistent with two transition states A and B :



A



B

a ($R^4 = R^5 = H$) ; A : 5a (threo) : 77 %; B : 5a' (erythro) : 23 %.

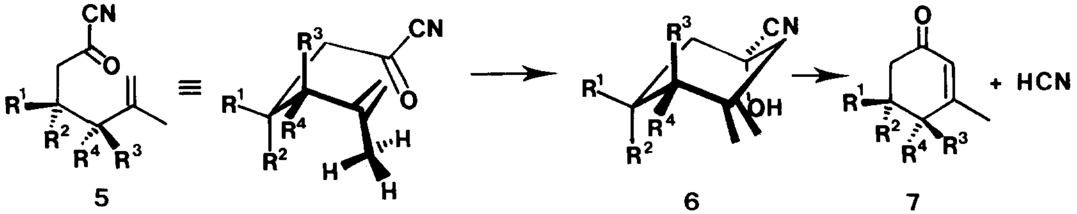
d ($R^4 = H$, $R^5 = CH_3$) ; A : 5d (threo) : 42 %; 5d' (erythro) : 58 %.

f ($R^4 = R^5 = CH_3$) ; A : 5f (threo) : 48 %; 5f' (erythro) : 52 %.

We assume that the allylsilane approaches the s-cis ethylenic acyl cyanide and attains a transitional state geometry which maximizes the C-Si hyperconjugation (*i.e.* the C-Si bond takes position parallel to the π orbital of the double bond)(8). The chlorotrimethylsilane is eliminated after a chloride anion transfer from the stereoproximal tetrachloride titanate.

B - INTRAMOLECULAR ENE CYCLISATION OF 5-METHYL-5-HEXENOYL CYANIDES :

Vapor phase pyrolysis (180-220 °, vector gas : hydrogen, 2 min.) of the 5-methyl-5-hexenoyl cyanides 5b-g results in *exclusive* formation of 3-methyl-2-cyclohexenones 7 and hydrogen cyanide :

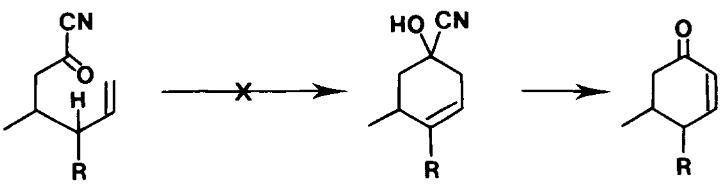


5 6 7

with : $R^1 = CH_3$, $R^2 = R^3 = R^4 = H$.............. b
$R^1 = R^2 = CH_3$, $R^3 = R^4 = H$.............. c
$R^1 = CH_3$, $R^4 = CH_2Si(CH_3)_3$, $R^2 = R^3 = H$ d
$R^1 = CH_3$, $R^3 = CH_2Si(CH_3)_3$, $R^2 = R^4 = H$ d'
$R^1 = R^2 = CH_3$, $R^3 = CH_2Si(CH_3)_3$, $R^4 = H$ e
$R^1 = R^3 = CH_3$, $R^4 = CH_2Si(CH_3)_3$, $R^2 = H$ f
$R^1 = R^4 = CH_3$, $R^3 = CH_2Si(CH_3)_3$, $R^2 = H$ f'
$R^1 = R^2 = R^4 = CH_3$, $R^3 = CH_2Si(CH_3)_3$.... g

This result confirms the high reactivity of acyl cyanides as heteroenophile (2).

Hexenoyl cyanides bearing a methyl group at the 5 position are necessary to get the cyclisation : 3-methyl-5-hexenoyl cyanide (6) and acyl cyanide 5a are unchanged even with forcing conditions (330 °, 4 min.) :



with : R = H
$R = CH_2Si(CH_3)_3$ 5a.

In conclusion, these two reactions (methallyltrimethylsilanes addition on α,β-ethylenic acyl cyanides and thermal cyclisation) leading to 3-methyl-2-cyclohexenones open up uncharted areas in natural products synthesis.

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