and olefin-free petroleum ether (150 ml., b.p. 30–60°). A mixture of 1-chloro-1-phenylmercaptopentadiene-1,3 (**12**) and 1-chloro-2-methyl-1-phenylmercaptobutadiene (**8**) was collected in 60% yield (12.7 g., 0.060 mole) and had the following properties: b.p. 74–77° (0.1 mm.); n^{25}D 1.6202; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 252 mμ (ε 20,930), shoulder 280 mμ (ε 10,950); ν^{neat} 1635 and 1605 (C═C), 1375 and near 2900 (CH_3), and 915 and 990 cm.$^{-1}$ (weak CH═CH_2); n.m.r. spectrum[12] (neat) C_6H_5 (complex, 423–445 c.p.s.), ═CH (complex, partly under phenyl hydrogens, 453–330 c.p.s.), ═CH_2 (complex, 304–328 c.p.s.), $C_6H_5CCl{=}C(CH_3){-}CH{=}CH_2$ (doublet, 121 and 126 c.p.s., wt. 1.0), and $C_6H_5{-}S{-}CCl{=}CH{-}CH{=}CH{-}CH_3$ (complex, 90–103 c.p.s., wt. 1.9); v.p.c. (Perkin-Elmer Model 154, silicone oil D. C. 200, on Chromosorb W, column set at 204°, carrier gas, He, pressure of 20 p.s.i.) showed two partly superimposed peaks, the smaller one being 1-chloro-2-methyl-1-phenylmercaptobutadiene (**8**) proved by injection of an authentic sample. A sample of the reaction mixture was redistilled through a spiral-wire column for analysis: b.p. 70–71° (0.01 mm.); n^{23}D 1.6208.

Anal. Calcd. for $C_{11}H_{11}ClS$: C, 62.69; H, 5.26; S, 15.22. Found: C, 62.41; H, 4.99; S, 15.26.

Reduction of the Mixture of 1-Chloro-2-methyl-1-phenylmercaptobutadiene (8) and 1-Chloro-1-phenylmercaptopentadiene-1,3 (12) with Raney Nickel.—The reduction was carried out as described for **8**. Vapor phase chromatography of the heptane solution showed the presence of three compounds (other than heptane). The compounds were identified as cyclohexane, isopentane, and *n*-pentane. The ratio of isopentane to *n*-pentane was 1 to 1.6 (according to n.m.r. spectrum, the ratio of **8** to **12** was 1 to 1.9).

1-*n*-Butylmercapto-1-chloropentadiene-1,3 and 1-*n*-Butylmercapto-1-chloro-2-methylbutadiene. The Reaction between Dichlorocarbene and *n*-Butyl α-Methylallyl Sulfide.—This reaction was carried out as described for **7** using *n*-butyl α-methylallyl sulfide (14.4 g., 0.10 mole), ethyl trichloroacetate (26.5 g., 0.14 mole), sodium methoxide (16.4 g., 0.30 mole), and olefin-free petroleum ether (175 ml., b.p. 30–60°). In addition to impure recovered sulfide (proved by v.p.c.; 3.1 g., 0.022 mole), there was obtained a crude mixture of 1-*n*-butylmercapto-1-chloropentadiene-1,3 and 1-*n*-butylmercapto-1-chloro-2-methylbutadiene (8.2 g., 0.043 mole, 43% yield; b.p. 73–75° at 0.7 mm.; n^{22}D 1.5278). This fraction was redistilled through a spiral-wire column to give 5.9 g. (0.031 mole) of product: 31% yield; b.p. 67–71 (0.7 mm.); n^{23}D 1.5313; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$ 237 mμ (ε 12,200) and 279 mμ (ε 10,300); ν^{neat} 1610 and 1635 cm.$^{-1}$ (weak, C═C); n.m.r. spectrum[12] (neat) $H_2C{=}CH$ (two quartets, 410, 419, 421, and 430 c.p.s. and 428, 437, 439, and 448 c.p.s.), ═CH–CH═CH– (complex, 333–418 c.p.s.), ═CH_2 (complex, 303–329 c.p.s.), SCH_2 (complex, 151–176 c.p.s., wt. 9.5), n-$C_4H_9{-}S{-}CCl{=}C(CH_3)CH{=}CH_2$ (doublet, 120 and 123 c.p.s.; wt. 3.0), n-$C_4H_9{-}S{-}CCl{=}CH{-}CH{=}CHCH_3$ (complex, 97–110 c.p.s.), $CH_2{-}CH_2$ (complex, 72–97 c.p.s.), CH_3 (complex, 42–61 c.p.s.), and small impurity peaks near 195 and 215 c.p.s.; v.p.c. (Perkin-Elmer Model 154, silicone oil D. C. 200, on Chromosorb W, column set at 198°, carrier gas, He, pressure of 15 p.s.i.) showed two nearly superimposed peaks, probably due to *cis*- and *trans*-1-*n*-butylmercapto-1-chloropentadiene-1,3 with a shoulder on the first peak, proved to be 1-*n*-butylmercapto-1-chloro-2-methylbutadiene by injection, and small peak due to an unknown impurity.

This lower-boiling impurity was very difficult to remove from the mixture of butadienes. After two distillations through a spiral-wire column a fraction (2.5 g., 0.013 mole, 13%; b.p. 68–69° at 0.7 mm.; n^{29}D 1.5300) was collected, which showed only a small impurity (<3%) in the v.p.c. and the n.m.r. spectrum.

Anal. Calcd. for $C_9H_{15}ClS$: C, 56.67; H, 7.93; S, 16.81. Found: C, 56.55; H, 8.15; S, 16.71.

Reduction of the Mixture of 1-*n*-Butylmercapto-1-chloropentadiene-1,3 and 1-*n*-Butylmercapto-1-chloro-2-methylbutadiene with Raney Nickel.—The reduction was carried out as described for **8** with the mixture of butadienes (fraction, b.p. 67–71° at 0.7 mm.; n^{23}D 1.5313). Vapor phase chromatography of the heptane solution showed the presence of three compounds (other than heptane). The compounds were identified as *n*-butane, isopentane, and *n*-pentane. The ratio of isopentane to *n*-pentane was 1 to 3.7 (according to n.m.r. spectrum the ratio of 1-*n*-butylmercapto-1-chloro-2-methylbutadiene to 1-*n*-butylmercapto-1-chloropentadiene-1,3 was 1 to 3.75).

Dithiolium Derivatives. V.[1] 1,3-Dithiol-2-ylidenes[2]

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The synthesis of 1,3-dithiol-2-ylidene derivatives from dithiocarboxylic acids and α-halo ketones is described. Dithiocarboxylic acids derived from compounds with active methylene groups and carbon disulfide, in their tautomeric form as *α,β*-unsaturated *gem*-dithiols, were condensed with α-halo ketones at room temperature to give 4-hydroxy-1,3-dithiolan-2-ylidene derivatives. Dehydration of these derivatives under mild conditions afforded the corresponding 1,3-dithiol-2-ylidenes, which also were prepared in some cases by the condensation of 2-methylthio-1,3-dithiolium perchlorates with active methylene compounds. 1,3-Dithiol-2-ylidenes were converted into 1,3-dithiolium perchlorates. N.m.r. and infrared data of the new products are discussed.

1,3-Dithiol-2-ylidene derivatives have been prepared by the condensation of 2-methylthio-1,3-dithiolium cations with compounds containing an active methylene group.[1b] Recently[3] it has been shown that α-halo ketones readily form 1,3-dithiols with a *gem*-dithiol. Since condensation of carbon disulfide with active methylene derivatives leads to dithio acids, which exist as *α,β*-unsaturated *gem*-dithiols,[4,5] condensation of these derivatives with α-halo ketones should provide a convenient alternate pathway for the synthesis of certain 1,3-dithiol-2-ylidene derivatives, some of which could not be obtained by the earlier method. It is interesting to note that these β-keto dithio acids can also serve as intermediates in the synthesis of 1,2-dithiolium systems.[4]

Dithio acids have been shown to condense with α-halo ketones to produce β-keto dithio esters, which require strongly acidic conditions to be cyclized to 1,3-dithiolium salts.[1d,6] It was therefore surprising to find that, in several instances, reaction of α-halo ketones (**1**) with β-keto dithio acids (**2**) in alcohol under mild alkaline conditions resulted in spontaneous ring closure to form the 4-hydroxy-1,3-dithiolan-2-ylidene derivatives **3**, and, in one case, the unsaturated 1,3-dithiol-2-ylidene (**4d**).

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(1) (a) E. Campaigne and R. D. Hamilton, *J. Org. Chem.*, **29**, 2877 (1964); (b) E. Campaigne and R. D. Hamilton, *ibid.*, **29**, 1711 (1964); (c) E. Campaigne, R. D. Hamilton, and N. W. Jacobsen, *ibid.*, **29**, 1708 (1964); (d) E. Campaigne and N. W. Jacobsen, *ibid.*, **29**, 1703 (1964).

(2) Contribution No. 1263. This research was supported by a grant from the Mead-Johnson Corp., Evansville, Ind. We gratefully acknowledge this support.

(3) E. Campaigne and F. Haaf, *J. Heterocyclic Chem.*, **1**, 163 (1964).

(4) A. Thuillier and J. Vialle, *Bull. soc. chim. France*, 1398 (1959); 2182, 2187, 2194 (1962).

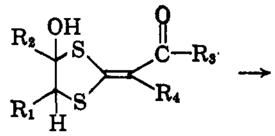
(5) R. Gompper and W. Töpfl, *Ber.*, **95**, 2861 (1962).

(6) D. Leaver, W. A. H. Robertson, and D. M. McKinnon, *J. Chem. Soc.*, 5104 (1962).

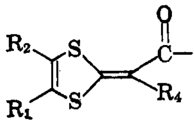
$R_1CHXCOR_2 + R_3COCR_4{=}C(SH)_2 \longrightarrow$

1a, $R_1 = H$; $R_2 = C_6H_5$
b, $R_1 = H$; $R_2 = p\text{-}BrC_6H_4$
c, $R_1 = H$; $R_2 = p\text{-}NO_2C_6H_4H$
d, $R_1, R_2 = C_6H_5$
e, $R_1 = H$; $R_2 = CH_3$

2a, $R_3 = C_6H_5$; $R_4 = H$
b, $R_3 = CH_3$; $R_4 = H$
c, $R_3 = OC_2H_5$; $R_4 = CN$

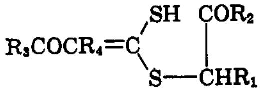


3a, $R_1, R_4 = H$; $R_2, R_3 = C_6H_5$
b, $R_1, R_4 = H$; $R_2 = p\text{-}NO_2C_6H_4$; $R_3 = C_6H_5$
c, $R_1, R_4 = H$; $R_2 = CH_3$; $R_3 = C_6H_5$
d, $R_1, R_4 = H$; $R_2 = C_6H_5$; $R_3 = CH_3$



4a, $R_1, R_4 = H$; $R_2, R_3 = C_6H_5$
b, $R_1, R_4 = H$; $R_2 = p\text{-}BrC_6H_4$; $R_3 = C_6H_5$
c, $R_1, R_4 = H$; $R_2 = p\text{-}NO_2C_6H_4$; $R_3 = C_6H_5$
d, $R_1, R_2 = C_6H_5$; $R_3 = C_6H_5$; $R_4 = H$
e, $R_1, R_4 = H$; $R_2 = CH_3$; $R_3 = C_6H_5$
f, $R_1, R_4 = H$; $R_2 = C_6H_5$; $R_3 = CH_3$
g, $R_1, R_2 = C_6H_5$; $R_3 = CH_3$; $R_4 = H$
h, $R_1 = H$; $R_2 = C_6H_5$; $R_3 = OC_2H_5$; $R_4 = CN$
i, $R_1, R_2 = C_6H_5$; $R_3 = C_6H_5$; $R_4 = CO_2C_2H_5$
j, $R_1 = H$; $R_2 = C_6H_5$; $R_3 = C_6H_5$; $R_4 = CN$
k, $R_1 = H$; $R_2 = C_6H_5$; $R_3 = CH_3$; $R_4 = CO_2C_2H_5$
l, $R_1 = H$; $R_2 = C_6H_5$; $R_3 = CH_3$; $R_4 = COCH_3$

In general, the 1,3-dithiol-2-ylidene derivatives (**4**) were obtained in excellent yield by acidic treatment of the 4-hydroxy-1,3-dithiolan-2-ylidene derivatives (**3**) which crystallized from solution, or by similar treatment of the reaction mixtures in those cases where **3** did not crystallize. Earlier studies[1d] suggest that the initial step involves formation of the β-keto dithio esters (**5**)



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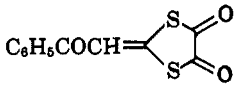

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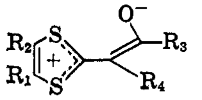
which were not isolated but which were in equilibrium in the reaction mixture with the hydroxydithiolanes **3**. In certain cases, the insolubility of **3** caused its precipitation, thus shifting the equilibrium. In other cases, it was necessary to add acid to shift the equilibrium by dehydration of **3** to form **4**.

The structure of the 1,3-dithiol-2-ylidene derivatives was confirmed in two cases (**4a** and **4h**) by independent syntheses. Ethyl cyanoacetate condensed with 2-methylthio-4-phenyl-1,3-dithiolium perchlorate to give **4h**,[1b] but this compound was obtained in better yield from the sodium salt of **2c** and phenacyl bromide. An attempt to synthesize **4a** from 2-methylthio-4-phenyl-1,3-dithiolium perchlorate and acetophenone failed.[7] The reaction of the dithiolium perchlorate with ethyl benzoylacetate in acetic acid–pyridine gave **4a** in poor yield rather than the expected 2-(α-carbethoxyphenacylidene)-4-phenyl-1,3-dithiole. Since condensation of ethyl benzoylacetate with carbon disulfide failed to give the dithio carboxylic acid, this compound could not be prepared by either method. Condensation of 2-methylthio-4,5-diphenyl-1,3-dithiolium perchlorate with ethyl benzoylacetate, however, produced the corresponding α-carbethoxyphenacylidene derivative **4i** in poor yield. Benzoylacetonitrile and ethyl acetoacetate condensed with 2-methylthio-4-phenyl-1,3-dithiolium perchlorate to give **4j** and **4k**, respectively.

Oxalyl chloride has been shown to condense with *gem*-dithiols, forming 1,3-dithiolane-4,5-diones which are satisfactory derivatives.[3,8] Under similar conditions, 2-phenacylidene-1,3-dithiolane-4,5-dione (**6**) was obtained by condensation of **2a** and oxalyl chloride.

All of the 1,3-dithiol-2-ylidene derivatives seemed to exist in the more stable 1,3-dithiole structures **4** rather than as dipolar dithiolium structures **7**. This was evident from the instability of the perchlorates **8a** and **8b** which were precipitated from solution by the addition of perchloric acid but reverted to the neutral compounds on attempted recrystallization from ethanol,[1b] and from the relatively high τ-values for protons at position R_1 (compounds **4a**, **4e**, **4f**, **4h**, **4j**, and **4k**, Table I). Strong carbonyl bands in the infrared spectra of compounds **4a–g**, and **4i–j** (Table II) were further evidence for their existence in the dithiole form. These bands were close to the absorption of the carbonyl groups in the 4-hydroxy-1,3-dithiolan-2-ylidenes **3**, in which conjugation is less likely. Furthermore, the carbonyl absorption in **3** and **4** occurred at frequencies (1590–1630 cm.$^{-1}$) comparable with those found for carbonyl groups attached to simple dialkylated α,β-unsaturated dithiols.[4] The structure of the dithiolium perchlorates **8** were assigned on the basis of analysis and lack of carbonyl absorption in the infrared spectra of the crude salts.



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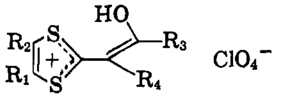

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8a, $R_1, R_4 = H$; $R_2, R_3 = C_6H_5$
b, $R_1, R_2 = C_6H_5$; $R_3 = CH_3$; $R_4 = H$
c, $R_1 = H$; $R_2 = C_6H_5$; $R_3 = CH_3$; $R_4 = COCH_3$

The n.m.r. spectra of the various 1,3-dithiol-2-ylidene derivatives which have been prepared are summarized in Table II. It has previously been reported[1b] that **4l** existed in acidic solution as the dithiolium salt **8c** since the C-5 proton gave a τ-value of 1.88. The n.m.r. spectrum of this compound has now been determined in deuteriochloroform, and the C-5 proton appears with the aromatic protons of the benzene ring, in the range of τ 2.30–2.75, in agreement with C-5 proton τ-values of 1,3-dithiol-2-ylidene compounds which cannot stabilize a proton in the salt form by chelation. Such compounds gave peaks for the C-5 proton in the range of τ 2.72–2.75 in trifluoroacetic acid[1b] and in the range 2.71–2.96 (**4h** and **4j**, Table II) in deuteriochloroform. The C-5 proton of **4h** appears at τ 2.72 in trifluoroacetic acid,[1b] a $\Delta\tau$-value of -0.24. Since the $\Delta\tau$ for the C-5 proton of **4l** in these two solvents must be in the range of -0.42 to -0.87, there is a definite, intensified deshielding effect when this compound is measured in acidic medium, probably due to salt formation.

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[7] D. Leaver and D. M. McKinnon [*Chem. Ind.* (London), 461 (1964)] have reported that the reaction of dithiolium iodide with sodioacetophenone led to decomposition. They prepared 2-phenacylidene-4-phenyl-1,3-dithiole (**4a**) from sodium benzoylacetate and the dithiolium salt.

[8] J. Jentzsch, J. Fabian, and R. Mayer, *Ber.*, **95**, 1764 (1962).

TABLE I

N.M.R. PEAKS OF 1,3-DITHIOL-2-YLIDENE DERIVATIVES[a]

<table>
<tr><th></th><th colspan="4">N.m.r. (J, c.p.s.) [*n*][b] proton signals of substituents at</th></tr>
<tr><th>Compd.</th><th>R_1</th><th>R_2</th><th>R_3</th><th>R_4</th></tr>
<tr><td>4a</td><td>3.17 [1]</td><td colspan="3">1.92–2.76 m [11]</td></tr>
<tr><td>4a[c]</td><td>3.11 d (1.2)
3.21 } [1]</td><td colspan="3">1.92–2.76 m [11]</td></tr>
<tr><td>4d</td><td colspan="4">2.22–2.98 m [16]</td></tr>
<tr><td>4e</td><td>3.71 q (1.5) [1]</td><td>7.78 d (1.5) [3]</td><td colspan="2">1.96–2.72 m [6]</td></tr>
<tr><td>4f</td><td>3.17 d (1.2)
3.28 } [1]</td><td>2.45–2.75 m [5]</td><td>7.82 [3]</td><td>3.29 d (1.2)
3.38 } [1]</td></tr>
<tr><td>4g</td><td colspan="2">2.78 [10]</td><td>7.80 [3]</td><td>3.38 [1]</td></tr>
<tr><td>4h</td><td>2.96 [1]</td><td>2.42–2.64 m [5]</td><td></td><td>5.70 q [2], 8.67 t [3]</td></tr>
<tr><td>4i</td><td colspan="3">2.34–2.75 m [15]</td><td>5.97 q [2], 9.18 t [3]</td></tr>
<tr><td>4j</td><td>2.71
2.72 } [1]</td><td colspan="2">1.88–2.58 m [10]</td><td></td></tr>
<tr><td>4k</td><td colspan="2">2.33–2.70 m [6]</td><td>7.39 [3]</td><td>5.60 q [2], 8.57 t [3]</td></tr>
<tr><td>4l[d]</td><td colspan="2">2.30–2.75 m [6]</td><td colspan="2">7.35 [6]</td></tr>
</table>

[a] Measurements were made in deuteriochloroform at concentrations of 6–8% w./v. at 31°, using a Varian A-60 spectrometer at 60 Mc./sec. Chemical shifts are recorded on the frequency independent τ-scale relative to internal tetramethylsilane. Spin–spin coupling values (J) are in c.p.s. measured on the 500-c.p.s. scale; d = doublet, t = triplet, q = quartet, m = multiplet. [b] Number of protons, by integration, in brackets. [c] Prepared by condensation of 2-methylthio-4-phenyl-1,3-dithiolium perchlorate with ethyl benzoylacetate. [d] Sample supplied by R. D. Hamilton.

TABLE II

PHYSICAL DATA ON PREPARATION OF 4-HYDROXY-1,3-DITHIOLAN-2-YLIDENE AND 1,3-DITHIOL-2-YLIDENE DERIVATIVES[a]

Compd.	% yield	M.p., °C.	Formula	Calcd., % C	Calcd., % H	Calcd., % S	Found, % C	Found, % H	Found, % S	Characteristic infrared peaks, cm.$^{-1}$[b]
3a	64	153–154	$C_{17}H_{14}O_2S_2$	64.95	4.49	20.39	65.15	4.45	20.17	3350 (OH), 1605 (CO)
3b	64	176–178 dec.	$C_{17}H_{13}NO_4S_2$	56.81	3.64	17.84	56.96	3.80	17.64	3180 (OH), 1595 (CO)
3c	57	121–122	$C_{12}H_{12}O_2S_2$	57.11	4.79	25.41	56.90	4.82	25.12	3290 (OH), 1600 (CO)
3d	54	112–113	$C_{12}H_{12}O_2S_2$	57.11	4.79	25.41	57.25	4.88	25.27	3320 (OH), 1630 (CO)
4a	81[c]	132–134	$C_{17}H_{12}OS_2$	68.89	4.08	21.64	68.75	4.02	21.65	1600 (CO)
4b	76	198–199	$C_{17}H_{11}BrOS_2$	54.41	2.95	17.09	54.66	3.07	17.22	1600 (CO)
4c	79	218–219	$C_{17}H_{11}NO_3S_2$	59.80	3.25	18.79	59.96	3.52	19.09	1590 (CO)
4d	67	229–230	$C_{23}H_{16}OS_2$	74.16	4.33	17.22	74.24	3.93	17.08	1595 (CO)
4e	86	117–118	$C_{12}H_{10}OS_2$	61.52	4.30	27.33	61.25	4.57	27.06	1595 (CO)
4f	17	152–154	$C_{12}H_{10}OS_2$	61.52	4.30	27.33	60.87	4.36	27.76	1610 (CO)
4g	13	149–150	$C_{18}H_{14}OS_2$	69.95	4.54	20.66	70.08	4.63	20.62	1610 (CO)
4h[d]	71	133–134	$C_{14}H_{11}NO_2S_2$	58.11	3.83	22.16	58.27	3.91	22.30	2200 (CN), 1675 (CO_2R)
4i	16	158–159	$C_{26}H_{20}O_3S_2$	70.24	4.54	14.43	70.48	4.65	14.74	1665 (CO_2R), 1595 (CO)
4j	44	190–191	$C_{18}H_{11}NOS_2$	67.27	3.45	19.95	67.17	3.38	19.58	2200 (CN), 1600 (CO)
4k	26	98–100	$C_{15}H_{14}O_3S_2$	58.80	4.60	20.93	59.10	4.88	20.85	1660 (CO_2R), 1595 (CO)

[a] See ref. 10. [b] Potassium bromide mulls, Perkin-Elmer Model 137 spectrophotometer. [c] Obtained in 19% yield by the reaction of 2-methylmercapto-4-phenyl-1,3-dithiolium perchlorate with ethyl benzoylacetate. [d] Previously reported; ref. 1b.

The τ-values for the C-5 protons of compounds **4a**, **4e**, **4f**, **4h**, and **4j** are quite close to values for the vinylic proton at R_4 (**4a**, **4d**, **4e**, **4f**, and **4g**), the latter varying from the aromatic region, τ 1.9–2.9, to 3.38 and the former from the aromatic region to 3.71 for compound **4e**. Splitting of this peak into a quartet by the adjacent methyl group is clear evidence of a double bond at C-4–C-5 in **4e**, and implies a lack of ring current in these compounds. The presence of additional electronegative groups at R_4 should increase the deshielding of the molecule, causing a downfield shift of the C-5 proton, which is seen in **4h**, **4j**, **4k**, and **4l**. The chemical shift for the C-5 protons in 2,2-dibenzyl-1,3-dithioles, which cannot involve resonance of a charge at the 2-carbon, has been found in the range of τ 3.9–4.9.[3]

In some cases, unusual splitting was observed for the C-5 proton. In **4j** two singlets and in **4f** a doublet and a singlet were assigned to the C-5 proton. The best explanation for this splitting seemed to be the existence of a mixture of *cis* and *trans* isomers. The C-5 proton environment in such isomers would be slightly different, thus giving rise to two different signals. The observation that one of the signals in **4f** was a doublet could be explained by long-range coupling of the C-5 proton with the proton attached to the *exo* double bond at R_4 in one of the isomers, but not in the other. Such long-range coupling across hetero atoms has been observed in many cases.[9] The same splitting was found in a sample of **4a** prepared by condensation of 2-methylthio-4-phenyl-1,3-dithiolium perchlorate and ethyl benzoylacetate. A doublet and singlet were observed accounting for 1 proton, while a sample prepared from the dithio carboxylic acid and phenacyl bromide showed only a singlet. Attempts to detect the conversion of one isomer into the other by examining the n.m.r. spectrum at higher temperatures (40–130°), were unsuccessful.

Experimental[10]

Preparation of 4-Hydroxy-1,3-dithiolan-2-ylidenes (3a–d).—The hydroxy-1,3-dithiolane derivatives, **3a–d**, listed in Table II all crystallized as yellow solids from a reaction mixture of the

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(9) S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964).

(10) All melting points were determined in soft-glass capillaries using a Mel-Temp heated-block apparatus, and are corrected. Analyses were performed by the Midwest Microlab, Inc., Indianapolis, Ind.

dithio acids **2a** or **2b**, prepared as previously described,[4,5] the appropriate α-halo ketone, and sodium bicarbonate in methanol or ethanol. They were recrystallized from acetone or cyclohexane for analysis. The following preparation is typical.

2-Phenacylidene-4-phenyl-4-hydroxy-1,3-dithiolane (**3a**).—To the solution of 4.9 g. (0.025 mole) of **2a**[4] in 200 ml. of ethanol, 4.0 g. of sodium bicarbonate and 5.0 g. (0.025 mole) of phenacyl bromide (**1a**) were added. After stirring for 24 hr. at room temperature, the precipitate was collected by filtration, washed with water, and recrystallized from acetone to give 5.0 g. of **3a** as yellow crystals.

2-Phenacylidene-4-phenyl-1,3-dithiole (**4a**).—The solution of 2.0 g. of **3a** in 25 ml. of concentrated sulfuric acid was poured into 150 ml. of chilled ethanol at a rate which did not allow the temperature to exceed 20°. By the addition of water a yellow solid was precipitated, which was collected and dried. After recrystallization from 1-propanol 1.52 g. (81%) of **4a** was obtained as deep yellow plates which melted at 132–134°. Compound **4c** (Table I) was obtained from **3b** in the same manner.

A solution of 1.62 g. (5.0 mmoles) of 2-methylthio-4-phenyl-1,3-dithiolium perchlorate[1b] and 1.15 g. (6.0 mmole) of ethyl benzoylacetate in 25 ml. of glacial acetic acid, containing 0.2 ml. of pyridine, was refluxed for 9 hr. After removal of the solvent, the residue was extracted with hot benzene; the benzene solution was decolorized with Norit and evaporated. The solid residue, obtained in 19% yield, was recrystallized from cyclohexane, and had the identical infrared spectrum and melting point of **4a**, above, but showed a slight difference in n.m.r. (see Table II).

2-Phenacylidene-4-methyl-1,3-dithiole (**4e**).—The solution of 1.0 g. of **3c** in 100 ml. of chloroform was saturated with hydrogen chloride at 0° and kept for 3 hr. at room temperature. After washing with water and drying, the solvent was removed and the residue was recrystallized from cyclohexane to give 0.80 g. (86%) of **4e** as yellow crystals.

2-Acetylidene-4-phenyl-1,3-dithiole (**4f**).—The solution of 1.3 g. of **3d** in 150 ml. of ether was saturated with hydrogen chloride at 0° and kept at room temperature for 5 hr. The ether solution was washed with aqueous sodium bicarbonate solution and dried. After removal of the solvent, the residue was recrystallized from 1-propanol to give 0.2 g. of **4f** as a brown solid.

2-Phenacylidene-4-*p*-bromophenyl-1,3-dithiole (**4b**).—A solution of 4.4 g. (22.5 mmoles) of **2a**, 4.0 g. of sodium bicarbonate, and 6.2 g. (22.5 mmoles) of *p*-bromophenacyl bromide (**1b**) in 200 ml. of ethanol was stirred for 24 hr. at room temperature. The solution was filtered, and 60 ml. of concentrated sulfuric acid was added to the chilled filtrate which was let stand at room temperature for several hours. Addition of water completed the precipitation of yellow solid, which was collected, dried, and recrystallized from acetone to give 6.4 g. of **4b** as deep yellow crystals.

2-Phenacylidene-4,5-diphenyl-1,3-dithiole (**4d**).—A mixture of 3.9 g. (20 mmoles) of **2a**, 4.0 g. of sodium bicarbonate, and 4.6 g. (20 mmoles) of desyl chloride (**1d**) in 100 ml. of ethanol was stirred for 24 hr. at room temperature. The precipitate was collected by filtration, washed with water, and dried. After recrystallization from an ethyl acetate–chloroform mixture (2:1), 5.0 g. of **4d** was obtained as yellow needles.

2-Acetonylidene-4,5-diphenyl-1,3-dithiole (**4g**).—A mixture of 4.0 g. of crude **2b**, 4.0 g. of sodium bicarbonate, and 4.6 g. of **1d** in 25 ml. of ethanol was stirred for 16 hr. at room temperature, then water was added, and the precipitate was extracted with ether. The ether extracts were dried and saturated with hydrogen chloride at 0°. After standing 1 hr., the ether solution was washed with water, then aqueous sodium bicarbonate solution, and dried. After removal of the solvent, an oil was obtained which crystallized upon trituration with ethyl acetate. Recrystallization from cyclohexane gave 0.8 g. of **4g** as yellow needles.

Ethyl 4-Phenyl-1,3-dithiol-2-ylidenecyanoacetate (**4h**).—A solution of 35 mmoles of the disodium salt of carbethoxycyanodithioacetic acid[5] and 7.0 g. (35 mmoles) of **1a** in 100 ml. of ethanol was stirred for 18 hr. at room temperature and then filtered. To the chilled filtrate, 50 ml. of concentrated sulfuric acid was added. After 3 hr. at room temperature the precipitate was collected by filtration, washed with water, dried, and recrystallized from ethanol to give 7.2 g. of **4h**. The melting point of a mixture of **4h** with a sample,[1b] prepared from 2-methylthio-4-phenyl-1,3-dithiolium perchlorate and ethyl cyanoacetate, was not depressed.

1,3-Dithiol-2-ylidenes 4i, 4j, and 4k.—Compounds **4i**, **4j**, and **4k** were prepared by the following general procedure. A mixture of 5.0 mmoles of 2-methylthio-1,3-dithiolium perchlorate and 6.0 mmoles of the active methylene compound in 25 ml. of glacial acetic acid containing 0.2 ml. of pyridine was heated in an oil bath to 130° for 9–15 hr. The solvent was removed under vacuum and the residue was extracted twice with 50-ml. portions of hot benzene. The benzene solution was decolorized with Norit, evaporated, and the residue was recrystallized from cyclohexane (see Table I).

2-Phenacylidene-1,3-dithiolane-4,5-dione (**6**).—A solution of 6.4 g. (0.05 mole) of oxalyl chloride in 30 ml. of chloroform was added dropwise to a cold mixture of 9.8 g. (0.05 mole) of **2a** and 12.8 g. of sodium carbonate in 150 ml. of chloroform. The mixture was kept under nitrogen and stirred at room temperature for 4 hr. The precipitate was collected by filtration and extracted several times with boiling chloroform. The extracts were evaporated, leaving 3.4 g. (27%) of **6** as yellow crystals, which melted at 193–196°. Four recrystallizations from chloroform raised the melting point to 202–203°; $\nu_{\max}^{\mathrm{KBr}}$ 1695 cm.$^{-1}$ (CO).

Anal. Calcd. for $C_{11}H_6O_3S_2$: C, 52.78; H, 2.42; S, 25.62. Found: C, 52.58; H, 2.41; S, 25.82.

2-Methylthio-4,5-diphenyl-1,3-dithiolium Perchlorate.—A suspension of 23.1 g. (0.1 mole) of **1d** in 300 ml. of ethanol was added to a solution of 0.1 mole of sodium methyltrithiocarbonate[6] in 200 ml. of ethanol with stirring at −40°. The mixture was stirred for 2 hr. at room temperature, and then poured into water. The yellow oil which separated overnight was dissolved in an equal volume of concentrated sulfuric acid, and the resulting red-brown solution diluted with 300 ml. of ethyl acetate and chilled to −40°. The oil which remained after decanting the solvent was warmed to 50° with three volumes of 70% perchloric acid, diluted with 500 ml. of ethyl acetate and chilled to −40°. After some time 14 g. (35%) of yellow needles were collected and recrystallized from glacial acetic acid; these had m.p. 158–160°, τ (CF_3CO_2H) 2.57 (10) and 6.78 (3).

Anal. Calcd. for $C_{16}H_{13}ClO_4S_3$: C, 47.92; H, 3.27; S, 23.99. Found: C, 48.18; H, 3.43; S, 24.14.

2-Phenacylidene-4-phenyl-1,3-dithiolium Perchlorate (**8a**).—To the solution of 0.2 g. of **4a** in 15 ml. of warm ethyl acetate, 30 ml. of 70% perchloric acid was added dropwise. The mixture was let stand overnight at room temperature and the precipitate was collected on a sintered-glass filter to give 0.12 g. (45%) of **8a** as an orange solid, m.p. 186–188° dec., $\nu_{\max}^{\mathrm{KB}}$ 3220–3170 and 1075–1120 cm.$^{-1}$.

Anal. Calcd. for $C_{17}H_{13}ClO_5S_2$: C, 51.45; H, 3.30; Cl, 8.93; S, 16.16. Found: C, 51.73; H, 3.45; Cl, 9.03; S, 16.10.

2-Acetonylidene-4,5-diphenyl-1,3-dithiolium Perchlorate (**8b**).—Acetone (*ca.* 2 ml.) was added to a suspension of 50 mg. of **4g** in 5 ml. of 70% perchloric acid and the mixture was warmed on a steam bath for a few minutes. After cooling, the precipitate was collected to give 50 mg. (76%) of **8b** as yellow crystals, m.p. 159–162° dec., $\nu_{\max}^{\mathrm{KBr}}$ 3250–3200 and 1070–1130 cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{15}ClO_5S_2$: C, 52.61; H, 3.68; Cl, 8.63; S, 15.61. Found: C, 52.75; H, 3.84; Cl, 9.39; S, 15.06.