Reactions of Chlorosulfanyl Derivatives of Cyclobutanones with Different Nucleophiles

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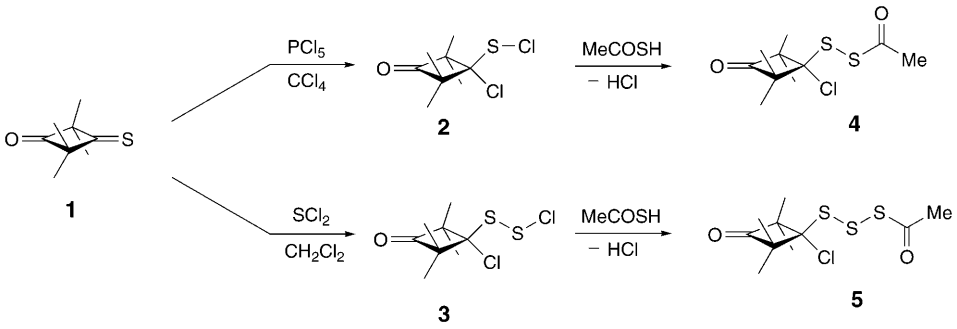
The reactions of 3-chloro-3-(chlorosulfanyl)-2,2,4,4-tetramethylcyclobutan-1-one (**2**) with N, O, S, and P nucleophiles occur by substitution of Cl at the S-atom. Whereas, in the cases of secondary amines, alkanols, phenols, thiols, thiophenols, and di- and trialkyl phosphates, the initially formed substitution products were obtained, the corresponding products with allyl and propargyl alcohols undergo a [2,3]-sigmatropic rearrangement to give allyl and allenyl sulfoxides, respectively. Analogous substitution reactions were observed when 3-chloro-3-(chlorodisulfanyl)-2,2,4,4-tetramethylcyclobutan-1-one (**3**) was treated with N, O, and S nucleophiles. The reaction of **3** with Et_3P led to an unexpected product *via* cleavage of the S–S bond (*cf. Scheme 13*). In the reactions of **2** with primary amines and H_2O, the substitution products react further *via* elimination of HCl to yield the corresponding thiocarbonyl *S*-imides and the thiocarbonyl *S*-oxide, respectively. Whereas the latter could be isolated, the former were not stable but could be intercepted by MeOH (*Scheme 4*) or adamantanethione (*Scheme 5*). The structures of some of the substitution products were established by X-ray crystallography.

1. Introduction. – Some years ago, it has been reported that the reaction of 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1**) with PCl_5 and SCl_2 provides the chlorosulfanyl derivative **2** and chlorodisulfanyl derivative **3**, respectively, in good yield [1] (*Scheme 1*). Due to the polar character of the S–Cl bond in **2** and **3**, a nucleophilic substitution

Scheme 1

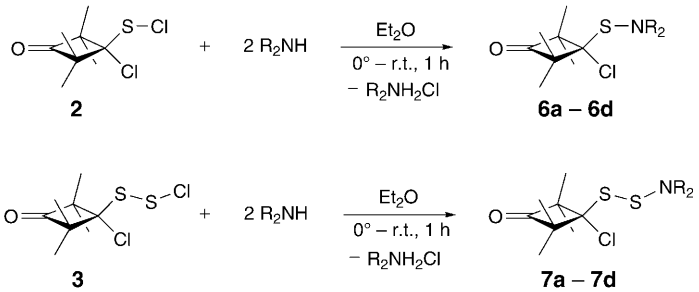


[1]) Part of the planned Ph.D. thesis of *A. M.*, Universität Zürich.

of Cl is possible. It is already known that the reactions of **2** and **3** with thioacetic S-acid give the corresponding stable thio-esters **4** and **5** [2]. As **2** and **3** represent stable and easily accessible sulfanyl chlorides, their derivatization with various nucleophiles could be examined.

2. Results and Discussion. – 2.1. *Reactions of Chlorosulfanyl and Chlorodisulfanyl Derivatives* **2** *and* **3***, respectively, with N Nucleophiles.* In a first set of experiments, chlorosulfanyl compound **2** and the corresponding chlorodisulfanyl derivative **3** were reacted with 2 equiv. of secondary amines (R_2NH) as nucleophiles (*Scheme 2*). The reactions were carried out in analogy to procedures described for transformations of simple sulfanyl chlorides [3][4]. The nucleophilic substitution at the S-atom was accomplished under mild conditions, and hardly any by-products were formed. The required reaction times are relatively short, and the 3-chloro-3-(aminosulfanyl)cyclobutanones **6** and their disulfanyl variants **7** were formed in good yields. The products **6** and **7** (*Scheme 2*) were separated by filtration from the precipitated amine hydrochlorides that were formed as second products. The crude products showed a purity of *ca.* 90%, and, if possible, they were further purified by crystallization[2]). In the cases of compounds **6a** and **7a**, suitable crystals for an X-ray crystal-structure determination were obtained (*Fig. 1*).

Scheme 2



a R–R = $-(CH)_2O(CH_2)_2-$ **b** R–R = $-(CH_2)_5-$ **c** R–R = $-(CH_2)_4-$ **d** R = Et

In an analogous series, **2** and **3** were reacted with primary amines. In this case, subsequent HCl elimination of the adducts **8** to give sulfinimides **9** (thiocarbonyl *S*-imides) should be possible (*Scheme 3*) [6–9]. These and related ylides are important building blocks for cycloadditions and other reactions [8][10], including conversions with amines [11], alkenes [12][13], and metal-organic compounds such as PhLi [14] or RMgBr [15]. In general, sulfinimides are reactive intermediates, which easily undergo further reactions. However, in a few cases, the isolation of a sulfinimide is possible when it is further stabilized by π-acceptor groups, as in compound **10** [16].

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[2]) It was not possible to apply other purification techniques, as decomposition occurred during chromatography on either SiO_2 or Al_2O_3, as well as by the attempted microdistillation.

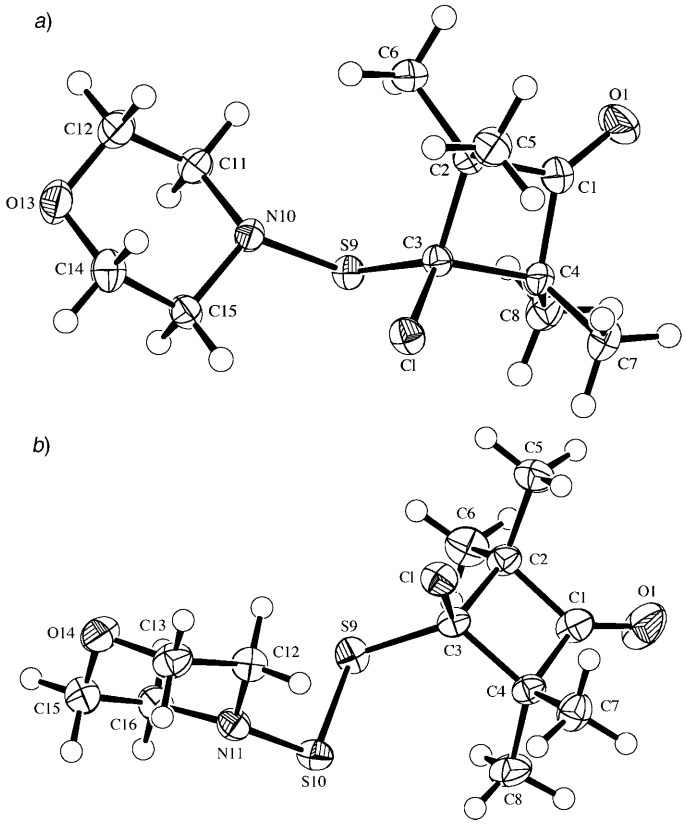
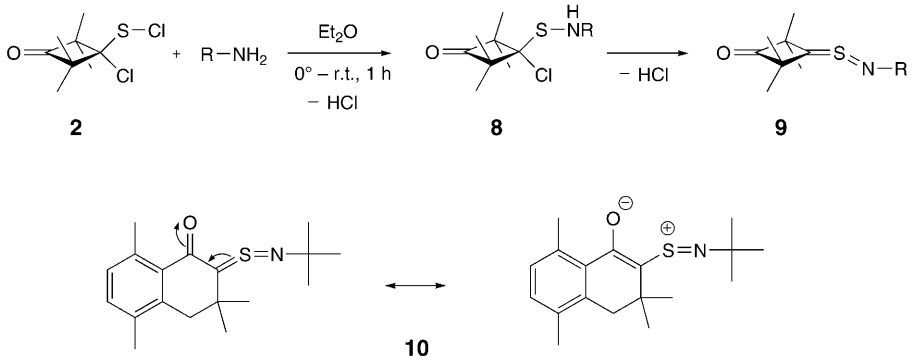


Fig. 1. *ORTEP Plots* [5] *of the molecular structures of* a) **6a** *and* b) **7a** (arbitrary numbering of atoms; 50% probability ellipsoids)

Scheme 3



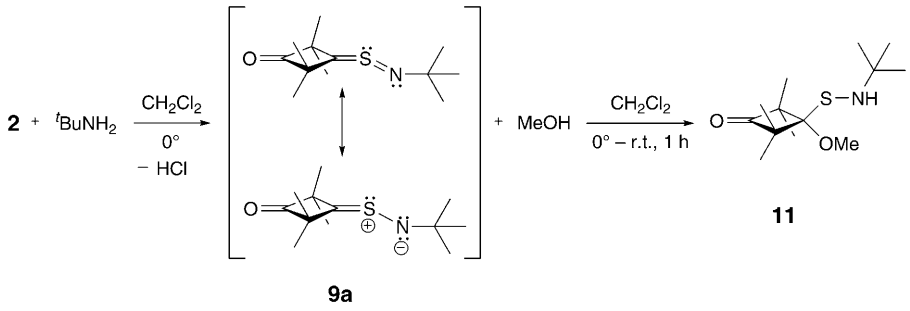
Sulfinimides are also accessible *via* the reaction of the corresponding sulfanyl chlorides with silylated amines [17]. They display a characteristic absorption at 480–500 nm,

and some examples exist as red or orange crystals [18–20]. Furthermore, they can often be identified by specific MS fragmentations [21].

The compounds **2** and **3** were treated with 3 or more equiv. of a primary amine. To avoid a reaction of the amine with 2 equiv. of the electrophile, the chlorosulfanyl compound was added to a solution of the amine in the corresponding solvent. Unfortunately, the expected sulfinimides of type **9** could not be isolated from any of the reactions with ^{t}BuNH$_2$, cyclohexylamine, PhCH$_2$NH$_2$ or PhNH$_2$. In all experiments, mixtures of compounds were formed that could neither be separated nor identified, and several variations of the reaction conditions did not improve the result. On the other hand, a hint for the intermediate formation of **9** may be the coloration of the reaction mixture.

Therefore, we tried to trap the reactive intermediate in the reaction with ^{t}BuNH$_2$ in analogy to the procedures applied with thiocarbonyl ylides [22–24]. In this experiment, MeOH was added to the mixture after 1 min, and workup after 1 h gave compound **11**, which actually points to the intermediary occurrence of the sulfinimide [3] (*Scheme 4*).

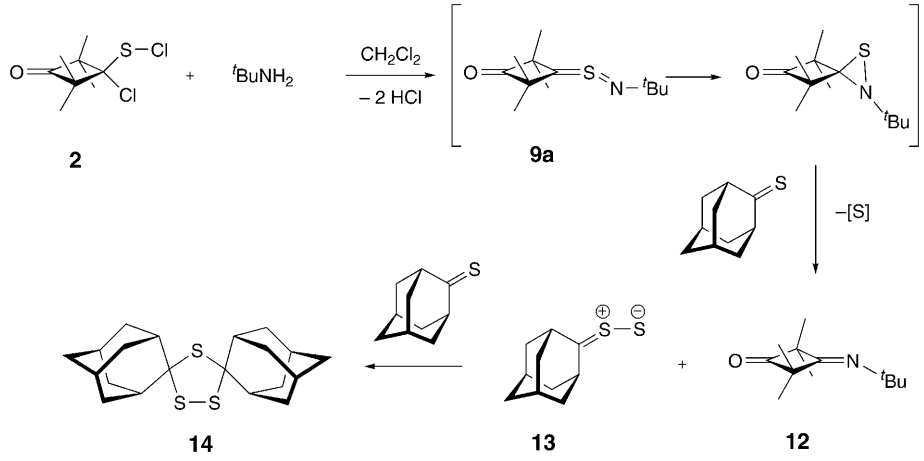
Scheme 4



Most likely, **11** was formed by the addition of MeOH to sulfinimide **9a**. A nucleophilic substitution of Cl at C(2) of the intermediate of type **8** by MeOH according to an S_N2 mechanism can be excluded, as such reactions are not known in similar sterically crowded cyclobutanone derivatives. However, a reaction *via* an S_N1 mechanism is feasible, but the thereby formed sulfonium ion equals the protonated form of sulfinimide **9a**. Under the basic reaction conditions, it is most likely that deprotonation to give **9a** occurs very fast. On the other hand, the addition of MeOH could take place already at the protonated intermediate. A direct formation of the thiaziridine by cyclization of the primarily formed cation can be excluded, because, to the best of our knowledge, there are no experimental data available for a ring opening of thiaziridines to give thiocarbonyl *S*-imides. All known reactions which are formulated *via* intermediate thiaziridines proceed by elimination of S (cleavage of the S,N and S,C bonds) or *via* rearrangement to give a thionitrone (cleavage of the S,C bond) [25].

In some cases, sulfinimides react further to the corresponding thiaziridines, which easily form imines by elimination of sulfur [22] (see *Scheme 5*). Therefore, as a second, more significant indication of an intermediate sulfinimide, we attempted to trap **9a** with adamantanethione in a 1,3-dipolar cycloaddition, in analogy to related reactions [26]. For this purpose, the reaction with ^{t}BuNH$_2$ and **2** was carried out as usual, and, after

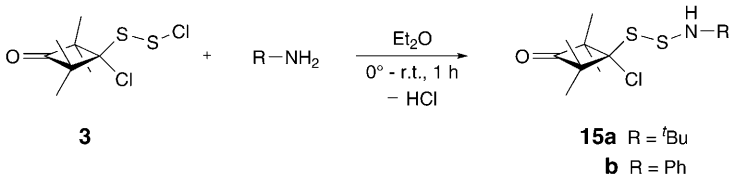
Scheme 5



a short time, adamantanethione was added to the mixture. After usual workup, the known imine **12** and trithiolane **14** were obtained, but not the desired [2+3] cycloadduct. A plausible mechanistic explanation for the formation of these compounds is shown in *Scheme 5*. The key-step is the S-transfer reaction from the intermediate thiaziridine onto adamantanethione to give **12** and adamantane *S*-sulfide (**13**, a thiosulfine) [25]. The latter undergoes a spontaneous [2+3] cycloaddition with adamantanethione to give the 1,2,4-trithiolane **14**.

The reaction of **2** with $PhCH_2NH_2$ was expected to give rise to a 1,4-H shift in the intermediate 1,3-dipole of type **9** (see [27]); however, no corresponding product was obtained. The analogous reaction of **3** with $^tBuNH_2$ was accomplished without any complication. As, in this case, a HCl elimination in the initially formed substitution product **15** is not possible, **15a** was obtained in good yield (*Scheme 6*). Similarly, the reaction of **3** with $PhNH_2$ yielded the corresponding product **15b**.

Scheme 6

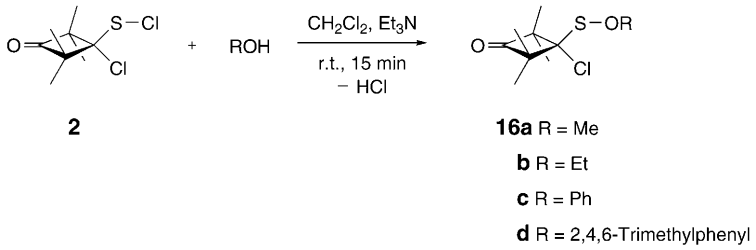


In summary, reactions of chlorosulfanyl derivative **2** and chlorodisulfanyl derivative **3** with secondary amines proceeded smoothly leading to products **6** and **7**, respectively, which can be isolated in good yield and in a relatively pure state. As a result of their instability, further purification by chromatography or distillation was not possible, and therefore, no correct elemental analyses could be obtained. Similarly, the reactions of **3** with $^tBuNH_2$ and $PhNH_2$ yielded the substitution products **15**. On the other hand, we were unable to isolate pure products of the reactions of **2** with primary amines.

However, two different quenching experiments indicate the interim formation of sulfinimides of type **9** by elimination of HCl from the initially formed substitution product **8**.

2.2. *Reactions of* **2** *and* **3** *with O Nucleophiles.* Some reactions of chlorosulfanyl compounds with O nucleophiles, in most cases aliphatic alcohols [28–30] or phenols [31], are described to occur *via* substitution of Cl. For the reactions with **2** and **3**, we chose some alcohols and phenols, as well as AcOH and H_2O. The conversions of **2** with MeOH, EtOH, and phenol in CH_2Cl_2 in the presence of Et_3N proceeded smoothly at room temperature and gave the crude substitution products **16** in high yields (*Scheme 7*). Unfortunately, these oily compounds decomposed during the attempted chromatographic purifications. Therefore, their yields were determined by ^{1}H-NMR measurements with 1,1,2,2-tetrachloroethane as an internal standard.

Scheme 7



2

16a R = Me
b R = Et
c R = Ph
d R = 2,4,6-Trimethylphenyl

The reactions with ^{i}PrOH and ^{t}BuOH, as well as with their alkoxides, led to complex mixtures of mainly decomposition products, and the spectroscopic analysis of the crude mixture gave no hint for the presence of the expected products of type **16**. With 2,4,6-trimethylphenol as the nucleophile, the conversion proceeded again with a high yield of the crude solid product **16d**, which was purified by crystallization. Furthermore, its structure was established by X-ray crystallography (*Fig. 2*).

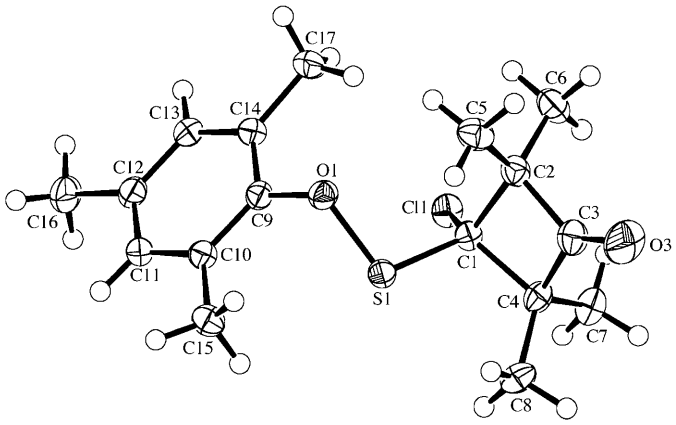
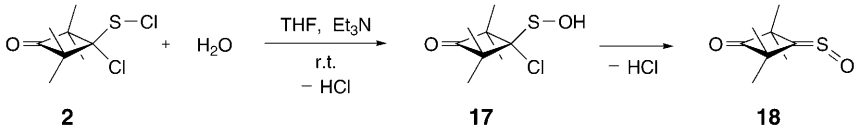


Fig. 2. *ORTEP Plot* [5] *of the molecular structure of* **16d** (arbitrary numbering of atoms; 50% probability ellipsoids)

The reaction of **2** with H_2O, using THF as the solvent instead of the usually applied CH_2Cl_2, led to the expected sulfine **18**, which was formed by consecutive substitution of Cl at the S-atom to give **17**, followed by HCl elimination (*Scheme 8*). The known **18** [32], a thiocarbonyl *S*-oxide, was purified by crystallization.

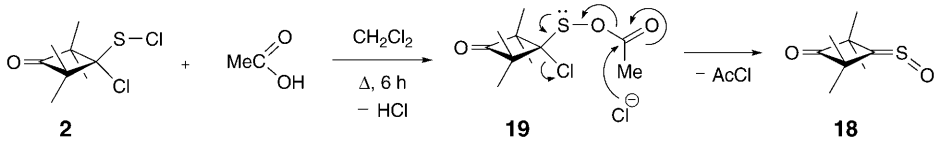
Scheme 8



2 **17** **18**

With AcOH and **2** in CH_2Cl_2, no reaction was observed at room temperature. At higher temperature, *i.e.*, in boiling CH_2Cl_2, **18** was formed again as the main product, probably *via* elimination of AcCl from the initially formed substitution product **19** (*Scheme 9*).

Scheme 9



2 **19** **18**

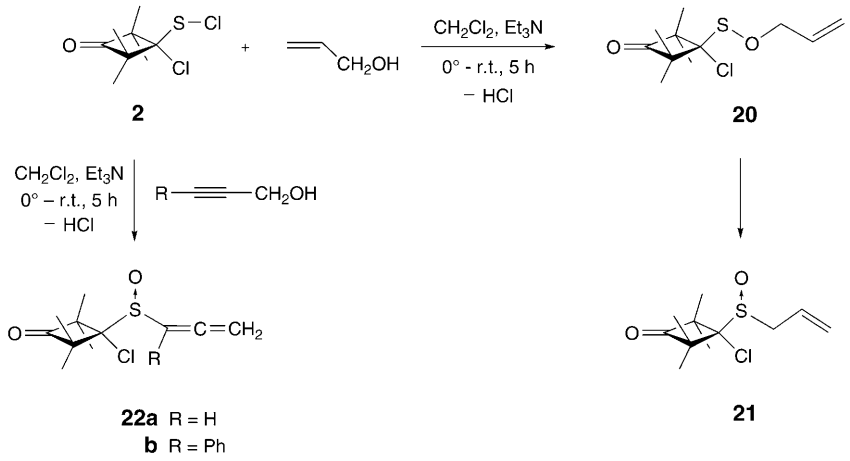
Of special interest are the conversions of **2** with allyl and propargyl alcohols (*Scheme 10*). In these cases, the initially formed substitution products of type **20**, *i.e.*, allyl and allenyl sulfenates, respectively, could undergo a [2,3]-sigmatropic rearrangement to give the corresponding sulfoxides. Such reactions using simple sulfanyl chlorides, have been published by *Raj et al.* [33], and *Scheufler* and *Maier* [34] (for earlier work see refs. cit. in [33][34], and *e.g.*, [35][36]).

Indeed, the reactions of **2** with allyl alcohol, propargyl alcohol, and 3-phenylprop-2-yn-1-ol led to the rearranged products, the sulfoxides **21**, **22a**, and **22b**, respectively[3]) (*Scheme 10*). After purification by either chromatography or crystallization, the products were obtained as colorless oils or crystals. Due to the newly formed stereogenic center at the S-atom, the cyclobutane core bears, instead of pair-wise diastereotopic Me groups of the starting material or the primary substitution product, four diastereotopic Me groups. Therefore, the rearranged products are easily distinguishable from the initially formed substitution products by NMR spectroscopy.

In a second series of experiments, chlorodisulfanyl compound **3** was reacted with three representative O nucleophiles. With MeOH, the reaction proceeded smoothly to give **23a** as a colorless oil (*Scheme 11*). Due to decomposition during the purification process, the yield could only be determined by NMR measurement with an internal standard. As in the case of **2**, the reaction of **3** with 2,4,6-trimethylphenol occurred

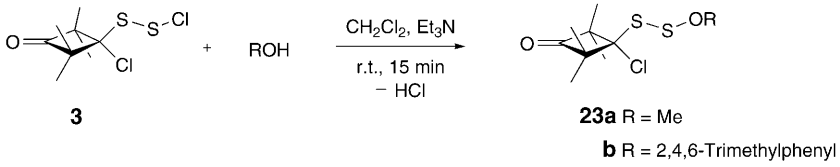
[3]) With cinnamyl alcohol as the nucleophile, a mixture of decomposition products was obtained.

Scheme 10



smoothly to yield **23b** as a colorless solid, which was purified by recrystallization. On the other hand, the attempted conversion of **3** with propargyl alcohol to give the corresponding rearranged product (*cf. Scheme 10*) was unsuccessful, as neither one of the expected products, *i.e.*, the primarily formed substitution products of type **23** (R = HC≡C–CH_2) and its rearranged disulfanyl *S*-monoxide, could be detected[4]).

Scheme 11



2.3. *Reactions of* **2** *and* **3** *with P Nucleophiles.* Reactions of P nucleophiles with simple sulfanyl chlorides are well-known. Among others, conversions with dialkyl [38], trialkyl [39][40], disilyl [41], and trisilyl phosphites [42], as well as with related compounds [43][44], have been described. In the present study, dialkyl (or diaryl) and trialkyl phosphites were used as nucleophiles in the reactions with **2** and **3**. Both types of nucleophiles should lead to the same products, as has already been shown with a sulfanyl chloride, which is similar to **2** [45].

Dialkyl (or diaryl) phosphites may exist in two tautomeric forms, in one of which the P-atom bears a lone electron pair. It, therefore, possesses nucleophilic properties and can attack the S-atom of the sulfanyl chlorides by replacing Cl in a S_N2 reaction. After deprotonation of the phosphonium ion **24**, the corresponding thiophosphate **25** is formed (*Scheme 12*).

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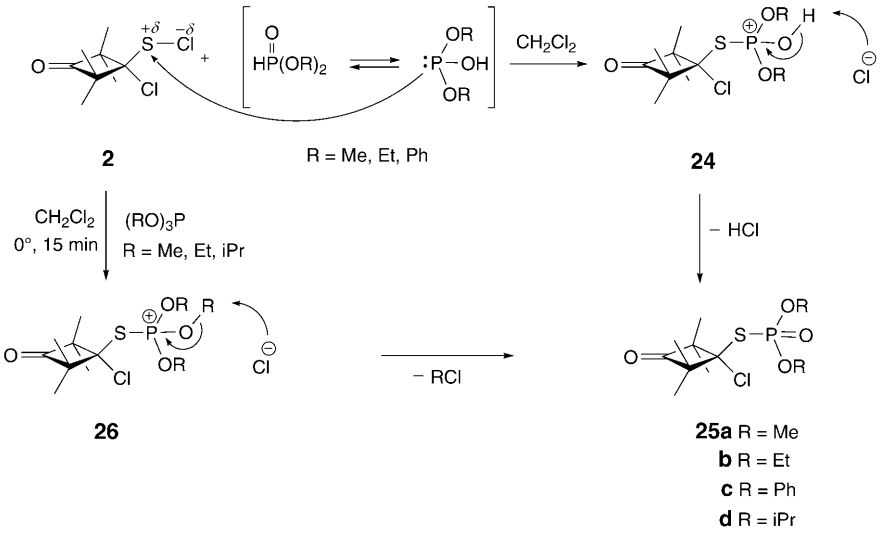
[4]) Several disulfanyl *S*-monoxides have been isolated as stable compounds (see, *e.g.*, [37]).

Scheme 12



The reaction of **2** in CH_2Cl_2 at 0° was carried out with dimethyl, diethyl, and diphenyl phosphites. In the first two cases, a quantitative conversion to the expected products **25a** and **25b** was observed, and they could be isolated in good yields after crystallization (*Scheme 12*). It is worth mentioning that no base is needed for a complete conversion. The reaction of **2** with diphenyl phosphite proceeded less smoothly, however, and **25c** was obtained in 35% yield after crystallization.

When trialkyl phosphites were used instead of the dialkyl derivatives, the same products **25** were obtained. Their formation follows a similar reaction pathway *via* intermediate **26** as found for the *Michaelis–Arbuzov* reaction. The reaction with trimethyl and triethyl phosphites gave **25a** and **25b**, again in high yields (*Scheme 12*). However, the yield of the product of the reaction with triisopropyl phosphite, **25d**, was significantly lower. This product could be purified by recrystallization, and its structure was established by X-ray crystallography (*Fig. 3*).

Similar reactions were carried out with chlorodisulfanyl compound **3**, but, in these cases, only mixtures of compounds were formed that could neither be separated nor identified. Although the reaction conditions were varied significantly, no products could be isolated. Only in one experiment with a tenfold excess of triethyl phosphite, one main product was formed, which could be isolated by crystallization. Unexpectedly, this product proved to be **25b**, identical with the product of the reaction of triethyl phosphite with **2** (*Scheme 13*).

This result can be explained by the following mechanism: upon substitution of Cl by the phosphite, the corresponding phosphonium ion **27** is formed. Two pathways are possible for the stabilization of this compound: *a*) attack of Cl at one of the EtO groups would lead to the *Michaelis–Arbuzov* product, in analogy to the reaction with **2**; *b*) an additional phosphite molecule may attack the second S-atom, in analogy to the initial reaction of Ph_3P with dipyridyl disulfide in the *Corey–Nicolaou* lactonization

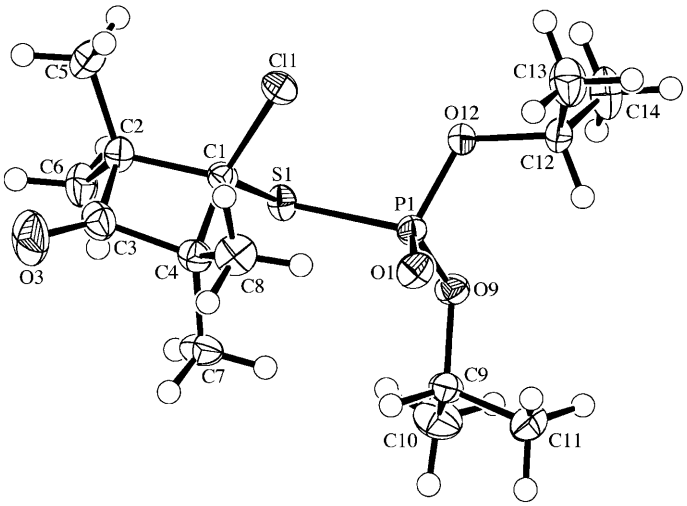
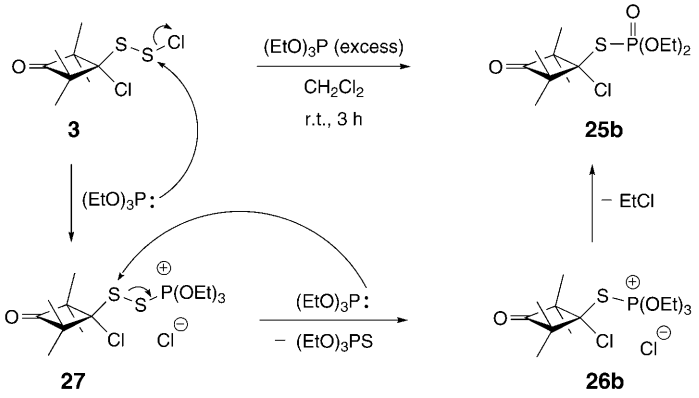


Fig. 3. *ORTEP Plot* [5] *of the molecular structure of* **25d** (arbitrary numbering of atoms; 50% probability ellipsoids)

Scheme 13



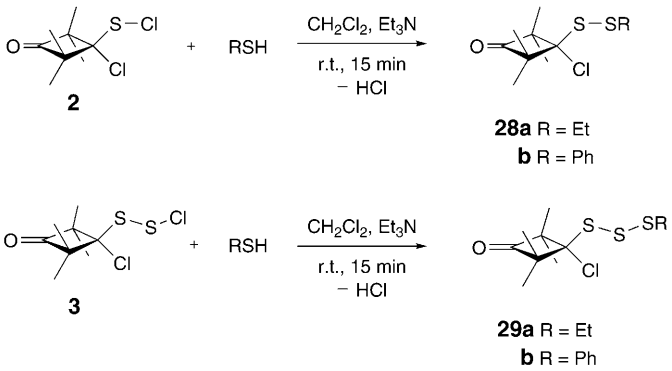
[46][47] and similar reactions, and triethoxy thiophosphate is released as the leaving group. Stabilization of the newly formed phosphonium ion **26b** now occurs in an *Michaelis–Arbuzov* reaction, as depicted in *Scheme 12*. The mass spectrum of the crude reaction mixture indeed confirmed the presence of the proposed triethyl thiophosphate. This reaction pathway is certainly favored by the huge excess of the phosphite.

2.4. *Reactions of* **2** *and* **3** *with S Nucleophiles.* The reaction of sulfanyl chlorides with S nucleophiles represents a standard method for the elongation of the S-chain in polysulfanes [48][49]. The application of thiocarbonyl compounds as nucleophiles has been described recently [50][51], and the reaction of thioacetic *S*-acid with **2** and **3** [2], as well as with a similar sulfanyl chloride [45], was already mentioned in the introduction

(*Scheme 1*). The resulting esters were used for the synthesis of S-rich heterocycles. Therefore, only a few reactions should be performed in this study to elucidate if SH compounds are appropriate nucleophiles for reactions with **2** and **3**.

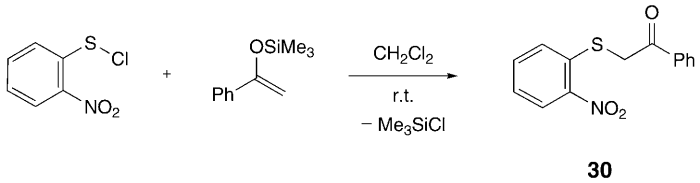
A thiol and a thiophenol, EtSH and PhSH, respectively, have been selected as reagents. Both reactions with either **2** or **3** proceeded very smoothly and led, in quantitative yield, to almost pure products. An additional purification by means of chromatography was not possible due to decomposition; however, crystallization was successful in the cases of **28b** and **29b** (*Scheme 14*). In conclusion, thioles and thiophenols are convenient nucleophiles in reactions with **2** and **3** to give the corresponding di- and trisulfanes, respectively.

Scheme 14



2.5. *Attempted Reactions of* **2** *and* **3** *with C Nucleophiles.* In the last section, reactions of **2** and **3** with selected C nucleophiles were investigated. For this purpose, organolithium and *Grignard* compounds, silyl enol ethers, enolates of carbonyl and β-dicarbonyl compounds, cyanide, and CH_2N_2 have been applied. Silyl enol ethers should be convenient enol equivalents to react with **2** and **3**, as no bases are required. As a reference reaction, the trimethylsilyl enol ether of acetophenone was treated with commercially available *o*-nitrophenylsulfanyl chloride. Even without the addition of a *Lewis* acid, the expected product **30** was obtained in good yield [52] (*Scheme 15*).

Scheme 15



Under the same conditions, **2** did not undergo a reaction. Additional experiments with different *Lewis* acids and under various conditions only led to the formation of acetophenone and decomposition products, but not to the desired sulfane. Unfortunately, the result could not be improved by using other C nucleophiles. The desired sul-

fane could not be isolated with NaCN, CH_2N_2, MeMgBr, (trifluoromethyl)trimethylsilane (*Ruppert*'s reagent [53–55]) nor with the enolates of *N*-methyl-*N*-phenylacetamide or β-dicarbonyl compounds (dimethyl malonate, acetylacetone). Besides unconverted starting material, only decomposition or side products (*e.g.*, **1** and **18**) were obtained in small amounts[5]). The analogous reactions with **3** led to similar results and only decomposition products were obtained. Therefore, chlorosulfanyl compounds **2** and **3** are not appropriate substrates to react with C nucleophiles.

3. Conclusions. – It has been shown that the chlorosulfanyl compounds **2** and **3** undergo substitution reactions at the S-atom with various nucleophiles and, therefore, are convenient building blocks for the synthesis of several organosulfur compounds. In the case of **2**, the reactions with N, O, S, and P nucleophiles occur smoothly, and the products are stable if no subsequent HCl elimination is possible. In the reactions with primary amines and H_2O, HCl elimination in the initially formed substitution products leads to reactive thiocarbonyl *S*-imides and the stable thiocarbonyl *S*-oxide (a sulfine), respectively. The intermediate thiocarbonyl *S*-imides formed in the reactions with primary amines can be detected by interception with either MeOH or adamantanethione. Unexpectedly, the reactions of **2** and **3** with C nucleophiles do not lead to the expected substitution products.

Experimental Part

1. *General*. See [57]. M.p.: *Mettler-FP-5* or *Büchi B-450* apparatus; uncorrected. IR Spectra: *Perkin-Elmer 781* or *Perkin-Elmer 1600-FT-IR* spectrophotometer. ^{1}H- and ^{13}C-NMR spectra: *Bruker AC-300* or *Bruker ARX-300* instrument (300 and 75.5 MHz, resp.) or *Bruker DRX-600* instrument (600 and 150.9 MHz, resp.), in $CDCl_3$; multiplicities of the C-atoms determined with DEPT technique. MS: *Finnigan MAT-90* or *Finnigan SSQ-700* instrument (CI (NH_3)). Elemental analyses were performed by the Mikroanalytisches Laboratorium des Organisch-Chemischen Instituts der Universität Zürich.

2. *Reactions of* **2** *and* **3** *with N Nucleophiles*. 2.1. *Reactions with Secondary Amines. General Procedure.* To a soln. of *3-chloro-3-(chlorosulfanyl)-2,2,4,4-tetramethylcyclobutanone* (**2**; 113.5 mg, 0.5 mmol) or *3-chloro-3-(chlorodisulfanyl)-2,2,4,4-tetramethylcyclobutanone* (**3**; 130 mg, 0.5 mmol) in Et_2O (3 ml) at 0° was added the respective secondary amine (1 mmol). The yellow color of the mixture disappeared immediately, and a precipitate formed. After stirring for 60 min, the inorg. salts were removed by filtration, and the solvent was evaporated to yield the product as an oily substance. If possible, the oil was further purified by trituration and crystallization.

3-Chloro-2,2,4,4-tetramethyl-3-[(morpholin-4-yl)sulfanyl]cyclobutanone (**6a**). Reaction of **2** with morpholine. Yield: 97 mg (70%). Colorless crystals. M.p. 63–65° (hexane). IR (neat): 2966*m*, 2915*m*, 2858*s*, 2338*m*, 1788v*s*, 1465*w*, 1453*w*, 1138*w*, 1111*s*, 1095*m*, 909*w*, 833*w*. ^{1}H-NMR: 1.34 (*s*, 2 Me); 1.35 (*s*, 2 Me); 3.10 (*t*, J = 4.6, 2 CH_2N); 3.62 (*t*, J = 4.7, 2 CH_2O). ^{13}C-NMR: 22.0 (*q*, 2 Me); 23.3 (*q*, 2 Me); 57.5 (*t*, 2 CH_2N); 67.5 (*t*, 2 CH_2O); 69.5 (*s*, 2 Me_2C); 84.3 (*s*, SCCl); 217.1 (*s*, C=O). CI-MS: 280 (36, $[M(^{37}Cl)+1]^+$), 278 (97, $[M(^{35}Cl)+1]^+$), 242 (75, $[M-Cl]^+$), 88 (100, $[C_4H_9NO+1]^+$).

Suitable crystals for the X-ray crystal-structure determination were obtained from hexane at −40°.

3-Chloro-2,2,4,4-tetramethyl-3-[(piperidin-1-yl)sulfanyl]cyclobutanone (**6b**). Reaction of **2** with piperidine. Yield: 85 mg (62%). Colorless oil. IR (neat): 2997*m*, 2974*m*, 2938*s*, 2912*m*, 1789*m*, 1468v*s*, 1385*s*, 1370*s*, 1112*w*, 1089*m*, 1049*m*, 976*w*, 954*w*, 916*w*, 827*s*, 801*m*. ^{1}H-NMR: 1.39 (*s*, 2 Me); 1.45 (*s*, 2

[5]) In a control experiment, the known reaction of *o*-nitrophenylsulfanyl chloride with diethyl malonate [56] was successfully repeated.

Me); 1.56–1.61 (*m*, 3 CH_2); 3.12 (*t*, *J* = 5.3, 2 CH_2N). ^{13}C-NMR: 22.0 (*q*, 2 Me); 23.2 (*q*, 2 Me); 23.5 (*t*, CH_2); 27.0 (*t*, 2 CH_2); 58.8 (*t*, 2 CH_2N); 68.0 (*s*, 2 Me_2C); 89.7 (*s*, SCCl); 217.8 (*s*, C=O). CI-MS: 276 (60, $[M(^{35}Cl)+1]^+$), 240 (100, $[M-Cl]^+$), 86 (10, $[C_5H_{11}N+1]^+$).

3-Chloro-2,2,4,4-tetramethyl-3-[(pyrrolidin-1-yl)sulfanyl]cyclobutanone (**6c**). Reaction of **2** with pyrrolidine. Yield: 110 mg (84%). Colorless oil. IR (neat): 2997*w*, 2967*m*, 2935*s*, 2869*m*, 1785v*s*, 1465*m*, 1382*w*, 1365*w*, 1173*w*, 1137*w*, 1028*m*, 980*w*, 915*w*, 887*w*, 834*w*. ^{1}H-NMR: 1.39 (*s*, 2 Me); 1.43 (*s*, 2 Me); 1.78–1.82 (*m*, 2 CH_2); 3.19–3.23 (*m*, 2 CH_2N). ^{13}C-NMR: 21.7 (*q*, 2 Me); 23.2 (*q*, 2 Me); 25.6 (*t*, 2 CH_2); 57.4 (*t*, 2 CH_2N); 67.7 (*s*, 2 Me_2C); 89.5 (*s*, SCCl); 217.8 (*s*, C=O). CI-MS: 262 (83, $[M(^{35}Cl)+1]^+$), 226 (100, $[M-Cl]^+$), 70 (10).

3-Chloro-3-[(diethylamino)sulfanyl]-2,2,4,4-tetramethylcyclobutanone (**6d**). Reaction of **2** with Et_2NH. Yield: 102 mg (78%). Colorless oil. IR (neat): 2997*w*, 2964*w*, 2932*m*, 2867*m*, 1785v*s*, 1465*m*, 1382*w*, 1366*w*, 1170*w*, 1027*m*, 917*w*, 834*w*. ^{1}H-NMR: 1.05 (*t*, *J* = 7.1, 2 $MeCH_2$); 1.28 (*s*, 2 Me); 1.37 (*s*, 2 Me); 3.09 (*q*, *J* = 7.1, 2 CH_2N). ^{13}C-NMR: 13.1 (*q*, 2 $MeCH_2$); 21.4 (*q*, 2 Me); 21.7 (*q*, 2 Me); 51.3 (*t*, 2 CH_2N); 66.9 (*s*, 2 Me_2C); 89.3 (*s*, SCCl); 217.1 (*s*, C=O). CI-MS: 264 (54, $[M(^{35}Cl)+1]^+$), 228 (100, $[M-Cl]^+$), 74 (6, $[C_4H_{11}N+1]^+$).

3-Chloro-2,2,4,4-tetramethyl-3-[(morpholin-4-yl)disulfanyl]cyclobutanone (**7a**). Reaction of **3** with morpholine. Yield: 119 mg (79%). Colorless crystals. M.p. 58–60° (hexane). IR (neat): 2973*m*, 2921*m*, 2859*s*, 2338*m*, 1786v*s*, 1465*w*, 1453*w*, 1382*w*, 1138*w*, 1366*w*, 1112*s*, 1098*m*, 931*w*, 838*w*. ^{1}H-NMR: 1.42 (*s*, 2 Me); 1.43 (*s*, 2 Me); 3.04 (*t*, *J* = 4.8, 2 CH_2N); 3.70 (*t*, *J* = 4.8, 2 CH_2O). ^{13}C-NMR: 23.3 (*q*, 2 Me); 23.4 (*q*, 2 Me); 56.2 (*t*, 2 CH_2N); 67.0 (*t*, 2 CH_2O); 69.2 (*s*, 2 Me_2C); 84.0 (*s*, SCCl); 216.5 (*s*, C=O). CI-MS: 310 (4, $[M(^{35}Cl)+1]^+$), 278 (5), 242 (5), 88 (65, $[C_4H_9NO+1]^+$), 86 (100, $C_4H_8NO^+$).

Suitable crystals for the X-ray crystal-structure determination were obtained from hexane at −40°.

3-Chloro-2,2,4,4-tetramethyl-3-[(piperidin-1-yl)disulfanyl]cyclobutanone (**7b**). Reaction of **3** with piperidine. Yield: 103 mg (67%). Colorless oil. IR (neat): 2999*m*, 2972*m*, 2938*s*, 2910*m*, 2870*w*, 1793*m*, 1469v*s*, 1383*s*, 1370*s*, 1112*w*, 1098*m*, 1048*m*, 972*w*, 953*w*, 916*w*, 829*s*, 802*m*. ^{1}H-NMR: 1.41 (*s*, 2 Me); 1.43 (*s*, 2 Me); 1.59–1.66 (*m*, 3 CH_2); 3.02 (*t*, *J* = 5.6, 2 CH_2N). ^{13}C-NMR: 22.6 (*t*, CH_2); 23.4 (*q*, 2 Me); 23.5 (*q*, 2 Me); 26.8 (*t*, 2 CH_2); 58.0 (*t*, 2 CH_2N); 69.2 (*s*, 2 Me_2C); 84.1 (*s*, SCCl); 217.1 (*s*, C=O). CI-MS: 308 (31, $[M(^{35}Cl)+1]^+$), 240 (25), 84 (100, $C_5H_{10}N^+$).

3-Chloro-2,2,4,4-tetramethyl-3-[(pyrrolidin-1-yl)disulfanyl]cyclobutanone (**7c**). Reaction of **3** with pyrrolidine. Yield: 118 mg (80%). Colorless oil. IR (neat): 2998*w*, 2965*m*, 2934*s*, 2868*m*, 1786v*s*, 1465*m*, 1383*w*, 1364*w*, 1174*w*, 1136*w*, 1029*m*, 980*w*, 915*w*, 889*w*, 835*w*. ^{1}H-NMR: 1.42 (*s*, 4 Me); 1.80–1.84 (*m*, 2 CH_2); 3.12–3.14 (*m*, 2 CH_2N). ^{13}C-NMR: 23.4 (*q*, 4 Me); 25.7 (*t*, 2 CH_2); 55.3 (*t*, 2 CH_2N); 69.1 (*s*, 2 Me_2C); 84.3 (*s*, SCCl); 217.0 (*s*, C=O). CI-MS: 294 (7, $[M(^{35}Cl)+1]^+$), 226 (6), 70 (100, $C_4H_8N^+$).

3-Chloro-3-[(diethylamino)disulfanyl]-2,2,4,4-tetramethylcyclobutanone (**7d**). Reaction of **3** with Et_2NH. Yield: 128 mg (87%). Colorless oil. IR (neat): 2996*w*, 2971*m*, 2935*m*, 2868*m*, 1785v*s*, 1465*m*, 1382*m*, 1365*w*, 1168*w*, 1027*m*, 914*w*, 829*w*. ^{1}H-NMR: 1.20 (*t*, *J* = 7.1, 2 $MeCH_2$); 1.42 (*s*, 2 Me); 1.44 (*s*, 2 Me); 3.01 (*q*, *J* = 7.1, 2 CH_2N). ^{13}C-NMR: 13.7 (*q*, 2 $MeCH_2$); 23.3 (*q*, 2 Me); 23.5 (*q*, 2 Me); 52.0 (*t*, 2 CH_2N); 69.1 (*s*, 2 Me_2C); 84.2 (*s*, SCCl); 217.1 (*s*, C=O). CI-MS: 296 (2, $[M(^{35}Cl)+1]^+$), 228 (2), 72 (100, $C_4H_{10}N^+$).

2.2. *Reactions with Primary Amines. 3-{[(*tert*-Butyl)amino]sulfanyl}-3-methoxy-2,2,4,4-tetramethylcyclobutanone* (**11**). To a soln. of **2** (113.5 mg, 0.5 mmol) in CH_2Cl_2 (3 ml) at 0° was added ^{t}BuNH$_2$ (73 mg, 1 mmol). After stirring for 10 min at 0°, 0.5 ml of MeOH was added, and stirring was continued for 60 min at r.t. Then, the solvent was evaporated, and, after addition of of Et_2O (5 ml), the insoluble residue was removed by filtration. Evaporation of the solvent yielded 111 mg (86%) of **11**. Colorless oil. ^{1}H-NMR: 1.19 (*s*, 3 Me); 1.34 (*s*, 2 Me); 1.35 (*s*, 2 Me); 2.12 (*s*, NH); 3.52 (*s*, MeO). ^{13}C-NMR: 20.9 (*q*, 2 Me); 21.2 (*q*, 2 Me); 29.8 (*q*, 3 Me); 53.9 (*s*, MeO); 66.3 (*s*, 2 Me_2C); 96.0 (*s*, S*C*OMe); 220.4 (*s*, C=O). CI-MS: 260 (11, $[M(^{35}Cl)+1]^+$), 187 (100, $[M-{}^t$BuNH$]^+$).

Reaction of **2** *with* ^{t}*BuNH*$_2$ *in the presence of Adamantanethione.* To a soln. of **2** (113.5 mg, 0.5 mmol) in CH_2Cl_2 (3 ml) at 0° was added ^{t}BuNH$_2$ (73 mg, 1 mmol). After stirring for 10 min at 0°, adamantanethione (166 mg, 1 mmol) and ^{t}BuNH$_2$ (37 mg, 0.5 mmol) were added, and stirring was continued for 60 min at r.t. Then, the solvent was evaporated, and the mixture was separated by prep. TLC (SiO_2, CH_2Cl_2/hexane 1:1). Only **14** (80 mg, 44%) [24] and decomposition products were obtained.

*3-[[(*tert*-Butyl)amino]disulfanyl}-3-chloro-2,2,4,4-tetramethylcyclobutanone* (**15a**). To a soln. of **3** (130 mg, 0.5 mmol) in Et_2O (3 ml) at 0° was added ^{t}BuNH$_2$ (73 mg, 1 mmol). The color of the mixture changed from yellow to red, and a precipitate formed. After stirring for 60 min, the inorg. salts were removed by filtration, and the solvent was evaporated to yield **15a** (102 mg, 69%). Colorless oil. IR (neat): 3368*m*, 2994*w*, 2973*m*, 2933*m*, 2868*m*, 1788v*s*, 1464*m*, 1385*m*, 1365*w*, 1167*w*, 1025*m*, 915*w*, 829*w*. ^{1}H-NMR: 1.21 (*s*, 3 Me); 1.41 (*s*, 2 Me); 1.46 (*s*, 2 Me); 3.60 (*s*, NH). ^{13}C-NMR: 22.7 (*q*, 2 Me); 23.5 (*q*, 2 Me); 29.5 (*q*, 3 Me); 56.0 (*s*, Me_3C); 69.1 (*s*, 2 Me_2C); 91.0 (*s*, SCCl); 217.1 (*s*, C=O). CI-MS: 298 (42, $[M(^{37}Cl)+1]^+$), 296 (100, $[M(^{35}Cl)+1]^+$), 175 (18), 74 (15, $[C_4H_{11}N+1]^+$).

3-Chloro-2,2,4,4-tetramethyl-3-[(phenylamino)disulfanyl]cyclobutanone (**15b**). Analogous to the reaction with ^{t}BuNH$_2$, **3** was treated with PhNH$_2$ (93 mg, 1 mmol), leading to **15b** (112 mg, 71%). Yellow oil. IR (neat): 3368*m*, 2973*m*, 2923*m*, 2868*w*, 1789v*s*, 1610*s*, 1553*s*, 1474*m*, 1389*w*, 1352*w*, 1293w, 1248*m*, 1172*w*, 1039*m*, 913*w*, 843*w*. ^{1}H-NMR: 1.40 (*s*, 2 Me); 1.43 (*s*, 2 Me); 5.60 (*s*, NH); 7.33–6.94 (*m*, 5 arom. H). ^{13}C-NMR: 22.9 (*q*, 2 Me); 23.4 (*q*, 2 Me); 69.2 (*s*, 2 Me_2C); 89.9 (*s*, SCCl); 116.9, 122.1, 129.2 (3*d*, 5 arom. CH); 144.6 (*s*, arom. C); 216.4 (*s*, C=O). CI-MS: 318 (14, $[M(^{37}Cl)+1]^+$), 316 (35, $[M(^{35}Cl)+1]^+$), 280 (100, $[M-Cl]^+$), 94 (21, $[C_6H_7N+1]^+$).

3. *Reactions of* **2** *and* **3** *with O Nucleophiles. General Procedure.* To a soln. of **2** (113.5 mg, 0.5 mmol) or **3** (130 mg, 0.5 mmol) in CH_2Cl_2 (3 ml) at 0° was added the respective O nucleophile (0.5 mmol). After stirring for 10 min at r.t., Et_3N (50.6 mg, 0.5 mmol) was added slowly, and stirring was continued for 60 min. Then, the solvent was evaporated, and, after addition of 5 ml of Et_2O, the insoluble residue was removed by filtration. Evaporation of the solvent yielded the product as an oily substance.

3-Chloro-3-[(methoxy)sulfanyl]-2,2,4,4-tetramethylcyclobutanone (**16a**). Reaction of **2** with MeOH. Yield: 92% (estimated by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as internal standard). Colorless oil. IR (neat): 2978*s*, 2937*m*, 2873*m*, 1789v*s*, 1770*m*, 1464*s*, 1381*w*, 1362*w*, 1246*w*, 1178*m*, 1134*m*, 1028*s*, 917*m*, 887*m*, 838*m*, 793*w*, 742*w*. ^{1}H-NMR: 1.37 (*s*, 2 Me); 1.45 (*s*, 2 Me); 3.89 (*s*, MeO). ^{13}C-NMR: 20.2 (*q*, 2 Me); 24.0 (*q*, 2 Me); 67.3 (*q*, MeO); 68.6 (*s*, 2 Me_2C); 89.1 (*s*, SCCl); 216.3 (*s*, C=O). CI-MS: 187 (100, $[M-Cl]^+$), 188 (10), 155 (8).

3-Chloro-3-[(ethoxy)sulfanyl]-2,2,4,4-tetramethylcyclobutanone (**16b**). Reaction of **2** with EtOH. Yield: 88% (estimated by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as internal standard). Colorless oil. IR (neat): 2975v*s*, 2934*s*, 2868*m*, 1790v*s*, 1464*s*, 1383*m*, 1366*w*, 1245*w*, 1169*m*, 1135*m*, 1026*s*, 914*m*, 884*m*, 836*m*, 792*w*, 738*w*. ^{1}H-NMR: 1.27 (*t*, $J=7.0$, *Me*CH_2); 1.39 (*s*, 2 Me); 1.45 (*s*, 2 Me); 4.01 (*q*, $J=7.0$, MeCH_2O). ^{13}C-NMR: 16.1 (*q*, *Me*CH_2); 20.3 (*q*, 2 Me); 24.4 (*q*, 2 Me); 68.5 (*s*, 2 Me_2C); 75.8 (*t*, MeCH_2O); 89.1 (*s*, SCCl); 216.4 (*s*, C=O). CI-MS: 239 (36, $[M(^{37}Cl)+1]^+$), 237 (100, $[M(^{35}Cl)+1]^+$), 201 (47), 191 (47), 166 (21), 163 (20), 131 (19).

3-Chloro-2,2,4,4-tetramethyl-3-[(phenoxy)sulfanyl]cyclobutanone (**16c**). Reaction of **2** with PhOH. Yield: 84% (estimated by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as internal standard). Colorless oil. IR (neat): 3383*s* (br.), 2973*s*, 2932*m*, 1784*s*, 1598*s*, 1583*s*, 1493v*s*, 1463*s*, 1381*w*, 1365*m*, 1263*m*, 1026*w*, 917*m*, 826*s*, 755*w*. ^{1}H-NMR: 1.43 (*s*, 2 Me); 1.44 (*s*, 2 Me); 7.06–7.31 (*m*, 5 arom. H). ^{13}C-NMR: 20.4 (*q*, 2 Me); 23.8 (*q*, 2 Me); 68.7 (*s*, 2 Me_2C); 88.4 (*s*, SCCl); 117.5, 123.4, 129.2 (3*d*, 5 arom. CH); 160.4 (*s*, Ph); 215.9 (*s*, C=O). CI-MS: 249 (100, $[M-Cl]^+$), 250 (16).

3-Chloro-2,2,4,4-tetramethyl-3-{[(2,4,6-trimethylphenyl)oxy]sulfanyl}cyclobutanone (**16d**). Reaction of **2** with 2,4,6-trimethylphenol. Yield: 104 mg (64%). Colorless crystals. M.p. 53–55° (hexane). IR (ATR): 2980*w*, 2964*m*, 2930*m*, 1785v*s*, 1769*s*, 1473*m*, 1458*s*, 1380*w*, 1364*m*, 1242*w*, 1190*s*, 1124v*s*, 1027*m*, 953*w*, 887*w*, 854*s*, 803v*s*, 781*m*, 741*m*, 676*w*. ^{1}H-NMR: 1.41 (*s*, 2 Me); 1.48 (*s*, 2 Me); 2.21 (*s*, *p*-*Me*C_6H_2); 2.37 (*s*, 2 *o*-*Me*C_6H_2); 6.76 (*s*, 2 arom. H). ^{13}C-NMR: 15.8 (*q*, 2 *o*-*Me*C_6H_2); 20.4 (*q*, 2 Me); 20.6 (*q*, *p*-*Me*C_6H_2); 24.4 (*q*, 2 Me); 68.9 (*s*, 2 Me_2C); 87.8 (*s*, SCCl); 129.5 (*s*, 2 arom. C); 129.6 (*d*, 2 arom. CH); 133.9, 155.2 (2*s*, 2 arom. C); 216.0 (*s*, C=O). CI-MS: 291 (27, $[M-Cl]^+$), 287 (39), 191 (21), 153 (23), 152 (53), 135 (100), 136 (61).

Suitable crystals for the X-ray crystal-structure determination were obtained from hexane at −40°.

3-Chloro-2,2,4,4-tetramethyl-3-[(propa-1,2-dien-1-yl)sulfanyl]cyclobutanone S-*Oxide* (**22a**). Reaction of **2** with propargyl alcohol. Yield: 27 mg (11%). Colorless crystals. M.p. 74–75° (hexane). IR (ATR): 3047*m*, 2963*m*, 1931*m*, 1772v*s*, 1456*s*, 1443*m*, 1383*w*, 1366*m*, 1247*w*, 1167*m*, 1139*m*, 1114*w*, 1065*s*, 1052v*s*, 1022*s*, 929*w*, 889*s*, 853*m*, 845*m*, 796*m*, 760*w*. ^{1}H-NMR: 1.34 (*s*, Me); 1.39 (*s*, Me); 1.44 (*s*, Me); 1.78 (*s*, Me); 5.2–5.4 (*m*, CH_2=C); 6.30 (*t*, $J=6.3$, CH=C). ^{13}C-NMR: 21.1 (*q*, Me); 21.3 (*q*,

Me); 22.4 (*q*, Me); 22.9 (*q*, Me); 65.9 (*q*, Me_2C); 69.0 (*s*, Me_2C); 82.0 (*t*, CH_2=C); 90.1 (*s*, SCCl); 96.5 (*d*, CH=C); 209.4 (*s*, CH=C=CH_2); 214.2 (*s*, C=O). CI-MS: 266 (38, $[M(^{37}Cl)+NH_4]^+$), 264 (100, $[M(^{35}Cl)+NH_4]^+$), 247 (13, $[M(^{35}Cl)+1]^+$), 190 (11).

3-Chloro-2,2,4,4-tetramethyl-3-[(1-phenylpropa-1,2-dien-1-yl)sulfanyl]cyclobutanone S-*Oxide* (**22b**). Reaction of **2** with 3-phenylprop-2-yn-1-ol. Yield: 103 mg (57%). Colorless crystals. M.p. 54–58° (hexane). IR (ATR): 3059*m*, 2986*m*, 2972*m*, 2906*w*, 2866*w*, 1958*m*, 1922*w*, 1788v*s*, 1489*m*, 1463*m*, 1443*s*, 1425*m*, 1382*m*, 1365*m*, 1243*m*, 1170*m*, 1136*w*, 1109*w*, 1080*s*, 1019*s*, 979*m*, 935*w*, 912*m*, 875*s*, 828*w*, 765*s*, 707*s*, 700*s*, 660*m*. ^{1}H-NMR: 1.34 (*s*, Me); 1.41 (*s*, Me); 1.46 (*s*, Me); 1.87 (*s*, Me); 5.61, 5.72 (*AB*, *J* = 13.6, CH_2=C); 7.31–7.48 (*m*, 5 arom. H). ^{13}C-NMR: 22.4 (*q*, Me); 22.5 (*q*, Me); 22.8 (*q*, Me); 23.9 (*q*, Me); 65.9 (*q*, Me_2C); 69.9 (*s*, Me_2C); 85.4 (*t*, CH_2=C); 87.8 (*s*, SCCl); 93.6 (*d*, CH=C); 128.3, 128.8, 129.2 (3*d*, 5 arom. CH); 131.6 (*s*, arom. C); 209.4 (*s*, CH=C=CH_2); 214.2 (*s*, C=O). CI-MS: 323 (12, $[M(^{35}Cl)+1]^+$), 287 (100, $[M-Cl]^+$), 259 (22), 132 (24), 115 (18).

3-Chloro-2,2,4,4-tetramethyl-3-[(prop-2-enyl)sulfanyl]cyclobutanone S-*Oxide* (**21**). Reaction of **2** with allyl alcohol. Yield: 76 mg (61%). Colorless crystals. M.p. 56–57° (hexane). IR (ATR): 3088*w*, 2976*m*, 2936*w*, 2871*w*, 1791v*s*, 1777v*s*, 1637*w*, 1463*m*, 1447*m*, 1420*w*, 1382*m*, 1368*m*, 1247*w*, 1174*w*, 1083*m*, 1046v*s*, 1022*m*, 987*m*, 961*w*, 931*m*, 891*w*, 864*m*, 835*w*, 793*w*, 724*w*. ^{1}H-NMR: 1.36 (*s*, Me); 1.39 (*s*, Me); 1.47 (*s*, Me); 1.78 (*s*, Me); 3.35–3.42, 3.66–3.73 (2*m*, CH_2S); 5.49–5.52 (*m*, CH_2=CH); 5.93–6.07 (*m*, CH_2=CH). ^{13}C-NMR: 21.2 (*q*, Me); 21.5 (*q*, Me); 22.1 (*q*, Me); 22.8 (*q*, Me); 55.9 (*t*, CH_2S); 65.7 (*q*, Me_2C); 69.2 (*s*, Me_2C); 89.7 (*s*, SCCl); 123.8 (*t*, CH_2=CH); 126.3 (*d*, CH_2=CH); 213.9 (*s*, C=O). CI-MS: 266 (15, $[M(^{35}Cl)+NH_4]^+$), 251 (37, $[M(^{37}Cl)+1]^+$), 250 (12), 249 (100, $[M(^{35}Cl)+1]^+$). Anal. calc. for $C_{11}H_{17}ClO_2S$ (248.77): C 53.11, H 6.89, S 12.89; found: C 53.06, H 6.68, S 12.67.

Reaction of **2** *with* H_2O. To a soln. of **2** (113.5 mg, 0.5 mmol) in THF (3 ml) at r.t. was added H_2O (3 ml). After stirring for 45 min at r.t., CH_2Cl_2 (5 ml) was added, and the mixture was separated. After drying of the org. phase ($MgSO_4$) and evaporation of the solvent, the residue was purified by prep. TLC (SiO_2; CH_2Cl_2/hexane 1:1). Subsequent recrystallization from hexane yielded **18** (67 mg, 79%) [31].

Reaction of **2** *with AcOH*. To a soln. of **2** (113.5 mg, 0.5 mmol) in CH_2Cl_2 (3 ml) at r.t. was added AcOH (30.3 mg, 0.5 mmol), and the mixture was heated under reflux for 6 h. After cooling to r.t., the solvent was evaporated. Purification of the residue by prep. TLC (SiO_2; CH_2Cl_2/hexane 1:1) yielded **18** (66 mg, 78%).

3-Chloro-3-(methoxydisulfanyl)-2,2,4,4-tetramethylcyclobutanone (**23a**). Reaction of **3** with MeOH. Yield: 74% (estimated by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as internal standard). Colorless oil. IR (neat): 2975*s*, 2939*s*, 2877*m*, 1787v*s*, 1773*m*, 1466*s*, 1380*w*, 1363*w*, 1243*w*, 1180*m*, 1133*m*, 1030*s*, 916*m*, 889*m*, 840*w*, 795*w*, 744*w*. ^{1}H-NMR: 1.42 (*s*, 2 Me); 1.46 (*s*, 2 Me); 3.66 (*s*, MeO). ^{13}C-NMR: 22.8 (*q*, 2 Me); 23.4 (*q*, 2 Me); 63.5 (*q*, MeO); 68.6 (*s*, 2 Me_2C); 86.7 (*s*, SCCl); 216.4 (*s*, C=O). CI-MS: 272 (27, $[M(^{35}Cl)+NH_4]^+$), 219 (100, $[M-Cl]^+$), 191 (17), 159 (84).

3-Chloro-2,2,4,4-tetramethyl-3-{[(2,4,6-trimethylphenyl)oxy]disulfanyl}cyclobutanone (**23b**). Reaction of **3** with 2,4,6-trimethylphenol. Yield: 95 mg (53%). Colorless solid. M.p. 98–100° (hexane). IR (KBr): 2972*s*, 2932*s*, 2865*w*, 1762*s*, 1603*m*, 1490*s*, 1449*m*, 1312*m*, 1201*s*, 1151*m*, 1027*m*, 921*m*, 834*m*, 737*w*. ^{1}H-NMR: 1.45 (*s*, 2 Me); 1.46 (*s*, 2 Me); 2.20 (*s*, *p*-*Me*C_6H_2); 2.22 (*s*, 2 *o*-*Me*C_6H_2); 6.94 (*s*, 2 arom. H). ^{13}C-NMR: 15.9 (*q*, 2 *o*-*Me*C_6H_2); 20.4 (*q*, 2 Me); 22.4 (*q*, 2 Me); 23.7 (*q*, *p*-*Me*C_6H_2); 69.3 (*s*, 2 Me_2C); 89.5 (*s*, SCCl); 123.3, 127.9 (2*s*, 3 arom. C); 129.6 (*d*, 2 arom. CH); 151.9 (*s*, arom. C); 216.9 (*s*, C=O). CI-MS: 323 (56, $[M-Cl]^+$), 152 (48), 153 (100). Anal. calc. for $C_{17}H_{23}ClO_2S_2$ (358.95): C 56.88, H 6.46, S 17.87; found: C 56.61, H 6.38, S 17.66.

4. *Reactions of* **2** *and* **3** *with P Nucleophiles. General Procedure.* To a soln. of **2** (113.5 mg, 0.5 mmol) or **3** (130 mg, 0.5 mmol) in CH_2Cl_2 (3 ml) at 0° was added the respective P nucleophile (0.5 mmol). After stirring for 60 min, the solvent was evaporated yielding the product as an oil, which was further purified by crystallization.

S-*(1-Chloro-2,2,4,4-tetramethyl-3-oxocyclobutyl)* O,O-*Dimethyl Thiophosphate* (**25a**). Reaction of **2** with $(MeO)_2POH$. Yield: 141 mg (94%) of crude **25a**; 118 mg (73%) after crystallization from hexane. Reaction of **2** with $(MeO)_3P$. Yield: 145 mg (96%) of crude **25a**; 132 mg (88%) after crystallization from hexane. Colorless crystals. M.p. 48–49° (hexane). IR (KBr): 2996*m*, 2974*m*, 2937*m*, 2871*w*, 1790v*s*, 1768*m*, 1465*s*, 1379*w*, 1364*w*, 1273v*s*, 1180*m*, 1043v*s*, 918*m*, 841*s*, 552*s*. ^{1}H-NMR: 1.42 (*s*, 2 Me);

1.58 (*s*, 2 Me); 3.87 (*d*, *J*(H,P) = 12.8, 2 MeO). ^{13}C-NMR: 21.7 (*q*, 2 Me); 23.8 (*q*, 2 Me); 54.3 (*dq*, *J*(C, P) = 6.9, 2 MeO); 69.8 (*d*, *J*(C,P) = 4.9, 2 Me_2C); 82.4 (*d*, *J*(C,P) = 5.8, SCCl); 216.5 (*s*, C=O). CI-MS: 320 (37, $[M(^{37}Cl)+NH_4]^+$), 318 (100, $[M(^{35}Cl)+NH_4]^+$), 301 (11, $[M(^{35}Cl)+1]^+$). Anal. calc. for $C_{10}H_{18}ClO_4PS$ (300.74): C 39.94, H 6.03, S 10.66; found: C 39.75, H 5.83, S 10.42.

S-*(1-Chloro-2,2,4,4-tetramethyl-3-oxocyclobutyl)* O,O-*Diethyl Thiophosphate* (**25b**). Reaction of **2** with $(EtO)_2POH$. Yield: 158 mg (96%) of crude **25b**; 139 mg (85%) after crystallization from hexane. Reaction of **2** with $(EtO)_3P$. Yield: 162 mg (99%) of crude **25b**; 137 mg (83%) after crystallization from hexane. Colorless crystals. M.p. 30–32° (hexane). IR (KBr): 2985*s*, 2938*m*, 2907*m*, 1789*s*, 1468*s*, 1384*m*, 1265*s*, 1165*m*, 1021*m*, 926*w*, 833*w,* 745*w*, 559*s*. ^{1}H-NMR: 1.39 (*td*, *J*(H,H) = 7.1, *J*(H,P) = 0.8, 2 $MeCH_2$); 1.43 (*s*, 2 Me); 1.58 (*s*, 2 Me); 4.13–4.31 (*m*, $MeCH_2O$). ^{13}C-NMR: 15.9 (*dq*, *J*(C,P) = 7.4, 2 Me); 21.7 (*q*, 2 Me); 23.8 (*q*, 2 Me); 64.3 (*td*, *J*(C,P) = 7.1, $MeCH_2O$); 69.8 (*d*, *J*(C,P) = 4.7, 2 Me_2C); 82.5 (*d*, *J*(C,P) = 5.8, SCCl); 216.7 (*s*, C=O). CI-MS: 348 (38, $[M(^{37}Cl)+NH_4]^+$), 346 (100, $[M(^{35}Cl)+NH_4]^+$), 331 (26, $[M(^{37}Cl)+1]^+$), 329 (66, $[M(^{35}Cl)+1]^+$). Anal. calc. for $C_{12}H_{22}ClO_4PS$ (328.79): C 43.84, H 6.74, S 9.75; found: C 43.73, H 6.48, S 9.55.

S-*(1-Chloro-2,2,4,4-tetramethyl-3-oxocyclobutyl)* O,O-*Diphenyl Thiophosphate* (**25c**). Reaction of **2** with $(PhO)_2POH$. Yield: 203 mg (92%) of crude **25c**; 78 mg (35%) after crystallization from hexane. Colorless crystals. M.p. 57–59° (hexane). IR (KBr): 2990*m*, 2928*w*, 2875*w*, 1789v*s*, 1588*s*, 1489v*s*, 1257*s*, 1204*s*, 1177*s*, 1156*s*, 1021*s*, 938v*s*, 827*w,* 774*s*, 690*s,* 616*w*. ^{1}H-NMR: 1.40 (*s*, 2 Me); 1.42 (*s*, 2 Me); 7.13–7.37 (*m*, 10 arom. H). ^{13}C-NMR: 21.9 (*q*, 2 Me); 23.6 (*q*, 2 Me); 70.2 (*d*, *J*(C,P) = 5.3, 2 Me_2C); 82.9 (*d*, *J*(C,P) = 6.1, SCCl); 120.9 (*dd*, *J*(C,P) = 4.8, 4 arom. CH); 125.8 (*dd*, *J*(C,P) = 4.9, 4 arom. CH); 129.8 (*d*, 2 arom. CH); 150.1 (*d*, *J*(C,P) = 9.5, 2 arom. CH); 216.2 (*s*, C=O). CI-MS: 442 (51, $[M(^{35}Cl)+NH_4]^+$), 344 (15), 252 (100). Anal. calc. for $C_{20}H_{22}ClO_4PS$ (424.88): C 56.54, H 5.22; found: C 56.10, H 5.29.

S-*(1-Chloro-2,2,4,4-tetramethyl-3-oxocyclobutyl)* O,O-*Diisopropyl Thiophosphate* (**25d**). Reaction of **2** with $(^iPrO)_3P$. Yield: 161 mg (90%) of crude **25d**; 82 mg (46%) after crystallization from hexane. Colorless crystals. M.p. 39–41° (hexane). IR (KBr): 2983*s*, 2936*m*, 2875*w*, 1787v*s*, 1764*m,* 1465*s*, 1386*m*, 1257*s*, 1110*m*, 974*s*, 832*w,* 766*m*, 600*s*. ^{1}H-NMR: 1.37 (*d*, *J* = 6.2, Me_2CH); 1.40 (*d*, *J* = 6.2, Me_2CH); 1.43 (*s*, 2 Me); 1.57 (*s*, 2 Me); 4.76–4.87 (*m*, 2 Me_2CH). ^{13}C-NMR: 21.9 (*q*, 2 Me); 23.6 (*q*, 2 Me); 23.8 (*q*, 2 Me); 23.9 (*q*, 2 Me); 69.9 (*d*, *J*(C,P) = 4.7, 2 Me_2C); 73.5 (*dd*, *J*(C,P) = 7.1, Me_2CH); 82.7 (*d*, *J*(C,P) = 6.0, SCCl); 217.0 (*s*, C=O). CI-MS: 376 (14, $[M(^{37}Cl)+NH_4]^+$), 374 (36, $[M(^{35}Cl)+NH_4]^+$), 359 (39, $[M(^{37}Cl)+1]^+$), 357 (100, $[M(^{35}Cl)+1]^+$).

Suitable crystals for the X-ray crystal-structure determination were obtained from hexane at −40°.

Reaction of **3** *with (EtO)$_3$P.* After usual workup and crystallization from hexane **25b** was obtained: 44 mg (34%). Colorless crystals. M.p. 30–32° (hexane).

5. *Reactions of* **2** *and* **3** *with S Nucleophiles. General Procedure.* To a soln. of **2** (113.5 mg, 0.5 mmol) or **3** (130 mg, 0.5 mmol) in CH_2Cl_2 (3 ml) at 0° was added the respective S nucleophile (0.5 mmol). After stirring for 10 min at r.t., Et_3N (50.6 mg, 0.5 mmol) was added slowly, and stirring was continued for 60 min. Then, the solvent was evaporated, and, after addition of Et_2O (5 ml), the insoluble residue was removed by filtration. Evaporation of the solvent yielded the product as an oily substance. Where possible, this was further purified by crystallization.

3-Chloro-3-(ethyldisulfanyl)-2,2,4,4-tetramethylcyclobutanone (**28a**). Reaction of **2** with EtSH. Yield: 99% (estimated by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as internal standard). Colorless oil. IR (neat): 2973v*s*, 2932*s*, 2869*m*, 1789v*s*, 1464*s*, 1455*s*, 1381*m*, 1366*w*, 1249*m*, 1131*m*, 1095*w*, 1026*m*, 915*w*, 830*m*. ^{1}H-NMR: 1.33 (*t*, *J* = 7.4, $MeCH_2$); 1.43 (*s*, 2 Me); 1.48 (*s*, 2 Me); 2.99 (*q*, *J* = 7.4, $MeCH_2S$). ^{13}C-NMR: 14.0 (*q*, $MeCH_2$); 22.3 (*q*, 2 Me); 23.5 (*q*, 2 Me); 33.8 (*t,* $MeCH_2S$); 69.0 (*s*, 2 Me_2C); 89.0 (*s*, SCCl); 216.6 (*s*, C=O). CI-MS: 218 (12), 217(100, $[M-Cl]^+$), 189 (52).

3-Chloro-2,2,4,4-tetramethyl-3-(phenyldisulfanyl)cyclobutanone (**28b**). Reaction of **2** with PhSH. Yield: 127 mg (84%). Colorless crystals. M.p. 47–48° (hexane). IR (KBr): 2973*s*, 2932*m*, 1784*s*, 1598*s*, 1583*s*, 1493v*s*, 1463*s*, 1381*w*, 1365*m*, 1263*m*, 1026*w*, 917*m*, 826*s*, 755*w*. ^{1}H-NMR: 1.39 (*s*, 2 Me); 1.45 (*s*, 2 Me); 7.21–7.34 (*m*, 3 arom. H); 7.59–7.62 (*m*, 2 arom. H). ^{13}C-NMR: 22.5 (*q*, 2 Me); 23.4 (*q*, 2 Me); 69.1 (*s*, 2 Me_2C); 87.9 (*s*, SCCl); 127.6, 128.8, 129.6 (3*d*, 5 arom. CH); 136.8 (*s*, arom. C); 216.2 (*s*, C=O). CI-MS: 267 (19), 266 (17), 265 (100, $[M-Cl]^+$). Anal. calc. for $C_{14}H_{17}ClOS_2$ (300.89): C 55.89, H 5.70, S 21.32; found: C 56.02, H 5.50, S 21.05.

Table. *Crystallographic Data for Compounds* **6a**, **7a**, **16d**, *and* **24d**

		6a	**7a**	**16d**	**24d**
Crystallized from		hexane	hexane	hexane	hexane
Empirical formula		$C_{12}H_{20}ClNO_2S$	$C_{12}H_{20}ClNO_2S_2$	$C_{17}H_{23}ClO_2S$	$C_{14}H_{26}ClO_4PS$
Formula weight		277.81	309.87	326.88	356.84
Crystal color, habit		colorless, prism	colorless, prism	colorless, prism	colorless, prism
Crystal dimensions [mm]		0.15×0.15×0.23	0.25×0.30×0.30	0.22×0.25×0.28	0.15×0.25×0.28
Temp. [K]		160(1)	160(1)	160(1)	160(1)
Crystal system		monoclinic	monoclinic	orthorhombic	monoclinic
Space group		$P2_1/n$	$C2/c$	$Pca2_1$	$P2_1/c$
Z		4	8	4	4
Reflections for cell determination		13595	21144	45294	29614
2θ Range for cell determination [°]		4–60	4–55	4–60	4–60
Unit cell parameters	a [Å]	6.1117(2)	20.2280(3)	24.3189(3)	12.0776(2)
	b [Å]	13.5317(4)	13.3852(3)	6.1656(1)	10.8647(1)
	c [Å]	16.8950(6)	14.4498(3)	11.2385(2)	15.1497(2)
	β [°]	100.208(2)	130.3281(9)	90	111.7564(9)
	V [Å^3]	1375.13(8)	2982.6(1)	1685.11(5)	1846.33(4)
D_x [g cm^{-3}]		1.342	1.380	1.288	1.284
μ(MoK_α) [mm^{-1}]		0.420	0.530	0.352	0.417
Scan type		ϕ and ω	ϕ and ω	ω	ϕ and ω
$2\theta_{(max)}$ [°]		60	55	60	60
Transmission factors [min; max]		0.844; 0.946	0.801; 0.879	0.797; 0.929	0.842; 0.942
Total reflections measured		24256	33254	42276	51692
Symmetry independent reflections		4009	3421	4901	5406
Reflections with $I>2\sigma(I)$		2702	2962	4367	4508
Reflections used in refinement		4009	3419	4897	5405
Parameters refined; restraints		158	167	197; 1	199
Final	$R(F)$ [$I>2\sigma(I)$ reflections]	0.0442	0.0326	0.0343	0.0342
	$wR(F^2)$ (all data)	0.1174	0.0774	0.0864	0.0919
Weighting parameters [a; b][a]		0.0576; 0.2756	0.0310; 3.1386	0.0413; 0.5216	0.0473; 0.5655
Goodness-of-fit		1.032	1.066	1.039	1.047
Secondary extinction coefficient		–	–	–	0.010(1)
Final Δ_{max}/σ		0.001	0.001	0.001	0.002
$\Delta\rho$ (max; min) [e Å^{-3}]		0.36; −0.59	0.42; −0.37	0.26; −0.34	0.47; −0.58

[a]) $w^{-1}=\sigma^2(F_o^2)+(aP)^2+bP$ where $P=(F_o^2+2F_c^2)/3$.

3-Chloro-3-(ethyltrisulfanyl)-2,2,4,4-tetramethylcyclobutanone (**29a**). Reaction of **3** with EtSH. Yield: 97% (estimated by ^{1}H-NMR with 1,1,2,2-tetrachloroethane as internal standard). Colorless oil. IR (neat): 2973v*s*, 2932*s*, 2869*m*, 1787v*s*, 1464*s*, 1381*m*, 1366*w*, 1253*m*, 1131*m*, 1026*m*, 915*m*, 885*w*, 830*m*, 739*w*. ^{1}H-NMR: 1.39 (*t*, $J=7.3$, *Me*CH$_2$); 1.43 (*s*, 2 Me); 1.46 (*s*, 2 Me); 2.93 (*q*, $J=7.3$, MeC*H*$_2$S). ^{13}C-NMR: 14.0 (*q*, *Me*CH$_2$); 22.3 (*q*, 2 Me); 23.5 (*q*, 2 Me); 33.8 (*t*, MeCH$_2$S); 69.0 (*s*, 2 Me$_2$*C*); 89.0 (*s*, SCCl); 216.6 (*s*, C=O). CI-MS: 218 (12), 217(100, $[M-Cl]^+$), 189 (52).

3-Chloro-2,2,4,4-tetramethyl-3-(phenyltrisulfanyl)cyclobutanone (**29b**). Reaction of **3** with PhSH. Yield: 114 mg (68%). Colorless crystals. M.p. 42–43° (hexane). IR (ATR): 2976*m*, 2934*w*, 1786v*s*,

1767*s*, 1574*w*, 1475*w*, 1451*s*, 1435*m*, 1377*w*, 1361*w*, 1020*m*, 908*m*, 886*w*, 828*m*, 733v*s*, 686v*s*. ^{1}H-NMR: 1.39 (*s*, 2 Me); 1.44 (*s*, 2 Me); 7.25–7.38 (*m,* 3 arom. H); 7.56–7.59 (*m,* 2 arom. H). ^{13}C-NMR: 22.9 (*q*, 2 Me); 23.3 (*q*, 2 Me); 69.1 (*s*, 2 Me_2C); 87.3 (*s*, SCCl); 128.2, 129.1, 129.9 (3*d*, 5 arom. CH); 136.7 (*s*, arom. C); 215.9 (*s*, C=O). CI-MS: 297 (18, $[M-Cl]^+$), 265 (21), 218 (100). Anal. calc. for $C_{14}H_{17}ClOS_3$ (332.95): C 50.51, H 5.15, S 28.89; found: C 56.49, H 5.02, S 28.73.

6. *X-Ray Crystal-Structure Determination of* **6a**, **7a**, **16d**, *and* **25d** (*Table* and *Figs. 1–3*)[6]). All measurements were performed on a *Nonius KappaCCD* diffractometer [58] using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in *Figs. 1–3*. Data reduction was performed with *HKL Denzo* and *Scalepack* [59]. The intensities were corrected for *Lorentz* and polarization effects, and absorption corrections based on the multi-scan method [60] were applied. Equivalent reflections, other than the *Friedel* pairs for **16d**, were merged. The structures were solved by direct methods using SIR92 [61], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me groups). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was applied in the case of **25d**. In **7a**, **16d**, and **25d**, two, four, and one reflections, resp., whose intensities were considered to be extreme outliers, were omitted from the final refinement. Refinement of the absolute structure parameter [62] of **16d** yielded a value of $-0.05(5)$, which confidently confirms that the refined coordinates correspond with the true absolute structure. Neutral atom scattering factors for non-H-atoms were taken from [63a], and the scattering factors for H-atoms were taken from [64]. Anomalous dispersion effects were included in F_c [65]; the values for f' and f'' were those of [63b]. The values of the mass attenuation coefficients are those of [63c]. All calculations were performed using the SHELXL97 [66] program.

REFERENCES

[1] K. N. Koch, G. Mlostoń, A. Senning, *Eur. J. Org. Chem*. **1999**, 83.
[2] G. Mlostoń, A. Majchrzak, A. Senning, I. Sotøfte, *J. Org. Chem*. **2002**, *67*, 5690.
[3] K. Oka, S. Hara, *Tetrahedron Lett.* **1977**, *8*, 695.
[4] C. D. Gabbutt, J. D. Hepworth, B. M. Heron, M. Kanjia, *Tetrahedron* **1994**, *50*, 827.
[5] C. K. Johnson, 'ORTEP II', Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
[6] I. El-Sayed, M. F. Abdel-Megeed, S. M. Yassin, A. Senning, *Phosphorus, Sulfur, Silicon* **1994**, *86*, 239.
[7] L. N. Markovskii, V. M. Timoshenko, Yu. G. Shermolovich, *Zh. Org. Khim.* **1995**, *31*, 161; *Chem. Abstr.* **1996**, *124*, 116274.
[8] H. W. Roesky, A. May, M. Noltemeyer, *J. Fluorine Chem.* **1993**, *62*, 77.
[9] G. Mlostoń, J. Romański, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1993**, *76*, 2147.
[10] T. Saito, S. Motoki, *J. Org. Chem.* **1977**, *42*, 559.
[11] S. Tamagaki, K. Sakaki, S. Oae, *Bull. Chem. Soc. Jpn.* **1974**, *47*, 3084.
[12] T. Saito, S. Motoki, *Chem. Lett*. **1978**, 591.
[13] T. Saito, S. Motoki, *J. Org. Chem*. **1979**, *44*, 2493.
[14] S. Holm, J. A. Boerma, N. H. Nilsson, A. Senning, *Chem. Ber.* **1976**, *109*, 1069.
[15] T. Saito, M. Nakane, S. Motoki, *Bull. Chem. Soc. Jpn.* **1984**, *57*, 1429.
[16] I. Crossland, *Acta Chem. Scand. B* **1977**, *10*, 890.
[17] A. May, H. Roesky, D. Stalke, F. Pauer, G. M. Sheldrick, *Chem. Ber.* **1990**, *123*, 1475.
[18] S. Tamagaki, K. Sakaki, S. Oae, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 2608.

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[6]) CCDC-600725–600728 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre*, *via* www.ccdc.cam.ac.uk/data_request/cif.

[19] K. Oka, S. Hara, *Tetrahedron Lett*. **1977**, 2939.
[20] E. M. Burgess, H. R. Penton, *J. Am .Chem. Soc.* **1973**, *95*, 279.
[21] T. Saito, S. Motoki, *J. Org. Chem*. **1977**, *42*, 3922.
[22] G. Mlostoń, J. Fabian, *Pol. J. Chem.* **1999**, *73*, 683.
[23] R. Huisgen, G. Mlostoń, E. Langhals, *Helv. Chim. Acta* **2001**, *84*, 1805.
[24] G. Mlostoń, J. Romański, A. Linden, H. Heimgartner, *Pol. J. Chem.* **1996**, *70*, 880.
[25] G. Mlostoń, M. Celeda, H. W. Roesky, E. Parisini, J.-T. Ahlemann, *Eur. J. Org. Chem.* **1998**, 459.
[26] G. Mlostoń, J. Romański, H. Heimgartner, *Pol. J. Chem.* **1996**, *70*, 437.
[27] G. Mlostoń, J. Romański, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **1995**, *78*, 1067.
[28] S. Braverman, D. Ytzhak, *Tetrahedron* **1990**, *46*, 2975.
[29] M. E. Sitzmann, W. H. Gilligan, *J. Org. Chem.* **1983**, *48*, 3354.
[30] E. O. John, J. M. Shreeve, *J. Fluorine Chem.* **1987**, *36*, 429.
[31] W. G. Phillips, K. W. Ratts, *J. Org. Chem.* **1972**, *37*, 1526.
[32] B. Zwanenburg, A. Wagenaar, L. Thijs, J. Strating, *J. Chem. Soc., Perkin Trans. 1* **1973**, 73.
[33] C. P. Raj, N. A. Dhas, M. Cherkinski, A. Gedanken, S. Braverman, *Tetrahedron Lett*. **1998**, *39*, 5413.
[34] F. Scheufler, M. E. Maier, *Eur. J. Org. Chem*. **2000**, 3945.
[35] P. Bickart, F. W. Carson, J. Jacobus, E. G. Miller, K. Mislow, *J. Am. Chem. Soc.* **1968**, *90*, 4869; R. Tang, K. Mislow, *J. Am. Chem. Soc.* **1970**, *92*, 2100.
[36] D. A. Evans, G. C. Andrews, C. L. Sims, *J. Am. Chem. Soc.* **1971**, *93*, 4956.
[37] E. Block, S. Naganathan, D. Putman, S. H. Zhao, *Pure Appl. Chem.* **1993**, *65*, 625; R. Bauer, W. Breu, H. Wagner, W. Weigand, *J. Chromatogr.* **1991**, *541*, 464.
[38] J. Michalski, B. Mlotkowska, A. Skowrońska, *J. Chem. Soc., Perkin Trans. 1* **1974**, 319.
[39] D. C. Morrison, *J. Am. Chem. Soc.* **1955**, *77*, 181.
[40] A. K. Bhattacharya, G. Thyagarajan, *Chem. Rev.* **1981**, *81*, 415.
[41] M. G. Blackburn, T. W. Maciej, *J. Chem. Soc., Perkin Trans. 1* **1985**, 1419.
[42] J. Chojnowski, M. Cypryk, W. Fortuniak, J. Michalski, *Synthesis* **1977**, 683.
[43] A. Skowrońska, R. Dembiński, R. Kamiński, J. Michalski, *Tetrahedron Lett*. **1987**, *28*, 4209.
[44] K. A. Petrov, N. K. Bliznyuk, V. A. Savostenok, *Zh. Obshch. Khim*. **1961**, *31*, 1361; *Chem. Abstr.* **1961**, *55*, 23317e.
[45] G. Mlostoń, A. Majchrzak, M. Rutkowska, M. Woznicka, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **2005**, *88*, 2624.
[46] E. J. Corey, K. C. Nicolaou, *J. Am. Chem. Soc.* **1974**, *96*, 5614; E. J. Corey, K. C. Nicolaou, L. S. Melvin Jr., *J. Am. Chem. Soc.* **1975**, *97*, 653 and 654.
[47] E. J. Corey, D. J. Brunelle, *Tetrahedron Lett.* **1976**, 3409; T. Sasaki, M. Inoue, M. Hirama, *Tetrahedron Lett.* **2001**, *42*, 5299.
[48] R. Steudel, *Chem. Rev.* **2002**, *102*, 3905.
[49] R. Steudel, K. Hassenberg, V. Münchow, O. Schumann, J. Pickard, *Eur. J. Inorg. Chem.* **2000**, *92*, 921.
[50] A. Majchrzak, A. Janczak, G. Mlostoń, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **2003**, *86*, 2272.
[51] A. Majchrzak, G. Mlostoń, A. Linden, H. Heimgartner, *Helv. Chim. Acta* **2004**, *87*, 790.
[52] I. L. Finar, A. J. Montgomery, *J. Chem. Soc.* **1961**, 367.
[53] R. P. Singh, J. M. Shreeve, *Tetrahedron* **2000**, *56*, 7613.
[54] G. K. S. Prakash, A. K. Yudin, *Chem. Rev.* **1997**, *97*, 757.
[55] G. Mlostoń, G. K. S. Prakash, G. A. Olah, H. Heimgartner, *Helv. Chim. Acta* **2002**, *85*, 1644.
[56] I. V. Koval, T. G. Panasenko, *Zh. Org. Khim.* **1989**, *25*, 1677; *Chem. Abstr.* **1990**, *112*, 197734.
[57] G. Mlostoń, J. Romański, H. Heimgartner, *Pol. J. Chem*. **2001**, *75*, 975
[58] R. Hooft, *KappaCCD Collect Software*, Nonius BV, Delft, The Netherlands, 1999.
[59] Z. Otwinowski, W. Minor, in 'Methods in Enzymology', Vol. 276, 'Macromolecular Crystallography', Part A, Eds. C. W. Carter Jr., R. M. Sweet, Academic Press, New York, 1997, p. 307.
[60] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33.
[61] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *SIR92*, *J. Appl. Crystallogr.* **1994**, *27*, 435.
[62] H. D. Flack, G. Bernardinelli, *Acta Crystallogr., Sect. A* **1999**, *55*, 908; H. D. Flack, G. Bernardinelli, *J. Appl. Crystallogr.* **2000**, *33*, 1143.

[63] a) E. N. Maslen, A. G. Fox, M. A. O'Keefe, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992 Vol. C, Table 6.1.1.1, p. 477; b) D. C. Creagh, W. J. McAuley, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992 Vol. C, Table 4.2.6.8, p. 219; c) D. C. Creagh, J. H. Hubbell, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992 Vol. C, Table 4.2.4.3, p. 200.
[64] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.
[65] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781.
[66] G. M. Sheldrick, SHELXL97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

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