

Reaction of ketenealkylsilylacetals with ethyl propiolate

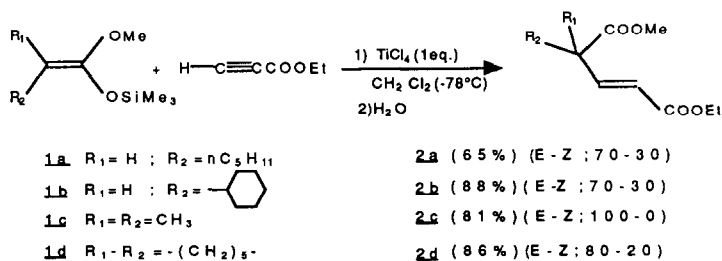
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Abstract : The reaction of ketenealkylsilylacetals with ethyl propiolate in the presence of different Lewis acids is reported to give Michaël-type additions or a [2+2] cycloaddition.

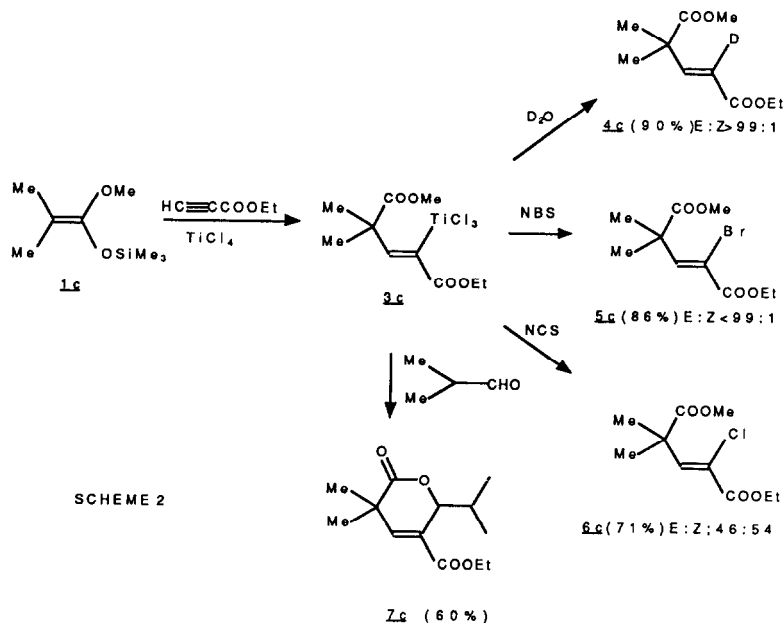
The Lewis acid catalyzed reaction of methyl or ethyl propiolate had been reported to give cyclobutenes via a [2+2] cycloaddition with mono or disubstituted olefins (1), enamines (2) and silylenoethers (3), or α,β -ethylenic esters via an ene-reaction with tri or tetrasubstituted olefines (1a). Our interest in the chemistry of ketenealkylsilylacetals (4) led us to investigate their comportement towards ethyl propiolate. There are few results in the litterature concerning the reaction of propiolic acid derivatives with keteneacetals : it was reported that 1,1-diethoxyethylene gave a cyclobutene derivative with ethyl propiolate by a thermal [2+2] cycloaddition (5) and that a ketenealkylsilylacetal gave a Michaël type-addition with propiolic acid in the presence of titanium tetrachloride (6).

We first studied the reaction of ketenealkylsilylacetals 1a-1d with ethyl propiolate in methylene chloride in the presence of titanium tetrachloride (30 minutes at -78°C , followed by quenching, with water at this temperature). We found that the reaction required one molar equivalent of titanium

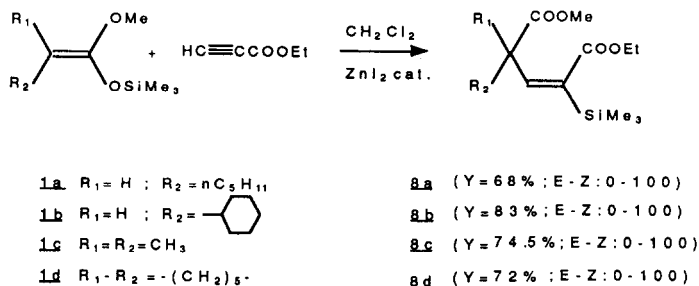


SCHEME 1

tetrachloride, leading thus cleanly in good yield to products 2a-2d (7) (scheme 1). The fact that one equivalent of titanium tetrachloride was necessary and the known syn-addition of titanates on the triple bond of acetylenic derivatives (8) have suggested the formation of compounds 2, which are chiefly E isomers, mainly by syn-addition of titanate ester enolates on ethyl propiolate. The presence of the expected titanate intermediate 3c was ascertained in the case of keteneacetal 1c by addition at -78°C of various electrophilesto the reaction mixture before quenching such as deuterium oxide, N-bromo and N-chloro succinimide and isobutyraldehyde (scheme 2) (7), leading in one step to highly fonctionalized compounds. However no reaction could be noticed with trimethylchlorosilane, allylbromide and ethylene oxide. Such an intermediate was unknown in the titanium case, however [α -(alkoxycarbonyl)vinyl] lithium, copper and recently aluminum (9) have been reported.

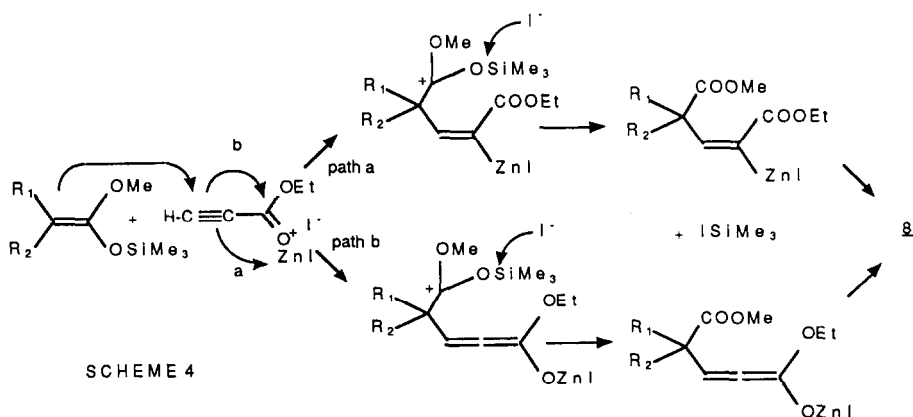


We studied also the reactivity of alkylsilylketeneacetals with ethyl propiolate in other reaction conditions. So we observed that in methylene chloride in the presence of a catalytic amount of zinc iodide Michaël-type products possessing a vinylic trimethylsilyl group were obtained (18 h ; 20°C). Our results are reported in the scheme 3. We observed in each case the formation of a single product.

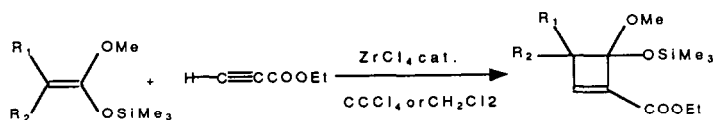


SCHEME 3

The Z stereochemistry of these unknown esters 8a-8d was deduced from their NMR spectra (10). Their formation can be interpreted by addition of the keteneacetals to the triple bond of the zinc activated ethyl propiolate leading to a vinylic zinc intermediate (path a) or a zinc allenoate (path b, scheme 4) and iodotrimethylsilane which subsequently could react together to give the esters 8. Such a mechanism can explain the transformation of the organozinc intermediate (11). The results led us to postulate the intermediate formation of a $[\alpha-(\text{ethoxycarbonyl})\text{vinyl}]$ zinc compound, however our attempts to trap it failed. Some α -trimethylsilyl α, β -ethylenic esters had been already reported (12) however their synthesis are less straightforward than those of esters 8.



In order to observe the common [2+2] cycloaddition we changed the nature of the Lewis acid. We found that in carbon tetrachloride or methylene chloride in the presence of a catalytic amount of zirconium tetrachloride this reaction occurred (18 hours ; 20°C). Our results are reported in the scheme 5. The cyclobutenes 9a-9d formed were characterized by their physical (7) and chemical properties (13). This reaction was not observed with carefully dried zirconium tetrachloride ; but the addition of diethyl ether (14) or water (0.5 - 1 equivalent) to the catalyst allowed the reaction to take place.



- 1a $R_1 = \text{H} ; R_2 = n\text{C}_3\text{H}_{11}$
1b $R_1 = \text{H} ; R_2 =$
1c $R_1 = R_2 = \text{CH}_3$
1d $R_1, R_2 = -(CH_2)_5-$

- 9a (51%)
9b (61%)
9c (70%)
9d (84%)

SCHEME 5

In conclusion the reaction of ketenealkylsilylacetals with ethyl propiolate leads to different highly functionalized products depending on the solvent and the Lewis acid used and illustrates the wealth of the chemistry of these compounds.

References

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- 13) The catalytic hydrogenation (Pd/C, ethyl acetate) gave the corresponding cyclobutanes (100% yields) which were easily transformed to α -carboethoxycyclobutanones (SiO₂, 20% H₂SO₄ ; 95% yields).
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