2,4,5-Triarylthiobenzophenones by Ring Transformation of 2,4,6-Triarylthiopyrylium Salts with Arylacetaldehydes[1]

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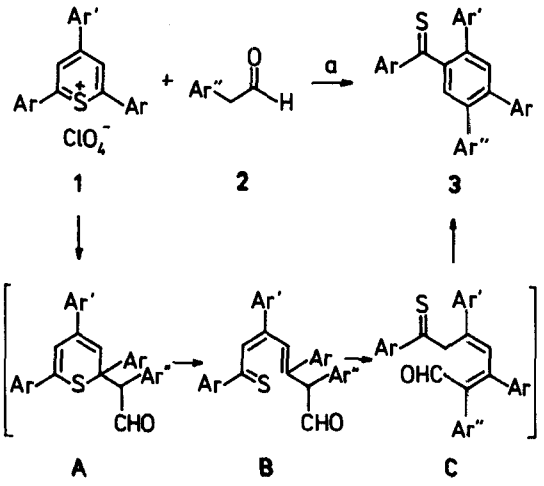
2,4,6-Triarylthiopyrylium salts **1** and arylacetaldehydes **2** react in the presence of sodium methoxide in methanol by a 2,5-[$C_4 + C_2$] ring transformation to give 2,4,5-triarylthiobenzophenones **3**. This ring transformation offers a new and efficient access to aryl substituted thiobenzophenones.

Although ring transformation reactions of thiopyrylium salts have been known for a long time,[2] until now only one example is reported where the sulfur atom of the thiopyrylium cation becomes part of a thiocarbonyl group. When the 2,4,6-triarylthiopyrylium salts **1** are treated with acetic anhydride and anhydrous sodium acetate 2-acetoxy-4,6-diarylthiobenzophenones are formed in moderate yield[3] besides 1,3,5-triarylbenzenes. Our continuing interest in the area of thiopyrylium chemistry and the first successful transformation of 2,4,6-triarylpyrylium salts with aldehydes as carbon nucleophiles[1] prompted us to investigate whether 2,4,6-triarylthiopyrylium salts **1** and aldehydes could also give ring transformation products.

By varying the aldehydes and the reaction conditions it was found that the thiopyrylium salts **1a–h** react smoothly with the arylacetaldehydes **2a,b** in the presence of sodium methoxide in refluxing methanol to give the 2,4,5-triarylthiobenzophenones **3a–p** in high yield (74–91 %). The thiobenzophenones **3** form deep blue to blue-green crystals and are more stable to light and air than the parent compound, thiobenzophenone[4] itself. These reactions also work with sodium ethoxide or piperidine acetate in ethanol, whereas triethylamine/acetic acid, triethylamine or sodium acetate give lower or no yield of thiobenzophenone **3**.

The reaction mechanism can be explained by assuming that the enolate, formed from the aldehyde **2** in the presence of base, adds preferentially to the 2-position[2] of the thiopyrylium salt **1** to give a 2*H*-thiopyran intermediate of type **A**. Electrocyclic ring opening,[5] proton shift, and condensation of the aldehyde group with the methylene moiety via **B** and **C** gives the thiobenzophenones **3**. In the course of this ring transformation a benzene ring is built up from four carbon atoms of the thiopyrylium cation and two carbon atoms of the aldehyde by connecting the former 2- and 4-positions of the heterocycle with a C_2-chain. Applying the nomenclature used for the classification of pyrylium ring transformations[6] the reaction can be characterized as a 2,5-[$C_4 + C_2$] transformation. This ring transformation clearly shows that it is possible, in contrast to the prevailing opinion,[2] to synthesize thiocarbonyl compounds from thiopyrylium salts in high yield.

The structure of the thiobenzophenones **3** was confirmed by the spectroscopic data (see Table) and by an independent synthesis of the triphenyl derivative **3a**. When the benzophenone **5**, prepared from 2,4,6-triphenylpyrylium perchlorate (**4**) and phenylacetaldehyde (**2a**) by ring transformation,[1] was treated with Lawesson's reagent (LR),[7] the compound obtained was identical in all respects to the thiobenzophenone **3a**. Since the thiopyrylium salt **1a** can be synthesized in high yield from the pyrylium salt **4**[2,8] it is evident that it is more convenient to prepare the thiobenzophenones **3** by heteroatom ex-



a: MeONa/MeOH, reflux, 1h, 74-91%

3	Ar	Ar'	Ar''
a	Ph	Ph	Ph
b	Ph	4-Me-C_6H_4	Ph
c	Ph	4-MeO-C_6H_4	Ph
d	Ph	4-Cl-C_6H_4	Ph
e	Ph	4-Br-C_6H_4	Ph
f	4-Me-C_6H_4	Ph	Ph
g	4-Cl-C_6H_4	Ph	Ph
h	4-Br-C_6H_4	Ph	Ph
i	Ph	Ph	4-F-C_6H_4
j	Ph	4-Me-C_6H_4	4-F-C_6H_4
k	Ph	4-MeO-C_6H_4	4-F-C_6H_4
l	Ph	4-Cl-C_6H_4	4-F-C_6H_4
m	Ph	4-Br-C_6H_4	4-F-C_6H_4
n	4-Me-C_6H_4	Ph	4-F-C_6H_4
o	4-Cl-C_6H_4	Ph	4-F-C_6H_4
p	4-Br-C_6H_4	Ph	4-F-C_6H_4

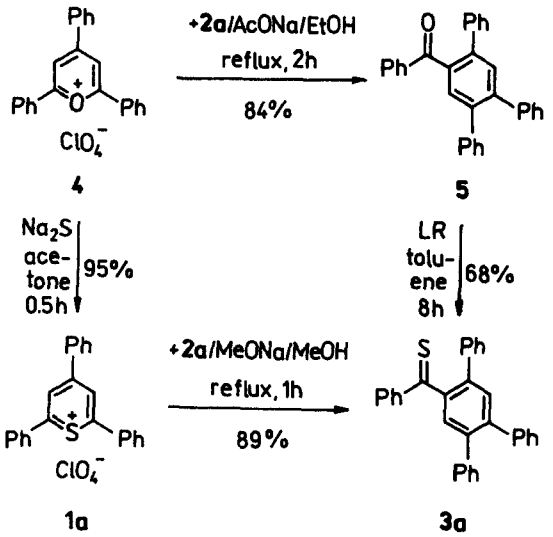
Scheme 1

Table. 2,4,5-Triarylthiobenzophenones 3

Product	Yield (%)	mp (°C)	VIS (MeCN) λ_{max} (nm) lg ε	^{1}H NMR ($CDCl_3$)[a] δ (ppm)
3a[b,c]	89	208–210	597 (2.320)	7.04–7.66 (m, 20 H, Ar-H), 7.39 (s, 1 H, 3-H), 7.56 (s, 1 H, 6-H)
3b	87	208–210	595 (2.315)	2.16 (s, 3 H, CH_3), 6.86–7.69 (m, 19 H, Ar-H), 7.38 (s, 1 H, 3-H), 7.51 (s, 1 H, 6-H)
3c	84	181–182	597 (2.346)	3.62 (s, 3 H, OCH_3), 6.58–7.66 (m, 19 H, Ar-H), 7.36 (s, 1 H, 3-H), 7.52 (s, 1 H, 6-H)
3d	84	215–216	597 (2.310)	7.03–7.63 (m, 19 H, Ar-H), 7.34 (s, 1 H, 3-H), 7.54 (s, 1 H, 6-H)
3e	80	223–224	597 (2.303)	7.05–7.66 (m, 19 H, Ar-H), 7.34 (s, 1 H, 3-H), 7.53 (s, 1 H, 6-H)
3f	85	216–218	595 (2.325)	2.19 (s, 3 H, CH_3), 2.25 (s, 3 H, CH_3), 6.91–7.62 (m, 18 H, Ar-H), 7.38 (s, 1 H, 3-H), 7.47 (s, 1 H, 6-H)
3g	77	232–234	598 (2.344)	7.04–7.56 (m, 18 H, Ar-H), 7.34 (s, 1 H, 3-H), 7.54 (s, 1 H, 6-H)
3h	89	251–253	597 (2.470)	7.00–7.53 (m, 18 H, Ar-H), 7.33 (s, 1 H, 3-H), 7.53 (s, 1 H, 6-H)
3i	81	214–216	597 (2.326)	6.80–7.64 (m, 19 H, Ar-H), 7.37 (s, 1 H, 3-H), 7.52 (s, 1 H, 6-H)
3j	91	202–204	597 (2.317)	2.15 (s, 3 H, CH_3), 6.81–7.67 (m, 18 H, Ar-H), 7.37 (s, 1 H, 3-H), 7.48 (s, 1 H, 6-H)
3k	89	225–226	594 (2.338)	3.63 (s, 3 H, OCH_3), 6.58–7.66 (m, 18 H, Ar-H), 7.35 (s, 1 H, 3-H), 7.49 (s, 1 H, 6-H)
3l	82	218–219	597 (2.323)	6.81–7.64 (m, 18 H, Ar-H), 7.32 (s, 1 H, 3-H), 7.50 (s, 1 H, 6-H)
3m	74	227–228	597 (2.317)	6.81–7.65 (m, 18 H, Ar-H), 7.32 (s, 1 H, 3-H), 7.50 (s, 1 H, 6-H)
3n	79	213–214	594 (2.311)	2.19 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 6.81–7.61 (m, 17 H, Ar-H), 7.37 (s, 1 H, 3-H), 7.44 (s, 1 H, 6-H)
3o	83	193–195	600 (2.344)	6.85–7.55 (m, 17 H, Ar-H), 7.33 (s, 1 H, 3-H), 7.51 (s, 1 H, 6-H)
3p	90	211–212	600 (2.373)	6.85–7.46 (m, 17 H, Ar-H), 7.34 (s, 1 H, 3-H), 7.50 (s, 1 H, 6-H)

[a] 3-H and 6-H denote the protons in 3- and 5-positions, respectively.
[b] ^{13}C NMR ($CDCl_3$, TMS): δ = 126.8, 126.9, 127.8, 127.9, 128.9, 129.1, 129.7, 129.8, 132.3, 132.4, 138.5, 139.0, 140.1, 140.4, 141.9, 146.1, 147.6, C=S 240.7.
[c] Mass spectrum (70 eV) *m/z* (%): 425 (M^+, 100).

change of pyrylium salts to thiopyrylium salts and subsequent transformation with arylacetaldehydes, than by the alternative approach via transformation of pyrylium salts and thionation.



Scheme 2

Melting points were measured on a Böetius apparatus. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 250 spectrometer (250 MHz for protons, 62.9 MHz for ^{13}C nuclei, $CDCl_3$, 25 °C, unless stated otherwise, hexamethyldisiloxane as internal standard) and VIS spectra were obtained on a Zeiss M 40 instrument (acetonitrile, 25 °C). Mass spectra were determined on a Finnigan MAT 111A spectrometer (70 eV, electron impact). The thiopyrylium salts **1a,c**,[8] **1b,f**[9] and **1d,e,g,h**[10] were prepared according to literature procedures. Phenylacetaldehyde **(2a)** (50% solution in diethyl phthalate) and Lawesson's reagent were provided by Fluka; 4-fluorophenylacetaldehyde **(2b)** was a gift from BASF AG, Ludwigshafen, Germany. Satisfactory microanalyses (C ± 0.35, H ± 0.15, S ± 0.30) were obtained for all the thiobenzophenones **3**.

Preparation of 2,4,5-Triarylthiobenzophenones 3 (cf. Table); General Procedure:

To a NaOMe solution, prepared by dissolving Na metal (0.12 g, 5 mmol) in abs. MeOH (20 mL), was added thiopyrylium perchlorate **1** (25 mmol) and arylacetaldehyde **2** (1.20 g of 50% diethyl phthalate solution of **2a**, 0.69 g **2b**, 5 mmol). The mixture was then heated under reflux for 1 h. During this time a crystalline precipitate of the thiobenzophenones **3** was formed. The mixture was cooled and the solid filtered off by suction, washed with H_2O and MeOH and recrystallized from EtOH/$CHCl_3$. If the reaction of the thiopyrylium salt **1a** with phenylacetaldehyde **(2a)** was performed in the presence of bases and solvents other than NaOMe/MeOH the following yields of the thiobenzophenone **3a** were obtained: NaOEt/EtOH, 64%; piperidine acetate/EtOH, 84%; Et_3N/AcOH (1 : 1 molar ratio)/EtOH, 25%; Et_3N/EtOH or NaOAc/EtOH, traces.

Independent Synthesis of the 2,4,5-Triphenylthiobenzophenone (3a)

According to a slight variation of Lawesson's original procedure[7] for the thionation of ketones, 2,4,5-triphenylbenzophenone[1] (2.06 g, 5 mmol) and Lawesson's reagent (1.61 g, 4 mmol) were heated under reflux in dry toluene (20 mL) for 8 h. After addition of MeOH (30 mL) the reaction mixture was cooled. The deep blue crystals formed were filtered off by suction and washed with MeOH; yield **3a**, 1.45 g, mp 208–210 °C (EtOH/$CHCl_3$); identical with the compound obtained from **1a** and **2a** by ring transformation.

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(1) Ring Transformations of Heterocyclic Compounds, VIII. For Part VII, see:
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