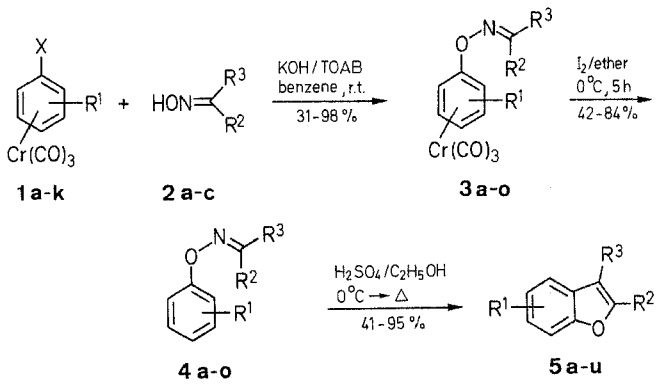

1a-k 2a-c 3a-o 4a-o 5a-u

TOAB = tetraoctylammonium bromide

1	X	R^1
a	Cl	H
b	F	*o*-CH_3
c	F	*m*-CH_3
d	F	*p*-CH_3
e	Cl	*o*-CH_3
f	Cl	*m*-OCH_3
g	Cl	*o*-Cl
h	Cl	*m*-Cl
i	Cl	*p*-Cl
j	Cl	*m*-(*n*-C_4H_9S)
k	Cl	*p*-(*n*-C_4H_9S)

2	R^2	R^3
a	CH_3	CH_3
b	CH_3	C_2H_5
c	$-(CH_2)_5-$	

3, 4	R^1	R^2	R^3
a	H	CH_3	CH_3
b	H	C_2H_5	CH_3
c	*o*-CH_3	CH_3	CH_3
d	*m*-CH_3	CH_3	CH_3
e	*p*-CH_3	CH_3	CH_3
f	*m*-CH_3	$-(CH_2)_5-$	
g	*p*-CH_3	$-(CH_2)_5-$	
h	*m*-OCH_3	CH_3	CH_3
i	*o*-Cl	CH_3	CH_3
j	*m*-Cl	CH_3	CH_3
k	*p*-Cl	CH_3	CH_3
l	*m*-Cl	$-(CH_2)_5-$	
m	*p*-Cl	$-(CH_2)_5-$	
n	*m*-(*n*-C_4H_9S)	CH_3	CH_3
o	*p*-(*n*-C_4H_9S)	CH_3	CH_3

5	R^1	R^2	R^3
a	H	CH_3	CH_3
b	H	C_2H_5	H
c	H	CH_3	H
d	7-CH_3	CH_3	H
e	6-CH_3	CH_3	H
f	4-CH_3	CH_3	H
g	5-CH_3	CH_3	H
h	6-CH_3	$-(CH_2)_4-$	
i	5-CH_3	$-(CH_2)_4-$	
j	6-OCH_3	CH_3	H
k	4-OCH_3	CH_3	H
l	7-Cl	CH_3	H
m	6-Cl	CH_3	H
n	4-Cl	CH_3	H
o	5-Cl	CH_3	H
p	6-Cl	$-(CH_2)_4-$	
q	4-Cl	$-(CH_2)_4-$	
r	5-Cl	$-(CH_2)_4-$	
s	6-(*n*-C_4H_9S)	CH_3	H
t	4-(*n*-C_4H_9S)	CH_3	H
u	5-(*n*-C_4H_9S)	CH_3	H

Nucleophilic Aromatic Substitution on Tricarbonylchromium-complexed Haloarenes: Synthesis of *O*-Aryloximes and Their Cyclization to Benzofurans

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A series of *O*-aryloximes have been prepared from tricarbonylchromium-complexed haloarenes in mild conditions. Title compounds are starting materials for benzofuran synthesis.

O-Aryloximes are useful organic reagents for the synthesis of benzofurans *via* a rearrangement paralleling the Fischer indole synthesis.[1] However the known synthetic methods allow the preparation mainly of compounds carrying electron withdrawing substituents on the aryl moiety.[2]

In a preliminary note[3] we communicated the possibility of obtaining in good yields acetonyl-*O*-aryloximes carrying both electron withdrawing and electron donating substituents on the aryl group and their cyclization to the 2-methyl-benzofurans.

In this paper we wish to communicate that such a method is of general applicability, allowing the preparation of compounds **4a–o**, some of which were hitherto unknown, and thus giving access to a rather broad range of substitution patterns in the final benzofurans. Starting materials were the tricarbonylchromium-complexed haloarenes **1a–k** and the ketoximes **2a–c**, which were made to react under solid-liquid phase transfer conditions (PTC) in benzene in the presence of an excess of powdered potassium hydroxide and with tetraoctylammonium bromide (TOAB) as catalyst. Most of the reactions were run at room temperature, the work-up was easy and the tricarbonylchromium-complexed *O*-aryloximes **3** were isolated in very good yields; the exception was **3i, n, o**, which were decomplexed directly. The *o*-dichlorobenzene tricarbonylchromium-complex **1g** did not react with **2c** (Table 1).

The *O*-aryloximes **4a–o** were obtained from the corresponding tricarbonylchromium-complexed compounds **3a–o** by iodine oxidation at 0 °C, in fair to high yields. All these compounds are new (the only exceptions being **4a**,[4] **4e**,[2] and **4k**[5] and no known procedures seem effective alternatives in achieving our range of substitution pattern (Table 2).

Products **3i, 3k** and **3m** remained practically unchanged when treated with a second molar equivalent of oxime even at 45 °C. However *para* complexed monochloro-*O*-aryloxime **3k** reacted with 1-butanethiol to give, after decomplexation with iodine, the *n*-butylthioderivative **4o**. Analogously **3j** reacted with 1-butanethiol to give **4n**. Compounds **4n–o** were also obtained by reacting tricarbonylchromium-complexed *m*- and *p*-butylthiochlorobenzenes **1j, k** with acetone oxime **2a**.

The reaction of butan-2-one oxime **2b**, employed as a mixture of *syn/anti* isomers, afforded a mixture of the corresponding *syn* and *anti*-*O*-aryl derivatives **4b** which were identified by ^{1}H-NMR spectra.

Table 1. Tricarbonylchronium-Complexed *O*-Aryloximes **3** Prepared

Product No.	Reaction Time (h)	Yield (%)	m.p. (°C)	Molecular Formula[a]	^{1}H-NMR ($CDCl_3$/TMS) δ (ppm)
3a	0.50	85	83	$C_{12}H_{11}CrNO_4$ (285.2)	2.0 (s, 6H, $2CH_3$); 4.7–4.9 (m, $1H_{arom}$); 5.3–5.7 (m, $4H_{arom}$)
3b[b]	4.25	80	79–81	$C_{13}H_{13}CrNO_4$ (298.2)	*anti*: 1.08 (t, 3H, $-CH_2-CH_3$, J = 7.5 Hz); 1.95 (s, 3H, CH_3); 2.46 (q, 2H, $-CH_2-CH_3$, J = 7.5 Hz); 4.68–4.9 (m, $1H_{arom}$); 5.38–5.66 (m, $4H_{arom}$) *syn*: 1.11 (t, 3H, $-CH_2-CH_3$, J = 7.5 Hz); 1.95 (s, 3H, CH_3); 2.36 (q, 2H, $-CH_2-CH_3$, J = 7.5 Hz); 4.68–4.9 (m, $1H_{arom}$); 5.38–5.66 (m, $4H_{arom}$)
3c	1.75	75	88–89	$C_{13}H_{13}CrNO_4$ (298.2)	2.1 [s, 6H, $C-(CH_3)_2$]; 2.3 (s, 3H, CH_3); 4.9 (m, $1H_{arom}$); 5.5 (m, $2H_{arom}$); 5.9 (d, $1H_{arom}$)
3d	1.00[c] 3.00[d]	98 75	77	$C_{13}H_{13}CrNO_4$ (298.2)	2.0 [s, 6H, $C-(CH_3)_2$]; 2.2 (s, 3H, CH_3); 4.6–4.8 (m, $1H_{arom}$); 5.2–5.7 (m, $3H_{arom}$)
3e	2.50	89	96	$C_{13}H_{13}CrNO_4$ (298.2)	2.0 [s, 6H, $C-(CH_3)_2$]; 2.2 (s, 3H, CH_3); 5.5 (s, $4H_{arom}$)
3f	2.00	55	114–115	$C_{16}H_{17}CrNO_4$ (339.3)	1.9 (m, 6H, cyclohexane); 2.6 (s, 3H, CH_3); 2.3–2.9 (m, 4H, cyclohexane); 5.1 (dd, 1H, H-4, J_o = 6.0 Hz, J_m = 1.2 Hz, arom); 5.7–6.1 (m, $3H_{arom}$)
3g	2.75	76	85–87	$C_{16}H_{17}CrNO_4$ (339.3)	1.5–1.8 (m, 6H, cyclohexane); 2.04 (s, 3H, CH_3); 2.1–2.6 (m, 4H, cyclohexane); 5.5 (s, $4H_{arom}$)
3h	1.75	84	112–114	$C_{13}H_{13}CrNO_5$ (315.2)	1.97 [s, 6H, $C-(CH_3)_2$]; 3.69 (s, 3H, CH_3); 4.76 (dd, 1H, H-4, J_o = 6.0 Hz, J_m = 1.25 Hz); 5.17 (dd, 1H, H-6, J_o = 7.5 Hz, J_m = 1.25 Hz); 5.5–5.7 (m, $2H_{arom}$)
3j	0.50	91	90	$C_{12}H_{10}ClCrNO_4$ (319.7)	2.0 [s, 6H, $C-(CH_3)_2$]; 5.15 (dd, 1H, H-4, J_o = 6.0 Hz, J_m = 1.2 Hz); 5.22 (dd, 1H, H-6, J_o = 6.0 Hz, J_m = 1.2 Hz); 5.6 (t, 1H, H-5, J_o = 6.0 Hz); 5.8 (d, 1H, H-2, J_m = 1.2 Hz)
3k	1.00	89	85	$C_{12}H_{10}ClCrNO_4$ (319.7)	2.0 [s, 6H, $C-(CH_3)_2$]; 5.5 (d, 2H, J = 6.5 Hz_{arom}); 5.7 (d, 2H, J = 6.5 Hz_{arom})
3l	0.50	73	96–98	$C_{15}H_{14}ClCrNO_4$ (359.7)	1.5–1.9 (m, 6H, cyclohexane); 2.2–2.7 (m, 4H, cyclohexane); 5.0 (dd, 1H, H-4, J_o = 6.5 Hz, J_m = 1.2 Hz); 5.2 (dd, 1H, H-6, J_o = 6.5 Hz, J_m = 1.2 Hz); 5.6 (t, 1H, H-5, J_o = 6.5 Hz); 5.75 (t, 1H, H-2, J_m = 1.2 Hz)
3m	1.25	31	87–89	$C_{15}H_{14}ClCrNO_4$ (359.7)	1.5–1.95 (m, 6H, cyclohexane); 2.15–2.6 (m, 4H, cyclohexane); 5.5 (d, 2H, J = 6.5 Hz_{arom}); 5.7 (d, 2H, J = 6.5 Hz_{arom})

[a] Satisfactory microanalyses obtained: C ±0.37, H ±0.18, N ±0.35 (Exception: **3j**, C −0.48).
[b] Mixture of *syn/anti* isomer 80:20 as inferred from ^{1}H-NMR spectrum.
[c] Reaction conducted starting from the corresponding chloro derivative.
[d] Reaction conducted starting from the corresponding fluoro derivative.

All the *O*-aryloximes **4a–o** underwent cyclization to benzofurans in good yields when refluxed in ethanol in the presence of 98% sulfuric acid (Table 3). It is noteworthy that attempts to cyclize the tricarbonylchromium-complexed *O*-aryloximes **3a–o** to the complexed benzofurans, in the above reaction conditions, resulted in the decomplexation to compounds **4** followed by cyclization to **5**. Cyclization of *m*-substituted *O*-aryloximes **4d, h, j, l, n**, gave the two possible isomers that were not separated. Their structure and relative ratio were inferred from the ^{1}H-NMR spectra of the crude mixtures. Only in the case of **4h** was it possible to isolate by column chromatography the pure 6-methoxy-2-methyl benzofuran **5j**. It is noteworthy that cyclization preferably occurs at the less hindered position of the arene ring. Compound **4b** gave two isomeric benzofurans in a 80:20 ratio: the 2,3-dimethyl benzofuran **5a** and the 2-ethyl derivative **5b**.

Many of compounds **5a–u** are new. Those previously reported (**5c–g** and **5j–o**) were prepared by completely different synthetic routes (Table 3).

The above described synthesis of *O*-aryloximes by S_NAr substitution on tricarbonylchromium-complexed haloarenes allows, therefore, a convenient entry to a rather broad range of differently substituted benzofurans, a class of compounds widely spread throughout nature and pharmacologically important.

^{1}H-NMR spectra were recorded on a Varian EM 390 spectrometer. All melting points are uncorrected. The microanalyses were performed on Perkin-Elmer 240 Elemental Analyzer. The tricarbonylchromium-complexed halogenoarenes **1a–k** were prepared according to literature procedures.[10-12]

Tricarbonylchromium-Complexed *O*-Aryloximes 3a–o; General Procedure:

To a vigorously stirred benzene solution (30 ml) of **1** (1.77 mmol), ground potassium hydroxide (297.4 mg, 5.31 mmol) and tetraoctylammonium bromide (267.9 mg, 0.49 mmol), the ketoxime **2** (1.77 mmol) is added. The reaction progress is monitored by TLC. After the completion of the reaction the solvent is evaporated, the residue extracted with ether (3 × 20 ml), dried with sodium sulfate and filtered over celite. Evaporation of the ether gives the crude products **3**, which is then purified by crystallization from diisopropylether (Table 1). The ether solutions of **3i, n, o** are directly used for decomplexation.

***n*-Butylthio-*O*-aryloximes 4n or 4o:**

To a vigorously stirred benzene solution (30 ml) of **3j** or **3k** (1.77 mmol), ground potassium hydroxide (297.4 mg, 5.31 mmol) and tetraoctylammonium bromide (273.4 mg, 0.5 mmol), the 1-butanethiol (159.6 mg, 1.77 mmol) is added. The reaction progress is monitored by TLC. When the substrate has disappeared, the solvent is evaporated under reduced pressure, the residue is extracted with ml (3 × 20 ml), filtered over celite and treated with iodine (see the following general decomplexation procedure).

Table 2. *O*-Aryloximes **4** Prepared

Product No.	Yield (%)	m.p. (°C) or b.p. (°C)/torr	Molecular Formula[a]	^{1}H-NMR ($CDCl_3$/TMS) δ (ppm)
4a	78	115/1	$C_9H_{11}NO$ (149.2)	1.9 (s, 3H, CH_3); 2.0 (s, 3H, CH_3); 6.7–7.6 (m, 5H$_{arom}$)
4b[b]	80	oil[c]	$C_{10}H_{13}NO$ (163.2)	*syn*-isomer: 1.13 (t, 3H, $-CH_2-CH_3$, J = 6.0 Hz); 2.02 (s, 3H, CH_3); 2.52 (q, 2H, $-CH_2-CH_3$, J = 6.0 Hz); 6.75–7.47 (m, 5H$_{arom}$) *anti*-isomer: 1.13 (t, 3H, $-CH_2-CH_3$, J = 7.2 Hz); 1.98 (s, 3H, CH_3); 2.26 (q, 2H, $-CH_2-CH_3$, J = 7.2 Hz); 6.75–7.74 (m, 5H$_{arom}$)
4c	56	oil[c]	$C_{10}H_{13}NO$ (163.2)	1.6 [s, 6H, $=C(CH_3)_2$]; 2.3 (s, 3H, *o*-CH_3); 6.8–7.9 (m, 4H$_{arom}$)
4d	55	77/0.8	$C_{10}H_{13}NO$ (163.2)	1.9 (s, 3H, CH_3); 1.95 (s, 3H, CH_3); 2.4 (s, 3H, *m*-CH_3); 6.7–7.3 (m, 4H$_{arom}$)
4e	81	60	$C_{10}H_{13}NO$ (163.2)	1.95 (s, 3H, CH_3); 2.05 (s, 3H, CH_3); 2.2 (s, 3H, *p*-CH_3); 6.8–7.1 (m, 4H$_{arom}$)
4f	80	oil[c]	$C_{13}H_{17}NO$ (203.3)	1.4–1.8 (m, 6H, cyclohexane); 2.1–2.68 (m, 4H, cyclohexane); 2.3 (s, 3H, CH_3); 6.6–7.1 (m, 4H$_{arom}$)
4g	70	46	$C_{13}H_{17}NO$ (203.3)	1.4–1.8 (m, 6H, cyclohexane); 2.2 (s, 3H, CH_3); 2.3–2.7 (m, 4H, cyclohexane); 7.0 (s, 4H$_{arom}$)
4h	74	oil[c]	$C_{10}H_{13}NO_2$ (179.2)	2.14 (s, 3H, CH_3); 2.2 (s, 3H, CH_3); 3.9 (s, 3H, OCH_3); 6.51–7.0 (m, 3H$_{arom}$); 7.2–7.5 (m, 1H$_{arom}$)
4i	42	oil[c]	$C_9H_{10}ClNO$ (183.6)	2.0 (s, 3H, CH_3); 2.1 (s, 3H, CH_3); 6.8–7.5 (m, 4H$_{arom}$)
4j	80	67/0.9	$C_9H_{10}ClNO$ (183.6)	2.0 (s, 3H, CH_3); 2.1 (s, 3H, CH_3); 6.8–7.3 (m, 4H$_{arom}$)
4k	84	oil[c]	$C_9H_{10}ClNO$ (183.6)	2.0 (s, 3H, CH_3); 2.1 (s, 3H, CH_3); 7.0–7.4 (m, 4H$_{arom}$)
4l	78	135–140/0.7	$C_{12}H_{14}ClNO$ (223.7)	1.5–1.85 (m, 6H, cyclohexane); 2.15–2.76 (m, 4H, cyclohexane); 6.71–7.28 (m, 4H$_{arom}$)
4m	73	oil[c]	$C_{12}H_{14}ClNO$ (223.7)	1.45–1.82 (m, 6H, cyclohexane); 2.2–2.75 (m, 4H, cyclohexane); 7–7.5 (m, 4H$_{arom}$)
4n	48	137/0.1	$C_{13}H_{19}NOS$ (237.4)	0.9 [t, 3H, $-(CH_2)_3-CH_3$, J = 6.5 Hz]; 1.3–1.8 [m, 4H, $CH_2-(CH_2)_2-CH_3$]; 2.0 (s, 3H, CH_3); 2.05 (s, 3H, CH_3); 2.9 (t, 2H, $S-CH_2$, J = 6.5 Hz); 6.9–7.4 (m, 4H$_{arom}$)
4o	84	130/0.1	$C_{13}H_{19}NOS$ (237.4)	0.9 [t, 3H, $-(CH_2)_3-CH_3$, J = 6.5 Hz]; 1.1–1.7 [m, 4H, $CH_2-(CH_2)_2-CH_3$]; 1.95 (s, 3H, CH_3); 2.05 (s, 3H, CH_3); 2.8 (t, 2H, $S-CH_2$, J = 6.5 Hz); 7–7.5 (m, 4H$_{arom}$)

[a] Satisfactory microanalyses obtained: C ±0.4, H ±0.31, N ±0.21 (Exceptions: **2c**, C −0.5, N −0.54; **2g**, C −0.64; **2l**, C +0.52).
[b] Mixture of *syn*/*anti* isomers (80:20) as inferred from ^{1}H-NMR spectrum.
[c] Unstable compound, purified by chromatography.

Table 3. Benzofurans **5** Prepared

Product No. (Ratio)	Yield[a] (%)	b.p. (°C)/torr	Molecular Formula[b] or Lit. b.p. (°C)/torr	^{1}H-NMR ($CDCl_3$/TMS)[c] δ (ppm)
5a + **b** (1 : 3)	60 (50–59)[6,7]	125/25	103/17[5] 100–102/15[7]	**5a**: 2.3 (s, 3H, CH_3-2); 2.55 (s, 3H, CH_3-3); 7.4–7.95 (m, 4H$_{arom}$) **5b**: 1.4 (t, 3H, $-CH_2-CH_3$, J = 7.5 Hz); 3.05 (q, 2H, $-CH_2-CH_3$, J = 7.5 Hz); 6.62 (s, 1H, H-3); 7.4–7.95 (m, 4H$_{arom}$)
5c	81 (56)[6]	105/16	76/8[9]	2.5 (s, 3H, CH_3); 6.3 (s, 1H); 7.1–7.6 (m, 4H$_{arom}$)
5d	87 (57)[8]	50/0.3	60/0.8[8]	2.55 (s, 3H, CH_3); 2.58 (s, 3H, CH_3); 6.3 (s, 1H, H-3); 6.8–7.3 (m, 3H$_{arom}$)
5e + **f** (1.7 : 1)	43 (60)[9]	41/1	83/10[8] 74/9[8]	**5e**: 2.4 (s, 6H, 2-CH_3); 6.3 (s, 1H, H-3); 6.9–7.4 (m, 3H$_{arom}$) **5f**: 2.4 (s, 6H, 2-CH_3); 6.4 (s, 1H, H-3); 6.9–7.4 (m, 3H$_{arom}$)
5g	42 (59)[8]	75/5	59/1[9]	2.4 (s, 6H, 2-CH_3); 6.3 (s, 1H, H-3); 6.9–7.3 (m, 3H$_{arom}$)
5h	41	150/20	$C_{13}H_{14}O$ (186.2)	1.8–1.9 (m, 4H, cyclohexane); 2.4 (s, 3H, CH_3); 2.5–2.7 (m, 4H, cyclohexane); 7.0 (dd, 1H, H-5, J_o = 7.5 Hz, J_m = 0.8 Hz); 7.2 (d, 1H, H-7, J_m = 0.8 Hz); 7.27 (d, 1H, H-4, J_o = 7.5 Hz)
5i	65	160/17	$C_{13}H_{14}O$ (186.2)	1.8–2.1 (m, 4H, cyclohexane); 2.4 (s, 3H, CH_3); 2.5–2.8 (m, 4H, cyclohexane); 6.9–7.4 (m, 3H$_{arom}$)
5j	–	140/15	122/12[a]	2.43 (d, 3H, CH_3, J = 1.19 Hz); 3.83 (s, 3H, OCH_3); 6.3 (m, 1H, H-3); 6.8 (dd, 1H, H-5, J_o = 8.4 Hz, J_m = 2.4 Hz); 6.9 (d, 1H, H-7, J_m = 2.4 Hz); 7.3 (d, 1H, H-4, J_o = 8.4 Hz)
5j + **k** (1.5 : 1)	70 (70)[9]	138/14	120/12[a]	**5k**: 2.45 (d, 3H, CH_3, J = 1.19 Hz); 3.93 (s, 3H, OCH_3); 6.49 (m, 1H, H-3); 6.64 (dd, 1H, H-5, J_o = 7.35 Hz, J_m = 1.3 Hz); 7.17 (m, 2H, AB part of AB system)
5l	83 (52)[8]	101/0.7	55/0.4[8]	2.5 (s, 3H, CH_3); 6.4 (s, 1H, H-3); 7.0–7.5 (m, 3H$_{arom}$)
5m + **n** (1.63 : 1)	74	75–80/0.25	C_9H_7ClO (166.6)	**5m**: 2.4 (s, 3H, CH_3); 6.25 (s, 1H, H-3); 6.9–7.4 (m, 3H$_{arom}$) **5n**: 2.4 (s, 3H, CH_3); 6.4 (s, 1H, H-3); 6.9–7.4 (m, 3H$_{arom}$)
5o	90	72–74/0.1	C_9H_7ClO (166.6)	2.4 (s, 3H, CH_3); 6.2 (s, 1H, H-3); 7.0–7.4 (m, 3H$_{arom}$)
5p + **q** (1.43 : 1)	84	135–140/0.3	$C_{12}H_{11}ClO$ (206.7)	**5p**: 1.8–2.0 (m, 4H, cyclohexane); 2.45–2.95 (m, 4H, cyclohexane); 7.165 (dd, 1H, H-5, J_o = 8.4 Hz, J_m = 1.8 Hz); 7.29 (d, 1H, H-4, J_o = 8.4 Hz); 7.4 (d, 1H, H-7, J_m = 1.8 Hz) **5q**: 1.8–2.0 (m, 4H, cyclohexane); 2.45–2.95 (m, 4H, cyclohexane); 7.05–7.14 (m, 2H, H-6 and H-5, AB part of ABX system); 7.28 (m, 1H, X part of ABX system)
5r	78	m.p. 68–69	$C_{12}H_{11}ClO$ (206.7)	1.73–1.95 (m, 4H, cyclohexane); 2.5–2.9 (m, 4H, cyclohexane); 7.0–7.4 (m, 3H$_{arom}$)
5s + **t** (1.43 : 1)	95	125–128/0.1	$C_{13}H_{16}OS$ (220.3)	**5s**: 0.9 [t, 3H, $-S-(CH_2)_3-CH_3$, J = 6.5 Hz]; 1.2–1.9 [m, 4H, $-S-CH_2-(CH_2)_2-CH_3$]; 2.4 (s, 3H, CH_3); 2.9 [t, 2H, $-S-CH_2-(CH_2)_2-$, J = 6.5 Hz]; 6.3 (s, 1H, H-3); 7.0–7.5 (m, 3H$_{arom}$) **5t**: 0.9 [t, 3H, $-S-(CH_2)_3-CH_3$, J = 6.5 Hz]; 1.2–1.9 [m, 4H, $-S-CH_2-(CH_2)_2-CH_3$]; 2.4 (s, 3H, CH_3-2); 2.96 [t, 2H, $-S-CH_2-(CH_2)_2-$, J = 6.5 Hz]; 6.5 (s, 1H, H-3); 7.0–7.5 (m, 3H$_{arom}$)
5u	51	202–205/0.1	$C_{13}H_{16}OS$ (220.3)	0.9 [t, 3H, $-S-(CH_2)_3-CH_3$, J = 6.5 Hz]; 1.2–1.8 [m, 4H, $-S-CH_2-(CH_2)_2-CH_3$]; 2.4 (s, 3H, CH_3); 2.8 [t, 2H, $-S-CH_2-(CH_2)_2-$, J = 6.5 Hz]; 6.31 (s, 1H, H-3); 7.0–7.5 (m, 3H$_{arom}$)

[a] Yield given in parenthesis refer to literature data.
[b] Satisfactory microanalyses obtained: C ±0.3, H ±0.06 (Exceptions: **5h**, C −0.84; **5m** + **n**, C −0.96).
[c] ^{1}H-NMR spectra were recorded on Varian XL-200 and Varian XL-300 spectrometers.

Decomplexation of 3a–o to *O*-aryloximes 4a–o; General Procedure:
An ethereal solution (60 ml) of **3** (1 mmol) is treated at 0 °C with iodine (254 mg, 1 mmol). After stirring for 5 h, the excess of iodine is destroyed with a saturated solution of sodium sulfite, the ether dried with sodium sulfate and evaporated. The crude products **4a–o** are purified by distillation (Table 2) or, in the case of **4b, c, f, i, k, m,** by column-chromatography on silica gel using petroleum-ether (40–60 °C)/ether (2:1) as eluent.

Benzofurans 5a–u; General Procedure:
To an ice cooled solution of **4** (2.8 mmol) in ethanol (25 ml) is added dropwise 98% sulfuric acid (0.44 ml, 8.8 mmol). The mixture is allowed to warm at room temperature and then refluxed until completion of the reaction (2–3 h). The ethanol solution is diluted with water (60 ml) and extracted with ether (4 × 20 ml). The organic layer is dried with sodium sulfate and evaporated. Crude **5** is purified by distillation (Table 3).

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