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FLASH PYROLYSIS: A ROUTE TO "α-KETENIC ESTERS".

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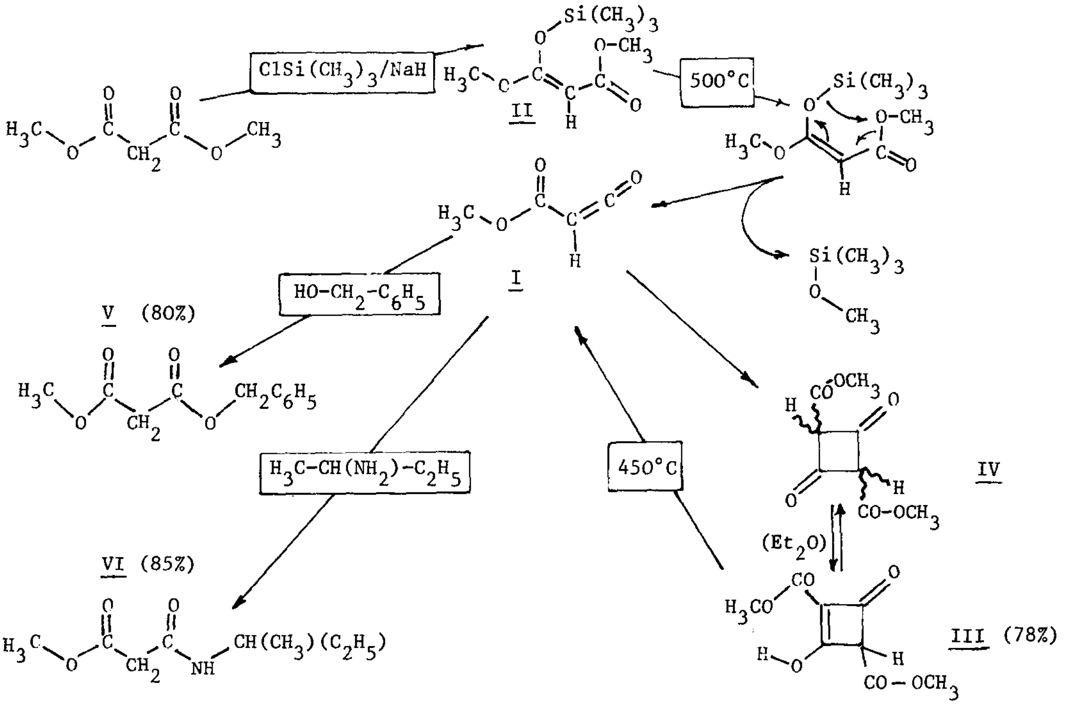
3-oxo 2-propenoic acid methyl ester has been prepared by flash vacuum pyrolysis and characterized by mass spectrometry and chemical trapping. Its four-membered cyclic dimers have been isolated.

We wish to report here the preparation of 3-oxo 2-propenoic acid methyl ester (I) by flash vacuum pyrolysis[1] at 500°C of 3-methoxy 3-trimethylsiloxy 2-propanoic methyl ester (II). To our knowledge, the only reported synthesis of an "α-ketenic ester" is that of trifluoromethyl derivative[2]. II was prepared from dimethylmalonic ester and has been shown to have the Z configuration[3].

The pyrolysis is likely to proceed via a six-centered, concerted, 1,5-rearrangement through elimination of methyltrimethylsilyl ether. This mechanism has already been described in the pyrolytic formation of α-allenic ketones[4], α-allenic esters[5] and acylketenes[6] (SCHEME)



The mass spectrum of I was recorded by use of a direct coupling of mass spectrometer to the pyrolyser[7]. However, when the pyrolysate of II is trapped in a matrix of various solvents ($CDCl_3$, CD_3COCD_3) at -196°C, only dimerisation products of I can be observed by low temperature (-80°C) NMR. When Et_2O is used as a trapping agent, a white precipitate appears upon thawing of the matrix. Analysis of the NMR ($CDCl_3$) and mass spectra of the collected precipitate is consistent with the enol dimer structure III[8] (see SCHEME). The total yield of formation of III from II is 78%. The solutions obtained when trapping with CH_3COCH_3 or CH_3CN contain mainly two products. It appears, after a GC/MS study, that these products are the dimer III (30%) and a isomer IV (70%); the close similarity of mass spectra of III and IV leads us tu suppose that IV has the keto-dimer structure shown on SCHEME[9]. Further attempts to isolate IV by TLC only yield reddish polymers.

When subjected to flash vacuum pyrolysis at 450°C, III yields the monomer I in a pure form as observed by direct coupling of the pyrolyser to a mass spectrometer. Above 850°C, III yields essentially carbon suboxyde C_3O_2 probably by formation of I and subsequent loss of methanol.

I has also been characterized by chemical trapping with an alcohol and with an amine: with benzylalcohol, I gives 80% of benzylmethylester V; and with 2-butylamine, I gives 85% of amidoester VI (see SCHEME). Such addition reaction may be of synthetic interest, as the alcoholic trapping of I gives better results than ester interchange[10] for the preparation of unsymetrical malonate derivatives. We think that this method of pyrolytic obtention of "α-ketenic esters" is general and further applications are currently under investigation .

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7 Mass Spectrum of I: {m/z, intensities at 70 eV}; 100 (M^{+},37), 69(100), 68(62), 40(56), 31(42), 41(28).

8 Experimental data of III. mp = 146-148°C; ^{13}C-NMR { ppm, off res. multiplicity, $CDCl_3$}: 181.8 (s), 172.3 (s), 167.7 (s), 156.4 (s), 86.1 (s), 78.5 (d), 56.6 (q), 52.8 (q); ^{1}H-NMR: 14.07 (1H), 5.38 (1H), 4.02 (3H), 3.98 (3H) {ppm, $CDCl_3$}; M.S.: 200 (M^{+},20), 69 (100), 59 (59), 140 (41), 172 (37), 44 (39), 100(27), 101(26).

9 Mass Spectrum of IV: 200 (M^{+},8), 69(100), 59(87), 101(77), 100 (35), 74(30), 140(11), 172(11).

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