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STUDIES ON MESOIONIC COMPOUNDS—IV[1]

SYNTHESIS AND REACTIONS OF 4-THIOSYDNONE DERIVATIVES[2]

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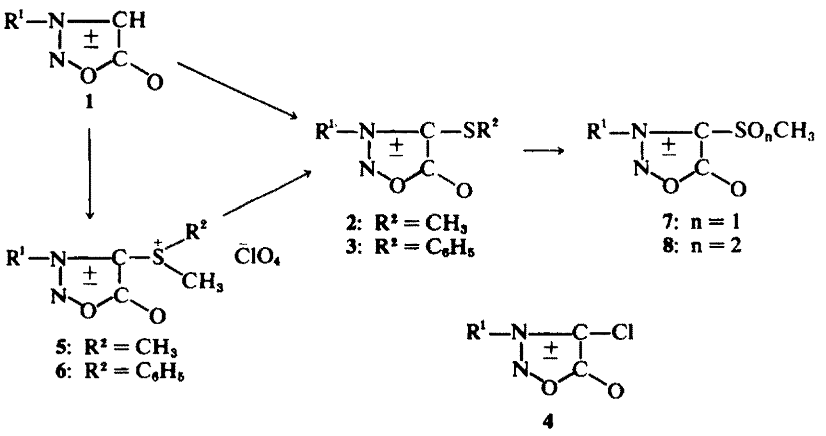
Abstract—Various 4-methylthiosydnones were prepared by the reaction of 3-substituted sydnones with DmSO and acetyl chloride, while the reaction with methyl phenyl sulfoxide and acetyl chloride gave 4-chlorosydnones. Treatment of 3-substituted sydnones with DmSO and methyl phenyl sulfoxide together with acetyl perchlorate, followed by refluxing with aqueous potassium chloride gave 4-methylthio- and 4-phenylthiosydnones via the corresponding 4-dimethyl- and 4-methylphenyl-sulfonium perchlorates, respectively. Oxidation of 4-methylthiosydnones with hydrogen peroxide gave 4-methyl-sulfinyl- and 4-methylsulfonylsydnones.

Mesoionic compounds as exemplified by sydnones, sydnonimines, etc., have been investigated rather extensively because of their unique electronic structures and biological activities.[3] One of these sydnonimine derivatives, N-ethoxycarbonyl-3-morpholinosydnonimine (Molsidmine†), was recently reported and has been used clinically as an antianginal drug.[5]

In the course of our synthetic programs to look for pharmacologically active mesoionic compounds, a number of sydnone derivatives have been prepared. The present paper deals with synthesis of 4-thiosydnone derivatives, *viz,* sulfides, sulfoxides, sulfones and sulfonium salts.

Since Ohta[6] first reported the substitution reaction at the 4-position of 4-bromo-3-phenylsydnone with a sulfur compound, little work has been done in this area except a few examples of the substitution reaction via 4-lithium[7] or 4-acetoxymercuric 3-phenylsydnones.[8] On the other hand, introduction of methylthio or phenylthio groups into other aromatic[9] and heterocyclic ring systems[10] by the use of dimethyl sulfoxide or methyl phenyl sulfoxide has been reported. This prompted us to explore the possibilities of direct introduction of a methylthio or phenylthio group at the 4-position of 3-substituted sydnones by the use of dimethyl sulfoxide or methyl phenyl sulfoxide, and to see if the sulfides thus obtained could serve as intermediates for the synthesis of other unknown derivatives of sydnones.

From a point of view of the chemistry of sydnones, it has also been an interesting problem to introduce an electron-donating methylthio group[11]



SCHEME 1

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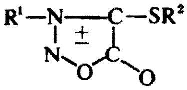
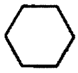
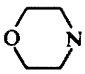
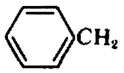
†Generic name: marketed as "Morial®" in Japan.

Table 1.



2 and 3

No.	R^1	R^2	M.p. °C (Solvent[a])	Yield %	Formula	Calcd./Found % C	H	N
2a	CH_3	CH_3	94–96 ($AcOEt-Et_2O$)	21	$C_4H_6O_2N_2S$	32·86 32·87	4·14 4·05	19·17 19·13
2b	C_2H_5	CH_3	40·5–42·5 (Et_2O-P.E.)	19	$C_5H_8O_2N_2S$	37·48 37·73	5·03 4·89	17·49 17·55
2c	iso-C_3H_7	CH_3	54–56·5 ($AcOEt-Et_2O$)	37	$C_6H_{10}O_2N_2S$	41·36 41·50	5·79 5·81	16·08 16·33
2d	t-C_4H_9	CH_3	78–79·5 (AcOEt-P.E.)	40	$C_7H_{12}O_2N_2S$	44·66 44·62	6·43 6·38	14·88 14·69
2e		CH_3	56–57·5 ($AcOEt-Et_2O$)	57	$C_9H_{14}O_2N_2S$	50·45 50·61	6·59 6·47	13·07 13·33
2f	$(CH_3)_2N$	CH_3	52–54 (AcOEt)	42 93[b]	$C_5H_9O_2N_3S$	34·28 33·96	5·18 5·16	23·99 24·06
2g		CH_3	90–92·5 (AcOEt)	46	$C_7H_{11}O_3N_3S$	38·70 38·82	5·10 5·17	19·34 19·61
2h		CH_3	101·5–102 (EtOH-hexane)	43	$C_9H_8O_2N_2S$	51·91 51·90	3·89 3·80	13·46 13·17
2i		CH_3	75–77 ($AcOEt-Et_2O$)	75	$C_{10}H_{10}O_2N_2S$	54·04 54·01	4·53 4·52	12·60 12·62
3	$(CH_3)N$		74–75 (C_6H_6-n-hexane)	96[c]	$C_{10}H_{11}O_2N_3S$	50·62 50·79	4·67 4·72	17·71 17·60

[a] P.E.: light petroleum.
[b] Yield from **5b**.
[c] Yield from **6**.

at the 4-position, because all attempts to introduce electron-donating substituents at this position had been unsuccessful.[3]

3-Substituted sydnones (**1**) which are fairly unstable to acidic reagents[3] were carefully treated with dimethyl sulfoxide and acetyl chloride at low temperatures to give the corresponding 4-methylthio compounds (**2**) which are summarized in Table 1.

When chloromethyl methyl ether was used in place of acetyl chloride,[10] complete decomposition of the sydnone ring had occurred, which might be due to the effect of the hydrogen chloride generated during the reaction.

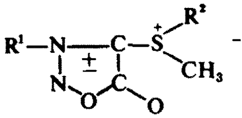
Treatment of **1** with methyl phenyl sulfoxide[9a] and acetylchloride, on the other hand, did not afford the anticipated 4-phenylthiosydnones (**3**), but 4-chlorosydnones (**4**) and methyl phenyl sulfide were obtained. The chlorination of **1** can be reasonably accounted for by an assumption that chlorine is generated by the oxidation of hydrogen chloride

Table 2. Spectral data of 4-methylthio- and 4-phenylthiosydnones (**2** and **3**)

No.	NMR[a]	IR[b]		UV[c]	max (ε)
2a	2·35	1730	1745	309	6650
2b	2·35	1733	1749	309	6460
2c	2·35	1749	1790[d]	310	6620
2d	2·37	1737		312	6420
2e	2·35	1747		310	6750
2f	2·38	1753		316	6750
2g	2·38	1760		318	6520
2h	2·28	1754	1775[d]	326	5770
2i	2·00	1740		314	6220
3	—	1744[d]	1759	310	8040

[a] The chemical shifts of the Me proton of the methylthio group in the NMR in $CDCl_3$ (δ ppm).
[b] The IR absorption spectra of the sydnone CO group in Nujol (cm^{-1}).
[c] The UV absorption spectra of the sydnone ring in EtOH (nm).
[d] Shoulder.

Table 3.



$^-ClO_4$ **5** and **6**

No.	R^1	R^2	M.p. °C	Yield %	Formula	Calc/Found % C	H	N
5a	iso-C_3H_7	CH_3	163·5–164^a	25	$C_7H_{13}O_6N_2SCl$	29·12	4·54	9·71
						28·95	4·42	9·73
5b	$(CH_3)_2N$	CH_3	152–154^a	46	$C_6H_{12}O_6N_3SCl$	24·87	4·18	14·50
						24·79	4·07	14·59
6	$(CH_3)_2N$		143^a	93	$C_{11}H_{14}O_6N_3SCl$	37·56	4·01	11·95
						37·40	4·11	11·91

^{a}Decomposition.

with methyl phenyl sulfoxide and that the hydrogen chloride is generated from acetyl chloride and moisture in the reaction mixture.*

In order to avoid the chlorination, 3-dimethylaminosydnone (**1**) was treated with methyl phenyl sulfoxide and acetyl perchlorate to give methylphenylsulfonium perchlorate (**6**), which upon treatment with aqueous potassium chloride gave **3** at the refluxing temperature. On merely standing **6** in dimethyl sulfoxide at room temperature for a while, **3** was also obtained in excellent yield.† Similarly, treatment of **1** with dimethyl sulfoxide and acetyl perchlorate, followed by refluxing with aqueous potassium chloride gave **2** via dimethylsulfonium perchlorates (**5**). The sulfonium perchlorates (**5** and **6**) thus obtained are listed in Table 3.

It is noteworthy that 4-methylthiosydnones (**2**) including 3-dimethylamino- and 3-morpholino-4-methylthiosydnones (**2f** and **2g**) which possess electron-donating substituents at their 3- and 4-positions[14] were obtained as stable crystalline substances and recovered unchanged even when heated above their m.ps.

Table 4. Spectral data of sulfonium perchlorates of sydnones (5 and 6)

No.	NMR^a	IR^b	
5a	3·34 (6H)	1772	1760
5b	3·34 (6H)	1798	
6	3·80 (3H)	1787	

^{a}The chemical shifts of the Me proton of the sulfonium group (δ ppm) in the NMR.

^{b}The IR absorption spectra of the sydnone CO group in Nujol (cm^{-1}).

Oxidations[15] and reductions[16] of sydnones resulted in some cases in the ring cleavage. In the present case, sydnones (**2**) were oxidized smoothly to the corresponding 4-methylsulfinylsydnones (**7**) or 4-methylsulfonylsydnones (**8**) with hydrogen peroxide in acetic acid by controlling the quantity of the peroxide; 1·2–1·3 equivalents of the peroxide gave **7** and 3 equivalents of the peroxide gave **8**. The sulfoxides (**7**) and sulfones (**8**) obtained are summarized in Table 5.

However, **3** was resistant to the oxidation with hydrogen peroxide in acetic acid or sodium metaperiodate in aqueous methanol at room temperature and recovered unchanged. At an elevated temperature, the oxidation of **3** with hydrogen peroxide or sodium metaperiodate resulted in the decomposition.

As for the reduction, elimination of 4-substituents to give 3-phenylsydnone was observed when 4-methylsulfinyl- and 4-methylsulfonylsydnones (**7f** and **8e**) were treated with sodium borohydride in methanol at room temperature. The ring decomposition, however, was observed with 3-dimethylamino-4-methylsulfinylsydnone (**7d**), whereas 3-benzyl-4-methylsulfonylsydnone (**8f**) and 4-methylthio-3-phenylsydnone (**2h**) were recovered unchanged under the same conditions.

EXPERIMENTAL

All m.ps were taken on a micro hot-stage apparatus and are uncorrected. UV and IR spectra were recorded on Hitachi Model EPI-2 and Perkin-Elmer Model 450 spectrophotometers, respectively. NMR spectra were recorded on a Varian Model A-60 spectrophotometer using TMS as internal standard.

Preparation of 3-*substituted sydnones* (**1**). Me,[17] Et,[18] i-Pr,[19] t-Bu,[19] cyclohexyl,[14] dimethylamino,[20] morpholino,[20] benzyl[16] and phenyl[21] sydnones were prepared according to the literature.

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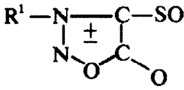
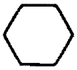
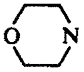
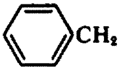
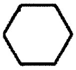
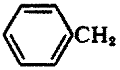
*Recently, the direct reduction of methyl phenyl sulfoxide with acetyl chloride to give chlorine has been reported,[12] while it was pointed out that the complete removal of water from the sulfoxide was very difficult.[13]

†It is assumed that this reaction is a transfer reaction of methyl perchlorate from **6** to dimethyl sulfoxide on the basis of NMR studies.

Table 5.  7 and 8

No.	R¹	M.p. °C	Yield %	Formula	Calcd./Found % C	H	N
n = 1							
7a	CH$_3$	55·5–58	60	$C_4H_6O_3N_2S$	29·62 29·39	3·73 3·79	17·28 17·02
7b	iso-C$_3$H$_7$	88–90	68	$C_6H_{10}O_3N_2S$	37·88 37·74	5·30 5·31	14·73 15·08
7c		75–77	49	$C_9H_{14}O_3N_2S$	46·94 46·88	6·13 6·09	12·17 12·13
7d	(CH$_3$)$_2$N	96–97·5	92	$C_5H_9O_3N_3S$	31·41 31·14	4·74 4·60	21·98 21·85
7e		90–92·5	72	$C_7H_{11}O_4N_3S$	38·70 38·82	5·10 5·17	19·34 19·61
7f		158–160	93	$C_9H_8O_3N_2S$	48·21 48·36	3·60 3·83	12·49 12·41
7g		158·5–160*	92	$C_{10}H_{10}O_3N_2S$	50·41 50·64	4·23 4·34	11·76 11·69
n = 2							
8a	CH$_3$	147–148	25	$C_4H_6O_4N_2S$	26·96 26·73	3·39 3·31	15·73 15·60
8b	iso-C$_3$H$_7$	109–110·5	57	$C_6H_{10}O_4N_2S$	34·94 34·78	4·89 4·80	13·59 14·09
8c		112–113	78	$C_9H_{14}O_4N_2S$	43·89 44·06	5·73 5·69	11·38 11·44
8d	(CH$_3$)$_2$N	180–181*	62	$C_5H_9O_4N_3S$	28·98 29·06	4·38 4·28	20·28 20·49
8e		156·5–157·5	87	$C_9H_8O_4N_2S$	45·00 44·95	3·36 3·38	11·66 11·69
8f		142·5	67	$C_{10}H_{10}O_4N_2S$	47·24 46·94	3·96 3·75	11·02 10·94

*Decomposition.

General procedure for the preparation of 4-methylthiosydnones (**2**)

(a) To a stirred soln of **1** (0·042 mol) in molecular sieve (type 3A)-dried DMSO (12 g), was added acetyl chloride (0·084 mol) dropwise below 15° under the protection from the moisture. After stirring overnight at room temp, the mixture was extracted with AcOEt (150 ml). The extract was washed with sat NaHCO$_3$aq, dried over Na$_2$SO$_4$ and evaporated to give an oily residue. Trituration with a small amount of ether under ice-cooling gave crystals, which were recrystallized from the solvent listed in Table 1 to afford **2**. In the case of **2b**, an oily residue was purified by column chromatography on silica gel (AcOEt) and crystallized.

(b) A suspension of **5** (0·011 mol) in sat KClaq (32 ml) was heated to reflux for 8 h. The mixture was extracted with CHCl$_3$, and the CHCl$_3$ extract was washed with water and dried over Na$_2$SO$_4$. Evaporation of the solvent *in vacuo* gave a crystalline residue, which was recrystallized from the solvent listed in Table 1 to give **2**.

3-*Dimethylamino-4-phenylthiosydnone* (**3**)

(a) A suspension of **6** (1 g) in sat KClaq (30 ml) was heated to reflux for 1 h and cooled to room temp. The ppt formed was collected and washed with water. Recrystallization from the solvent listed in Table 1 yielded **3**.

(b) A mixture of **6** (2 g) and DMSO (6 ml) was stirred for 45 min at room temp and then diluted with CHCl$_3$ (50 ml). The organic layer was washed with water and dried over Na$_2$SO$_4$. Evaporation of the solvent under reduced pres-

Table 6. Spectral data of 4-methylsulfinylsydnones (7)

			IR[b]				
No.	NMR[a]		CO		SO	UV[c]	max (ε)
7a	3·21	1750		1733[d]	1018	297	(7270)
7b	3·23		1758		1051	299	(6770)
7c	3·25		1754		1039	299	(6910)
7d	3·29		1770		1056	303	(6790)
7e	3·20	1754		1767[d]	1037	304	(6810)
7f	3·25	1773		1755	1066	308	(6140)
7g	3·03		1762		1038	303	(6360)

[a] The chemical shifts of the Me proton of the methylsulfinyl group in $CDCl_3$ (δ ppm) in the NMR.

[b] The IR absorption spectra of the sydnone carbonyl group and sulfinyl group in Nujol (cm^{-1}).

[c] The UV absorption spectra of the sydnone ring in EtOH (nm).

[d] Shoulder.

Table 7. Spectral data of 4-methylsulfonylsydnones (8)

			IR[b]					
No.	NMR[a]		CO		SO_2		UV[c]	max (ε)
8a	3·33		1768		1327	1148	292	(7320)
8b	3·30	1802[d]		1770	1316	1147	296	(6740)
8c	3·32		1776		1329	1141	293	(7390)
8d	3·31	1812[d]		1789	1328	1143	300	(7000)
8e	3·29	1791		1766[d]	1338	1147	304	(6010)
8f	2·89	1818[d]		1782	1324	1142	299	(6410)

[a] The chemical shifts of the Me proton of the methylsulfonyl group in $CDCl_3$ (δ ppm) in the NMR.

[b] The IR absorption spectra of the sydnone CO group and sulfonyl group in Nujol (cm^{-1}).

[c] The UV absorption spectra of the sydnone ring in EtOH (nm).

[d] Shoulder.

sure gave a crystalline residue, which was recrystallized from the solvent listed in Table 1 to afford **3**.

General procedure for the preparation of dimethyl- and methylphenylsulfonium perchlorates (**5** *and* **6**)

(a) To a stirred soln of **1** (0·03 mol) in a mixture of DMSO (0·03 mol) and Ac_2O (15 ml), was added acetyl perchlorate[22] prepared from 70% $HClO_4$ (4·28 g) and Ac_2O (15 ml) dropwise at − 15°. After being stirred for 1 h at room temp, the ppt was collected and washed with ether. Recrystallization from AcOH gave **5**.

(b) In similar experiments as described in (a) with only exception that DMSO was replaced by methyl phenyl sulfoxide, a series of reactions started with **1** yielded **6**.

General procedure for the preparation of 4-methylsulfinylsydnones (**7**)

To a stirred soln of **2** (2·8 mmol) in AcOH (2·5 ml), was added 1·2 equivs of 30% H_2O_2 under ice-cooling. After being allowed to stand for 3 days at room temp, the mixture was diluted with AcOEt (50 ml), the AcOEt layer was washed with sat $NaHCO_3$aq and water, and dried over Na_2SO_4. Evaporation of the solvent *in vacuo* gave an oily residue, which was crystallized under ice-cooling. Recrystallization from AcOEt-n-hexane gave **7**.

(b) **2** was treated as described in (a). The mixture was poured into ice water. The ppt formed was collected and washed with water. Recrystallization from EtOH yielded **7**.

General procedure for the preparation of 4-methylsulfonylsydnones (**8**)

(a) To a stirred soln of **2** (1·5 mmol) in AcOH (1·5 ml), was added 3 equivs of 30% H_2O_2 under ice-cooling. The mixture was allowed to stand for 3 days at room temp and poured into ice water. The ppt formed was collected and washed with water. Recrystallization from EtOH gave **8**.

(b) A mixture of **2f** (1·1 g, 5 mmol) and 30% H_2O_2 (1·7 g, 15 mmol) in AcOH (7 ml) was warmed at 50–60° for 3 h. To the mixture cooled to room temp was added ether to give a ppt, which was recrystallized from EtOH to yield **8f** (0·9 g).

Chlorination of **1** *with methyl phenyl sulfoxide and acetyl chloride.* To a stirred soln of 3-isopropylsydnone (3·8 g, 0·03 mol) in methyl phenyl sulfoxide (4·8 g, 0·034 mol) and AcOH (6 ml), was added acetyl chloride (2·5 g, 0·032 mol) dropwise under ice-cooling. After stirring for 1 h at the same temp, the mixture was extracted with AcOEt (100 ml). The extract was washed with sat $NaHCO_3$ aq and water and dried over Na_2SO_4. After evaporation of the solvent under reduced pressure, an oily residue was taken up in ether and cooled in a dry ice-acetone bath, to which light petroleum was added and the ppt was collected, followed by washing with light petroleum to give crude crystals. Recrystallization from ether-light petroleum gave 2·9 g (60%) of 4-chloro-3-isopropylsydnone, m.p. 30–32°. (Found: C, 36·83; H, 4·31; N, 17·32. Calcd. for $C_5H_7O_2N_2Cl$: C, 36·93; H, 4·34; N, 17%·23%.) IR_{max}^{Nujol} cm^{-1}: 1762, 1740. NMR ($CDCl_3$) δ ppm: 1·70 (6H, d), 4·88 (1H, m). The mother soln was concentrated under reduced pressure and subjected to distillation to afford colorless liquid (3·2 g), of which the IR spectrum was identical with that of methyl phenyl sulfide. Similarly, 3-dimethylaminosydnone (2·3 g, 0·0165 mol) was treated as described above to afford 1·9 g (65%) of 4-chloro-3-dimethylaminosydnone, m.p. 61–61·5°. (Found: C, 29·52; H, 3·71; N, 25·65. Calcd. for $C_4H_6O_2N_3Cl$: C, 29·38; H, 3·71; N, 25·65%); IR_{max}^{Nujol} cm^{-1}: 1770, 1734; NMR ($CDCl_3$) δ ppm: 3·13 (6H, s).

Reduction with sodium borohydride

(a) To a stirred soln of **7f** (192 mg, 0·86 mmol) in 10 ml of MeOH, was added $NaBH_4$ (45 mg, 1·18 mmol) under ice-cooling and the soln was stirred for 2 h at room temp. After the excess of the reagent had been decomposed by addition of 0·1 ml of AcOH, the mixture was concentrated to dryness under reduced pressure. To the residue was added water and the ppt was filtered and washed with water, yielding 72 mg (52%) of crystals, m.p. 134–135·5° (from water).

(b) **8e** (200 mg, 1 mmol) was treated with $NaBH_4$ (45 mg, 1·18 mmol) in MeOH (10 ml) as described in (a) to yield 61 mg (38%) of crystals, m.p. 129–131° (from water). The IR and NMR spectra of these substances obtained in (a) and (b) were identical with those of 3-phenylsydnone.

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REFERENCES

[1] Part III of this series. K. Masuda, T. Kamiya and K. Kashiwa, *Chem. Pharm. Bull. Tokyo* **19**, 559 (1971)

[2] Presented at the *Annual Meeting of the Pharmaceutical Society of Japan*. Sapporo, July (1970)

[3a] F. H. C. Stewart, *Chem. Rev.* **64**, 129 (1964); M. Ohta and H. Kato, *Nippon Kagaku Zasshi* **86**, 661 (1965); L. B. Kier and E. B. Roche, *J. Pharm. Sci.* **56**, 149 (1967); [b] E. Ackermann, *Pharmazie* **22**, 537 (1967); M. Ohta and H. Kato, *Nonbenzenoid Aromatics* (Edited by J. P. Snyder) Vol. 1, Chapt 4. Academic Press, New York and London (1969)

[4] K. Masuda, T. Kamiya, Y. Imashiro and T. Kaneko, *Chem. Pharm. Bull. Tokyo* **19**, 72 (1971)

[5] T. Sato, M. Iwamoto and J. Kurihara, *Jap. J. Clin. Pharmacol.* **1**, 17 (1970); S. Toyama, H. Nomura, T. Yamagami, T. Amamiya and K. Suzuki, *Jap. J. Clin. Med.* **28**, 1594 (1970)

[6] M. Ohta and H. Kato, *Bull. Chem. Soc. Japan* **30**, 210 (1957)

[7] N. Suciu and G. Mihai, *Tetrahedron* **24**, 37 (1968)

[8] V. A. Mofeder, *Zh. Obs. Khim.* **38**, 2184 (1968)

[9a] R. Oda and K. Yamamoto, *Nippon Kagaku Zasshi* **85**, 133 (1964); K. Hirose and S. Ukai, *Yakugaku Zasshi* **86**, 187 (1966); *Chem. Pharm. Bull. Tokyo* **16**, 195 (1968); [b] E. Goethals and P. de Radzitzky, *Bull. Soc. Chim. Belg.* **73**, 546 (1964)

[10] K. Anzai and S. Suzuki, *Agr. Biol. Chem. Tokyo* **30**, 597 (1966); E. A. Gray, R. M. Hulley and B. K. Snell, *J. Chem. Soc.* (C) 986 (1970)

[11] C. C. Price and S. Oae, *Sulfur Bonding*, Chap 2. Ronald Press, New York (1962)

[12] T. Numata and S. Oae, *Chem. Ind.* 277 (1973)

[13] D. Barnard, J. M. Fabian and H. P. Koch, *J. Chem. Soc.* 2442 (1949)

[14] K. Masuda, Y. Imashiro and T. Kaneko, *Chem. Pharm. Bull. Tokyo* **18**, 128 (1970)

[15] M. Hashimoto and M. Ohta, *Bull. Chem. Soc. Japan* **31**, 1048 (1958); H. Kato and M. Ohta, *Ibid.* **35**, 1418 (1962); F. H. C. Stewart, *Chem. Ind.* 1718 (1962)

[16] W. Baker, W. D. Ollis and V. D. Poole, *J. Chem. Soc.* 307 (1949); J. C. Earl, *Rec. Trav. Chim.* **75**, 346 (1956)

[17] D. L. Hammick and D. J. Voaden, *J. Chem. Soc.* 3303 (1961)

[18] V. F. Vasiléva and V. G. Yashunskii, *Chem. Abstr.* **58**, 9053 (1963)

[19] L. B. Kier and D. Dhawan, *J. Pharm. Sci.* **51**, 1058 (1962)

[20] K. Masuda, Y. Imashiro and T. Kaneko, in preparation

[21] J. C. Earl and A. W. Mackney, *J. Chem. Soc.* 899 (1935)

[22] H. Burton and P. F. G. Praiee, *Ibid.* 1203 (1950); *Ibid.* 2034 (1950)