

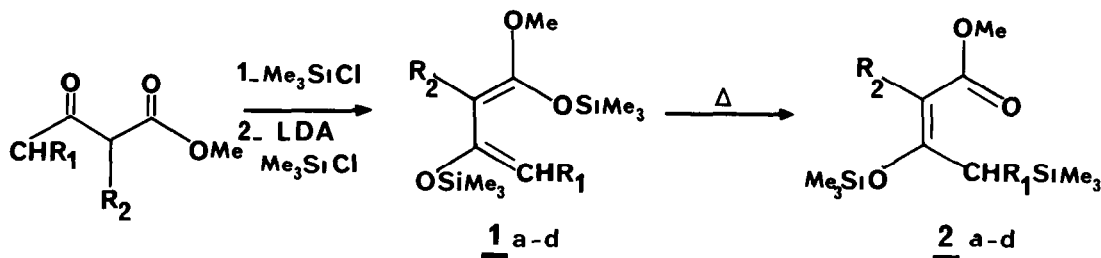
FLASH VACUUM PYROLYSIS OF 1-METHOXY-1,3-BIS(TRIMETHYLSILOXY)-1,3-DIENES
SYNTHESIS OF α -ALLENIC ACIDS

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Abstract Flash vacuum pyrolysis at 680-700°C of 2- and 4- substituted 1-methoxy-1,3-bis(trimethylsiloxy)-1,3-butadienes yields α -allenic silyl esters which, upon hydrolysis, provide a direct route to α -allenic acids with good overall yield

The preparation of 2- and 4- substituted 1-methoxy-1,3-bis(trimethylsiloxy)-1,3-butadienes (1a-d) in two steps from β -keto esters has recently been described ^{1,2,3} (Cf scheme 1) It has been reported ² that products (1a-d) after undergoing a stereospecific thermal rearrangement lead to (2a-d) Although it has been stated that (1a-b) could be distilled safely below 80°C ², we were unable to obtain the 2- substituted compounds (1c) and (1d) but only the rearranged products (2c) and (2d) On the other hand, the products (1b), (1a) and its rearranged form (2a) were isolated



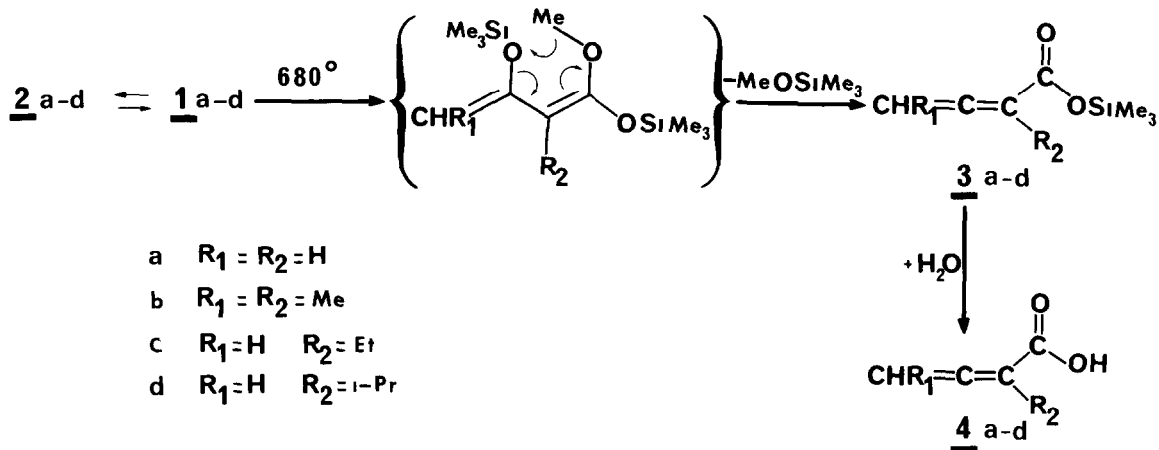
Scheme 1.

At 680-700°C, under flash vacuum pyrolysis conditions ⁴, (1a,b) and (2a,c,d) yielded the corresponding α -allenic silyl esters (3a-d) through the elimination of trimethylsilyl-methyl ether. The reaction seemed to proceed through a 1,5 rearrangement according to Scheme 2. This rearrangement presents the closest analogy with the 1,5 rearrangement as proposed in our previous paper ⁵ on thermal decomposition of β -keto-trimethylsilyl enol ether.

The α -allenic silyl esters (3a-d) were unstable and thermally labile compounds ⁶ which could not be isolated in significant yields. However, upon conventional hydrolysis ⁷ they yielded the stable corresponding α -allenic acids (4a-d).

On a preparative scale, when 4-5 gr of starting material (1a,b) and (2a,c,d) were subjected to pyrolysis, between 60 and 40% theoretical yield of pure acids (4a-d) were obtained (see Table 1). As compounds (1a) and (2a) gave similar yields of acid (4a), it is suggested that (2a,c,d) rearranged to (1a,c,d) at high temperatures prior to its

decomposition into silyl esters (3a-d)



Scheme 2

Table 1 Isolated yields of α -allenenic acids (4a-d)

Precursor	R ₁	R ₂	Product	Yield %	mp of (<u>4a-d</u>) (Litt)
<u>1a</u>	H	H	<u>4a</u>	50	64 (65) ⁷
<u>1b</u>	Me	Me	<u>4b</u>	43	45 (25) ⁸ and (55) ⁹
<u>2a</u>	H	H	<u>4a</u>	43	64 (65) ⁸
<u>2c</u>	H	Et	<u>4c</u>	60	73 (72) ⁸
<u>2d</u>	H	i-Pr	<u>4d</u>	56	44 - 10

The spectroscopic data of the isolated acids (4a-d) were in good agreement with previously published data ^{7,8,9} We believe that this method can compare favourably with previous preparations of α -allenenic acids ^{7,8,9}

References and notes

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- 3/(1a-d) were prepared with 80-70% yield according to N SLOUGHI, G ROUSSEAU and J M CONIA, Synthesis 58 (1982)
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- 10/(4d) 2-(1-methyl-ethyl)-2,3-butadienoic acid ¹H NMR (CCl₄, 90 MHz, δ in ppm), 5.2 (d, J=2.5 Hz, 2H), 2.67 (m, 1H), 1.09 (d, J=7 Hz, 6H) M S (70 eV, m/z, intensities) 126 (M⁺, 4), 39 (100), 43 (98), 41(75), 84 (50), 81(40), 66 (22), 83 (20), 65 (20), 45 (14)

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