

Synthesis of 2-Acyl-3-Methylthiofurans from 3-Methylthio-2-pentene-1,5-dione Enolates

M. Tinggaard, P. Hansen, P. K. Mogensen, O. Simonsen and J. Becher*

Department of Chemistry, Odense University,
DK-5230 Odense M, Denmark
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2-Acyl-3-methylthiofurans **3** are obtained in fair yields from 3-methylthio-2-pentene-1,5-dione enolates **1** by reaction with iodine. In a similar reaction 1-phenyl-3-methylthio-4-nitro-2-buten-1-one gave 3-methylthio-2-nitro-5-phenylfuran **11**. In the crystalline state the 2-benzoyl-3-methylthio-5-phenylfuran **3b** showed a non-bonded sulfur-oxygen interaction as inferred from an X-ray diffraction determination, with a S...O distance of 2.871(5) Å.

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Introduction.

Furans and furan derivatives are found in many natural products and biologically active compounds. Sulfur containing furans are often parts of flavouring constituents in food, for example in coffee [1] and meat [2].

Some 2-alkylthiofurans have been obtained by ring closure reactions *via* α -oxoketene dithioacetals [3]. A few direct ring closure reactions to 3-alkylthiofurans are also known [4], but normally 3-alkylthiofurans are obtained from 3-halogenofurans using butyllithium and a dialkyl disulfide [5].

Apart from being related to natural products, this substituted furans are of interest due to the possibility of easy functionalization of the alkylthio group.

It is known that 2,4,6-triphenylpyrylium as well as 2,4,6-trimethylpyrylium salts undergoes ring contraction to 2-acylfurans [6] when oxidized under aqueous conditions.

In this type of reaction a 1,3,5-triphenyl-1,5-pentanedione enolate was suggested as a likely intermediate [7], however the reaction was only used for the few examples mentioned above.

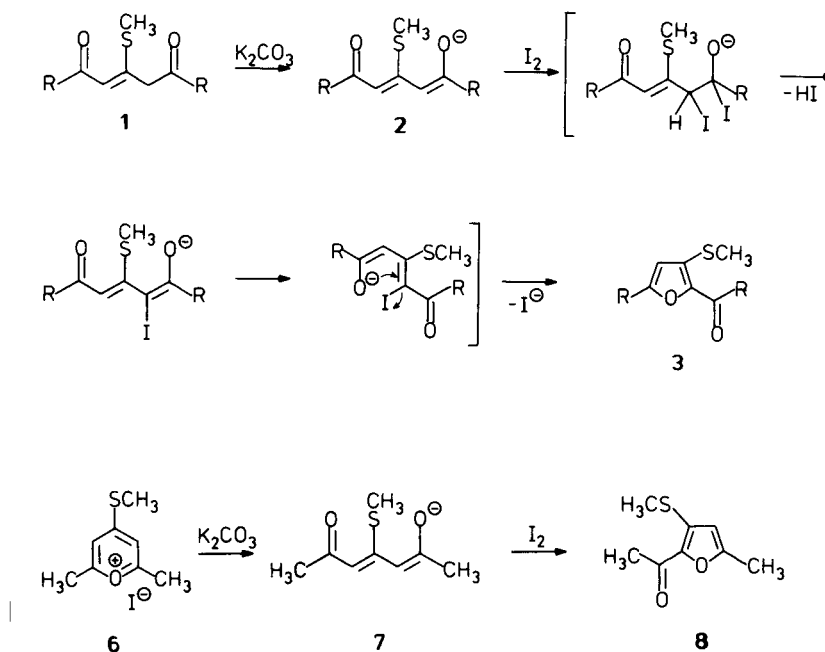
Nesvadba and Kuthan [8] described the oxidation of 1,2,4,6-tetraphenylpyridinium salts which in a related ring contraction gives 2-benzoyl-1,3,5-triphenylpyrrole in fair yield.

Therefore, it was of interest to investigate, if the readily available 3-methylthio-2-pentene-1,5-dione [9] and their enolates could be used as starting materials for the preparation of 3-methylthiofurans.

Results.

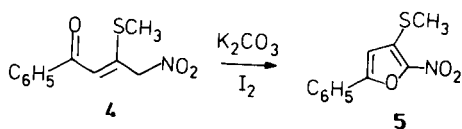
The 3-methylthiofurans **3** were all prepared by dissolving the diketones **1** in acetone with an excess of potassium carbonate followed by addition of an excess of iodine, this

Scheme 1



method gave compounds **3** in 60-90% yields. Formation of the furans **3** is rationalized in Scheme 1 where the intermediate 2-iodo-2-pentene-1,5-dione enolate ring closes to furans **3** *via* elimination of an iodine anion. This ring closure has resemblance to other synthesis of the furan ring such as the Feist-Benary synthesis [10], and the substitution by iodine at carbon-2 in the 2-pentene-1,5-dione enolates resembles the substitution at carbon-2 in the parent glutacetaldehyde anion [11]. Related anions such as the enolate of the methylthio ketone **4** which was obtained as described by Kobayashi *et al* [14] gave the expected nitro furan **5** under the same reaction conditions, whereas the 2-acetyl-3-methylthiofuran **8** was obtained from pyrylium salt **6** *via* the anion **7**.

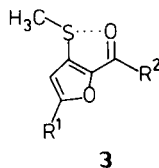
Scheme 2



Structure of 2-Acyl-3-methylthiofurans.

The ir spectra of 2-acyl-3-methylthiofurans **3** all showed C=O absorptions below or around 1600 cm⁻¹. This relatively low carbonyl band is probably a result of the electron distribution **II** ↔ **III** (see Scheme 4).

Scheme 3



The equivalent 2-acetyl-3-methylthiofuran (R¹ = R² = CH₃) **8** showed the ir carbonyl absorption at 1635 cm⁻¹ which again is lower than the normal value of 1675 cm⁻¹ found for 2-acetylfuran [12]. This lowering of the carbonyl absorption in the ir spectra is due to a non-bonded S...O interaction and has not been described in the furan series before, but it is well known for other five-membered heterocyclic systems [13].

Structure of Furans **3** Results from X-ray Structure Determination of **3b**.

The structure of compound **3b** (R¹ = R² = C₆H₅) determined by X-ray diffraction gave bond distances which corresponds very well to the low carbonyl absorptions seen in the ir spectra, the S...O distance of 2.871 Å falls well within the range 2.03-3.25 Å for non-bonded S...O interactions as classified by Kucsman and Kapovits [13]. According to this classification **3b** has a S...O, 1,5 interaction of the type **I** which in this case can be specified to **II**. In Table V **3b** has been compared with related compounds

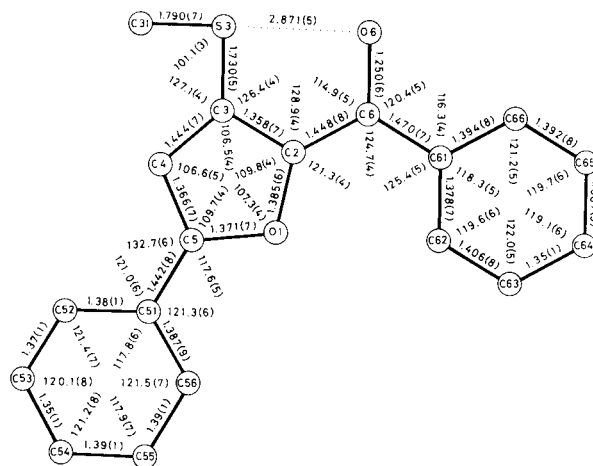


Figure 1.

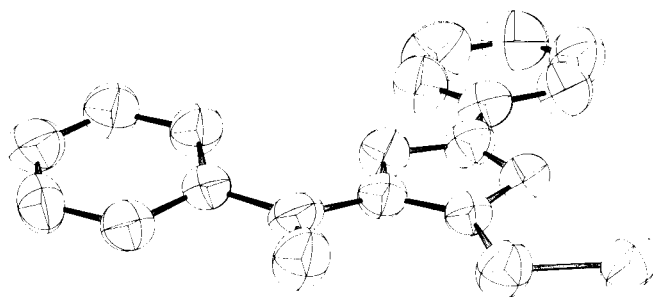
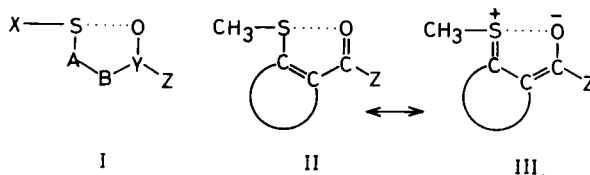


Figure 2.

Scheme 4



of type **II**. Shortenings are seen for the bonds S-C and C-C (especially compared to methyl 2-(methylthio)benzoate, whereas the C=O bond (1.250(6) Å) is distinctly longer than a normal carbonyl bond (1.19-1.22 Å) [18]. The C=C bond in the furan ring (1.358(7) Å) is significantly longer than C=C in unsubstituted furan (1.322(6) Å) [19]. These bond lengths considerations leads to the conclusion that the mesomeric form **III** must have some weight in the description of **3b**. The S...O contact distance (2.871(5) Å) is 0.38 Å shorter than the sum of the Van der Waals radii for S and O (S: 1.85 Å; O: 1.40 Å) [20]. The rather long S...O distance in **3b** is probably caused by an increase of the angles S-A-B and A-B-Y when the bond A-B is part of a five-membered ring instead of a six-membered ring (see Table 1). The five-membered ring S3-C3-C2-C6-O6 (see **II** and Figure 1) constitute a nearly planar system (Figure 2)

Table I

Compound No.	R ¹	R ²	Yield (%)	MP (°C) (Crystallized form)	Molecular formula (MW)	Analysis	
						Calcd./Found C	H
3a	2-thienyl	2-thienyl	65	162-163 (MeOH)	C ₁₄ H ₁₀ O ₂ S ₃ (306.43)	54.87	3.29
						55.00	3.30
3b	phenyl	phenyl	90	125-126 (MeOH)	C ₁₈ H ₁₄ O ₂ S (294.37)	73.44	4.79
						73.43	4.81
3c	<i>p</i> -methoxy-phenyl	<i>p</i> -methoxy-phenyl	64	124-125 (MeOH)	C ₂₀ H ₁₈ O ₄ S (354.42)	67.77	5.12
						67.56	5.13
3d	<i>p</i> -bromo-phenyl	<i>p</i> -bromo-phenyl	88	192-194 (MeOH)	C ₁₈ H ₁₂ Br ₂ O ₂ S (452.42)	47.81	2.67
						47.84	2.67
3e	<i>p</i> - <i>t</i> -butyl-phenyl	<i>p</i> - <i>t</i> -butyl-phenyl	83	144-146 (MeOH)	C ₂₆ H ₂₀ O ₂ S (406.59)	76.81	7.44
						77.13	7.42
3f	2-furyl	2-furyl	64	149-151 (EtOH)	C ₁₄ H ₁₀ O ₄ S (274.29)	61.31	3.67
						61.37	3.65
3g	<i>p</i> -methyl-phenyl	<i>p</i> -methyl-phenyl	62	121-122 (MeOH)	C ₂₀ H ₁₆ O ₂ S (322.42)	74.51	5.63
						74.58	5.70
3h	4-diphenyl	4-diphenyl	41	200-202 (MeOH)	C ₃₀ H ₂₂ O ₂ S (446.56)	80.69	4.97
						80.93	4.97
3i	2-naphthyl	2-naphthyl	63	185-186 (MeOH)	C ₂₆ H ₁₈ O ₂ S (394.49)	79.16	4.60
						79.35	4.54

Table II

Compound No.	IR [cm ⁻¹] ν C=O	UV λ max [nm] EtOH (log ε)	Mass (M ⁺) (relative intensity %)
3a	1585	300 (4.36)	306 (100) 291 (10) 289 (11) 273 (30)
		405 (4.35)	245 (15) 111 (70) 108 (17) 83 (9) 39 (22)
3b	1605	230 (3.66); 278 (4.01)	294 (100) 279 (16) 277 (13) 261 (41)
		365 (3.93)	215 (10) 105 (56) 102 (12) 77 (66)
3c	1610	231 (4.08); 285 (4.34)	354 (100) 339 (10) 337 (18) 321 (22) 191 (9)
		377 (4.34)	163 (12) 135 (70) 92 (12) 77 (18)
3d	1605	224 (4.21); 283 (4.53)	454 (54) 452 (100) 450 (50) 435 (16) 340 (60)
		371 (4.38)	338 (62) 185 (48) 183 (48) 157 (20) 155 (20)
3e	1600	278 (4.61)	406 (100) 391 (26) 389 (11) 349 (12)
		370 (4.49)	317 (31) 161 (19) 57 (18)
3f	1605	224 (3.81); 279 (4.35)	274 (100) 257 (20) 245 (35) 213 (20)
		383 (4.31)	151 (19) 95 (92) 39 (28)
3g	1600	227 (3.97); 276 (4.38)	322 (100) 307 (20) 289 (36) 119 (40)
		367 (4.28)	91 (42) 65 (10) 28 (9)
3h	1600	294 (4.46)	447 (33) 446 (100) 429 (12) 413 (33)
		381 (4.07)	181 (52) 178 (16) 153 (32) 152 (48)
3i	1605	279 (4.43); 298 (4.32)	295 (18) 294 (57) 261 (21) 211 (12)
		382 (4.30)	155 (41) 152 (27) 128 (12) 127 (100)

with the torsion angles C31-S3-C3-C2: -177.1(5)°; S3-C3-C2-C6 = 0.9(9)° and C3-C2-C6-O6: -3.4(9)°. This is in agreement with a conformational *ab initio* MO study carried out for Z-3-(fluorothio)-2-propenal [13] which gave minimum energy to a planar conformation of type I. Figure 1 shows bond distances, bond angles and the atom numbering system; the positional and equivalent isotropic thermal parameters are given in Table VI. Figure 2 shows a perspective drawing of **3b** (ORTEP).

EXPERIMENTAL

X-ray Crystallographic Data of **3b**.

C₁₈H₁₄O₂S, mol wt = 294.37. A crystal with the dimensions 0.26 x 0.26 x 0.16 mm was selected for intensity measurements. F(000) = 616, orthorhombic P2₁2₁, a = 5.552(4), b = 15.018(3), c = 17.647(3) Å. The unit cell volume is 1471 Å³, Z = 4. The measured and the calculated density is d_m = 1.33 and d_c = 1.329 g·cm⁻³, respectively. The X-ray intensity data were collected on an Enraf-Nonius CAD-4F diffractometer using

Table III

Compound No.	¹ H-NMR [ppm] (DMSO-d ₆)/TMS (internal)
3a	2.5 (s, 3H, SCH ₃), 6.7 (s, 1H, CH), 7.1-8.4 (m, 6H, H arom)
3b	2.5 (s, 3H, SCH ₃), 6.8 (s, 1H, CH), 7.3-8.3 (m, 10H, H arom)
3c	2.6 (s, 3H, SCH ₃), 6.7 (s, 1H, CH), 6.9-8.4 (m, 8H, H arom), 3.9 (s, 3H, OCH ₃), 4.0 (s, 3H, OCH ₃)
3d	2.5 (s, 3H, SCH ₃), 6.8 (s, 1H, CH), 7.3-8.4 (m, 8H, H arom)
3e	2.5 (s, 3H, SCH ₃), 6.8 (s, 1H, CH), 7.3-8.3 (m, 8H, H arom), 1.3 (m, 9H, <i>t</i> -butyl), 1.3 (m, 9H, <i>t</i> -butyl)
3f	2.5 (s, 3H, SCH ₃), 6.7 (s, 1H, CH), 6.5-7.7 (m, 6H, H arom)
3g [a]	2.5 (s, 3H, SCH ₃), 7.2-8.1 (m, 8H, H arom), 2.35 (s, 3H, CH ₃), 2.45 (s, 3H, CH ₃)
3h	2.55 (s, 3H, SCH ₃), 6.9 (s, 1H, CH), 7.2-8.4 (m, 18H, H arom)
3i	2.55 (s, 3H, SCH ₃), 6.9 (s, 1H, CH), 7.4-8.4 (m, 14H, H arom)

[a] The nmr spectrum of **3g** was obtained in deuteriochloroform.

graphite-monochromatized MoK α -radiation ($\lambda_{\text{MoK}\alpha 1} = 0.71073 \text{ \AA}$), $T = 295 \text{ K}$. Lattice parameters were determined from 25 diffractometer setting angles ($7.80 < \theta < 13.23^\circ$). The data collection range was ($2 < \theta < 27.5^\circ$), ($h \ 0-7, k \ 0-19, l \ 0-22$). Three reflections were used for orientation control every 100 reflections, intensity check every third hour of exposure time, with one reflection. A total of 1861 reflections were measured in the $\omega/2\theta$ mode with scan angle $\Delta\omega = (1.80 + 0.35 \tan\theta)^\circ$. A total of 901 reflections were considered as observed ($I > 2.5\sigma(I)$). Lorentz and polarization correction were applied, no absorption correction was made; $\mu = 0.211 \text{ mm}^{-1}$.

The structure was solved with direct methods. Anisotropic full-matrix least squares refinement of non H-atoms. Positional parameters for six H-atoms from a difference density map; the remaining eight H-atom positions were calculated. Refinements of $H(x,y,z)$ with $\sin \theta/\lambda < 0.40 \text{ \AA}^{-1}$; fixed isotropic H-temperature factor. Only half of the H-atoms refined to "realistic" positions;

Table IV

Compound No.	¹³ C-NMR [ppm] (DMSO-d ₆)/TMS (internal)					
	$\delta \text{ C (2)}$	$\delta \text{ C (3)}$	$\delta \text{ C (4)}$	$\delta \text{ C (5)}$	$\delta \text{ SCH}_3$	$\delta \text{ C=O}$
3a	152.05	132.54	105.33	143.74	15.54	171.42
3b	156.49	131.77	105.58	145.37	15.50	180.19
3c	156.57	131.53	104.21	145.30	15.71	178.81
3d	155.73	132.24	106.17	145.39	15.72	179.17
3e		134.41	105.10	145.59	15.72	179.98
3f		138.66	105.41		15.53	167.42
3g [a]	156.21	134.13	106.50	144.37	15.11	178.81
3h	156.48	135.50	105.80	144.50	15.76	180.05
3i	156.77	139.35	106.15	145.50	15.79	180.20

[a] The nmr spectrum of **3g** was obtained in deuteriochloroform.

Table V

Bond Distances [Å] and Angles [°] in the Ring System (II) Compared with the Corresponding Bonds in Related Compounds

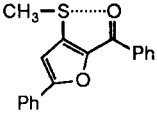
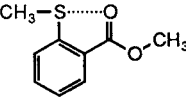
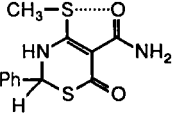
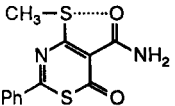
Compound	Reference	CH ₃ -S	S-C	C=C	C-C	C=O	S...O	<O-C-C	<C-C-C	<C-C-S
 3b		1.790(7)	1.730(5)	1.358(7)	1.448(8)	1.250(5)	2.871(5)	114.9(5)	128.9(4)	126.4(4)
	[21]	1.793(6)	1.760(4)	1.407(7)	1.480(7)	1.196(6)	2.721(4)	124.9(8)	121.0(7)	120.6(6)
	[22]	1.809(2)	1.741(2)	1.407(2)	1.498(2)	1.229(2)	2.657(2)	118.3(2)	117.8(2)	120.1(2)
	[23]	1.815(2)	1.748(2)	1.388(2)	1.504(2)	1.224(2)	2.664(2)	120.2(2)	119.5(2)	121.4(2)

Table VI

Fractional Coordinates and Equivalent Isotropic Thermal Parameters of Non H-Atoms in **3b** with e.s.d.'s in Parentheses

Atom	x	y	z	B _{eq}
S 3	0.3511(3)	0.26046(9)	0.63466(9)	5.7(1)
O 1	0.4600(7)	0.0099(2)	0.5814(2)	4.8(3)
O 6	0.7409(8)	0.1655(2)	0.7047(2)	6.2(4)
C 2	0.514(1)	0.0875(3)	0.6202(3)	4.5(4)
C 3	0.357(1)	0.1527(3)	0.6001(3)	4.2(4)
C 4	0.191(1)	0.1131(3)	0.5467(3)	4.9(4)
C 5	0.264(1)	0.0270(3)	0.5366(3)	5.0(5)
C 6	0.708(1)	0.0910(3)	0.6748(3)	5.0(5)
C 31	0.092(1)	0.3042(3)	0.5871(4)	6.5(5)
C 51	0.175(1)	-0.0445(4)	0.4898(3)	5.3(5)
C 52	-0.031(1)	-0.0341(5)	0.4469(3)	6.8(8)
C 53	-0.114(2)	-0.1007(5)	0.4007(4)	8.0(7)
C 54	0.007(2)	-0.1786(6)	0.3963(4)	8.6(8)
C 55	0.215(2)	-0.1932(4)	0.4384(4)	9.1(9)
C 56	0.293(1)	-0.1257(4)	0.4861(4)	6.8(6)
C 61	0.858(1)	0.0145(3)	0.6966(3)	4.4(4)
C 62	0.813(1)	-0.0730(3)	0.6779(3)	5.7(5)
C 63	0.972(1)	-0.1399(4)	0.7024(3)	6.1(5)
C 64	1.171(1)	-0.1212(4)	0.7435(4)	6.2(5)
C 65	1.218(1)	-0.0335(4)	0.7634(3)	5.8(5)
C 66	1.063(1)	0.0337(3)	0.7394(3)	4.9(4)

the other half part were included in the refinements with fixed calculated positions $\sum w(|F_o| - |F_c|)^2$ minimized; final R = 0.064 and wR = 0.062; w = 1 when $|F_c| < 80$ otherwise w = $(40/F_o)^2$. S = 1.55. $(\Delta/\sigma)_{max} = 0.05$ (non H-atoms). Minimum and maximum in final $\Delta\rho$ map = -0.36 and 0.75 e Å⁻³. Scattering factors from International Tables for X-ray Crystallography [15]. Computer programs from SHELX 76 [16] and X-RAY 76 [17].

1,5-Bis(4-diphenyl)-3-methylthio-2-pentene-1,5-dione (**2h**).

To a stirred solution of potassium *t*-butoxide (4.5 g, 0.04 mole) and 4-acetyldiphenyl (3.9 g, 0.02 mole), dissolved in dry tetrahydrofuran, was added 3,3-bis(methylthio)-1-(4-diphenyl)-2-propen-1-one (6.0 g, 0.02 mole). The mixture was stirred at room temperature for 20 hours. The reaction mixture is poured into water (ca 600 ml 0°) with stirring, and treated with a 2% solution of acetic acid. The precipitate is collected and dried. The brown crystals were recrystallized from cyclohexane and ethyl acetate (1:1), crude yield 94%, mp 120°; ¹H-nmr (deuteriochloroform/TMS): δ = 2.55 (s, 3H, -SCH₃), 4.75 (s, 2H, -CH₂), 7.0 (s, 1H, =CH), 7.4-8.6 ppm (aromatic); ¹³C-nmr (deuteriochloroform/TMS): δ = 15.5 (-SCH₃), 45 (-CH₂), 114 (=CH), 126-147 (aromatic), 186 (C=O), 193 ppm (-C=O); ms: (relative intensity %) 433 (8), 198 (14), 181 (100), 153 (17), 152 (20), 48 (26), 47 (35).

Anal. Calcd. for C₃₀H₂₄S₂: C, 80.33; H, 5.39 (448.58). Found: C, 80.32; H, 5.74.

1,5-Bis(2-naphthyl)-3-methylthio-2-pentene-1,5-dione (**2i**).

The general method described by Potts *et al* [9] was used. To a stirred solution of potassium *t*-butoxide (4.5 g, 0.04 mole) and methyl 2-naphthyl ketone (3.4 g, 0.02 mole), dissolved in dry tetrahydrofuran, was added 3,3-bis(methylthio)-1-(2-naphthyl)-2-penten-1-one (5.17 g, 0.02 mole). The mixture was stirred at room temperature for 20 hours. The reaction mixture is poured into water (ca. 600 ml 0°) with stirring, and treated with a 2% solution of acetic acid. The precipitate was collected and dried.

The brown crystals were recrystallized from ethyl acetate, crude yield, 90%, mp 151°; ¹H-nmr (deuteriochloroform/TMS): δ = 2.5 (s, 3H, -SCH₃), 4.75 (s, 2H, -CH₂), 7.0 (s, 1H, -CH), 7.4-8.6 ppm (m, 14H, aryl); ¹³C-nmr (deuteriochloroform/TMS): δ = 15.55 (-SCH₃), 45 (-CH₂), 110 (=CH), 123-137 (aromatic), 187 (C=O), 194 ppm (C=O); ms: (relative intensity %) 396 (6), 381 (8), 156 (12), 155 (100), 127 (59).

Anal. Calcd. for C₂₆H₂₀S₂: C, 78.76; H, 5.08 (396.50). Found: C, 79.14; H, 5.14.

2-(Aroyl or heteroaryl)-5-(aryl or heteroaryl)-3-(methylthio)furans 3. General Procedure.

To a solution of 1,5-di(aryl)-3-methylthio-2-pentene-1,5-dione **1** (10 mmoles) and acetone (100 ml, 20°) was added with stirring an aqueous solution of potassium carbonate (20 ml 1M) and the mixture was stirred at room temperature for 1¼ hour whereupon iodine (8 g) was added and the stirring continued at room temperature for 22 hours. Chloroform (100 ml) was then added to the dark solution and the mixture extracted with a solution of sodium thiosulphate (1M) to remove the excess iodine. The organic phase was dried (sodium sulfate) and the solvent evaporated *in vacuo*. The crude product was recrystallized from a suitable solvent to give compounds **3** as pale yellow crystals.

2-Acetyl-5-methyl-3-(methylthio)furan (**8**).

Compound **8** was obtained by the method described in reference [7] with 2,6-dimethyl-4-methylthiopyrylium iodide as the starting material. The crude product was recrystallized from cyclohexane to give pale yellow crystals of **8**, yield 1.2 g (70%), mp 101-102°; ir (potassium bromide): ν = 1635 cm⁻¹ (C=O); uv: λ max (log ε) = 221 (3.74), 271 (3.94), 313 (3.97) nm; ¹H-nmr (deuteriochloroform/TMS): δ = 2.3-2.5 (3 x 3H, 2 x CH₃ + SCH₃), 6.2 ppm (s, 1H, CH); ¹³C-nmr (deuteriochloroform/TMS): δ = 185.56 (C=O), 156.14 (C₂), 145.44 (C₃), 133.97 (C₄), 107.66 (C₅), 25.86 (CH₃), 15.49 (SCH₃), 14.13 ppm (CH₃); ms: m/e (relative intensity) = 170 (73), 155 (42), 137 (35), 43 (100), 28 (16).

Anal. Calcd. for C₈H₁₀O₂S: C, 56.45; H, 5.92 (170.23). Found: C, 56.11; H, 5.85.

3-Methylthio-5-phenyl-2-nitrofurans (**5**).

Compound **5** was obtained by the same method as described for compounds **3**. The starting material **4** was obtained according to reference [14] by Kobayashi *et al*. From ketone **4** the general method resulted in formation of a dark reaction product. This crude product was washed with ether (70 ml) and recrystallized from toluene to give pale yellow crystals of **5**, yield 0.6 g (25%), mp 140-142°; uv: λ max (log ε) = 272 (4.11), 338 (4.05), 381 nm (4.16); ¹H-nmr (deuteriochloroform/TMS): δ = 2.3 (s, 3H, -SCH₃), 6.8 (s, 1H, CH), 7.2-8.0 ppm (m, 5H, aryl); ¹³C-nmr (deuteriochloroform/TMS): δ = 155.96 (C₂), 125-135 (aryl + C₃ + C₄), 105.91 (C₅), 15.59 ppm (-SCH₃); ms: m/e (relative intensity %) = 235 (51), 205 (18), 161 (27), 145 (30), 105 (100), 102 (43), 77 (38).

Anal. Calcd. for C₁₁H₉NO₂S: C, 56.16; H, 3.86; N, 5.95 (235.26). Found: C, 56.45; H, 3.83; N, 5.85.

Microanalyses were carried out by NOVO A/S Bagsvaerd, Denmark. The ir spectra were obtained on a Perkin-Elmer 580 and the uv spectra were obtained on a Varian Cary 219. The ¹H and ¹³C-nmr spectra were obtained on a 250 MHz Bruker AC 250 spectrometer. Mass spectra were obtained on a Varian MAT 311 A. Melting points are uncorrected, and were obtained with a Büchi apparatus. Yields are given for analytically pure products.

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