Journal of Organometallic Chemistry, 50 (1973) 113–119

REACTIONS OF 2,2-DIALKYL-1-OXA-3-AZA-2-STANNACYCLOPENTANES AND 2,2-DIALKYL-1,3-DIAZA-2-STANNACYCLOPENTANES WITH CARBON DISULFIDE AND PHENYL ISOTHIOCYANATE

SHIZUYOSHI SAKAI*, YOJI FUJIMURA and YOSHIO ISHII

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Chikusa-ku, Nagoya, 464 (Japan)

(Received June 27th, 1972)

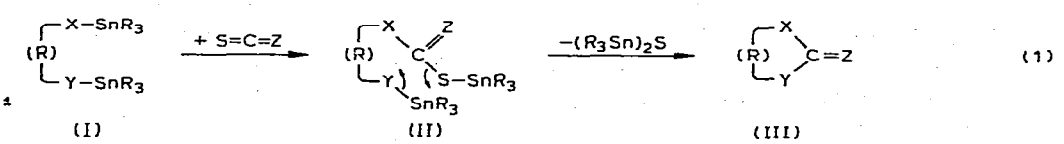
SUMMARY

Contrary to the reaction of 2,2-dialkyl-1-oxa-3-aza-2-stannacyclopentane with carbon disulfide at room temperature which yields oxazolidine-2-thione and dialkyltin sulfide, the reaction of *N*-substituted 2,2-dialkyl-1-oxa-3-aza-2-stannacyclopentane gave a stable 1/1 adduct of carbon disulfide across the Sn–N bond at 0°, and afforded a mixture of thiazolidine-2-thione and oxazolidine-2-thione at moderate reaction temperature. Phenyl isothiocyanate reacted with 3-methyl-2,2-dibutyl-1-oxa-3-aza-2-stannacyclopentane to form 2-phenylimino-1,3-thiazolidine and -oxazolidine. The unusual effect of *N*-methyl substituent in the dialkyl-1-oxa-3-aza-2-stannacyclopentane is reported.

1,3-Dimethyl-2-dibutyl-1,3-diaza-2-stannacyclopentane reacted with carbon disulfide at 0° to give *N*,*N'*-dimethylimidazolidine-2-thione and a small amount of the 1/2 adduct which could not be converted to the imidazolidine-2-thione but to an insoluble matter by heating it *in vacuo* at 150°.

INTRODUCTION

The unusual high reactivity of bis(trialkylstannyl) derivatives of diols, mercaptoalkanols, alkanolamine, and diamines toward carbon disulfide or isothiocyanates to afford a cyclic thiocarbonyl or iminocarbonyl compound and bis(trialkyltin) sulfide was previously demonstrated[1–3].



(1)

(I) (II) (III)

X,Y=O,S, or NR'; Z=S or NR"

* Present address: Department of Industrial Chemistry, Faculty of Engineering, Shizuoka University, Hamamatsu, 430 (Japan).

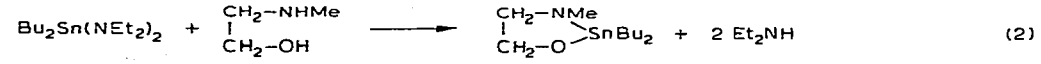
In reaction (1), we assumed that the formation of an intermediate compound such as (II) followed by the elimination reaction of bis(trialkylstannyl) sulfide may have led to the cyclic compound (III).

In this paper, we report the reaction of carbon disulfide or isothiocyanate with 2,2-dialkyl-1-oxa-3-aza-2-stannacyclopentane or 2,2-dialkyl-1,3-diaza-2-stannacyclopentane. The reactions of 2,2-alkyl-1-oxa-3-aza-2-stannacyclopentane and of *N*-substituted analogues were compared in the present investigation.

RESULTS AND DISCUSSIONS

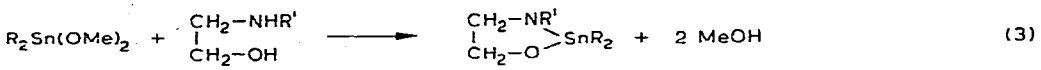
Preparations of 2,2-dialkyl-1-oxa-3-aza-2-stannacyclopentane

The transamination reaction of bis(diethylamino)dibutyltin with 2-(methylamino)ethanol to afford 3-methyl-2,2-dibutyl-1-oxa-3-aza-2-stannacyclopentane was successful, as was reported in the preparation of 2,2-dibutylstanna-1,3-diaza-2-stannacyclopentane[4].



(2)

Mehrotra and Gupta reported that the reaction between dialkoxydialkyltin and glycol yielded cyclic dialkoxydialkyltin and alcohols[5]. We found that the treatment of ethanolamines with dimethoxydibutyltin or dimethoxydiethyltin at 100° followed by distillation of the reaction mixture gave 2,2-dibutyl- or 2,2-diethyl-1-oxa-3-aza-2-stannacyclopentane in 10–79% yield. Some amounts of the viscous distillation residue showed the same IR spectrum as the corresponding 1-oxa-3-aza-2-stannacyclopentane, suggesting the formation of the polymeric 1-oxa-3-aza-2-stannacyclopentane homologue.

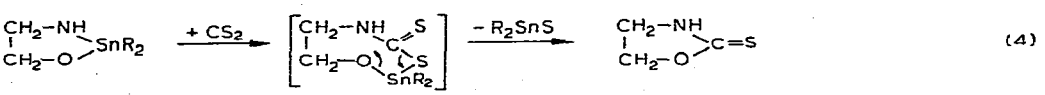


(3)

In general[6], amino–tin compounds react with alcohols or amines to form alkoxy–tin compounds or other amino–tin compounds as in the case of the reaction (2). However, the nitrogen–tin bonds could be derived from the organotin methoxide and aminoalkanols [reaction (3)].

Reaction of cyclic dialkyltin(IV) compounds

The reaction of 2,2-dialkyl-1-oxa-3-aza-2-stannacyclopentanes with carbon disulfide at 110° has been reported to yield dialkyltin sulfide and diethylene orthocarbonate in good yield, the latter being formed via ethylene thionocarbonate[7]. Carbon disulfide reacted exothermically with 2,2-dibutyl- or 2,2-diethyl-1-oxa-3-aza-2-stannacyclopentane [(IVa) or (IVb)] at room temperature, giving dialkyltin sulfide and 1,3-oxazolidine-2-thione (VI) in moderate yields.



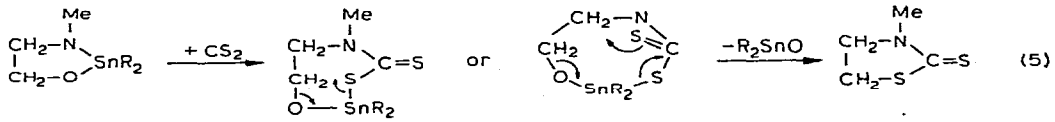
(4)

(IVa); R=Bu
(IVb); R=Et

(V) (VI)

In the reaction of the unsubstituted dialkyl-1-oxa-3-aza-2-stannacyclopentane [(IVa) or (IVb)], dialkyltin sulfide was eliminated from the 1/1 adduct, and it is suggested that the elimination reaction takes place through a transition state such as (V), analogously in the reaction of 2,2-dialkyl-1-oxa-3-aza-2-stannacyclopentane[7,8].

On the other hand, the reaction of the *N*-methyl-substituted derivative [(IVc) or (IVd)] with carbon disulfide at 60° gave 3-methyl-1,3-thiazolidine-2-thione (VIII) through reaction path (5), accompanied by the formation of small amounts of 3-methyl-1,3-oxazolidine-2-thione (N–Me-VI).



(IVc); R=Et
(IVd); R=Bu

(VII a) (VII b) (VIII)

In the reaction path (5), dialkyltin oxide should be obtained, but it could not be detected because excess amounts of carbon disulfide were used to exclude the reaction of thiocarbonyl group in the thiazolidine-2-thione with dialkyltin oxide, which reacted preferentially with carbon disulfide to be converted to dialkyltin sulfide[9].

The results of reaction of the substituted 1-oxa-3-aza-2-stannacyclopentanes and carbon disulfide are summarized in Table 1.

TABLE 1

REACTION OF 2,2-DIALKYL-1-OXA-3-AZA-2-STANNACYCLOPENTANES WITH CARBON DISULFIDE

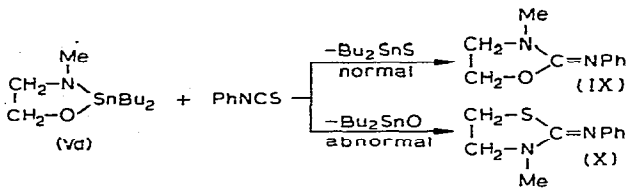
Reactant	*Reaction conditions*		*Product yields* (%)	
	Temp. (°C)	*Time* (*h*)	*Oxazolidinethione*	*Thiazolidinethione*
(IVa)	R.t.	5–6	60(VI)	
(IVb)	R.t.	5–6	73(VI)	
(IVc)	40–60	3	22[N–Me-(VI)]	48(VIII)
(IVd)	60	10	< 5[N–Me-(VI)]	80(VIII)

Carbon disulfide reacted exothermally with the *N*-substituted 1-oxa-3-aza-2-stannacyclopentanes (IVc), (IVd). When the reaction temperature was kept below 10° and the reaction mixture was cooled, a stable insertion product [(VII); R = Et] of carbon disulfide across a tin–nitrogen bond in (IVc) was obtained, which showed ν(NCS) bands at 1485 and 1385 cm^{-1} in the IR spectrum. However, any stable adduct of the unsubstituted 1-oxa-3-aza-2-stannacyclopentane (IVa) or (IVb) and carbon disulfide could not be isolated. The effects of *N*-methyl substituent in these reactions were of great interest, but the mechanisms of these effects are not clear as yet.

In the reaction of 3-methyl-2,2-dibutyl-1-oxa-3-aza-2-stannacyclopentane with excess amounts of carbon disulfide, 3-methyl-1,3-oxazolidine-2-thione was hardly formed (see Table 1), but in the equimolar reaction of carbon disulfide in

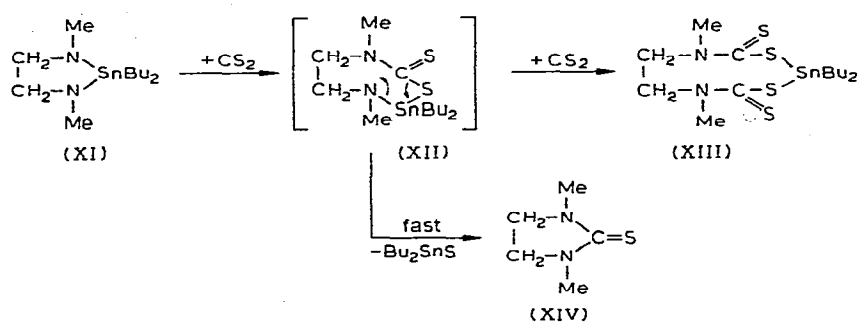
carbon tetrachloride, 3-methyl-1,3-thiazolidine-2-thione (VIII) was formed in the first stage of the reaction, while 3-methyloxazolidine-2-thione appeared mainly in the latter stage.

The unusual elimination products were also obtained in the reaction of 3-methyl-2,2-dibutyl-1-oxa-3-aza-2-stannacyclopentane (Vd) and phenyl isothiocyanate to give a mixture of 2-(phenylimino)oxazolidine (IX) and -thiazolidine (X), which were isolated and identified as picrates.



(6)

1,3-dimethyl-2,2-dibutyl-1,3-diaza-2-stannacyclopentane (XI) prepared *in situ* reacted violently with carbon disulfide at 0° to the 1/2 adduct [(XIII); 3%], 1,3-dimethyl-1,3-diaza-2-stannacyclopentane [(XIV); 89%] and dibutyltin sulfide.



(7)

The 1/2 adduct (XIII) was heated *in vacuo* for 3 h at 150°, to afford an insoluble product in ordinary organic solvents, which gave the same elementary analyses as (XIII), suggesting that the soluble 1/2 adduct would convert a polymeric structure by heating and that the cyclic thiourea (XIV) would be formed from the 1/1 adduct (XII).

EXPERIMENTAL

Melting points and boiling points were not corrected. NMR and IR spectra were recorded on a JEOL C-60HL spectrometer and a JASCO DS-403G spectrometer, respectively. All reactions and measurements of spectra were performed in dry nitrogen and in strictly dried solvents. 2,2-Dibutyl-1,3-diaza-2-stannacyclopentane was prepared by the method reported by Yoder and Zuckerman[4]. Bis(diethylamino)dibutyltin, and dimethoxydialkyltin compounds were prepared by the usual methods[6,10,11].

Reaction of dimethoxydibutyltin with 2-aminoethanol

Equimolar amounts of dimethoxydibutyltin and 2-aminoethanol were added

to a distillation flask equipped with nitrogen inlet, stirrer, condenser and drying tube, and gradually heated to 10° for a few hours. Then, the reaction mixture was distilled *in vacuo*, giving 2,2-dibutyl-1,3-diaza-2-stannacyclopentane (IVa) in a 10% yield; b.p. 106–109°/0.3 mm. (Found: C, 40.98: H, 7.98. $C_{10}H_{23}ONSn$ calcd.: C, 41.16; H, 7.89%.) IR ($CHCl_3$): ν(N–H) 3400 and ν(C–O) 1050 cm^{-1}. NMR ($CHCl_3$): τ 6.35 (CH_2–O, t, 5.3 Hz), 7.25 (CH_2–N, t, 5.3 Hz), 7.9 (NH, br, s) and ≈8.7 (Et–Sn, m).

Reaction of bis(diethylamino)dibutyltin with 2-(methylamino)ethanol

Equimolar quantities (each 40 mmoles) of bis(diethylamino)dibutyltin and 2-(methylamino)ethanol were added to the distillation flask. The reactants were heated with stirring under nitrogen atmosphere for a few hours at 110°, and diethylamine was distilled off. The mixture was distilled *in vacuo*, affording 3-methyl-2,2-dibutyl-1,3-diaza-2-stannacyclopentane in a 54% yield; b.p. 150–152°/0.3 mm. (Found: C, 43.99; H, 8.44; N, 4.72. $C_{11}H_{25}NOSn$ calcd.: C, 43.38; H, 8.18; N, 4.58%.) IR ($CHCl_3$): ν(C–O) 1050 cm^{-1}. NMR ($CHCl_3$): τ 6.18 (CH_2–O, t, 5.0 Hz), 7.36 (CH_2–N, t, 5.0 Hz), 7.57 (CH_3–N, s) and ≈9 (Bu–Sn, br, m).

Reaction of 2,2-butyl-1-oxa-3-aza-2-stannacyclopentane (IVa) with CS_2

The 1-oxa-3-aza-2-stannacyclopentane (IVa) and excess amounts of CS_2 were mixed under nitrogen atmosphere and kept for several hours at room temperature, to separate the crystals of 1,3-oxazolidine-2-thione (VI) in a 60% yield; m.p. (CCl_4): 97.5–98.5° (lit.[11] 98–99°). (Found: C, 34.83; H, 4.85; S, 31.23. C_3H_5ONS calcd.: C, 34.95; H, 4.85; S, 31.07%.) IR (KBr): ν(NH) 3200, ν(NCS) 1530, 1290 and ν(C=S) 1170 cm^{-1}. NMR ($CHCl_3$): τ 6.16 (CH_2–N, t, 9.0 Hz), and 5.23 (CH_2–O, t, 9.0 Hz).

Reaction of 2,2-diethyl-1-oxa-3-aza-2-stannacyclopentane (IVb) with CS_2

An excess amount of CS_2 was allowed to react (IVb) (2.35 g, 10 mmoles) for several hours at room temperature. The crystals were separated from the reaction mixture by cooling in a refrigerator in a 73% yield; m.p. 96–98°; its IR and NMR spectra were the same as those of pure 1,3-oxazolidine-2-thione mentioned above.

Reaction of 3-methyl-2,2-diethyl-1-oxa-3-aza-2-stannacyclopentane (IVc) with CS_2

The 3-methyl-1-oxa-3-aza-2-stannacyclopentane [(IVc); 1.0 g; 4 mmoles] was slowly added to an excess amount of CS_2 (5 g) below 10°, kept at 5° for several hours, and filtered, giving the 1/1 adduct (VII) in a 29% yield; m.p. 107–109°. (Found: C, 29.42; H, 5.31. $C_8H_{17}ONSn$ calcd.: C, 29.54; H, 5.21%.) IR (KBr): ν(NCS) 1485, 1385, ν(C–O) 1060 and ν(Sn–S) 365 cm^{-1}. NMR ($CHCl_3$): τ ≈ 8.9(Et–Sn, m), 6.52 (CH_3–H, s) and 6.03 (br, s, NCH_2CH_2O).

On the other hand, when the mixture of 3-methyl-1-oxa-3-aza-2-stannacyclopentane [(IVc); 1.0 g; 4 mmoles] and CS_2 (5 g) was heated for 4 h at 60° and distilled, diethyltin sulfide (75% yield; b.p. 95–100°/0.7 mm; ν(Sn–S) 312 cm^{-1}) and the mixture (b.p. 110–113°/0.7 mm) of 3-methyloxazolidine-2-thione (22% yield) and 3-methylthiazolidine-2-thione (48% yield) were obtained. The ratio of these products was calculated from their peak area in the NMR spectrum. The isolations and identifications of the pure products are given below.

Reaction of 3-*methyl*-2,2-*dibutyl*-1-*oxa*-3-*aza*-2-*stannacyclopentane* (*IVd*) *with* CS_2

(*A*). *Reaction without solvent.* Carbon disulfide (5.0 g; 70 mmoles) was added to the distillation flask which contained the 3-methyl-1-oxa-3-aza-2-stannacyclopentane [(IVd); 6.6 g; 22 mmoles] and which was equipped with a condenser, a nitrogen inlet and receivers. Then, heat evolution was observed. The reaction mixture was kept for 10 h at 60°, and distilled, giving 3-methyl-1,3-thiazolidine-2-thione [(VIII); 84% yield] contaminated by small amounts of 3-methyl-1,3-oxazolidine-2-thione; b.p. 130–132°/0.6 mm. Recrystallization of the crude products from toluene/n-hexane mixture gave pure 3-methylthiazolidin-2-thione (VIII); m.p. 69.5–70.5°. IR ($CHCl_3$): ν(NCS) 1503, and ν(C=S) 1108 cm^{-1}. NMR ($CHCl_3$): τ 6.73 (CH_3–N, s), 6.58 (CH_2–S, t, 7.5 Hz) and 5.85 (CH_2–N, t, 7.5 Hz); MS (*m/e*) parent peak 133. IR and NMR spectra coincided well with those of the authentic sample[13].

(*B*). *Reaction in carbon tetrachloride.* Equimolar amounts of CS_2 were added to the solution of the 3-methyl-1-oxa-3-aza-2-stannacyclopentane [(IVd); 20 vol %] in CCl_4 at room temperature. The reaction mixture showed the band of ν(NCS) at 1490 and 1390, ν(C=S) at 1190 and ν(C–O) at 1065 cm^{-1} in the IR spectrum and the peaks at $\tau \approx 8.6$ (Bu–Sn, m), 6.54 (CH_3–N, br, s) and 6.12 (OCH_2CH_2N, br, s) in the NMR spectrum, indicating the formation of the 1/1 adduct of CS_2 across a Sn–N bond in (IVd). Then, the reaction mixture was heated for 16 h at 80°, and filtered to separate crystals formed, from which 3-methylthiazolidine-2-thione [(VIII); 40% yield] and 3-methyloxazolidine-2-thione (30% yield) were obtained by fractional recrystallizations. The IR and NMR spectra of the latter were the same as those of an authentic sample[13]. The filtrate was distilled, giving liquid dibutyltin sulfide in an 85% yield; b.p. 150–170°/0.8 mm; IR ν(Sn–S) 355 cm^{-1}.

Reaction of 3-*methyl*-2,2-*dibutyl*-1-*oxa*-3-*aza*-2-*stannacyclopentane* (*IVd*) *with phenyl isothiocyanate*

Phenyl isothiocyanate (1.4 g; 10.4 mmoles) was slowly added to the flask containing the 3-methyl-1-oxa-3-aza-2-stannacyclopentane (IVd) at ice-bath temperature, where heat evolution was observed. The reaction mixture was distilled, affording the mixture (b.p.: 125–128°/0.5 mm) of 2-(phenylimino)-1,3-thiazolidine (29% yield) and 2-(phenylimino)-1,3-oxazolidine (23% yield), the composition of which was determined by the NMR spectrum of the distillate. However, isolation by crystallization or by column chromatography failed, so small amounts of picric acid were added to the solution of the reaction mixture in ethanol, and the picrates were isolated by fractional recrystallizations.

2-(Phenylimino)-1,3-thiazolidine (X): IR (CCl_4): ν(C=N) 1625 cm^{-1}; NMR ($CHCl_3$) τ 7.26 (CH_3–N, s), 7.23 (CH_2–S, t, 6.0 Hz) and $\approx$3 (Ph, m). Its picrate: m.p. 135.5–137°; IR (KBr) ν(C=N) 1638 cm^{-1}. (Found: C, 45.62; H, 3.36; N, 16.35. $C_{16}H_{15}O_7N_5S$ calcd.: C, 45.61; H, 3.56; N, 16.63%.) NMR and IR spectra coincided well with those of authentic sample prepared by Dains' method[14].

2-(Phenylimino)-1,3-oxazolidine (IX): IR (CCl_4): ν(C=N) 1680 cm^{-1}; NMR ($CHCl_3$) τ 7.33 (CH_3–N, s), 6.92 (CH_2–N, t, 7.5 Hz), 5.86 (CH_2–O, t, 7.5 Hz) and $\approx$3 (Ph, m). Its picrate: m.p.: 171–173°; IR (KBr) ν(C=N) 1694 cm^{-1}. (Found: C, 47.22; H, 3.76; N, 16.92. $C_{16}H_{15}O_8N_5$ calcd.: C, 47.41; H, 3.70; N, 17.28%.)

Reaction of 1,3-*dimethyl*-2,2-*dibutyl*-1,3-*diaza*-2-*stannacyclopentane* (*XI*) *with* CS_2

The mixture of bis(diethylamino)dibutyltin (4.7 g; 15 mmoles) and *N,N'*-

dimethylethylenediamine (1.3 g; 15 mmoles) was slowly added, and diethylamine was slowly distilled off in nearly quantitative yield. 1,3-dimethyl-2,2-dibutyl-1,3-diaza-2-stannacyclopentane (XI) thus prepared *in situ* was cooled to 0°, an excess amount (5 g) of CS_2 was added dropwise, and heat evolution occurred violently. The mixture was kept for several hours below 5°, and filtered to separate the fine solid, which was the 1/2 adduct (XIII); yield 3%; m.p. 216–218°. (Found: C, 35.86; H, 6.23. $C_{14}H_{28}N_2S_4Sn$ calcd.: C, 35.67; H, 5.94%.) IR (KBr): ν(NCS) 1483, 1390, 1625, ν(C=S) 1190, ν(C–S) 685 and ν(Sn–S) 360 cm^{-1}. NMR ($CHCl_3$): $\tau \approx 8.7$ (Bu–Sn) 6.58 (CH_3–N, br, s) and 5.78 (CH_2–N, br, s), which was heated *in vacuo* (0.1 mm) for 3 h at 150°, to insoluble polymer showing the same IR spectrum. (Found: C, 36.22; H, 6.23. $C_{14}H_{28}N_2S_4Sn$ calcd. C, 35.67; H, 5.94%.)

The filtrate was kept in a refrigerator at 0°, and filtered to afford needle crystals of ethylene thiourea (XIV) in an 89% yield; m.p. 109–111°; IR (KBr) ν(NCS) 1510, 1325, 1285 and ν(C=S) 1110 cm^{-1}; NMR ($CHCl_3$) τ 6.95 (CH_3–N, s) and 6.45 (CH_2–N, s), which coincided well with those of an authentic sample[2].

REFERENCES

1 S. Sakai, Y. Kiyohara, K. Itoh and Y. Ishii, *J. Org. Chem.*, 35 (1970) 2347.
2 S. Sakai, Y. Asai, Y. Kiyohara, K. Itoh and Y. Ishii, *Organometal. Chem. Syn.*, 1 (1970/1971) 45.
3 S. Sakai, H. Niimi and Y. Ishii, *J. Organometal. Chem.*, 25 (1970) C23.
4 C. H. Yoder and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 88 (1966) 4831.
5 R. C. Mehrotra and V. D. Gupta, *J. Organometal. Chem.*, 4 (1965) 145.
6 K. Jones and M. F. Lappert, *J. Organometal. Chem.*, 3 (1965) 295; *J. Chem. Soc.*, (1965) 1944.
7 S. Sakai, Y. Fujimura and Y. Ishii, *J. Org. Chem.*, 35 (1970) 2344.
8 S. Sakai, Y. Kobayashi and Y. Ishii, *J. Org. Chem.*, 36 (1971) 1176.
9 W. T. Reichle, *Inorg. Chem.*, 1 (1962) 650.
10 G. P. Mack, *U.S. Pat.* 2745820; *Chem. Abstr.*, 51 (1957) 6219.
11 G. S. Sasin, *J. Org. Chem.*, 18 (1953) 1142.
12 M. G. Ettlinger, *J. Amer. Chem. Soc.*, 72 (1950) 4792.
13 T. C. Owen, *J. Chem. Soc. C*, (1967) 1373.
14 F. D. Deins, *J. Amer. Chem. Soc.*, 44 (1922) 1637.