Synthesis of α-Oxo Sulfines from Enol Silyl Ethers and Thionyl Chloride

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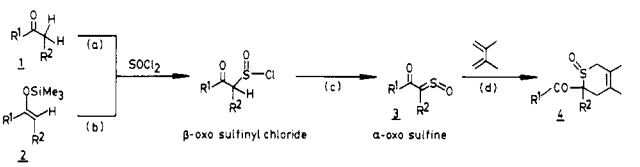
The reaction of some α-methylene ketones **1** with thionyl chloride leads to α-oxo sulfines **3** provided the ketone is sufficiently enolized. The reaction of trimethylsilyl enol ethers **2** is a more efficient and versatile method for the synthesis of α-oxo sulfines **3**. The isolation of **3** is only possible if they crystallize from the reaction mixture. If this is not the case sulfines **3** are entrapped by cycloaddition reaction with 2,3-dimethyl-1,3-butadiene. Sulfines **3** can also serve as the diene component in Diels–Alder reactions with electron rich alkenes, e.g., ethyl vinyl ether.

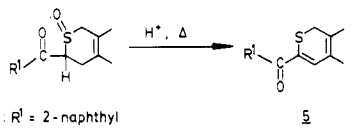
For the preparation of sulfines (thione *S*-oxides) several synthetic pathways are now available.[1] The most important routes to these sulfur-centered heterocumulenes are oxidation of thiocarbonyl containing compounds[2-4] and alkylidenation of sulfur dioxide with α-silyl carbanions.[5-7] The dehydrohalogenation of sulfinyl chlorides is also an attractive method were it not that its scope is virtually limited to a few diaryl sulfines[8,9] and some mono-[10] and dialkyl sulfines.[11] Suitable sulfinyl halides for functionalized sulfines are difficult to obtain if at all. The possibility of preparing such sulfinyl chlorides from active methylene compounds is frequently considered in the literature[12] but was met with limited success.

As is apparent from the recent review by Oka[12] the course of the reaction of thionyl chloride with various methylene compounds is strongly dependent on the nature of the starting material, the reaction conditions, and the ratio of reagent and substrate used. In a few isolated examples sulfines were reported as products from these reactions.[13-15] Recently we found that reaction of thionyl chloride with some dihydrothiophene derivatives, e.g., 3-oxo-2,3-dihydrobenzo[*b*]thiophene, leads to α-oxo sulfines which either could be isolated or be trapped by a cycloaddition reaction with 2,3-dimethyl-1,3-butadiene.[16] The first step in this formation of sulfines from active α-methylene ketones probably is C-sulfinylation at the α-carbon atom to give β-oxo sulfinyl chlorides. These notoriously unstable compounds then undergo a spontaneous dehydrohalogenation to **3** (reaction a and c in Scheme I). For some well enolized ketones no base is needed in this sequence, however if this is not the case, the presence of a base, e.g., triethylamine, is required to cause the reaction. Treatment of **1c** with thionyl chloride in the absence of base led to no reaction. By using triethylamine as the base α-oxo sulfine **3c** could be isolated as its cycloadduct **4c**. The isolation of the sulfine **3c** itself is not possible, because on contact with water hydrolysis[1] to starting ketone takes place. The scope of the synthesis of α-oxo sulfines from α-methylene ketones is very limited, however. For instance, acetophenone and 1-indanone fail to produce the corresponding sulfines upon treatment with thionyl chloride and triethylamine. Deviating reactions of similar ketones, e.g., the formation of β-chloro sulfenyl chlorides, have been reported in the literature.[12]

Scheme I



Scheme II



As is apparent from the above discussion the presence of the enol form of the methylene ketone is of utmost importance. We, therefore, decided to consolidate the enol structure through the enol silyl ether. Gratifyingly, a variety of enol silyl ethers smoothly react with thionyl chloride to produce α-oxo sulfines which can be trapped as their Diels–Alder adducts[17] (Scheme I, reaction b, c, and d). The results are compiled in the Table I. The first step in this sequence is the formation of β-oxo sulfinyl chlorides from **2** with elimination of trimethylsilyl chloride. Subsequent dehydrochlorination, as before, then gives sulfines **3**. In some cases, e.g., 1-[(trimethylsilyl)oxy]-1-indene, the sulfine itself crystallizes out within a few minutes.[17a] The presence of a base is not required in this case. Probably, here the enol silyl ether serves partly as an HCl scavenger. In the other cases, however, the addition of base is absolutely essential. 2,6-Lutidine was the base of choice (tri-

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(17) (a) For a preliminary publication see: Lenz, B. G.; Regeling, H.; Zwanenburg, B. *Tetrahedron Lett.*, in press. (b) In a private communication Professor I. W. J. Still, University of Toronto, Canada, informed us that the reaction of the trimethylsilyl enol ether of 4-thiochromanone 1,1-dioxide with thionyl chloride gives the corresponding α-oxo sulfine which was trapped by cycloaddition reactions.

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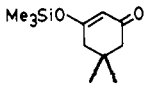
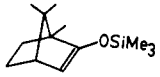
Table I. Synthesis of Compounds 4 according to Scheme I

starting materials					products[a]		
no.	R^1	R^2	reactn temp, °C	reactn time, h	no.	yield, %	mp, °C
1a	EtO	EtOOC	0	3	4a	23	oil
2a	EtO	EtOOC	20	24	4a	33	
2a			−20	1	4a	53	
2b	MeO	C_6H_5	20	24	4b	59[b]	116
1c	C_6H_5	C_6H_5S	20	12	4c	24[b]	118-120
2d	C_6H_5	$C_6H_5SO_2$	−20	24	4d	48	125
2e	C_6H_5	C_6H_5	20	40	4e	35	139-142
2e			20	20	4e	28[c]	
2f	C_6H_5	H	−78	0.5	4f[d]	84	122-127 (E + Z)
2f			0	2	4f[d]	37	
2f			20	12	4f[d]	9[b]	
2g	4-MeC_6H_4	H	−78	1.5	4g[d]	77	90-92 (E); 152-161 (Z)
2h	4-$MeOC_6H_4$	H	−78	1	4h[d]	67	112-118 (E); 133-148 (Z)
2i	4-ClC_6H_4	H	−78	0.5	4i[d]	78	112-117 (E); 148-165 dec (Z)
2j	2-naphthyl	H	−78	0.5	4j[d]	41	138-148 (E)
2k	2-MeC_6H_4	H	−78	0.5	4k[d]	33	108-123 (E + Z)
						R^1, R^2	
2l			0	8	4l	 68	88-89
2m			20	12	4m	 34	oil
1n			0	1	4n	 55	197 dec
2o			20	24	4o	 26	152; $[\alpha]_D$ 8.7° (c 1.0, $CHCl_3$)

[a] 2,6-Lutidine was used as base unless stated wise. [b] Triethylamine was used as base. [c] 4-(Dimethylamino)pyridine was used as base. [d] Obtained as a mixture of diastereomers.

ethylamine is not efficient, e.g., the result obtained for **4f** is only a yield of 9%). The use of more than 1 equiv of base does not improve the yields of the trapping products **4**. Attempts to promote the reaction with Lewis acids,[18] such as $ZnCl_2$, led to a significantly decreased yield of **4**, probably due to sensitivity of sulfines **3** toward released HCl.

The differences in the synthesis of **3** by both methods (reaction a, c and b, c, respectively) can be best demonstrated for the case of bis(ethoxycarbonyl) sulfine (**3a**). The yield of (trapped) sulfine **3a** that is made via enol silyl ether **2a** is higher (53%) and the reaction proceeds more smoothly (−20 °C, 0.5 h) than that directly from diethyl malonate (**1a**) (23% yield, 0 °C, 3 h).

The reaction temperature has to be carefully controlled, as shown for benzoyl sulfine (**3f**). The yield of the cycloadduct is much higher when the reaction is performed at −78 °C. This demonstrates, too, that the dienophilicity of the benzoyl sulfines **3f–k** is large enough to give a cycloaddition reaction, even at low temperatures.

The dihydrothiapyran *S*-oxides **4f–k** were obtained as a mixture of diastereomers, most probably arising from (*E*)- and (*Z*)-benzoyl sulfines **3f–k**. The diastereomers **4g–j** could be separated by careful crystallization. No isomerization (*E*–*Z*) of a pure isomer was observed upon treatment with pyridine (20 °C, 2 h). The structure of *E* and *Z* isomers was tentatively assigned by means of ^1H NMR spectroscopy by regarding position and coupling constants of the protons at C_2 and C_3 of the $COCHCH_2$ group.[19]

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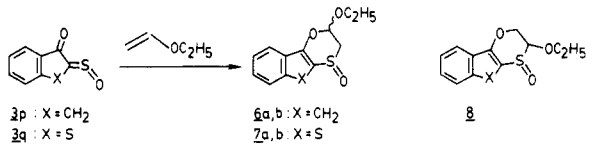
Scheme III



3p : X = CH_2
3q : X = S

6a,b : X = CH_2
7a,b : X = S

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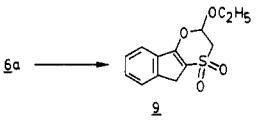
Scheme IV



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Upon heating, especially under acid catalysis, dihydrothiapyran S-oxides **4f–k** give a Pummerer rearrangement to thiapyrans. Heating of, e.g., **4j**, with *p*-toluenesulfonic

(19) The relative configuration of the substituents at the 1- and 2-position can be established by assuming that the inductive and deshielding effect of the sulfoxide function on the proton at the 2-position is larger in the *E* isomer than in the *Z* isomer and consequently this proton absorbs at lower field (4.72–4.93 ppm). The spacial arrangement of the protons at the 2- and 3-position can be deduced from the vicinal coupling constants. Inspection of molecular models reveals that two similar dihedral angles (approximately 60°) in the *E* isomer would lead to a triplet and a doublet for the $COCHCH_2$ group with J = 6.8–7.2 Hz. In the *Z* isomer a high (approximately 150°) and a small (60°) dihedral angle result in a double doublet for the methine proton at C_2 with J = 10.2–10.5 Hz and J = 4.2–4.8 Hz. The benzoyl group in this isomer deshields one proton of the vicinal methylene group giving rise to a geminal coupling. Since these protons are also coupled with the methine proton at C_2 this explains the rather indistinct signal of the methylene protons at C_3 in the *Z* isomer.

acid produced **5** in 82% yield (Scheme II). This rearrangement is most probably also responsible for the long melting ranges of the dihydrothiapyrans **4f–k** (see Table I).

An interesting aspect of this type of sulfines is that they can serve as diene component in cycloaddition reactions with electron-rich olefins like ethyl vinyl ether. Thus, the stable α-oxo sulfines **3p**[17a] and **3q**[16] react smoothly with ethyl vinyl ether to give the heterocycles **6** and **7**, respectively (Scheme III). The cycloadduct **7** was obtained as a mixture of diastereomers. Only one diastereomer (**6a**) was found in the reaction of **3p**; however, on standing in $CDCl_3$ (7 d, 5 °C), **6b** was also formed. No structural assignment (*E* or *Z*) could be made for the configuration of the diastereomers **6a,b** and **7a,b**, respectively. For an unambiguous proof of the regiochemistry of this cycloaddition **6a** was oxidized to the corresponding sulfone (Scheme IV). The ^1H NMR spectrum of the oxidation product shows the methine proton at 5.73 ppm which is almost the same position as in the starting sulfoxide (5.67 ppm). This observation can only be explained by assigning structure **6** to the cycloadduct. If the regioisomer **8** had been formed the oxidation would have affected the chemical shift of the methine proton to a considerable extent. Morever, the change of position of the methylene protons adjacent to the sulfoxide group upon oxidation (3.23 → 3.47 ppm) is in full accordance with the proposed structure **6**.

The reaction of silyl enol ethers with thionyl chloride is a general and facile manner for the preparation of a variety of α-oxo sulfines. For instance, the remarkable reactive α-oxo sulfines **3f–k** (which are in fact thioaldehyde S-oxides) can be easily synthesized from the silyl enol ethers of substituted acetophenones and can be trapped by a cycloaddition reaction at low temperatures. The isolation of the sulfines **3** is only possible if they crystallize from the reaction mixture.[16,17a] On attempts to isolate the sulfines in the other cases, hydrolysis[1] to the starting methylene compounds is observed.

Experimental Section

Melting points were determined on a Reichert hot stage microscope and are uncorrected. ^1H NMR spectra were recorded on a Varian EM-390 spectrometer with Me_4Si as internal standard. IR spectra were recorded on a Perkin-Elmer 298 infrared spectrophotometer. Elemental analyses were performed by J. Diersmann (Micro Analytical Department of our university). Mass spectra were obtained with a VG 7070 mass spectrometer. Dichloromethane was dried with P_4O_{10} and distilled from K_2CO_3. 3-Oxo-2,3-dihydrobenzo[*b*]thiophene 1,1-dioxide[20] and the trimethylsilyl enol ethers of diethyl malonate,[21] methyl phenylacetate,[21] acetophenone,[22] dimedone,[23] and *d*-camphor[24] were prepared as described in the literature. Thionyl chloride was distilled from triphenyl phosphite. The trimethylsilyl enol ethers of substituted acetophenones were all prepared following the procedure described for the unsubstituted case.[22] The spectral features are as expected (no., yield, bp. **2g**, 86%, 79–81 °C (2.0 mm); **2h**, 83%, 81–83 °C (1.0 mm); **2i**, 23%, 98–102 °C (3.6 mm); **2j**, decomposed upon heating, crude product was used; **2k**, 41%, 49–52 °C (0.6 mm)).

1-Phenyl-1-[(trimethylsilyl)oxy]-2-(phenylsulfonyl)ethene (2d). A solution of α-(phenylsulfonyl)acetophenone (2.6 g, 10 mmol) in dry THF (15 mL) was added at −78 °C to 10 mmol of lithium diisopropylamide in THF (40 mL) and was stirred for 30 min. Chlorotrimethylsilane (3 mL) was added at −78 °C. After stirring for 1 h at room temperature, the solvent was removed in vacuo. The residue was extracted with ether, and the combined extracts were filtered and concentrated to give **2d** as a colorless powder containing 25% of starting ketone: ^1H NMR ($CDCl_3$) δ 0.33 (s, 9 H, $SiMe_3$), 6.10 (s, 1 H, C=CH), 7.34–7.56, 7.90–8.07 (m, 10 H, aromatic).

General Procedure for Thiapyran 1-Oxides 4a,c,n. To a solution of ketone (5 mmol), base (10 mmol, see Table I), and 2,3-dimethyl-1,3-butadiene (4–5 mL) in dry CH_2Cl_2 (20 mL) was added thionyl chloride (5 mmol) and the reaction mixture was stirred at the temperature and for the period indicated in Table I. The reaction mixture was washed twice with water and dried ($MgSO_4$) and the solvent was removed in vacuo. The resulting crude product was purified by flash column chromatography (silica gel, 60 H, Merck, light petroleum–ethyl acetate) and recrystallized from light petroleum–toluene.

2,2-Bis(ethoxycarbonyl)-3,6-dihydro-4,5-dimethyl-2*H*-thiapyran 1-oxide (4a): chromatographed with light petroleum–ethyl acetate (2:3); MS (chemical ionization), *m/e* 289 (M^+ + 1, 100), 166 (6); IR (neat) 1720 (C=O) and 1050 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23, 1.30 (t, 6 H, OEt), 1.70, 1.78 (s, 6 H, $CH_3C{=}CCH_3$), 2.55–3.70 (m, 4 H, CH_2), 4.27 (q, 4H, OEt); calcd for $C_{13}H_{20}O_5S$ (M + 1) *m/e* 289.1110, found *m/e* 289.1110.

2-Benzoyl-2-(phenylthio)-3,6-dihydro-4,5-dimethyl-2*H*-thiapyran 1-oxide (4c): chromatographed with light petroleum–ethyl acetate (1:1); MS, *m/e* 356 (M^+), 338, 308, 247, 228, 215, 199; IR (KBr) 1650 (C=O) and 1050 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (s, 3 H, CH_3), 1.50 (s, 3 H, CH_3), 1.80–3.33 (m, 4 H, CH_2), 7.14–8.02 (m, 10 H, aromatic). Anal. Calcd for $C_{20}H_{20}O_2S_2$: C, 67.38; H, 5.65. Found: C, 67.09, 67.18; H, 5.66, 5.61.

2,3-Dihydro-3-oxobenzo[*b*]thiophene-2-spiro-2′-(3′,6′-dihydro-4′,5′-dimethyl-2′*H*-thiapyran) 1,1,1′-trioxide (4n): chromatographed with light petroleum–ethyl acetate (2:3); IR (KBr) 1710 (C=O), 1310, 1145 (SO_2) and 1065 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.81 (s, 6 H, CH_3), 2.94 (s, 2 H, $SOCH_2$), 3.74 and 4.47 (ABq, 2 H, *J* = 16.5 Hz, CH_2), 7.74–8.07 (m, 4 H, aromatic). Anal. Calcd for $C_{14}H_{14}O_4S_2$: C, 54.18; H, 4.55. Found: C, 54.15, 54.20; H, 4.50, 4.48.

General Procedure for Thiapyran 1-Oxides 4a,b,d–m,o. To a solution of trimethylsilyl enol ether (5 mmol), base (5 mmol, see Table I), and 2,3-dimethyl-1,3-butadiene (4–5 mL) in dry CH_2Cl_2 (20 mL) was added thionyl chloride (5 mmol) and the reaction mixture was stirred at the temperatures and for the period indicated in Table I. The reaction mixture was washed twice with water. The water layers were extracted once with CH_2Cl_2 (10 mL). The combined organic layers were washed with 5% $NaHCO_3$ (20 mL), dried ($MgSO_4$), and evaporated in vacuo. The crude product was purified by flash column chromatography (silica gel, 60 H, Merck, light petroleum–ethyl acetate) and was recrystallized from light petroleum–toluene.

2-(Methoxycarbonyl)-2-phenyl-3,6-dihydro-4,5-dimethyl-2*H*-thiapyran 1-oxide (4b): chromatographed with light petroleum–ethyl acetate (3:7); IR (KBr) 1720 (C=O) and 1040 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70, 1.77 (s, 6 H, $CH_3C{=}CCH_3$), 2.67–3.45 (m, 4 H, CH_2), 3.67 (s, 3 H, OCH_3), 7.36–7.47 (m, 5 H, aromatic). Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52. Found: C, 64.43, 64.53; H, 6.54, 6.50.

2-Benzoyl-2-(phenylsulfonyl)-3,6-dihydro-4,5-dimethyl-2*H*-thiapyran 1-oxide (4d): chromatographed with light petroleum–ethyl acetate (3:7); IR (KBr) 1645 (C=O), 1330 and 1150 (SO_2) and 1055 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20, 1.33 and 1.52 (s, 6 H, CH_3), 2.55–4.0 (m, 2 H, CH_2), 3.03 (br s, 2 H, CH_2), 7.3–8.1 (m, 10 H, aromatic). Anal. Calcd for $C_{20}H_{20}O_4S_2$: C, 61.83; H, 5.19. Found: C, 61.39, 61.74; H, 5.08, 4.96.

2-Benzoyl-2-phenyl-3,6-dihydro-4,5-dimethyl-2*H*-thiapyran 1-oxide (4e): chromatographed with light petroleum–ethyl acetate (3:7); IR (KBr) 1650 (C=O) and 1040 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 and 1.63 (s, 6 H, CH_3), 2.67 and 3.57 (ABq, 2 H, *J* = 18 Hz, CH_2), 3.00 and 3.57 (ABq, 2 H, *J* = 17.5 Hz, CH_2), 7.26–7.47 (m, 10 H, aromatic). Anal. Calcd for $C_{20}H_{20}O_2S$: C, 74.04; H, 6.21. Found: C, 74.13, 74.12; H, 6.27, 6.29.

2-Benzoyl-2,6-dihydro-4,5-dimethyl-2*H*-thiapyran 1-oxide (4f): chromatographed with light petroleum–ethyl acetate (1:4);

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(24) Simchen, G.; Kober, W. *Synthesis* **1976**, 259.

the *Z* isomer was obtained by fractional recrystallization (light petroleum–toluene); IR (KBr) 1670 (C=O) and 1025 (S=O) cm^{-1}; *E* isomer ^1H NMR ($CDCl_3$) δ 1.70 (s, 6 H, CH_3), 2.64 (d, 2 H, *J* = 6.90 Hz, $COCCH_2$), 3.47 (br s, 2 H, $SOCH_2$), 4.80 (t, 1 H, *J* = 6.90 Hz, CH), 7.40–7.60 (m, 3 H, aromatic), 7.85–8.03 (m, 2 H, aromatic); *Z* isomer ^1H NMR ($CDCl_3$) δ 1.72 (s, 6 H, CH_3), 2.17–3.17 (m, 2 H, $COCCH_2$), 3.40 (br s, 2 H, $SOCH_2$), 4.43 (dd, 1 H, *J* = 10.5 Hz and *J* = 4.20 Hz, CH), 7.44–7.60 (m, 3 H, aromatic), 7.86–7.97 (m, 2H, aromatic). Anal. Calcd for $C_{14}H_{16}O_2S$: C, 67.71; H, 6.49. Found: C, 67.80, 67.55; H, 6.45, 6.44.

2-(4-Methylbenzoyl)-3,6-dihydro-4,5-dimethyl-2*H*-thiapyran 1-oxide (4g): chromatographed with light petroleum–ethyl acetate (1:9); *E* and *Z* isomers separated by fractional recrystallization (light petroleum–toluene); IR (KBr) 1665 (C=O) and 1035 (S=O) cm^{-1}; *E* isomer ^1H NMR ($CDCl_3$) δ 1.72 (s, 6 H, $CH_3C{=}CCH_3$), 2.38 (s, 3 H, 4-CH_3), 2.64 (d, 2 H, *J* = 6.90 Hz, $COCCH_2$), 3.47 (br s, 2 H, $SOCH_2$), 4.74 (t, 1 H, *J* = 6.90 Hz, CH), 7.27 and 7.90 (ABq, 4 H, *J* = 8.10 Hz, aromatic). Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.66; H, 6.92. Found: C, 68.71, 68.85; H, 6.92, 6.98. *Z* isomer ^1H NMR ($CDCl_3$) δ 1.77 (s, 6 H, $CH_3C{=}CCH_3$), 2.40 (s, 3 H, 4-CH_3), 2.94–3.26 (m, 2 H, $COCCH_2$), 3.37 (br s, 2 H, $SOCH_2$), 4.40 (dd, 1 H, *J* = 10.5 Hz and *J* = 4.5 Hz, CH), 7.24 and 7.77 (ABq, 4 H, *J* = 8.10 Hz, aromatic). Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92. Found: C, 68.86, 68.71; H, 6.98, 6.98.

2-(4-Methoxybenzoyl)-3,6-dihydro-4,5-dimethyl-2*H*-thiapyran 1-oxide (4h): chromatographed with light petroleum–ethyl acetate (1:9); *E* and *Z* isomers separated by fractional recrystallization (light petroleum–toluene); IR (KBr) 1650 (C=O) and 1040 (S=O) cm^{-1}; *E* isomer ^1H NMR ($CDCl_3$) δ 1.75 (s, 6 H, $CH_3C{=}CCH_3$), 2.64 (d, 2 H, *J* = 6.90 Hz, $COCCH_2$), 2.60 (br s, 2 H, $SOCH_2$), 3.85 (s, 3 H, OCH_3), 4.72 (t, 1 H, *J* = 6.90 Hz, CH), 6.94 and 7.97 (ABq, 4 H, *J* = 8.70 Hz). Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52. Found: C, 64.93, 64.75; H, 6.60, 6.56. *Z* isomer ^1H NMR ($CDCl_3$) δ 1.75 (s, 6 H, $CH_3C{=}CCH_3$), 2.14–2.98 (m, 2 H, $COCCH_2$), 3.37 (br s, 2 H, $SOCH_2$), 3.85 (s, 3 H, OCH_3), 4.40 (dd, 1 H, *J* = 10.2 Hz and *J* = 4.80 Hz, CH), 6.92 and 7.90 (ABq, 4 H, *J* = 8.70 Hz, aromatic). Anal. Calcd for $C_{15}H_{18}O_3S$: C, 64.72; H, 6.52. Found: C, 64.93, 64.75; H, 6.60, 6.56.

2-(4-Chlorobenzoyl)-3,6-dihydro-4,5-dimethyl-2*H*-thiapyran 1-oxide (4i): chromatographed with light petroleum–ethyl acetate (3:7); *E* and *Z* isomers separated by fractional recrystallization (light petroleum-toluene); IR (KBr) 1670 (C=O) and 1040 (S=O) cm^{-1}; *E* isomer ^1H NMR ($CDCl_3$) δ 1.75 (s, 6 H, CH_3), 2.65 (d, 2 H, *J* = 7.20 Hz, $COCCH_2$), 3.50 (br s, 2 H, $SOCH_2$), 4.72 (t, 1 H, *J* = 7.20 Hz, CH), 7.45 and 7.96 (ABq, 4 H, *J* = 8.40 Hz, aromatic). Anal. Calcd for $C_{14}H_{15}ClO_2S$: C, 59.46; H, 5.35. Found: C, 59.40, 59.63; H, 5.39, 5.42. *Z* isomer ^1H NMR ($CDCl_3$) δ 1.77 (s, 6 H, CH_3), 2.17–3.40 (m, 4 H, CH_2), 4.44 (dd, 1 H, *J* = 10.2 Hz and *J* = 4.20 Hz, CH), 7.44 and 7.86 (ABq, 4 H, *J* = 8.40 Hz, aromatic). Anal. Calcd for $C_{14}H_{15}ClO_2S$: C, 59.46; H, 5.35. Found: C, 59.55, 59.32; H, 5.33, 5.29.

2-(2-Naphthoyl)-3,6-dihydro-4,5-dimethyl-2*H*-thiapyran 1-oxide (4j): chromatographed with light petroleum–ethyl acetate (1:4); *E* isomer obtained by fractional recrystallization (light petroleum–toluene); IR (KBr) 1655 (C=O) and 1040 (S=O) cm^{-1}; *E* isomer ^1H NMR ($CDCl_3$) δ 1.73 (s, 6 H, CH_3), 2.70 (d, 2 H, *J* = 6.90 Hz, $COCCH_2$), 3.50 (s, 2 H, $SOCH_2$), 4.93 (t, 1 H, *J* = 6.90 Hz, CH), 7.50–8.07 (m, 6 H, aromatic), 8.53 (s, 1 H, aromatic). Spectral features of the *Z* isomer: ^1H NMR ($CDCl_3$) δ 1.77 (s, 6 H, CH_3), 2.20–3.17 (m, 2 H, $COCCH_2$), 3.37 (s, 2 H, $SOCH_2$), 4.58 (dd, 1 H, *J* = 10.2 Hz and *J* = 4.2 Hz, CH), 7.50–8.07 (m, 6 H, aromatic), 8.40 (s, 1 H, aromatic). Anal. (E isomer) Calcd for $C_{18}H_{22}O_2S$: C, 72.45; H, 6.08. Found: C, 72.03, 72.22; H, 6.07, 6.08.

2-(2-Methylbenzoyl)-3,6-dihydro-4,5-dimethyl-2*H*-thiapyran 1-oxide (4k): chromatographed with light petroleum–ethyl acetate (1:4); IR (KBr) 1680 (C=O) and 1050 (S=O) cm^{-1}; spectral features of the *E* isomer ^1H NMR ($CDCl_3$) δ 1.67 (s, 3 H, $CH_3C{=}CCH_3$), 2.45 (s, 3 H, 2-CH_3), 2.5–3.67 (m, 4 H, CH_2), 4.65 (dd, 1 H, *J* = 7.2 Hz and *J* = 5.7 Hz, CH), 7.17–7.43 (m, 3 H, aromatic), 7.63–7.73 (m, 1 H, aromatic). Spectral features of the *Z* isomer: ^1H NMR ($CDCl_3$) δ 1.75 (s, 6 H, $CH_3C{=}CCH_3$), 2.45 (s, 3 H, 2-CH_3), 2.5–3.67 (m, 4 H, CH_2), 4.20 (dd, 1 H, *J* = 11.4 Hz and *J* = 4.5 Hz, CH), 7.17–7.43 (m, 3 H, aromatic), 7.63–7.73 (m, 1 H, aromatic). Anal. of (*E* + *Z*) mixture Calcd for $C_{15}H_{18}O_2S$: C, 68.67; H, 6.92. Found: C, 68.85, 68.58; H, 6.98, 6.97.

1,3-Dioxo-5,5-dimethylcyclohexane-2-spiro-2′-(3′,6′-dihydro-4′,5′-dimethyl-2′*H*-thiapyran) 1′-oxide (4l): chromatographed with light petroleum–ethyl acetate (3:2); IR (KBr) 1720, 1690 (C=O) and 1070 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85 (s, 3 H, 5-CH_3), 1.17 (s, 3 H, 5-CH_3), 1.70 (s, 6 H, 4′- and 5′-CH_3), 2.34–3.52 (m, 8 H, CH_2). Anal. Calcd for $C_{14}H_{20}O_3S$: C, 62.66; H, 7.51. Found: C, 62.63, 62.75; H, 7.47, 7.57.

Cyclohexanone-2-spiro-2′-(3′,6′-dihydro-4′,5′-dimethyl-2′*H*-thiapyran) 1′-oxide (4m): chromatographed with ethyl acetate; IR (neat) 1700 (C=O) and 1050 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.70, 1.73 (s, 6 H, CH_3), 3.20 (s, 2 H, $SOCH_2$), 1.87–2.47 (m, 10 H, remaining protons); MS, *m/e* 226 (M^+, 6), 178 (38), 163 (100); calcd for $C_{12}H_{19}O_2S$ (M + 1) *m/e* 227.1106, found *m/e* 227.1100.

1,7,7-Trimethyl-2-oxobicyclo[2.2.1]heptane-3-spiro-2′-(3′,6′-dihydro-4′,5′-dimethyl-2′*H*-thiapyran) 1′-oxide (4o): chromatographed with light petroleum–ethyl acetate (3:7); IR (KBr) 1730 (C=O) and 1050 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.85, 0.97, 1.05 (s, 9 H, CH_3's of camphor), 2.50–3.60 (m, 4 H, $CH_2C{=}CCH_2$), 1.56–1.87 (m, 11 H, remaining protons); MS (chemical ionization), *m/e* 281 (M^+ + 1, 100), 233 (10), 217 (20), 165 (5); calcd for $C_{16}H_{25}O_2S$ (M + 1) *m/e* 281.1575, found *m/e* 281.1566.

2-(2-Naphthoyl)-4,5-dimethyl-6*H*-thiapyran (5). A solution of **4j** (0.12 g, 0.53 mmol) in xylene (10 mL) containing a few crystalls of *p*-toluenesulfonic acid monohydrate was heated under reflux for 30 min. The solvent was evaporated and the residue was purified by flash column chromatography on silica gel (type 60 H, Merck) with light petroleum–ethyl acetate (1:9) to give 90 mg (82%) of **5** as a yellow oil which crystallized on standing: mp 100–102 °C; IR (KBr) 1620 (C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.77, 1.95 (s, 6 H, CH_3), 3.26 (s, 2 H, CH_2), 6.77 (s, 1 H, C=CH), 7.43–7.9 (m, 6 H, aromatic), 8.17 (s, 1 H, aromatic); calcd for $C_{18}H_{16}OS$ (M^+) *m/e* 280.3916, found *m/e* 280.3910.

2,3-Dihydroindeno[1,2-*b*]-2-ethoxy-1,4-oxathiin 4-Oxide (6). A solution of sulfine **3p** (0.30 g, 1.7 mmol) in CH_2Cl_2 (5 mL) and ethyl vinyl ether (5 mL) was stirred at room temperature for 12 h. The solvent was concentrated in vacuo and the residue was chromatographed on silica gel (60 H). Byproducts were removed with ethyl acetate as eluent. Elution with ethyl acetate containing 2% ethanol delivered **6a** (0.25 g, 59%): mp 119–121 °C (light petroleum–toluene); IR (KBr) 1610 (C=C) and 1030 (SO) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.23 (t, 3 H, *J* = 7.2 Hz, CH_3), 3.03 and 3.43 (d of ABq, 2 H, *J* = 14.4 Hz and *J* = 3.0 Hz, CH_2SO), 3.50 and 3.97 (ABq, 2 H, *J* = 22.2 Hz, indene CH_2), 3.58 (q, 2 H, *J* = 7.2 Hz, OCH_2), 5.67 (t, 1 H, *J* = 3.0 Hz, CH), 7.23–7.5 (m, 4 H, aromatic). Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.37, 62.60; H, 5.57, 5.59. The other diastereomer **6b** was chromatographed on silica gel with ethanol–ethyl acetate (1:9): mp 94–96 °C (light petroleum–toluene); IR (KBr) 1610 (C=C) and 1040 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.33 (t, 3 H, *J* = 7.3 Hz, CH_3), 2.83 (d of ABq, 1 H, *J* = 13.5 Hz and *J* = 9.0 Hz, CH_2SO), 3.15 (d of ABq, 1 H, *J* = 13.5 Hz and *J* = 1.8 Hz, CH_2SO), 3.43 and 3.83 (ABq, 2 H, *J* = 21.0 Hz, indene CH_2), 3.77–4.07 (m, 2 H, OCH_2), 5.63 (dd, 1 H, *J* = 9.0 Hz and *J* = 1.8 Hz, CH), 7.2–7.4 (m, 4 H, aromatic); MS, *m/e* 250 (M^+, 13), 202 (37) and 72 (100). Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.52, 62.30; H, 5.63, 5.64.

2,3-Dihydrobenzo[*b*]thiopheno[2,3-*b*]-2-ethoxy-1,4-oxathiin 4-Oxide (7). A solution of sulfine **3g** (0.50 g, 2.5 mmol) in dichloromethane (10 mL) and ethyl vinyl ether (10 mL) was allowed to react for 12 h at room temperature. The solvent was removed and the residue was chromatographed on silica gel with light petroleum–ethyl acetate (3:7) to give first diastereomer **7a** (0.1 g, 15%): mp 83–85 °C (light petroleum–toluene); IR (CCl_4) 1590 (C=C) and 1045 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.37 (t, 3 H, *J* = 7.2 Hz, CH_3), 3.02 (d of ABq, 1 H, *J* = 14.4 Hz and *J* = 9.0 Hz, CH_2SO), 3.32 (d of ABq, 1 H, *J* = 14.4 Hz and *J* = 1.8 Hz, CH_2SO), 3.83 and 4.18 (q of ABq, 2 H, *J* = 9.6 Hz and *J* = 7.2 Hz, OCH_2), 5.77 (dd, 1 H, *J* = 9.0 Hz and *J* = 1.8 Hz, CH), 7.23–7.83 (m, 4 H, aromatic). Anal. Calcd for $C_{12}H_{12}O_3S_2$: C, 53.71; H, 4.51. Found: C, 53.98, 53.73; H, 4.66, 4.46. Further elution delivered the diastereomer **7b** (0.42 g, 65%): mp 122–128 °C (light petroleum–toluene); IR (KBr) 1590 (C=C) and 1040 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.20 (t, 3 H, = 6.9 Hz, CH_3), 3.15

(d of ABq, 1 H, J = 14.4 Hz and J = 2.1 Hz, CH_2SO), 3.62 (d of ABq, 1 H, J = 14.4 Hz and J = 3.0 Hz, CH_2SO), 3.61–4.0 (m, OCH_2), 5.77 (unsymmetrical t, 1 H, J = 3.0 Hz and J = 2.1 Hz, CH), 7.3–7.9 (m, 4 H, aromatic). Anal. Calcd for $C_{12}H_{12}O_3S_2$: C, 53.71; H, 4.51. Found: C, 53.71, 53.77; H, 4.50, 4.48.

2,3-Dihydroindeno[1,2-*b*]-2-ethoxy-1,4-oxathiin 4,4-Dioxide (9). To a solution of **6a** (0.19 g, 0.76 mmol) in chloroform (10 mL) monoperphthalic acid (1.5 mmol) in chloroform (3 mL) was added. After stirring for 0.5 h at room temperature the reaction mixture was washed once with aqueous sodium carbonate, dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by flash column chromatography on silica gel with light petroleum–ethyl acetate (7:3) to give **9** (0.10 g, 50%) as colorless crystals: mp 127–129 °C (light petroleum–toluene); IR (KBr) 1615 (C=C), 1390 and 1295 (S=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.32 (t, 3 H, J = 7.2 Hz, CH_3), 3.47 (d, 2 H, J = 4.8 Hz, CH_2SO_2), 3.70 (s, 2 H, indene CH_2), 3.7–4.17 (m, 2 H, OCH_2), 5.73 (dd, 1 H, J = 6.0 Hz and J = 4.8 Hz), 7.3–8.5 (m, 4 H, aromatic). Anal. Calcd for $C_{13}H_{14}So_4S$: C, 58.63; H, 5.30. Found: C, 58.57, 58.60; H, 5.33, 5.30.

Registry No. **1a**, 105-53-3; **1c**, 16222-10-9; **1n**, 1127-35-1; **2a**, 17906-37-5; **2b**, 40195-27-5; **2d**, 96745-89-0; **2e**, 72223-17-7; **2f**, 13735-81-4; **2g**, 54731-27-0; **2h**, 55991-65-6; **2i**, 58518-76-6; **2j**, 52119-18-3; **2k**, 59790-53-3; **2l**, 10416-78-1; **2m**, 6651-36-1; **2o**, 56613-17-3; **3p**, 95683-64-0; **3q**, 96746-17-7; **4a**, 96745-90-3; **4b**, 96745-91-4; **4c**, 96745-92-5; **4d**, 96745-93-6; **4e**, 96745-94-7; *cis*-**4f**, 96745-95-8; *trans*-**4f**, 96745-96-9; *cis*-**4g**, 96745-97-0; *trans*-**4g**, 96745-98-1; *cis*-**4h**, 96745-99-2; *trans*-**4h**, 96746-00-8; *cis*-**4i**, 96746-01-9; *trans*-**4i**, 96746-02-0; *cis*-**4j**, 96746-03-1; *trans*-**4j**, 96746-04-2; *cis*-**4k**, 96746-05-3; *trans*-**4k**, 96746-06-4; **4l**, 96746-07-5; **4m**, 96746-08-6; **4n**, 96746-09-7; **4o**, 96746-10-0; **5**, 96746-11-1; *cis*-**6**, 96746-12-2; *trans*-**6**, 96746-13-3; *cis*-**7**, 96746-14-4; *trans*-**7**, 96746-15-5; **9**, 96746-16-6; α-(phenylsulfonyl)acetophenone, 3406-03-9; 2,3-dimethyl-1,3-butadiene, 513-81-5; thionyl chloride, 7719-09-7; ethyl vinyl ether, 109-92-2; 2,6-lutidine, 108-48-5.

Twin Benzoannulation of Naphthalene via 1,3-, 1,6-, and 2,6-Naphthodiyne Synthetic Equivalents. New Syntheses of Triphenylene, Benz[*a*]anthracene, and Naphthacene

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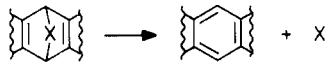
New syntheses of triphenylene (**4**), benz[*a*]anthracene (**5**), naphthacene (**6**), and the tetramethylated derivatives **17** and **25** are described that feature, as the key step, the formal Diels–Alder cycloaddition between a naphthodiyne synthon (**1**, **2**, or **3**) and a furan (**10** or **14**). Subsequent deoxygenation affords the arene in 16–28% overall yield from dibromo ditosylate **7**, **8**, or **9**. The latter are prepared in two steps from commercially available 2,3- or 2,7-dihydroxynaphthalene, and, with phenyllithium, serve as synthetic equivalents of **1**, **2**, and **3**. The X-ray structure of the anti isomer of **23** is discussed in some detail.

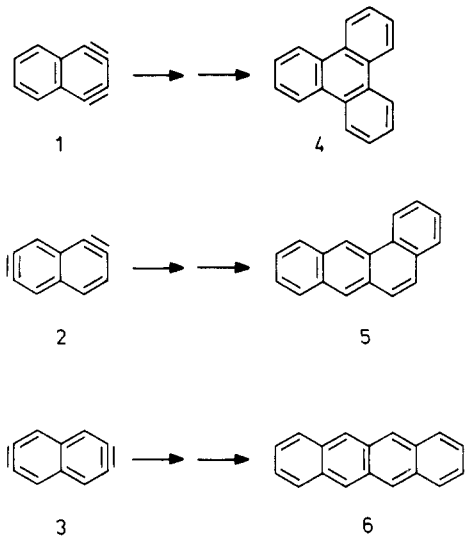
The extrusion of a bridging atom or atoms from suitable Diels–Alder adducts has been widely used to synthesize arenes, i.e., **A** → **B**.[1] In particular, the use of benzynes and other arynes in this methodology has proven to be a powerful tool for the synthesis of polycyclic aromatic hydrocarbons (PAH).[2]



A B

The pioneering work of Hart[3] and our own recent study[4] have illustrated the utility of bis(aryne) synthetic equivalents in the synthesis of PAH and related molecules. For example, in our previous paper we reported[4] a new chrysene synthesis using a synthetic equivalent of 1,5-naphthodiyne.

We now describe synthetic equivalencies of 1,3-naphthodiyne (**1**), 1,6-naphthodiyne (**2**), and 2,6-naphthodiyne (**3**), and illustrate their utility in new syntheses of triphenylene (**4**), benz[*a*]anthracene (**5**), and naphthacene (**6**), respectively.



1 4

2 5

3 6

Previous examples of these naphthodiyne synthons are the tetramethyl derivative of **3** [3a,b,d] and 1,4-dibromo-

† Author to whom inquiries regarding the X-ray crystallographic data should be directed.

(1) For reviews, see: (a) Wong, H. N. C.; Ng, T.; Wong, T. *Heterocycles* **1983**, *20*, 1815. (b) Wong, H. N. C.; Ng, T.; Wong T.; Xing, Y. D. *Heterocycles* **1984**, *22*, 875.

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