Photochemistry of Mercaptoles[1]

ROBERT E. KOHRMAN[2] AND GLENN A. BERCHTOLD*

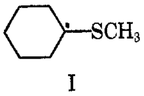
Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Received April 21, 1971

The photochemistry of 1,1-bis(methylthio)cyclohexane and several cyclic mercaptoles containing a carbon-carbon double bond (**7**, **14**) or an aromatic ring (**19**, **23**, **24**, **28**, **31**, **33**) has been studied. The observed results are compared with the photochemical reactions of simple, cyclic mercaptoles.

Previous investigations of the photochemical reactions of cyclic mercaptoles derived from cyclohexanone and cyclopentanone established two major pathways of reaction.[3] These are indicated in Scheme I for the mercaptoles of cyclohexanone. When $n = 3$, path a was the major pathway and gave predominantly the cis product **1**. When $n = 2$, the predominant reaction was *via* path b to products derived from the thione **2**.

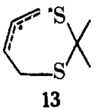
The effects of other changes in the structure of the mercaptole on the reaction course on irradiation in cyclohexane have been investigated. The results are summarized in Table I. Irradiation of the acyclic mercaptole **3** yielded mainly **4** and **6** along with a small amount of **5**. Initial homolytic cleavage of the C–S bond of **3** to structure I and $CH_3S\cdot$ seems obvious, but the



I

poor material balance prevents further conclusions on the pathway. If **5** and CH_3SH are formed from hydrogen atom transfer between the radicals, there is no addition of CH_3SH to **5** to form *cis*-1,2-bis(methylthio)cyclohexane by an intermolecular pathway analogous to formation of **1**. The hydrogen atom source for converting structure I to **4** is not the solvent since a similar product mixture is obtained from irradiation of **3** in Freon-113 (47% reaction: 17% **4**, 3% **5**, and 11% **6**).

Derivatives of 1,3-dithiacyclohept-5-ene were irradiated to determine whether cleavage of the allylic C–S bond would be the preferred path. Irradiation of **7** gave **8** as the major product. Formation of **8** suggests involvement of the diradical **13**. Products **9**, **10**, and **11** undoubtedly arise from acetone thione which



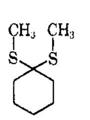
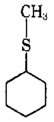
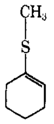
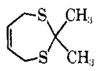
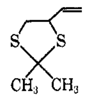
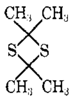
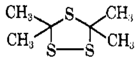
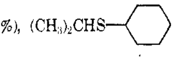
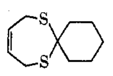
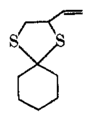
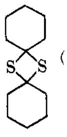
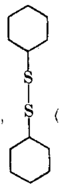
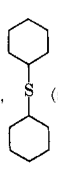
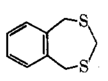
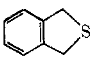
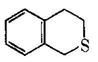
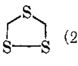
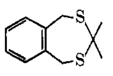
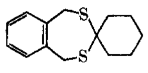
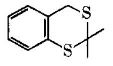
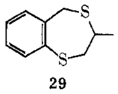
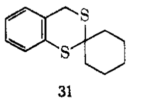
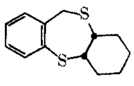
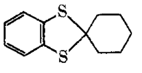
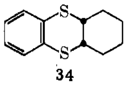
13

may be formed from **13** or from initial cleavage as previously observed.[3] Product **12** may arise from reaction of **13** or thione with solvent.[3] Photolysis of **14** proceeds in similar fashion except no trithiolane product is observed. If any dihydrothiophene (or thiophene) were formed, its presence would have gone undetected in the removal of the solvent.

The benzo[*e*]-1,3-dithiacyclohept-5-ene analogs **19**, **23**, and **24** were also studied for comparison with **7** and **14**. In all three cases, the major photochemical

TABLE I

PRODUCTS FROM IRRADIATION OF MERCAPTOLES IN CYCLOHEXANE

Mercaptole	Time, hr	Mercaptole consumed, %	Products (% conversion)
 **3**	4	65	 **4** (27%),  **5** (2%), CH_3SSCH_3 **6** (18%)
 **7**	18	89	 **8** (25%),  **9** (4%), $(CH_3)_2CHSSCH(CH_3)_2$ **10** (3%)  **11** (8%),  **12** (4%)
 **14**	15	89	 **15** (11%),  **16** (13%),  **17** (2%),  **18** (5%)
 **19**	10	93	 **20** (38%),  **21** (10%),  **22** (2%)
 **23**	8	85	**20** (41%), **9** (14%) **10** (9%), **11** (3%)
 **24**	12	95	**20** (13%), **16** (15%), **17** (6%), **18** (2%),  **25** (1%)
 **28**	41	67	 **29** (15%), **9** (4%), **10** (3%)
 **31**	42	87	 **32** (5%), **16** (6%), **17** (6%), **18** (2%)
 **33**	16	62	 **34** (16%)

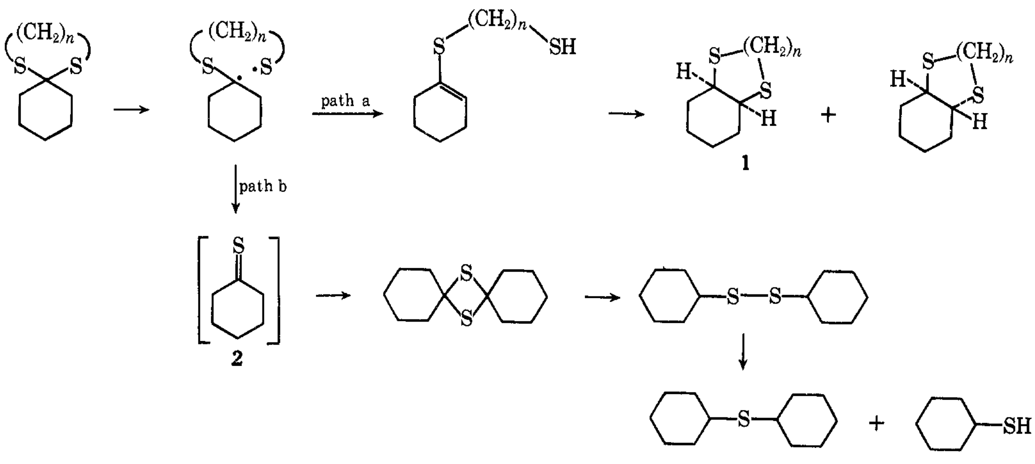
---

[1] This research has been supported by National Science Foundation Grant No. GP-7831 and by National Institutes of Health Grant No. AI-09300.

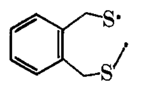
[2] National Institutes of Health Predoctoral Fellow, 1966–1968.

[3] J. D. Willett, J. R. Grunwell, and G. A. Berchtold, *J. Org. Chem.*, **33**, 2297 (1968).

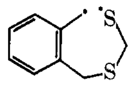
SCHEME I



reaction involves elimination of thione and formation of 2,5-dihydro-3,4-benzothiophene (**20**). All other products, except **21**, are derived from thione as described earlier. The presence of **21** represents a previously unobserved extrusion of sulfur on irradiation of mercaptoles. Whether the reaction occurs through initial homolytic cleavage to form **26** or **27** which eliminates thioformaldehyde and cyclizes to **20** or eliminates sulfur and cyclizes to **21** is open to question.



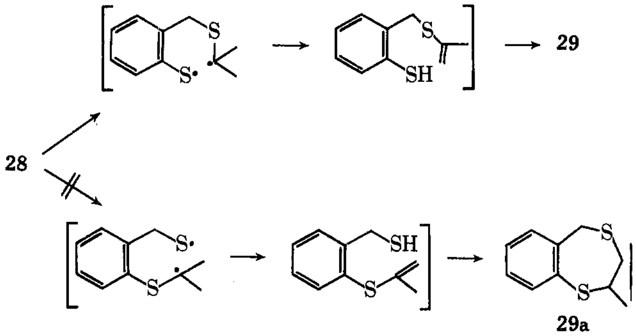
26



27

Photolysis of **28** gave the rearrangement product **29** (analogous to the formation of **1**[3]) in addition to **9** and **10** in low yield. No **29a** was observed. The initial C–S bond cleavage occurs only in the direction to give the more stable thiyl radical as indicated in Scheme II. Irradiation of **31** and **33** produced products from the same photochemical rearrangement. The structure of **29** was established by synthesis of an authentic sample (see Experimental Section).

SCHEME II



Experimental Section[4]

Photochemical Studies.—The photochemical results are listed in Table II. Photolysis solvents were purified by the following procedures. Cyclohexane (Eastman Spectrograde) was distilled under N_2 from BaO through a 2-ft Vigreux column. *tert*-Butyl alcohol (Eastman reagent) was distilled under N_2 from Na through a 2-ft column. Freon-113 (Allied Chemical Co.) was distilled under N_2 from NaH through a 2-ft Vigreux column. In general, the solvents were distilled directly into the photolysis vessel and degassed with prepurified N_2 for 2–3 hr, and the photolysis was carried out under an atmosphere of N_2.

TABLE II

PHOTOCHEMICAL EXPERIMENTS

Compd irradiated (g)	Solvent (ml)	Time, hr	Components of product mixture (% yield)
3 (0.618)	Cyclohexane (75 ml)	4	**3** (35%), **4** (27%), **5** (2%), **6** (18%)
3 (3.385)	Freon-113 (600)	15.5	**3** (53%), **4** (17%), **5** (3%), **6** (11%)
7 (2.427)	Cyclohexane (600)	18	**7** (11%), **8** (25%), **9** (4%), **10** (3%), **11** (8%), **12** (4%)
14 (3.92)	Cyclohexane (600)	15	**14** (11%), **15** (11%), **16** (13%), **17** (2%), **18** (5%)
19 (5.27)	Cyclohexane (600)	10	**19** (7%), **20** (38%), **21** (10%), **22** (2%)
23 (3.42)	Cyclohexane (600)	3	**23** (15%), **9** (14%), **10** (9%), **11** (3%), **20** (41%)
24 (2.85)	Cyclohexane (600)	12	**24** (5%), **16** (15%), **17** (6%), **18** (2%), **20** (13%), **25** (1%)
28 (3.32)	Cyclohexane (600)	41	**28** (67%), **9** (4%), **10** (3%), **29** (15%)
31 (3.80)	Cyclohexane (600)	42	**31** (13%), **16** (6%), **17** (6%), **18** (2%), **32** (5%)
33 (2.21)	Cyclohexane (600)	16	**33** (38%), **34** (16%)

The light source was a Rayonet photochemical reactor, Model RPR 100 (Southern New England Ultraviolet Co.), reactor barrel 10 (diameter) × 15 in. (depth) with 16 lamps (2537 Å) in a circular bank.

Solutions were stirred with a magnetic stirring bar, and quartz vessels were equipped with a water-cooled condenser. Photolyses were monitored by ir or glpc with aliquots withdrawn at convenient intervals of time. Products were characterized by

---

[4] Infrared spectra were taken on a Perkin-Elmer Model 237 or 337 spectrophotometer. Ultraviolet spectra were taken on a Cary Model 14 spectrophotometer. The nmr spectra were taken on a Varian A-60 or T-60, and chemical shift data are reported in parts per million downfield from tetramethylsilane as an internal standard at 0.00. Mass spectra were run on a Hitachi Perkin-Elmer RMU-6D mass spectrometer with an ionizing potential of 80 eV and are expressed in per cent relative intensity relative to the most intense peak as 100%. Melting points were taken on a Thomas-Hoover "Uni Melt" and are corrected. Gas chromatographic analyses and isolations were carried out on either an F & M Model 810 research gas chromatograph or a Hewlett-Packard Model 5750 gas chromatograph with thermal conductivity detectors using 0.25-in.-diameter columns of the following type: 6 ft, 10% SE-30; 4 ft, 20% SE-30; 4 ft, 10% LAC-446; or 4 ft, 20% Versamid-800 (all on 60–80 mesh Chromosorb P). Microanalyses were performed by Scandinavian Microanalytical Laboratory, Herlev, Denmark, Galbraith Laboratories, Knoxville, Tenn., or Mrs. Nancy Alvord, of this department.

collection from glpc and comparison with authentic samples. Glpc yields are based on the addition of a known amount of hydrocarbon as an internal standard after irradiation.[5]

1,1-Bis(methylthio)cyclohexane (3).—To a solution of cyclohexanone (50.8 g, 0.52 mol) in 250 ml of benzene in a three-necked flask equipped with a Dry Ice condenser and a gas inlet tube was added methyl mercaptan (50 g, 1.04 mol). Hydrogen chloride gas was bubbled through the solution for 2 hr. The solvent was removed under reduced pressure, and the residue was dissolved in ether. The solution was washed with 5% NaOH solution and saturated NaCl solution and dried ($MgSO_4$). The ether was removed under reduced pressure and the residue was distilled to give 70.2 g (77%) of **3**: bp 68–70° (0.4 mm); ir (CCl_4) 2965, 2850, 1445, 1270, 1250, 1180, 1130, 1010, 950, and 865 cm^{-1}; uv max (cyclohexane) 237 nm (ϵ 991); nmr ($CDCl_3$) δ 1.05–1.90 (10 H, m) and 2.02 ppm (6 H, s); mass spectrum *m/e* (rel intensity) 176 (10), 128 (70), 88 (14), 80 (100), 78 (14), 60 (21), 54 (16), 45 (12), 41 (18), and 39 (13).

Anal. Calcd for $C_8H_{16}S_2$: C, 54.48; H, 9.14; S, 36.37. Found: C, 54.66; H, 9.24; S, 36.45.

Cyclohexyl Methyl Sulfide (4).—Sulfide **4** was prepared in 65% yield according to the procedure of Weibull,[6] bp 77–78° (20 mm) [lit.[6] bp 68–68.5° (18 mm)].

Cyclohexenyl Methyl Sulfide (5).—The structure of **5** was assigned on the basis of the following spectral data: ir (CCl_4) 2920, 1647, 1445, and 1132 cm^{-1}; mass spectrum *m/e* (rel intensity) 128 (54), 113 (22), 100 (15), 85 (38), 81 (100), 80 (54), 79 (50), 77 (17), 71 (13), 67 (11), 61 (11), 59 (13), 53 (32), 51 (15), 45 (29), 41 (43), and 39 (39).

Dimethyl Disulfide (6).—The authentic sample of **6** was purchased from Eastman Organic Chemicals.

2,2-Dimethyl-1,3-dithiacyclohept-5-ene (7).—*cis*-1,4-Dichloro-2-butene[7] was converted to *cis*-2-butene-1,4-dithiol diacetate in 47% yield with thiolacetic acid in pyridine, bp 91–92° (0.08 mm) [lit.[8] bp 81–83° (0.1 mm)]. The dithiol diacetate was converted to *cis*-2-butene-1,4-dithiol in 74% yield with KOH in methanol, bp 55–56° (0.2 mm) [lit.[9] bp 80–81° (11 mm)].

To a solution of 11.6 g (0.2 mol) of acetone in 200 ml of benzene containing 20 mg of *p*-toluenesulfonic acid was added 24.0 g (0.20 mol) of *cis*-2-butene-1,4-dithiol. The mixture was heated under reflux for 18 hr while the water formed was removed by a Dean-Stark trap. The mixture was cooled, washed with 10% NaOH solution and water, and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue was purified by column chromatography on silicic acid with pentane as eluent. The product was further purified by distillation, repeated fractional recrystallizations from pentane at low temperature (Dry Ice–isopropyl alcohol), and short-path distillation to give 6.82 g (21%) of pure **7**: bp 58–61° (0.4 mm); ir (CCl_4) 3015, 2960, 2910, 2855, 1650, 1438, 1380, 1362, 1162, 1150, and 1112 cm^{-1}; uv max (cyclohexane) 227 nm (ϵ 1840) and 257 (398); nmr (CCl_4) δ 1.68 (6 H, s), 3.2–3.4 (4 H, m) and 5.8–6.0 ppm (2 H, m); mass spectrum *m/e* (rel intensity) 160 (27), 106 (58), 95 (12), 86 (16), 85 (36), 75 (11), 74 (28), 72 (12), 59 (79), 58 (12), 57 (13), 45 (35), 43 (100), 42 (62), and 41 (75).

Anal. Calcd for $C_7H_{12}S_2$: C, 52.44; H, 7.54; S, 40.00. Found: C, 52.70; H, 7.74; S, 39.79.

2,2-Dimethyl-4-vinyl-1,3-dithiacyclopentane (8).—To a solution of 16.8 g (0.100 mol) of 86% KOH in 75 ml of methanol was added 30 g of CS_2, followed by slow addition of 7 g (0.10 mol) of butadiene monoxide (K and K Laboratories). The solution was stirred for 12 hr at room temperature and the excess CS_2 was removed under reduced pressure. Water was added to the residue and the mixture was extracted with ether. The ether layer was washed with water and dried ($MgSO_4$). The solvent was removed under reduced pressure to give 13.3 g (83%) of crude 3-butene-1,2-dithiol trithiocarbonate as a light orange oil. Attempts to induce crystallization were unsuccessful. The product darkened rapidly on exposure to the atmosphere. A small sample was short path distilled: bp 120° (0.7 mm); ir (CCl_4) 1635, 1425, 1075, 975, 930, 808, and 735 cm^{-1}; nmr (CCl_4) δ 3.6–4.1 (3 H, m) and 4.8–6.6 ppm (4 H, m); mass spectrum *m/e* (rel intensity) 162 (35), 108 (14), 86 (58), 85 (100), 71 (11), 64 (15), 54 (15), 53 (19), 45 (41), and 39 (28).

Anal. Calcd for $C_5H_6S_3$: C, 37.00; H, 3.73; S, 59.28. Found: C, 37.20; H, 3.61; S, 59.37.

A solution of crude 3-butene-1,2-dithiol trithiocarbonate (10.73 g, 0.066 mol) in 50 ml of ether was added with stirring to a slurry of 3.8 g (0.10 mol) of $LiAlH_4$ in 100 ml of ether, and the mixture was stirred overnight at room temperature. The excess hydride was decomposed with water, and the mixture was acidified with 6 *N* HCl. The layers were separated and the aqueous layer was extracted with ether. The ether extracts were combined, washed with water, and dried ($MgSO_4$). The solvent was removed under reduced pressure to give 6.88 g (86%) of 3-butene-1,2-dithiol. Further attempts to purify the material resulted in decomposition.

A 2.4-g sample of 3-butene-1,2-dithiol was converted to **8** by reaction with acetone using the procedure described for the preparation of **7**. The product was obtained as a light yellow oil (3.05 g). Attempted distillation resulted in decomposition. It could be collected from glpc programmed from 50° up at 4°/min: ir (CCl_4) 3060, 2940, 2900, 1850, 1640, 1440, 1368, 1160, 984, and 919 cm^{-1}; nmr (CCl_4) δ 1.70 (6 H, s), 3.10 (2 H, m), 4.20 (1 H, m), and 4.8–6.0 ppm (3 H, m); mass spectrum *m/e* (rel intensity) 160 (15), 145 (32), 106 (77), 99 (10), 88 (10), 87 (15), 86 (98), 86 (66), 84 (31), 75 (31), 74 (26), 59 (100), 45 (26), 41 (22), and 39 (18).

Anal. Calcd for $C_7H_{12}S_2$: C, 52.44; H, 7.54; S, 40.00. Found: C, 52.28; H, 7.51; S, 40.05.

2,2,4,4-Tetramethyl-1,3-dithietane (9).—Assignment of structure to this product is based on its identity with **9** obtained from irradiation of 2,2-dimethyl-1,3-dithian-5-one[10] where the structural assignment was based on the following data: mp 77.0–77.5°; ir (KBr) 2990, 2950, 2920, 2850, 1460, 1450, 1380, 1160, 1135, 920, and 570 cm^{-1}; uv max (hexane) 234 nm (ϵ 138) and 302 (30); nmr (CCl_4) δ 1.87 (12 H, s); mass spectrum *m/e* (rel intensity) 150 (2), 149 (2), 148 (10), 74 (55), 59 (100), and 41 (17).

Anal. Calcd for $C_6H_{12}S_2$: C, 48.59; H, 8.15; S, 43.24. Found: C, 48.81; H, 8.09; S, 43.15.

Diisopropyl Disulfide (10).—The authentic sample of **10** was purchased from Wateree Chemical Co.

3,3,5,5-Tetramethyltrithiolane (11).—A mixture of 58 g (1 mol) of acetone and 20 g of phosphorus pentasulfide was heated under reflux for 12 hr, poured onto crushed ice, and extracted with ether. The ether extract was dried ($MgSO_4$) and the solvent was removed under reduced pressure. The residue was distilled to obtain 12.4 g (7%) of **11**, bp 85–87° (18 mm) [lit.[11] bp 75° (10 mm)].

Cyclohexyl Isopropyl Sulfide (12).—A solution of sodium ethoxide was prepared by dissolving 9.2 g (0.4 g-atom) of Na in 250 ml of ethanol. A dewar condenser was attached to the flask and 30.4 g (0.4 mol) of isopropyl mercaptan was slowly added to the solution with stirring. To this solution was added 65.2 g (0.4 mol) of cyclohexyl bromide in 100 ml of ethanol. A cloudy white precipitate formed almost immediately. The mixture was refluxed for 12 hr. The solution was cooled, water (400 ml) was added, and the mixture was extracted with pentane. The pentane extracted was dried ($MgSO_4$), and the solvent was removed under reduced pressure. Distillation of the residue afforded 9.04 g (14%) of **12**: bp 121–122° (35 mm); ir (CCl_4) 2960, 1453, 1387, 1340, 1247, 1205, 1168, 1055, 1000, and 890 cm^{-1}; nmr (CCl_4) δ 1.20 (6 H, d), 1.2–2.6 (11 H, m), and 2.90 ppm (1 H, septet).

Anal. Calcd for $C_9H_{18}S$: C, 68.28; H, 11.46; S, 20.25. Found: C, 68.10; H, 11.28; S, 20.36.

1,6-Dithiaspiro[6.5]undec-3-ene (14).—Mercaptole **14** was prepared in 48% yield from cyclohexanone and *cis*-2-butene-1,4-dithiol by the same procedure described for the preparation of **7**: bp 117° (1.0 mm); ir (CCl_4) 3010, 2910, 2845, 1440, 1396, 1265, and 1005 cm^{-1}; uv max (cyclohexane) 248 nm (ϵ 3120) and 280 (639); nmr (CCl_4) δ 1.4–2.2 (10 H, m), 3.2–3.5 (4 H, m) and 5.4–5.9 ppm (2 H, m); mass spectrum *m/e* (rel intensity) 200 (28), 146 (32), 135 (10), 114 (16), 85 (16), 82 (10), 81 (100), 71 (13), 55 (12), 45 (15), 41 (13), and 39 (14).

Anal. Calcd for $C_{10}H_{16}S_2$: C, 59.94; H, 8.05; S, 32.01. Found: C, 60.06; H, 7.96; S, 32.03.

2-Vinyl-1,4-dithiaspiro[4.5]decane (15).—Mercaptole **15** was prepared from cyclohexanone and 3-butene-1,2-dithiol by the procedure described for the preparation of **8**. Attempted purifi-

---

(5) The internal standards used were $n\text{-}C_{12}H_{26}$ (The Matheson Co.), $n\text{-}C_{14}H_{30}$, $n\text{-}C_{15}H_{32}$, $n\text{-}C_{16}H_{34}$, $n\text{-}C_{17}H_{36}$, or $n\text{-}C_{18}H_{38}$ (Aldrich Chemical Co.).

(6) Z. Weibull, *Ark. Kemi*, **23**, 25 (1946).

(7) K. Mislow and H. M. Hellman, *J. Amer. Chem. Soc.*, **73**, 244 (1951).

(8) W. Autenreith and R. Hennings, *Ber.*, **34**, 1774 (1901).

(9) A. Luttringhaus and S. Kabuss, *Z. Naturforsch.*, **166**, 761 (1961).

(10) R. Yaffe and G. A. Berchtold, unpublished results.

(11) F. Asinger and M. Thiel, *Angew. Chem.*, **79**, 667 (1958).

cation by distillation resulted in decomposition. Purification could be effected by collection from glpc: ir (CCl_4) 3075, 2918, 2845, 1840, 1658, 1630, 1442, 1262, 1118, 980, and 916 cm^{-1}; mass spectrum *m/e* (rel intensity) 200 (12), 157 (47), 146 (39), 115 (51), 86 (58), 81 (100), and 71 (32).

Anal. Calcd for $C_{10}H_{16}S_2$: C, 59.92; H, 8.05. Found: C, 59.86; H, 7.86.

7,14-Dithiadispiro[5.1.5.1]tetradecane (16), Dicyclohexyl Disulfide (17), and Dicyclohexyl Sulfide (18).—The structures of products **16–18** were established by spectral comparison with material reported previously.[3]

1,5-Dihydro-2,4-benzodithiepin (19).—To a solution of 112.5 g (0.426 mol) of α,α′-dibromo-*o*-xylene (Aldrich Chemical Co.) in 200 ml of ethanol was added 56.4 g (0.752 mol) of thiourea and the mixture heated under reflux for 5 hr. A solution of 50 g of NaOH in 500 ml of water was added and the solution was heated under reflux for an additional 2 hr. The mixture was cooled, acidified with 6 *N* HCl, and extracted with ether. The ethereal extract was washed with water and dried ($MgSO_4$). The solvent was removed and the residue was distilled under reduced pressure to give 54.1 g (75%) of 1,2-benzenedimethanethiol, bp 105–107° (0.25 mm) [lit.[8] bp 160° (20 mm)].

To 15.0 g of a 40% aqueous solution of formaldehyde was added 34.0 g (0.187 mol) of 1,2-benzenedimethanethiol followed by 10 ml of concentrated HCl. The solution was stirred for 10 min, ether was added, and the precipitate which formed was collected by filtration. The product was sublimed at 45° (0.05 mm) to give 22.5 g (62%) of white crystals: mp 155–156° (lit.[8] mp 152–153°); ir ($CHCl_3$) 2985, 2900, 1494, 1455, 1430, 1380, 1150, and 895 cm^{-1}; uv max (cyclohexane) 255 nm (ε 1550); nmr ($CDCl_3$) δ 3.90 (2 H, s), 4.00 (4 H, s) and 7.28 (4 H, s); mass spectrum *m/e* (rel intensity) 182 (42), 136 (15), 135 (100), 134 (14), 104 (28), and 91 (14).

1,3-Dihydroisothionaphthene (20).—Product **20** was prepared in 55% yield in these laboratories by Dr. A. L. Maycock as previously described,[12] bp 49–57° (0.5 mm) [lit.[12] bp 94.7° (5 mm)].

Isothiochromane (21).—Compound **21** was prepared in 57% yield from 4-oxoisothiochromane as previously reported,[13] bp 65–66° (0.4 mm) [lit.[13] bp 129° (13 mm)].

1,2,4-Trithiolane (22).—The structure of **15** was established by comparison of its mass spectrum with that which is published.[14]

1,5-Dihydro-3,3-dimethyl-2,4-benzodithiepine (23).—To 14.1 g (0.083 mol) of 1,2-benzenedimethanethiol was added 10 ml of acetone, and HCl gas was passed through the mixture at a rapid rate. A white milky precipitate formed immediately and crystallized when water was added. The product was collected by filtration, dried, and sublimed at 60° (0.5 mm) to give 12.5 g (72%) of white crystals: mp 136–137°; ir ($CHCl_3$) 2970, 2920, 2850, 1492, 1450, 1439, 1380, 1365, 1160, and 1147 cm^{-1}; uv max (cyclohexane) 252 nm (ε 1490); nmr ($CDCl_3$) δ 1.74 (6 H, s), 3.92 (4 H, s) and 7.15 ppm (4 H, s); mass spectrum *m/e* (rel intensity) 210 (13), 136 (31), 135 (100), 134 (17), 106 (12), 104 (17), 91 (17), and 59 (12).

3,4-Benzo-1,6-dithiaspiro[6.5]undecane (24).—Mercaptole **24** was prepared from 25.5 g (0.15 mol) of 1,2-benzenedimethanethiol, 19.6 g (0.20 mol) of cyclohexanone, and 0.020 g of *p*-toluenesulfonic acid by the same procedure described for the preparation of **7** except that the reflux period was 7 hr. After the solvent was removed the solid was shaken with 2 l. of ether. The ether was filtered, concentrated, and cooled in the refrigerator. The mercaptole crystallized and was collected by filtration in a yield of 16.6 g (43%), mp 95–98°. An additional recrystallization from ether gave mp 96.5–98°; ir ($CHCl_3$) 3055, 3010, 2920, 2845, 1492, 1445, 1395, 1250, 1185, and 1008 cm^{-1}; uv max (cyclohexane) 231 nm (ε 4580) and 254 (1290); nmr ($CDCl_3$) δ 1.40–1.80 (6 H, m), 1.90–2.10 (4 H, m), 3.94 (4 H, s), and 7.15 ppm (4 H, s); mass spectrum *m/e* (rel intensity) 250 (16), 217 (17), 136 (35), 135 (100), 115 (18), 105 (19), 91 (17), and 81 (31).

Anal. Calcd for $C_{14}H_{18}S_2$: C, 67.15; H, 7.25; S, 25.61. Found: C, 67.23; H, 7.31; S, 25.50.

Cyclohexyl Mercaptan (25).—The authentic sample of **25** was purchased from Aldrich Chemical Co.

2,2-Dimethyl-1,3-benzodithiin (28).—To a slurry of 24 g (0.634 mol) of lithium aluminum hydride in 1000 ml of tetrahydrofuran was added, dropwise with stirring, 92.0 g (0.5 mol) of 2,3-dithiosulfindene[15] in 100 ml of tetrahydrofuran. The mixture was stirred for 8 hr at room temperature. The excess hydride was decomposed with water, and the mixture acidified with 6 *N* HCl. Water (1 l.) was added and the mixture was extracted with ether. The ether extract was washed with water and dried ($MgSO_4$), and the ether was removed under reduced pressure. The residue was distilled to give 73.7 g (94%) of *o*-α-toluenedithiol, bp 90–92° (0.5 mm) [lit.[16] bp 125–126° (12 mm)].

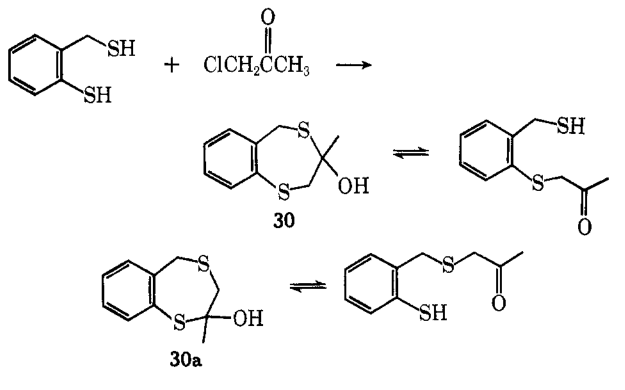
Mercaptole **28** was prepared in 85% yield from 5.84 g (0.0374 mol) of *o*-α-toluenedithiol and 3.0 g (0.0517 mol) of acetone in 30 ml of benzene by the procedure described for the preparation of **7**: bp 78–82° (0.2 mm) [lit.[16] bp 140–141° (12 mm)]; ir (CCl_4) 3065, 2965, 2920, 1570, 1472, 1450, 1386, 1368, 1160, 1110, and 1070 cm^{-1}; uv max (cyclohexane) 232 nm (ε 5740) and 262 (4920); nmr ($CDCl_3$) δ 1.59 (6 H, s), 3.68 (2 H, s), and 7.18–7.30 ppm (4 H, m); mass spectrum *m/e* (rel intensity) 196 (100), 181 (18), 163 (60), 153 (25), 122 (98), 78 (24), 77 (15), 59 (16), and 39 (10).

5,6-Benzo-1,4-dithia-2-hydroxy-2-methylcycloheptane (30).—To a solution of 15.6 g (0.10 mol) of *o*-α-toluenedithiol in 100 ml of anhydrous ether was added 2.30 g of Na metal and a small amount of methanol. After the Na was dissolved, chloroacetone (9.25 g, 0.10 mol) was slowly added and the solution was stirred for 8 hr. Water was added and the mixture was extracted with ether. The ether extract was dried ($MgSO_4$) and the ether was removed under reduced pressure. The white crystalline residue (20.2 g, 95%) was recrystallized from CCl_4: mp 95–98°; ir ($CHCl_3$) 3460, 2960, 1409, 1330, 1200, 1070, and 900 cm^{-1}; nmr ($CDCl_3$, room temperature) δ 1.62 (3 H, s), 3.05 (2 H, s), 3.50 (1 H, d, J = 15 Hz), 4.57 (1 H, d, J = 15 Hz), 4.48 (1 H, s), and 7.10–7.80 ppm (4 H, m); nmr (C_2Cl_4, 112°) δ 1.78 (1 H, t, J = 8 Hz), 2.11 (3 H, s), 3.57 (2 H, s), 3.88 (2 H, d, J = 8 Hz), and 6.9–7.7 ppm (4 H, m); mass spectrum *m/e* (rel intensity) 212 (2), 194 (35), 160 (70), 156 (22), 154 (55), 153 (100), 135 (41), 134 (11), 123 (20), 122 (35), 121 (34), 91 (20), 77 (15), 76 (30), 68 (14), 45 (36), and 39 (14).

Anal. Calcd for $C_{10}H_{12}OS_2$: C, 56.57; H, 5.70; S, 30.19. Found: C, 56.05; H, 5.86; S, 29.02. Further attempts at purification did not improve the purity.

The product from the reaction of *o*-α-toluenedithiol and chloroacetone in the presence of 1 equiv of base existed initially in the cyclic form (**30**) at room temperature (see Scheme III) but was converted in solution to the mercapto ketone form on heating in tetrachloroethylene. The ring opening was observed from the nmr spectrum and established the structure as **30** rather than **30a** since the spectrum at 112° showed absorption for the SH hydrogen atom as a triplet (J = 8 Hz) at 1.78 and the benzylic hydrogen atoms as a doublet (J = 8 Hz) at 3.88 ppm.

SCHEME III



5,6-Benzo-1,4-dithia-2-methylcycloheptene (29).—To a solution of 2.12 g (0.01 mol) of **30** in 40 ml of pyridine was added slowly 2.5 g of $POCl_3$. The mixture was stirred at room temperature for 5 hr, and the solution was poured onto crushed ice. The aqueous mixture was extracted with ether. The ether extracts were washed with 6 *N* HCl and water and dried ($MgSO_4$). Removal of the solvent gave 1.49 g (77%) of white, crystalline 5,6-benzo-1,4-dithia-2-methylcycloheptene that was sublimed

---

(12) J. A. Oliver and P. A. Ongley, *Chem. Ind. (London)*, 1024 (1965).

(13) P. Cagniant and D. Cagniant *Bull. Soc. Chim. Fr.*, 1998 (1959).

(14) K. Morita and S. Kobayashi, *Chem. Pharm. Bull.*, **15**, 989 (1967).

(15) F. S. Fowkes and E. W. McClelland, *J. Chem. Soc.*, 187 (1941).

(16) A. Luttringhaus and K. Hägele, *Angew. Chem.*, **67**, 304 (1955).

at 80° (0.1 mm): mp 100–102°; ir (CCl_4) 3040, 2980, 2945, 1575, 1468, 1438, 1413, 1286, 1200, and 1088 cm^{-1}; nmr ($CDCl_3$) δ 1.80 (3 H, d, J = 1.2 Hz), 4.50 (2 H, s), 5.78 (1 H, q, J = 1.2 Hz), and 7.2–7.6 ppm (4 H, m); mass spectrum *m/e* (rel intensity) 194 (34), 162 (12), 161 (100), 153 (18), 135 (59), 134 (15), 121 (11), 90 (15), 77 (12), 59 (12), and 45 (12).

Anal. Calcd for $C_{10}H_{10}S_2$: C, 61.81; H, 5.19; S, 33.01. Found: C, 61.75; H, 5.13; S, 33.18.

To a solution of 97 mg (5.0 mmol) of the above olefin in 50 ml of ethanol was added 388 mg of palladium-on-carbon catalyst (Matheson). The flask was equipped with a magnetic stirrer and placed under 1 atm of hydrogen. After 12 hr, 300 mg of catalyst was added, and the material was hydrogenated for an additional 12 hr. The catalyst was removed by filtration with the aid of Celite and washed with hot methanol, and the solvent was removed under reduced pressure. The residue contained starting olefin and **29** (13% yield) that was collected from glpc (LAC-446): ir (CCl_4) 3060, 2962, 2905, 1470, 1440, 1410, 1372, 1238, 1152, and 1000 cm^{-1}; nmr ($CDCl_3$) δ 1.29 (3 H, d, J = 7 Hz), 2.36–3.40 (3 H, m), 3.74 (1 H, d, J = 15 Hz), 4.18 (1 H, d, J = 15 Hz), and 7.0–7.7 ppm (4 H, m); mass spectrum *m/e* (rel intensity) 196 (100), 155 (19), 154 (64), 153 (72), 150 (25), 136 (24), 135 (57), 121 (22), 91 (15), 78 (10), 77 (22), 45 (14), 44 (12), 40 (13), and 39 (13).

Anal. Calcd for $C_{10}H_{12}S_2$: C, 61.18; H, 6.16; S, 32.66. Found: C, 61.27; H, 6.22; S, 32.86.

2,3-Benzo-1,5-dithiaspiro[5.5]undecane (31).—Mercaptole **31** was prepared in 74% yield from 9.2 g (0.104 mol) of cyclohexanone and 15.6 g (0.10 mol) of *o*-α-toluenedithiol by the same procedure described for the preparation of **7**: bp 120–124° (0.07 mm); ir (CCl_4) 3065, 2940, 2860, 1570, 1470, 1450, 1272, 1120, and 1012 cm^{-1}; uv (cyclohexane) 231 nm (ϵ 6000), 263 (469); nmr ($CDCl_3$) δ 1.4–2.0 (10 H, m), 3.71 (2 H, s), and 6.95–7.4 ppm (4 H, m); mass spectrum *m/e* (rel intensity) 237 (15), 236 (100), 203 (57), 193 (21), 154 (10), 153 (26), 147 (15), 123 (84), 121 (26), 81 (12), 78 (10), and 45 (10).

Anal. Calcd for $C_{13}H_{16}S_2$: C, 66.05; H, 6.82; S, 27.13. Found: C, 65.91; H, 6.89; S, 26.98.

***cis*-2,3-Benzo-1,5-dithiabicyclo[5.4.0]undecane (32).**—The identification of **32** is based slowly on spectral data: ir (CCl_4) 3050, 2910, 2840, 1470, 1443, 1408, 1268, and 1005 cm^{-1}; mass spectrum *m/e* (rel intensity) 226 (30), 203 (10), 155 (17), 154 (70), 153 (100), 124 (12), 123 (19), 122 (11), 121 (17), 109 (10), 81 (17), 77 (22), 45 (12), 41 (12), 40 (13), and 39 (19).

2,3-Benzo-1,4-dithiaspiro[4.5]decane (33).—Mercaptole **33** was prepared in 55% yield from 2.60 g (26 mmol) of cyclohexanone and 3.55 g (25 mmol) of 1,2-benzenedithiol by the procedure described for the preparation of **7**: bp 120–123° (0.25 mm); ir (CCl_4) 3040, 2910, 2840, 1440, 1254, 1112, 1005, and 975 cm^{-1}; uv max (cyclohexane) 238 nm (ϵ 12,100), 273 (3070), 292 (2220), 302 (2100), and 312 (1600); nmr (CCl_4) δ 1.3–1.9 (6 H, m), 2.1–2.4 (4 H, m) and 7.05 ppm (4 H, m); mass spectrum *m/e* (rel intensity) 222 (45), 179 (100), 166 (17), 153 (8), 81 (8), and 77 (7).

Anal. Calcd for $C_{12}H_{14}S_2$: C, 64.81; H, 6.35; S, 28.84. Found: C, 65.03; H, 6.42; S, 29.08.

***cis*-3,4-Benzo-2,5-dithiabicyclo[4.4.0]decane (34).**—To a solution of 416 mg (2.81 mmol) of *cis*-1,2-cyclohexanedithiol[3] in 50 ml of ethanol was added 393 mg (2.75 mmol) of cuprous oxide. The mixture was heated under reflux for 40 hr, cooled, and filtered. The red cuprous salt was dried and dissolved in 25 ml of quinoline containing 5 ml of pyridine. *o*-Dibromobenzene (589 mg, 2.5 mmol) was added and the mixture was heated under reflux for 12 hr. The solution was cooled and poured into a stirred mixture of ice and hydrochloric acid. The mixture was stirred 2 hr and extracted with ether. The ether extracts were washed with 3 N HCl, 10% $NaHCO_3$, and water and dried ($MgSO_4$). After removal of the solvent, the product (14% yield) was collected by glpc: ir (CCl_4) 3060, 2940, 2860, and 1460 cm^{-1}; nmr (CCl_4) δ 1.4–2.2 (8 H, m), 3.3–3.7 (2 H, m), and 6.9–7.1 ppm (4 H, m); mass spectrum *m/e* (rel intensity) 222 (100), 179 (27), 153 (23), 142 (35), 140 (80), 96 (19), 81 (59), 80 (20), 79 (10), 77 (12), 41 (13), and 39 (12).

Anal. Calcd for $C_{12}H_{14}S_2$: C, 64.82; H, 6.35. Found: C, 65.29; H, 6.49.

Registry No.—**3,** 4479-55-4; **5,** 4410-13-3; **7,** 14198-71-1; **8,** 31443-07-9; **9,** 31443-08-0; **12,** 7133-39-3; **14,** 31443-10-4; **15,** 31443-11-5; **19,** 7216-19-5; **23,** 14198-73-3; **24,** 31443-14-8; **28,** 6247-53-6; **29,** 31443-21-7; **30,** 31442-16-0; **31,** 31443-17-1; **32,** 31443-18-2; **33,** 7127-65-3; **34,** 31443-19-3; 3-butene-1,2-dithiol trithiocarbonate, 31443-20-6.

Photocyclization of Acrylanilides[1]

YOSHIRO OGATA,* KATSUHIKO TAKAGI, AND IWAO ISHINO

Department of Applied Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, Japan

Received April 2, 1971

Ultraviolet irradiation of acrylanilides (I) has been found to afford a cyclization product, 3,4-dihydrocarbostyrils (II); *e.g.*, methacrylanilide (Ib) in *n*-hexane gives IIb in a quantum yield of 0.26 and *N*-methylmethacrylanilide (Id) gives IId in a quantum yield of 0.24. The sensitizing and quenching studies suggest that the reaction occurs *via* an excited singlet state and that the formation of an enol precursor IV is less favorable. Their quantum yields tend to decrease with increasing solvent polarity, which is attributable to an increase of the efficiency of intersystem crossing with increasing the polarity of solvent.

It is known that the photolysis of *N*-phenylacylamides undergoes acyl migration to *o*- and *p*-acylanilines,[2–4] but that acrylanilides with an α,β-unsaturated acyl group photocyclize[5] without rearrangement except in the case of benzanilides which give both rearranged and cyclized products.[6]

Ultraviolet irradiation of *N*-allylanilines affords mainly anilines together with small amounts of ortho and para rearranged products.[7] However, *N*-allylaniline gives a cyclized product, *i.e.*, quinoline, in the presence of oxidizing agents such as $FeCl_3 \cdot 6H_2O$. Similarly, photolysis of aryl acrylates gives *o*- and *p*-acrylphenols without cyclization to lactones.[8]

---

(1) Contribution No. 168.

(2) (a) For the review of the photo-Fries rearrangement see D. Bellus and P. Hrdlovic, *Chem. Rev.*, **67**, 599 (1967); (b) J. C. Anderson and C. B. Reese, *J. Chem. Soc.*, 1781 (1963); (c) H. Kobsa, *J. Org. Chem.*, **27**, 2293 (1962); (d) R. A. Finnegan and A. W. Hagen, *Tetrahedron Lett.*, 365 (1963); (e) Y. Ogata, K. Takagi, and I. Ishino, *Tetrahedron*, **26**, 2703 (1970).

(3) (a) H. Shizuka, *Bull. Chem. Soc. Jap.*, **42**, 52, 57, 909 (1969); (b) H. Shizuka and I. Tanaka, *ibid.*, **41**, 2343 (1968).

(4) (a) D. Elad, D. V. Rao, and V. I. Stenberg, *J. Org. Chem.*, **30**, 3252 (1965); (b) D. V. Rao and V. Lamberti, *ibid.*, **32**, 2896 (1967); (c) J. S. Bradshaw, R. D. Knudsen, and E. L. Loveridge, *ibid.*, **35**, 1219 (1970).

(5) (a) P. G. Cleveland and O. L. Chapman, *Chem. Commun.*, 1064 (1967); (b) O. L. Chapman and W. R. Adams, *J. Amer. Chem. Soc.*, **89**, 4243 (1967); (c) O. L. Chapman and W. R. Adams, *ibid.*, **90**, 2333 (1968).

(6) B. S. Thyagarajan, N. Kharash, H. B. Lewis, and W. Wolf, *Chem. Commun.*, 614 (1967).

(7) Y. Ogata and K. Takagi, *J. Org. Chem.*, **35**, 1642 (1970).

(8) (a) H. Obara and H. Takahashi, *Bull. Chem. Soc., Jap.*, **40**, 1012 (1966); (b) H. Obara, H. Takahashi, and H. Hirano, *ibid.*, **42**, 560 (1969); (c) H. Obara, H. Takahashi, and J. Onodera, *Kogyo Kagaku Zasshi*, **72**, 309 (1969).