Reactions of Thioketones with Dichlorocarbene[1])

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Dedicated to Prof. *Andrzej Jończyk* on the occasion of his 60th birthday

The reactions of sterically crowded cycloalkanethiones of type **2** with $CHCl_3$/NaOH under phase-transfer catalysis (PTC) with benzyl(triethyl)ammonium chloride (TEBA) as catalyst afforded the corresponding 'gem.-dichlorothiiranes' of type **3** in good yields (*cf. Scheme 2* and *Table*). The desulfurization, which, in some cases, occurred spontaneously, led to (dichloromethylidene)cycloalkanes of type **4**. Similar results were obtained using *Seyferth*'s reagent in boiling benzene. In the case of 2,2,6,6-tetramethylcyclohexanethione, reaction under PTC conditions after 3 h yielded only the corresponding dichloromethylidene derivative; on the other hand, workup after 1 h gave (2,2,6,6-tetramethylcyclohexylidene)methanethione (thioketene **9**; *Scheme 5*).

1. Introduction. – Various methods are known for the preparation of thiiranes from different starting materials [1]. For example, thioketones and reactive diazo compounds afford 2,5-dihydro-1,3,4-thiadiazoles, which extrude N_2 to give thiiranes *via* thiocarbonyl ylides as intermediates [2][3]. On the other hand, less reactive diazo compounds (*e.g.*, dimethyl diazomalonate) react with thioketones only in the presence of $[Rh_2(OAc)_4]$ (*cf.* [4] and refs. cited therein). Whereas in the first case the reaction pathway involves a 1,3-dipolar cycloaddition as the key step, the decomposition of the diazo compound generating a carbenoid initiates the formation of a thiocarbonyl ylide in the second case. The formation of thiocarbonyl methanides from thioketones and $:CH_2$, generated by photolysis of CH_2N_2, was evidenced by low-temperature experiments in matrices [5].

Dichlorocarbene is one of the best-known and most frequently used carbenes [6]. It can be formed conveniently by dehydrochlorination of $CHCl_3$ with strong bases. The most efficient method for its generation is the phase-transfer catalysis (PTC) elaborated for the preparative organic chemistry by *Makosza* [7]. However, other methods which involve thermal decomposition of trichloroacetates and (phenyl)-(trichloromethyl)- or (bromodichloromethyl)(phenyl)mercury (*Seyferth*'s reagents) are also well-known [6].

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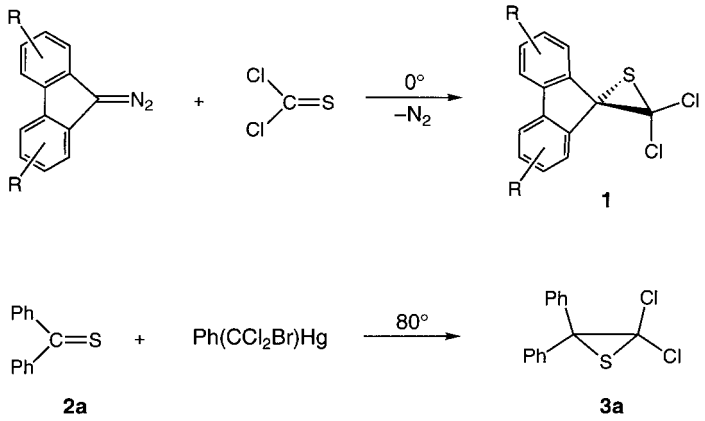
[1]) Presented in preliminary form by *G. M.* at the 14th International Symposium on the Organic Chemistry of Sulfur, Łódź 1990.

[2]) Postdoctoral stay at the University of Zürich (February 1997 – July 1998).

[3]) In part from the diploma thesis of *A. S.*, University of Łódź, 1996.

Geminal dichlorothiiranes are only scarcely reported compounds. A long-known method used for their preparation with only limited application is the reaction of diazo compounds with thiophosgene (Cl_2CS) [8]. This method was recently used by *Harpp* and co-workers to synthesize a series of 3′,3′-dichlorospiro[fluorene-9,2′-thiiranes] of type **1** and related compounds [9] (*Scheme 1*). In the second reported method for the synthesis of 'gem-dichlorothiiranes', (bromodichloromethyl)(phenyl)mercury in boiling benzene was used [10]. By this method, thiobenzophenone (**2a**) was converted into thiirane **3a** (*Scheme 1*).

Scheme 1



The aim of our present work was to establish a new method for the synthesis of 'gem-dichlorothiiranes' starting with thioketones and using PTC conditions. For this study, we selected the non-enolizable thioketones **2a**–**i** (*cf. Table*) to avoid the formation of enethiolates[4]). Although $:CCl_2$ generated by PTC methodology was widely used to convert olefins and imines into dichlorocyclopropanes and dichloroaziridines, respectively, to the best of our knowledge there are no analogous conversions with thiocarbonyl compounds reported (*cf.* [6][7]).

2. Results. – Typically, the two-phase system of the colored solution of a thioketone **2** in $CHCl_3$ and a concentrated aqueous NaOH solution containing catalytic amounts of benzyl(triethyl)ammonium chloride (TEBA) was stirred at room temperature. The reactions were in all cases fast, and the color of the starting material disappeared within 3–20 min. After usual workup and evaporation of the solvent, thiiranes **3** were obtained as crystalline, colorless products (*Scheme 2*, *Table*).

The thiiranes **3** were characterized by elemental analyses, IR, ^{13}C-NMR, and mass spectra. The signal of CCl_2 in the ^{13}C-NMR spectrum (C_6D_6) was found at 85–75 ppm, and all compounds showed a strong C–Cl absorption in the IR spectrum between 780 and 730 cm^{-1}.

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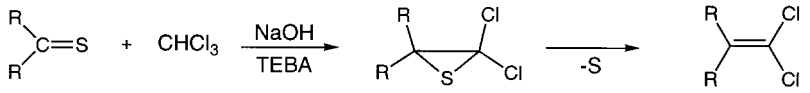
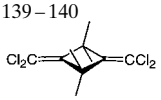
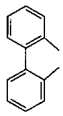
[4]) *Stang* and *Christensen* studied the reaction of isopropylidenecarbene with enolizable dialkyl thioketones and obtained divinyl sulfides as products of the insertion of the carbene into the SH-group of ene-thiols [11].

Scheme 2



2a – g **3a – g** **4b – d, 4g**

Table. *2,2-Dichlorothiiranes* **3** *and 1,1-Dichloroalkenes* **4** *Prepared from Thioketones* **2** *and* $CHCl_3$ *under Two-Phase Conditions*

2	R, R	**3**		**4**	
		M.p. [°]	Yield [%]	M.p. [°]	Yield [%]
a	Ph, Ph	79 – 81	80	–	
b		59 – 61	91	64 – 66	37
c		58 – 68 2 : 1 adducts *cis*/*trans* 4 : 1	82	139 – 140 	46
d		65 – 67	61	–	
e		82 – 83	83	–	
f		105 – 107	63	125 – 130°/12 Torr.	51
g		–		35 – 37°	46
h		112 – 114	80	119 – 121	65
i		–		–	

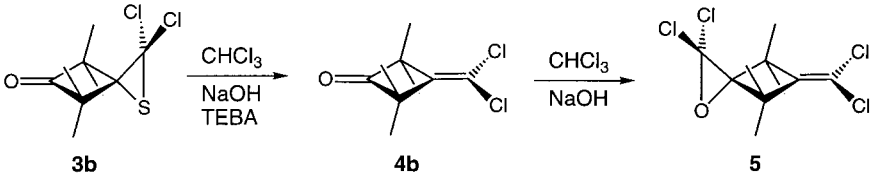
By the above-described procedure, 2,2-dichloro-3,3-diphenylthiirane (**3a**, *cf.* [8][10]) was obtained in 80% yield as a stable crystalline material[5]). Similarly, the spirocycloaliphatic derivatives **3b – e** were stable and could be stored at room

[5]) Thiofluorenone (**2i**) and 4,4′-dimethoxythiobenzophenone were treated under the same conditions, but we were not able to isolate the corresponding thiiranes of type **3**. Their instability has already been observed by *Harpp* and co-workers [9].

temperature without decomposition. However, in the case of indan derivative **3h**, a spontaneous desulfurization took place at room temperature. After two months, a crystalline sample of **3h** had partially decomposed to afford a *ca.* 1:1 mixture of **3h** and the corresponding dichloroalkene **4h**; the products were separated by chromatography.

The spirocyclic dichlorothiirane **3b**, which, in the crystalline state, was stable at room temperature, underwent desulfurization under the conditions of its formation: after 1 h, the red color of **2b** disappeared and **3b** could be isolated in 91% yield. The ^{1}H-NMR spectrum ($CDCl_3$) of **3b** showed two *singlets* at 1.75 and 1.15 ppm for the four Me groups. However, after a reaction time of 7 h, no **3b** could be detected by TLC. The ^{1}H-NMR analysis revealed the presence of dichloroalkene **4b** as the main product with only one signal at 1.35 ppm for all four Me groups. It was accompanied by a minor product **5** with Me signals at 1.58 and 1.22 ppm. The ratio of **4b**/**5** was *ca.* 77:23; after 10 h reaction, it changed to 71:29. Chromatographic workup yielded **4b** and the new compound **5**; the latter showed no C=O absorption in the IR spectrum. In the EI-MS, $M^{+\cdot}$ appeared at *m*/*z* 290, with the characteristic pattern of a compound with four Cl-atoms, and the elemental analysis confirmed the molecular formula $C_{10}H_{12}Cl_4O$. These data correspond to a product formed from **2b** and two :CCl_2 and elimination of sulfur. Therefore, we proposed the structure of the spirocyclic oxirane **5** (*Scheme 3*). This structure was supported by the ^{13}C-NMR data: two *singlets* for sp^2-C-atoms were found at 148.3 and 113.2 ppm, three *singlets* for C(2), C(3), and C(4/6) appeared at 88.6, 81.8, and 48.5 ppm, respectively.

Scheme 3



3b **4b** **5**

In the case of 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**2c**), the color of the solution disappeared within 1 h, and a mixture of bisthiiranes *cis*-**3c** and *trans*-**3c** was formed (*Scheme 4*). The *cis*/*trans* ratio in the crude mixture was 4:1[6]). In the ^{1}H-NMR spectrum ($CDCl_3$), the signal for all four Me groups of *trans*-**3c** showed two Me absorptions at 2.02 and 0.86 ppm. When the reaction mixture was stirred for 7 h, two new products **7** and **8**, in addition to *cis*-**3c** and *trans*-**3c**, were identified by ^{1}H-NMR spectroscopy. After 14 h stirring, product **7**, with Me absorptions at 1.78 and 1.25 ppm, had disappeared completely. The final product **8**, with only one Me absorption at 1.45 ppm, was isolated in 46% yield and was identified as 1,3-bis(dichloromethylidene)-2,2,4,4-tetramethylcyclobutane (**8**; *Scheme 4*). For the intermediate product, we propose the structure of 2,2-dichloro-5-(dichloromethylidene)-4,4,6,6-tetramethyl-1-thiaspiro[2.3]hexane (**7**).

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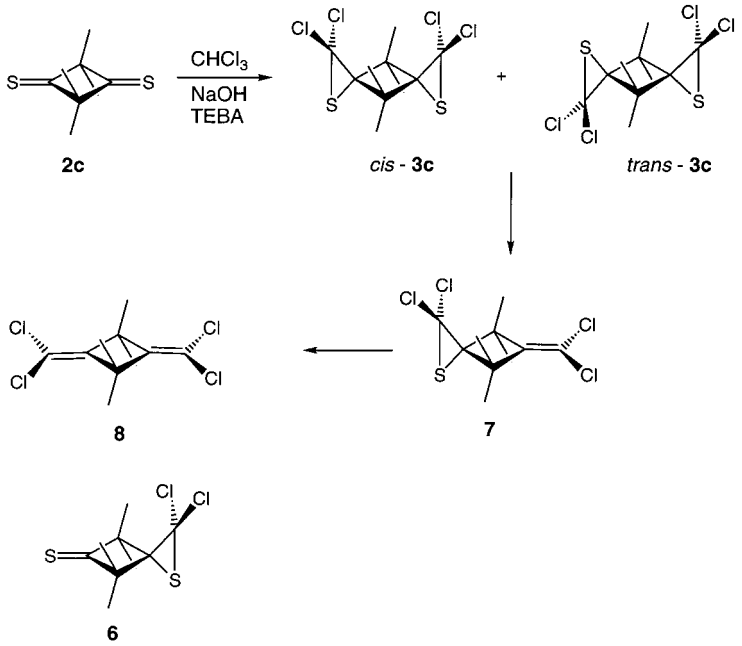
[6]) Separation of *cis*-**3c** and *trans*-**3c** could be achieved neither by column chromatography nor by recrystallization. Isolation of the mono-adduct **6** was not attempted.

Scheme 4



A similar reaction course was observed with 2,2,5,5-tetramethylcyclopentanethione (**2f**). To isolate thiirane **3f**, the reaction had to be carried out at 0–5° to avoid desulfurization. A complete elimination of sulfur was observed after 3 h stirring at room temperature.

With respect to **2f**, the homologous cyclohexanethione **2g** showed a somewhat different behavior. After 3 h under PTC conditions at room temperature, chromatographic workup afforded dichloroalkene **4g** as the only product (46% yield). All attempts to isolate the expected thiirane **3g** were unsuccessful. Unexpectedly, workup, after 1 h[7]), by chromatography or distillation, yielded a violet-colored liquid, which, in the IR spectrum, showed a very intense absorption band at 1740 cm^{-1}. By comparison with spectra of an authentic sample[8]), this product was identified as thioketene **9** (*Scheme 5*)[9]). The yield of isolated **9** was rather low, but no other product could be obtained. In an analogous experiment, we examined the crude mixture by IR spectroscopy. When **2g** had been completely consumed, no absorption at 1740 cm^{-1} could be detected. Therefore, the formation of thioketene **9** must take place during workup.

To compare scope and limitations of the synthesis of dichlorothiiranes **3** under the described PTC conditions with *Seyferth*'s procedure, some additional experiments with

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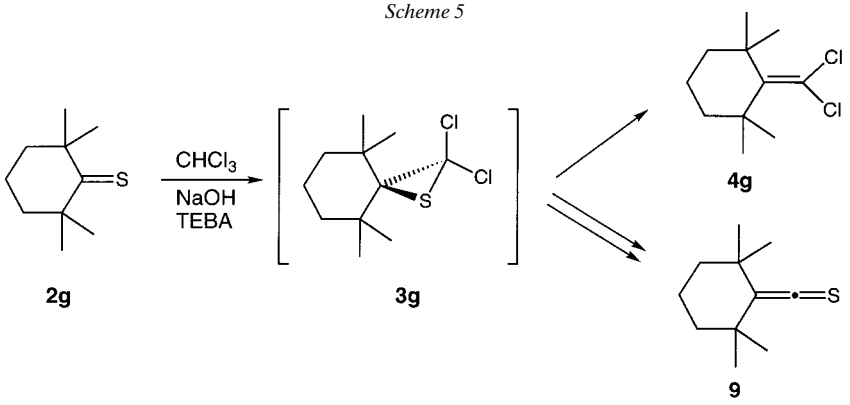
7) After this time, no **2g** could be detected by TLC.

8) We thank Prof. Dr. *E. Schaumann*, University of Clausthal-Zellerfeld, for kindly providing us with an original sample and the IR spectrum.

9) Similarly, the sterically crowded di(*tert*-butyl) thioketone under analogous conditions gave the corresponding thioketene in *ca.* 18% yield.

Scheme 5



2a–**c** and **2h** were carried out. Typically, the reactions were performed with (phenyl)(trichloromethyl)mercury in boiling benzene until the color of the thioketone disappeared (12–24 h). In the case of **2a**, workup after 12 h gave dichloroalkene **4a** as the main product (40%) and dichlorothiirane **3a** in 9% yield. In addition, 44% of benzophenone was isolated.

The reaction with monothione **2b** afforded thiirane **3b** in 84% yield, whereas, in the case of dithione **2c**, monoadduct **6** (*cf. Scheme 4*) was formed (*ca.* 10%) along with *cis*-**3c** and *trans*-**3c**. Under similar conditions, after 12 h, **2h** yielded a 2:1 mixture of **3h** and **4h**. This result is in accordance with our observation that **3h** is less stable than **3b** and **3c**.

3. Discussion. – It is well-known that the two-phase system of $CHCl_3$ and aqueous NaOH in the presence of a quarternary ammonium salt contains $:CCl_3^-$ and $:CCl_2$ as reactive species [6][7]. Principally, thioketones are able to react with both reagents. Therefore, the formation of thiiranes **3** can be rationalized by mechanisms involving dichlorocarbene or trichloromethyl anion as shown in *Scheme 6*.

In the case of the 'carbene mechanism' the reaction can occur either as a two-step process *via* an intermediate thiocarbonyl ylide **A** or concerted *via* a transition state of type **B**. It is worth noting that no products of **A** trapped by thioketones **2** were observed in our experiments, although, in general, thiocarbonyl ylides easily undergo 1,3-dipolar cycloadditions with thioketones as dipolarophiles (*cf.* [12][13]). On the other hand, the reaction pathway *via* nucleophilic addition of $:CCl_3^-$ onto **2** cannot be excluded. In this case, the anion can attack the C=S group in a carbophilic or a thiophilic fashion to give intermediates **C** and **D**, respectively.

Similar interpretations are conceivable in the case of reactions with *Seyferth*'s reagent. Furthermore, the dichlorocarbene transfer to thioketones can also occur *via* a 'free carbene' or *via* the direct interaction between the organomercury compound and the thioketone (*cf.* [10])[10]).

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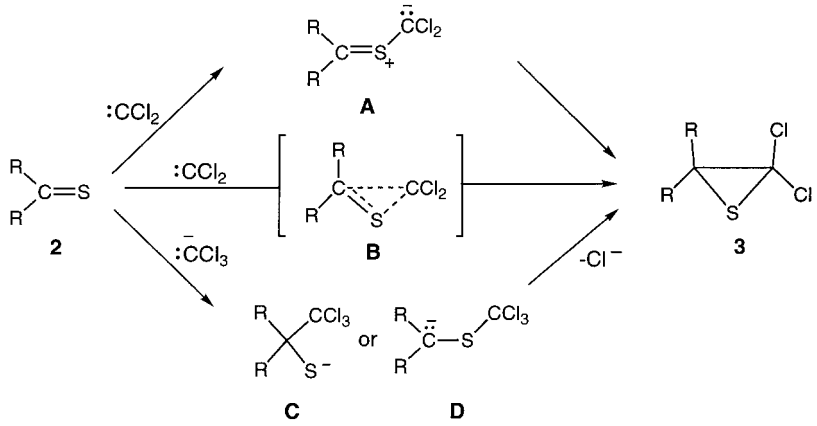
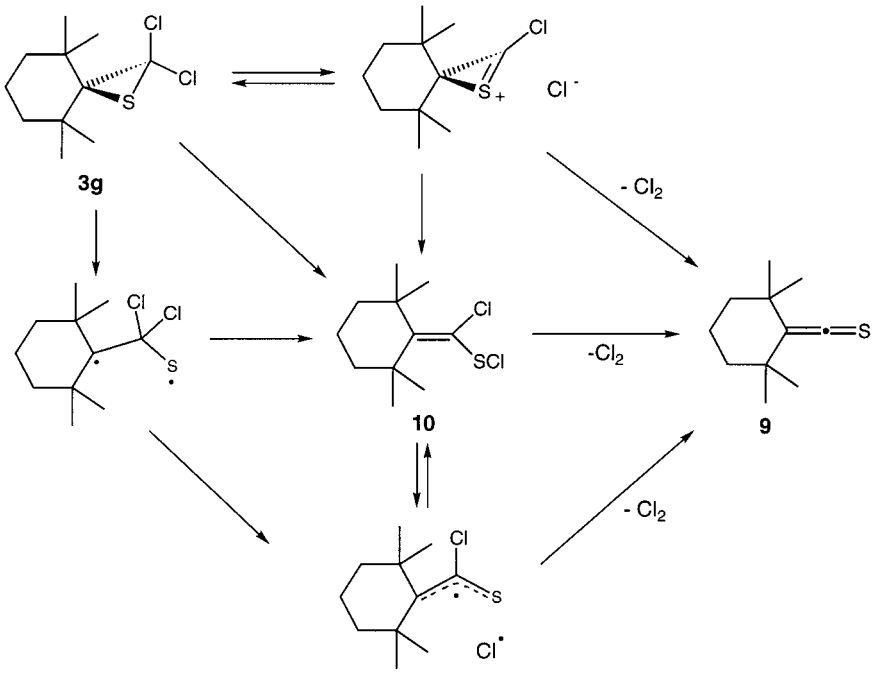
[10]) A procedure for the generation of pure dichlorocarbene is the cheletropic cycloreversion of 11,11-dichloro-1,6-methano[10]annulene/9,9-dichloro-4a,8a-methanonaphthalene [14]. Because of the very low yields in the preparation of the precursor, this method is of little importance for preparative work. For an analogous photochemical generation of dichlorocarbene, see [15].

Scheme 6



The formation of dichloro alkenes **4** under two-phase conditions results from a smooth desulfurization of the primarily formed thiiranes **3** (*Scheme 2*). Based on our previous results [4] we propose that in this desulfurization :CCl_2 is involved. This electrophilic carbene is especially able to interact with an electron lone pair of the S-atom. Thiophosgene formed thereafter is immediately hydrolyzed under the basic conditions.

Scheme 7



The formation of thioketene **9** from sterically crowded dichlorothiirane **3g**[9]) is an unexpected result. Among the methods for the synthesis of thioketenes, no procedure involving thiiranes is known [16]. Formally, the transformation **3g** → **9** requires elimination of Cl_2, which can be explained by ionic as well as by radical mechanisms (*Scheme 7*). In both cases, the unsaturated α-chlorosulfenyl chloride **10**, an isomer of **3g**, may be a key intermediate which, after elimination of Cl_2, yields **9**[11]). An anlogous intermediate formed from 'gem-dihalodiarylthiiranes' has been proposed to explain the formation of benzo[*b*]thiophene derivatives [10].

In conclusion, a new and efficient method for the preparation of 2,2-dichlorothiiranes from non-enolizable thioketones under simple two-phase reaction conditions has been elaborated.

We thank the analytical sections of our institutes for spectra and analyses and Mrs. *M. Celeda* (University of Łódź) for her excellent technical assistance. Financial support of this work by the *Polish State Committee for Scientific Research* (KBN grants No. 2 P303 059 05 and 3 T09A 007 16), the *Swiss National Science Foundation*, and *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged. *J.R.* thanks the *Dr. Helmut Legerlotz Foundation* for a scholarship.

Experimental Part

1. *General*. M.p.: Determined in a capillary, *SMP-20* melting-point apparatus (*Aldrich*), uncorrected. IR Spectra: *Specord-71-IR* spectrophotometer, in KBr, in cm^{-1}. NMR Spectra (^1H: 200 or 400 MHz, and ^{13}C: 50.4 or 100.7 MHz): *Varian-Gemini 200* or *Bruker-400* spectrometer, in $CDCl_3$ unless otherwise stated, δ in ppm, TMS (= 0 ppm) as internal standard. EI-MS: *Finnigan MAT-90* spectrometer; 70 eV. Elemental analyses were performed in laboratories of the Center of Molecular and Macromolecular Studies, PAN in Łódź and the University of Zürich.

2. *Starting Materials. Thiobenzophenone* (**2a**) was prepared from benzophenone with *Lawesson*'s reagent [18], *2,2,4,4-tetramethyl-3-thioxocyclobutanone* (**2b**), *2,2,4,4-tetramethylcyclobutane-1,3-dithione* (**2c**), and *adamantanethione* (**2e**) were obtained by thionation of the corresponding ketones with P_2S_{10} in pyridine according to [19][20], *2,2,4,4-tetramethylcyclobutanethione* (**2d**), *2,2,5,5-tetramethylcyclopentanethione* (**2f**), *2,2,6,6-tetramethylcyclohexanethione* (**2g**), and *1,1,3,3-tetramethylindan-2-thione* (**2h**) were prepared from the corresponding ketones in EtOH solns. passing through mixed streams of H_2S and HCl gas in the presence of trimethyl orthoformate as catalyst [20][21]. For the preparation of fluorene-9-thione (**2i**), a similar procedure was applied [22], and for *di*(tert-*butyl*)*thioketone* (**2j**) a protocol involving reaction of di(*tert*-butyl)ketonimine lithium salt with CS_2 was applied [23]. Benzyl(triethyl)ammonium chloride (TEBA) was synthesized from triethylamine and benzylchloride [24]. $CHCl_3$ was purified to remove EtOH according to [25].

3. *Preparation of 'gem-Dichlorothiiranes* **3** *from Thioketones* **2** *under PTC Conditions. General Procedure.* A soln. of **2** (5 mmol) in freshly purfied $CHCl_3$ (10 ml) and an aq. soln. of NaOH (10 ml, 50%) containing 0.2 g of TEBA, was vigorously stirred. When necessary, the reaction flask was placed in a water bath to keep the temp. below 20°. Progress of the reaction was monitored by TLC, and stirring was stopped as soon as no **2** was detected; reaction times between 10 min and 1 h were needed. The mixtures were poured into H_2O, 50 ml of CH_2Cl_2 were added, the organic phase was separated, repeatedly washed with H_2O, dried ($CaCl_2$), filtered, and evaporated. The brownish residues were separated by CC (SiO_2; pentane or petroleum ether, in some cases with increasing amounts of CH_2Cl_2). Reaction times are given in parentheses, and reported yields refer to isolated **3**. Anal. pure samples were obtained after recrystallization from pentane or MeOH (cooling with dry ice).

2,2-Dichloro-3,3-diphenylthiirane (**3a**) (20 min): 1.13 g (80%). M.p. 79–81° (MeOH) ([8]: 89–90°). IR: 2980*w*, 1495*m*, 1450*m*, 1110*m*, 820v*s*, 780*s*, 720*s*. ^1H-NMR (C_6D_6): 7.45–7.4, 7.15–6.9 (2*m*, 10 arom. H). ^{13}C-NMR (C_6D_6): 139.5 (*s*, 2 arom. C); 129.9, 129.6, 128.3 (3*d*, 10 arom. CH); 81.5 (*s*, C(2)); 67.2 (*s*, C(3)). EI-MS: 282 (3), 280 (4, $M^{+\cdot}$), 258 (39), 210 (100, $[M-S]^+$), 178 (74), 165 (84).

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11) Sterically crowded α-chlorosulfenyl chlorides have been prepared recently by the reaction of Cl_2 with corresponding thioketones (*cf.* [17]). In several cases, an equilibrium with the starting materials was proposed to explain the instability of α-chlorosulfenyl chlorides (refs. cited in [17]).

2,2-Dichloro-4,4,6,6-tetramethyl-1-thiaspiro[2.3]hexan-5-one (**3b**) (15 min): 1.09 g (91%). M.p. 59–61° (pentane). IR: 2900*s*, 1785v*s* (C=O), 1450*s*, 1360*m*, 1280*m*, 1150*m*, 1020*m*, 915*s*, 805v*s*, 760*s*, 690*m*. ^{1}H-NMR: 1.43, 0.91 (2*s*, 4 Me). ^{13}C-NMR (C_6D_6): 210.5 (*s*, C=O); 77.4 (*s*, C(2)); 72.1 (*s*, C(3)); 64.8 (*s*, C(4), C(6)); 23.3, 22.1 (2*q*, 4 Me). EI-MS: 239 (< 1, $M^{+\cdot}$), 205 (30), 203 (90), 175 (69), 133 (43), 81 (75), 70 (100). Anal. calc. for $C_9H_{12}Cl_2OS$ (239.16): C 45.20, H 5.06, Cl 29.65, S 13.41; found: C 45.20, H 5.04, Cl 29.39, S 13.65.

cis- *and* trans-*2,2,7,7-Tetrachloro-4,4,8,8-tetramethyl-1,6-dithiadispiro[2.1.2.1]octane* (*cis*-**3c** and *trans*-**3c**, resp.) (20 min): 1.39 g (82%) as a *ca.* 4:1 *cis*/*trans* mixture[12]. M.p. 58–68° (pentane). IR: 2900*s*, 1460*s*, 1380*s*, 1250*s* (br.), 1130*w*, 1020*m*, 890*m*, 820v*s* (br.), 770v*s* (br.), 700*s*, 680*s*. ^{1}H-NMR: 2.26, 1.00 (2*s*, 4 Me of *cis*-**3c**); 1.56 (*s*, 4 Me of *trans*-**3c**). ^{1}H-NMR (C_6D_6): 2.02, 0.86 (2*s*, 4 Me); 1.36 (*s*, 4 Me). ^{13}C-NMR (C_6D_6): *cis*-**3c**: 75.0 (*s*, 2 CCl_2); 74.7 (*s*, C(3), C(5)); 51.5 (*s*, C(4), C(8)); 27.8, 21.7 (2*q*, 4 Me); *trans*-**3c**: 78.1 (*s*, 2 CCl_2); 74.6 (*s*, C(3), C(5)); 51.6 (*s*, C(4), C(8)); 29.0 (*q*, 4 Me). EI-MS: 340 (20), 338 (38, $M^{+\cdot}$), 336 (28), 264 (25), 209 (67), 207 (100), 187 (36), 168 (52), 133 (45), 83 (22). Anal. calc. for $C_{10}H_{12}Cl_4S_2$ (338.14): C 35.52, H 3.57, Cl 41.94, S 18.97; found: C 35.74, H 3.62, Cl 42.14, S 18.33.

2,2-Dichloro-4,4,6,6-tetramethyl-1-thiaspiro[2.3]octane (**3d**) (10 min): 687 mg (61%). M.p. 65–67° (MeOH). IR: 2900v*s*, 1450*s*, 1365*s*, 1270*s*, 1240*m*, 1180*m*, 1030*w*, 920*m*, 820v*s*, 765*s*, 690*s*. ^{1}H-NMR: 1.88 (*s*, CH_2); 1.63, 1.18 (2*s*, 4 Me). ^{13}C-NMR (C_6D_6): 76.9 (*s*, C(2)); 49.0 (*t*, CH_2); 41.0 (*s*, C(4), C(6)); 39.3 (*s*, C(3)); 30.9, 26.6 (2*q*, 4 Me). Anal. calc. for $C_9H_{14}Cl_2S$ (225.18): C 48.00, H 6.27, Cl 31.49, S 14.24; found: C 47.68, H 6.17, Cl 31.23, S 14.38.

3′,3′-Dichlorospiro[tricyclo[3.3.1.1^{3,7}]decane-2,2′-thiirane] (**3e**) (60 min): 1.03 g (83%). M.p. 82–83° (pentane). IR: 2800*s*, 1450*m*, 1360*w*, 1230*m*, 1200*m*, 1110*m*, 970*m*, 900*m*, 800v*s*, 780*s*, 750*s*, 700*m*. ^{1}H-NMR (C_6D_6): 1.98, 1.61 (2 br. *m*, 14 H). ^{13}C-NMR (C_6D_6): 84.2 (*s*, CCl_2); 67.6 (*s*, C(2)); 37.0, 36.8, 36.4 (3*t*, 5 CH_2); 38.3, 26.9, 26.6 (3*d*, 4 CH). Anal. calc. for $C_{11}H_{14}Cl_2S$ (249.20): C 53.02, H 5.66, Cl 28.45, S 12.87; found: C 53.29, H 5.88, Cl 28.01, S 12.67.

2,2-Dichloro-4,4,7,7-tetramethyl-1-thiaspiro[2.4]heptane (**3f**) (2 h): 753 mg (63%). M.p. 105–107° (MeOH). IR: 2950*s*, 1470v*s*, 1370*s*, 1240*m*, 1140*w*, 1010*w*, 845*s*, 785v*s*, 740*s*, 700*m*. ^{1}H-NMR: 1.85–1.7 (*m*, 2 CH_2); 1.58, 1.03 (2*s*, 4 Me). ^{13}C-NMR: 79.7 (*s*, C(2)); 79.2 (*s*, C(3)); 46.5 (*s*, C(4), C(7)); 40.9, 27.2 (2*q*, 4 Me); 31.2 (*t*, 2 CH_2). Anal. calc. for $C_{10}H_{16}Cl_2S$ (239.21): C 50.21, H 6.74, Cl 29.64, S 13.40; found: C 50.11, H 6.58, Cl 29.78, S 13.21.

3′,3′-Dichloro-1,1,3,3-tetramethylspiro[indan-2,2-thiirane] (**3h**) (15 min): 1.15 g (80%). M.p. 112–114° (MeOH). IR: 2950*s*, 1480*m*, 1450*w*, 1380*m*, 1370*s*, 800v*s*, 780*s*, 750v*s*, 730*s*. ^{1}H-NMR: 7.40, 7.18 (2*m*, 4 arom. H); 1.89, 1.45 (2*s*, 4 Me). ^{1}H-NMR (C_6D_6): 7.15–7.05, 6.95–6.85 (2*m*, 4 arom. H); 1.66, 1.27 (2*s*, 4 Me). ^{13}C-NMR: 148.6 (*s*, 2 arom C); 127.8, 121.9 (2*d*, 4 arom. CH); 78.8, 78.4 (2*s*, CCl_2, C(2)); 49.9 (*s*, C(1), C(3)); 29.8, 28.6 (2*q*, 4 Me). EI-MS: 287 (2, $M^{+\cdot}$), 286 (15, $[M-1]^+$), 273 (11), 253 (10), 251 (30), 201 (12), 184 (15), 157 (100), 152 (11), 141 (20), 115 (16). Anal. calc. for $C_{14}H_{16}Cl_2S$ (287.25): C 58.54, H 5.61, Cl 24.68, S 11.16; found: C 58.16, H 5.66, Cl 24.58, S 11.12.

*Reaction with 9*H*-Fluorene-9-thione* (**2i**). After 10 min reaction, no **2i** could be detected. There was no thiirane **3i** present as the characteristic signals in the ^{13}C-NMR spectrum ($CDCl_3$, 77.3 and 60.3 ppm [9]) were absent. Instead, two signals of an unknown compound 73.9 and 73.3 ppm were observed. The instability of the expected **3i** has already been reported [8][26].

4. *Formation of (Dichloromethylidene)cycloalkanes* **4** *from Thioketones* **2** *under PTC Conditions.* 4.1. *Reaction of* **2b**. To a soln. of **2b** (780 mg, 5 mmol) in $CHCl_3$ (10 ml) containing 0.2 g of TEBA, 50% aq. NaOH soln. (10 ml) was added. The two-phase system was stirred vigorously at r.t. for 7 h. After usual workup and CC (SiO_2; petroleum ether with increasing amounts of CH_2Cl_2), two fractions were isolated. Recrystallization afforded anal. pure samples of **4b** and **5**; reported yields refer to amounts isolated after CC.

3-(Dichloromethylidene)-2,2,4,4-tetramethylcyclobutanone (**4b**): 367 mg (37%), isolated as the more polar fraction. M.p. 64–66° (MeOH). IR: 2900*m*, 1790v*s* (C=O), 1650*w* (C=C), 1450*s*, 1180*m*, 985v*s*, 900*s*, 870*s*, 820*w*. ^{1}H-NMR: 1.35 (*s*, 4 Me). ^{13}C-NMR: 216.7 (*s*, C=O); 146.6 (*s*, $=CCl_2$); 114.7 (*s*, C(3)); 63.8 (*s*, C(2), C(4)); 20.2 (*q*, 4 Me). EI-MS: 207 (1, $M^{+\cdot}$), 180 (31), 177 (55), 145 (23), 143 (100), 107 (83). Anal. calc. for $C_9H_{12}Cl_2O$ (207.10): C 52.20, H 5.84, Cl 34.24; found: C 52.40, H 6.02, Cl 34.15.

2,2-Dichloro-5-(dichloromethylidene)-4,4,6,6-tetramethyl-1-oxaspiro[2.3]hexane (**5**): 233 mg (17%), isolated as the less polar fraction. M.p. 98–100° (pentane). IR: 2900*s*, 1640*s* (C=C), 1460*s*, 1415*m*, 1380*s*, 1260*m*, 1040*s*, 1010*s*, 900v*s*, 860v*s* (br.), 820*s*. ^{1}H-NMR: 1.58, 1.22 (2*s*, 4 Me). ^{13}C-NMR: 148.3 (*s*, $=CCl_2$); 113.2 (*s*, (C(5)); 88.6 (*s*, C(3)); 81.8 (*s*, C(2)); 20.5, 19.7 (2*q*, 4 Me). EI-MS: 290 (30, $M^{+\cdot}$), 277 (40), 275 (100), 273 (71), 255 (25), 253 (25), 189 (23), 177 (26), 175 (26), 155 (44), 119 (20), 101 (20), 77 (26). Anal. calc. for $C_{10}H_{12}Cl_4O$ (290.02): C 41.41, H 4.17, Cl 48.90; found: C 41.74, H 4.37, Cl 49.23.

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[12]) A similar *cis*/*trans* ratio was established in the crude mixture by ^{1}H-NMR.

4.2 *Reaction of* **2c**, **2f**–**h**. The reactions were carried out according to the *General Procedure* (*Exper. 3*). However, the magnetic stirring was continued, until the primarily formed thiirane **3** had disappeared. After usual workup and evaporation of the solvent, the residue was separated by CC (SiO_2; pentane).

1,3-Bis(dichloromethylidene)-2,2,4,4-tetramethylcyclobutane (**8**) (14 h): 630 mg (46%). M.p. 139–140° (MeOH). IR ($CHCl_3$): 2900*s*, 1630v*s* (C=C), 1460*s*, 1380*s*, 1200*s*, 905v*s*, 870*s*. ^{1}H-NMR: 1.45 (*s*, 4 Me). ^{13}C-NMR: 149.6 (*s*, 2 $=CCl_2$); 113.0 (*s*, C(1), C(3)); 50.6 (*s*, C(2), C(4)); 25.3 (*q*, 4 Me). EI-MS: 274 (28, $M^{+\bullet}$), 272 (22), 261 (36), 259 (96), 241 (23), 239 (95), 237 (100), 223 (26), 221 (26), 204 (20), 202 (33), 201 (22). Anal. calc. for $C_{10}H_{12}Cl_4$ (274.02): C 43.83, H 4.42, Cl 51.75; found: C 43.55, H 4.59, Cl 51.94.

1-(Dichloromethylidene)-2,2,5,5-tetramethylcyclopentane (**4f**) (3 h): 528 mg (51%), purified additionally by bulb-to-bulb distillation at 125–130°/12 Torr. IR (neat): 2880v*s*, 1600*m* (C=C), 1460*s*, 1370*m*, 1230*m*, 920*s*, 880*m*, 860v*s*, 800*w*. ^{1}H-NMR: 1.58 (*s*, 2 CH_2); 1.23 (*s*, 4 Me). ^{13}C-NMR (C_6D_6): 166.6 (*s*, $=CCl_2$); 122.6 (*s*, C(1)); 48.1, 47.3 (2*s*, C(2), C(5)); 41.1, 41.0 (2*t*, 2 CH_2); 28.8, 26.1 (2*q*, 4 Me). EI-MS: 207 (1, $M^{+\bullet}$), 171 (49), 152 (28), 150 (45), 135 (17), 115 (39), 83 (100). Anal. calc. for $C_{10}H_{16}Cl_2$ (207.14): C 57.98, H 7.79, Cl 34.23; found: C 57.83, H 7.65, Cl 34.11.

1-(Dichloromethylidene)-2,2,6,6-tetramethylcyclohexane (**4g**) (3 h): 508 mg (46%). M.p. 35–37° (MeOH/CH_2Cl_2). IR (neat): 2890*s*, 1530*m* (C=C), 1470*s*, 1370*m*, 1230*m*, 1160*m*, 1000*m*, 900*s*, 860v*s*, 790*m*, 730*m*. ^{1}H-NMR: 1.48 (br. *s*, 3 CH_2); 1.35 (*s*, 4 Me). ^{13}C-NMR (C_6D_6): 150.9 (*s*, $=CCl_2$); 119.4 (*s*, C(1)); 43.8 (*t*, 2 CH_2); 38.5 (*s*, C(2), C(6)); 29.2 (*q*, 4 Me); 17.6 (*t*, CH_2). EI-MS: 221 (1, $M^{+\bullet}$), 150 (18), 143 (17), 116 (18), 115 (27), 109 (17), 96 (28), 81 (15), 69 (100), 55 (23). Anal. calc. for $C_{11}H_{18}Cl_2$ (221.17): C 59.74, H 8.20, Cl 32.06; found: C 59.91, H 8.34, Cl 31.90.

5. *Formation of 2-(Dichloromethylidene)-1,1,3,3-tetramethylindan* (**4h**) *by Decomposition of* **3h**. At r.t., **3h** underwent a spontaneous but slow desulfurization. After 2 months, a *ca.* 1:1 mixture of **3h** and **4h** was present. After 8 months, the mixture was separated by CC (SiO_2; petroleum ether/CH_2Cl_2 8:2). Yield of **4h**: *ca.* 65%. Colorless crystals. M.p. 119–121° (MeOH). IR: 2900*s*, 1570*s* (C=C), 1490*s*, 1460*s*, 1370*m*, 1260*m*, 1130*m*, 1050*w*, 1040*m*, 905*s*, 870v*s*, 720v*s*, 690*w*. ^{1}H-NMR: 7.3–7.2, 7.2–7.1 (2*m*, 4 arom. H); 1.59 (*s*, 4 Me). ^{13}C-NMR: 155.1 (*s*, $=CCl_2$); 148.7 (*s*, 2 arom. C); 127.5, 122.4 (2*d*, 4 arom. CH); 50.2 (*s*, C(1), C(3)); 27.4 (*q*, 4 Me). EI-MS: 255 (3, $M^{+\bullet}$), 241 (60), 239 (100), 223 (13), 221 (12), 219 (41), 184 (19), 152 (11). Anal. calc. for $C_{11}H_{14}Cl_2$ (255.19): C 65.89, H 6.32; found: C 66.14, H 6.08.

6. *Formation of Thioketenes* **9** *from Thioketones under PTC Conditions. (2,2,6,6-Tetramethylcyclohexylidene)methanethione* (**9**). The reaction with **2g** (5 mmol) was carried out according to the *General Procedure* (*Exper. 3*). After 75 min at r.t., the originally violet color of the mixture turned brownish, and **2g** had disappeared (TLC). After usual workup, the brown oily residue was separated by CC (SiO_2; pentane): 100 mg (12%) of **9**[13]), identified by comparison with an authentic sample[8]). IR (neat): 1740v*s* (C=C=S). ^{1}H-NMR: 1.57 (*s*, CH_2); 1.35 (*s*, 2 CH_2); 1.15 (*s*, 4 Me).

Di(tert-*butyl)thioketene*. An analogous reaction was carried out with di(*tert*-butyl)thioketone. TLC revealed complete consumption of the starting material after 20 min. However, the violet color of the org. phase remained dominant. ^{1}H-NMR Analysis ($CDCl_3$) of the crude mixture showed a quite complicated pattern of signals between 2.0 and 1.0 ppm with a dominant *s* at 1.26 ppm. The IR spectrum of the mixture showed a very strong absorption band at 1740 cm^{-1}. Destillative workup afforded a violet-colored main fraction at 95–100°/0.3 Torr which was identified as di(*tert*-butyl)thioketene. Subsequent CC (SiO_2; pentane) afforded 153 mg (18%). ^{1}H-NMR: 1.26 (*s*, 6 Me). ^{13}C-NMR: 272.5 (*s*, C=*C*=S); 100.5 (*s*, *C*=C=S); 31.9 (*q*, 6 Me). All data corresponded well to those reported [16b].

7. *Reactions of Thioketones* **2** *with (Phenyl)(trichloromethyl)mercury* (*Seyferth*'s reagent). A soln. of $PhHgCCl_3$ (871 mg, 2.2 mmol) and 2 mmol of **2** in abs. benzene (5 ml) was heated to reflux, until TLC (SiO_2; hexane/CH_2Cl_2 8:2) indicated complete consumption of **2**. The mixture was cooled to r.t. and precipitated PhHgCl was filtered. The clear filtrate was evaporated, and the oily residue was chromatographed (SiO_2; pentane with increasing amounts of CH_2Cl_2). Reported yields refer to chromatographically purified products. When necessary, additional recrystallization was applied to obtain anal. pure samples.

Reaction with **2b** (26 h): CC with hexane/CH_2Cl_2 9:1 afforded 402 mg (84%) of **3b**.

Reaction with **2c** (24 h): CC afforded mono-adduct **6** as the less polar fraction followed by *cis*-**3c**/*trans*-**3c** 8:2.

2,2-Dichloro-4,4,6,6-tetramethyl-1-thiaspiro[2.3]hexane-5-thione (**6**): 255 mg (50%). Orange crystals. M.p. 53–55° (MeOH). IR: 2970*s*, 2920*m*, 1455*s* (br.), 1410*m*, 1380*m*, 1370*m*, 1360*m*, 1320*s*, 1110*s*, 910*m*, 810v*s* (br.),

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[13]) A similar yield of **9** was obtained after a bulb-to-bulb distillation of the crude mixture at 100°/0.3 Torr.

770*s* (br.), 740*m*. ^{1}H-NMR: 1.81, 1.22 (2*s*, 4 Me). ^{13}C-NMR: 271 (*s*, C=S); 76.9 (*s*, C(2)); 74.9 (*s*, C(3)); 67.3 (*s*, C(4), C(6)); 27.5, 26.3 (2*q*, 4 Me). CI-MS (NH_3): 256 (43, $[M+1]^+$), 254 (51), 239 (18), 221 (46), 219 (61), 185 (14), 183 (14), 182 (14), 180 (15), 103 (16), 86 (100), 71 (18). Anal. calc. for $C_9H_{12}Cl_2S_2$ (255.23): C 42.35, H 4.74, Cl 27.78, S 25.13; found: C 42.02, H 4.70, Cl 27.59, S 24.95.

Cis- and *trans*-**3c** (4:1): 156 mg (23%). Colorless crystals. M.p. 58–68°.

Reaction with **2h** (12 h): CC yielded a mixture of **3h** and its desulfurization product **4h** (2:1) in a total yield of *ca.* 20%.

Reaction with **2a** (12 h): CC afforded **3a** (50 mg, 9%) and *1,1-dichloro-2,2-diphenylethene* (**4a**) (198 mg, 40%). **4a**: Colorless crystals. M.p. 76–77° ([27]: 77–79°). Identified by comparison of its spectra and physical properties with those reported in [27]. In addition to **3a** and **4a**, benzophenone (92 mg, 44%) was isolated as the most polar fraction.

Reaction with **2e** (3 h): After this time, the initially orange color of the mixture changed to black. After usual workup, no reasonable product could be isolated from the black residue. The only material isolated after CC was adamantanone (50 mg, 16%).

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