Studies on Mesoionic Compounds. Part 10.[1] Synthesis and Chemical Properties of Mesoionic 1,2,5-Thiadiazolium-3-olates [2]

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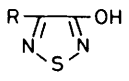
The preparation of a novel mesoionic heterocycle is described; derivatives of 4-aryl-5-alkyl-1,2,5-thiadiazolium-3-olates (6a—f) are obtained by treatment of α-*N*-substituted aminophenylacetamides with sulphur monochloride followed by base.

RECENTLY Ollis and Ramsden [3] have shown that five-membered mesoionic heterocycles are classified into type A and type B in which the atoms contributing two electrons each to the π-system are non-adjacent or adjacent. More than fifty representatives of type A have been described, but only eight of type B. We now report the synthesis of new mesoionic heterocycles of type B, the 1,2,5-thiadiazolium-3-olates (6).

Most of the preparations of type B mesoionic compounds or their salts involve ring alkylation of the corresponding heteroaromatic derivatives, *e.g.*, 1,2-oxazolium-4-olate [4,5] and -4-aminide,[5] 1,2-diazolium-4-olate [6] and -4-aminide,[5] and 1,2-thiazolium-4-aminide [5] systems. Thus, alkylation of 3-hydroxy-1,2,5-thiadiazoles,[7] easily obtainable from α-aminoacetamides with either thionyl chloride, *N*-sulphinylaniline [8] or sulphur monochloride,[9] at N-5 should yield the mesoionic compounds (6). However, methylation of 3-hydroxy-4-phenyl-1,2,5-thiadiazole (1a) with dimethyl sulphate or methyl fluorosulphonate gave the thiadiazolone (2); methylation with diazomethane yielded the methyl ether (3) as the major product with some (2). This approach therefore failed.

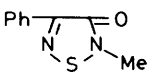
We therefore investigated the ring closure of α-*N*-substituted aminoacetamides (4). Benzaldehyde was converted into α-methylaminophenylacetamide (4a) by treatment of its cyanohydrin with methylamine followed by conversion into the amide;[10] other amides (4b—e) and (4g—j) were analogously prepared. 1,2,3,4-Tetrahydroisoquinoline-1-carboxamide (4f),[11] α-phenylaminopropionamide (4k),[12] piperidine-2-carboxamide (4l),[13] and prolinamide (4m) [14] were prepared by reported



(1a,b)

a; R = Ph

b; R = *p*-MeOC$_6$H$_4$



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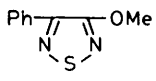
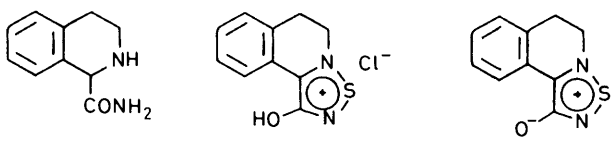


(3)

methods. Although treatment of (4a) with thionyl chloride or *N*-sulphinylaniline resulted in recovery of the amide (4a), reaction occurred with sulphur monochloride in dimethylformamide at 60 °C to give the crystalline salt (5a). The free base (6a) was obtained as yellow crystals on treatment of (5a) with sodium hydrogencarbonate or more favourably triethylamine. The i.r. spectrum of (6a) showed a strong absorption band at 1 550 cm^{-1} which is attributed to carbonyl stretching. In the mass spectrum of (6a) peaks at *m/e* 192 (M^+) and 118 (PhC≡$\overset{+}{N}$Me, base peak) were observed. These, along with the n.m.r. [δ 4.2 (NMe) and 7.35—8.0 (Ph)] and u.v. data [$\lambda_{max.}$ 252 and 376 nm (log ε 3.70 and 4.01)] could support the formulation of this product as the mesoionic structure (6a). The other amides (4b—m) were submitted to the above process; mesoionic compounds (6b—f) were obtained from the amides (4b—f).

(4a-e,g-m) (5a-e) (6a-e)

a, R^1 = Ph, R^2 = Me
b, R^1 = *p*-MeOC$_6$H$_4$, R^2 = Me
c, R^1 = *p*-ClC$_6$H$_4$, R^2 = Me
d, R^1 = Ph, R^2 = C$_5$H$_{11}$
e, R^1 = *p*-ClC$_6$H$_4$, R^2 = C$_6$H$_{11}$
g, R^1 = Ph, R^2 = PhCH$_2$
h, R^1 = *p*-MeOC$_6$H$_4$, R^2 = PhCH$_2$
i, R^1 = R^2 = Ph
j, R^1 = Ph, R^2 = *p*-MeOC$_6$H$_4$
k, R^1 = Me, R^2 = Ph
l, R^1, R^2 = -[CH$_2$]$_4$-
m, R^1, R^2 = -[CH$_2$]$_3$-

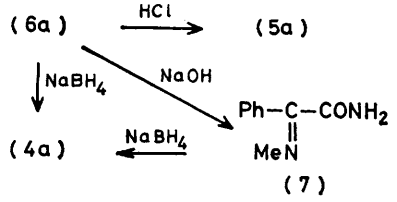


(4f) (5f) (6f)

The benzylamino-derivatives (4g and h) gave 3-hydroxy-1,2,5-thiadiazoles (1a and b) with loss of benzyl. The arylaminoacetamides (4i and j) yielded no mesoionic product; considerable amounts of aromatic amine were detected in the reaction mixture. The three compounds (4k—m), not containing the phenylacetamide structure, gave no identifiable product. It seems that only α-alkylaminoarylacetamides can form mesoionic 4-aryl-5-alkyl-1,2,5-thiadiazolium-3-olates by this method, and it may be that a 4-aryl group is required to stabilise the system.

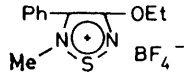
The new mesoionic compounds (6) were inactive to dipolarophiles such as dimethyl acetylenedicarboxylate. These compounds (6) seem to be stable to acid, but to be

sensitive to alkali. For example, compound (6a) formed the hydrochloride (5a) on treatment with hydrochloric acid; the action of dilute sodium hydroxide on (6a) gave α-methyliminophenylacetamide (7), reduction of which with sodium borohydride afforded the original amide (4a). Similarly, reduction of (6a) with sodium borohydride gave the amide (4a) (Scheme).



SCHEME

We have reported [15] that *exo-O*-alkylated sydnone could be converted into *exo*-sulphur analogue by treatment with sodium hydrosulphide. Our attempts to extend this procedure to the salt (8), the Meerwein alkylation product of (6a), were unsuccessful. Thus, on the reaction of (8) with sodium hydrosulphide only the imino-amide (7) was isolated. The action of methylamine on the salt (8), on the other hand, afforded 5-methyl-3-methylamino-4-phenyl-1,2,5-thiadiazolium fluoroborate (9), which on treatment with base underwent decomposition without formation of any mesoionic product. These results suggest that the mesoionic 1,2,5-thiadiazole system is labile.



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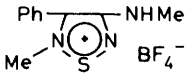

(9)

EXPERIMENTAL

General experimental details are given in Part 6.[15]

2-Methyl-4-phenyl-1,2,5-thiadiazol-3-one (2).—(*a*) A mixture of 3-hydroxy-4-phenyl-1,2,5-thiadiazole [9] (1a) (356 mg) and methyl fluorosulphonate (362 mg) in dioxan (5 ml) was refluxed for 8 h. After evaporation, the residue was dissolved in chloroform, washed with dilute sodium carbonate solution, and then dried (Na_2SO_4). Evaporation and distillation gave *2-methyl-4-phenyl-1,2,5-thiadiazol-3-one* (2) (180 mg, 47%) as crystals, b.p. 85—90 °C at 0.1 mmHg (bath temp.), m.p. 72—74 °C (Found: C, 56.2; H, 3.9; N, 14.5. $C_9H_8N_2OS$ requires C, 56.25; H, 4.2; N, 14.55%), $\nu_{max.}$ (KBr) 1 650 cm^{-1} (CO), δ ($CDCl_3$) 3.4 (3 H, s, NMe), 7.2—7.55 (3 H, m, arom.), and 8.2—8.5 (2 H, m, arom.), *m/e* 192 (M^+).

(*b*) A mixture of (1a) (1.78 g) and dimethyl sulphate (1.39 g) was heated at 120 °C for 1.5 h. After cooling, the mixture was washed with ether and recrystallised from hexane to give compound (2) (1.4 g, 73%) as needles, m.p. 72—74 °C, identical with the product obtained above.

Methylation of the Hydroxythiadiazole (1a) *with Diazomethane.*—Ethereal diazomethane [from *N*-nitrosomethylurea (3 g), 50% potassium hydroxide (10 ml), and ether (20 ml)] was added to a solution of (1a) (1 g) in methanol (5 ml), and the mixture was allowed to stand at room temperature (1 h). Evaporation and recrystallisation of the residue from hexane gave the *2-methyl compound* (2) (240 mg, 22%) as needles, m.p. 71—74 °C.

The mother-liquor was concentrated and distilled to afford the *methyl ether* (3) (630 mg, 58%) as an oil, b.p. 100—105 °C at 1 mmHg (bath temp.) (Found: C, 56.0; H, 4.05; N, 14.8. $C_9H_8N_2OS$ requires C, 56.25; H, 4.2; N, 14.55%), $\nu_{max.}$ (film) 1 250 cm^{-1} (ether), δ ($CDCl_3$) 4.05 (3 H, s, OMe), 7.1—7.5 (3 H, m, arom.), and 7.85—8.2 (2 H, m, arom.).

Preparation of α-N-Substituted Amino-acid Amides (4).—(*a*) 2-*N*-Substituted amino-acetonitrile derivatives were prepared by the following two methods.

Method A. A mixture of equimolar amounts of aromatic aldehyde, sodium hydrogen sulphite (saturated aqueous solution), sodium cyanide (30% solution), and the amine was stirred at room temperature for 2—3 h. Extraction with chloroform and evaporation gave the corresponding amino-nitrile.

Method B. The aldehyde, sodium hydrogensulphite, and sodium cyanide were treated as above. The resulting cyanohydrin was isolated by extraction with chloroform and evaporation, and then heated with amine in ethanol under reflux for 1 h. Concentration of the mixture gave the amino-nitrile.

The amino-nitrile, thus obtained, was dissolved in ice-cooled sulphuric acid (3—5 times volume of nitrile), and left overnight at room temperature. The mixture was poured onto ice and made alkaline with 30% potassium hydroxide. The crystalline precipitate was collected and recrystallised to give the *amide* (4). These results are summarised in the Table.

(*b*) The amides (4f and k—m) were prepared according to reported methods.

3-Hydroxy-1,2,5-thiadiazolium Chlorides (5).—(*a*) A mixture of (4a) (1.64 g) and sulphur monochloride (6.8 g) in dimethylformamide (30 ml) was heated at 60 °C for 2 h. The solvent was removed under reduced pressure to give a crystalline residue. Addition of methanol, filtration, and evaporation of the filtrate gave crystals, which were then washed with chloroform and dried to afford *3-hydroxy-5-methyl-4-phenyl-1,2,5-thiadiazolium chloride* (5a) (1.76 g, 77%), needles, m.p. 167—170 °C (from ethanol) (Found: C, 47.4; H, 3.9; N, 12.25. $C_9H_9ClN_2OS$ requires C, 47.25; H, 3.95; N, 12.25%), δ (CD_3OD) 4.3 (3 H, s, NMe), and 7.5—7.9 (5 H, m, Ph).

(*b*) Similarly, compounds (4b—f) (0.01 mol) were treated with sulphur monochloride (4 g, 0.03 mol) in dimethylformamide (40 ml) at 60 °C for 1—3 h. Work-up in the same way as above gave the *salts* (5b—f); m.p.s and yields: (5b), 131—134 °C, 84%; (5c), 141—143 °C, 74%; (5d), 127—133 °C, 79.5%; (5e), 133—134 °C, 59%; (5f), 189—193 °C, 98%.

1,2,5-Thiadiazolium-3-olates (6).—(*a*) A solution of triethylamine (0.8 g) in ethanol (5 ml) was added to a suspension of the compound (5a) (1.76 g) in ethanol (15 ml), and the mixture was stirred at room temperature for 30 min. The precipitate was filtered off and recrystallised from ethanol to give *5-methyl-4-phenyl-1,2,5-thiadiazolium-3-olate* (6a) (1.11 g, 75%) as yellow needles, m.p. 174—176 °C (Found: C, 56.3; H, 4.25; N, 14.8. $C_9H_8N_2OS$ requires C, 56.25; H, 4.2; N, 14.55%), $\nu_{max.}$ (KBr) 1 550 cm^{-1} (CO), $\lambda_{max.}$ (EtOH) 252 (log ε 3.70) and 376 nm (4.01), δ [$(CD_3)_2SO$] 4.2 (3 H, s, NMe) and 7.35—8.0 (5 H, m, Ph), *m/e* 192 (M^+), 178, 160, 118 (base peak), 104, and 77.

α-*N*-Substituted amino-acetamides (4) $R^1CH(NHR^2)CONH_2$

Cmpd	Method [a]	R^1	R^2	M.p./°C	Yield [b] (%)	Formula	Analysis (%) Found (Required) C	H	N
(4a)	A	Ph	Me	160—163 [c,d]	58	$C_9H_{12}N_2O$	65.7 (65.85)	7.15 (7.35)	17.2 (17.05)
(4b)	B	*p*-$MeOC_6H_4$	Me	174—176 [d]	15	$C_{10}H_{14}N_2O_2$	61.6 (61.85)	7.05 (7.25)	14.2 (14.4)
(4c)	A	*p*-ClC_6H_4	Me	153—154 [e]	49	$C_9H_{11}ClN_2O$	54.65 (54.4)	5.3 (5.6)	14.35 (14.1)
(4d)	A	Ph	C_6H_{11}	117—118 [d]	81	$C_{14}H_{20}N_2O$	72.15 (72.35)	8.8 (8.7)	12.2 (12.05)
(4e)	A	*p*-ClC_6H_4	C_6H_{11}	73—75 [e]	86	$C_{14}H_{19}ClN_2O$	62.75 (63.05)	7.0 (7.2)	10.3 (10.5)
(4g)	B	Ph	$PhCH_2$	121 [d]	69	$C_{15}H_{16}N_2O$	75.0 (74.95)	6.75 (6.7)	11.4 (11.65)
(4h)	B	*p*-$MeOC_6H_4$	$PhCH_2$	127—128 [d]	44	$C_{16}H_{18}N_2O_2$	71.35 (71.1)	6.7 (6.7)	10.3 (10.35)
(4i)	B	Ph	Ph	130—131 [e]	56	$C_{14}H_{14}N_2O$	74.15 (74.3)	6.3 (6.25)	12.1 (12.35)
(4j)	B	Ph	*p*-$MeOC_6H_4$	114—116 [e]	47	$C_{15}H_{16}N_2O_2$	70.25 (70.3)	6.55 (6.3)	11.2 (10.95)
(4f)		*o*-$CH_2CH_2C_6H_4$		185—187 [d,f]					
(4k)		Me	Ph	144—145 [e,g]					
(4l)		$-[CH_2]_4-$		141—142 [e,h]					
(4m)		$-[CH_2]_3-$		92—95 [e,i]					

[a] Preparation method of α-aminoacetonitrile. [b] Based on aldehyde. [c] Lit. m.p. 155 °C (ref.10). [d] Recrystallised from isopropy alcohol. [e] Recrystallised from benzene. [f] Lit. m.p. 182—183 °C (ref. 11). [g] Lit. m.p. 144 °C (ref. 12). [h] Lit. m.p. 144—146 °C (ref. 13). [i] Lit. m.p. 93 °C (ref 14).

(*b*) The salt (5b) was treated in the same way as above to give compound (6b). Salts (5c—f) were added to saturated sodium hydrogencarbonate solution, and the mixtures stirred at room temperature for 30 min. Extraction with chloroform, evaporation, and recrystallisation gave the compound (6c—f). 4-p-*Methoxyphenyl*-5-*methyl*-1,2,5-*thiadiazolium*-3-*olate* (6b) was obtained as yellow plates (60%), m.p. 187—189 °C (from ethanol) (Found: C, 53.9; H, 4.4; N, 12.65. $C_{10}H_{10}N_2O_2S$ requires C, 54.05; H, 4.55; N, 12.6%), $\nu_{max.}$ (KBr) 1 560 cm^{-1} (CO), $\lambda_{max.}$ (EtOH) 245 (log ε 3.74), 302 (3.72), and 387 nm (4.19), δ ($CDCl_3$) 3.9 (3 H, s, OMe), 4.2 (3 H, s, NMe), and 7.0 and 7.85 (4 H, AB q, *J* 9 Hz, arom.), *m/e* 222 (M^+); 4-p-*chlorophenyl*-5-*methyl*-1,2,5-*thiadiazolium*-3-*olate* (6c) gave yellow needles (65%), m.p. 187—188 °C (from isopropyl alcohol) (Found: C, 47.4; H, 2.95; N, 12.2. $C_9H_7ClN_2OS$ requires C, 47.7; H, 3.1; N, 12.35%), $\nu_{max.}$ (KBr) 1 580 cm^{-1} (CO), $\lambda_{max.}$ (EtOH) 263 (log ε 3.84), and 382 nm (4.04), δ (CD_3OD) 4.1 (3 H, s, NMe), and 7.55 and 7.9 (4 H, AB q, *J* 8 Hz, arom.), *m/e* 226 (M^+); 5-*cyclohexyl*-4-*phenyl*-1,2,5-*thiadiazolium*-3-*olate* (6d) gave yellow prisms (73%), m.p. 198—200 °C (from isopropyl alcohol) (Found: C, 64.8; H, 6.45; N, 11.0. $C_{14}H_{16}N_2OS$ requires C, 64.6; H, 6.2; N, 10.8%), $\nu_{max.}$ (KBr) 1 570 cm^{-1} (CO), $\lambda_{max.}$ (EtOH) 270 (log ε 3.53) and 376 nm (3.94), δ ($CDCl_3$) 0.9—2.5 (11 H, m, aliph.) and 7.5 (5 H, s, Ph); 4-p-*chlorophenyl*-5-*cyclohexyl*-1,2,5-*thiadiazolium*-3-*olate* (6e) gave yellow needles (77%), m.p. 177—178 °C (from ethyl acetate–chloroform) (Found: C, 57.3; H, 5.1; N, 9.75. $C_{14}H_{15}ClN_2OS$ requires C, 57.05; H, 5.15; N, 9.5%), $\nu_{max.}$ (KBr) 1 570 cm^{-1} (CO), $\lambda_{max.}$ (EtOH) 265 (log ε 3.71) and 380 nm (3.99), δ ($CDCl_3$) 1.0—2.4 (10 H, m, aliph.), 4.3—4.9 (1 H, m, NCH<), and 7.5 (4 H, s, arom.), *m/e* 294 (M^+); 5,6-*dihydroisoquinolino*[2,1-b][1,2,5]*thiadiazolium*-1-*olate* (6f) gave yellow needles (65%), m.p. 227—228 °C (from isopropyl alcohol) (Found: C, 58.75; H, 3.7; N, 13.85. $C_{10}H_8N_2OS$ requires C, 58.8; H, 3.95; N, 13.7%), $\nu_{max.}$ (KBr) 1 570 cm^{-1} (CO), $\lambda_{max.}$ (EtOH) 248 (log ε 3.86), 282 (3.67), and 400 nm (4.18), δ ($CDCl_3$) 3.4 (2 H, t, *J* 7 Hz, NCH_2CH_2), 4.65 (2 H, t, *J* 7 Hz, NCH_2CH_2), 7.25—7.6 (3 H, m, arom)., and 9.0—9.25 (1 H, m, arom.), *m/e* 204 (M^+).

Reaction of α-N-*Benzylaminoacetamide Derivatives* (4g and h) *with Sulphur Monochloride*.—A mixture of (4g and h) (0.01 mol) and sulphur monochloride (4 g) in dimethylformamide (40 ml) was heated at 60 °C for 3 h. After evaporation, methanol was added to the residue and the mixture was filtered. Concentration of the filtrate and recrystallisation of the residue gave 3-*hydroxy*-4-*phenyl*-1,2,5-*thiadiazole* (1a) as prisms (180 mg, 10%), m.p. 168 °C (from isopropyl alcohol), identical with an authentic sample (m.p. 167—170 °C),[9] and 3-*hydroxy*-4-p-*methoxyphenyl*-1,2,5-*thiadiazole* (1b) as leaflets (1.4 g, 67%), m.p. 191—194 °C (from benzene) (Found: C, 52.1; H, 3.6; N, 13.35. $C_9H_8N_2O_2S$ requires C, 51.9; H, 3.85; N, 13.45%), $\nu_{max.}$ (KBr) 3 000—2 500 cm^{-1} (OH), δ [$(CD_3)_2CO$] 3.8 (3 H, s, OMe) and 6.9 and 8.1 (4 H, AB q *J* 9 Hz, arom.), *m/e* 208 (M^+).

α-*Methyliminophenylacetamide* (7) *and Its Reduction with Sodium Borohydride*.—A mixture of compound (6a) (726 mg) and 10% sodium hydroxide solution (10 ml) was stirred at room temperature for 30 min. Extraction with chloroform, evaporation, and recrystallisation of the residue from benzene gave the *amide* (7) (234 mg, 38%) as cubes, m.p. 144—145 °C (Found: C, 66.7; H, 6.05; N, 17.35. $C_9H_{10}N_2O$ requires C, 66.65; H, 6.2; N, 17.25%), $\nu_{max.}$ (KBr) 3 350, 3 050 (NH_2), and 1 620 cm^{-1} (CO), δ ($CDCl_3$) 3.3 (3 H, s, NMe), 6.2—7.0 (2 H, broad peak, NH_2), and 7.1—8.0 (5 H, m, Ph), *m/e* 162 (M^+).

To the above amide (7) (200 mg) in methanol (5 ml) was added sodium borohydride (76 mg) at room temperature. After stirring for 1 h and evaporation, the residue was dissolved in chloroform, washed with water, and dried (Na_2SO_4). Concentration and recrystallisation of the residue from isopropyl alcohol gave α-*methylaminophenylacetamide* (4a) (112 mg, 55%), m.p. 157—162 °C, identical with an authentic sample.

Reduction of Compound (6a) *with Sodium Borohydride.*—Sodium borohydride (38 mg) was added portionwise to a cooled solution of compound (6a) (100 mg) in methanol (2 ml) with stirring. After 10 min, the mixture was filtered and the filtrate was diluted with chloroform. The chloroform solution was worked up as above to give the *amide* (4a) (55 mg, 64.5%), m.p. 164—167 °C (from isopropyl alcohol). The i.r. spectrum of this product was identical with that of an authentic sample.

3-Ethoxy-5-methyl-4-phenyl-1,2,5-thiadiazolium Fluoroborate (8).—A mixture of the mesoionic compound (6a) (768 mg) and triethyloxonium fluoroborate [16] (1.4 g) in dichloromethane (10 ml) was stirred at room temperature for 30 min. Evaporation yielded a solid, which was recrystallised from benzene–ethanol to afford the *thiadiazolium fluoroborate* (8) (712 mg, 58%) as leaflets, m.p. 134—137 °C (Found: C, 43.05; H, 4.45; N, 8.95. $C_{11}H_{13}BF_4N_2OS$ requires C, 42.9; H, 4.25; N, 9.1%), δ [$(CD_3)_2CO$] 1.4 (3 H, t, *J* 7 Hz, OCH_2-*Me*), 4.45 (3 H, s, NMe), 4.7 (2 H, q, *J* 7 Hz, OCH_2Me), and 7.5—8.0 (5 H, m, Ph).

5-Methyl-3-methylamino-4-phenyl-1,2,5-thiadiazolium Fluoroborate (9).—Methylamine solution (30% in ethanol) (260 mg) in acetonitrile (2 ml) was added to a cooled solution of the ethoxy-compound (8) (308 mg) in acetonitrile (3 ml). The mixture was allowed to stand at room temperature for 24 h. After evaporation, addition of cyclohexane to the chilled solution gave a precipitate. Recrystallisation from isopropyl alcohol afforded the *methylamino-compound* (9) (92 mg, 31%) as needles, m.p. 174—177 °C (Found: C, 41.2; H, 4.25; N, 14.2. $C_{10}H_{12}BF_4N_3S$ requires C, 41.0; H, 4.15; N, 14.35%), δ [$(CD_3)_2CO$] 3.05 (3 H, d, *J* 5 Hz, NH*Me*), 4.3 (3 H, s, NMe), 6.6—7.1 (1 H, broad peak, N*H*Me), and 7.7 (5 H, s, Ph), *m/e* 191 (*M* − $MeBF_4$, base peak).

Thanks are due to Mr. M. Morikoshi for mass spectral measurements and to Mr. H. Hori for microanalyses.

[0/999 *Received*, 27*th June*, 1980]

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