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Syntheses of 1,3-Dithiol-2-ylidene and 1,3-Oxathiol-2-ylidene Derivatives[1,2]

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1,3-Dithiol-2-ylidene and 1,3-oxathiol-2-ylidene derivatives were prepared by a simple method. 2-Immonio-1,3-dithiole, 2-immonio-1,3-oxathiole, and 2-immonio-1,3-dithiolane were condensed with a variety of active methylene compounds giving the corresponding 2-ylidene derivatives readily. Some active methylene compounds, however, gave ketene S,N-acetals in the reaction with 2-immonio-1,3-oxathiole.

Fulvenes including hetero atoms in their molecules are interesting as "heterofulvenes"[4] and 1,3-dithiol-2-ylidene derivatives have been conveniently termed 1,4-dithiafulvenes (I).[5] During a study of possible applications of the reactivity of N-(1,3-dithiol-2-ylidene)tertiary iminium salts (II)[6] and N-(1,3-oxathiol-2-ylidene)tertiary iminium salts (III),[1] we found a convenient method for obtaining I and 1,3-oxathiol-2-ylidene derivatives (IV). Since, like I, IV are iso π-electronic with heptafulvenes (VIII), from which they can be formally derived by replacement of two C=C double bonds with two hetero atoms, IV can be termed "1,4-oxathiafulvenes."

Although 1,4-dithiafulvenes have been prepared by a number of methods,[7] IV have received little attention and only a few compounds of this type have been prepared.[8]

Jutz[9] has reported the preparation of dicyanoheptafulvenes (VIII: R=R'=CN) from immonioheptafulvenes and malononitrile in the presence of acetic anhydride and triethylamine. When Jutz's method was applied to 4-phenyl-N-(1,3-dithiol-2-ylidene)piperidinium hydrosulfate (II), using a variety of active methylene compounds, the corresponding 1,4-dithiafulvenes (I) were obtained readily. This reaction proceeded at room temperature or on brief reflux in methylene chloride solution in the presence of triethylamine with or without acetic anhydride. The active methylene compounds used in this reaction were malononitrile, dimedone, indane-1,3-dione, ethyl cyanoacetate, acetyl acetone, benzoyl acetone, deoxybenzoine, ethyl acetoacetate, barbituric acid, nitromethane, nitroethane, and cyanoacetamide and the corresponding 1,4-dithiafulvenes (I) were prepared as shown in Table I. Under the conditions used here no product was obtained with the weakly acidic fluorenone,

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[1] This paper forms Part VI in a series of the Studies on Heterocyclic Cation Systems Preceding paper, Part V: K. Hirai and T. Ishiba, *Chem. Pharm. Bull.* (Tokyo), **20**, 304 (1972).

[2] The article has been previously reported in a preliminary form; K. Hirai, Abstracts of papers presented at the Symposium of Heterocyclic Chemistry, Tokyo, Nov. 1970, p. 57; K. Hirai, *Tetrahedron Letters*, **1971**, 1137.

[3] Location: *Sagisu, Fukushima-ku, Osaka.*

[4] For review, see: *a*) E.D. Bergmann, *Chem. Rev.*, **68**, 41 (1968); *b*) H. Prinzbach and E. Futterer, "Advances in Heterocyclic Chemistry," Vol. 7, Academic Press, New York and London, 1966, p. 103.

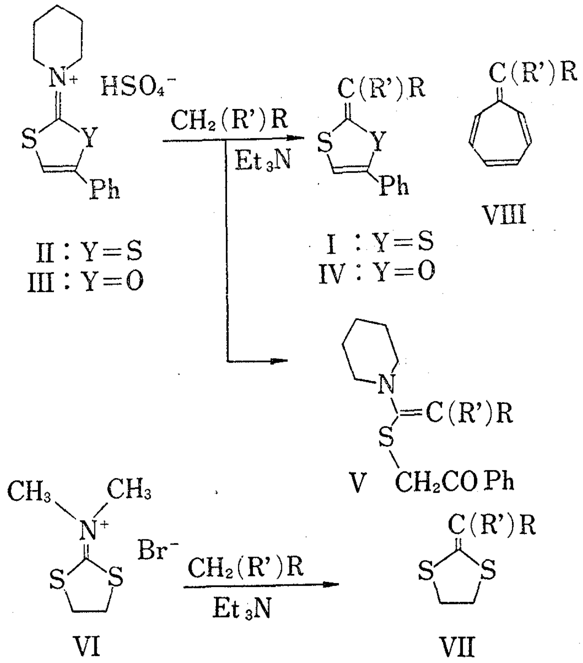
[5] W. Kirmse and L. Horner, *Ann.*, **614**, 4 (1958).

[6] *a*) E. Campaigne and N.W. Jacobsen, *J. Org. Chem.*, **29**, 1703 (1964); *b*) A. Takamizawa and K. Hirai, *Chem. Pharm. Bull.* (Tokyo), **17**, 1924 (1969).

[7] *a*) E. Campaigne and R.D. Hamilton, *J. Org. Chem.*, **29**, 1711 (1964); *b*) E. Campaigne and F .Haaf, *ibid.*, **30**, 732 (1965); *c*) A. Lüttringhaus, E. Futterer, and H. Prinzbach, *Tetrahedron Letters*, **1963**, 1209; *d*) H. Behringer and R. Wiedenmann, *ibid.*, **1965**, 3705.

[8] *a*) H. Yamaguchi, *Chem. Pharm. Bull.* (Tokyo), **16**, 997 (1968); *b*) W. Drenth and H.J.De Gruijter, *Trav. Chim.*, **89**, 379 (1970).

[9] C. Jutz, *Ber.*, **97**, 2050 (1964).



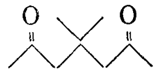
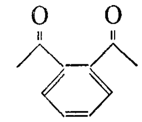
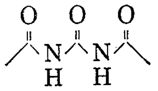
Ph=phenyl or *p*-hydroxyphenyl

Chart 1

p*K*a 25,[10] and the starting material was recovered. Since the starting materials, II and III, are both stable and easily accessible, and the reaction proceeds readily under much milder conditions than those described before,[7] this method has many advantages for the preparation of I.

The formation of 1,4-dithiafulvenes from 2-immonio-1,3-dithiole (II) and active methylene compounds suggested the synthesis of 1,4-oxathiafulvenes from 2-immonio-1,3-oxathiole (III) instead of II. Therefore, the reaction of III with indane-1,3-dione in the presence of triethylamine was carried out in methylene chloride solution, and 2-(5-phenyl-1,3-oxathiol-2-ylidene) indane-1,3-dione (IVb), mp 230—232° (decomp.), was obtained. In a similar manner, dimedone and ethyl acetoacetate were allowed to react with III giving the corresponding 1,4-oxathiafulvenes (IV) as shown in Table II. The phy-

TABLE I. 1,4-Dithiafulvenens (I)

Compound	R	R'	Yield (%)	mp[a] (°C)	Formula	Analysis (%)							
						Calcd.				Found			
						C	H	N	S	C	H	N	S
Ia	CN	CN	56	175—176[b]	$C_{12}H_6N_2S_2$	59.48	2.50	11.57	25.46	59.49	2.53	11.65	26.23
Ib			50	188—189	$C_{17}H_{16}O_2S_2$	64.55	5.10		20.20	64.76	5.18		20.27
Ic	CN	$COOC_2H_5$	92	132[c,d]	$C_{14}H_{11}O_2NS_2$	58.11	3.81	4.84	22.16	58.38	3.64	4.96	21.94
Id	CH_3CO	CH_3CO	56	147—149[e]	$C_{14}H_{12}O_2S_2$	60.86	4.35		23.21	61.07	4.43		23.34
Ie			64	249—250[f,g] (decomp.)	$C_{18}H_{10}O_2S_2$	67.08	3.13		19.90	66.94	2.75		19.69
If	C_6H_5CO	CH_3CO	61	158—159	$C_{19}H_{14}O_2S_2$	67.45	4.17		18.95	66.67	4.00		18.57
Ig	C_6H_5	C_6H_5CO	46	162—163	$C_{23}H_{16}OS_2$	74.18	4.33		17.22	74.08	4.46		16.95
Ih	CH_3CO	$COOC_2H_5$	67	101—102[h]	$C_{15}H_{14}O_3S_2$	58.82	4.61		20.92	58.79	4.75		20.52
Ii				>275[f]	$C_{13}H_8O_3S_2$	51.32	2.65	9.21	21.08	50.72	2.87	9.14	20.23
Ij	H	NO_2	91	126—129	$C_{10}H_7O_2NS_2$	50.64	2.98	5.91	27.03	50.78	2.68	5.98	26.59
Ik	CN	$CONH_2$	79	236—237[f] (decomp.)	$C_{12}H_8ON_2S_2$	55.39	3.10	10.77	24.64	55.09	3.06	10.69	24.45
Il	CH_3	NO_2	71	142—144	$C_{11}H_9O_2NS_2$	52.57	3.61	5.58	25.52	52.36	3.69	5.64	25.92
Im[i]	$COCH_3$	COOEt	69	203—205 (decomp.)	$C_{15}H_{14}O_4S_2$	55.90	4.35		19.88	55.71	4.66		20.06

a) Recryst. from EtOH; *b*) lit.[7a] mp167—168°; *c*) lit.[7a] mp 131—132°; *d*) lit.[7b] mp 134°; *e*) lit.[7a] mp144—146°; *f*) Recryst. from DMF; *g*) lit.[7a] 255—256°; *h*) lit.[7b]mp 98—100°; *i*) Ph=*p*-hydroxyphenyl

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10) D.J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York and London, 1965, p. 10.

sicochemical properties of these 1,4-dithia/oxathia-fulvenes will be fully discussed in the following paper.[11]

However, similar reaction of III with cyanoacetamide and ethyl cyanoacetate failed to give the corresponding 1,4-oxathiafulvenes and the corresponding ketene S,N-acetals (V) were obtained (Table III). The reaction of III with other active methylene compounds proceeded in another way giving thiophene and related derivatives.[12]

This reaction was also applied to N-(1,3-dithiolan-2-ylidene)dimethylammonium bromide (VI)[13] and the corresponding 1,3-dithiolan-2-ylidenes (VII) were obtained. Therefore, the reaction does not necessarily require the 6π-electron ring system and is general for compounds having the cation stabilized by three α-hetero atoms.[14]

Table II. Spectral Data of 1,4-Dithiafulvenes (I)

Compd.	UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm($\log \varepsilon$)	NMR$^{a)}$ (=CH-)			IR $\nu_{\max}$ cm^{-1}	
		$CDCl_3$	DMSO-d_6	CF_3COOD	$CHCl_3$	KBr
Ia	228,384 (4.31,4.46)	7.02		7.25$^{b)}$		2200
Ib	236,274,396 (4.35,3.95,4.50)	7.43	8.17	8.02	1683^{W},1587^{S}, 1397^{S}	
Ic	222,315,382 (4.29,3.57,4.42)	7.12, 7.07	7.92, 7.85	7.30, 7.25$^{c)}$		2200, 1674^{S}, 1442^{VS}, 1292^{VS}, 1175^{S}
Id	235,284,390 (4.34, 3.83, 4.45)		8.02	8.07$^{d)}$	1635^{W}, 1580^{S}, 1373^{VS}, 1336^{VS}, 1302^{S}	
Ie	239, 423 (4.70, 4.72)		8.10	7.45		1658^{S}, 1498^{S}, 1480^{VS}
If	233, 306, 400 (4.40, 3.87,4.46)	7.32, 7.29	8.02, 7.97	8.05		1562^{S}, 1365^{S}, 1340^{VS}
Ig	238, 327, 419 (4.36, 3.57, 4.43)	7.05	7.72	8.13		1586^{W}, 1555^{m}, 1393^{VS}, 1335^{VS}
Ih	232, 303, 385 (4.37, 3.63, 4.45)	7.28, 7.23	7.95, 7.88	8.08	1665^{S}, 1600^{S}, 1378^{VS}, 1357^{S}	
Ii	234, 395 (sat)		8.07	7.88		1730, 1705, 1510^{b}
Ij	237, 313, 429, (4.28, 3.57, 4.46)	7.13^{d} (J=1.2), 7.12	7.92^{d} (J=1.2), 7.90			
Ik	225, 380, (4.29, 4.41)		7.77 7.70			2198, 1668, 1652
Il	239, 320, 436, (4.32,3.84, 4.47)	7.12				
Im$^{e)}$	235, 258, 290(sh), 393 (4.20, 4.25,4.03, 4.39)		7.62, 7.68			1660^{S}, 1553^{S}, 1250^{VS}, 1100^{S}

a) δ value in ppm from the internal standard TMS at 60 MHz; coupling constant in H_z; b) lit.$^{7a)}$ 7.27;
c) lit.$^{7a)}$ 7.28; d) lit.$^{7a)}$ 8.12; e) ph=p-hydroxyphenyl

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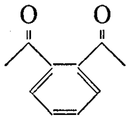
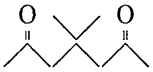
11) K. Hirai and H. Sugimoto, *Chem. Pharm. Bull.* (Tokyo), in contribution.
12) The result has been reported in a preliminary form: K. Hirai and T. Ishiba, *Chem. Pharm. Bull.* (Tokyo), **19**, 2194 (1971).
13) T.P. Johnston and A. Gallagher, *J. Org. Chem.*, **29**, 2442 (1964).
14) T. Nakai, *Yuki Gosei Kagaku Kyokai Shi*, **28**, 708 (1970).

Table III. 1,4-Oxathiafulvenes (IV)

Compd.	R	R′	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd. C	H	S	Found C	H	S
IVa	CH_3CO	$COOC_2H_5$	22	139—141[a]	$C_{15}H_{14}O_4S$	62.06	4.86	11.05	61.18	4.76	10.97
IVb			46	230—232[b] (decomp.)	$C_{18}H_{10}O_3S$	70.59	3.29	10.47	70.78	3.09	8.96
IVc			59	164—165[a]	$C_{17}H_{16}O_3S$	67.99	5.37	10.68	68.05	5.45	10.65

a) Recryst. from AcOEt; b) Recryst. from EtOH

Table IV. Spectral Data of 1,4-Oxathiafulvenes (II)

Compd.	UV λ_{max}^{EtOH} nm (log ε)	NMR (CH-, δ ppm) CDCl₃	DMSO-d_6	CF_3COOD	IR ν_{max} cm^{-1}
IVa	230, 290, 350 (4.26, 3.90, 4.34)	6.78	7.65	7.73	1697^{S}, 1610^{m}, 1460^{VS}, 1440^{VS}, ($CHCl_3$)
IVb	232, 305, 384 (4.54, 4.12, 4.52)		7.86	7.98	1708^{W}, 1669^{S}, 1527^{VS} (KBr)
IVc	228, 264, 361 (4.17, 4.06, 4.40)	6.92	7.82	7.55	1663^{m}, 1604^{S}, 1455^{S}, 1440^{VS} ($CHCl_3$)

Table V. Ketene S,N-Acetals (V)

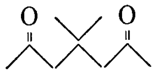
Compd.	R	R′	Yield (%)	mp[a] (°C)	Formula	Analaysis (%) Calcd. C	H	N	S	Found C	H	N	S
Va	CN	$CONH_2$	25	148—149	$C_{17}H_{19}O_2N_3S$	61.99	5.82	12.76	9.74	61.82	5.44	12.43	9.46
Vb	CN	$COOC_2H_5$	84	120—121	$C_{19}H_{22}O_3N_2S$	63.67	6.19	7.82	8.95	63.77	6.02	8.00	8.73

a) Recryst. from EtOH

Table VI. Spectral Data of Ketene S, N-Acetals (V)

Compd.	UV λ_{max}^{EtOH} nm(log ε)	NMR (δ ppm, $CDCl_3$)	IR λ_{max}^{KBr} cm^{-1}
Va	247, 276, 330 (4.18, 3.91, 4.14)	5.42(SCH_2)	2190, 1690, 1640, 1610
Vb	247, 277, 331 (4.14, 3.91, 4.17)	5.36(SCH_2)	2200, 1693 1535, 1270, 1152

Table VII. 1,3-Dithiolan-2-ylidenes (VI)

Compound	R	R′	Yield (%)	mp[a] (°C)	Formula	Analysis (%) Calcd C	H	N	S	Found C	H	N	S
VIIa	CN	$CONH_2$	26	186—190	$C_6H_6ON_2S_2$	38.72	3.25	15.05	34.45	38.50	3.33	14.63	34.16
VIIb	H	NO_2	44	105—106[b,c]	$C_4H_5O_2NS_2$	29.43	3.09	8.59	39.29	29.41	3.21	8.37	39.08
VIIc			37	197—198	$C_{11}H_{14}O_2S_2$	54.54	5.83		26.46	54.56	6.00		26.23
VIId	CN	$COOC_2H_5$	72	102—103[b,c]	$C_8H_9O_2NS_2$	44.66	4.22	6.51	29.79	44.74	4.26	6.24	26.91

a) Recryst. from EtOH; b) lit.[15] mp 107—109°; c) lit.[16] mp 117°; d) lit.[17] mp 102—103°; e) lit.[17] mp 104.5—105°

Table VIII. Spectral Data of 1,3-Dithiolan-2-ylidenes (VI)

Compd.	UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm (log ε)	NMR (δ ppm, $CDCl_3$)	IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}
VIIa	317 (4.26)	3.23 (CH_2), 3.55 (CH_2), 7.27 (NH_2)[a]	2200, 1660,
VIIb	218, 355 (3.55, 4.20)	3.52 (CH_2CH_2), 7.54 (=CH-)	1519
VIIc	247, 342 (4.07, 4.24)	1.07 ($2\times CH_3$), 2.50 ($2\times CH_2$), 3.35 ($2\times CH_2$)	1651, 1603
VIId	318 (4.30)	$1.33^{t)}$ (J=7,3Hz), 3.65 ($2\times CH_2$), $4.30^{q)}$ (J=7,2Hz)	2200, 1696, 1275, 1167

a) in DMSO-d_6

Experimental[18]

4-Phenyl-1,3-dithiol-2-ylidene Derivatives (I), 5-Phenyl-1,3-oxathiol-2-ylidene Derivatives (IV), 1-Piperidino-1-phenacylthio-2,2-disubstituted Ethylene Derivatives (V), and 1,3-Dithiolan-2-ylidene Derivatives (VII)——Compounds Ia—e, IVa—c, Va,b, and VIIa—d were prepared by the following general method. To a mixture of 0.7 g of one of N-(4-phenyl-1,3-dithiol-2-ylidene)piperidinium hydrosulfate (II), N-(5-phenyl-1,3-oxathiol-2-ylidene)piperidinium hydrosulfate (III), or N-(1,3-dithiolan-2-ylidene)diemthylammonium bromide (VI), 0.7 g of active methylene compound, and 1 g of Ac_2O in 10 ml of CH_2Cl_2, 0.8 g of Et_3N was added dropwise to give a clear solution (in some cases Ac_2O was not added). After allowing the mixture to stand at room temperature for 2—4 hr or, alternatively, refluxing it for 30—60min, dil. HCl was added and the CH_2Cl_2 layer was separated, dried, and evaporated. The residual crystals were recrystallized from appropriate solvents. When an oily product was obtained it was purified and solidified by SiO_2–acetone column chromatography. The results are summarized in Tables I, II, III, and IV.

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15) R. Gompper and H. Schaefer, *Ber.*, **100**, 591 (1967).

16) R. Mayer and K. Schaefer, *J. Prakt. Chem.*, **26**, 279 (1964).

17) B.R. O'Connor and F.N. Jones, *J. Org. Chem.*, **35**, 2002 (1970).

18) Melting points are uncorrected.