Studies on Reactions of Thioketones with Trimethyl(trifluoromethyl)silane Catalyzed by Fluoride Ions

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Treatment of 2,2,4,4-tetramethylcyclobutane-1,3-dione (**6**) in THF with CF_3SiMe_3 in the presence of tetrabutylammonium fluoride (TBAF) yielded the corresponding 3-(trifluoromethyl)-3-[(trimethylsilyl)oxy]-cyclobutanone **7** (*Scheme 1*) *via* nucleophilic addition of a CF_3^- anion at the C=O group and subsequent silylation of the alcoholate. Under similar conditions, the 'monothione' **1** reacted to give thietane derivative **8** (*Scheme 2*), whereas in the case of 'dithione' **2** only the dispirodithietane **9**, the dimer of **2**, was formed (*Scheme 3*). A conceivable mechanism for the formation of **8** is the ring opening of the primarily formed CF_3 adduct **A** followed by ring closure *via* the S-atom (*Scheme 2*). In the case of thiobenzophenones **4**, complex mixtures of products were obtained including diarylmethyl trifluoromethyl sulfide **10** and 1,1-diaryl-2,2-difluoroethene **11** (*Scheme 4*). Obviously, competing thiophilic and carbophilic addition of the CF_3^- anion took place. The reaction with 9*H*-fluorene-9-thione (**5**) yielded only 9,9′-bifluorenylidene (**14**; *Scheme 6*); this product was also formed when **5** was treated with TBAF alone. Treatment of **4a** with TBAF in THF gave dibenzhydryl disulfide (**15**; *Scheme 7*), whereas, under similar conditions, **1** yielded the 3-oxopentanedithioate **17** (*Scheme 9*). The reaction of dithione **2** with TBAF led to the isomeric dithiolactone **16** (*Scheme 8*), and **3** was transformed into 1,2,4-trithiolane **18** (*Scheme 10*).

Introduction. – In recent years, there has been a growing interest in fluorinated organic compounds [1–3]. The presence of F-atoms, especially in CF_3 groups, modifies the physicochemical and biological properties of these materials [2–4]. One of the most important features is their increased lipophilicity. Among several methods applied for the preparation of fluorinated systems, the nucleophilic trifluoromethylation with trimethyl(trifluoromethyl)silane (CF_3SiMe_3, '*Rupert*'s compound' [5]) is the method of choice for the introduction of a CF_3 group [6]. In the presence of F^-, CF_3SiMe_3 reacts efficiently with ketones and aldehydes as well as with carboxylic acid derivatives. Whereas reactions with carbonyl compounds give trifluoromethylated alcohols [7][8], carboxylic esters are converted – under controlled conditions – to trifluoromethyl ketones [9][10][3]). In contrast to carbonyl compounds, imines are less reactive towards CF_3SiMe_3, and special conditions are necessary to perform the

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[1]) Sabbatical at the Loker Hydrocarbon Institute, USC, Los Angeles, CA 90089, 09.96–03.97.

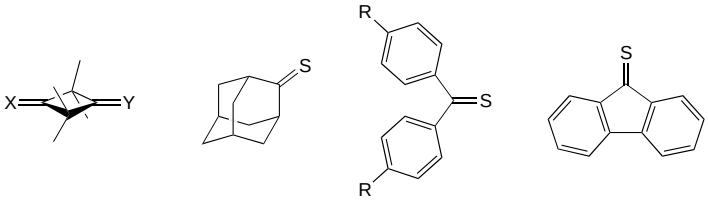
[2]) Presented in preliminary form by *G. M.* at the 18th International Symposium on the Organic Chemistry of Sulfur, Florence, 1998.

[3]) For reactions with other C=O compounds see [6].

reaction. In the presence of *N*-(trimethylsilyl)imidazole and CsF, the expected secondary amines with the CF_3 group at C(α) are obtained [11a]. A similar reaction with 2*H*-azirines was also reported [11b]. *Prakash et al.* have reported on trifluoromethylation of sulfonaldimines as well as sulfinimines [11c–f].

Fluorinated sulfurorganic compounds, especially trifluoromethyl sulfides, attract attention as agrochemicals [12] and pharmaceuticals [13]. The main reason for the biological activity of these compounds is their high lipophilicity; the CF_3S group is recognized as the most lipophilic substituent known [4b][14]. In a recent review, the methods applied for the preparation of trifluoromethyl sulfides are summarized [15]. On the one hand, the CF_3S group can be introduced by the reaction of CF_3SCl or CF_3SSCF_3 with organometallic reagents and, on the other hand, organic sulfides undergo substitution reaction with CF_3X (X = Cl, Br, I) under different conditions (*e.g.*, phase-transfer catalysis). Another approach reported recently is based on the reaction of CF_3SiMe_3 with disulfides or thiocyanates in the presence of F^- ions [16][17a]. Similarly, *N*-substituted trifluorothioacetamides were obtained in reactions with isothiocyanates [17b]. Under these conditions, the nucleophilic CF_3^- anion is the reactive intermediate.

Thiocarbonyl compounds, especially thioketones, can also be considered useful starting materials for the preparation of trifluoromethyl sulfides *via* thiophilic addition of a CF_3^- anion generated from CF_3SiMe_3. So far, very little is known about reactions of thiocarbonyl compounds with silanes. However, two recent publications show that aromatic thioketones and some sulfines undergo thiophilic addition with allyl(trimethyl)silane in the presence of tetrabutylammonium fluoride (TBAF) to afford allyl sulfides and sulfoxides, respectively, in good yields [18]. These observations prompted us to investigate the behavior of aromatic and cycloaliphatic thioketones towards CF_3SiMe_3 with TBAF as a catalyst. As model compounds, we selected the easily available and relatively stable 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1**), 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**2**), adamantanethione (**3**), thiobenzophenones **4a**–**d**, and 9*H*-fluorene-9-thione (**5**). To compare the behavior of the thiones with that of the parent ketone, 2,2,4,4-tetramethylcyclobutane-1,3-dione (**6**) was also included [18b].



1 X = O, Y = S
2 X = Y = S
6 X = Y = O

3

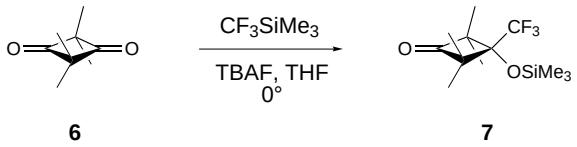
4a R = H
b R = Me
c R = F
d R = MeO

5

Results and Discussion. – The original protocol applied for 'nucleophilic trifluoromethylation' of benzophenone, adamantanone, *etc.* with CF_3SiMe_3 and TBAF [7] was modified by using commercially available TBAF solution (1M in THF) carefully dried over activated molecular sieves (4 Å). This modification proved to be crucial for

successful conversion of carboxylic esters to trifluoromethyl ketones [9] (*cf.* also [10]). Under these conditions, the reaction of dione **6** with *ca.* 1.2 equiv. of CF_3SiMe_3 at *ca.* 0° was completed after 2 min, and no evolution of gaseous CHF_3 was observed[4]). The analysis of the crude mixture by ^{19}F-NMR spectroscopy revealed the presence of two signals at −62.24 (minor) and −67.70 ppm (major)[5]). A spectrum taken after 1 h showed no significant changes of the mixture. The minor signal was indicative of CF_3SiMe_3 and the major one corresponded to the 1:1 adduct **7** (*Scheme 1*), which was isolated after aqueous workup in 74% yield. It is worth mentioning that the cyclobutanone ring was conserved[6]). This result can be explained by the fact that the initially formed alcoholate is silylated immediately [18b].

Scheme 1



6 **7**

Under similar conditions, the reaction with monothione **1** was finished after 15 min when the red color of the solution disappeared. The ^{19}F-NMR spectrum of the crude mixture indicated the formation of a new product containing a CF_3 group absorbing at −67.50 ppm[7]). Unexpectedly, the ^{1}H-NMR spectrum showed four signals for Me groups at 1.70, 1.46, 1.41, and 1.40 ppm indicating that the strained cyclobutanone ring was transformed into a new nonsymmetric system. Characteristic signals in the ^{13}C-NMR spectrum are two *singlets* for olefinic C-atoms at 127.5 and 119.2 ppm. Based on these data, the structure of thietane derivative **8** was proposed (*Scheme 2*). The colorless product, isolated after chromatography in 70% yield, was found to be stable at room temperature.

Analogous to the reaction with **6**, the CF_3^- anion generated in the system CF_3SiMe_3/F^- undergoes nucleophilic addition onto the more electrophilic C=O group to give intermediate **A**, which opens the ring to form the stabilized thiolate **B**. Ring closure *via* the more nucleophilic S-atom leads to the formation of thietanolate **C**, which is trapped by CF_3SiMe_3 to yield **8**. As a consequence, the CF_3^- anion is set free to start the next reaction cycle. Analogous ring-opening/ring-closure processes leading to the four-membered thiolactone isomer of **1** were reported to occur on treatment with NaH in DMSO [20].

On treatment of dithione **2** with CF_3SiMe_3/TBAF at 0°, the orange-red color of the solution changed to pale red within 3 min, and a red solid precipitated. No new CF_3-containing product could be detected by ^{19}F-NMR spectroscopy. The red solid isolated by means of chromatography showed only one Me signal at 1.39 ppm. The ^{13}C-NMR spectrum indicated high symmetry in the molecule, which, according to its MS (*m*/*z*

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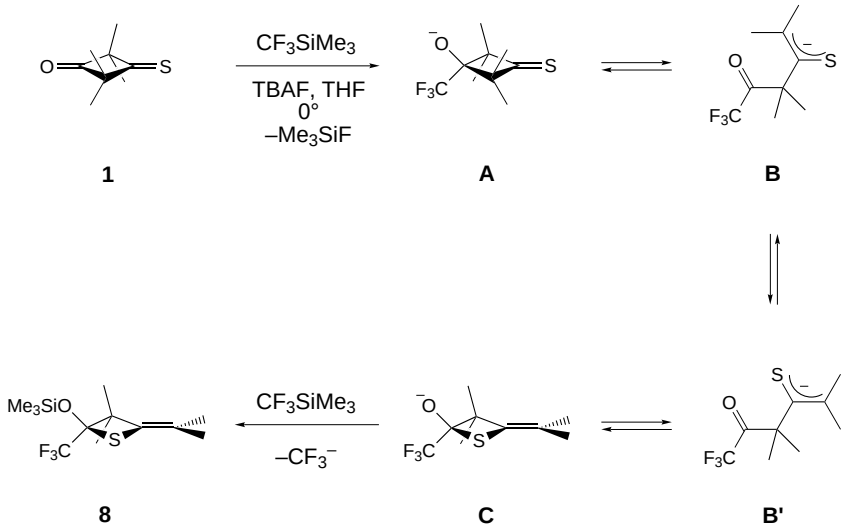
4) It is known that TBAF is a very hygroscopic substance, and its commercial THF-solution contains a significant amount of H_2O, which immediately decomposes CF_3SiMe_3.

5) As internal standard, $CFCl_3$ was used.

6) Under several basic conditions, ring-opening reactions of **6** were observed [19].

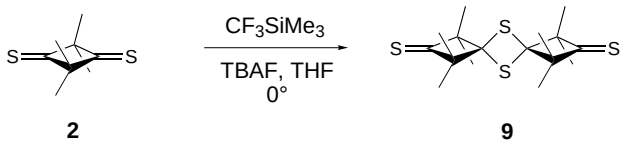
7) For the purified product in $CDCl_3$, this signal appeared at −76.04 ppm (see *Exper. Part*).

Scheme 2



345), is a dimer of **2**. All data confirm structure **9** for the new product[8]) (*Scheme 3*). The formation of **9** is remarkable! In contrast to other thioketones, which spontaneously form dimers and trimers [21][22], **2** is known not to undergo such oligomerizations.

Scheme 3



In the case of adamantanethione (**3**), no reaction was observed – even after 8 h – when it was treated with CF_3SiMe_3/TBAF under the above-mentioned conditions.

Aromatic thioketones **4** reacted very sluggishly with CF_3SiMe_3/TBAF, and a conversion was achieved only under rigorous exclusion of moisture. Reactions were carried out at room temperature, and, after 3–4 h, the initially blue solutions turned yellow. The crude mixtures were analyzed quantitatively by ^{19}F-NMR spectroscopy with weighed amounts of trifluoromethylbenzene as the internal standard. In all cases, two fluorinated products were present revealing ^{19}F-resonances at *ca.* –40 and –90 ppm, respectively[9]). The isolation of both remarkably nonpolar products was achieved by means of preparative TLC. Yields of fluorinated products as established by NMR, were not satisfactory (*ca.* 30–40% in total), and, therefore, it was presumed that some

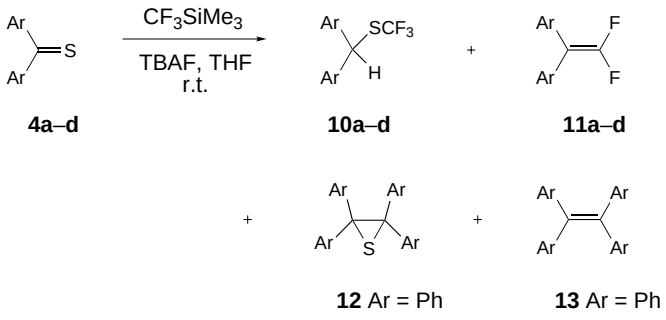
[8]) The structure of the isomeric 1,2-dithietane (head-to-head dimer) can be excluded on the basis of the NMR data.

[9]) In addition, several minor products containing F-atoms were detected but not identified.

products were nonfluorinated. For this reason, the mixture obtained from the reaction of **4a** was thoroughly separated.

As the least polar fractions, the fluorinated products **10a** and **11a** were obtained, followed by tetraphenylthiirane (**12**) and a small portion of tetraphenylethene (**13**) (*Scheme 4*). The main fluorinated product **10a** showed a signal in the ^{19}F-NMR spectrum at -41.12 ppm, and this chemical shift is typical for the CF_3S group [23]. This substance is the expected product of the thiophilic addition of CF_3^- onto **4a**. The second fluorinated product was identified as **11a** (*cf.* [24]). Its formation can be explained by a carbophilic addition of CF_3^-, followed by elimination of F^- by cyclization to give 2,2-difluoro-3,3-diphenylthiirane, which spontaneously extrudes the S-atom. An analogous conversion of this thiirane was observed earlier in the reaction of **4a** with difluorocarbene [24].

Scheme 4



a Ar = Ph **b** Ar = 4-MeC_6H_4 **c** Ar = 4-FC_6H_4 **d** Ar = 4-MeOC_6H_4

The formation of **12** in the reaction of **4a** with CF_3SiMe_3/TBAF is rather unexpected. Plausible mechanistic explanations are shown in *Scheme 5*. The intermediate carbanion **D**, which is the precursor of **10a**, can react with **4a** to give **G**, which, *via* an intramolecular S_N2 reaction, forms the thiirane **12**. On the other hand, a dissociation of **D** leads to diphenylcarbene **E**, which intercepts **4a** to give thiocarbonyl ylide **F** that cyclizes to yield **12**. Desulfurization of **12** under the reaction conditions leads to **13**.

When a THF solution of **5** and CF_3SiMe_3 was treated with TBAF, a vigorous reaction ensued, the olive-green color of the solution changed immediately to orange, and 9,9′-bifluorenylidene (**14**; *Scheme 6*) precipitated as an orange solid. No other product was detected in the mixture, and the known **14** [25] was isolated in almost quantitative yield.

9*H*-Fluorene-9-thione (**5**) shows a strong tendency to undergo thiophilic reactions with nucleophiles [26]. For this reason, a reaction of **5** with CF_3^- can easily afford an anion of type **D** (*Scheme 5*), which, subsequently, decomposes to give fluorenylidene[10]). Its dimerization is probably the source of **14**[11]).

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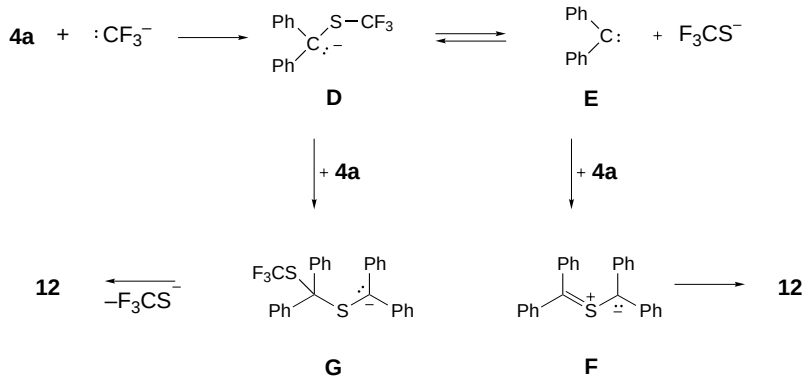
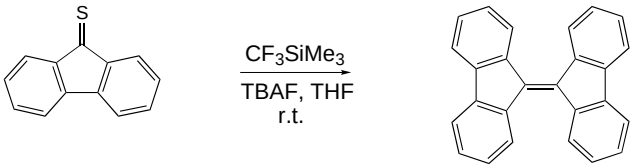
[10]) A reaction mechanism without participation of CF_3SiMe_3 may also be taken into account (see below).

[11]) Many routes leading to **14** starting from **5** or its dimer (the hetero-*Diels-Alder* adduct [27]) are described [28]. In these procedures, the corresponding thiirane was never observed. For preparation of the thiirane, see [29].

Scheme 5



Scheme 6



In extension of the above described studies, we decided to investigate reactions of thioketones mediated by F^-. Despite the fact that the reactivity of thioketones has been extensively studied [30], no reactions induced by F^- have been reported so far. On the other hand, F^- gained great importance as a powerful catalyst in organic synthesis [31] as shows properties of a strong base with poor nucleophilicity. In *Pearson*'s classification, F^- belongs to the hard bases [32].

The reactions described below were carried out using commercially available TBAF dissolved in THF after rigorous drying over activated molecular sieves (4 Å). Thiobenzophenone (**4a**) was treated with equimolar amounts of TBAF at room temperature, and, after 12 h, the blue color of **4a** disappeared. Chromatographic workup gave a colorless solid as the main product[12]). During determination of the melting point (153–155°), the substance turned blue indicating that **4a** was formed by thermal decomposition. The ^{1}H-NMR spectrum shows a *multiplet* (7.40–7.30 ppm) for aromatic H-atoms and a *singlet* at 4.80 ppm (ratio 10:1). In the ^{13}C-NMR spectrum, in addition to only one set of signals for Ph, a signal for CH (DEPT analysis) appears at 59.7 ppm. Whereas the EI-MS shows a peak with *m*/*z* 198 (82%) corresponding to $M^{+\cdot}$ of **4a**, the CI-MS (NH_3) indicated the presence of a dimeric compound +2 H-atoms (*m*/*z* 418, *i.e.*, [*M* of **15** + NH_4]$^+$). Finally, the structure of the product has been unequivocally established by X-ray crystallography as dibenzhydryl disulfide (**15**, *Scheme 7, Figure*).

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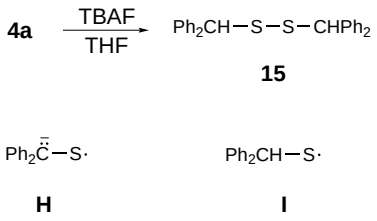
[12]) Several minor products were also formed but not characterized.

Scheme 7



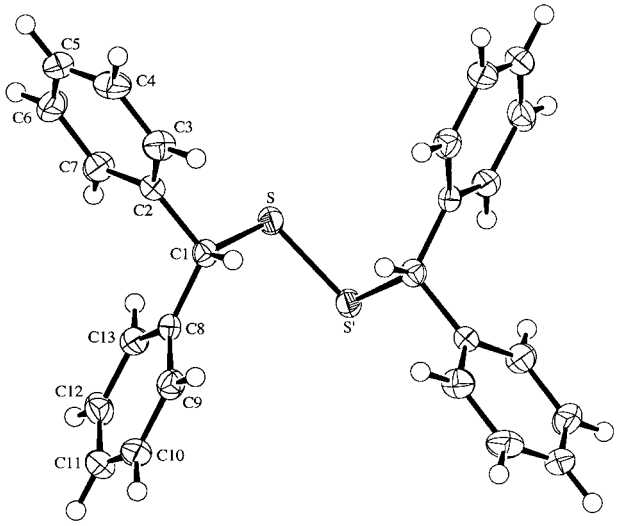


Figure. *ORTEP Plot* [33] *of the molecular structure of* **15** (50% probability ellipsoids, arbitrary numbering of atoms)

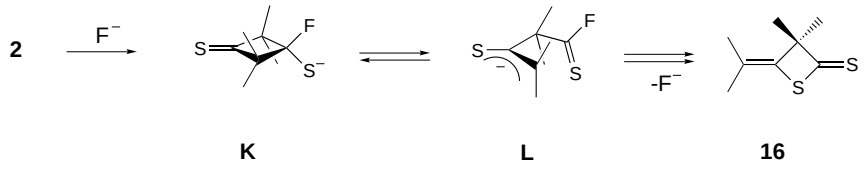
The formation of **15** from **4a** has been described previously, *e.g.*, by *Staudinger* and *Freudenberger* on treatment with NaSH in EtOH [34]. *Ohno et al.* obtained this compound in quantitative yield by treatment of **4a** with EtONa in EtOH at room temperature in the dark [35a]. A mechanism *via* a single-electron transfer (SET) to give the radical anion **H** as an intermediate has been proposed. Dimerization followed by protonation then yields **15**. Alternatively, **H** can be protonated to give the radical **I**, which dimerizes. The reaction of **4a** with EtONa in THF also yielded **15** along with benzhydryl sulfide as the main product. *Alper* and *Paik* reported the formation of **15** from **4a** in the reaction with cyclopentadienylmetal carbonyl anions in THF [35b]. Similar to the previous paper, a SET-mechanism was postulated and the solvent was indicated as the source of H-radicals. It is worth mentioning that a dithietane structure ('head-to-tail' dimer) was ascribed to the product isolated after the treatment of **4a** with sodium acetylide in liquid NH_3 [36a], but this conclusion is questionable, as the reported melting point (152–153°) is almost identical to that of **15** (151–152°)

reported by *Ohno et al.* [35a][13]). The experiment was repeated by *Schönberg et al.*, and the product was described as dibenzhydryl (**15**) [36c]. The reproduced IR spectrum (KBr) of the compound is in perfect agreement with that for product **15** isolated in our experiment. Whereas no convincing data on the formation of 1,3-dithietanes by base-catalyzed dimerization of aromatic thioketones are available, dimerization of some aliphatic representatives to yield 1,3-dithietanes in the presence of pyridine was reported [36c].

Under similar conditions to those described for **4a**, **5** reacted immediately to give **14** (*Scheme 6*) as the sole product. Apparently, the reactive thioketone **5** behaves identically in the presence of CF_3SiMe_3/TBAF or only TBAF.

Treatment of the cycloaliphatic dithione **2** with TBAF solution led to the formation of a single product that was identified as the isomeric thietanethione **16** [37] (*Scheme 8*). The reaction was completed after 5 min at 0° and afforded **16** in high yield. The mechanistic pathway leading to **16** corresponds to earlier presented ring-opening/ring-closure processes. In the present case, F^- attacks the C=S group in a carbophilic fashion, in agreement with the HSAB concept, to give intermediate **K**, which undergoes ring opening to **L**.

Scheme 8



K **L** **16**

To our surprise, the reaction of TBAF with monothione **1** afforded a completely different product. By means of ^{1}H-NMR analysis of the crude mixture, dione **6** and a new product **17** with a set of 3 *singlets* for Me groups and the typical signals for an i-Pr group were present. After separation of the two products by chromatography, **17** was obtained as a yellow oil, which solidified at room temperature. Based on EI-MS (*m*/*z* 314) and high-resolution (HR) MS (314.1370; $C_{16}H_{26}O_2S_2$), we concluded that the molecule has been formed from two molecules of **1**. The most surprising fact is the presence of two additional H-atoms, which is unequivocally confirmed both by ^{1}H- and ^{13}C-NMR spectra. Taking into account all these data, the structure of the product can tentatively be ascribed to 3-oxopentanedithioate **17** (*Scheme 9*)[14]). In analogy to the reaction of **4a**, a likely explanation is an initial SET with participation of F^- and THF as the H donor.

The reaction of adamantanethione (**3**) with TBAF solution also led to an astonishing result. After 4 h at room temperature, the reaction mixture was separated chromatographically and colorless crystals of 1,2,4-trithiolane **18** were isolated as the sole product (*Scheme 10*). Its structure was confirmed by comparison with an authentic sample [22][38].

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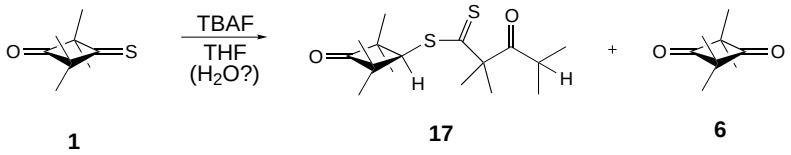
[13]) The information given in [21] concerning the dimer of thiobenzophenone is wrong; the indicated paper relates to dimers of aliphatic thioketones exclusively (see [36b]).

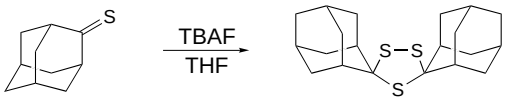
[14]) At the moment, a convincing explanation for the formation of **17**, as well as of **15**, is missing. Further studies are needed to gain more insight on the reactions of thioketones and the naked F^-.

Scheme 9

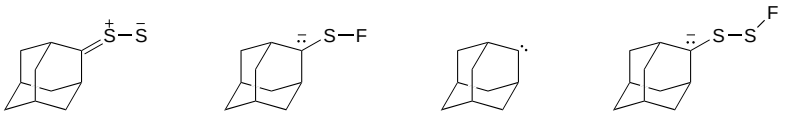


1 **17** **6**

Scheme 10



3 **18**



M **N** **O** **P**

In the light of the known mechanism leading to 1,2,4-trithiolanes [38][39], the formation of **18** results from the 1,3-dipolar cycloaddition of an intermediate **M** (adamantanethione *S*-sulfide) with **3**. The generation of **M** from **3** under the described conditions is not clear[15]). However, it is likely that the thiophilic addition of F^- to **3** gives an intermediate anion **N**, which, subsequently, decomposes to adamantylidene (**O**) by transfer of FS^- to another molecule of **3** to give **P**. By elimination of F^-, the latter converts to **M**.

Conclusions. – The presented results show that – in general – thioketones are less reactive towards CF_3SiMe_3 than ketones. The course of the reaction strongly depends on the type of thioketone. Thiobenzophenones **4** react to give products that are formed *via* addition of CF_3^- in the thiophilic and carbophilic mode. The anion generated by the thiophilic addition is probably also the key intermediate for the formation of thiiranes. Furthermore, thioketones were shown to undergo reactions with F^-. The type of products formed in TBAF solutions differs depending on the structure of the thioketone. Explanations of reaction pathways leading to the isolated products require the assumption of thiophilic as well as carbophilic addition of F^- onto the C=S group.

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[15]) The formation of **18** from **3** has been observed under different conditions, *e.g.*, on treatment with nitrile sulfides or S_8 [40], with organic azides [38][41], sodium thiophenolate [42], P_4S_{10} [43], or with SiO_2 [22].

Experimental Part

1. *General.* M.p.: *Melt-Temp.-II* apparatus (*Aldrich*); in capillary; uncorrected. IR Spectra: *Specord-75* IR spectrometer; in KBr or neat for oily materials; absorptions in cm^{-1}. ^1H-, ^{19}F-, and ^{13}C-NMR Spectra: *Varian Gemini 200* or *Varian VXR 200* instruments; in $CDCl_3$; δ in ppm rel. to TMS (=0 ppm) for ^1H and ^{13}C or to $CFCl_3$ (=0 ppm) for ^{19}F. MS: *Hewlett-Packard GC/MS 5890/5971A* or *Finnigan MAT INCOS 50*. Elemental analyses were performed at the *Galbraith Laboratory* (Knoxville, Tennessee).

2. *Starting Materials.* Trimethyl(trifluoromethyl)silane (CF_3SiMe_3) was synthesized from bromo(trifluoro)-methane and chloro(trimethyl)silane according to [44]. *2,2,4,4-Tetramethyl-3-thioxocyclobutanone* (**1**) and *2,2,4,4-tetramethylcyclobutane-1,3-dithione* (**2**) were obtained as a mixture after heating *2,2,4,4-tetramethylcyclobutane-1,3-dione* (**6**) [45] with P_4S_{10} in pyridine and were separated by chromatography (see [46]). *Adamantanethione* (**3**) was prepared from adamantanone and P_4S_{10} [47]. *9H-Fluorene-9-thione* (**5**) was synthesized from 9*H*-fluoren-9-one by treatment with HCl and H_2S [48] (for a modified procedure, see [28]). *Thiobenzophenone* (**4a**) and its derivatives **4b**, **4c**, and **4d** were prepared from the corresponding ketones by heating in toluene soln. with *Lawesson*'s reagent (*LR*) according to [49] and were purified by chromatography on SiO_2. Activated molecular sieves (4 Å) were prepared by heating small portions (2–3 g) of commercial sieves in a round-bottomed flask with a flame at *ca.* 10^{-1} Torr for *ca.* 10 min and were immediately used for the reaction. The THF soln. of tetrabutylammonium fluoride (TBAF, 1M) was purchased from *Sigma-Aldrich*.

3. *Fluoride-Ion-Mediated Reactions with CF_3SiMe_3.* 3.1. *Reaction with* **6**. To a soln. of **6** (280 mg, 2 mmol) and CF_3SiMe_3 (355 mg, 2.5 mmol) in abs. THF (2 ml) in a 25-ml round bottomed flask (N_2 atmosphere) equipped with a magnetic stirrer were added *ca.* 300 mg of freshly activated molecular sieves (4 Å)[16]. The flask was closed with a rubber septum and stirred at r.t. for 2 h. In another flask, similarly equipped with a magnetic stirrer, a diluted soln. of TBAF (0.5 ml of commercial 1M soln. in THF was diluted with 2 ml of abs. THF) was treated under N_2 with *ca.* 300 mg of freshly activated molecular sieves (4 Å). The flask was closed with a rubber septum, and the soln. was stirred magnetically for 2 h. Then, by means of a syringe 0.25 ml of the predried soln. containing *ca.* 0.05 mmol TBAF was added dropwise to the soln. of **6**, cooled with an ice bath. No evolution of gaseous products was observed and, after 2 min, a sample was taken *via* syringe to check the progress of reaction (^{19}F-NMR). A small excess of CF_3SiMe_3 was evidenced by the presence of an *s* at −62.24 ppm; another *s* at −67.70 ppm was assigned to the product **7**. After 1 h, the mixture showed virtually the same ratio of CF_3SiMe_3 and **7**. The mixture was diluted with 20 ml of CH_2Cl_2 and washed with 20 ml of H_2O (3×). The org. phase was dried ($MgSO_4$), and the solvent was evaporated to give 450 mg of a colorless oil. After microdistillation, an anal. pure product was isolated as a colorless liquid.

2,2,4,4-Tetramethyl-3-(trifluoromethyl)-3-[(trimethylsilyl)oxy]cyclobutanone (**7**): 420 mg (74%). Colorless liquid, distilled at 95–97°/20 Torr. IR (neat): 2971*s*, 1783v*s* (C=O), 1472*s*, 1256v*s*, 1026v*s*, 874*s*, 839v*s*. ^1H-NMR: 1.26 (*s*, 2 Me); 1.23 (*q*, J(H,F) = 1.8, 2 Me); 0.18 (*q*, J(H,F) = 0.6, Me_3Si). ^{13}C-NMR: 218.9 (C=O); 125.6 (*q*, ^1J(C,F) = 284.4, CF_3); 79.9 (*q*, ^2J(C,F) = 28.1, C(3)); 63.0 (C(2), C(4)); 22.1 (2 Me); 18.8 (*q*, J(C,F) = 3.2, 2 Me); 1.4 (*q*, J(C,F) = 1.8, Me_3Si). ^{19}F-NMR: −67.7 (CF_3). EI-MS: 267 (4, $[M-Me]^+$), 213 (7), 212 (53, $[M-Me_2C{=}C{=}O]^{+\cdot}$), 120 (39), 77 (41), 70 (100, $[Me_2C{=}C{=}O]^{+\cdot}$). Anal. calc. for $C_{12}H_{21}F_3O_2Si$ (282.38): C 51.04, H 7.50; found: C 50.98, H 7.32.

3.2. *Reaction with* **1**. According to the procedure in *3.1*, **1** (312 mg, 2 mmol) was reacted with CF_3SiMe_3 (355 mg, 2.5 mmol). After 15 min at 0–5°, the reaction was finished and, after aq. workup and evaporation of CH_2Cl_2, 415 mg of a colorless oil were obtained. Anal. pure product, **8**, was obtained by distillation at *ca.* 20 Torr.

2-Isopropylidene-3,3-dimethyl-4-(trifluoromethyl)-4-[(trimethylsilyl)oxy]thietane (**8**): 415 mg (70%). Colorless liquid, distilled at 108–110°/20 Torr. IR (neat): 2950*s*, 1280*s*, 1240*s*, 1180v*s*, 1130*s*, 1080*s*, 850v*s*. ^1H-NMR: 1.70, 1.46, 1.41 (3*s*, 3 Me); 1.40 (*q*, J(H,F) = 1.6, Me–C(3) *cis* to CF_3); 0.22 (*s*, Me_3Si). ^{13}C-NMR: 124.6 (*q*, ^1J(C,F) = 282.7, CF_3); 127.5, 119.2 (C=C); 84.2 (*q*, ^2J(C,F) = 30.3, C(4)); 58.5 (C(3)); 24.9, 22.4 (br.); 21.4, 19.4 (4 Me); 1.20 (Me_3Si). ^{19}F-NMR: −76.04 (*s*, CF_3). EI-MS: 298 (56, $M^{+\cdot}$), 283 (23, $[M-Me]^+$), 209 (22), 187 (21), 127 (17), 96 (100), 81 (55). Anal. calc. for $C_{12}H_{21}F_3OSSi$ (298.44): C 48.30, H 7.09, F 19.10, S 10.74; found: C 48.70, H 7.28, F 18.84, S 10.95.

3.3. *Reaction with* **2**. According to the general procedure in *3.1*, **2** (328 mg, 2 mmol) was reacted with CF_3SiMe_3 (355 mg, 2.5 mmol). After 3 min at 0–5°, the ruby-red color of the mixture changed to pale red, and a colored solid precipitated from the THF soln., which dissolved completely after warming the soln. to r.t. After

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16) After activation, molecular sieves were immediately transferred to the reaction flask and used for drying of the TBAF soln. All operations have been carried out under a stream of N_2 to prevent contact with air moisture.

typical aq. workup and evaporation of the org. solvents, the red residue (310 mg) was chromatographed on prep. TLC plates (SiO_2; petroleum ether/CH_2Cl_2 9:1) to afford 240 mg of a red crystalline material. Anal. pure product, **9**, was obtained after crystallization.

1,1,3,3,7,7,9,9-Octamethyl-5,10-dithiadispiro[3.1.3.1]decane-2,8-dithione (**9**): 240 mg (70%). Red needles. M.p. 194–195° (hexane). IR (KBr): 2968*s*, 2920*m*, 1448*s*, 1377*m*, 1360*m*, 1302*s*, 1146*m* (C=S), 924*s*. ^{1}H-NMR: 1.39 (*s*, 8 Me). ^{13}C-NMR: 280.3 (C=S); 68.0 (C(1), C(3), C(7), C(9)); 55.1 (C(4), C(6)); 26.0 (8 Me). EI-MS: 345 (100, $M^{+\bullet}$), 173 (11), 172 (7), 96 (11). HR-MS: calc. for $C_{16}H_{24}S_4$: 345.083913; found: 345.085700. Anal. calc. for $C_{16}H_{24}S_4$ (344.63): C 55.77, H 7.02, S 37.21; found: C 55.92, H 7.03, S 37.70.

3.4. *Attempted Reaction with* **3**. According to the general procedure in *3.1*, after 8 h at r.t. the orange color of the soln. was unchanged. After dilution with CH_2Cl_2, washing with H_2O, drying ($MgSO_4$), and evaporation, the orange residue obtained was identified as unchanged **3** (^{13}C-NMR).

3.5. *Reaction with* **4a–d**. In all cases, the reaction was carried out according to the general procedure. After 3–4 h, the initially blue-colored soln. turned yellow. A sample of decolorized mixture was diluted with $CDCl_3$ and examined by ^{19}F-NMR spectroscopy. Two major fluorinated products revealing absorptions at *ca.* −40 and −90 ppm, resp., were found in all cases and left unchanged after the aq. workup. The yields of fluorinated products **10** and **11** were established directly in the crude mixture by standard NMR analysis with a weighed portion of α,α,α-trifluorotoluene. The mixtures were separated on prep. TLC plates (SiO_2; pentane or pentane with increasing amount of CH_2Cl_2). In the cases of **4b–d**, separation was limited to fluorinated products. As a rule, geminal-difluoroethenes **11** were isolated as the less polar fractions.

Diphenylmethyl Trifluoromethyl Sulfide (**10a**): Yield: crude **10a** 30%; isolated 78 mg (22%). Colorless liquid, b.p. 105–108°/0.75 Torr. ^{1}H-NMR: 7.40–7.36, 7.24–7.21 (*m*, 10 arom. H); 5.67 (br. *s*, CH). ^{13}C-NMR: 139.2 (2 arom. C); 130.1 (*q*, ^1J(C,F) = 306.4, CF_3); 128.8, 128.2, 127.9 (10 arom. CH); 53.5 (CH). ^{19}F-NMR: −41.12 (CF_3S). EI-MS: 268 (0.3, $M^{+\bullet}$), 167 (100, $[M-CF_3]^+$), 165 (34), 152 (15). Anal. calc. for $C_{14}H_{11}F_3S$ (268.30): C 62.67, H 4.13, S 11.95; found: C 62.73, H 4.22, S 12.07.

1,1-Difluoro-2,2-diphenylethene (**11a**). Yield: crude **11a** 8%; isolated 15 mg (6%). Colorless liquid, b.p. 92–94°/0.75 Torr ([50]: 91–97°/1.5 Torr). ^{13}C-NMR: 153.8 (*t*, ^1J(C,F) = 291.2, CF_2); 134.3 (2 arom. C); 129.6, 128.4, 127.5 (10 arom. CH); 97.3 (*t*, ^2J(C,F) = 17.5, *C*=CF_2). ^{19}F-NMR: −88.32 (CF_2).

2,2,3,3-Tetraphenylthiirane (**12**): 109 mg (45%), after chromatography with pentane/CH_2Cl_2 8:2. Colorless crystals, m.p. 172–174° (MeOH) ([50]: 177–179°). ^{13}C-NMR: 140.1 (1 arom. C); 130.9, 127.1, 126.6 (10 arom. CH); 66.6 (C(2), C(3)).

1,1,2,2-Tetraphenylethene (**13**): 12 mg (3%), after chromatography with pentane/CH_2Cl_2 8:2. Colorless crystals. M.p. 201–206° ([50]: 203–205°).

Bis(4-methylphenyl)methyl Trifluoromethyl Sulfide (**10b**): Yield: crude **10b** 26%; isolated 84 mg (21%). Colorless oil, purified by distillation at 105–108°/0.75 Torr. ^{13}C-NMR: 137.6, 136.4 (4 arom. C); 131.6 (*q*, ^1J(C,F) = 306.4, CF_3); 129.4, 128.0 (8 arom. CH); 53.1 (br., CH); 21.0 (2 Me). ^{19}F-NMR: −40.72 (CF_3S). Anal. calc. for $C_{16}H_{15}F_3S$ (296.35): C 64.85, H 5.10, S 10.82; found: C 64.79, H 5.13, S 10.28.

1,1-Difluoro-2,2-bis(4-methylphenyl)ethene (**11b**). Yield: crude **11b** 15%; isolated 29 mg (9%). Colorless needles. M.p. 54–56° (MeOH). ^{13}C-NMR: 153.6 (*t*, ^1J(C,F) = 290.3, CF_2); 137.2, 131.5 (4 arom. C); 129.4, 128.9 (8 arom CH); 95.9 (*t*, ^2J(C,F) = 18.0, *C*=CF_2); 21.1 (2 Me). ^{19}F-NMR: −89.17 (CF_2). Anal. calc. for $C_{16}H_{14}F_2$ (244.29): C 78.67, H 5.78, F 15.55; found: C 79.09, H 6.11, F 15.14.

Bis(4-fluorophenyl)methyl Trifluoromethyl Sulfide (**10c**): Yield: crude **10c** 28%; isolated 110 mg (20%), after chromatography and distillation at 90–93°/0.75 Torr. ^{13}C-NMR: 162.3 (*d*, ^1J(C,F) = 246.3, 2 arom. CF); 134.7 (2 arom. C); 129.7 (*q*, ^1J(C,F) = 306.7, CF_3); 129.8, 116.0 (8 arom. CH); 52.0 (CH). Anal. calc. for $C_{14}H_9F_5S$ (304.28): C 55.26, H 2.98, S 10.54; found: C 54.97, H 2.91, S 10.45.

1,1-Difluoro-2,2-bis(4-fluorophenyl)ethene (**11c**): Yield: crude **11c** 5%; not isolated in pure form. Identified in the mixture with **10c** after attempted chromatographic separation on prep. TLC plates. ^{19}F-NMR: −88.46 (CF_2).

Bis(4-methoxyphenyl)methyl Trifluoromethyl Sulfide (**10d**). Yield: crude **10d** 29%; isolated 92 mg (21%). Colorless crystals, m.p. 36–38° (MeOH). ^{13}C-NMR: 159.1, 131.3 (4 arom. C); 129.9 (*q*, ^1J(C,F) = 306.0, CF_3); 129.2, 113.7 (8 arom. CH); 55.1 (MeO); 52.6 (br., CH). Anal. calc. for $C_{16}H_{15}F_3O_2S$ (328.35): C 58.53, H 4.60, S 9.77; found: C 58.81, H 4.68, S 9.89.

1,1-Difluoro-2,2-bis(4-methoxyphenyl)ethene (**11d**): Yield: crude **11d** 7%; isolated 26 mg (5%). Colorless crystals. M.p. 50–52° (pentane) ([51]: 53–54°). ^{19}F-NMR: −90.38 (CF_2).

4. *Fluoride-Ion-Induced Conversions of Thioketones. General Procedure.* A mixture of 2 mmol of the corresponding thioketone in 2 ml of abs. THF and *ca.* 300 mg of freshly activated molecular sieves (4 Å) was stirred in a *Schlenk* flask. In a second *Schlenk* flask, 5 ml of commercial TBAF soln. in THF was diluted with

3 ml of abs. THF and dried with activated molecular sieves. After 2 h at r.t., 3 ml of predried TBAF soln. (*ca.* 1.5 mmol. TBAF) were added portionwise by means of a syringe to the soln. of a thioketone cooled to 0–5°. The cooled soln. was stirred for 30 min, then the cooling bath was removed, and stirring was continued at r.t., until the initial color of thioketone disappeared or completely changed. The mixture was diluted with 20 ml of CH_2Cl_2, washed with H_2O (29 ml, 3 ×), and the org. phase was dried and evaporated. Separation of products was achieved by means of chromatographic techniques, followed by crystallization. Reported yields refer to amounts obtained after chromatography.

4.1. *Reaction with* **4a**. Reaction time 12 h; chromatography: SiO_2, petroleum ether. *Bis(diphenylmethyl) Disulfide* (**15**): 195 mg (49%). Colorless crystals, m.p. 153–155° (MeOH/CH_2Cl_2) ([34]: 151–152°). IR: 3026*w*, 1495*m*, 1450*m*, 1082*w*, 1030*w*, 750*m*, 721*m*, 700*s*, 627*m*. ^{1}H-NMR: 7.40–7.30 (*m*, 20 arom. H); 4.80 (*s*, 2 CH). ^{13}C-NMR: 140.1 (2 arom. C); 128.9, 128.3, 127.4 (10 arom. CH); 59.7 (2 CH). EI-MS: 198 (82, $Ph_2CS^{+\bullet}$), 165 (100), 121 (93), 77 (43). CI-MS (NH_3): 417 (7), 416 (21, $[M+NH_4]^+$), 352 (10), 199 (14, $Ph_2CHS^{+\bullet}$), 184 (5), 182 (6), 168 (14), 167 (100). Anal. calc. for $C_{26}H_{22}S_2$ (398.59): C 78.35, H 5.56, S 16.09; found: C 77.95, H 5.65, S 16.73.

4.2. *Reaction with* **5**. The first drop of TBAF soln. initiated a vigorous reaction to give an orange-colored product. Chromatographic workup (SiO_2 column, hexane/CH_2Cl_2 8:2) gave 198 mg (60%) of *9-(9*H*-fluoren-9-ylidene)-9*H*-fluorene* (**14**): Orange crystals. M.p. 182–185° (Et_2O) ([25]: 182–187°).

4.3. *Reaction with* **2**. Five min after the addition of the TBAF soln., the red color of the mixture changed to orange, and TLC revealed complete conversion of **2**. The sole product of the reaction was isolated chromatographically (prep. TLC plates, SiO_2; petroleum ether/CH_2Cl_2 9:1). Physical and spectral properties matched those reported for *4-isopropylidene-3,3-dimethylthietane-2-thione* (**16**) [20]. Yield: 293 mg (85%). Orange oil, distilled at 108–110°/12 Torr ([20]: 112–116/20 Torr). ^{1}H-NMR: 1.80 (*s*, Me); 1.67 (*s*, Me); 1.40 (*s*, 2 Me). ^{13}C-NMR: 243.0 (C=S); 130.7, 122.3 (C=C); 73.9 (C(3)); 25.0 (2 Me); 21.7 (Me); 19.9 (Me).

4.4. *Reaction with* **1**. After 3 h, the red color of the soln. changed to yellow-green, and the conversion of **1** was complete (TLC). After typical workup, the crude mixture was examined by means of ^{1}H-NMR spectroscopy. The spectrum revealed an *s* at 1.32 ppm (assigned to **6**) along with three other *s* at 1.64, 1.43, and 1.17. The ratio of **6** and the new product, established on the basis of integrals of Me groups, was *ca.* 1:1. The mixture was separated (SiO_2 column; petroleum ether with increasing amount of CH_2Cl_2), and two fractions were isolated.

Compound **6:** Chromatography with petroleum ether/CH_2Cl_2 1:1:37 mg (12%). Colorless crystals, identical with an authentic sample [45].

2,2,4,4-Tetramethyl-3-oxocyclobutyl 2,2,4-Trimethyl-3-oxopentanedithioate (**17**): 147 mg (47%), isolated as a slightly more polar fraction than **6**, with petroleum ether/CH_2Cl_2 1:1 and purified by crystallization. Yellow crystals. M.p. 62–63° (hexane at −20°). ^{1}H-NMR: 4.20 (*s*, H–C(3)); 2.84 (*sept.*, J = 6.6, Me_2CH); 1.64 (*s*, 2 Me); 1.43 (*s*, 2 Me); 1.17 (*s*, 2 Me); 1.09 (*d*, J = 6.6, Me_2CH). ^{13}C-NMR: 241.0 (C=S); 218.6 (C=O, cyclobutanone); 211.8 (C(3)=O); 69.3, 61.0 (C(1′), C(2)); 57.5 (C(2′), C(4′)); 36.9 (C(4)); 26.7 (2 Me); 24.9 (2 Me); 21.7 (2 Me); 20.3 (2 Me). EI-MS: 314 (3, $M^{+\bullet}$), 299 (2, $[M-Me]^+$), 244 (15, $[M-Me_2C{=}C{=}O]^{+\bullet}$), 174 (18), 173 (19), 158 (21), 131 (5), 98 (15), 97 (100), 87 (8). HR-MS: Calc. for $C_{16}H_{26}O_2S_2$: 314.13724; found: 314.13700. Anal. calc. for $C_{16}H_{26}O_2S$ (314.50): C 61.11, H 8.33, S 20.39; found: C 61.45, H 8.57, S 20.89.

4.5. *Reaction with* **3**: The reaction was complete after 1 h at 0–5° and 4 h at r.t., and the mixture was separated chromatographically.

Dispiro[adamantane-2,2′-[1,2,4]trithiolane-5′,2″-adamantane] (**18**): 233 mg (64%). Colorless prisms. M.p. 203–206° (EtOH/CH_2Cl_2) ([52]: 193–195°). Identified by comparison of the ^{13}C-NMR spectra with that of an authentic sample.

5. *X-Ray Crystal-Structure Determination of* **15**[17]). All measurements were made on a *Nonius KappaCCD* diffractometer [53] with 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 a view of the molecule is shown in the *Figure*. Data reduction was performed with *HKL Denzo* and *Scalepack* [54]. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method [55] was applied. The structure was solved by direct methods using SIR92 [56], which revealed the

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[17]) Crystallographic data (excluding structure factors) for the structure of **15** reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication No. CCDC-179554. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

positions of all non-H-atoms. The molecule has C_2 symmetry. The non-H-atoms were refined anisotropically. All of the H-atoms were fixed in geometrically calculated positions (d(C–H) = 0.95 Å), and each was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom. Refinement of the structure was carried out on F using full-matrix least-squares procedures, which minimized the function $\Sigma w(|F_o| - |F_c|)^2$. A correction for secondary extinction was not applied. The absolute structure was determined by refinement of the absolute structure parameters [57], which yielded a value of 0.01(4). Neutral-atom scattering factors for non-H-atoms were taken from [58a] and the scattering factors for H-atoms from [59]. Anomalous dispersion effects were included in F_c [60]; the values for f' and f'' were those of [58b], and the values of the mass attenuation coefficients were those of [58c]. All calculations were performed using the teXsan crystallographic software package [61].

Table. *Crystallographic Data of* **15**

Crystallized from	AcOH
Empirical formula	$C_{26}H_{22}S_2$
M_r [g mol^{-1}]	398.58
Crystal color, habit	colorless, needle
Crystal dimensions [mm]	0.08 × 0.20 × 0.35
Temp. [K]	160(1)
Crystal system	monoclinic
Space group	$C2$
Z	2
Reflections for cell determination	16093
2θ range for cell determination [°]	4 – 60
Unit-cell parameters a [Å]	17.7978(3)
b [Å]	5.7598(1)
c [Å]	12.3326(2)
β [°]	124.5945(9)
V [Å^3]	1040.71(3)
D_x [g cm^{-3}]	1.272
μ(MoK_α) [mm^{-1}]	0.264
Scan type	ϕ and ω
$2\theta_{(max)}$ [°]	60
Transmission factors (min; max)	0.889; 0.985
Total reflections measured	15892
Symmetry independent reflections	3017
Reflections used [$I > 2\sigma(I)$]	2847
Parameters refined	127
Final R	0.0330
wR ($w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$)	0.0364
Goodness-of-fit	2.270
Final Δ_{max}/σ	0.0006
$\Delta\rho$ (max; min) [e · Å^{-3}]	0.20; – 0.21

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