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HETEROCYCLIC SILYL ENOL ETHER CHEMISTRY[1] : SYNTHESIS AND REACTIVITY OF 3-TRIMETHYLSILOXYFURAN AND 3-TRIMETHYLSILOXYTHIOPHENE

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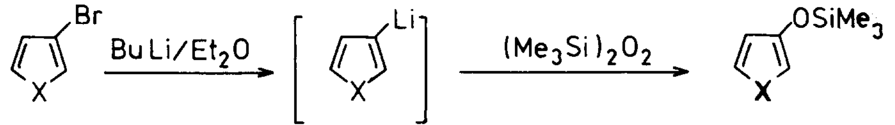
Summary. The preparation of the title compounds is reported starting from the corresponding bromo derivatives.3-Trimethylsiloxyfuran gives rise easily to cycloadditions affording bicyclic tetrahydrofuranonic systems.

Heterocyclic silyl enol ethers are versatile synthons in organic chemistry : 2-trimethylsiloxy-furan has been widely used in synthesis of butenolides[2-4] and through 2,5-bis(trimethylsiloxy)-furan[5], -thiophene[6] and -pyrrole[6] a rapid entry into the synthesis of lignans and related systems has been envisioned.

As a part of our interest in the development of the chemistry of heterocyclic silyl enol ethers[6,7], we report now the preparation of 3-trimethylsiloxy-furan 1 and 3-trimethylsiloxy-thiophene 2 and the preliminary results of their reactional behaviour with electrophiles and with dienophiles in [4+2] cycloadditions.

1 and 2 were prepared by reaction[8] of the corresponding heterocyclic anions generated from 3-bromofuran 3 and 3-bromothiophene 4 with bis-(trimethylsilyl)peroxide which acts here as a very suitable new reagent for electrophilic oxysilylation.



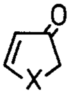
3 X=O
4 X=S

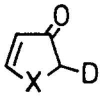
1 X= O
2 X= S

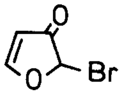
Whereas 1 is a colourless volatile liquid which can be stored for more than one month in freezer (-10°) under nitrogen , 2 is a yellow oil that after some weeks at -25° slowly starts to polymerize giving a black mirror on the surface of the flask where it is stored.

Protonolysis and deuterolysis of 1 and 2 gave 3,[2H]-furanones[10] 5,7 and 3,[2H]

-thiophenones[10] 6, 8; bromination of 1 at low temperature gave the bromoderivative 9, whereas 2 gave a polybrominated system even using a molar defect of bromine.[11]


5 X=O
6 X=S


7 X=O
8 X=S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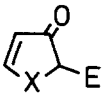
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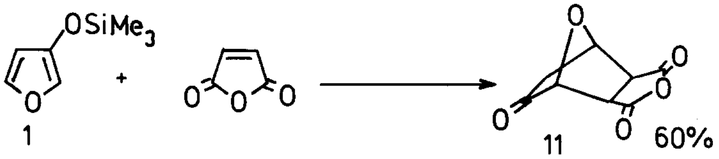
Moreover reactions with carbon electrophiles generally did not give the expected products of general formula 10. The presence of Lewis Acids led in fact to an uncontrolled degradation of the heterocyclic rings.

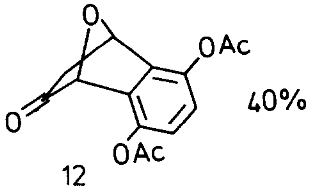
3-Trimethylsiloxy-furan 1 showed anyway its major synthetic perspectives in Diels-Alder reactions with dienophiles.

Addition of maleic anhydride (1 eq.) to compound 1 (2 eq.) at room temperature and without solvent resulted in the formation of a solid that, after crystallisation, showed to be the adduct 11.



Its spectral properties[12] were in perfect accordance with the exo geometry reported in the scheme.

Treatment of 1 with p-benzoquinone in refluxing benzene followed by acetic anhydride-pyridine gave compound 12[13] and reaction of 1 with dimethyl-acetylendicarboxylate in the same reaction conditions gave, after vacuum distillation, the adduct 13[14] as an oil. Its further desilylation induced with trifluoroacetic acid in CCl_4 gave the ketone 14.[15]



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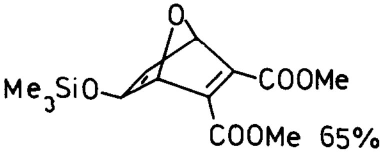

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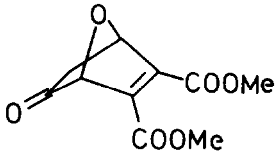

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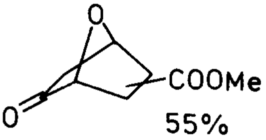

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The tendency of 1 to $[4+2]$ cycloadditions was confirmed by the formation of 15 (55% yield ca.)[16] by the reaction with methylacrylate in neat at 95°C for 20 h. With that dienophile furan gives thermal cycloadditions in comparable

yields only under high pressure.[17]
Further applications of **1** in synthesis, especially regarding the preparation of antraquinonic nuclei, are currently under investigation.

References and notes.

- 1). For the former paper of the series see ref.6 .
- 2). A.Pelter, R.Al-Bayati, W.Lewis Tetrahedron Lett. **23**, 353 (1982).
- 3). M.Asaoka, N.Yanagida, K.Ishibashi, H.Takei Tetrahedron Lett. **22**, 4269 (1981).
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- 5). P.Brownbridge, T.H.Chan Tetrahedron Lett. 21, 3423 (1980).
- 6). L.Lozzi, A.Ricci, M.Taddei J.Org.Chem. **49**, 3408 (1984).
- 7). M.Fiorenza, G.Reginato, A.Ricci, M.Taddei, P.Dembech J.Org.Chem. **49**, 551 (1984).
- 8). In a typical procedure to a solution of 3-lithium-thiophene, prepared from 3-bromothiophene (3 g , 18.4 mmol)in dry Et_2O (25 ml) and a 1.6 M solution of BuLi in hexane stirred at $-78^{\circ}C$ for 2 h. , bis-(trimethylsilyl)-peroxide (3.27 g , 18.4 mmol) was added slowly with a syringe. The solution was warmed up to room temperature, pentane (25 ml) was added and a fine solid so formed was separated by centrifugation.The clear solution was concentrated and after Kugelrohr distillation, 2 was obtained as a yellow oil. 1.6 g , 60% yield.

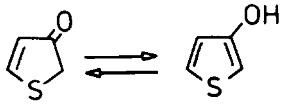
Warning . Use of bis-(trimethylsilyl)peroxide (prepared following ref. 9) never gave us troubles due to explosions or other kind of uncontrolled reactions in presence of metal surfaces or warming up. Nevertheless in presence of the peroxide all the reactions were carried out under a fume cupboard with safety glass windows.

2 b.p. 125-130° at 0.2 mmHg . The product obtained in such a way can be impure of hexamethyldisiloxane up to 20%. Nmr δ ($CDCl_3$/TMS) 0.37 (s,9H,Me_3Si), 6.2 (m, 1H, H_2), 6.60 (dd, 1H, J = 4.5 Hz, H_4), 7.0 (m, 1H, H_5). M/S (m/e) : 156 (M^+), 141(base), 73.

1 b.p.105-110°C at 15 mmHg . Nmr δ 0.24 (s, 9H, Me_3Si), 6.1 (m, 1H, H_4), 7.14 (d, 1H, J =1.5Hz, H_2), 7.2 (m, 1H, H_5). M/S (m/e) 172 (M^+), 157, 73.

- 9). P.G.Cokos, A.G.Davies, N.Fazal, J.Organomet.Chem. **99**, C31 (1975).
- 10). **5** nmr δ (CCl_4/TMS) 4.7 (m, 2H, CH_2), 6.0 (m, 1H, H_4), 7.66 (d, 1H, J = 2Hz H_5). M/S (m/e) : 84 (M^+,base), 54 (M^+-CH_2O).

6 nmr δ (CCl_4/TMS) 3.4 (m, 2H, CH_2), 6.0 (m, 1H, H_4), 8.2 (s, 1H, H_5).



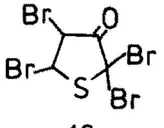
6a 6b

6 shows broad nmr signals, probably for the equilibration between the two

forms **6a** and **6b**.

-11). **9** nmr **δ** (CCl_4/TMS) 5.2 (m, 1H, H_2), 6.4 (m, 1H, H_4), 8.0 (m, 1H, H_5). M/S (m/e) 162-164 (M^+), 82-84 (M^+-Br).

Bromination of **2** gave at -78^{0}C a product with the following nmr signals : 4.94 (d, 1H, J = 4.5 Hz) and 5.53 (d, 1H, J = 4.5 Hz) to which the possible structure **16** of 2,2,4,5-tetrabromo, 3-tetrahydrothiophenone has been assigned.



16

-12). **11** nmr **δ** (CCl_4/TMS) 2.4 (m, 2H, CH_2) 3.76 (d of an AB system, 1H,J = 9Hz, CHCOO) 3.91 (d of an AB system, 1H, J = 9Hz, CHCOO) 4.83 (s, 1H, CHO), 5.40 (d, 1H, J = 4.5 Hz, CHO-CO). M/S (m/e) 182 (M^+), 154 (M^+-CO), 81 (base).

-13). **12** nmr**δ** ($CDCl_3$/TMS) 1.35 (d, 1H, J = 11 Hz CH_2-Hendo), 1.58 (dd, 1H, J = 11 Hz and J = 3 Hz, CH_2-Hexo), 2.47 (s, 6H, COOMe), 4.29 (s, 1H, CHCO), 4.80 (d, 1H, J = 3 Hz, CH-O), 7.2 (m, 2H, Arom.). M/S (m/e) 248 (M^+-28), 234 (M^+- CH_2=C=O), 43 (base).

-14). **13** nmr **δ**(CCl_4/TMS) 0.26 (s, 9H, Me_3Si), 3.77(s,6H, COOMe), 5.0 (m, 1H, H_3), 5.4 (m, 1H, CHO), 5.6 (m, 1H, CHO). M/S (m/e) 298 (M^+), 283 (M^+-15), 73(base).

-15). **14** nmr **δ** (CCl_4/TMS) 2.05 (s, 1H, J = 37 Hz, CH_2-H endo), 2.35 (dd, 1H, J = 37 Hz and J = 4 Hz, CH_2-H exo), 3.72 (s, 6H, COOMe), 4.90 (s, 1H, CHCO), 5.33 (d, 1H, J = 4 Hz, CH-O). M/S (m/e) 211 (M^+-15), 153 (base).

-16). **15** M/S (m/e) 170 (M^+), 142 (M^+-28), 114 (M^+-56), 84 ($\underbrace{\mathrm{CH{=}CH{-}CO{-}CH_2\overset{+}{-}O}}$), 59 (COOMe), 55 (base, $\underbrace{\mathrm{CH{-}CH{=}CH{-}\overset{+}{O}}}$).

-17). W.C.Dauben, H.O.Krabbenhoft J.Am.Chem.Soc., **98**, 1992 (1976).

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