Gas-phase Thermolyses. Part 3.[1] Gas-phase Thermolysis of Silylated Thionocarboxylic Acid Derivatives: a Route to Thioketens?

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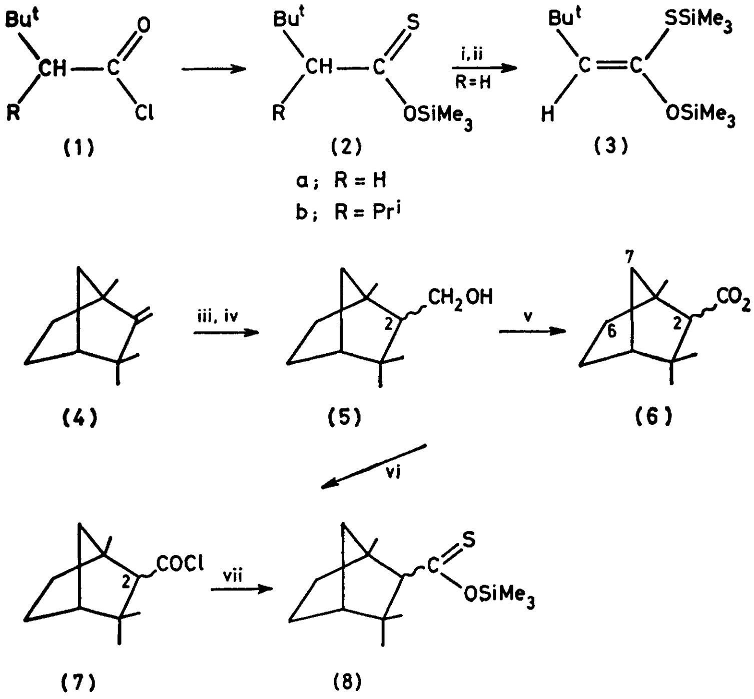
The unimolecular gas-phase thermolytic decomposition of three silylated thionocarboxylic acid derivatives (2b), (3), and (8) have been studied by the flash vacuum thermolysis–field ionization mass spectrometry technique in the temperature range from 783 to 1 404 K in order to elucidate its possible applicability as a route to thioketens. Only very minor amounts of the expected thioketens were found, whereas the corresponding ketens were obtained as the major products. A possible mechanism for keten formation is discussed.

THE β-elimination of hydrogen chloride from acyl chlorides containing an α-hydrogen atom is perhaps the most important synthetic pathway to ketens.[2] The possible corresponding formation of thioketens from thioacyl chlorides can, however, be applied only in exceptional cases.[3,4] Alternatively, thionocarboxylic carboxylic acid *silyl* esters are found to be *ca.* 62 kJ mol^{-1} more stable than the corresponding thiolo compounds.[7] Hence, the thermodynamically unfavourable thiono to thiolo rearrangement together with the known ready elimination of silyl ethers from silylated carboxylic acid derivatives,[8] suggest the use of silylated



SCHEME 1 *Reagents:* i, Pr$^i_2$NLi; ii, Me$_3$SiCl; iii, B$_2$H$_6$; iv, H$_2$O$_2$; v, Cr^{VI} or Mn^{VII}; vi, SOCl$_2$; vii, $\mathrm{Me}\overset{\mathrm{S^-}}{\overset{|}{\mathrm{C}}}\mathrm{{=}NSiMe_3}$

esters may be expected to yield thioketens upon thermolysis. However, this method may be of limited value, since a competing reaction analogous to the Chapman rearrangement is expected to lead to thiolocarboxylate esters[5] rather than alcohol elimination. Thus, to our knowledge only one example of thioketen formation from a thionoester has been reported,[6] the thioketen being isolated as its dimer.

In contrast to *alkyl* thionocarboxylates thionocarboxylic acid derivatives as thioketen precursors. In this paper we report on the gas-phase thermolyses of three silylated thionocarboxylic acid derivatives in order to study the possible formation of thioketens. The starting materials (2b), (3), and (8) (see Scheme 1) have been chosen so as to provide sterically stabilized products, which would facilitate subsequent preparative operations.

The thionoester (2a) was synthesized by reaction of the acyl chloride (1a) with a dithiocarbamidate followed by silylation of the intermediate by chlorotrimethylsilane as reported by Kricheldorf and Leppert.[9] The sterically highly hindered ester (2b) was prepared by a reaction of (1b) with the anion of *N*-trimethylsilylthioacetamide, adopting the method of Lüke.[10] The thionoester (2a) could be reacted further with lithium di-isopropylamine and chlorotrimethylsilane to the keten *OS*-acetal (3). A similar conversion was not observed in the case of (2b).

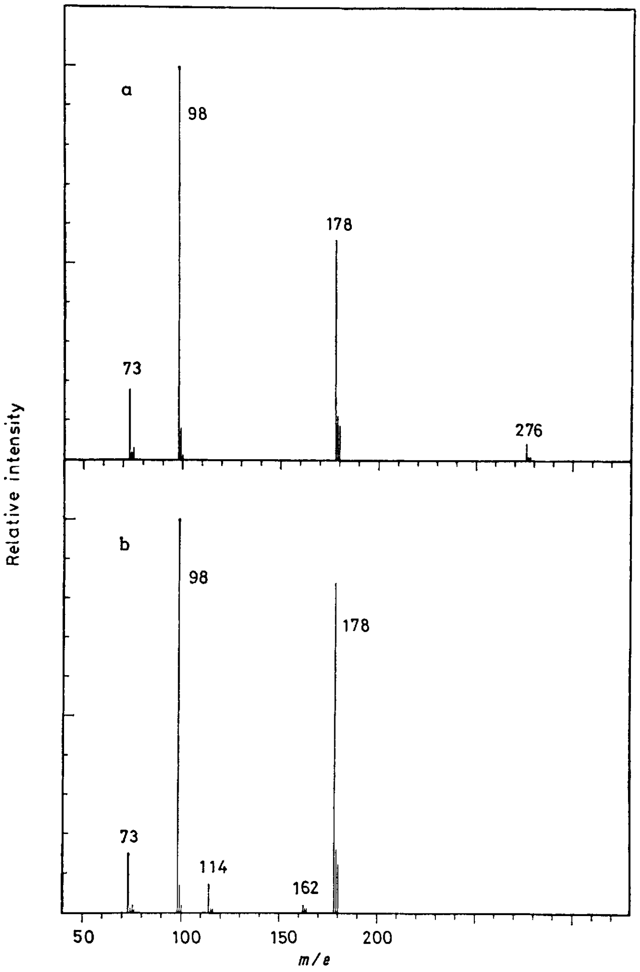


FIGURE 1 Field ionization mass spectra obtained after thermolysis of (3) at 1 043 K (a) and 1 404 K (b)

The precursor (7) to the thionoester (8) was prepared from homofenchene (4) by a procedure similar to that reported for the synthesis of 2-t-butyl-3,3-dimethylbutyryl chloride.[11] By using $KMnO_4$ in the presence of tetra-n-butylammonium bromide [12] in the oxidation of (5) to (6) instead of chromium trioxide the yield could be raised from 43 to 75%. The final silylation of (7) into (8) was performed as mentioned above using the metallated *N*-trimethylsilylthioacetamide reagent.

Compounds (5)—(8) can exist as *exo*- and/or *endo*-conformers. The primary alcohol (5) exhibits two sets of three methyl ^1H n.m.r. signals, which strongly suggests the presence of both possible configurations at C-2. Similarly, more than three methyl signals and two signals for 2-H are observed for compounds (7) and (8). The carboxylic acid (6) apparently exists exclusively as a single conformer. However, the very small difference expected in the ^4J coupling between *exo*-2-H and *exo*-6-H, and *endo*-2-H and *anti*-7-H, respectively (see *exo*- and *endo*-2-fenchol [13]), unfortunately affords no possibilities for the determination of the actual configuration.

Gas-phase Thermolyses of (2b), (3), *and* (8).—The unimolecular gas-phase thermolytic decomposition of the silylated thionocarboxylic acid derivatives (2b), (3), and (8) were studied by the flash vacuum thermolysis–field ionization mass spectrometry (f.v.t.–f.i.m.s.) technique [14,15] (see Experimental section) in the temperature range from 783 to 1 404 K. Field ionization is known to give intense molecular ions and little fragmentation.[14]

In Figures 1a and 2a the f.i.m.s. spectra obtained from the thermolysis at 1 043 K of compounds (3) and (8), respectively, are shown. At this temperature the compounds are almost completely decomposed. Lowering the thermolysis temperature to 783 K did not change the composition of the product mixture, but only the relative yields. Also the absolute yields are changed, as *ca.* 95% of the starting materials were recovered.

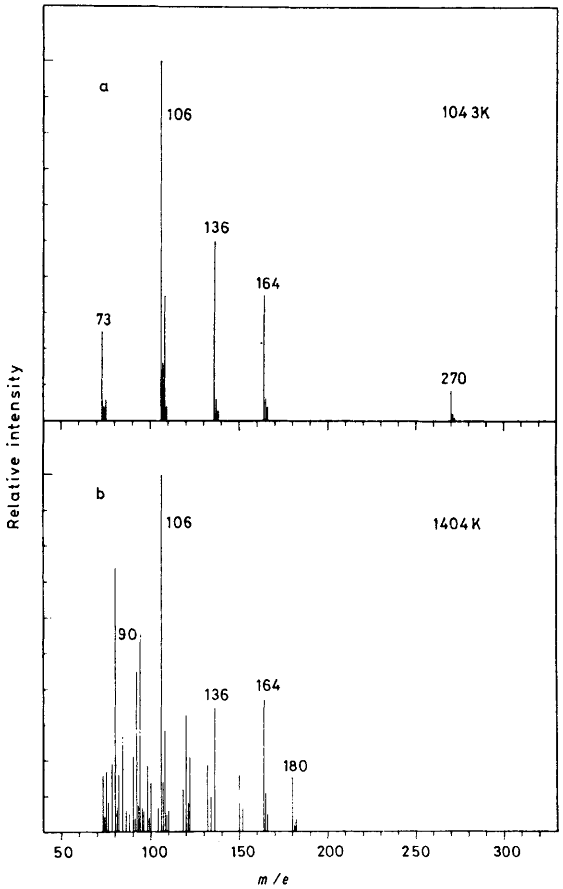
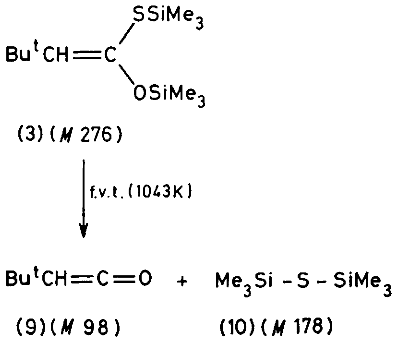


FIGURE 2 Field-ionization mass spectra obtained after thermolysis of (8) at 1 043 K (a) and 1 404 K (b)

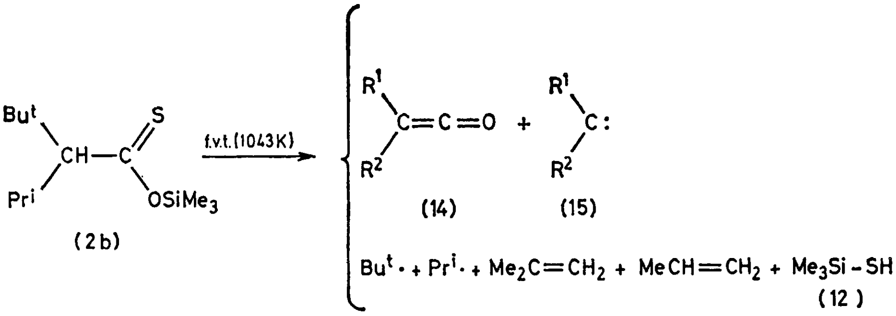
The spectrum depicted in Figure 1a exhibits two peaks at *m*/*e* 178 and 98. The compound responsible for the latter peak evidently does not contain sulphur, since only an isotopic cluster corresponding to ^{13}C and ^{18}O is seen, whereas the characteristic ^{34}S isotopic peak is lacking. The isotopic cluster surrounding the peak of *m*/*e* 178 is consistent with the presence of two trimethylsilyl groups and one sulphur atom, as the relative intensities of the peaks of *m*/*e* 178/179/180/181 were found and calculated to be 1.00/0.19/0.12/0.02 and 1.00/0.18/0.13/0.02, respectively. On this basis the thermolysis of (3) is then formulated as in Scheme 2.



Scheme 2

An analogous analysis of the spectrum depicted in Figure 2a leads to the conclusion that compound (8) upon thermolysis decomposes into the keten (11) and trimethylsilanethiol (12). Additionally a product exhibiting a molecular ion at *m*/*e* 136, which may be assigned to carbene (13) or an isomeric species, is formed (Scheme 3).

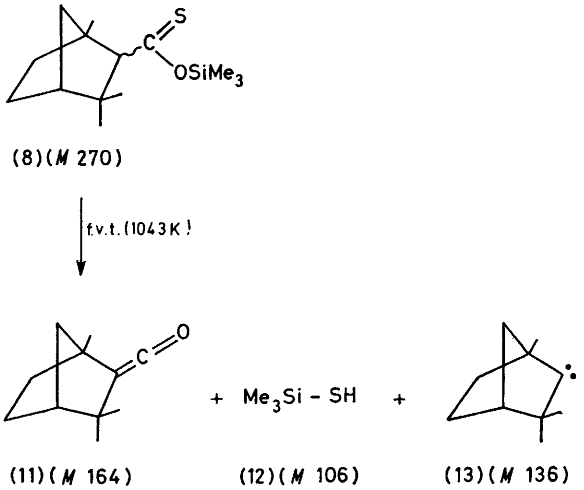
In contrast to these very simple fragmentation reactions compound (2b) exhibits a rather complicated decomposition pattern. The product mixture consists of the three possible ketens (14) and the three possible carbenes (15) together with t-butyl and s-propyl radicals, methylpropene and propene as products of consecutive radical decomposition, and the thiol (12). However, no indication of any thioketen formation was found (Scheme 4).



a; $R^1 = Bu^t$, $R^2 = Pr^i$
b; $R^1 = Bu^t$, $R^2 = H$
c; $R^1 = H$, $R^2 = Pr^i$

Scheme 4

Changing the thermolysis temperature to 1 404 K, in the case of (2b), did not give rise to any new product formation, but caused only a change in the relative composition of the product mixture. For compounds (3) and (8), however, small changes are observed by elevating the thermolysis temperature, as new sets of peaks are developed in the f.i.m.s. spectra obtained following thermolysis at 1 404 K (Figures 1b and 2b). In both cases appearance of the new peaks can be rationalized as the result of competing thioketen formation. In the case of (8) the higher temperature also resulted in the appearance of a variety of new peaks of low intensity, caused by more pronounced degradation of the carbon skeleton, probably similar to the thermolytic pathways observed for (2b) (Scheme 5).

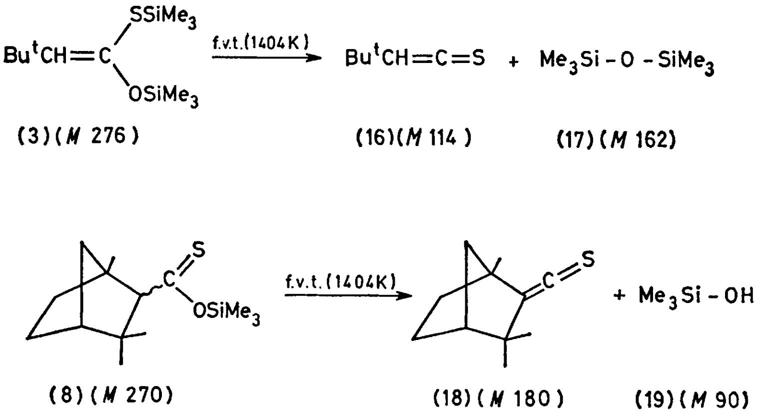


Scheme 3

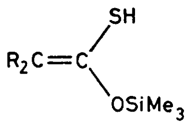
It should be noted that it is not possible to calculate the yields of the single species directly from the f.i.m.s. spectra, as the single compounds may exhibit rather different field ionization sensitivities.[14] However, as the ketens and thioketens probably exhibit comparable sensitivities,[15] it is obvious that only very minor amounts of the thioketens are formed.

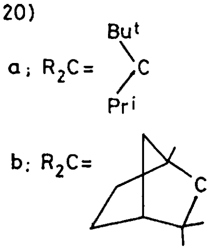
DISCUSSION

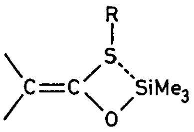
The elimination of trimethylsilanethiol (12) from (2b) or (8) and of bistrimethylsilyl sulphide (10) from (3) to give ketens is in apparent contrast to the relative strengths of Si–S and Si–O bonds.[7] Moreover, (2b) and (8) obviously cannot furnish ketens *via* a simple one-step process. A rationale for keten formation in these examples can be made by assuming primary enthiolization to give (20a and b), respectively, followed by β-elimination of Me_3Si–SH (12), whereas formation of thioketen (18) at the more elevated temperature probably results from the direct β-elimination of Me_3Si–OH (19) from (8). Elimination of Me_3Si–S–$SiMe_3$ (10) from (3) to give keten (9) would be in complete analogy to the invoked cleavage of (20).



SCHEME 5


(20)

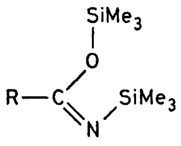


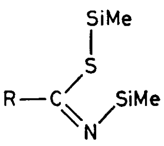

(21)

a; R = H
b; R = $SiMe_3$

Previously studied β-eliminations of silanols from *N*-silylcarbamates or imidocarboxylates have been proven to follow intramolecular pathways *via* four-centre transition complexes.[16] This non-ionic mechanism may also operate in the gas phase and thus be applied to the thermolysis of (3) as well as (2b) and (8) *via* (20). This leads to transition state (21a) from (20) and (21b) from (8). The driving force in each case seems to be the pronounced nucleophilicity of sulphur which permits attack at silicon thus overcoming the stability of the Si–O bond. Besides the electronic a steric effect may also favour transition states like (21) incorporating sulphur, as the larger size of sulphur compared with oxygen will diminish strain in the four-membered ring.

The reactivity of sulphur in four-centre transition states involving silicon is also obvious from the relative stabilities of bis-silylated amides (22) and thioamides (23). Thus compound (22; R = Ph) is gradually cleaved to give benzonitrile only at reflux temperature (*ca.* 470 K),[17] whereas the corresponding thio-compound (23; R = Ph) eliminates Me_3Si–S–$SiMe_3$ (10) *in situ* on silylation of *N*-trimethylsilylthiobenzamide at 253 K.[10]


(22)


(23)

In the cases of (8) and (2b) a second possible reaction mechanism, a primary thiono–thiolo rearrangement followed by rapid decomposition of the latter into the ketens (11) and (14), respectively, and the silanethiol (12), should *a priori* be considered. After thermolyses at 1 043 K only very minor amounts of the starting materials are recovered, which implies that possible primarily generated species are quantitatively decomposed into the observed products before reaching the detection system (ion source). In general it is believed that species with half lives less than *ca.* 10^{-3} s may escape detection.[18] However, assuming $\Delta H_r \simeq \Delta G_r \simeq -62$ kJ mol^{-1} (*i.e.* $\Delta S_r \simeq 0$)[7] for the thiolo–thiono rearrangement, the equilibrium constants for the thiono–thiolo system can, according to the van't Hoff equation, be calculated to be $\log_e K$ (293 K) $\simeq 25$ and $\log_e K$ (1 043 K) $\simeq 7$, respectively, *i.e.* even at the elevated temperature the thiolo–thiono rearrangement will be rather favourable. In the present case the latter rearrangement should compete with the possible rethermolytic β-elimination of silanethiol (12) from the thiolo-species, the latter totally suppressing the former, corresponding to quantitative rethermolysis. Based on the above figures and the fact that rethermolyses in general may be expected to occur to only a small extent [18] it seems unlikely that a primary thiono–thiolo rearrangement should be expected to play any major role in the thermolyses of (8) and (2b).

In conclusion, it appears that because of the electronic and possibly also steric effect of neighbouring sulphur the Si–O bond is readily cleaved in the silylated thiocarboxylic acid derivatives (2b), (3), and (8) to give ketens, thus excluding this method as a suitable route to thioketens.

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 257 spectrograph, and the ^1H n.m.r. spectra ($CDCl_3$) on Varian T60, Varian EM360, and Perkin-Elmer R32 instruments.

Flash Vacuum Thermolysis Technique.[18]—The f.v.t. technique used is based on the direct combination of a thermolysis unit with a double focusing mass spectrometer with a field ion source. The thermolysis unit is constructed as a modification of the Pye–Unicam PV4000 pre-column pyrolysis system, which is based on the Curie-point principle, *i.e.* the high frequency inductive heating in ferromagnetic materials. The thermolysis unit is connected directly to the ion source of the mass spectrometer *via* a heated line-of-sight inlet system.

Samples (*ca.* 50 μg) of the pure compound were introduced (micro-syringe) into the reactor *via* a heated injection block. The contact time in the hot zone has been estimated to be *ca.* 10^{-3}—10^{-4} s,[18] fulfilling the contact time requirement for f.v.t. equipment. According to the geometry of the system, thermolysis products with half-lives < *ca.* 10^{-3} s are assumed to escape detection.[18] The internal geometry of the reactor (length 40 mm, internal diameter 2 mm) combined with a low actual pressure (*P ca.* 10^{-4} Torr) assure a very low frequency of intermolecular collisions relative to the molecular–hot surface collison frequency, *i.e.* only unimolecular reactions take place.

The mass spectra were recorded on a Varian MAT CH 5D instrument equipped with a combined electron impact ionization–field ionization–field desorption ion source. The field ion emitter was a 10 μm tungsten wire activated in benzonitrile vapour.

Compounds (1a),[19] (1b),[20] (4),[21] and *N*-trimethylsilylthioacetamide (from thioacetamide and hexamethyldisilazane) [22] were prepared according to reported procedures.

3,3-*Dimethyl(thiobutanoic) Acid* O-*Trimethylsilyl Ester* (2a).—Compound (2a) was prepared by reaction of (1a) with 2-phenylethylamine–carbon disulphide–triethylamine followed by silylation with chlorotrimethylsilane–triethylamine,[9] yield 49%; b.p. 341—343 K at 11 mbar; i.r. exhibits no absorption in the carbonyl region; δ 0.35 (9 H, $SiMe_3$), 0.98 (9 H, Bu^t), and 2.64 (2 H, CH_2).

3,3-*Dimethyl*-2-*isopropyl(thiobutanoic) Acid* O-*Trimethylsilyl Ester* (2b).—*N*-Trimethylsilylthioacetamide (12.5 g, 0.086 mol) in hexane (15 ml) was slowly added to BuLi (0.086 mol) in hexane at 195 K. After 1 h (1b) (14.5 g, 0.082 mol) in hexane (20 ml) was slowly added and the solution was allowed to warm to room temperature. The precipitate was removed by filtration (with exclusion of moisture). The filtrate was concentrated *in vacuo* and the product was isolated by distillation, yield 54%; b.p. 356—358 K at 2 mbar; i.r. exhibits no absorption in the carbonyl region; δ 0.40 (9 H, $SiMe_3$), 0.97 and 1.09 (6 H, d, *J ca.* 7 Hz, diastereotopic Me of Pr^i), 1.02 (9 H, s, Bu^t), 2.00 (1 H, m, CH of Pr^i), and 2.77 (1 H, d, *J* 5 Hz, 2-H).

3,3-*Dimethyl*-1-*trimethylsiloxy*-1-*trimethylsilylthiobut*-1-*ene* (3).—Compound (2a) (9.4 g, 46 mmol) in dry THF (20 ml) was slowly added to a stirred solution of lithium di-isopropylamine (50 mmol) [prepared from di-isopropylamine (50 mmol) and an equimolar amount of BuLi in hexane] at 195 K. The stirring was continued for 3 h followed by dropwise addition of chlorotrimethylsilane (5.4 g, 50 mmol) in dry hexane (10 ml). The mixture was allowed to heat up to room temperature and the precipitated LiCl was removed by filtration after 20 h (exclusion of moisture). The solvent was removed *in vacuo* and the product isolated by distillation, yield 9.0 g (72%); b.p. 348—350 K (at 0.9 mbar); $\nu_{max.}$ 1 640 cm^{-1} (C=C); δ 0.23 and δ 0.27 (both 9 H, $SiMe_3$), 1.03 (9 H, Bu^t), and 4.70 (1 H, =CH) (Found: C, 52.65; H, 10.35; S, 11.1. $C_{12}H_{28}OSSi_2$ requires C, 52.15; H, 10.15; S, 11.6%).

1,3,3-*Trimethylbicyclo*[2.2.1]*heptan*-2-*ylmethanol* (5).—*Compound* (5) was prepared from (4) by reaction with diborane followed by oxidation of the resulting borane with H_2O_2,[11] yield 89%; m.p. 334 K; $\nu_{max.}$ (KBr) 3 340 cm^{-1} (OH); $[\alpha]_D^{20}$ −37.7° ($CDCl_3$); δ 0.8—1.8 [m, containing δ 0.83, 0.88, 0.96, 1.00, 1.03, and 1.12 (Me)] and 3.68 (d, *J* 7 Hz, CH_2O) (Found: C, 78.25; H, 12.15. $C_{11}H_{20}O$ requires C, 78.5; H, 12.0%).

1,3,3-*Trimethylbicyclo*[2.2.1]*heptane*-2-*carboxylic Acid* (6).—*Compound* (6) was preferentially prepared by oxidizing (5) according to ref. 12, yield 75%; m.p. 379 K, $[\alpha]_D^{20}$ −4.4° ($CDCl_3$); $\nu_{max.}$ (KBr) *ca.* 3 000br (OH) and 1 700 cm^{-1} (C=O); δ 0.9—2.3 [m, containing δ 1.02, 1.14, and 1.17 (Me)], 2.16 (d, *J ca.* 2 Hz, H-2), and 10.7br (OH) (Found: C, 72.5; H, 10.0. $C_{11}H_{18}O_2$ requires, C, 72.5; H, 9.95%).

1,3,3-*Trimethylbicyclo*[2.2.1]*heptane*-2-*carbonyl Chloride* (7).—*Compound* (7) was prepared by reaction between (6) and thionyl chloride, yield 60%; b.p. 347 K at 0.95 mbar; $\nu_{max.}$ (film) 1 805 cm^{-1} (C=O); δ 0.9—2.3 [m, containing δ 1.00, 1.09, 1.14, 1.17, and 1.25 (Me)] and 2.61 and 2.70 (both d, *J ca.* 2 Hz, *endo*- and *exo*-2-H) (Found: C, 65.85; H, 8.65. $C_{11}H_{17}ClO$ requires C, 65.8; H, 8.55%).

O-*Trimethylsilyl* 1,3,3-*Trimethylbicyclo*[2.2.1]*heptane*-2-*thiocarboxylate* (8).—The reaction was analogous to the above preparation of (2b) from (1b), yield 25%; b.p. 383 K at 1.1 mbar; i.r. exhibits no absorption in the carbonyl region; δ 0.41 (9 H, $SiMe_3$), 0.8—2.2 [m, containing δ 0.98, 1.00, 1.14, and 1.16 (Me)], and 2.76 and 2.87 (both d, *J ca.* 2 Hz, *endo*- and *exo*-2-H).

Compounds (2a), (2b), and (8) did not give satisfactory elemental analyses due to their highly hygroscopic nature.

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