Anal. Calcd for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.48; H, 8.96.

0.342 g (10.2%) of (±)5,6-Dehydro-11-desoxyprostaglandin E_2 (15, R = H) was eluted next: ir (film) 1740 (C=O) and 1710 cm^{-1} (CO_2H); nmr δ 5.65 (m, 2, CH=CH), 4.1 (m, 1, C_{15}–H) and 0.88 ppm (5, 3, J = 6Hz, CH_3); mass spectrum (70 eV) m/e (rel intensity) 334 (2), 316 (10), 263 (42), 244 (51), 181 (67), 163 (100), 43 (90).

Anal. Calcd for $C_{20}H_{30}O_4$: C, 71.82; H, 9.04. Found: C, 71.63; H, 8.88.

(±)3-(trans-1-octenyl)-1-trimethyl siloxy cyclopentene (19). 7.64 g of trans-1-bromo-1-octene (40 mmol) in 12 ml of ether was added over 30 min to 0.79 g of lithium wire containing 1% sodium in 40 ml of ether under argon with magnetic stirring. The reaction temperature was held at -5 to -10° for 2 hr. This solution was then added to a slurry of 3.80 g (20 mmol) of cuprous iodide in 20 ml of THF at -35°. After stirring at -35° for 15 min, a solution of 1.64 g (20 mmol) of cyclopent-2-enone in 4 ml of THF was added to the reaction mixture. Following a 10 min period at -40°, 5 ml of chlorotrimethyl silane was added to the reaction mixture and the cooling bath removed. On warming to room temperature, the reaction mixture was poured into 200 ml of hexane, 3 ml of triethyl amine and ice water. The hexane solution was separated, washed with saturated bicarbonate, dried over sodium sulfate and concentrated in vacuo. Short path distillation gave 5.211 g (97%) of enol ether (19): bp 93-98° (0.1 mm); ir (film) 1640 cm^{-1} (OC=CH);

nmr (CCl_4) 5.30 (m, 2, CH=CH), 4.42 (m, 2, OC=CH), 3.2 (m, 1, C=CH–CH–CH=CH), 0.91 (t, 3, CH_2CH_3), and 0.20 ppm [s, 9, $Si(CH_3)$]; mass spectrum (70 eV) m/e (rel intensity) 266 (8), 195 (25), 181 (100), 75 (18), 73 (90).

Anal. Calcd for $C_{16}H_{30}OSi$: C, 72.10; H, 11.35. Found: C, 71.97; H, 11.45.

(±)11,15-Desoxyprostaglandin E_2 methyl ester (20, R = CH_3). A solution of 1.33 g of silyl enol ether 19 (5 mmol) in 10 ml of tetrahydrofuran was added to a suspension of lithium amide prepared from 73 mg of lithium, 80 ml of ammonia, 30 ml of tetrahydrofuran and a trace of ferric nitrate. The reaction mixture was stirred magnetically and protected from atmospheric moisture by means of a nitrogen atmosphere. After stirring for 10 min at -35°, a solution of 4.45 g (20 mmol) of methyl cis-7-bromo-5-heptenoate in 5 ml of tetrahydrofuran was added over a 30 sec interval. Following an additional reaction period of 3 min at -35°, the reaction was quenched with ammonium chloride. The ammonia was evaporated under a stream of nitrogen and the resulting residue poured into 200 ml of ice water and 40 ml of acetic acid. This solution was then extracted with three 200 ml portions of ether, the combined ethereal extracts washed with brine, dried over sodium sulfate and concentrated in vacuo. Toluene (100 ml) was added and the mixture evaporated again to remove acetic acid. This residue was chromatographed on 300 g of silica gel, eluting with a gradient of 5-20% ethyl acetate-hexane (v/v) to yield 0.986 g (60%) of prostaglandin 20, R = CH_3. A small

sample of 20, R = CH_3 was evaporatively distilled for spectral analysis: ir (CCl_4) 1750 cm^{-1} (CO_2CH_3 and C=O); nmr δ 5.4 (m, 4, CH=CH), 3.65 (s, 3, OCH_3), and 0.89 ppm (t, 3, CH_3); mass spectrum (70 eV) m/e (rel intensity) 334 (2), 303 (3), 194 (20) and 109 (100).

Anal. Calcd for $C_{21}H_{34}O_3$: C, 75.40; H, 10.25. Found: C, 75.14; H, 10.25.

11,15-Desoxy Prostaglandin E_2 (20, R = H). A solution of 0.227 g of potassium hydroxide, 10 ml of water, 10 ml of tetrahydrofuran, 3 ml of methanol and 0.304 g of keto ester 20, R = CH_3 was stirred under nitrogen for 4 hr. Tlc analysis showed the absence of starting ester and the reaction mixture was diluted with 100 ml of water, extracted twice with 200 ml of ether, acidified to pH2 with concentrated hydrochloric acid, and extracted three times with 100 ml of ethyl acetate. The combined ethyl acetate solution were washed with brine, dried over sodium sulfate and concentrated in vacuo. The residue was evaporatively distilled at 150°/0.005 mm to yield 0.248 g of 20, R = H: ir (CCl_4) 1750 (C=O) and 1715 cm^{-1} (CO_2H); nmr δ 8.5 (s, 1, CO_2H), 5.4 (m, 4, CH=CH) and 0.89 ppm (t, 3, CH_3); mass spectrum m/e (rel intensity) 320 (1), 302 (1), 194 (7) and 109 (100).

Anal. Calcd for $C_{20}H_{32}O_3$: C, 74.96; H, 10.06. Found: C, 75.74; H, 10.12.

Remit check or money order for $4.00 for photocopy of $2.00 for microfiche, referring to code number JOC-74-2506.

References and Notes

(1) (a) Contribution No. 434 from the Institute of Organic Chemistry, Syntex Research. (b) Studies in Prostaglandins, No. 38. (c) The contents of this paper were the subject of lectures by J. Fried, presented at the University of Southern California (Nov 17, 1972), the University of California, Santa Cruz (Jan 8, 1973), and the Eidgenössische Technische Hochschule (Zurich) (May 9, 1973).

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(11) For another synthesis of 11,15-deoxyprostaglandin E_2 see K. F. Bernady and M. J. Weiss, *Tetrahedron Lett.*, 4083 (1972), and P. A. Grieco and J. J. Reap, *J. Org. Chem.*, **38**, 3413 (1973).

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Pyrolysis of Spirotrithianes

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Pyrolysis of spirotrithianes **3–7** at reduced pressure gave volatile mixtures consisting almost entirely of cyclic thioketones and their enethiols. At higher temperatures volatile products were mixtures of mercaptans and olefins. The nonvolatile residue of higher temperature pyrolysis of cyclohexanethione trimer contained dibenzothiophene, tetrahydrodibenzothiophene, octahydrodibenzothiophene,and spiro-2,2-pentamethylenebenzodithiolane (**13**). Bicyclo[2.2.1]heptane-2-thione (**1**) is a further example of a relatively stable thioketone.

Several methods for preparing aliphatic thioketones have been reported recently.[1–5] Each suffers from lack of generality. The absence of a general synthetic method for preparing thioketones, their instability, and the disagreeable odor of their intermediates all have slowed the investigation of the chemistry of the thiocarbonyl group. In the course of synthesis of thiols we prepared norbornanethione (**1**) by pyrolysis of trithiane **3** in good yield despite previous reports[6,7] that pyrolysis of trithianes is unsatisfactory for preparation of aliphatic thioketones. The results of pyrolyzing the structurally related spirotrithianes **4–7** at reduced pressure are shown in Table I.

These pyrolyses were stopped after generating workable quantities of red distillate and were not necessarily pushed to completion. Thioketone content of products was estimated from the absorption maximum at about 500 nm and enethiol content was estimated from nmr spectra.

Table I
Pyrolyses at Reduced Pressure

Pyrolysis of	Pressure, mm	Pot temp, °C (external)	Time, min	% distilling	Composition of distillate: % thione	Composition of distillate: % enethiol
3	~20	210–293	60	85	91	
3′	10	240–278	198	43	96	<1
4	13	195–247	30	10	>13	34
5	13–17	290–310	10	68	*a*	
6	13	165–210	80	45	>34	12
7	10	180–260	95	23	~33	32

[a] Red liquid distillate rapidly crystallized to give trimer.

Experimental Section

General. - Spectra were recorded using the following instruments: Cary model 14 (vis and uv); Perkin-Elmer model 137 and Beckman acculab 4 (ir); Varian T-60 (nmr), using tetramethylsilane as internal standard; A.E.I. MS-9 mass spectrometer. Vpc analyses were done on an Aerograph A-90-P gas chromatograph using silicone SE-30, 4% on 80-100 mesh chromosorb G (column a), silicone SE-52, 20% on chromosorb W (column b), silicone GE SF-96 (column c), or didecylphthalate, 15% on 60-80 mesh chromosorb W (column d). Melting points were determined on a Fisher-Johns apparatus and are uncorrected. Elemental analyses were performed by Chemalytics, Inc., Tempe, Arizona. Commercially available cycloolefins, bicyclo[2.2.1] heptene, bicyclo[3.2.1]-2-octene, cyclohexanethiol, dibenzothiophene, and thianthrene were used as standards in identifying pyrolysis products. 2,4-Dinitrophenyl derivatives were prepared by the method of Bost,[17] except that 2,4-dinitrofluorobenzene (FDNB) was used rather than 2,4-dinitrochlorobenzene.

1,3,5-Trithianes. - H_2S and HCl were bubbled simultaneously through alcoholic solutions of the ketones cooled with ice H_2O baths.[15,18] To make efficient use of H_2S, several preparations were carried out in series on a gas train. A 40% NaOH solution was used as a final trap. Gas flow through each reaction mixture was maintained until the maximum amount of white solid had formed. Reaction times in the gas train varied between 4 and 8 hr. The crude white solids were collected, washed with alcohol, vacuum dried to constant weight over NaOH, and recrystallized from $CHCl_3$-EtOH.

Recrystallized 4 had mp 98.1-99.5°;[15] recrystallized 5 had mp 100.3-101.5°;[15] recrystallized 6 had mp 74-75°.[18] Base-washed 5 and 6 were prepared as described for 3'.

tris-Bicyclo[3.2.1]octane-2-thione (7). - Bicyclo[3.2.1]-octan-2-one (9.3 g, 0.075 mol) in 30 ml of methanol was reacted by simultaneous bubbling of H_2S and HCl. An orange oil separated after 30 min, becoming quite viscous after 2 hr. Some ethanol (10 ml) was added after 2 hr, and the gas flow was maintained for 3 more hr. A crude white solid was obtained, 9.82 g (93% yield). Recrystallization from $CHCl_3$-EtOH gave 7.38 g of white crystals, mp 176.5-178.8°; nmr (CCl_4) all signals 0.8 - 3.03 ppm. Recrystallization from EtOH gave an analytical sample, mp 180.2-182.2°; mass spectrum (50 eV) m/e (rel intensity) 420.1955 (420.1979 calcd for $C_{24}H_{36}S_3^+$) (1), 280 (dimer$^+$) (37), 140 (monomer$^+$) (100).

Anal. Calcd for $C_{24}H_{36}S_3$: C, 68.51; H, 8.62; S, 22.85. *Found:* C, 68.62; H, 8.74; S, 21.79.

Oligomeric 2-Norbornanethione (3'). - 2-Norbornanone (22.0 g, 0.2 mol) in 180 ml of EtOH was reacted by simultaneous bubbling of H_2S and HCl to give 22.41 g (89% yield) of crude white solid, broad mp beginning at 135.5°. Three recrystallizations of a 6 g portion from $CHCl_3$-EtOH gave a highly crystalline sample[19] (2.73 g), mp 145-175°; mass spectrum (47 eV) m/e (rel intensity) 378 (1), 252 (18), 220 (8), 126 (100).

A $CHCl_3$ solution of 14.5 g of the crude white solid was washed first with 5% $NaHCO_3$ and then repeatedly with H_2O, dried (Na_2SO_4), and evaporated. Recrystallization from $CHCl_3$-EtOH provided 12.95 g of base-washed 3', broad mp beginning at 133°; the nmr spectrum was nearly identical to that of 3.

tris-2-Norbornanethione (3). Liquid H_2S procedure. - A solution of 11.02 g of 2-norbornanone (0.1 mol) in 100 ml of EtOH was added slowly to approximately 30 ml of liquid H_2S maintained at -55° by a dry ice-acetone bath. Hydrogen chloride gas was bubbled through the reaction solution for 1 hr. The reaction mixture was maintained at -55° for 2 more hr, and became opaque with crystal formation. The mixture was warmed cautiously (H_2S evolution) and partitioned between ice H_2O (500 ml) and petroleum ether (500 ml). The petroleum ether phase was washed with H_2O (6 x 100 ml) until the H_2O washes were neutral, dried (Na_2SO_4), and evaporated to dryness. A portion of the crude product (95% yield) was recrystallized from EtOH and gave an analytical sample, white crystals, mp 127-128° (82% yield); nmr (CCl_4) all signals 0.75-2.90 ppm; mass spectrum (70 eV) m/e 378.1484 (378.1510 calcd for $C_{21}H_{30}S_3^+$), 252 (dimer$^+$), 220, 127, 126 (monomer$^+$), 93, 67, 66.

Anal. Calcd for $C_{21}H_{30}S_3$: C, 66.61; H, 7.99; S, 25.40. Found: C, 66.87; H, 8.22; S, 24.71.

Trithiane Pyrolyses at Reduced Pressure. General Methods. - The trithianes were pyrolyzed with an equal weight of ordinary dry sand, except where stated otherwise.

Method A. - The still pot was equipped with a short path distillation apparatus. Reduced pressure was provided by a H_2O aspirator.

Method B. - A short glass tube, heated by an electrical heating tape, was used to connect the still pot with the receiver. A regulated partial vacuum (P) was established for the system, a dry ice-acetone bath was used to chill the receiver, and a steady temperature (T_1) was established for the glass tube. The temperature (T_2) of the still pot heater was monitored. The pyrolyses were often stopped after 1 or 2 hr, and were not necessarily pushed to completion.

Method C. - The still pot, containing a bed of sand, was heated to an externally measured temperature of 300 ± 10° and maintained there throughout the pyrolysis. Molten 5 was injected onto the sand. A room temperature or ice-chilled receiver was used.

Trithiane Pyrolyses at Atmospheric Pressure. Method D. - In a still pot equipped with a H_2O-cooled short path distillation apparatus, mixed trithiane and an equal weight of ordinary dry sand were pyrolyzed completely until no more distillate was collected (receiver at room temperature). Heating times varied from 50 to 120 min. The maximum temperatures attained by the still pot heater varied from 341 to 358°. The temperature at the still head was monitored.

Pyrolysis of *tris*-2-Norbornanethione (3) by Method A. - 3 (18.94 g, 0.05 mol) and an equal weight of dry sand were heated under reduced pressure. Red liquid (15.08 g) was collected in the still pot temperature range 210-293° over a period of 1 hr. Vpc analysis (column a, 162°) of the red liquid was done 90 min after collecting the product and showed 3 peaks with relative areas 91:8.5:0.5. The 8.5% component had approximately the same retention time as 2-norbornanethiol. Yield of 1 (based on 91% thioketone content, and minimal enethiol content) was 14.83 g, 77%. Mass spectrum (70 eV) of the red liquid, m/e 126.0482 (126.0503 calcd for $C_7H_{10}S^+$).

2-Norbornanethiol. - *Following a procedure for the reduction of thioketones,*[20] 6.32 g of the red liquid (crude 1) was reduced with $NaBH_4$ and gave 1.63 g of colorless liquid, bp 68.5-70.2° (15 mm); nmr (CCl_4)δ 0.65-2.4 (complex), 2.4-2.95 (very small signals), 2.95-3.45 (1 H), no signals downfield from 3.45 ppm. The nmr shows that the reduced product is predominantly the endo thiol.

Following a procedure describing the use of sodium cyanoborohydride,[21] 2.50 g of crude 1 was reduced with $NaBH_3CN$ using bromocresol green as the color indicator and dropwise additions of 2 N HCl in MeOH to maintain the pH. There was obtained 0.7 ml of colorless liquid, *bp 75-81° (23 mm); nmr (CCl_4)δ 0.65-2.4* (complex), 2.4-2.95 (much less than 1 H), 2.95-3.45 (almost 1 H), no signals downfield from 3.45 ppm. The nmr shows that the reduced product is predominantly the endo thiol. Ir (neat liquid) 1755 (weak, C=O due to a trace of norbornanone), 2570 cm^{-1} (strong, SH); mass spectrum (70 eV) m/e 128.0626 (128.0660 calcd for $C_7H_{12}S^+$).

Pyrolysis of Oligomeric 2-Norbornanethione (3') by Method B. - With T_1 = 132° and P = 10 mm, base-washed 3' (3.79 g, equivalent to 0.01 mol of 3) was heated starting from room temperature. Red-orange liquid (1.64 g) was collected in the T_2 temperature range 240-278° over a period of 3.3 hr, leaving 2.08 g of dark brown residue in the still pot, nmr (CCl_4) identical to that of 3'.

The red-orange liquid was warmed to room temperature and portions were promptly removed and characterized: uv-vis (heptane) max 217 nm (ε 5700), 239 (9900), 313 (12.9), 460 (sh), 497 (11.8), 561 (1.5)[22] - no decrease of absorbance was observed in the vis spectrum when it was recorded again 3.8 hr and 4 days later; nmr (CCl_4)δ 1.1-2.1 (complex, 6 H), 2.35 (2 H), 2.78 (1 H), 3.33 (1 H), 5.96 (<<1% of total integration) - no change was observed in this nmr spectrum when it was recorded again 4 days later; ir (neat film) no bands at or near 1640 (C=C), 1755 (C=O), 2550 (SH), 3020 cm^{-1} (=C-H); ir (neat liquid in cavity cell) still no bands were observable at 1640, 1755, 2550, or 3020 cm^{-1}; vpc (column b, 152°) showed 2 peaks with relative areas 96:4. The 4% component had the same retention time as 2-norbornanethiol. The above characterization was completed within 4 hr, except for recording the uv spectrum and re-recording of spectra.

The remaining neat red-orange liquid was stored at room temperature *for 5 to 6 days and portions were again removed and characterized.* At this time the red-orange liquid contained 64% thioketone (calculation based on ε_{497} = 11.8). The nmr spectrum was nearly unchanged. The vinyl signal at δ 5.96 now accounted for about 0.7% of the total integration (7% enethiol). The ir spectrum was nearly unchanged except for a new band at 1755 cm^{-1} (weak, C=O due to norbornanone). No bands were observable at 1640, 2550, or 3020 cm^{-1}. Vpc (column b, 150°) was unchanged except for a new peak (5%) which had the same retention time as norbornanone.

Pyrolysis of *tris*-Cyclopentanethione (4) by Method B. - With T_1 = 69° and P = 13 mm, 4 (3.0 g, 0.01 mol) was heated starting from room temperature. Red liquid (0.31 g) was collected in the T_2 temperature range 195-247° over a period of 30 min, leaving an amber liquid in the still pot which solidified rapidly on cooling to off-white crystals, 2.66 g, mp 92-98°; nmr (CCl_4) identical to that of 4.

The red liquid was warmed to room temperature and portions were promptly removed and characterized: dilutions for vis and nmr spectra were made 15 to 20 min after the red liquid was warmed to room temperature; vis (heptane) max 512 nm (with shoulders at 445, 473, 496, 520), 542, 579.[7] An 11% decrease of absorbance at 512 nm was observed in this vis spectrum when it was recorded again 5 hr later. Nmr (CCl_4) δ 1.4-2.9 (complex), 2.9-3.7 (impurity), 5.52 and 5.87 (4.2% of total integration, 34% enethiol). There was no measurable change in this nmr spectrum when it was recorded again 2.5 hr later. The ir (neat) spectrum was recorded 25 min after the red liquid was warmed to room temperature and showed bands at 1593 (C=C), 2520 (SH), and 3030 cm^{-1} (=C-H). Vpc analysis was done 70 min after warming the product to room temperature. By this time the red color of the liquid had faded to pale pink. No cyclopentene was present.

Pyrolyses of *tris*-Cyclohexanethione (5) by Method C. - 5 (3.38 g) was delivered onto 3.43 g of sand at 13 mm. There was an immediate collection of red liquid distillate, with the collection rate becoming quite slow by 10 min after injection, at which time the red distillate (2.30 g) began to crystallize rapidly to a white solid still bearing some orange color. The residual colored liquid was dissolved in heptane, vis max (main peak) centered at 507 nm (with shoulders at 453, 482, 526), 569.[7] A 6% decrease of absorbance at 507 nm was observed when this spectrum was re-recorded 90 min later. A portion of the largely solidified distillate was recrystallized from $CHCl_3$-EtOH, mp 99-100.5°.

Base-washed 5 (1.64 g) was delivered onto 1.71 g of sand at 15 mm. There was an immediate collection of red liquid distillate. The system was opened 4 min after injection, at which time white solid formed rapidly in the receiver.

Pyrolysis of *tris*-Cycloheptanethione (6) by Method B. - With T_1 = 105° and P = 13 mm, base-washed 6 (3.85 g, 0.01 mol) was heated starting from room temperature. Red liquid (1.72 g) was collected in the T_2 temperature range 165-210° over a period of 80 min, leaving a brown-amber residue in the still pot.

The red liquid was warmed to room temperature and portions were promptly removed and characterized (within 2 hr): vis (heptane) max 510 nm (with shoulders at 575, 585)[7]; nmr (CCl_4) δ 1.3-2.7 (complex), 3.0-3.25 (broad), 5.67-6.03 (not observed in an earlier and lower temperature pyrolysis of 6), 5.08-6.40 (1% of total integration, 12% enethiol). The neat liquid was still red after 24 hr at room temperature.

Pyrolysis of tris-Bicyclo[3.2.1]octane-2-thione (7) by Method B. - With T_1 = 112° (later increased to 150°) and P = 10 mm, 7 (3.15 g, 0.0075 mol) was heated starting from room temperature. Orange liquid (0.74 g) was collected in the T_2 temperature range 180-260° over a period of 95 min, leaving 2.35 g of pale amber solid (after cooling) in the still pot, nmr (CCl_4) identical to that of 7.

The orange liquid was warmed to room temperature and portions were promptly removed and characterized: uv-vis (heptane) max 219 nm, 231, 498 (main vis peak with shoulders 450, 505, 522), 563 - the vis spectrum for the same solution was *recorded again after 2 hr* and showed no decay of absorbance; ir (neat) 1630 (C=C), 2550 (SH), and 3020 cm^{-1} (=C-H); nmr (CCl_4) δ 1.0-3.3 (complex), 3.6 (broad, 1% of total integration), 5.25-5.43 (2.7% of total integration, 32% enethiol). The above spectral characterization was completed within 2 hr, except for recording the uv spectrum. The neat liquid still retained some of its orange color after 24 hr at room temperature.

Pyrolysis of Oligomeric 2-Norbornanethione (3') by Method D. - Pyrolysis of 5.79 g of base-washed 3' gave 2.64 g of hard black residue and 1.74 g of light orange liquid distillate, bp 132-183°.

Vpc (column d, 160°) showed 2 major peaks (relative areas 45:55) with retention times coincident with those of 2-norbornanethiol and norbornene respectively. Nmr (CCl_4) signals at δ 2.84 and 5.97 showed the presence of norbornene.[23] After further manipulation of the distillate, a trace of norbornanone was detected by vpc and by ir (neat liquid) 1755 cm^{-1} (C=O). A band was also observed at 2550 cm^{-1} (SH).

A portion of fresh distillate (1.22 g) was reacted with FDNB (0.005 mol) and, after work-up and two recrystallizations from EtOH, *gave two types of yellow crystals* (I and II). Physical separation with a spatula gave 0.86 g of I, mp 110-112°, and 30 mg of II, mp 120-122.5°. Nmr for II ($CDCl_3$) δ 1.0-2.75 (complex, 10 H), 3.11-3.45 (complex, ∿ 0.5 H), 3.45-3.9 (complex, ∿ 0.5 H), 7.62, 8.37, and 9.04 (3 Ar H), no vinyl signals were observed. I was recrystallized 4 more times to give an analytical sample (0.41 g of homogeneous appearing yellow crystals), mp 112-112.8°; nmr ($CDCl_3$) δ 1.0-2.75 (complex, 10 H), 3.11-3.45 (complex, ∿ 0.7 H), 3.45-3.9 (complex, ∿ 0.3 H), 7.62, 8.37, and 9.04 (3 Ar H), no vinyl signals *were observed. The nmr spectrum of this material, containing* ∿ 70% of the exo-2-DNP derivative and ∿ 30% of the endo-DNP derivative, was very nearly identical to the spectrum of the pure exo-2-DNP derivative.

Anal. Calcd for $C_{13}H_{14}N_2O_4S$: C, 53.05; H, 4.79; S, 10.89. Found: C, 52.85; H, 4.95; S, 10.14.

Pyrolysis of *tris*-Cyclopentanethione (4) by Method D. - Pyrolysis of 3.0 g of 4 (0.01 mol) gave 1.04 g of black charred solid residue and 1.18 g of extremely pale pink liquid distillate, bp 115-133°.

Vpc (column b, 152° and column c, 133°) showed 2 peaks with relative areas 75:25. The 25% component had the same retention time as cyclopentene. Nmr (CCl_4) signals at δ 2.22, 2.33, and 5.7 showed the presence of cyclopentene. Redistillation of 1.0 g of the liquid at 1 atm gave a 0.24 g center fraction, colorless liquid, bp 125-129° [cyclopentanethiol lit. bp 132.2°];[24] ir (neat) showed all the bands of cyclopentanethiol. A combined fraction (0.24 g) of the redistilled colorless liquid [estimated by vpc to contain 0.2 g of cyclopentanethiol (0.002 mol) and 0.04 g of cyclopentene] was reacted with FDNB (0.002 mol) and gave yellow crystals, mp 96-97°. Recrystallization (EtOH) provided an analytical sample, 0.32 g (60% yield), mp 96-97°; nmr (CCl_4) δ 1.5-2.5 (8 H), 3.5-3.95 (1 H), 7.62, 8.34, and 9.00 (3 Ar H), no vinyl signals were observed in the nmr spectrum.

Anal. Calcd for $C_{11}H_{12}N_2O_4S$: C, 49.25; H, 4.51; S, 11.95. Found: C, 49.30; H, 4.60; S, 11.61.

Pyrolysis of *tris*-Cyclohexanethione (5) by Method D. - Pyrolysis of 3.43 g of 5 (0.01 mol) gave an uncharred, light-yellow liquid residue and 2.13 g of colorless liquid distillate, bp 145-177°. Ir (neat) was identical to that of cyclohexanethiol. Nmr (CCl_4) was very similar to that of cyclohexanethiol except for extra signals at δ 5.6 (<2% of total integration, 12% cyclohexene) and δ 7.2 (also <2% of total integration).

Pyrolysis of *tris*-Cycloheptanethione (6) by Method D. - Pyrolysis of 3.85 g of base-washed 6 (0.01 mol) gave 1.45 g of hard brown-black residue and 1.66 g of colorless liquid distillate, bp 98-159°. Vpc (column a, 160°) showed 2 peaks with relative areas 84:16. The 84% component had the same retention time as cycloheptene. Redistillation of 1.39 g of the liquid at 1 atm gave 0.89 g of colorless cycloheptene (>99% pure by vpc); bp (of center portion) 105-106°; ir (neat) and nmr (CCl_4) spectra were identical to those of authentic cycloheptene.

Pyrolysis of *tris*-Bicyclo[3.2.1]octane-2-thione (7) by Method D. - Pyrolysis of 2.10 g of 7 (0.005 mol) gave 1.15 g of hard black residue and 0.45 g of colorless distillate which solidified on cooling, bp ~ 105-125°. Nmr (CCl_4) strong signals centered at δ 1.6, 1.7, 1.77,

2.31, 5.33 (d, broad), and 5.88 (t, broad) indicated the presence of bicyclo[3.2.1]-2-octene, but other signals were observed including a vinyl signal centered at δ 6.24.

Non-volatile Pyrolysis Products from *tris*-Cyclohexanethione (5). - 5 (6.85 g, 0.02 mol) was heated without sand in a still pot equipped with a H_2O-cooled reflux condenser and drying tube. A reflux of colorless liquid was established (oil bath 240°). Heating was stopped after 7.5 hr. Distillation of the resulting yellow liquid at 1 atm gave 3.86 g of colorless liquid, bp 74-190°, and left 2.27 g of high boiling yellow liquid residue in the still pot. Redistillation of the colorless liquid at 1 atm gave an initial fraction containing cyclohexene, and a center fraction (1.28 g), bp 155-157°. Ir (neat) and nmr (CCl_4) spectra of this fraction were identical to those of cyclohexanethiol except for a small signal at δ 7.2.

Vacuum distillation of 2.0 g of the pot residue gave 1.38 g of light yellow liquid, bp 108-152° (1 mm). A portion, distilled twice more using a micromolecular still, gave a colorless liquid distillate, bp ~100° (1 mm). The colorless liquid (146 mg) was chromatographed on preparative layers of silica gel HF_{254} (E. Merck) using heptane as the developing solvent (3 passes) giving approximately 84 mg of pale yellow oil (faster band) and 23 mg of pale yellow oil (slower band).

Spiro-2,2-pentamethylenebenzodithiolane (13). - Slower band, nmr (CCl_4) δ 1.3-1.92 (broad, 6 H), 1.92-2.35 (broad, 4 H), 6.8-7.33 (complex, 4 Ar H); mass spectrum (70 eV, 200°) m/e (rel intensity) 224 (4), 223 (7), 222 (47), 193 (8), 181 (10), 180 (13), 179 (100), 166 (15), 153 (8); mass spectrum (chem ionization with isobutane, 200°) base peak m/e 223; uv (heptane) max 237 nm, 274 (ε 28500, 8600); tlc (Eastman silica gel chromagram sheet with fluorescent indicator) with heptane as the solvent showed only a trace of contamination in this sample.

Octahydrodibenzothiophene (9). - The 84 mg sample (faster band on silica gel) was further chromatographed on a preparative layer of aluminum oxide HF_{254} using heptane as the developing solvent (2 passes) giving three bands (A, B, C). The fastest moving band (A) contained 4.9 mg of a cloudy glass; nmr (thick-walled tube, CCl_4) no signals observed downfield from δ 2.85; mass spectrum (chem ionization with isobutane) main peaks m/e 207, 193.

1,2,3,4-Tetrahydrodibenzothiophene (10). - Intermediate tlc band B contained 54.8 mg of colorless oil; nmr (CCl_4) δ 1.64-2.14 (broad, 4 H), 2.5-3.0 (broad, 4 H), 7.0-7.8 (complex, 4 Ar H); mass spectrum (70 eV, 175°) m/e (rel intensity) 190 (11), 189 (30), 188 (100), 187 (42), 161 (17), 160 (100), 147 (17), 115 (27), 43 (75), 42 (28), 41 (32), 40 (11), 39 (15); mass spectrum (chem ionization with isobutane, 175°) m/e (rel intensity) 245 (29), 189 (100); ir (neat) was identical to that of 10;[25] uv (heptane) max 232 nm (log ε 4.44), 264 (3.76), 270 (3.76), 288 (3.42), 298 (3.57).[26]

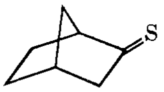
1,2,3,4-Tetrahydrodibenzothiophene-9,9-dioxide. - Following a procedure for the conversion of 10 to its sulfone,[27] about 40 mg of 10 was oxidized with 30% H_2O_2 to give white crystals (from EtOH), mp 185-187°. Ir (KBr) 1144 and 1289 cm^{-1} (SO_2).

Dibenzothiophene (11). - Slow moving tlc band C contained 22.7 mg of white crystals, mp 95.5-98°. Nmr (CCl_4) δ 7.2-7.5 (complex, 4 Ar H), 7.6-8.23 (complex, 4 Ar H), identical to that of authentic dibenzothiophene.

exo-2-Norbornanethiol. - S-Acetyl *exo*-2-norbornanethiol, bp 48-53° (0.26-0.15 mm), was prepared by addition of thioacetic acid to norbornene.[28] The thioacetate (68.11 g, 0.4 mol) was refluxed for 1 hr with 1 liter of alcoholic KOH (95% EtOH and 10% KOH in equal volumes). The reaction flask was cooled, and 5 N HCl was added to adjust to pH 7, causing the product to oil. The mixture was extracted with ether (900, 500, 250 ml), and the combined ether extracts were washed with H_2O (5 x 100 ml), dried (Na_2SO_4), and concentrated. Distillation gave 31.84 g (62% yield) of colorless liquid, bp 64.5-69.5° (13 mm); ir (neat liquid in cavity cell) 2570 cm^{-1} (SH). A portion was redistilled, bp (center fraction) 71.5° (19.3 mm); mass spectrum (70 eV) m/e 128; nmr (CCl_4) δ 1.0-2.4 (complex, 11 H), 2.6-3.0 (complex, 1 H).

2,4-Dinitrophenyl Derivative of *exo*-2-Norbornanethiol. - The exo thiol (1.28 g, 0.01 mol) was reacted with 1.86 g of FDNB (0.01 mol). Work-up and recrystallization from EtOH gave 2.66 g (90% yield) of yellow crystals, mp 117.5-118.3°. Two more recrystallizations gave an analytical sample (2.08 g), mp 118-118.9°; nmr ($CDCl_3$) δ 1.05-2.25 (complex, 8 H), 2.25-2.53 (complex, 2 H), 3.11-3.45 (complex, 1 H), 7.62, 8.37, and 9.04 (3 Ar H).

Anal. Calcd for $C_{13}H_{14}N_2O_4S$: C, 53.05; H, 4.79; S, 10.89. Found: C, 53.18; H, 4.75; S, 10.99.



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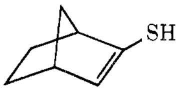

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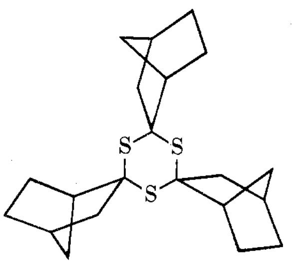
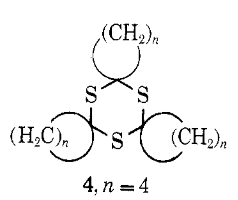
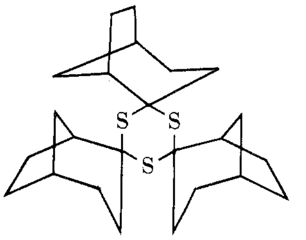


3, 3′



4, $n = 4$
5, $n = 5$
6, $n = 6$



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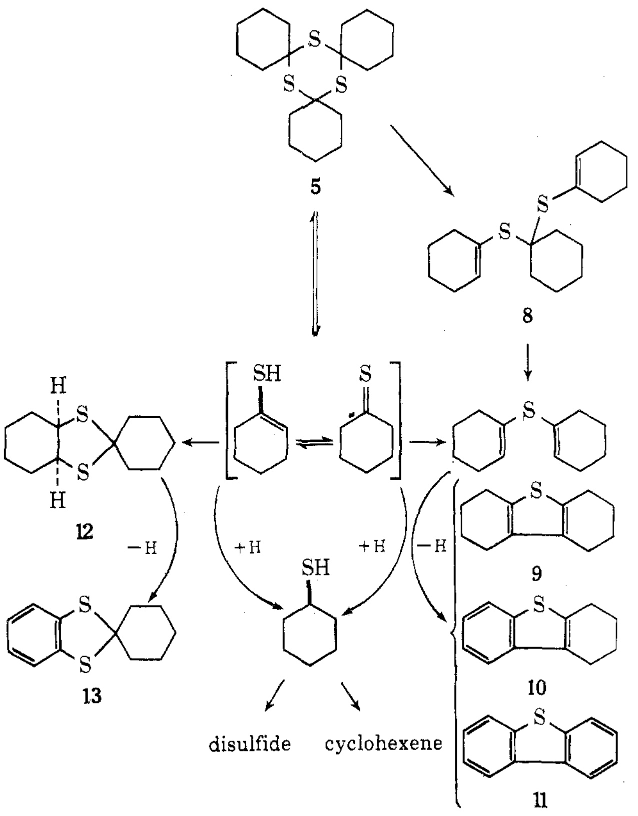
Two oligomers of norbornanethione, both evidently trimers from mass spectra, gave good yields of monomeric thioketone on pyrolysis at reduced pressure. Monomeric norbornanethione was found to be a remarkably stable thioketone. When initially generated it contained less than 1% (nmr) enethiol **2**, and after 5 days at room temperature 7% enethiol with 64% (visible) of the neat liquid surviving as the thioketone. In contrast to this stability, injection of molten cyclohexanethione trimer (**5**) onto sand at 300° instantly produced a red liquid (thioketone) in the condenser which became crystalline and colorless within minutes. The crystals were indistinguishable from the starting trimer.

The few previously reported stable thioketones involve heavily α-substituted rigid skeletons. Thiofenchone,[8,9] 2,2,4,4-tetramethyl-1,3-cyclobutanedithione,[10] and adamantanethione[11] are all rigid, highly hindered, nonenolizable thioketones. Thiocamphor[7,8] and thioketo steroids[12] possess rigidity and some quaternary α carbons. The trimer of adamantanethione is known, but no trimers have been prepared from any of the other stable thioketones. From the relative stability of norbornanethione it appears that the hindrance or conformation provided by the bicyclo[2.2.1]heptane skeleton is sufficient to stabilize the thioketone without the encumbering methyl groups of thiocamphor or thiofenchone. The thioketone stabilizing effect does not extend to its homolog, bicyclo[3.2.1]octane-2-thione. The qualitative order of stability of neat thioketones studied at room temperature is norbornanethione (days) > cycloheptanethione (days) > cyclopentanethione (hours) > cyclohexanethione (minutes). The major causes of fading of the red color are enolization and trimerization.

Freshly generated norbornanethione contained 4% (vpc) of a mixture of *exo*- and *endo*-2-norbornanethiol. These thiols were major products of atmospheric pressure pyrolysis. The appearance of a small amount of norbornanone was observed in several instances by ir, vpc, and mass spectrum after norbornanethione was manipulated or stored for prolonged periods at room temperature. Assuming that the fresh pyrolysis distillate contains 96% norbornanethione, as suggested by its nmr and vpc, pure norbornanethione has λ_{max} (heptane) 497 nm (ϵ 11.8). This value is close to that observed for other relatively stable thioketones.[7,8,11]

Cracking of trithianes at atmospheric pressure produced no thioketones but only pyrolysis products of thioketones which are characterized by hydrogen disproportionation and H_2S elimination. Pyrolyses of **3′**-**7** were pushed until no more distillate was collected, by which time the heating bath temperature was about 350°. Hard black residues were left after pyrolysis of **3′**, **4**, **6**, and **7**, while the residue from pyrolysis of cyclohexanethione trimer was a yellow oil. The distillates had the following compositions: from **3′**, 45% 2-norbornanethiol and 55% norbornene; from **4**, 75% cyclopentanethiol and 25% cyclopentene; from **5**, 88% cyclohexanethiol and 12% cyclohexene; from **6**, 84% cycloheptene; and bicyclo[3.2.1]-2-octene as the major product from **7**.

Scheme I



Cyclopentanethiol and 2-norbornanethiol were characterized as crystalline 2,4-dinitrophenyl (DNP) derivatives. The 2,4-dinitrophenyl-2-norbornyl sulfide was a mixture of endo and exo isomers which could not be completely separated by recrystallization. However, integration of the unique methine nmr signal showed that the major pyrolysis product was *exo*-2-norbornanethiol. Pure *exo*-2-norbornanethiol was prepared by addition of thioacetic acid to norbornene followed by saponification of *exo*-2-norbornyl thioacetate. *endo*-2-Norbornanethiol, containing some exo isomer, was prepared by $NaBH_4$ reduction of 2-norbornanethione. *endo*-2-Norbornanethiol is distinguished from the exo isomer by its exo methine proton resonance at 2.95–3.45 ppm in CCl_4; this methine resonance occurs at 2.6–3.0 ppm in *exo*-2-norbornanethiol. In the endo-DNP derivative the methine resonance occurs at 3.45–3.9 ppm and in the exo-DNP derivative at 3.11–3.45 ppm.

Distillation products from atmospheric pressure pyrolyses were generally more hydrogenated than the starting trithianes. Pot residues must then be relatively dehydrogenated. The dehydrogenation products of triscyclohexanethione, which appeared to give the least polymeric pot residue, were fractionated by molecular distillation followed by preparative tlc. Major components were identified as 1,2,3,4-tetrahydrodibenzothiophene (**10**), characterized as its crystalline sulfone, crystalline dibenzothiophene (**11**), 1,2,3,4,5,6,7,8-octahydrodibenzothiophene (**9**), and liquid spiro-2,2-pentamethylenebenzodithiolane (**13**).

Dehydrogenation product **13** had a chemical ionization mass spectral ion at *m/e* 223 (M + 1) with isotopic peak intensities expected for natural abundance ^{34}S and ^{13}C in a $C_{12}H_{14}S_2$ compound. It had a uv spectrum compatible with an *o*-dithiobenzene derivative.[13] Spiro structure **13** was assigned primarily on the basis of a four-proton multiplet at 1.9–2.3 ppm rather than a two-proton multiplet in this region required for the conceivable isomer hexahydrothianthrene. Under the dehydrogenative conditions hexahydrothianthrene, if present, could have been expected to undergo extensive dehydrogenation to thianthrene. Pyrolysis of thianthrene is known to give dibenzothiophene.[14] However, no thianthrene could be detected in any fractions. Further, the presence of hydrodibenzothiophenes suggests that the route to dibenzothiophene is one of those shown in Scheme I rather than *via* thianthrene. Fromm investigated the pyrolysis of triscyclohexanethione under similar conditions.[15] He did not examine the pot residue but did isolate a major volatile component to which he assigned structure **8** based on elemental analysis and the decolorization of bromine. Although the structural evidence is not compelling, compound **8** could be an intermediate between trimer **5** and dibenzothiophene. Katritzky and coworkers observed the formation of spiro dimer **12** on treatment of an ethereal ethanolic solution of cyclohexanethione monomer, from which the red color had faded, with diazomethane at 25°.[16] Since **13** was probably formed *via* **12**, the diazomethane used by Katritzky and coworkers is probably not necessary in the conversion of cyclohexanethione into its dithiolane dimer.

Although reduced pressure pyrolysis of trithianes is not necessarily a general method of preparing thioketones, it has some range of utility and is a very good method of preparation of 2-norbornanethione. The stability of norbornanethione compares favorably with the most stable thioketones known. Thus norbornanethione provides a good model for investigation of thioketone chemistry beyond enthiolization and trimerization.

Registry No.—**1**, 51849-44-6; **3**, 51849-42-4; **4**, 177-61-7; **5**, 177-58-2; **6**, 177-54-8; **7**, 51849-43-5; **9**, 15869-74-6; **10**, 16587-33-0; **10** sulfone, 51849-45-7; **11**, 132-65-0; **13**, 7127-65-3; bicyclo[3.2.1]octan-2-one, 5019-82-9; 2-norbornanone, 497-38-1; *endo*-2-norbornanethiol, 51849-46-8; *exo*-2-norbornanethiol 2,4-dinitrophenyl derivative, 51849-47-9; *endo*-2-norbornanethiol 2,4-dinitrophenyl derivative, 51849-48-0; cyclopentanethiol 2,4-dinitrophenyl derivative, 51849-49-1; *exo*-2-norbornanethiol, 51849-50-4.

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Decomposition of Sulfonyl Azides and *tert*-Butyl Azidoformate By Transition Metal Carbonyls

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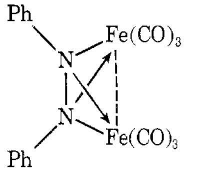
Iron and cobalt complexes $[Fe(RSO_2N)_2CO{\cdot}H_2O]_n$ and $[Co(RSO_2N)_2CO{\cdot}\frac{1}{2}H_2O]_n$ which are deficient of terminal and bridging metal carbonyls have been isolated from the reaction of methane-, benzene-, and *p*-toluenesulfonyl azide with iron pentacarbonyl, diiron nonacarbonyl, and dicobalt octacarbonyl. Hydrolysis of these with dilute hydrochloric acid leads to the corresponding *N,N'*-bis(sulfonyl)urea. Possible structures for the complexes involving coordination of a sulfonyl oxygen to the metal are presented and supporting evidence for such coordination is given. Free singlet sulfonyl nitrenes are not formed in these decompositions. The decomposition of *tert*-butyl azidoformate with iron pentacarbonyl and diiron nonacarbonyl gave impure complexes, still containing terminal and bridging carbonyls, which could be hydrolyzed to give mainly *tert*-butyl carbamate, di-*tert*-butyl iminodicarboxylate, and *N,N*-bis(*tert*-butoxycarbonyl)urea.

Despite the large volume of information available on the thermal and photochemical decomposition of organic azides,[1b,2-4] studies pertaining to the decomposition of organic azides by transition metal carbonyls have only recently appeared. Phenyl azide, which thermolyzes only above 120°, decomposes at room temperature in the presence of diiron nonacarbonyl to give a low yield of the nitrene product, azobenzene. The main product is the complex **1**, which decomposes spontaneously in solution to the urea complex **2**.[5]



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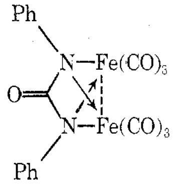

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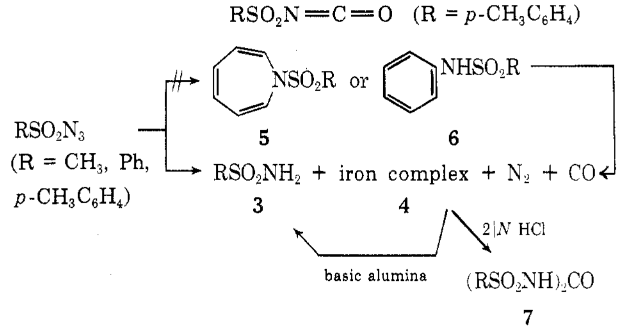
A similar complex was obtained from 2-azidobiphenyl, together with the urea and nitrene-derived products.[6] As part of our interest in generating sulfonyl nitrenes under mild conditions to study their behavior with aromatic compounds under kinetic control conditions,[3,7] we now report the results for the decomposition of sulfonyl azides and *tert*-butyl azidoformate by transition metal carbonyls.

Results and Discussion

The decomposition of excess methane-, benzene-, and *p*-toluenesulfonyl azide and *p*-toluenesulfonyl isocyanate with diiron nonacarbonyl at room temperature (heterogeneous) or iron pentacarbonyl at 60–65° (homogeneous) in benzene gave a low yield of the corresponding sulfonamide (**3**) and a high-melting amorphous iron complex (**4**) devoid of both terminal and bridging iron carbonyls. *N*-Sulfonylazepines (**5**), the expected aromatic addition products if discrete nitrenes were formed, were not detected nor were the corresponding sulfonanilides (**6**). Thus, no free singlet sulfonylnitrenes are generated in these catalyzed decompositions.



The nmr spectra of these complexes could not be obtained owing to their paramagnetic nature (*vide infra*) and their insolubility in solvents that did not effect their decomposition, and the mass spectra could not be determined owing to their insufficient volatility. Elemental analyses (reproducible from run to run) satisfied an empirical formula corresponding to $Fe(RSO_2N)_2CO{\cdot}H_2O$. Hydrolysis of these complexes with dilute hydrochloric acid gave the corresponding *N,N'*-bis(sulfonyl)urea (**7**) in high yield (70–80%), while chromatography on basic alumina gave the corresponding sulfonamide (80%). The crystal structure of the complexes obtained in this study could not be determined because of our inability to obtain them crystalline. They gave blue solutions in dimethyl sulfoxide from which the complex could not be recovered.

The stoichiometry of the reaction was found to be azide: $Fe_2(CO)_9$ = 4. For the decomposition of methanesulfonyl azide with diiron nonacarbonyl, the molar ratio of nitrogen to carbon monoxide evolved was 0.68. The calculated molar ratio, in which seven molecules of carbon monoxide are lost from diiron nonacarbonyl and four molecules of nitrogen are evolved from methanesulfonyl azide, is 0.57. The observed ratio is expected to be higher since a low yield of methanesulfonamide was also formed.

The decomposition of methanesulfonyl azide with dicobalt octacarbonyl in benzene at room temperature gave a