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FLASH VACUUM THERMOLYSIS OF β-KETO-TRIMETHYLSILYL-ENOL-ETHERS

SYNTHESIS OF ALLENIC AND FURANIC DERIVATIVES

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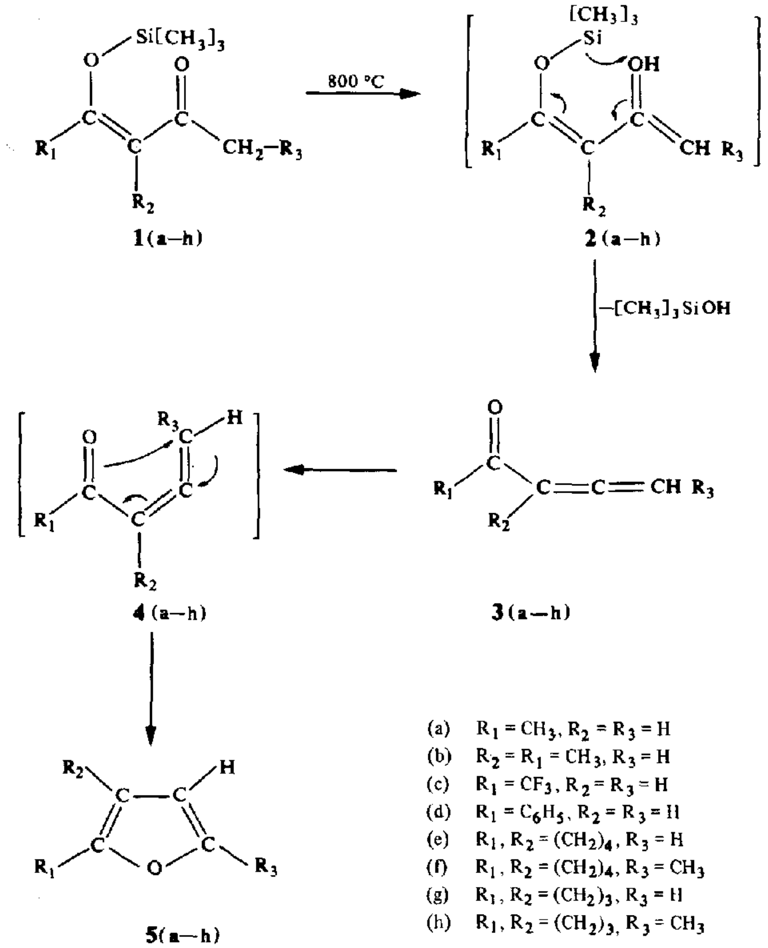
Abstract—Thermolysis at 800° of a series of β-keto-trimethylsilyl-enol-ethers allows the elimination of a trimethylsilanol molecule through a 1,5 rearrangement. The reaction products are furanic derivatives, which are obtained in often good yields through an allenic intermediate, which has been isolated.

Preliminary investigations of the thermolytic behaviour of a series of β-diketones demonstrated that upon heating above 750° under low pressures, these compounds yield little amounts of furanic derivatives; for instance acetylacetone yields about 5% of 2-methyl-furan.[1] This reaction seemed to be of both mechanistic and synthetic interest, and a study was undertaken to define the reaction pathway and optimize its yield. Since the first step of the reaction appeared to proceed through the enol form of the β-diketone, the blocking of one of the CO groups in the enol form was investigated and the corresponding β-keto-trimethylsilyl-enol-ethers **1a–h** were synthetized.

The thermal reactivity of **1a–h** was studied by flash vacuum thermolysis.[2] Reaction occurs above 800° and affords the corresponding furan **5a–h** together with α-allenic ketones **3a–h**.

The reaction seems to proceed through two consecutive steps as shown in Scheme 1.

The first step can be described as a 1,5 rearrangement



(a) $R_1 = CH_3, R_2 = R_3 = H$
(b) $R_2 = R_1 = CH_3, R_3 = H$
(c) $R_1 = CF_3, R_2 = R_3 = H$
(d) $R_1 = C_6H_5, R_2 = R_3 = H$
(e) $R_1, R_2 = (CH_2)_4, R_3 = H$
(f) $R_1, R_2 = (CH_2)_4, R_3 = CH_3$
(g) $R_1, R_2 = (CH_2)_3, R_3 = H$
(h) $R_1, R_2 = (CH_2)_3, R_3 = CH_3$

Scheme 1.

of the enol form of β-keto-trimethylsilyl-enol-ether **2a–h**, yielding α-allenic ketones **3a–h** through elimination of a trimethyl-silanol molecule.[3,4] A further rearrangement involving a substituent shift can yield the corresponding furanic derivatives **5a–h**.

The presence of trimethyl silanol, which rapidly yields hexamethyl disiloxane, can be ascertained by NMR and GC-MS.

The intermediacy of the α-allenic ketone **3** can be supported by using a reactor configuration allowing shorter contact times (Experimental): when the reaction is carried out in about 10^{-3} sec at 800°, good yields of **3** are obtained in most instances in the pyrolyzate as measured by glc and NMR (Table 1). However, thorough isolation and purification of these unstable compounds is more difficult and due to fast polymerization and hydrolysis, they can only be obtained in pure form in much lower yields. In all cases, formation of low yields (5–10%) of furans **5** is observed under these conditions.

On the other hand, a much longer contact time can be achieved by packing the reactor tube with quartz wool. When the reaction is carried out under these conditions, at the same temperature (800°), only traces of the α-allenic ketones **3** are to be found in the pyrolyzate, whereas, in most instances, a good yield of furan **5** is obtained. Quantification can be done by glc and NMR and yields are given in Table 1.

Additional proof of the intermediacy of the keto-allene **3** in the furan synthesis is obtained by thermolysing a sample of 1,2-pentadiene-4-one **3a** at 800° in a quartz wool packed reactor. GC-MS analysis of the pyrolyzate shows the presence of 9% of the unreacted keto-allene **3a** together with 80% of 2-methyl-furan **5a**.

On a preparative scale 2–5 g of starting material were subjected to thermolysis under conditions optimized for furan production, and the corresponding yield of furans **5b–f** isolated and purified were calculated and reported in Table 1. These yields compare favorably with the yields of the alternate methods of obtention of these compounds,[5-7] and since the starting material is easily available, we believe that thermolysis of β-keto-trimethylsilyl-enol-ether is a method of choice to prepare gram quantities of certain furanic derivatives, particularly tetrahydrobenzofurans such as **5e** and **f**.

Preparation of the keto allene **3a–h** have already been described and these products can be prepared in much higher yields using alternate methods.[8-10]

The thermolysis of the cyclic derivatives **1e–h** exhibits the superposition of another effects: the 6-membered ring derivatives **1e** and **f** yield low or negligible amounts of the expected α-allenic ketones whereas they can be converted to the corresponding tetrahydrobenzofuran (**5e** and **f**) in good yields. The opposite is observed with the 5-membered ring derivatives **1g** and **h**, which give fairly good yields of the cyclic α-keto allenes **3g** and **h**, while further thermal reactions only yield degradation products, furans **5g** and **h** being produced in low or negligible yields. Steric strains involved in the transition state **4** of the allene rearrangement probably account for these effects.

Upon thermolysis at 800°, **1f** yields 2-methyl- and 3-methyl-4,5,6,7-tetrahydrobenzofurans **5f** in a ratio of 9 : 1. As can be expected, the necessary substituent shift in the rearrangement described in transition state **4** involves preferentially the hydrogen over the Me group. However, when the reaction temperature is increased to 850°, practically equal amounts of 2-methyl- and 3-methyl-4,5,6,7-tetrahydrobenzofurans are obtained.

Upon thermolysis at temperatures above 900°, the previously reported retro-Diels-Alder reaction involving the 6-membered rings **5e** and **f** becomes predominant.[11]

EXPERIMENTAL

Preparation of the β-keto-trimethylsilyl-enol-ether.[12-14] A soln of 0.1 mole Et_3N and 0.12 mole trimethylsilyl-chloride in 100 ml anhyd ether was added to 0.1 mole β-diketone in 100 ml anhyd ether. The mixture was stirred for 6 hr at room temp. After

Table 1. Pyrolysis yields of β-keto-trimethylsilyl-enol ethers

REACTION :

$$\underset{\mathbf{1}\ (a\text{-}h)}{(CH_3)_3Si\text{-}O\text{-}C(R_1)\text{=}C(R_2)\text{-}CO\text{-}CH_2\text{-}R_3} \xrightarrow{800°C} \underset{\mathbf{3}\ (a\text{-}h)}{R_1\text{-}CO\text{-}C(R_2)\text{=}C\text{=}CH\text{-}R_3} + \underset{\mathbf{5}\ (a\text{-}h)}{(R_1)C\text{=}C(R_2)\text{-}C(R_3)\text{=}CH\text{-}O}$$

PRECURSOR[†]	R_1	R_2	R_3	YIELD (%) OF[*] α-ALLENIC KETONE,		YIELD (%)[*] OF FURAN,		PREPARATIVE YIELD[§] (%) OF FURAN,
1a	CH_3	H	H	3a	50	5a	55	-
1b	CH_3	CH_3	H	3b	60	5b	55	40
1c	CF_3	H	H	3c	40	5c	70	50
1d	C_6H_5	H	H	3d	25	5d	45	36
1e	$-(CH_2)_4-$		H	3e	25	5e	55	48
1f	$-(CH_2)_4-$		CH_3	3f	0	5f	55	50
1g	$-(CH_2)_3-$		H	3g	40	5g	5	-
1h	$-(CH_2)_3-$		CH_3	3h	40	5h	0	-

[†] MIXTURE OF E + Z ISOMERS (SEE EXPERIMENTAL). [*] EVALUATED BY NMR AND GC-MS

[§] ISOLATED PURE (SEE EXPERIMENTAL)

filtration over celite, the solvent was evaporated and the trimethylsilyl-enol-ether distilled under reduced pressure. Care should be taken to avoid the presence of moisture during the reaction or the distillation. Yields in all cases were higher than 85%.

Flash vacuum thermolysis experiments.[2] The reactor was a 8 × 1 cm (ID) quartz tube and the heating zone was approximately 5 cm long. The temp was monitored by a thermocouple sliding in a coaxial quartz tube 5 mm (OD). Pressure was kept at about 10^{-1} torr and the compound swept with argon. Between 0.3 and 5 g of starting material could be thermolyzed with this apparatus.

Separation of reaction mixtures. The pyrolyzate mixture was analyzed immediately at the end of the experiment by ^{1}H NMR, glc, and mass spectrometry. Furans were isolated by liquid chromatography on alumina (eluent: pentane). The α-allenic ketones, which are particularly unstable, were separated by vacuum distillation on the vacuum line followed by thin layer chromatography on silicagel (eluent: 10% EtOAc in pentane).

Spectral data. The spectral data of new compounds are listed below, together with those of known products which had not yet been published. ^{1}H NMR: CCl_4, 90 MHz, δ in ppm; ^{19}F NMR: CCl_4, δ in ppm after $CFCl_3$; Mass spectrometry: *m/e* and intensities at 70 eV electron energy.

β-keto-trimethylsilyl-enol-ether. For these compounds the ^{1}H NMR spectra show at most two isomers, these isomers have been reported to be inseparable,[15,16] however separation and quantification of these isomers could be obtained by glc on a 25 m quartz capillary column coated with CP-sil 5. Four different isomers (three for the ring containing compounds) can be expected for β-keto-trimethylsilyl-enol-ether (Scheme 2).

The two *Z*-isomers undergo a rapid 1,5-sigmatropic rearrangement and are undistinguishable by glc and NMR at room temp.[3,16,17]. In the case of compounds **1c** and **d**, two distinct isomers E_a and E_b can be expected. However, only the E_b form was observed in the ^{13}C and ^{1}H NMR spectra.[18]

4 - ((*Trimethylsilyl*)*oxy*) - 3 - *penten* - 2 - *one* **1a**

E_a and E_b (equiv), (75%). ^{1}H NMR[15]: 5.53 (s, 1H); 2.17 (s, 3H); 2.00 (s, 3H); 0.29 (s, 9H). MS: 172 (M^+, 14), 157 (100), 73 (91), 43 (91), 45 (70), 75 (38). *Z*, (25%). ^{1}H NMR[15]: 5.21 (s, 1H); 2.00 (s, 6H); 0.29 (s, 9H). MS: 172 (M^+, 9), 157 (100), 73 (77), 43 (71), 45 (41), 75 (36).

3 - *Methyl* - 4 - (*trimethylsilyloxy*) - 3 - *penten* - 2 - *one* **1b**

E_a and E_b (equiv), 30%). ^{1}H NMR[15]: 2.13 (s, 6H); 1.67 (s, 3H); 0.28 (s, 9H). MS: 186 (M^+, 7), 73 (100), 171 (86), 43 (83), 45 (49), 75 (34). *Z*, (70%). ^{1}H NMR[15]: 2.13 (s, 6H); 1.82 (s, 3H); 0.24 (s, 9H). MS: 186 (M^+, 8), 73 (100), 43 (96), 171 (92), 45 (50), 75 (31).

1,1,1 - *Trifluoro* - 4 - (*trimethylsilyloxy*) - 3 - *penten* - 2 - *one* **1c**

E_b, (65%). ^{1}H NMR: 5.7 (s, 1H); 2.36 (s, 3H); 0.33 (s, 9H). ^{19}F NMR: −80.0 (s, 3F). MS: 226 (M^+, 0.6), 43 (100), 73 (95), 45 (58), 77 (32), 211 (17), 157 (16). *Z*, (35%). ^{1}H NMR: 5.96 (s, 1H); 2.17 (s, 3H); 0.29 (s, 9H). ^{19}F NMR: −75.1 (s, 3F). MS: 226 (M^+, 0.2), 43 (100), 73 (60), 77 (39), 45 (34), 211 (31), 157 (9).

4 - *Phenyl* - (*trimethylsilyloxy*) - 2 - *buten* - 2 - *one* **1d**

E_b, (70%). ^{1}H NMR: 7.85 (m, 2H); 7.40 (m, 3H); 6.01 (s, 1H); 2.35 (s, 3H); 0.32 (s, 9H). MS: 234 (M^+, 19), 219 (100), 73 (55), 43 (49), 45 (40), 77 (36), 233 (33). *Z*, (30%). ^{1}H NMR: 7.69 (m, 2H); 7.40 (m, 3H); 6.25 (s, 1H); 2.09 (s, 3H); 0.21 (s, 9H). MS: 234 (M^+, 14), 219 (100), 73 (52), 43 (56), 45 (36), 77 (39), 233 (21).

1 - (2 - (*Trimethylsilyloxy*) - 1 - *cyclohexen* - 1 - *yl*) - *ethanone* **1e**

Z, (100%). ^{1}H NMR[15]: 2.23 (s, 3H); 2.20 (m, 4H); 1.62 (m, 4H); 0.28 (s, 9H). MS: 212 (M^+, 8), 197 (100), 73 (58), 43 (42), 45 (42), 75 (24), 169 (10).

1 - (2 - (*Trimethylsilyloxy*) - 1 - *cyclohexen* - 1 - *yl*) - *propanone* **1f**

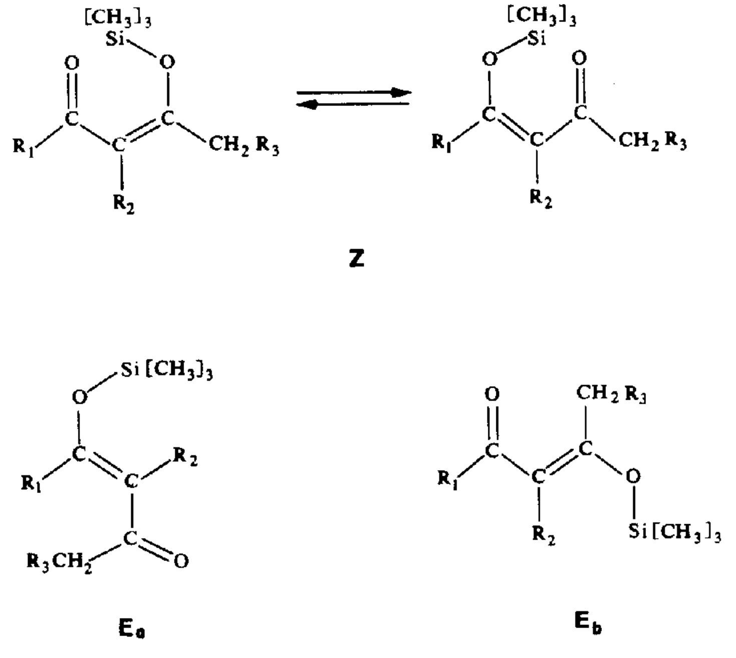
Z, (100%). ^{1}H NMR: 2.57 (q, J = 8 Hz, 2H); 2.17 (m, 4H); 1.6 (m, 4H); 0.97 (t, J = 8 Hz, 3H); 0.26 (s, 9H). MS: 226 (M^+, 9), 73 (100), 197 (94), 45 (45), 211 (43), 75 (39).

1 - (2 - (*Trimethylsilyloxy*) - 1 - *cyclopenten* - 1 - *yl*) - *ethanone* **1g**

E_b, (40%). ^{1}H NMR: 2.45 (m, 3H); 2.15 (m, 4H); 1.72 (q, 2H); 0.29 (s, 9H). MS: 198 (M^+, 8), 183 (100), 73 (59), 45 (40), 43 (36), 75 (30). *Z*, (60%). ^{1}H NMR: 2.45 (m, 3H); 2.15 (m, 4H); 1.72 (q, 2H); 0.25 (s, 9H). MS: 198 (M^+, 10), 183 (100), 73 (58), 45 (40), 75 (36), 43 (36).

1 - (2 - (*Trimethylsilyloxy*) - 1 - *cyclopenten* - 1 - *yl*) - *propanone* **1h**

E_b, (70%). ^{1}H NMR: 2.5 (m, 4H); 2.25 (t, 2H); 1.82 (q, 2H); 1.0 (t, 3H); 0.3 (s, 9H). MS: 212 (M^+, 17), 73 (100), 183 (93), 197 (41), 45 (46), 75 (22), 29 (21). *Z*, (30%). ^{1}H NMR: 2.5 (m, 6H); 1.82 (q, 2H); 1.04 (t, 3H); 0.26 (s, 9H). MS: 212 (M^+, 23), 183 (100), 73 (98), 197 (69), 45 (58), 75 (39), 29 (27).



Scheme 2.

α-Allenic ketones

Products **3a** and **3b** see Ref. 19.

5,5,5 - Trifluoro - 1,2 - pentadien - 4 - one ***3c***

^{1}H NMR: 6.06 (t, J = 8 Hz, 1H); 5.44 (d, J = 8 Hz, 2H). ^{19}F NMR: −76.8 (s, 3F). MS: 136 (M$^+$, 3.6), 39 (100), 38 (95), 67 (92), 69 (83), 37 (70).

4 - Phenyl - 1,2 - butadien - 4 - one ***3d***

^{1}H NMR: 7.82 (m, 2H); 7.4 (m, 3H); 6.06 (t, J = 6.5 Hz, 1H); 5.22 (d, J = 6.5 Hz, 2H). MS: 144 (M$^+$, 3.3), 105 (100), 77 (65), 51 (19).

2 - Ethenylidene - cyclohexanone ***3e***

^{1}H NMR: 4.96 (t, J = 3.5 Hz, 2H); 2.53 (m, 2H); 2.33 (m, 2H); 1.80 (m, 4H). MS: 122 (M$^+$, 68), 52 (100), 79 (87), 39 (83), 51 (61).

2 - Ethenylidene-cyclopentanone ***3g***

^{1}H NMR: 5.10 (t, J = 4.7 Hz, 2H); 2.73 (m, 2H); 2.25 (m, 2H); 1.95 (m, 2H). MS: 108 (M$^+$, 61), 79 (100), 52 (79), 51 (55), 39 (35).

2 - (1 - Methyl - ethenylidene) - cyclopentanone ***3h***

^{1}H NMR: 5.50 (m: 12 bands, J = 5 and 7 Hz, 1H); 2.65 (m, 2H); 2.20 (m, 2H); 1.95 (m, 2H); 1.77 (d, J = 7 Hz, 3H). MS: 122 (M$^+$, 89), 39 (100), 66 (71), 79 (56), 40 (48), 77 (31), 65 (27).

Furans

2 - Trifluoromethyl - furan ***5c***

^{1}H NMR^5: 7.55 (s, 1H); 6.8 (s, 1H); 6.5 (s, 1H). ^{19}F NMR: −65.7 (s, 3F). MS: 136 (M$^+$, 95), 39 (100), 38 (62), 57 (36), 69 (28), 86 (25), 117 (15).

4,5,6,7 - Tetrahydro-benzofuran ***5c***

^{1}H NMR: 7.09 (sext, J = 1.8 and 0.5 Hz, 1H); 6.02 (sext, J = 1.8 and 0.8 Hz, 1H), 2.55 (m, 2H); 2.42 (m, 2H); 1.79 (m, 4H). MS: 122 (M$^+$, 38), 94 (100), 39 (57), 51 (25).

2 - Methyl - 4,5,6,7 - tetrahydrobenzofuran ***5f***

^{1}H NMR: 5.62 (s, 1H); 2.48 (m, 2H); 2.32 (m, 2H); 1.75 (m, 4H); 2.17 (s, 3H). MS: 136 (M$^+$, 95), 43 (100), 108 (93), 39 (58), 121 (26), 93 (24).

5,6- Dihydro - 4H - cyclopenta(b)furan ***5g***

^{1}H NMR: 7.18 (bs, 1H); 6.10 (d, J = 2 Hz, 1H); 2.6 (m, 2H); 2.3 (m, 2H); 2.0 (m, 2H). MS: 108 (M$^+$, 64), 79 (100), 77 (62), 107 (41), 51 (39), 39 (31).

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