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REACTION OF SILYLKETENE ACETALS WITH ACRYLOYL AND MONO SUBSTITUTED ACRYLOYL CHLORIDES.

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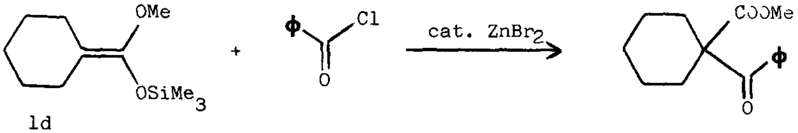
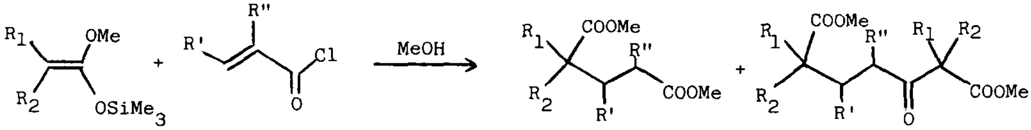
Summary : The reaction of silylketene acetals with acryloyl, methacryloyl and crotonyl chlorides gave, after addition of methanol, mainly substituted glutaric esters, probably via a [2 + 2] cycloaddition.

Silylketene acetals are C-acylated with saturated acid chlorides to provide β-keto esters (1). According to literature in the conditions used this reaction seemed limited to un- or mono-substituted ketene acetals. Applications of this reaction to the synthesis of methylketones (2a) or α-functionalized methylketones (2b) have been reported. In the presence of a Lewis acid, we have anticipated and checked that disubstituted as well as mono-substituted silylketene acetals could react with aliphatic or aromatic acid chlorides in a non-polar solvent, to lead to β-keto ester. For example, ketene acetal 1d mixed with benzoyl chloride in CCl_4 in the presence of zinc bromide led to the desired product with a satisfactory yield (80%) (3).



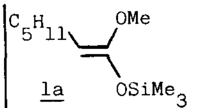
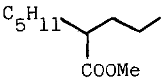
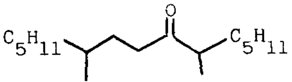
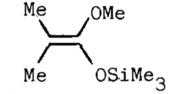
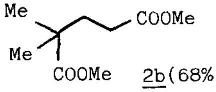
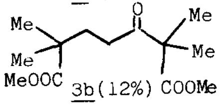
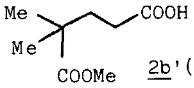
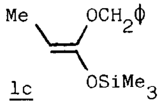
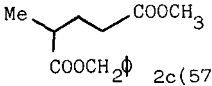
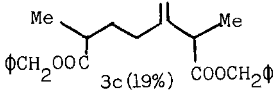
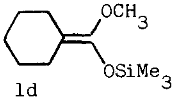
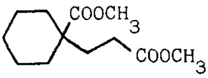
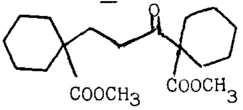
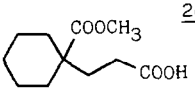
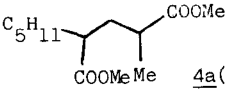
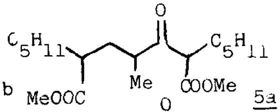
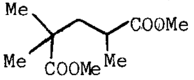
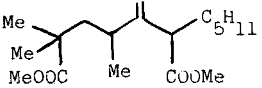
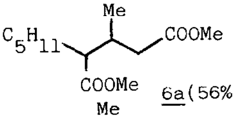
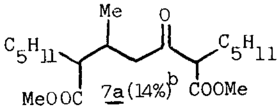
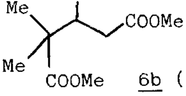
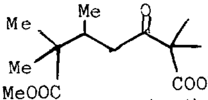
1d

The main purpose of this communication is to report the behavior of O-silylketene acetals with α,β-ethylenic acid chlorides. First we studied the reactivity of acryloyl chloride 8. When one equivalent of this acid chloride was added at room temperature to silylketene acetals 1 in CCl_4 solution without any Lewis acid, an exothermic reaction occurred. After 2-3 hours, the reaction was over and addition of methanol gave two compounds : the major product (75 to 85%) was a substituted glutaric ester and the minor one (25 to 15%) resulted from the coupling of two molecules of the ketene acetal with one of the acid chloride 8 (4). Our results are reported in the table (see entries 1,2,5).



1	R' = R'' = H	8	2	3
	R' = H R'' = Me	9	4	5
	R' = Me R'' = H	10	6	7

Table. Reaction of silylketene acetals with unsaturated acid chlorides

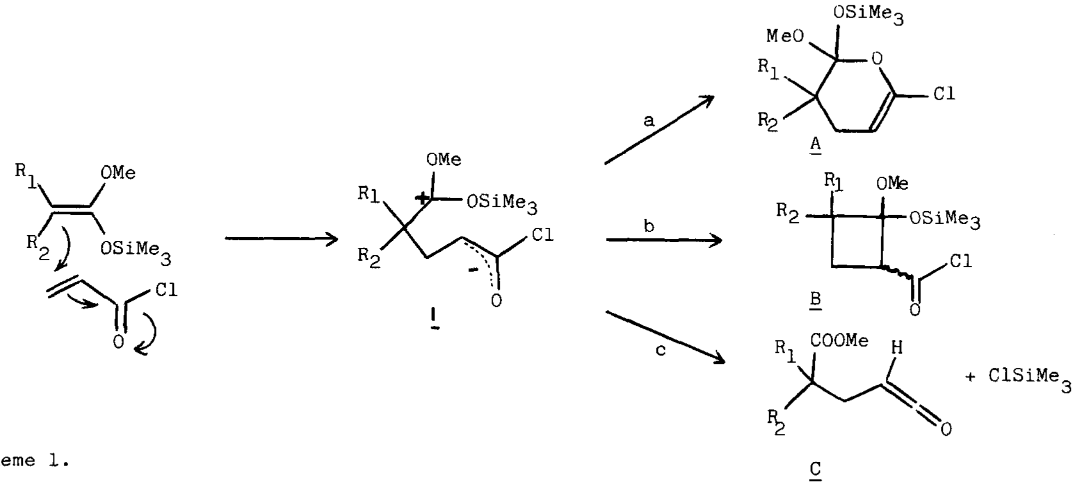
Entry	Ketene acetal 1	Reaction conditions	Products (Yield [a])
* Reaction with acryloyl chloride 8			
1	 1a	1) CCl_4(2h, 20°C) 2) MeOH	 2a(76%) +  3a(13%)
2	 1b	1) CCl_4 (3h, 20°C) 2) MeOH	 2b(68%) +  3b(12%)
3	1b	1) CCl_4(3h, 20°C) 2) aq. Na_2CO_3	 2b'(68%) + 3b (12%)
4	 1c	1) CCl_4(3h, 20°C) 2) MeOH-NEt_3	 2c(57%) +  3c(19%)
5	 1d	1) CCl_4 (2.5h, 20°C 2) MeOH	 2d(60%) +  3d (15%)
6	1d	1) CCl_4(2.5h,20°C) 2) aq. Na_2CO_3	 2d'(60%) + 3d (15%)
* Reaction with methacryloyl chloride 9			
7	1a	1) CH_2Cl_2 (3h,20°C) 2) MeOH	 4a(63%)[b] +  5a(11%)[b]
8	1b	1) CH_2Cl_2, $AlCl_3$ (6.5h, 20°C) 2) MeOH	 4b(63%) +  5b (11%)
* Reaction with crotonyl chloride 10			
9	1a	1) CH_3CN (3h,20°C) 2) MeOH	 6a(56%)[b] +  7a(14%)[b]
10	1b	1) CH_3CN (12h,40°C 2) MeOH	 6b (16%) +  7b (48%)
11	1b	1) CH_2Cl_2, $TiCl_4$ (0.5h, -80°C) 2) MeOH	6b (40%) + 7b (25%)

a) Products isolated by liquid chromatography ; b) the stereochemistry of the products was not determined.

If the alkoxy group of the ketene acetal was different from methoxy, a mixed glutaric ester was obtained (see entry 4) ; however during methanolysis, addition of triethylamine was necessary to avoid trans-esterification. In the same way, hemi-ester of substituted glutaric acids were synthetized by treating the intermediates with aqueous sodium carbonate (see entries 3 and 6).

Similar results were obtained from methacryloyl and crotonyl chloride in methylene chloride or acetonitrile (no reaction occured in CCl_4). The reaction of methacryloyl chloride 9 with disubstituted ketene acetal 1b was faster in the presence of a Lewis acid, $AlCl_3$; it led to similar reaction products (see entry 8). In the same way, the reaction of crotonyl chloride 10 with ketene acetal 1b could be run in acetonitrile or in methylene chloride in the presence of $TiCl_4$: it gave the same products 6b, 7b, but in different ratios (entries 10 and 11) and was also faster in the presence of $TiCl_4$.

As the rate of the reaction was sensitive to the polarity of the solvent (5), it seems that the first step of the reaction could involve the formation of a polar intermediate I which, a priori, could evolve through three different pathways : formation of dihydropyran A by a [4 + 2]cycloaddition (way a ; scheme 1), formation of cyclobutane acyl chloride by a [2 + 2]cycloaddition (way b, scheme 1) or formation of ketene C by chlorotrimethylsilane elimination (way c, scheme 1).

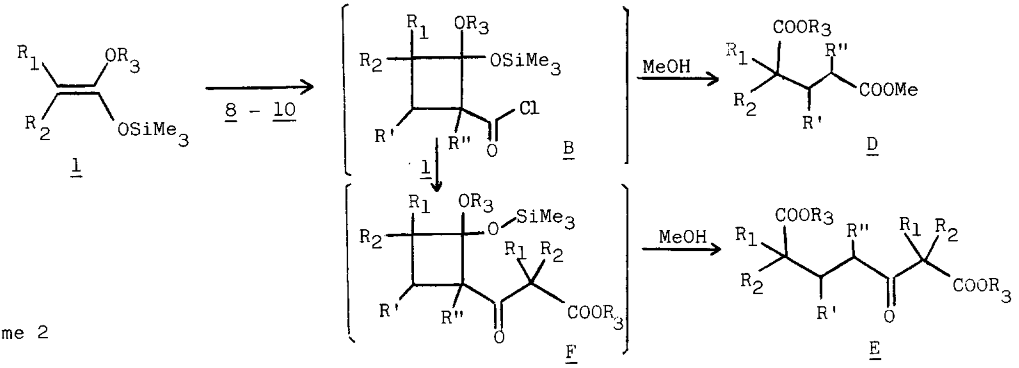


Scheme 1.

After the reaction of the ethylenic acid chloride with silylketene acetal and before methanolysis, the IR spectra of the crude reaction mixtures showed mainly a strong absorption at 1790-1795 cm^{-1}(acid chloride) and two weak ones at 1735 cm^{-1}(ester) and 2120 cm^{-1}(ketene). Their ^1H NMR spectra showed that the silicon atoms were fixed mainly to oxygens (δ=0.28-0.3 ppm (s)) and the formation of a small amount of chlorotrimethylsilane (δ= 0.42 ppm (s)). The methoxy groups gave signals at δ= 3.20-3.30 ppm (s) and a small one at 3.50-3.60 ppm (s). We also observed the absence of vinylic protons, except a weak multiplet around 4.70-4.80 ppm. All these indications rule out the formation of intermediate A and agree with the predominant formation of B (mixture of stereoisomers) next to a small amount of C.

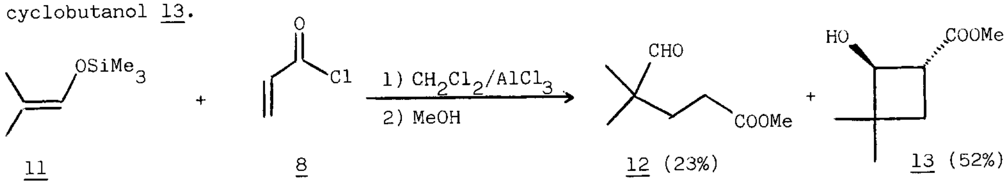
The more likely mechanism of this reaction is thus a [2+2]cycloaddition (5) which should lead to B. This acid chloride could subsequently partly react with a second molecule of ketene-acetal to give the cyclobutanic β-keto ester F (see scheme 2). The formation of the small amount of β-keto ketene C could take place either by a direct formation (way c, scheme 1) or by cleavage of the cyclobutane intermediate B.

The addition of methanol led to the two observed products D, E, by the known ring opening of this kind of cyclobutane compounds (6) (7) (addition of methanol on ketene C led to the same glutaric esters as B).



Scheme 2

An other indication of the [2 + 2]cycloaddition process from these unsaturated acid chlorides had been obtained by studying the reactivity of isobutyraldehyde trimethylsilylenol ether 11 with acryloyl chloride : at room temperature, in methylene chloride in the presence of 10% of $AlCl_3$ we isolated, after addition of methanol, the δ-aldehydo ester 12 and the cyclobutanol 13.



In the next paper is reported a completely different reaction which occurred with 3,3-dimethyl acryloyl chloride.

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1) Kramarova, E.N.; Baukov, Y.L.; Lutsenko, I.F. Zh. Obshch. Khim. 1973, 43, 1857 ; Rathke, M.W.; Sullivan, D.F. Tetrahedron Lett. 1973, 1297.

2) a) Schmidt, U.; Schwochau, M. Tetrahedron Lett. 1967, 4491 ; b) Wissner, A. J. Org. Chem., 1979, 44, 4617.

3) Rousseau, G. unpublished results.

4) All these products have been caracterized from their NMR, IR and mass spectra. Some of them have already been described : see Yamaguchi, M.; Tsukamoto, M.; Hirao, I. Chem. Lett., 1984, 375 and references cited therein.

5) Huisgen, R. Acc. Chem. Res., 1977, 10, 117 ; see also Roberts, J.D.; Sharts, C.M. Org. React., 1962, 12, 1.

6) It is known that this kind of α-difunctional cyclobutanic derivatives are unstable. See Lechevallier, A.; Huet, F.; Conia, J.M. Tetrahedron 1983, 39, 3329.

7) The formation of the keto diester E could also be interpreted by a C-acylation reaction followed by a Michael addition of silyl ketene acetal. See Kita, Y.; Segawa, J.; Haruta, J.; Fujii, T.; Tamura, Y. Tetrahedron Lett., 1980, 21, 3779 and RajanBabu, T.V. J. Org. Chem., 1984, 49, 2083. This seems unlikely from the NMR spectra of the crude reaction mixture, before addition of methanol.

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