55. Spiro[1,3-benzoxathiepin-4(5*H*),1′-cyclohexa[2,4]diene]-2,2′-dione, a Novel Heterocyclic Ring System

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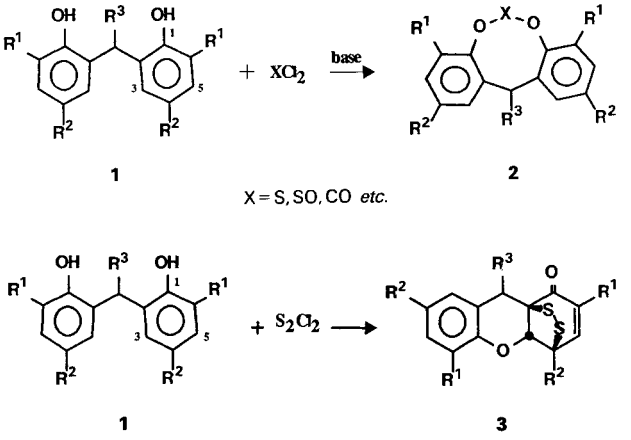
The 4,4′,6,6′-tetrasubstituted 2,2′-alkylidenebis(phenols) **1** reacted with ClSCOCl to give spiro[1,3-benzoxathiepin-4(5*H*),1′-cyclohexa[2,4]diene]-2,2′-diones **4**, together with cyclic carbonates **5**. The structures of the products were elucidated mainly by ^{13}C-NMR and ^{1}H-NMR spectroscopy.

Introduction. – The 2,2′-alkylidenebis(phenols) **1** react under cyclisation with divalent electrophiles such as $SOCl_2$, SCl_2, or $COCl_2$, through selective attack by the two O-atoms to give dibenzo[*d*,*g*][1,3,2]dioxathiocines [1] or cyclic carbonates [2], respectively, with an 8-membered ring structure (*Scheme 1*). However, with S_2Cl_2 **1** formed the novel tetracyclic product **3** [3] through a nucleophilic attack by the *ortho* and *para* C-atoms (C(2) and C(4)) of **1** [3].

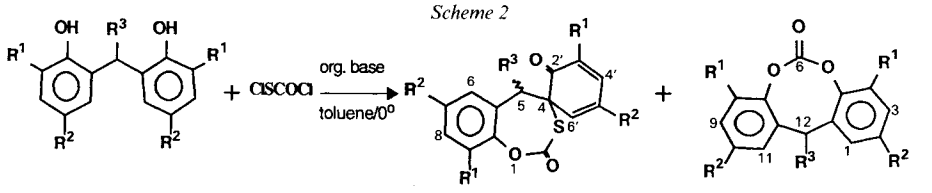
We now report a new type of cyclocondensation of the bis(phenols) **1** with divalent electrophiles such as chlorocarbonylsulfenyl chloride (ClSCOCl) affording spiro[1,3-benzoxathiepin-4(5*H*),1′-cyclohexa[2,4]diene]-2,2′-diones **4** together with cyclic carbonates **5** (see *Scheme 2*).

Scheme 1



Results. – At 0°, a toluene solution of ClSCOCl was added dropwise to a toluene solution of bis(phenol) **1** and pyridine (molar ratio 1:1:2), and the mixture was stirred at room temperature. Pure spirothiocarbonate **4** and carbonate **5** (*Scheme 2*) could be

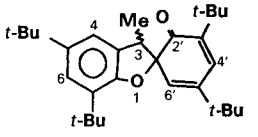
Scheme 2



1a $R^1 = R^2 = t$-Bu, R^3 = Me
b $R^1 = R^2 = t$-Bu, R^3 = Et
c $R^1 = t$-Bu, R^2 = Me, R^3 = H
d $R^1 = R^2 = t$-Bu, R^3 = H

4a $R^1 = R^2 = t$-Bu, R^3 = Me
b $R^1 = R^2 = t$-Bu, R^3 = Et
c $R^1 = t$-Bu, R^2 = Me, R^3 = H
d $R^1 = R^2 = t$-Bu, R^3 = H

5a $R^1 = R^2 = t$-Bu, R^3 = Me
b $R^1 = R^2 = t$-Bu, R^3 = Et
c $R^1 = t$-Bu, R^2 = Me, R^3 = H
d $R^1 = R^2 = t$-Bu, R^3 = H



6a

obtained by repeated chromatography on silica gel and recrystallisation from hexane (yields of **4** 7.3–21.2% and of **5** 4.5–11.8%). From the reaction of **1a**, a minor amount (3%) of the spirofurane **6a** was also isolated.

The structure elucidation of **4a–d** is based upon their ^{1}H-coupled ^{13}C-NMR spectra (δ(C) in *Table 1*; for reference compounds, see [4]) and on detailed ^{1}H-NOE experiments (δ(H) in *Table 2*) as well as on their mass and IR spectra given in the *Exper. Part.* The δ(C) and δ(H) are correlated by selective INEPT experiments [5]. The ^{1}H-NOE experiments in turn establish also the relative configuration at C(5) in **4a** or **4b**. *E.g.*, in **4b**, irradiation of CH_3CH_2–C(5) results in a strong NOE of H–C(6′), whereas practically no NOE is observed for this proton upon irradiation of H–C(5). The Et group at C(5) and H–C(6′) are, therefore, in a *cis*-relation to each other. The structures of **5a–d** follow from the symmetry of their ^{1}H-NMR spectra. A representative ^{13}C-NMR spectrum is given for **5d** (see *Exper. Part*). The structure of **6a** rests upon its lower mass (*m/z* 436) and its ^{13}C-NMR spectrum. It is a mixture of diastereoisomers, the major one having the Me group in *cis*-position to C(6′) (strong ^{1}H-NOE between Me and H–C(6′) in the major diastereoisomer and between H–C(6′) and H–C(3) in the minor one).

Discussion. – The novel oxathiepines **4** arise by attack of one of the phenolic O-atoms and one of the *ortho* C-atoms of the other phenolic moiety upon ClSCOCl. This is one of the rare examples where we find simultaneous C- and O-functionalisation of bis(phenol) nucleophiles. In *Scheme 3*, two possible modes of formation of **4** are represented. We believe that attack by the phenolic O-atom affording the chlorosulfenylcarboxylate **7** occurs preferentially; intermediate **7** can easily account for the by-products **5** and **6a**. The formation of the carbonates **5** most probably proceeds *via* S-extrusion from **7**. An analogous elimination of S is known to occur in the case of carbamoylsulfenyl chlorides – intermediates from the reaction of ClCOSCl and aliphatic amines – which yield the corresponding carbamoyl chlorides [6]; in a similar way, S is extruded from (dialkylthiocarbamoyl)sulfenyl chlorides [7]. Direct formation of the carbonates **5** from **4** under the reaction conditions could be excluded by a control experiment (see *Exper. Part*).

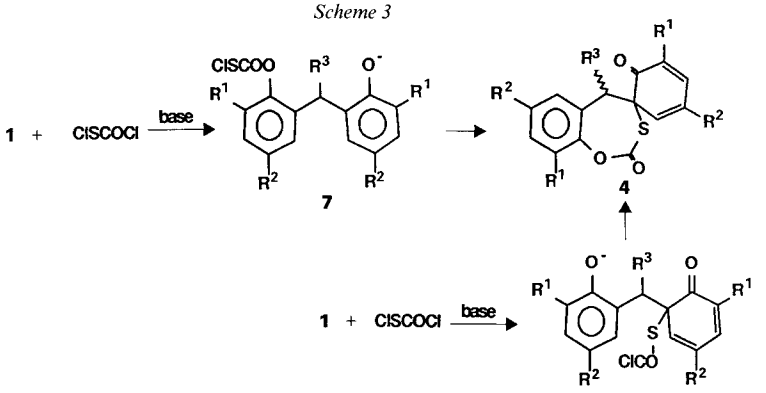
Table 1. *^{13}C-NMR Data* ($CDCl_3$) *of* **4a–d**

	4a	**4b**	**4c**	**4d**		**4a**	**4b**	**4c**	**4d**
C(2)	161.9	161.8	161.6	161.8	*Me*–C(5) or *Et*–C(5)	13.6	21.3, 12.4	–	–
C(4)	65.3	65.0	62.9	62.8	*Me*–C(7)	–	–	21.2	–
C(5)	37.4	44.0	35.0	36.2	$(CH_3)_3C$–C(7)	34.92	34.9	–	34.7
C(5a)	132.5	130.3	129.6	129.1	$(CH_3)_3C$–C(9)	34.82	34.8	34.4	34.8
C(6)	121.9	122.1	129.4	126.0					
C(7)	148.5	148.2	135.7	148.7	*Me*–C(5′)			21.7	
C(8)	123.2	122.9	127.5	123.6	$(CH_3)_3C$–C(3′)	34.85	34.9	34.6	34.9
C(9)	140.3	140.5	141.2	140.8	$(CH_3)_3C$–C(5′)	34.93	34.9	–	34.6
C(9a)	148.1	149.1	148.6	148.3	$(CH_3)_3$C–C(7)	31.6	31.5	–	31.5
C(2′)	195.7	195.1	194.4	195.3	$(CH_3)_3$C–C(9)	30.4	30.4	30.3	30.3
C(3′)	144.2	144.2	144.7	144.5	$(CH_3)_3$C–C(3′)	29.2	29.1	29.1	29.2
C(4′)	134.2	133.9	137.1	133.8	$(CH_3)_3$C–C(5′)	28.8	28.7		28.5
C(5′)	146.3	145.6	132.5	144.0					
C(6′)	122.5	122.3	127.2	124.4					

Table 2. *^{1}H-NMR Data* ($CDCl_3$) *of* **4a–d**

	4a	**4b**	**4c**	**4d**		**4a**	**4b**	**4c**	**4d**
H–C(5)	4.31	4.13	4.09, 2.54 (J = 14)	4.08, 2.59 (J = 14)	Me–C(5) or Et–C(5)	1.11	1.73, 1.33, 0.83	–	–
H–C(6)	7.18	7.18	6.94	7.10	Me–C(7)	–	–	2.39	–
H–C(8)	7.39	7.39	7.19	7.40	*t*-Bu–C(7)	1.36	1.37	–	1.36
H–C(4′)	6.85	6.83	6.50	6.82	*t*-Bu–C(9)	1.39	1.39	1.37	1.39
H–C(6′)	5.69	5.71	5.86	5.89	*t*-Bu–C(3′)	1.30	1.30	1.28	1.30
					Me–C(5′)	–	–	1.90	–
					t-Bu–C(5′)	1.10	1.10	–	1.10

Scheme 3



Formation of spirofuran derivative **6a**, a minor by-product of **4a**, could arise by direct attack of phenolate **7a** at the less hindered *ortho*-position of the second ring under elimination of chloride and COS. A direct formation of **6a** from **4a** under the reaction conditions could be excluded by a control experiment (see *Exper. Part*).

Conclusions. – Chlorocarbonylsulfenyl chloride is an interesting divalent electrophile with two reactive sites of rather different selectivity. Whereas the Cl–S group appears to react selectively with soft nucleophiles (in the same way as S_2Cl_2 [3]), *e.g.*, with the C-end of phenolates such as that corresponding to **1a** or thioles [6], the COCl group behaves like $SOCl_2$, SCl_2, $COCl_2$, or any other acid chloride, *i.e.*, it is reactive towards alcohols [8] and towards the hard O-end of phenolates such as that corresponding to **1a**.

Experimental Part

1. *General.* Flash chromatography (FC) [9]: silica gel (*Merck 60;* 230–400 mesh). TLC: silica gel; R_f values for hexane/toluene 7:3 (*A*) or hexane/toluene 4:1 (*B*). M.p.: *Tottoli (Büchi)*; uncorrected. IR Spectra (cm^{-1}): *Nicolet SX20*; unless specified otherwise, in KBr. ^1H- and ^{13}C-NMR Spectra: unless specified otherwise, in $CDCl_3$; *Varian Unity 500* (500 MHz, ^1H) and *Varian XL 300* (75.4 MHz, ^{13}C) spectrometers. MS: unless specified otherwise, EI-MS; *VG Micromass 70/70E* or *Finigan MAT 212-SS300;* FAB on *VG Micromass 70/70E* or *Hewlett-Packard HP5988A*.

2. *Starting Materials.* The bis(phenols) **1a**, **1d**, and **1c** are commercially available (*Isonox 129, Isonox 128,* and *Cyanox 2246,* from *Schenectady Chemicals,* US, and *American Cyanamid,* US, resp.). Preparation of **1b**, see [1].

3. *Spiro[1,3-benzoxathiepin-4(5*H*),1′-cyclohexa[2,4]diene]-2,2′-diones and Dibenzo[*d,g*][1,3]dioxocin-6-ones: General Procedure.* A soln. of 0.1 mol of chlorocarbonylsulfenyl chloride in 100 ml of toluene is added within 60 min at 0–5° to a stirred soln. of 0.1 mol of bis(phenol) **1** and 0.22 mol of pyridine in 130 ml of toluene. After stirring for 2 h at 0–5° and 23 h at r.t., the suspension is filtrated over a short silica-gel column and the filtrate evaporated. The crude mixture is then separated by FC (silica gel, hexane/toluene 4:1, 9:1, and 7:3). The major fractions are further purified, if required, by chromatography (*Method A*) and/or recrystallisation/washing (usually with hexane) (*Method B*). The carbonates **5** are eluated first, the spiro compounds **4** last (see below). In all cases, some unconverted **1** is isolated (9–25%); the reactions are not optimised and yields given without correction for unconverted **1**.

3.1. *From* **1a**: *3′,5′,7,9-Tetra(*tert*-butyl)-5-methylspiro[1,3-benzoxathiepin-4(5*H*),1′-cyclohexa[2,4]diene]-2,2′-dione* (**4a**; 14%). FC (hexane/toluene 4:1); purification, *Method B*. M.p. 197° (hexane). R_f 0.28 (*A*). IR: 1731, 1668, 1645. MS: 497 (56, $[M+1]^+$), 496 (37, M^+), 468 (32, $[M-CO]^+$), 436 (100, $[M-COS]^+$). Anal. calc. for $C_{31}H_{44}O_3S$ (496.76): C 74.95, H 8.93, S 6.46; found: C 74.82, H 9.11, S 6.76.

*2,4,8,10-Tetra(*tert*-butyl)-12-methyldibenzo[*d,g*][1,3]dioxocin-6-one* (**5a**; 11.8%). FC (hexane/toluene 4:1); purification, *Method A* (hexane/toluene 9:1). M.p. 150–151° (hexane). R_f 0.61 (*A*). IR: 1788. ^1H-NMR (values of

minor isomer in parentheses): 7.28, 7.19 (7.31, 7.14) (arom. H); 4.21 (4.28) (*q*, H–C(12)); 1.78 (1.68) (*d*, Me–C(12)); 1.40, 1.31 (1.42, 1.31) (*t*-Bu). MS: 464 (12, M^+), 406 (33), 405 (100, $[M - CO_2 - Me]^+$). Anal. calc. for $C_{31}H_{44}O_3$ (464.69): C 80.12, H 9.54; found: C 80.12, H 9.59.

*3′,5,5′,7-Tetra(*tert*-butyl)-3-methylspiro[benzofuran-2(3*H*),1′-cyclohexa[2,4]dien]-2′-one* (**6a**; mixture of diastereoisomers; *ca.* 3%). FC (hexane/toluene 4:1); purification, *Method A* (hexane/toluene 9:1). M.p. 118–125° (hexane). R_f 0.35 (*A*). IR ($CHCl_3$): 1684, 1652. ^{1}H-NMR (major isomer): 7.13 (H–C(6)); 6.92 (H–C(4)); 6.83 (H–C(4′)); 6.01 (H–C(6′)); 3.56 (H–C(3)); 1.42 (*t*-Bu–C(7)); 1.40 (Me–C(3)); 1.28 (*t*-Bu–C(5)); 1.23 (*t*-Bu–C(3′)); 1.14 (*t*-Bu–C(5′)). ^{13}C-NMR (major isomer): 201.1 (C(2′)); 154.6 (C(7a)); 144.6, 143.3, 143.1 (C(5), C(3′), C(5′)); 134.7 (C(4′)); 131.9 (C(7)); 129.5 (C(3a)); 128.1 (C(4)); 122.4 (C(6)); 118.8 (C(6′)); 93.3 (C(2)); 44.2 (C(3)); 34.5, 34.4, 34.3 (Me_3C); 31.8, 29.4, 28.7 (Me_3C); 16.8 (*Me*–C(3)). MS (FAB): 436.

3.2. *From* **1b**: *3′,5′,7,9-Tetra(*tert*-butyl)-5-ethylspiro[1,3-benzoxathiepin-4(5*H*),1′-cyclohexa[2,4]diene]-2,2′-dione* (**4b**; 21.2%). FC (hexane/toluene 7:3); purification, *Method B*. M.p. 144–146° (hexane). R_f 0.35 (*A*). IR: 1734, 1668, 1645. MS: 511 (< 1, $[M + 1]^+$), 450 (1, $[M - COS]^+$), 394 (4, $[M - COS - C_4H_8]^+$), 379 (2, $[M - COS - C_4H_8 - Me]^+$), 323 (1, $[M - COS - C_4H_8 - Me - C_4H_8]^+$), 57 (100, $C_4H_9^+$). Anal. calc. for $C_{32}H_{46}O_3S$ (510.78): C 75.25, H 9.08, S 6.28; found: C 75.44, H 9.27, S 6.20.

*2,4,8,10-Tetra(*tert*-butyl)-12-ethyldibenzo[*d,g*][1,3]dioxocin-6-one* (**5b**; 5.3%). FC (hexane/toluene 7:3); purification, *Method B*. M.p. 165–166° (hexane). R_f 0.66 (*A*). IR: 1785. ^{1}H-NMR (values of minor isomer in parentheses): 7.26, 7.15 (7.30, 7.11) (arom. H); 3.88 (3.92) (*t*, H–C(12)); 2.32 (2.05) (*quint.*, CH_3CH_2); 1.40, 1.30 (1.42, 1.31) (*t*-Bu); 0.96 (0.88) (*t*, CH_3CH_2). MS: 478 (4, M^+), 406 (30), 405 (100, $[M - CO_2 - Et]^+$). Anal. calc. for $C_{32}H_{46}O_3$ (478.71): C 80.29, H 9.69; found: C 79.99, H 9.90.

3.3. *From* **1c**: *3′,9-Di(*tert*-butyl)-5′,7-dimethyl-spiro[1,3-benzoxathiepin-4(5*H*),1′-cyclohexa[2,4]diene]-2,2′-dione* (**4c**; 7.3%). FC (hexane/toluene 4:1); purification, *Method B*. M.p. 175–176° (hexane). R_f 0.25 (*A*). IR: 1728, 1671, 1653. MS: 398 (7, M^+), 338 (29, $[M - COS]^+$), 323 (35, $[M - COS - Me]^+$), 282 (100, $[M - COS - C_4H_8]^+$), 225 (23, $[M - COS - C_4H_8 - C_4H_9]^+$). Anal. calc. for $C_{24}H_{30}O_3S$ (398.57): C 72.33, H 7.59, S 8.04; found: C 72.30, H 7.69, S 7.77.

*4,8-Di(*tert*-butyl)-2,10-dimethyldibenzo[*d,g*][1,3]dioxocin-6-one* (**5c**; 4.5%). FC (hexane/toluene 4:1); purification, *Method B*. M.p. 197–199° (hexane) ([2]: 201–202°). R_f 0.42 (*A*). IR: 1785. ^{1}H-NMR: 7.04, 6.95 (arom. H); 4.08, 3.66 (*AB*, $J = 15$, CH_2 C(12)); 2.29 (Me); 1.39 (*t*-Bu). MS: 366 (37, M^+), 323 (12), 322 (49, $[M - CO_2]^+$), 308 (23), 307 (100, $[M - CO_2 - Me]^+$), 265 (80, $[M - CO_2 - C_4H_9]^+$). Anal. calc. for $C_{24}H_{30}O_3$ (366.51): C 78.65, H 8.25; found: C 78,32, H 8.41.

3.4. *From* **1d**: *3′,5′,7,9-Tetra(*tert*-butyl)spiro[1,3-benzoxathiepin-4(5*H*),1′-cyclohexa[2,4]diene]-2,2′-dione* (**4d**; 9,9%). FC (hexane/toluene 9:1); purification, *Method A* (hexane/AcOEt 99:1), followed by *Method B*. M.p. 193–194° (hexane). R_f 0.10 (*B*). IR: 1726, 1672, 1644. MS: 482 (1, M^+), 422 (11, $[M - COS]^+$), 366 (100, $[M - COS - C_4H_8]^+$), 310 (20, $[M - COS - C_4H_8 - C_4H_8]^+$). Anal. calc. for $C_{30}H_{42}O_3S$ (482.73): C 74.65, H 8.77, S 6.64; found: C 74.59, H 8.89, S 6.84.

*2,4,8,10-Tetra(*tert*-butyl)dibenzo[*d,g*][1,3]dioxocin-6-one* (**5d**; 9.9%). FC (hexane/toluene 9:1); purification, *Method B*. M.p. 150° (hexane). R_f 0.38 (*B*). IR: 1786. ^{1}H-NMR: 7.28, 7.14 (arom. H); 4.12, 3.75 (*AB*, $J = 15$, CH_2 C(12)); 1.40, 1.30 (Me). ^{13}C-NMR: 150.7 (*s*, C(6)); 149.4 (C(4a)); 148.1 (C(2)); 139.2 (C(4)); 127.8 (*t*, C(12a)); 125.8 (C(1)); 123.3 (C(3)); 35.1, 34.7 (Me_3C); 34.9 (C(12)); 31.5 (Me_3C–C(2)); 30.3 (Me_3C–C(4)). MS: 450 (10, M^+). 407 (10), 392 (31), 391 (100, $[M - CO_2 - Me]^+$), 366 (23, $[M - CO - C_4H_8]^+$). Anal. calc. for $C_{30}H_{42}O_3$ (450.66): C 79.95, H 9.39; found: C 79.64, H 9.48.

Stability Test of **4a**. A mixture of 0.4 mmol of **4a**, 0.5 mmol of ClSCOCl, 1.0 mmol of pyridine, and 1.0 mmol of pyridine hydrochloride in 1.2 ml of toluene is stirred for 24 h at r.t. TLC: no formation of **5a** and/or **6a**.

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