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SYNTHETIC APPLICATIONS OF THE [2+2] CYCLOADDITION PRODUCTS OF KETENE ALKYLSILYLACETALS WITH ACRYLONITRILE

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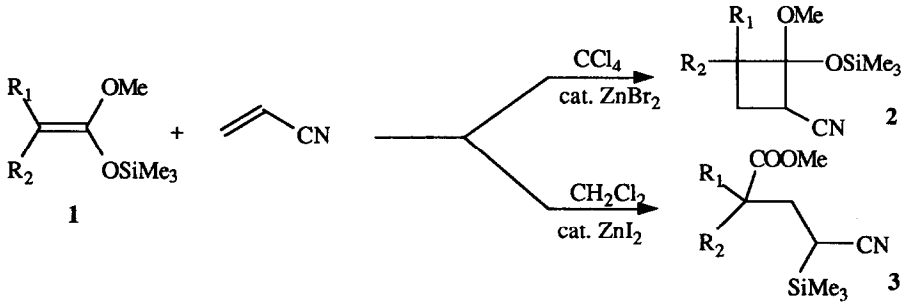
Abstract *: 2-Cyanocyclobutane alkylsilylacetals, obtained by a [2+2] cycloaddition reaction of ketene alkylsilylacetals and acrylonitrile, have allowed the synthesis of 2-cyanoclobutanones, 4-chloro-4-cyanobutanoates and 4-cyanobutanoates by respectively acidic catalysis, $FeCl_3$ cleavage and nBu_4NF treatment. The cycloadducts obtained from chloroketene alkylsilylacetals give 2-cyanocyclopropanecarboxylates by reaction with nBu_4NF.*

The catalyzed reaction of ketene alkylsilylacetals **1** with acrylonitrile was reported to take place via different pathways depending of the solvent and the Lewis acid used in the reaction.[1] In a non polar solvent such as tetrachloromethane in the presence of a catalytic amount of zinc bromide a [2+2] cycloaddition occured, while in dichloromethane and a catalytic amount of zinc iodide a Michael reaction was observed.[1a]

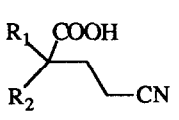


In this paper we want to report synthetic applications of the cyclobutanic compounds **2**.

2-Cyanocyclobutanone synthesis

There are some reports in the literature concerning the preparation of 2-cyanocyclobutanone dialkylacetals [2], however deprotection of the carbonyl group is difficult [2b] and 2-cyanocyclobutanones are usually obtained by hydrolysis of the corresponding enamines [3] or [2+2] cycloaddition with cyanoketenes. [4] In our case, the cyclobutanone alkylsilylacetals **2a-2e** have been deprotected in high yields using 20% sulfuric acid on silica gel.[5] The 2-cyanocyclobutanones **4a-4e** (see Table 1) were characterized by ^1H NMR, IR, mass spectra

and analytical analysis. These compounds were very sensitive and their purifications difficult. For example, chromatography on silica gel led partially to 4-cyanobutanoic acid derivatives **5** by cleavage of the cyclobutane ring. This cleavage becomes quantitative in an acidic medium.



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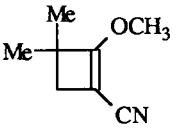
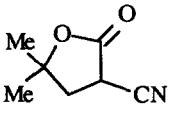
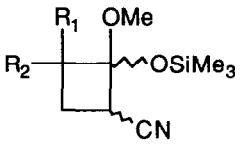


6e



7e

Table 1 **: Preparation of 2-cyanocyclobutanones 4a-4e by hydrolysis of 2-cyanocyclobutane alkylsilylacetals 2a-2e.**



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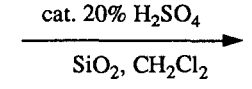
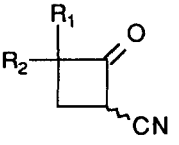




4 (%, yield)[a]

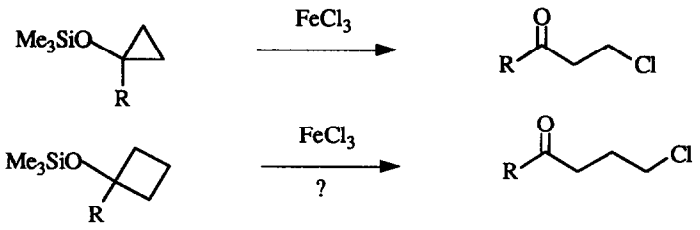
R1=nC_5H_{11} ; R_2=H	**2a**	**4a**	(82)[b]
R_1=cyclohexyl ; R_2=H	**2b**	**4b**	(80)[b]
R_1-R_2=-$(CH_2)_4$-	**2c**	**4c**	(85)
R_1-R_2=-$(CH_2)_5$-	**2d**	**4d**	(90)
R_1=R_2=Me	**2e**	**4e**	(90)

[a] Crude yield (purity ≥95%). [b] Diastereoisomeric mixture.

The enol form of 2-cyanocyclobutanones **4a-4e** could not be detected from their IR and ^1H NMR spectra, by contrast with the 2-cyanocyclohexanone for example, which is 30% enolized.[6] However, as in this latter case, the reaction with diazomethane in ether gave only the O-methylated products. So the enol ether **6e** was isolated in 86% yield, by reaction of diazomethane with the cyclobutanone **4e**. This cyclobutanone **4e**, when treated with 3-chloroperoxybenzoic acid in dichloromethane at room temperature, gave the lactone **7e** resulting, as expected[7] from the insertion of the oxygen atom between the carbonyl and the *gem*-dimethylated carbon.

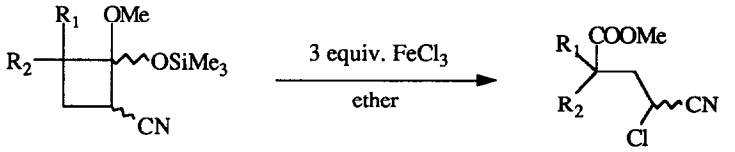
4-Chloro-4-cyanobutanoate synthesis

It has been reported that when trimethylsilyloxycyclopropanes were treated with ferric chloride, cleavage of the cyclopropane ring occured leading to β-chlorocarbonyl compounds.[8a] This reaction applied to 1-silyloxybicyclo[n.1.0]alkanes led to alkenones by ring enlargement.[8b] The radical nature of the reaction was recently demonstrated.[8c] Nothing is known about its possible extension to silyloxycyclobutane derivatives.



When 2-cyanocyclobutane alkylsilylacetals **2a-2e** were treated with 3 equivalents of $FeCl_3$ in anhydrous ether (18h, room temperature) the cleavage of the cyclobutane ring occured leading to methyl 4-chloro-4-cyanobutanoates **8a-8e** (see Table 2). These products were characterized by ^1H NMR, IR, mass spectra and elemental analysis and should be purified by distillation since during the silicagel chromatography, partial removal of the chlorine atom was observed.

Table 2 **: Preparation of 4-chloro-4-cyanobutanoates 8a-8e by reaction of 2-cyanocyclobutane alkylsilylacetals 2a-2e with $FeCl_3$.**

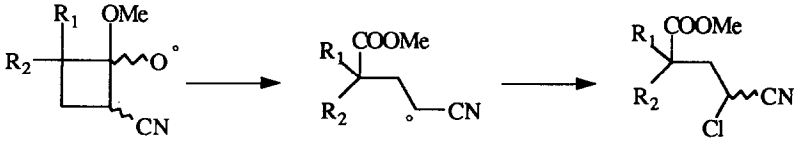


2 **8** (%yield)[a]

$R1=nC_5H_{11}$; R_2=H	**2a**	**8a**	(91)[b]
R_1=cyclohexyl ; R_2=H	**2b**	**8b**	(90)[b]
R_1-R_2=-$(CH_2)_4$-	**2c**	**8c**	(90)
R_1-R_2=-$(CH_2)_5$-	**2d**	**8d**	(90)
R_1=R_2=Me	**2e**	**8e**	(80)

[a] Crude yield (purity ≥ 95%). [b] Diastereoisomeric mixture.

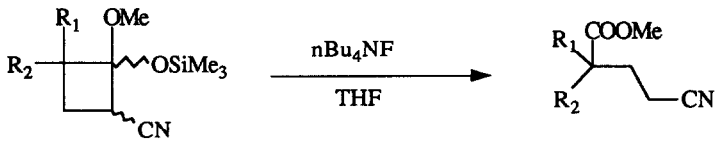
Similarly to the $FeCl_3$ cleavage of trimethylsilyloxycyclopropanes [8], the formation of products **8a-8e** occurs probably via a cyclobutyloxy radical [9], which opens into a cyano stabilized radical.



4-Cyanobutanoate synthesis

The Michael addition of ester enolates to acrylonitrile is possible only with soft carbanions, so the reported examples with monoesters involved only arylacetates.[10] In fact, 4-cyanobutanoates have been usually prepared by reaction of substituted malonates with acrylonitrile followed by a decarboxylation.[11] The reaction of 2-cyanocyclobutane alkylsilylacetals **2a-2e** with 1 equiv. of tetrabutylammonium fluoride in THF (4 h, room temperature) led in excellent yields to the open chain compounds **9a-9e** (see Table 3). These cyanoesters purified by liquid chromatography on silicagel were characterized by their spectral data and analytic properties.

Table 3 **: Preparation of 4-cyanobutanoates 9a-9e by reaction of 2-cyanocyclobutane alkylsilylacetals 2a-2e with tetrabutylammonium fluoride.**



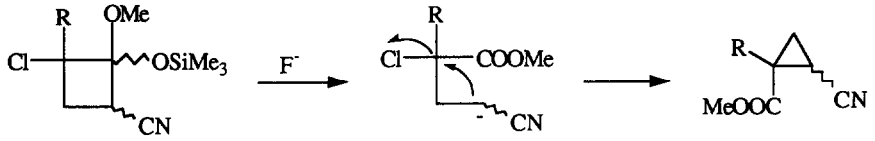
2		9 (%yield)[a]	
R1=nC_5H_{11} ; R_2=H	**2a**	**9a**	(95)
R_1=cyclohexyl ; R_2=H	**2b**	**9b**	(95)
R_1-R_2=-$(CH_2)_4$-	**2c**	**9c**	(85)
R_1-R_2=-$(CH_2)_5$-	**2d**	**9d**	(85)
R_1=R_2=Me	**2e**	**9e**	(90)

[a] Purified compound (purity ≥ 98%).

Our method, which can be conducted as a one pot procedure starting from the ketene acetal, is thus a convenient one to obtain 4-cyanobutanoates. Interestingly, 4-cyano-2,2-dialkylbutanoates **2c-2e**, are unknown products, which cannot be prepared using the previously reported procedures.[11]

2-Cyanocyclopropanecarboxylate synthesis

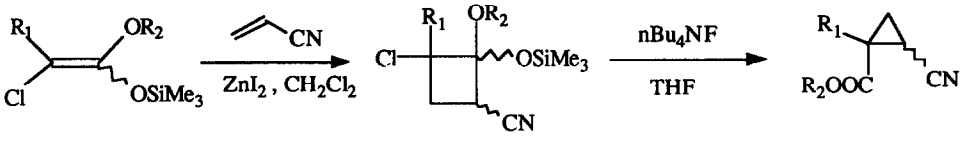
2-Cyanocyclopropanecarboxylates are useful intermediates which have been prepared by numerous methods.[12] We postulated that we could obtain these compounds by an intramolecular cyclisation of the anion resulting from the cleavage by a fluoride anion of 4-chloro-2-cyanocyclobutane alkylsilylacetals.



The desired chloroketene acetals **1** were prepared by the standard procedure [13] from the corresponding chloroesters (or chlorolactone). The reaction of these ketene acetals with acrylonitrile in dichloromethane (or

dichloroethane) at reflux in the presence of a catalytic amount of zinc iodide led to the corresponding 4-chloro-2-cyanocyclobutane alkylsilylacetals, which by a subsequent reaction with tetrabutylammonium fluoride led to 2-cyanocyclopropanecarboxylates (see Table 4). Compounds **2f-2h** and **10f-10h** were characterized from their spectral data and analytical properties. The ratios of isomers of ketene acetals **1f,1g** and cyclopropane carboxylates **10f,10g** were deduced from their ^1H NMR spectra. Assignment of the signals was made on the basis of relative chemical shifts and coupling constants (see also[14]).

Table 4 **: Preparation of 2-cyanocyclopropanecarboxylates 10f-10h by reaction of 4-chloro-2-cyanocyclobutane alkylsilylacetals 2f-2h with tetrabutylammonium fluoride.**



1		2 (%, Yield)[a]	10 (%, Yield)[b]
R_1=Me ; R_2=Et	**1f** : Z/E=66/34	**2f** (69)[c]	**10f** (83)[c] : Z/E=50/50
R_1=C_5H_{11} ; R_2=Et	**1g** : Z/E=66/34	**2g** (61)[c]	**10g** (80)[c] : Z/E=30/70
R_1- R_2=-$(CH_2)_4$-	**1h**	**2h** (23)	**10h** (47)[c] : Z/E ND[d]

[a]Crude yield (purity≥95%). [b]Pure material. [c]Isomeric mixture. [d]Not determined.

The necessity to made the [2+2] cycloaddition at reflux of dichloromethane (or even of 1,2-dichloroethane for the enol ether **1h**) shows the deactivation introduced by the presence of the chlorine atom. Besides, a very slow reaction was observed when zinc bromide was used as catalyst. None of the reactions observed with acetals **2a-2e** were successful.

In conclusion in this paper we have shown that 2-cyanocyclobutane alkylsilylacetals are useful intermediates, from which we were able to generate numerous compounds, which would be generally more difficult to obtain by other methods.

Experimental Part

Nuclear magnetic resonance spectra were recorded on Perkin Elmer R-32A (90 MHz) or Brucker AM250 (250 MHz). Mass spectra were determined with a Nermag R10-10 spectrometer at an ionizing voltage of 70 ev. Infrared spectra were recorded on a Perkin Elmer 682 spectrometer. Melting points were determined on a Reichert microscope. GLPC were recorded on a Intersmat IGC 120FB with 10% SE-30 2 m column. Column chromatography was performed with SDS silica gel (70-230 Mesh). Thin layer chromatography was performed on 0.25 mm Silica gel (Merck 60 F 254). Dry solvents were obtained as followed : diethylether was distilled over $LiAlH_4$, tetrahydrofuran was distilled over sodium-benzophenone and hexane over phosphoric anhydride. Triethylamine and diisopropyl amine were purified by distillation over calcium hydride and chlorotrimethylsilane by distillation over quinoline under argon.

The preparation and the description of 2-cyanocyclobutane alkylsilylacetals **2a-2e** have been already reported [1a].

Preparation of 2-cyanocyclobutanones 4a-4e : General Procedure. In a 25 ml flask, were placed 5 g of silicagel (70-200 mesh) and 2 ml of a 20% aqueous H_2SO_4 were dropped under stirring. 2 Mmol of cyclobutane acetal **2** in dichloromethane solution (10 mL) was then added. After 12 h. at room temperature, the solution was filtered. The silica gel was washed several times with CH_2Cl_2 and the filtrate was concentrated under vacuum. Analyticaly pure samples of **4a-4e** could be obtained by chromatography over SiO_2 (ether-hexane : 1-1).

*3-Pentyl-2-oxocyclobutanecarbonitrile **4a*** (mixture of diastereoisomers). IR (neat) cm^{-1}: 2240 (CN), 1795 (CO). ^1H NMR δ : 0.70 - 1.05 (m, 5H), 1.05 - 1.50 (m, 7H), 2.00 - 2.30 (m, 3H), 4.80 - 4.95 (m, 1H). MS : m/e 165 (M^+, 0.4), 84, 68, 55 (100), 41, 39. Anal. calcd. for $C_{10}H_{15}NO$: C, 72.68 ; H, 9.16. Found : C, 72.83 ; H, 9.08.

*3-Cyclohexyl-2-oxocyclobutanecarbonitrile **4b*** (mixture of diastereoisomers). IR (neat) cm^{-1}: 2240 (CN), 1790 (CO). ^1H NMR δ : 1.00 - 1.40 (m, 6H), 1.50 - 2.00 (m, 6H), 2.00 - 2.30 (m, 2H), 4.80 - 4.95 (m, 1H). MS : m/e 177 (M^+, 1.8), 124, 81 (100), 67, 55, 41, 39. Anal. calcd. for $C_{11}H_{15}NO$: C, 74.53 ; H, 8.54. Found : C, 74.80 ; H, 8.60.

*3,3-Tetramethylene-2-oxocyclobutanecarbonitrile **4c***. IR (neat) cm^{-1}: 2240 (CN), 1790 (CO). ^1H NMR δ : 1.50 - 1.95 (m, 8H), 2.20 (dd, J = 8 and 11 Hz, 1H). 2.30 (dd, J = 11 and 9 Hz, 1H), 4.05 (dd, J = 9 and 8 Hz, 1H). MS : m/e 122, 96, 68 (100), 67, 54, 39. Anal. calcd. for $C_9H_{11}NO$: C, 72.44 ; H, 7.44. Found : C, 72.61 ; H, 7.59.

*3,3-Pentamethylene-2-oxocyclobutanecarbonitrile **4d***. IR (neat) cm^{-1}: 2240 (CN), 1785 (CO). ^1H NMR δ : 1.30 - 1.90 (m, 10H), 2.15 (dd, J = 12 and 8 Hz, 1H), 2.20 (dd, J = 10 and 12 Hz, 1H), 4.05 (dd, J = 10 and 8 Hz, 1H). MS : m/e 136, 82, 81, 67 (100), 54, 41. Anal. calcd. for $C_{10}H_{13}NO$: C, 73.57 ; H, 8.03. Found : C, 73.69 ; H, 8.23.

*3,3-Dimethyl-2-oxocyclobutanecarbonitrile **4e***. IR (neat) cm^{-1} : 2245 (CN), 1800 (CO). ^1H NMR (250 MHz) δ : 1.23 (s, 3H), 1.27 (s, 3H), 2.10 (dd, J = 8.23 and 11.66 Hz, 1H), 2.30 (dd, J = 9.04 and 11.66 Hz, 1H), 4.15 (dd, J = 9.64 and 8.23 Hz, 1H). MS : m/e 124 (M^+ +1), 96, 55 (100), 41, 39. Anal. calcd. for C_7H_9NO : C, 68.25 ; H, 7.37. Found : C, 68.48 ; H, 7.50.

Preparation of 6e. To a 4 mmol of cyclobutanone **4e** were added at room temperature an excess of an ethereal solution of diazomethane. After 30 min., the excess of diazomethane was destroyed and the ethereal solution dried over Na_2SO_4. After removal of the solvent under vacuum the product was purified by chromatography (86%). IR (neat) cm^{-1} : 2210 (CN), 1640 (CC), 1340. ^1H NMR δ : 1.20 (s, 6H), 2.10 (s, 2H), 3,95 (s, 3H). MS : m/e 137 (M^+, 100), 122, 94, 80, 67, 55, 52, 41. Anal. calcd. for $C_8H_{11}NO$: C, 70.03 ; H, 8.09. Found : C, 70.40 ; H, 8,18.

Preparation of 7e. To 4 mmol of cyclobutanone **4e** in dichloromethane (5 ml) at 0°C were added 4 mmol of 3-chloroperoxybenzoic acid. After 1 h. at 0°C and 12 h.at room temperature the solid was filtered. The filtrate was concentrated under reduced pressure and purified by liquid chromatography (SiO_2, ether-hexane : 1-1). Solid mp 38°C (yield : 80%). IR ($CDCl_3$) cm^{-1} : 2260 (CN), 1775 (CO). ^1H NMR (250 MHz) δ : 1.42 (s, 3H), 1.58 (s,

3H), 2.43 (dd, J = 10.4 and 12.5 Hz, 1H), 2.58 (dd, J = 12.5 and 9.4 Hz, 1H), 3.90 (dd, J = 10.4 and 9.4 Hz, 1H). MS : m/e 140 (M^+ +1, 0.8), 124 (100), 94, 68, 59, 43. Anal. calcd. for $C_7H_9NO_2$: C, 60.40 ; H, 6.52 ; N, 10.07. Found : C, 60.17 ; H,6.67 ; N, 9.98.

Preparation of 4-chloro-4-cyanobutanoates 8a-8c. General procedure. In a 25 ml flask were placed 6 mmol of anhydrous $FeCl_3$, 6 ml of dry ether and 2 mmol of cyclobutane acetal **2** were added over 10 min. at 0°C. After removal of the cooling bath the mixture was stirred 12 h. at room temperature. The reaction was quenched by addition of 10 ml of water and 5 ml of ether. The organic phase was washed with water (pH 7). The aqueous phases were extracted with ether. The collected organic phases were washed with water (pH 7), dried (Na_2SO_4) and concentrated under vacuum. Analytical pure samples of **8a-8e** were obtained by liquid chromatography (SiO_2, ether-hexane : 5-95).

Methyl 4-chloro-4-cyano-2-pentylbutanoate 8a : Mixture of diastereoisomers : 70-30. IR (neat) cm^{-1}: 2220 (CN), 1740 (CO). ^1H NMR δ : 0.70 - 1.00 (m, 5H), 1.10 - 1.48 (m, 6H), 2.00 - 2.50 (m, 3H), 3.60, main isomer and 3.65, minor isomer (s, 3H), 4.40 - 4.60 (m, 1H). MS (main isomer) : m/e 196, 161, 87 (100), 55, 41. Anal. calcd. for $C_{11}H_{18}ClNO_2$: C, 57.12 ; H, 7.85 ; Cl 15.13. Found : C, 57.31 ; H, 7.99 ; Cl, 14.88.

Methyl 4-chloro-4-cyano-2-cyclohexylbutanoate 8b : Mixture of diastereoisomers : 66-34. IR (neat) cm^{-1}: 2220 (CN), 1740 (CO). ^1H NMR δ : 1.00 - 1.40 (m, 6H), 1.45 - 1.95 (m, 5H), 2.00 - 2.60 (m, 3H), 3.58, minor isomer and 3.60, main isomer (s, 3H), 4.35 - 4.60 (m, 1H). MS (main isomer) : m/e 208, 161, 87 (100), 55, 41. Anal. calcd. for $C_{12}H_{18}ClNO_2$: C, 59.23 ; H, 7.46. Found : C, 59.48 ; H, 7.68.

Methyl (2-chloro-2-cyanoethyl)-1-cyclopentanecarboxylate 8c. IR (neat) cm^{-1}: 2220 (CN), 1735 (CO). ^1H NMR δ : 1.45 - 1.95 (m, 8H), 2.00 - 2.50 (m, 2H), 3.70 (s, 3H), 4.40 - 4.70 (m, 1H). MS : m/e 215 (M^+, 0.3), 180, 141, 120, 93, 81 (100), 79, 67, 41. Anal. calcd. for $C_{10}H_{14}ClNO_2$: C, 55.80 ; H, 6.56. Found : C, 60.10 ; H, 6.30.

Methyl (2-chloro-2-cyanoethyl)-1-cyclohexanecarboxylate 8d. IR (neat) cm^{-1}: 2220 (CN), 1735 (CO). ^1H NMR δ : 1.00 - 1.80 (m, 10H), 1.95 - 2.60 (m, 2H), 3.65 (s, 3H), 4.30 - 4.60 (m, 1H). MS : m/e 229 (M^+, 0.3), 194, 170, 155, 142, 123, 95 (100), 81, 67, 55, 41. Anal. calcd. for $C_{11}H_{16}ClNO_2$: C, 57,62 ; H, 7.04. Found : C, 57.91 ; H, 7.28.

Methyl 4-chloro-4-cyano-2,2-dimethylbutanoate 8e. IR (neat) cm^{-1} : 2230 (CN), 1730 (CO). ^1H NMR δ : 1.30 (s, 6H), 2.25 - 2.55 (m, 2H), 3.70 (s, 3H), 4.62 (t, J = 10 Hz, 1H). MS : m/e 154, 130, 102, 94 (100), 89, 67, 55, 41, 39. Anal. calcd. for $C_8H_{12}ClNO_2$: C, 50.84 ; H, 6.40 ; N, 7.41 ; Cl, 18.75 . Found : C, 50.89 ; H, 6.41 ; N, 7.20 ; Cl, 18.64.

Preparation of 4-cyanobutanoate 9a-9e. General procedure. To a solution of 2 mmol of cyclobutane acetals **2a-2e** in THF (10 ml) was added at room temperature 1M sol. in THF of n-tetrabutylammonium fluoride. The mixture was stirred 2 h. at 20°C and then the solvent was removed under vacuum. The residue was taken into by water (5 ml) and extracted with ether (3 x 10 ml). The ethereal phase was dried (Na_2SO_4). After removal of the solvent, the residue was purified by liquid chromatography (SiO_2, ether-hexane : 20-80).

Methyl 4-cyano-2-pentylbutanoate 9a. IR (neat) cm^{-1} : 2245 (CN), 1740 (CO). ^1H NMR δ : 0.70 - 1.00 (m, 5H), 1.05 - 1.50 (m, 6H), 1.55 - 2.00 (m, 3H), 2.15 - 2.40 (m, 2H), 3.65 (s, 3H). MS : m/e 198 (M^+ +1, 0.6), 127, 87 (100), 82, 55, 41. Anal. calcd. for $C_{11}H_{19}NO_2$: C, 66.96 ; H, 9.71. Found : C, 67.38 ; H, 9.99.

Methyl 4-cyano-2-cyclohexylbutanoate ***9b***. IR (neat) cm^{-1} : 2245 (CN), 1735 (CO). ^1H NMR δ : 1.00 - 1.45 (m, 6H), 1.45 - 2.05 (m, 5H), 2.10 - 2.45 (m, 5H), 3.65 (s, 3H). MS : m/e 210 (M^+ +1, 0.8), 127, 87 (100), 55. Anal. calcd. for $C_{12}H_{19}NO_2$: C, 68.85 ; H, 9.16. Found ; C, 69.19 ; H, 9.01.

Methyl (2-cyanoethyl)-1-cyclopentanecarboxylate ***9c***. IR (neat) cm^{-1} : 2245 (CN), 1735 (CO). ^1H NMR δ : 1.45 - 1.90 (m, 8H), 1.95 - 2.40 (m, 4H), 3.65 (s, 3H). MS : m/e 180 (M^+ -1, 2), 141, 120, 93, 81 (100), 79, 67, 59, 41. Anal. calcd. for $C_{10}H_{15}NO_2$: C, 66.26 ; H, 8.35. Found : C, 66.51 ; H, 8.60.

Methyl (2-cyanoethyl)-1-cyclohexanecarboxylate ***9d***. IR (neat) cm^{-1} : 2240 (CN), 1730 (CO). ^1H NMR δ : 1.00 - 1.80 (m, 10H), 1.85 - 2.35 (m, 4H), 3.65 (s, 3H). MS : m/e 195 (M^+, 1.1), 155, 136, 108, 95 (100), 81, 67, 55, 41. Anal. calcd. for $C_{11}H_{17}NO_2$: C, 67.65 ; H, 8.78. Found : C, 67.80 ; H, 9.01.

Methyl 4-cyano-2,2-dimethylbutanoate ***9e***. IR (neat) cm^{-1} : 2245 (CN), 1740 (CO). ^1H NMR (250 MHz) δ : 1.20 (s, 6H), 2.05 (t, J = 8 Hz, 2H), 2.35 (t, J = 8 Hz, 2H), 3.70 (s, 3H). MS : m/e 140 (M^+ -15), 96 (100), 69, 55, 41, 39. Anal. calcd. for $C_8H_{13}NO_2$: C, 61.90 ; H, 8.45. Found ; C, 62.22 ; H, 8.30.

2-Chloroketene alkylsilylacetals 1f-1h were made from the corresponding 2-chloroesters (or chloro lactone) by reaction with lithium diisopropylamide (THF, -78°C) followed by addition of chlorotrimethylsilane.[13]

2-Chloro-1-ethoxy-1-trimethylsilyloxy-1-propene ***1f***: 55% yield. bp 68°C/12 mmHg. Z-E mixture : 66-34. IR (neat) cm^{-1} : 1695 (CC). ^1H NMR δ : 0.20 (s, 9H), 1.20 (t, J = 6 Hz, 3H), 1.90 E isomer and 1.95 Z isomer (s, 3H,), 3.8, Z isomer and 3.9, E isomer (q, J = 6 Hz, 2H,). MS (Z isomer) : m/e 210-208 (M^+), 103, 93, 90, 73 (100), 55, 43.

2-Chloro-1methoxy-1-trimethylsilyloxy-1-heptene ***1g*** : 86% yield. bp 54°C/6.10^{-2} mmHg. Z-E mixture : 66-34. IR (neat) cm^{-1} : 1690 (CC). ^1H NMR δ : 0.20 (s, 9H), 1.10 - 1.60 (m, 5H), 2.05 - 2.35 (m, 6H), 3.55 , Z isomer and 3.60, E isomer (s, 3H). MS (Z isomer) : m/e 252-250 (M^+), 193, 89, 73 (100), 55, 45.

2,3,4,5-Tetrahydro-6-chloro-7-trimethylsilyloxy-7-oxepine ***1h*** : 68% yield. bp 104°C/12 mmHg. IR (neat) cm^{-1} : 1685 (CC). ^1H NMR δ : 0.20 (s, 9H), 1.45 - 2.05 (m, 4H), 2.35 - 2.60 (m, 2H), 3.80 - 4.10 (m, 2H). MS : m/e 222-220 (M^+), 93, 73 (100), 67.

Preparation of 4-chloro-2-cyanocyclobutane alkylsilylacetals 2f-2g. A mixture of 2 mmol of keteneacetal **1f-1h**, 3 mmol of acrylonitrile, 5 ml of solvent and 0.2 mmol of zinc iodide (65 mg) was heated under reflux. After completion of the reaction (monitored by tlc) 5 ml of 10% aqueous sodium bicarbonate and 5 ml of ether were added. The aqueous phase was extracted with ether (3 x 5 ml). The organic phases were combined and dried over sodium sulfate. After filtration and removal of the solvents under vacuuo, the crude product was used for the subsequent reaction. Analytical samples were obtained by liquid chromatography (SiO_2, ether-hexane : 5-95).

3-Chloro-2-ethoxy-3-methyl-2-trimethylsiloxycyclobutanecarbonitrile ***2f***. A mixture of four diastereoisomers in the ratio 66-18-8-8 was obtained in CH_2Cl_2 after 18 h. at reflux. IR (neat) cm^{-1} : 2235 (CN). ^1H NMR δ : 0.25 (s, 9H), 1.30 (t, J = 8 Hz, 3H), 1.55 (s, 3H, one isomer), 2.20 - 2.50 (m, 1H), 4.20 (q, J = 8 Hz, 2H, one isomer), 4.25 (q, J = 8 Hz, one isomer). MS (main isomer) : m/e 263-261 (M^+), 226, 185, 113, 93, 73 (100), 45. Anal. calcd. for $C_{11}H_{20}ClNO_2Si$: C, 50.56 ; H, 7.72. Found : C, 50.81 ; H, 7.98.

3-Chloro-2-methoxy-3-pentyl-2-trimethylsiloxycyclobutanecarbonitrile ***2g***. A mixture of four diastereoisomers in the ratio 69-23-4-4 was obtained in CH_2Cl_2 after 48 h. at reflux. IR (neat) cm^{-1} : 2240 (CC). ^1H NMR δ : 0.25 (s, 9H), 0.70 - 1.05 (m, 5H), 1.05 - 1.55 (m, 6H), 1.85 - 2.00 (m, 2H), 2.10 - 2.40 (m, 1H),

3.65 (s, 3H, one isomer), 3.70 (s, 3H, one isomer). MS (main isomer) : m/e 288 (M^+-15), 268, 171, 89, 73 (100), 55, 43. Anal. calcd. for $C_{14}H_{26}ClNO_2Si$: C, 55.42 ; H, 8.64. Found :C, 55.80 ; H, 8.32.

4-Chloro-9-oxa-1-trimethylsiloxybicyclo[5.2.0]nonanecarbonitrile ***2h***. A mixture of two diastereoisomers was obtained in 1,2-dichloroethane after 48 h. at reflux. IR (neat) cm^{-1} : 2240 (CN). ^1H NMR (250 MHz) δ : 0.25 (s, 9H), 1.60 - 2.10 (m, 6H), 2.15 - 2.38 (m, 1H), 2.45 - 2.58 (m, 1H), 3.05 - 3.25 (m, 1H), 3.65 - 3.75 (m, 2H). MS (main isomer) : m/e 275-273 (M^+), 157, 95, 93, 81, 73 (100), 67, 55, 45. Anal. calcd. for $C_{12}H_{20}ClNO_2Si$: C, 52.73 ; H, 7.38. Found : C, 53.01 ; H, 7.58.

Preparation of 2-cyanocyclopropanecarboxylates 10f-10h. General procedure. To a mixture of 2 mmol of chlorocyclobutane alkylsilylacetals **2f-2g** and 10 ml of THF were added 2 mmol of a 1M solution of tetrabutylammonium fluoride in THF (2 ml). After 2 h. at room temperature the solvent was removed and to the residue were added 5ml of water and 5 ml of ether. The organic phase was separated and the aqueous phase was extracted with ether (3 x 5 ml). The combined ethereal phases were dried over sodium sulfate. The solvent was removed under reduced pressure and the products were purified by liquid chromatography (SiO_2, ether-hexane).

Ethyl 3-cyano-2-methylcyclopropanecarboxylate ***10f***. This compound is already known.[15] IR neat cm^{-1} : 2935 (CN), 1740 (CO).1H NMR (250 MHz) CN and COOEt anti δ : 1.20 (dd, *J* =4.7 and 6.25 Hz, 1H), 1.30 (t, *J* =6.3 Hz, 3H), 1.55 (s, 3H), 1.70 (dd, *J* =4.7 and 9.4 Hz, 1H), 2.10 (dd, *J* =6.25 and 9.4 Hz, 1H),;4.20 (q, *J* =6.3 Hz, 2H).CN and COOEt syn δ : 1.15 (dd, *J* =4.7 and 6.25 Hz, 1H), 1.30 (t, *J* =6.3 Hz, 3H), 1.50 (s, 3H), 1.65 (dd, *J* =4.7 and 6.25 Hz, 1H), 1.95 (dd, *J* =6.25 and 9.4 Hz, 1H),;4.20 (q, *J* =6.3 Hz, 2H).

Methyl 3-cyano-2-pentylcyclopropanecarboxylate ***10g***. IR (neat) cm^{-1} : 2240 (CN), 1740 (CO). ^1H NMR (250 MHz) δ : CN and COOMe anti : 0.80 - 0.95 (m, 5H), 1.15 (dd, *J* = 4.7 and 9.4 Hz, 1H), 1.25 - 1.40 (m, 6H), 1.75 (dd, *J* = 4.7 and 6.25 Hz, 1H), 1.95 (dd, *J* = 6.25 and 9.4 Hz, 1H), 3.70 (s, 3H).CN and COOMe syn : 0.80 - 0.95 (m, 5H),1.20 (dd, *J* = 4.7 and 6.25, 1H) 1.25 - 1.40 (m, 6H), 1,80 (dd, *J* = 4.7 and 9.4 Hz, 1H), 2.10 (dd, *J* = 6.25 and 9.4 Hz, 1H), 3.70 (s, 3H). MS (main isomer) : m/e 196 (M^+ +1), 142, 113, 95, 87 (100), 82, 69, 55, 41, 39. Anal. calcd. for $C_{11}H_{17}NO_2$: C, 67.65 ; H, 8.78. Found : C, 67.81 ; H, 8.53.

4-Oxa-3-oxo-spiro[6.2]nonanecarbonitrile ***10h***. A mixture of two diastereoisomers was obtained (non determined ratio). Solid. mp : 118°C ± 10°C. IR ($CDCl_3$) cm^{-1} : 2240 (CN), 1730 (CO). ^1H NMR (250 MHz) δ : 1.30 (t, *J* = 6.33, 2H), 1.58 - 1.85 (m, 4H), 1.90 - 2.15 (m, 2H + 1Ha), 2.30 (dd, *J* = 6.38 and 9.5 Hz, 1Hb), 4.25 - 4.38 (m, 2H). MS (main isomer) : m/e 165 (M^+, 11), 137, 106, 79 (100), 67, 55, 41, 39. Anal. calcd. for $C_9H_{11}NO_2$: C, 65.42 ; H, 6.72. Found : C, 65.81 ; H, 6.83.

References

1) a)Quendo, A.; Rousseau, G. *Synth. Commun.* **1989**, *19*, 1551.
b)Ali, S.M.; Rousseau, G. *Tetrahedron* **1990**, *46*, 7011.

2) a) Barrick, P.L.; U.S. Patent 2,437,289 ; *Chem. Abstracts* **1948**, *42*, 4199i.
b) Amice, P.; Conia, J.M. *Bull. Soc. Chim. Fr.* **1974**, 1015.
c) Scheeren, H.W.; Frisson, A.E. *Synthesis* **1983**, 794.

3) Kuehne, M.E. *J. Am. Chem. Soc.* **1959**, *81*, 5400 ; Ficini, J.; Touzin, A.M. *Bull. Soc. Chim. Fr.* **1972**, 2385 ; Madsen, O.; Lawesson, S.O. *Tetrahedron* **1974**, *30*, 3481 ; Cobb, R.L.; Mahan, J.E. *J. Org. Chem.* **1977**, *42*, 1948.

4) a) *tert*-Butylcyanoketene : Moore, H.W.; Gheorghiu, M.D. *Chem. Soc. Rev.* **1981**, *10*, 289 ; Al-Husaini, A.H.; Moore, H.W. *J. Org. Chem.* **1985**, *50*, 2597.
b) Alkynylcyanoketenes : Nguyen, N.V.; Chow, K.; Moore, H.W. *J. Org. Chem.* **1987**, *52*, 1315.
c) Chlorocyanoketenes : Malherbe, R.; Rist, G.; Bellus, D. *J. Org. Chem.* **1983**, *48*, 860 ; Fishbein, P.L.; Moore, H.W. *J. Org. Chem.* **1985**, *50*, 3226 ; Fishbein, P.L.; Moore, H.W. *J. Org. Chem.* **1984**, *49*, 2190.

5) Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J.M. *Synthesis* **1978**, 63.

6) Kulp, S.S.; Schmoyer, R.W.; Freeze, D.E.; Buzas, J. *J. Org. Chem.* **1975**, *40*, 453.

7) Hassal, C.H. *Org. Reactions* **1957**, *9*, 73 ; Lee, J.B.; Uff, B.C. *Rev. Chem. Soc.* **1967**, *21*, 429 ; Krow, G. R. in "*Comprehensive Organic Synthesis*" Vol.7, Trost, B.M. editor, Pergamon Press **1991**, p.671.

8) a) Schaafsma, S.E.; Steinberg, H.; De Boer, T.J. *Rec. Trav. Chim. Pays Bas* **1966**, *85*, 70 and 73.
b) Ito, Y.; Fujii, S.; Saegusa, T. *J. Org. Chem.* **1976**, *41*, 2073.
c) Blanco, L.; Mansouri, A. *Tetrahedron Lett.* **1988**, *29*, 3239.

9) Meyer, K.; Rocek, J. *J. Am. Chem. Soc.* **1972**, *94*, 1209.

10) Grob, C.A.; Weissbach, O. *Helv. Chim. Acta* **1961**, *44*, 1736.

11) Bruson, H.A. *Org. Reactions* **1949**, *5*, 79 ; Mathieu, J.; Weill-Raynal, J. *Formation of C-C Bonds*, Vol. 2, Georg Thieme and Masson Publishers **1975**, p. 164.

12) McCoy, L.L. *J. Am. Chem; Soc.* **1960**, *82*, 6416 ; Bonavent, G.; Causse, M.; Guitard, M.; Fraisse-Jullien, R. *Bull. Soc. Chim. Fr.* **1964**, 2462 ; Schmidt, U.; Schroer, R.; Hockrainer, A. *Justus Liebigs Ann. Chem.* **1970**, *733*, 180 ; Payne, G.B.; Johnson, M.R. *J. Org. Chem.* **1968**, *33*, 1285 ; Villieras, J.; Disnar, J.R.; Normant, J.F. *J. Organomet. Chem.* **1974**, *81*, 295 ; Ducker, S.; Sudre, J.P.; Vessiere, R. *C. R. Acad. Sci. Ser. C* **1974**, *278*, 537 ; Tsuda, T.; Ohoi, F.; Ito, S.; Saegusa, T. *J. Chem. Soc. , Chem. Commun.* **1975**, 327 ; Doyle, M.P.; Davidson, J.G. *J. Org. Chem.* **1980**, *45*, 1538 ; De Vos, M.J.; Krief, A. *Tetrahedron Lett.* **1979**, 1891 ; Jonczyk, A.; Makosza, M. *Synthesis* **1976**, 387 ; Babler, J.H.; Invergo, B.J. *Tetrahedron Lett.* **1981**, *22*, 2743 ; Bhattacharjee, S.S.; Ila, H.; Junjappa, *Synthesis* **1982**, 301 ; Doyle, M.P.; Dorow, R.L.; Tamblyn, *J. Org. Chem.* **1982**, *47*, 4059 ; Makosza, M.; Kwast, A.; Kwast, E.; Jonczyk, A. *J. Org. Chem.* **1985**, *50*, 3722 ; Hirao, T.; Harano, Y.; Yamana, Y.; Hamada, Y.; Nagata, S.; Agawa, T. *Bull. Chem.. Soc. Jpn* **1986**, *59*, 1341 ; Yoneda, R.; Santo, K.; Harusawa, S.; Kurihara, T. *Synth. Commun.* **1987**, *17*, 921 ; Tinant, B.; Wu, S.; Declercq, J.P.; Van Meerssche, M.; Ma Samba, W.; De Mesmaecker, A.; Viehe, H.G. *J. Chem. Soc., Perkin Trans. 2* **1988**, 1045 ; Chen, C.; Liao, Y.; Huang, Y. *Tetrahedron* **1989**, *45*, 3011 ; Hori, M.; Kataoka, T.; Shimizu, H.; Tsutsumi, K.; Yoshimátsu, M. *Heterocycles* **1990**, *30*, 295 and *J. Org. Chem.* **1990**, *55*, 2458, see also [14, 15].

13) Ainsworth, C.; Chen, F.; Kuo, Y.N. *J. Organometal. Chem.* **1972**, *46*, 59.

14) McCoy, L.L. *J. Org. Chem.* **1960**, *25*, 2078.

15) Stork, G.; Cohen, J.F. *J. Am. Chem. Soc.* **1974**, *96*, 5270.