Reactions of Sulfanyl Chlorides with Thiocamphor and Thiofenchone: *Wagner–Meerwein* Rearrangement of an Intermediate Thiocarbonylium Ion

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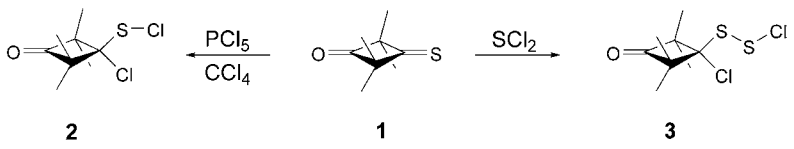
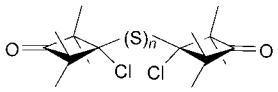
The reaction of sulfanyl and disulfanyl chlorides with thiocamphor (**6**) in the presence of Et_3N leads to unsymmetrical di- and trisulfanes, respectively (*Schemes 2* and *4*). A reaction mechanism *via* a thiocarbonylium ion, which is immediately deprotonated, is proposed. The formation of a minor product **10** in the absence of a base, resulting from a *Wagner–Meerwein* rearrangement, is an additional evidence for the intermediacy of a thiocarbonylium ion (*Scheme 3*). On the other hand, the non-enolizable thiofenchone (**13**) reacts with sulfanyl chlorides in CH_2Cl_2/Et_3N to give exclusively products with a rearranged bicyclic skeleton (*Scheme 5*). A *Wagner–Meerwein* rearrangement of the intermediate thiocarbonylium ion is the key step. The structures of the products **10** and **14**, which have rearranged bicyclic systems, have been established by X-ray crystallography.

1. Introduction. – In a recent report [1], reactions of the sterically crowded 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1**) with PCl_5 and SCl_2 to give the stable α-chlorosulfanyl chloride **2** and α-chlorodisulfanyl chloride **3**, respectively, have been described (*Scheme 1*). These products were shown to add easily to **1** to give symmetrically substituted polysulfanes **4** [2][3]. On the other hand, **2** and **3** are highly electrophilic reagents, which react smoothly with enolizable thiocarbonyl-functionalized N-heterocycles like 1*H*-imidazole-2-thiones or thiouracil to give the corresponding di- and trisulfanes of type **5**, respectively [2].

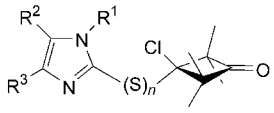
Scheme 1



2 **1** **3**



4 n = 2, 3



5 n = 2, 3

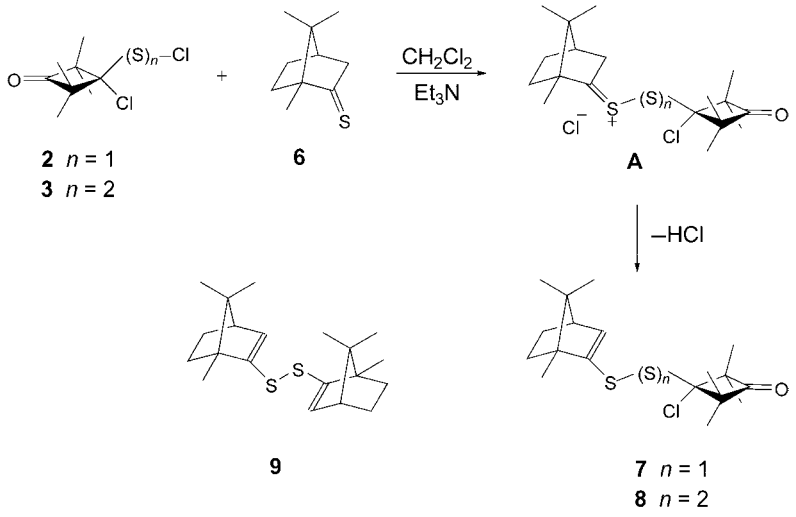
[1]) Part of the planned Ph.D. thesis of *A. M.*, Universität Zürich.

Sulfur transfer *via* a thiocarbonylium ion with subsequent hydrolysis was observed when **2** or **3** were reacted with non-enolizable thiocarbonyl compounds (*e.g.*, thiobenzophenone, 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione) in wet THF. The products isolated from these reactions correspond to symmetrical polysulfanes of type **4**, which contain three or five S-atoms [2].

In our ongoing study focused on the application of thiocarbonyl compounds for the preparation of S-rich molecules, we were interested in reactions of **2** and **3** with enolizable thioketones. Based on our experience, thiocamphor (**6**) was selected as an easily accessible [4], relatively stable, and almost non-odorous substrate. To compare the reactivity of similarly substituted thioketones, thiofenchone was reacted under similar conditions.

2. Results and Discussion. – 2.1. *Reactions with Thiocamphor* (**6**). The reactions of **2** and **3** with thiocamphor (**6**) in a molar ratio of 1:1 were carried out in abs. CH_2Cl_2 in the presence of an equimolar amount of Et_3N at room temperature. The color of **6** disappeared within a few min, and, after evaporation of the solvent, the crude products were analyzed by NMR spectroscopy. The yields of the obtained products (*ca.* 70%) were determined by ^{1}H-NMR spectroscopy after addition of a weighed amount of 1,1,2,2-tetrachloroethane as an external standard. In both cases, the NMR spectra showed a *doublet* for an olefinic CH group (δ(H): 6.24 and 6.33 ppm, resp.; δ(C): 153.3 and 139.4 ppm, resp.). Other signals observed in the spectra confirmed the presence of the bicyclic moiety as well as the substituted cyclobutanone. The CI-MS (NH_3) indicated the molecular formula of the corresponding di- and trisulfane **7** and **8** (*Scheme 2*). Although the spectroscopic data convincingly established the structures, all attempts to obtain the products in an analytically pure form were in vain. During chromatography, both products decomposed, and only unconverted **6**, along with small amounts of the known symmetrical disulfane **9** [5], was isolated.

Scheme 2



2 *n* = 1
3 *n* = 2

6

A

9

7 *n* = 1
8 *n* = 2

We assumed that the instability of **7** and **8** may be a result of the lability of the C–Cl bond, but all experiments aimed towards the substitution of the Cl-atom by nucleophiles such as morpholine and sodium thiophenolate led to complex mixtures of decomposition products.

The presence of Et_3N is crucial for the smooth reaction leading to **7** and **8**, as, in its absence, complex mixtures were formed. In one of the experiments with **2** and **6**, chromatographic workup gave traces of a product **10**, which is an isomer of **7**. Its structure was unambiguously determined by X-ray crystallography (*Fig. 1*).

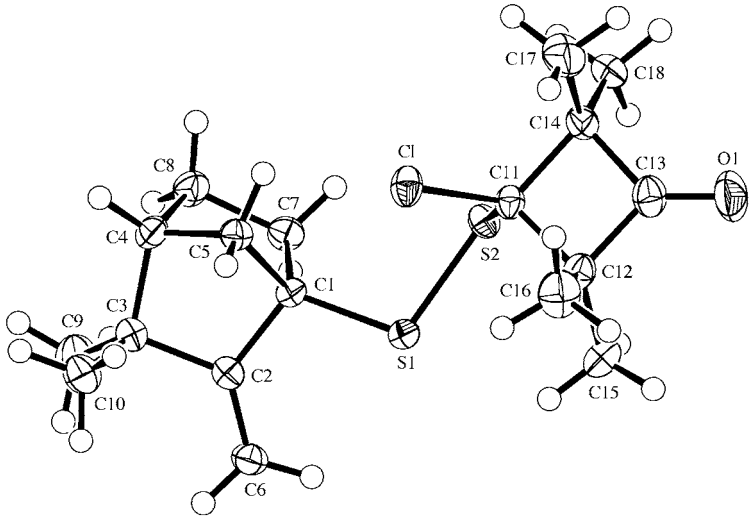


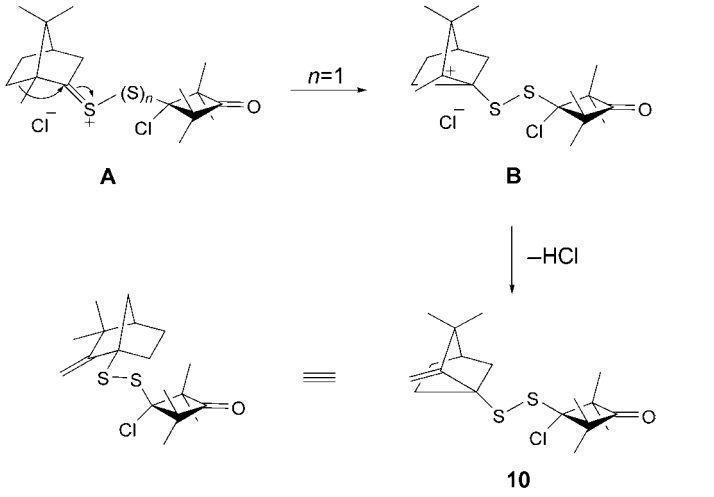
Fig. 1. *ORTEP Plot* [6] *of the molecular structure of* **10** (50% probability ellipsoids, arbitrary numbering of atoms)

The structure presented in *Fig. 1* shows that the bicyclic skeleton corresponds to a rearranged product formed *via* a *Wagner–Meerwein* rearrangement [7]. It seems that, in the absence of Et_3N, the intermediate thiocarbonylium salt **A** ($n=1$) is not spontaneously transformed into **7**, but undergoes a 1,2-shift to give the carbenium ion **B**, which by deprotonation yields **10** (*Scheme 3*).

The results obtained with α-chlorosulfanyl chloride **2** prompted us to carry out similar reactions with the commercially available (nitrophenyl)sulfanyl chlorides **11a** and **11b**. The progress of the conversions was monitored by ^{1}H-NMR spectroscopy. Both sulfanyl chlorides reacted with **6** much more slowly than **2** and **3** and, in the case of **11a**, even after 72 h, 12% of **6** were still recovered (*Table 1*). Therefore, the reactions were repeated at 100° in CCl_4/toluene solution. After 3 h heating and chromatographic workup, the corresponding disulfanes **12a** and **12b** were isolated in 57 and 42% yield, respectively (*Scheme 4*). Unlike the analogous products **7** and **8**, no decomposition was observed during isolation and purification.

2.2. *Reactions with Thiofenchone* (**13**). The reactions of **13** with sulfanyl chlorides were carried out under analogous conditions to those described for **6** (*Sect. 2.1*). Whereas, in the case of **2**, the reaction was complete after 2 min, 24 h were necessary in the case of **3**. The crude products **14** and **15** (*Scheme 5*) were analyzed by NMR

Scheme 3



Scheme 4

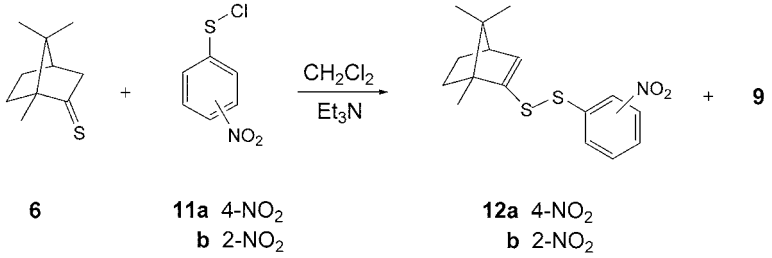


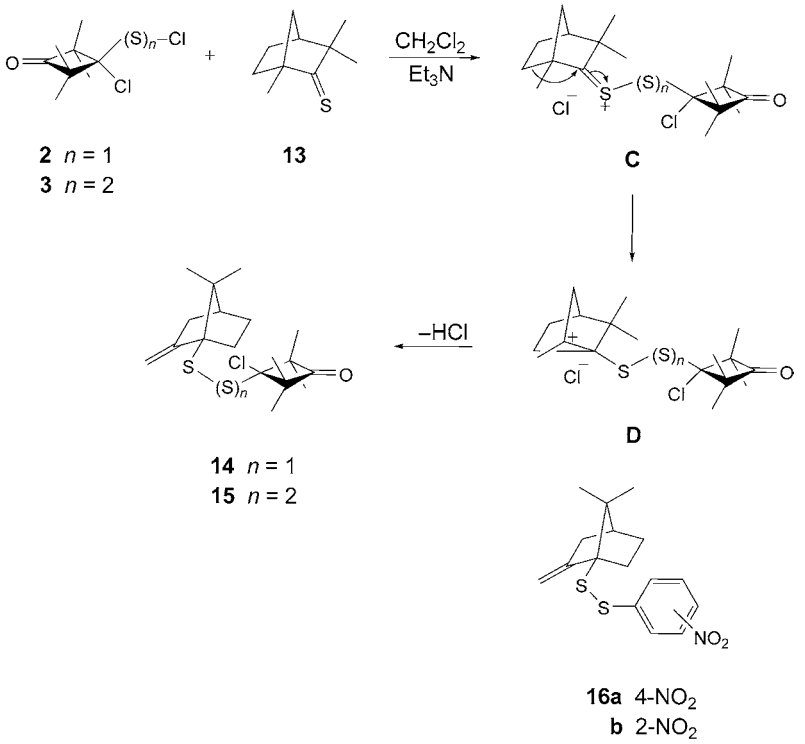
Table 1. *Reactions of* **6** *with (Nitrophenyl)sulfanyl Chlorides* **11** *in* CH_2Cl_2

11	Temp. [°]	Time [h]	**12** [%]	**9** [%]	**6** [%]
a 4-NO_2	r.t.	1	13	17	69
	r.t.	72	32	29	12
	100°[a])	3	57	traces	2
b 2-NO_2	r.t.	1	59	3	4
	100°[a])	3	42	traces	25

[a]) Reaction carried out in CCl_4/toluene 1 : 1.

spectroscopy. The products obtained in the two experiments showed *triplet*-like signals for two H-atoms at δ 5.24/4.88 and 5.18/4.89 ppm with $J = 1.9 – 2.4$ Hz, respectively. This pattern is characteristic for the olefinic CH_2 group. In the ^{13}C-NMR spectra, the corresponding signals of **14** appeared at δ 154.2 (*s*) and 106.2 (*t*) ppm, and at 153.2 (*s*) and 106.4 (*t*) in the case of **15**. The other signals in the NMR spectra showed that both products have similar structures, and the CI-MS confirmed that they differ by only one S-atom.

Scheme 5



All these data indicated that the formation of **14** and **15** occurred *via* rearrangement of the bicyclic skeleton in a manner, which corresponds to a *Wagner–Meerwein* rearrangement. In the case of **14**, the product was obtained in crystalline form, and its structure was confirmed by X-ray crystallography (*Fig. 2*)[2]).

In contrast to **14**, the trisulfane **15** could not be isolated in pure form. Chromatography on SiO_2 plates led to partial decomposition of the main product, and only a mixture of the known symmetric bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutyl)tri- and -tetrasulfanes **4** ($n = 3,4$) [3] was isolated as a minor fraction.

The (nitrophenyl)sulfanyl chlorides **11a** and **11b** reacted with **13** to give disulfanes of type **16** *via Wagner–Meerwein* rearrangement of the intermediate thiocarbonylium cation (*Scheme 5*). Similar to the reaction with **6**, longer reaction times than with **2** were needed to complete the reactions.

In conclusion, the results described show that thiocarbonylium cations, formed by electrophilic addition of sulfanyl chlorides to thioketones, are stabilized by deprotonation. Whereas vinylic polysulfanes are formed in the case of the enolizable thiocamphor (**6**), the direct deprotonation is not possible in the case of the non-enolizable thiofenchone (**13**). In this system, a *Wagner–Meerwein* rearrangement

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[2]) Repeated recrystallization from hexane gave a single crystal that proved to be racemic, although the solid obtained after chromatography was optically active (see *Exper. Part*).

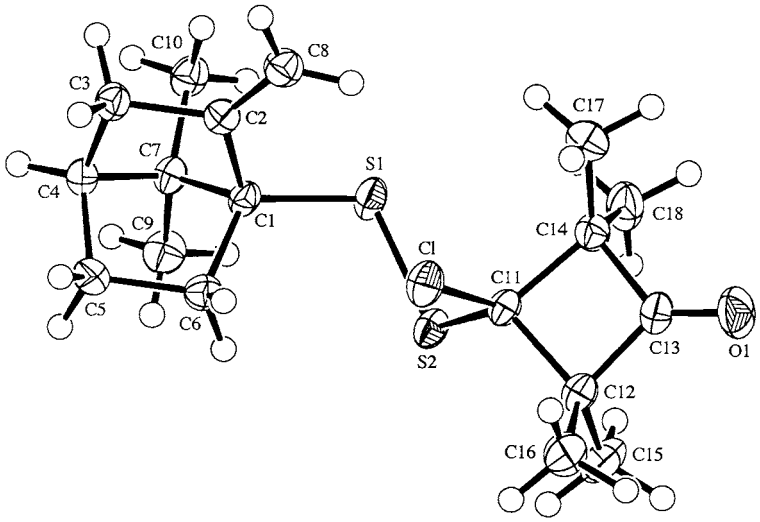

Fig. 2. *ORTEP Plot* [6] *of the molecular structure of* **14** (50% probability ellipsoids, arbitrary numbering of atoms)

occurs prior to the deprotonation. The course of this reaction is in accordance with already described transformations of the *in situ* generated thiocarbonylium cation formed by protonation of the transient thiofenchone *S*-methylide [8][9].

We thank the analytical units of the Institute of Organic Chemistry of the University of Zürich for spectra and analyses. Financial support of this work by the *Swiss National Science Foundation* and *F. Hoffmann-La Roche AG*, Basel, is gratefully acknowledged. *G. M.* acknowledges financial support by the *Polish State Committee for Scientific Research* (grant No. 4 T09A 046 25).

Experimental Part

1. *General*. See [2]. 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 $CDCl_3$. MS: *Finnigan MAT-90* or *Finnigan SSQ-700* instrument (EI, 70 eV, or CI (NH_3)). Elemental analyses were performed by the Mikroanalytisches Laboratorium des Organisch-chemischen Instituts der Universität Zürich.

2. *Starting Materials. (−)-(1*R,*4*R*)-1,7,7-Trimethylbicyclo[2.2.1]heptane-2-thione* (=*thiocamphor*; **6**) and *(−)-(1*R,*4*S*)-1,3,3-Trimethylbicyclo[2.2.1]heptane-2-thione* (*thiofenchone*; **13**) were prepared according to [4] by treatment of a soln. of the corresponding ketones in MeOH with a mixture of HCl and H_2S gas in the presence of equal amounts of methyl orthoformate. *3-Chloro-3-(chlorosulfanyl)-2,2,4,4-tetramethylcyclobutanone* (**2**) and *3-chloro-3-(chlorodisulfanyl)-2,2,4,4-tetramethylcyclobutanone* (**3**) were obtained from *2*,2,4,4-tetramethyl-3-thioxocyclobutanone according to a protocol described in [1]. The (4-nitrophenyl)- and (2-nitrophenyl)sulfanyl chlorides (**11a** and **11b**, resp.) are commercially available (*Aldrich*).

3. *Reactions of* **6** *with Sulfanyl Chlorides. General Procedure*. To a soln. of **6** (84.5 mg, 0.5 mmol) and Et_3N (50.6 mg, 0.5 mmol) in CH_2Cl_2 (3 ml) at r.t. was added a soln. of the corresponding sulfanyl chloride (0.5 mmol) in CH_2Cl_2 (2 ml). The color of the soln. changed significantly. After the indicated time, the solvent was evaporated, and the residue was triturated with Et_2O and filtered to remove the inorg. salts. The solvent was again evaporated, the residue was dissolved in $CDCl_3$, and the yield of the product was determined by ^{1}H-NMR spectroscopy with respect to a weighed amount of 1,1,2,2-tetrachloroethane as an external standard.

3.1. *Reaction with* **2**. Reaction time 2 min. Color change from orange to yellow. Yield (^{1}H-NMR): 74% of *3-chloro-2,2,4,4-tetramethyl-3-{2-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]disulfanyl}cyclobutanone* (**7**). ^{1}H-NMR: 6.24 (*d*, *J* = 3.4, H–C(3′)); 2.39 (*t*, *J* = 3.5, 1 H); 1.94–1.82 (*m*, 1 H); 1.61–1.51 (*m*, 1 H); 1.50, 1.47, 1.42, 1.41 (4*s*, 4 Me); 1.24–1.12 (*m*, 1 H); 1.07 (*s*, Me); 1.06–0.95 (*m*, 1 H); 0.84, 0.79 (2*s*, 2 Me). ^{13}C-NMR: 216.7 (*s*, C(1)); 141.2 (*s*, C(2′)); 135.3 (*d*, C(3′)); 88.1 (*s*, C(3)); 69.4 (*s*, C(2), C(4)); 57.6 (*s*, C(1′)); 56.6 (*s*, C(7′)); 52.4 (*d*, C(4′)); 31.5 (*t*, C(6′)); 25.4 (*t*, C(5′)); 23.5, 23.1, 22.6, 22.3 (4*q*, 2 Me–C(2), 2 Me–C(4)); 19.5, 19.3 (2*q*, 2 Me–C(7′)); 11.4 (*q*, Me–C(1′)). CI-MS (NH_3): 361 (10), 359 (88, $[M+1]^+$), 323 (100, $[M-Cl]^+$), 169 (7).

An analogous reaction was carried out in the absence of Et_3N. After stirring the mixture for 1 h (orange → yellow), the solvent was evaporated, and the residue was separated by prep. TLC (hexane/Et_2O 15:1): *ca.* 9 mg (5%) of *3-chloro-2,2,4,4-tetramethyl-3-{[(1*R*,4*R*)-3,3-dimethyl-2-methylidenebicyclo[2.2.1]hept-1-yl]disulfanyl}cyclobutanone* (**10**). Colorless crystals. M.p. 86.9–87.1° (hexane). Single crystals suitable for an X-ray crystal-structure determination were grown from hexane.

3.2. *Reaction with* **3**. Reaction time: 2 min. Color change from orange to yellow. Yield (^{1}H-NMR): 62% of *3-chloro-2,2,4,4-tetramethyl-3-{3-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]trisulfanyl}cyclobutanone* (**8**). ^{1}H-NMR: 6.33 (*d*, *J* = 3.4, H–C(3′)); 2.44 (*t*, *J* = 3.6, 1 H); 1.93–1.88 (*m*, 1 H); 1.61–1.50 (*m*, 1 H); 1.46 (*s*, 2 Me); 1.43 (*s*, 2 Me); 1.18–1.13 (*m*, 1 H); 1.11 (*s*, Me); 1.07–1.00 (*m*, 1 H); 0.84, 0.81 (2*s*, 2 Me). ^{13}C-NMR: 216.2 (*s*, C(1)); 141.6 (*s*, C(2′)); 139.4 (*d*, C(3′)); 87.6 (*s*, C(3)); 69.0 (*s*, C(2), C(4)); 57.3 (*s*, C(1′)); 56.8 (*s*, C(7′)); 52.7 (*d*, C(4′)); 31.6 (*t*, C(6′)); 25.2 (*t*, C(5′)); 23.6, 23.3, 22.9, 22.3 (4*q*, 2 Me–C(2), 2 Me–C(4)); 19.6, 19.3 (2*q*, 2 Me–C(7′)); 11.7 (*q*, Me–C(1′)). CI-MS (NH_3): 457 (19), 455 (33), 391 (40, $[M+1]^+$), 365 (16), 359 (52), 355 (100, $[M-Cl]^+$), 335 (23), 323 (61), 169 (44, $[C_{10}H_{16}S+1]^+$).

3.3. *Reaction with* **11a**. Reaction time: 1 h and 3 d at r.t., and 3 h at 100° (CCl_4/toluene 1:1) (see *Table 1*). Color change from brown to orange. The mixture was separated by prep. TLC (hexane/Et_2O 20:1) to yield 21 mg (13%), 51 mg (32%), and 91 mg (57%), resp., of *1-(4-nitrophenyl)-2-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]disulfane* (**12a**). Pale yellow crystals. M.p. 93–95° (hexane). $[\alpha]_D^{23} = -170.9$ (*c* = 1.1, $CHCl_3$). IR (KBr): 2951*m*, 1593*m*, 1577*m*, 1511*s*, 1473*m*, 1362*m*, 1336*s*, 1176*w*, 1105*m*, 1078*w*, 851*m*, 838*m*, 794*w*, 741*m*, 710*w*, 680*w*. ^{1}H-NMR: 8.09, 7.52 (*AA′BB′*, *J* = 9.0, 4 arom. H); 6.00 (*d*, *J* = 3.4, H–C(3)); 2.29 (*t*, *J* = 3.5, H–C(4)); 1.85–1.76 (*m*, 1 H); 1.60–1.47 (*m*, 1 H); 1.09–1.03 (*m*, 1 H); 1.05 (*s*, Me); 1.02–0.82 (*m*, 1 H); 0.71, 0.63 (2*s*, 2 Me). ^{13}C-NMR: 145.6, 145.2, 139.4 (3*s*, 2 arom. C, C(2)); 134.7 (*d*, C(3)); 125.2, 122.9 (2*d*, 4 arom. CH); 56.5 (*s*, C(1)); 56.2 (*s*, C(7)); 51.4 (*d*, C(4)); 30.7 (*t*, C(6)); 24.5 (*t*, C(5)); 18.5, 18.3 (2*q*, 2 *Me*–C(7)); 10.4 (*q*, *Me*–C(1)). CI-MS: 322 (100, $[M+1]^+$), 169 (16, $[C_{10}H_{16}S+1]^+$). Anal. calc. for $C_{16}H_{19}NO_2S_2$ (321.46): C 59.78, H 5.96, N 4.36, S 19.95; found: C 59.76, H 6.19, N 4.31, S 19.71.

3.4. *Reaction with* **11b**. Reaction time: 1 h at r.t. and 3 h at 100° (CCl_4/toluene 1:1), (see *Table 1*). Color change from brown to orange. The mixture was separated by prep. TLC (hexane/Et_2O 20:1) to yield 94 mg (59%) and 68 mg (42%), resp., of *1-(2-nitrophenyl)-2-[(1*R*,4*R*)-1,7,7-trimethylbicyclo[2.2.1]hept-2-en-2-yl]disulfane* (**12b**). Yellow oil. $[\alpha]_D^{23} = -30.9$ (*c* = 0.9, $CHCl_3$). IR (film): 2952*m*, 1590*m*, 1567*m*, 1513*s*, 1449*m*, 1304*m*, 1101*w*, 1039*m*, 852*m*, 728*m*, 732*s*, 710*m*, 681*w*, 653*w*. ^{1}H-NMR: 8.17 (*dd*, *J* = 9.6, 1.3, 1 arom. H); 8.00 (*dd*, *J* = 9.4, 1.2, 1 arom. H); 7.57–7.52, 7.28–7.22 (2*m*, 2 arom. H); 5.88 (*d*, *J* = 3.4, H–C(3)); 2.25 (*t*, *J* = 3.5, H–C(4)); 1.82–1.73, 1.54–1.46, 1.09–1.05 (3*m*, 3 H); 1.07 (*s*, Me); 1.03–0.83 (*m*, 1 H); 0.70, 0.68 (2*s*, 2 Me). ^{13}C-NMR: 144.7, 139.4, 136.1 (3*s*, 2 arom. C, C(2)); 132.8, 132.7 (2*d*, 2 arom. C); 126.5 (*d*, C(3)); 125.0, 124.9 (2*d*, 2 arom. C); 56.4, 56.2 (2*s*, C(1), C(7)); 51.3 (*d*, C(4)); 30.6, 24.6 (2*t*, C(6), C(5)); 18.6, 18.3 (2*q*, 2 Me–C(7)); 10.4 (*q*, Me–C(1)). CI-MS: 322 (100, $[M+1]^+$), 169 (18, $[C_{10}H_{16}S+1]^+$). Anal. calc. for $C_{16}H_{19}NO_2S_2$ (321.46): C 59.78, H 5.96, N 4.36, S 19.95; found: C 59.64, H 6.16, N 4.13, S 19.90.

4. *Reactions of* **13** *with Sulfanyl Chlorides.* According to the *General Procedure.* 4.1. *Reaction with* **2**. Reaction time: 2 min. Color change from orange to colorless. Prep. TLC (hexane/Et_2O 15:1) gave 96 mg (54%) of *3-chloro-3-{2-[(1*S*,4*S*)-7,7-dimethyl-2-methylidenebicyclo[2.2.1]hept-1-yl]disulfanyl}-2,2,4,4-tetramethylcyclobutanone* (**14**) as a colorless oil. After recrystallization from hexane, 14 mg (8%) of **14** were obtained as colorless crystals. M.p. 73–75° (hexane). $[\alpha]_D^{23} = -143.6$ (*c* = 1, AcOEt). IR (KBr): 2995*w*, 2956*m*, 2936*m*, 2873*w*, 1788*vs*, 1768*m*, 1656*w*, 1465*m*, 1454*w*, 1384*m*, 1367*w*, 1171*w*, 1027*w*, 977*w*, 915*w*, 887*w*, 831*w*, 699*w*. ^{1}H-NMR (600 MHz, C_6D_6): 5.24 (*t*-like, *J* ≈ 2.2, 1 H of $=CH_2$); 4.88 (*t*-like, *J* ≈ 1.9, 1 H of $=CH_2$); 2.51–2.45 (*m*, H_{exo}–C(6′), H_{exo}–C(3′)); 2.06 (*dt*, *J* = 16.1, 1.8, H_{endo}–C(6′)); 1.95–1.89 (*m*, H_{exo}–C(5′)); 1.84 (*t*, *J* = 3.4, H–C(4′)); 1.70–1.64 (*m*, H_{endo}–C(3′)); 1.57, 1.47 (2*s*, Me–C(2), Me–C(4)); 1.41 (*s*, Me–C(2), Me–C(4)); 1.39–1.32 (*m*, H_{endo}–C(5′)); 0.98, 0.84 (2*s*, 2 Me–C(7′)). ^{13}C-NMR (150.9 MHz, C_6D_6): 217.0 (*s*, C(1)); 154.2 (*s*, C(2′)); 106.2 (*t*, $=CH_2$); 86.1 (*s*, C(3)); 70.4, 68.1 (2*s*, C(2), C(4)); 66.5 (*s*, C(1′)); 50.5 (*s*, C(7′)); 43.7 (*d*, C(4′)); 37.1 (*t*, C(6′)); 33.8 (*t*, C(3′)); 28.0 (*t*, C(5′)); 23.8, 23.7, 23.6, 21.8 (4*q*, 2 Me–C(2), 2 Me–C(4)); 19.6,

19.4 (2*q*, 2 Me–C(7′)). CI-MS (NH_3): 325 (13), 324 (21), 323 (100, $[M-Cl]^+$), 169 (17, $[C_{10}H_{16}S+1]^+$). Anal. calc. for $C_{18}H_{27}ClOS_2$ (358.99): C 60.22, H 7.57, S 17.86; found: C 60.67, H 7.95, S 17.84.

Single crystals suitable for an X-ray crystal-structure determination were grown from hexane.

4.2. *Reaction with* **3**. Reaction time: 24 h. No color change. Yield (^{1}H-NMR): 28% of *3-chloro-3-[3-[(1S,4S)-7,7-dimethyl-2-methylidenebicyclo[2.2.1]hept-1-yl]trisulfanyl}-2,2,4,4-tetramethylcyclobutanone* (**15**). ^{1}H-NMR (600 MHz, C_6D_6): 5.18 (*t*-like, $J\approx2.4$, 1 H of $=CH_2$); 4.89 (*t*, $J\approx2.0$, 1 H of $=CH_2$); 2.52–2.45 (*m*, 2 H); 2.08–1.66 (*m*, 4 H); 1.57, 1.46, 1.43, 1.41 (4*s*, 2 Me–C(2), 2 Me–C(4)); 1.40–1.33 (*m*, 1 H); 1.07, 0.89 (2*s*, 2 Me–C(7′)). ^{13}C-NMR (150.9 MHz, C_6D_6): 217.6 (*s*, C(1)); 153.2 (*s*, C(2′)); 106.4 (*t*, $=CH_2$); 87.4 (*s*, C(3)); 71.0, 69.2 (*s*, C(2), C(4)); 67.0 (*s*, C(1′)); 50.3 (*s*, C(7′)); 44.5 (*d*, C(4′)); 37.0 (*t*, C(6′)); 34.6 (*t*, C(3′)); 28.1 (*t*, C(5′)); 23.4, 23.1, 23.0, 22.4 (4*q*, 2 Me–C(2), 2 Me–C(4)); 20.0, 19.6 (2*q*, 2 Me–C(7′)). CI-MS (NH_3): 367 (5), 355 (19, $[M-Cl]^+$), 327 (12), 323 (100), 201 (9), 199 (20), 169 (66, $[C_{10}H_{16}S+1]^+$), 167 (5).

4.3. *Reaction with* **11a**. Reaction time: 1 h. Color change from brown to orange. The mixture was separated by prep. TLC (hexane/Et_2O 20:1) to yield 51 mg (32%) of *1-[(1S,4S)-7,7-dimethyl-2-methylidenebicyclo[2.2.1]-hept-1-yl]-2-(4-nitrophenyl)disulfane* (**16a**)[3]) and 27 mg (32%) of **13**.

Data of **16a**: Yellow oil. $[\alpha]_D^{23}=-163.1$ ($c=0.9$, $CHCl_3$). IR (film): 2947*m*, 1596*w*, 1577*m*, 1513*s*, 1474*m*, 1367*w*, 1334*s*, 1108*m*, 1075*m*, 1009*w*, 977*w*, 885*w*, 851*m*, 757*w*, 741*m*, 681*w*. ^{1}H-NMR: 8.09, 7.62 (*AA′BB′*, $J=9.1$, 4 arom. H); 5.15 (*t*-like, $J\approx2.5$, 1 H of $=CH_2$); 4.85 (*t*-like, $J\approx2.1$, 1 H of $=CH_2$); 2.48–2.41 (*m*, 1 H); 2.12–1.93 (*m*, 2 H); 1.83–1.73 (*m*, 2 H); 1.51–1.38 (*m*, 1 H); 1.26–1.18 (*m*, 1 H); 0.95, 0.82 (2*s*, 2 Me). ^{13}C-NMR: 152.8 (*s*, C(2)); 147.8, 145.0 (2*s*, C(1), C(4)); 124.9, 122.8 (2*d*, 4 arom. CH); 105.1 (*t*, $=CH_2$); 66.7 (*s*, C(1)); 49.6 (*s*, C(7)); 42.8 (*d*, C(4)); 35.9 (*t*, C(6)); 32.5 (*t*, C(3)); 26.7 (*t*, C(5)); 18.8, 18.7 (2*q*, 2 Me–C(7)). CI-MS (NH_3): 340 (20), 339 (100, $[M+NH_4]^+$, 322 (20, $[M+1]^+$), 169 (17, $[C_{10}H_{16}S+1]^+$), 167 (8). Anal. calc. for $C_{16}H_{19}NO_2S_2$ (321.46): C 59.78, H 5.96, N 4.36, S 19.95; found: C 59.94, H 6.01, N 4.15, S 19.70.

4.4. *Reaction with* **11b**. Reaction time: 1 h. Color change from brown to orange. The mixture was separated by prep. TLC (hexane/Et_2O 20:1) to yield 79 mg (49%) of *1-[(1S,4S)-7,7-dimethyl-2-methylidenebicyclo[2.2.1]-hept-1-yl]-2-(2-nitrophenyl)disulfane* (**16b**)[3]) and 4 mg (5%) of **13**. Yellow crystals. M.p. 67–69° (hexane). $[\alpha]_D^{23}=-60.3$ ($c=1.0$, $CHCl_3$). IR (film): 2965*m*, 1654*m*, 1589*m*, 1565*m*, 1514*s*, 1448*m*, 1384*w*, 1334*s*, 1304*s*, 1096*m*, 1039*m*, 973*w*, 900*m*, 852*m*, 785*m*, 734*s*, 709*w*. ^{1}H-NMR: 8.09 (*dd*, $J=8.3$, 1.2, 1 arom. H); 8.14 (*dd*, $J=8.2$, 1.3, 1 arom. H); 7.61–7.56, 7.27–7.19 (2*m*, 2 arom. H); 5.24 (*t*, $J=2.5$, 1 H of $=CH_2$); 4.86 (*t*, $J=2.1$, 1 H of $=CH_2$); 2.44 (*d*, $J=16.1$, 1 H); 2.07–1.92 (*m*, 2 H); 1.80–1.72 (*m*, 2 H); 1.41–1.33 (*m*, 1 H); 1.22–1.13 (*m*, 1 H); 0.97, 0.83 (2*s*, 2 Me). ^{13}C-NMR: 153.1 (*s*, C(2)); 144.6, 138.6 (2*s*, 2 arom. C); 132.6, 127.2, 124.9, 124.8 (4*d*, 4 arom. CH); 105.0 (*t*, $=CH_2$); 66.3 (*s*, C(1)); 49.6 (*s*, C(7)); 42.7 (*d*, C(4)); 36.0 (*t*, C(6)); 32.0 (*t*, C(3)); 26.9 (*t*, C(5)); 18.8 (*q*, 2 Me–C(7)). CI-MS (NH_3): 340 (16), 339 (100, $[M+NH_4]^+$, 322 (82, $[M+1]^+$), 169 (12, $[C_{10}H_{16}S+1]^+$). Anal. calc. for $C_{16}H_{19}NO_2S_2$ (321.46): C 59.78, H 5.96, N 4.36, S 19.95; found: C 59.58, H 6.23, N 4.28, S 19.91.

5. *X-Ray Crystal-Structure Determination of* **10** *and* **14** (see *Table 2*, and *Figs. 1* and *2*)[4]). All measurements were made on a *Nonius KappaCCD* diffractometer [10] with graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream 700* cooler. Data reduction was performed with *HKL Denzo* and *Scalepack* [11]. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method [12] was applied. Equivalent reflections, other than *Friedel* pairs for **10**, were merged. Data collection and refinement parameters are given in *Table 2*, and views of the molecules are shown in *Figs. 1* and *2*. The structure of **10** was solved by direct methods with SIR92 [13], which revealed the positions of all non-H-atoms. In the case of **14**, the structure was solved by heavy-atom *Patterson* methods [14], which revealed the positions of the S- and Cl-atoms. All remaining non-H-atoms were located in a *Fourier* expansion of the *Patterson* solution, which was performed with DIRDIF 94 [15]. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom ($1.5U_{eq}$ for the Me groups). Refinement of each structure was carried out on F^2 by full-matrix least-squares procedures, which minimized the function $\Sigma w\left(F_o^2-F_c^2\right)^2$. A correction for secondary

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[3]) In contrast to the analogous reaction with **6**, the yield of **16a** (and **16b**) decreased significantly after longer reaction time or at increased temp.

[4]) CCDC-221849-221850 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccde.cam.ac.uk/cibts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 IEZ, U.K.; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Table 2. *Crystallographic Data of* **10** *and* **14**

	10	**14**
Crystallized from	hexane	hexane
Empirical formula	$C_{18}H_{27}ClOS_2$	$C_{18}H_{27}ClOS_2$
Formula weight [g mol^{-1}]	358.98	358.98
Crystal color, habit	colorless, prism	colorless, plate
Crystal dimensions [mm]	$0.10 \times 0.12 \times 0.25$	$0.02 \times 0.07 \times 0.25$
Temperature [K]	160(1)	160(1)
Crystal system	monoclinic	triclinic
Space group	$P2_1$	$P\bar{1}$
Z	2	2
Reflections for cell determination	36333	31804
2θ Range for cell determination [°]	4 – 60	4 – 52
Unit cell parameters a [Å]	6.3437(1)	6.7667(2)
b [Å]	11.1033(2)	11.1820(4)
c [Å]	13.2624(2)	12.3873(4)
α [°]	90	88.370(2)
β [°]	91.3277(6)	86.078(2)
γ [°]	90	82.374(2)
V [Å^3]	933.90(3)	926.65(5)
Dx [g cm^{-3}]	1.276	1.286
μ(MoK_α) [mm^{-1}]	0.428	0.431
Scan type	ϕ and ω	ω
$2\theta_{(max)}$ [°]	60	52
Transmission factors (min; max)	0.869; 0.963	0.820; 0.996
Total reflections measured	43942	14008
Symmetry independent reflections	5450	3618
Reflections with $I > 2\sigma(I)$	4695	2932
Reflections used in refinement	5450	3618
Parameters refined; restraints	205; 1	206
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0328	0.0407
$wR(F^2)$ (all data)	0.0737	0.1085
Weighting parameters [a; b][a])	0.0360; 0.1051	0.0543; 0.4305
Goodness-of-fit	1.034	1.037
Secondary extinction coefficient	–	0.009(2)
Final Δ_{max}/σ	0.001	0.001
$\Delta\rho$(max; min) [e Å^{-3}]	0.22; -0.32	0.34; -0.33

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

extinction was applied for **14**. In the case of **10**, refinement of the absolute structure parameter [16] yielded a value of $-0.10(4)$, which confidently confirms that the refined coordinates represent the true enantiomorph. Neutral-atom scattering factors for non-H-atoms were taken from [17a], and the scattering factors for H-atoms were taken from [18]. Anomalous dispersion effects were included in F_c [19]; the values for f' and f'' were those of [17b]. The values of the mass attenuation coefficients are those of [17c]. All calculations were performed using the SHELXL97 [20] program.

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