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REACTION OF SILYLKETENE ACETALS WITH 3,3-DIMETHYLACRYLOYL CHLORIDE.

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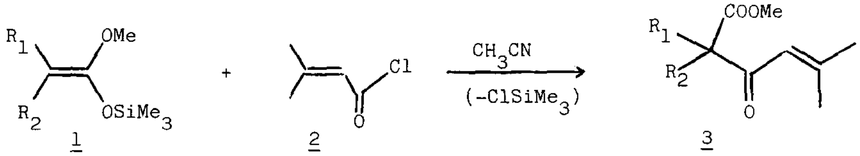
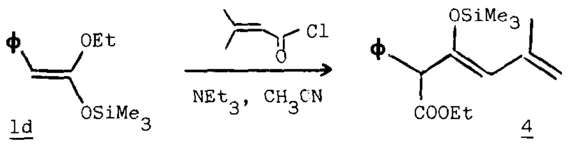
Summary : The reaction of silylketene acetals with 3,3-dimethylacryloyl chloride in acetonitrile gave γ,δ-ethylenic β-keto esters 3. Application to a new synthesis of (±)-turmerone is described.

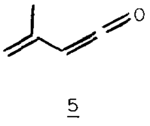
In the preceding paper we have reported that the reaction of acryloyl and mono substituted acryloyl chlorides with silylketene acetals, gave, after addition of methanol, mainly glutaric esters, probably via a polar [2 + 2]cycloaddition.

In the case of 3,3-dimethylacryloyl chloride 2 a completely different reaction took place. In acetonitrile without any catalyst, the C-acylation of ketene acetals 1 was observed (4), to produce γ,δ-ethylenic β-keto esters 3.



Our results are reported in the table. In all cases studied satisfactory yields were obtained, except with phenylketene acetal 1d, for which the main reaction ($\geqslant$ 50%) was hydrolysis (formation of ethyl phenylacetate). In this latter case, we found that the addition of one equivalent triethylamine (1) gave rapidly trimethylsilyl enol ether 4 probably via ketene 5. The silyl enol ether 4 could be easily transformed by acid hydrolysis into the β-keto ester 3d.



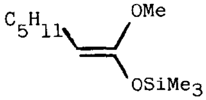
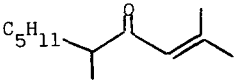
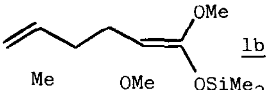
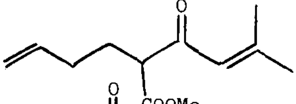
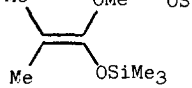
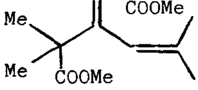
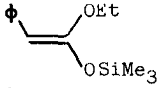
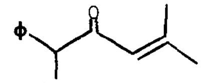
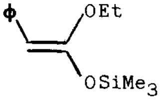
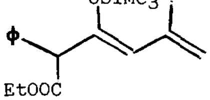
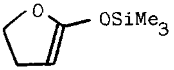
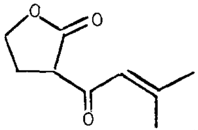


We can interpret the C-acylation of ketene acetals with 3,3-dimethylacryloyl chloride 2, instead of the probable [2 + 2]cycloaddition observed with acryloyl chloride, by the steric hindrance of the β carbon of 2.

Since decarbethoxylation of β-keto esters is a well-known reaction (2), this method is an access to alkyl isopropenyl ketones. For example from keto ester 3a we obtained hexyl isopropenyl ketone 3d (85%) and from ester benzyl isopropenyl ketone (70%).

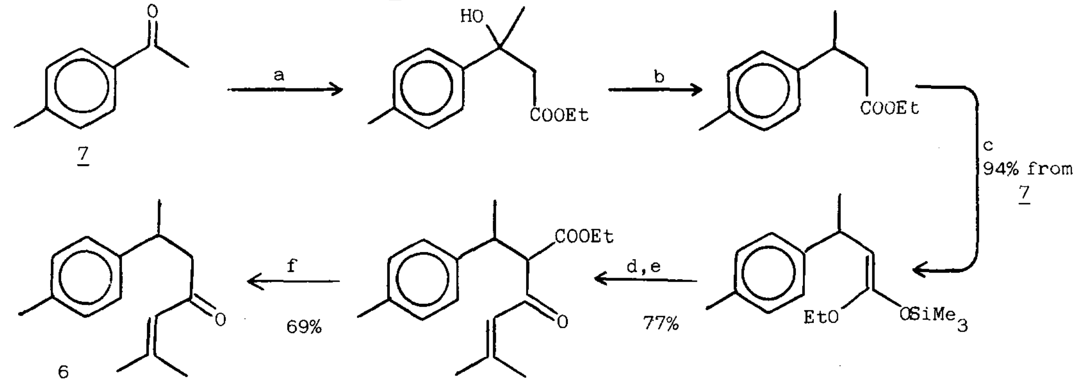
This reaction was illustrated by a new synthesis of (±)- turmerone 6 (3) (see the scheme).

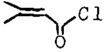
Table : Reaction of silylketene acetals 1 with 3,3-dimethyl acryloyl chloride 2

Ketene acetal 1		Reaction condition	Product 3 (yields [(a)])	
	1a	CH_3CN, 40°, 2 h		3a (70%)
	1b	CH_3CN, 20°, 3 h		3b (70%)
	1c	CH_3CN, 40°, 8 h		3c (70%)
	1d	CH_3CN, 40°, 8 h		3d (30%)
	1d	CH_3CN, 1 eq. NEt_3, 20°, 0.5 h		4 (62%)
	1e	CH_3CN, 20°, 12 h		3e (80%)

a) products isolated by liquid chromatography

Scheme : Synthesis of (±)-turmerone 6



a) $BrCH_2COOEt/Zn(Ag)$ benzene-THF ; b) H_2-Pd/C (EtOH, $HClO_4$) ; c) LDA-$ClSiMe_3$ (THF) ;
d)  2, CH_3CN (1 eq. NEt_3) ; e) THF (aq. HCl) ; f) Ref. (2).

REFERENCES

1) Rathke, M.W.; Sullivan, D.F. Tetrahedron Lett., 1973, 1297.

2) Krapcho, A.P.; Lovey, A.J. Tetrahedron Lett., 1973, 957.

3) Precedent synthesis: Sato, S.; Matsuda, I.; Izumi, Y. Tetrahedron Lett., 1985, 26, 1527 ; Motoyoshiya, J.; Miyajima, M.; Hirakawa, K.; Kakurai, T. J. Org. Chem., 1985, 50, 1326 ; Meyers, A.I.; Smith, R.K. Tetrahedron Lett., 1979, 2749 and references cited.

4) In methylene chloride in the presence of a Lewis acid, the same reaction took place in lower yield.

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