Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

EXCHANGE REACTIONS OF ORGANOTIN CARBOXYLATES*

A. DAVID COHEN** AND CLYDE R. DILLARD

Department of Chemistry, Brooklyn College of the City University of New York, Brooklyn, N.Y. 11210 (U.S.A.)

(Received July 8th, 1970)

SUMMARY

Triorganotin carboxylates were found to react with diorganotin dichlorides according to the following reactions:

$$R_2SnCl_2 + R'_3Sn(OOCR'') \rightarrow R_2SnCl(OOCR'') + R'_3SnCl$$

$$R_2SnCl_2 + 2\,R'_3Sn(OOCR'') \rightarrow R_2Sn(OOCR'')_2 + 2\,R'_3SnCl$$

($R = CH_3$ or C_6H_5; $R' = CH_3$, C_6H_5 or n-C_4H_9 and $R'' = CH_3$, CH_2Cl, or C_6H_5).

In addition, reaction of $R_2SnCl(OOCR'')$ with $R'_3Sn(OOCR'')$ in a 1/1 mole ratio was found to give $R_2Sn(OOCR'')_2$.

These reactions were followed by use of NMR techniques as well as by isolation of the products. These reactions afford a convenient method for the synthesis of diorganotin halide carboxylates and diorganotin dicarboxylates. The scope of these reactions as well as the IR spectra of the products are discussed.

INTRODUCTION

Redistribution or exchange reactions of electronegative groups X and Y (X or Y = mono- or bidentate ligand) between diorganotin(IV) compounds, equation (1), are of considerable synthetic utility:

$$R_2SnX_2 + R_2SnY_2 \rightarrow 2\,R_2SnXY \qquad (1)$$

For example, this type of reaction has been used to synthesize dibutyltin halide acetates[1-3], dialkyltin halide methoxides[3], dialkyl-[4] and diphenyltin[5] chloride 8-hydroxyquinolinates, dialkyltin halide hydrides[6-8], dimethyltin halide acetates[9], dimethyltin halide tropolonates[10], and dimethyltin halide dithiocarbamates[11].

However, attempts to prepare compounds of the type (p-XC_6H_4COO)-$SnCl(CH_3)_2$, ($X = H$, Cl, CH_3O or CH_3), *via* the above type of reaction, were unsuccessful. When the reactions were run in either chloroform or benzene, the only

---

[*] Presented in part at the 158th National Meeting of the American Chemical Society, New York, N.Y., September 1969.

[**] Taken from a thesis submitted by A.D.C. to The City University of New York in partial fulfillment of the requirements of the Ph.D. degree, February, 1970.

pure product obtained was $(p\text{-}XC_6H_4COO)_2Sn(CH_3)_2$. Attempts to prepare dimethyltin chloride benzoate using other methods[12-14] were also unsuccessful. To determine whether the isolation of only $(p\text{-}XC_6H_4COO)_2Sn(CH_3)_2$ was due merely to its insolubility relative to $(p\text{-}XC_6H_4COO)SnCl(CH_3)_2$, mixtures of methyltin chlorides and methyltin carboxylates were examined by means of NMR spectroscopy. In the course of these studies a hitherto unreported reaction system was discovered and several new compounds were prepared.

EXPERIMENTAL

NMR spectra were recorded in $CDCl_3$ with a Varian Associates A-60A spectrometer, using tetramethylsilane as an internal standard. IR spectra were recorded as KBr disks or nujol mulls using Beckman IR-10 or Perkin–Elmer 21 spectrophotometers.

Dimethyltin oxide, dimethyltin dichloride, diphenyltin dichloride, trimethyltin chloride, triphenyltin chloride, and triphenyltin acetate were obtained from M & T Chemicals, Inc. The melting points of these compounds, after recrystallization from a suitable solvent, agreed with literature values. Trimethyltin chloroacetate[15], triphenyltin benzoate[16], and trimethyltin benzoate were synthesized according to the interfacial polymerization technique[16].

Tin was determined gravimetrically as SnO_2 by degrading the compounds in H_2SO_4 according to the method of Okawara, Webster and Rochow[17] as modified by Okawara and Wada[18]. Microanalyses (C, H and Cl) were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

NMR studies

Solutions were prepared by dissolving methyltin chlorides and methyltin carboxylates in amounts which gave the desired mole ratio of reactants in $CDCl_3$. The concentrations of the final solutions ranged from 5–13%. The mixtures were transferred to sample tubes, TMS added as internal standard, and the spectra were

TABLE 1

NMR EVIDENCE FOR EXCHANGE BETWEEN METHYLTIN CHLORIDES AND METHYLTIN BENZOATES[a]

Composition of mixture	Mole ratio	SnC_2 species		SnC_3 species	
		τ^b	J^c	τ^b	J^c
R_2SnCl_2/R_3SnCl[d]	1/1	8.78	69.2	9.33	58.8
$R_2SnCl_2/R_3Sn(OOCR')$[e]	1/1	8.83	77.5	9.34	59.2
$R_2SnCl_2/R_3Sn(OOCR')$	1/2	8.86	82.9	9.34	59.6
$R_3SnCl/R_2Sn(OOCR'')_2$[f]	1/1	8.88	83.7	9.35	59.2
R_2SnCl_2	Pure compound	8.80	68.9		
R_3SnCl	Pure compound			9.35	57.8
$R_3Sn(OOCR')$	Pure compound			9.37	58.7
$R_2Sn(OOCR'')_2$	Pure compound	8.88	83.8		
$R_2SnCl(OOCR)$	Pure compound	8.88	76.5		

[a] In $CHCl_3$ or $CDCl_3$. [b] TMS = 10 ppm. [c] $J(^{119}Sn\text{–}C\text{–}H)$, in Hz. [d] $R = CH_3$. [e] $R' = C_6H_5$. [f] $R'' = p\text{-}CH_3OC_6H_4$.

obtained. Typical results are shown in Table 1. The observed reactions were essentially complete within the time of preparation of the samples because no changes in the spectra were observed after standing at room temperature for considerable periods of time.

Syntheses via exchange reactions

Since, in every case, the conditions were similar, details will be given only for those exchange reactions which involved new compounds.

Dimethyltin chloride chloroacetate. A solution of 0.85 g (3.9 mmoles) dimethyltin dichloride in 5 ml benzene was added to a hot solution of 1.00 g (3.9 mmoles) trimethyltin chloroacetate in 10 ml benzene. Evaporation of a portion of the solvent and cooling the mixture yielded 0.77 g (72%) of small, colorless squares of crude dimethyltin chloride chloroacetate, m.p. 122–125°. This compound was also prepared, in a yield of 90%, by reaction of dimethyltin dichloride with dimethyltin bis(chloroacetate) in a 1/1 mole ratio, equation (1), m.p. 126.5–128°. (Found: C, 17.79; H, 3.13; Cl, 25.16; Sn, 42.86. $C_4H_8Cl_2O_2Sn$ calcd.: C, 17.30; H, 2.91; Cl, 25.53; Sn, 42.74%.) NMR spectral data: $J(^{119}Sn{-}C{-}H)$ 74.8 Hz; $\tau(Sn{-}CH_3)$ 8.83; $\tau(OOCCH_2Cl)$ 5.20.

Dimethyltin bis(chloroacetate). A solution of 0.42 g (1.95 mmoles) dimethyltin dichloride and 1.00 g (3.9 mmoles) trimethyltin chloroacetate in 11 ml benzene was concentrated by evaporation. Cooling to room temperature yielded 0.49 g (76%) of dimethyltin bis(chloroacetate), m.p. 166–168°; lit.[19] 162–165°. The NMR spectrum of this product was very nearly the same as that obtained for pure dimethyltin bis(chloroacetate) synthesized from dimethyltin oxide and chloroacetic acid; $J(^{119}Sn{-}C{-}H)$ 81.5 Hz; $\tau(Sn{-}CH_3)$ 8.88; $\tau(OOCCH_2Cl)$ 5.87.

Dimethyltin chloride chloroacetate with trimethyltin chloroacetate. A solution of 0.54 g (1.95 mmoles) dimethyltin chloride chloroacetate and 0.50 g (1.95 mmoles) trimethyltin chloroacetate in 11 ml benzene was concentrated and cooled to room temperature to yield 0.51 g (78%) of dimethyltin bis(chloroacetate), m.p. 166–168°; lit.[19] 162–165°.

Attempted reverse reaction. A solution of 0.50 g (1.49 mmoles) dimethyltin bis(chloroacetate) and 0.89 g (4.47 mmoles) trimethyltin chloride in 5 ml benzene was concentrated and cooled to yield 0.35 g of crude dimethyltin bis(chloroacetate), m.p. 155–160°; lit.[19] 162–165°. The NMR spectrum of this product showed the presence of a small amount of trimethyltin chloride (τ 9.37). There was no evidence of $(CH_3)_3Sn(OOCCH_2Cl)$ or of $(CH_3)_2SnCl_2$.

Diphenyltin chloride benzoate. A solution of 1.21 g (3.5 mmoles) diphenyltin dichloride in 10 ml ligroin was added to a solution of 1.00 g (3.5 mmoles) trimethyltin benzoate in 15 ml ligroin. Removal of about 18 ml of solvent under vacuum and cooling in the freezer overnight yielded 1.33 g (88%) of a white powder of diphenyltin chloride benzoate, m.p. 71.5–73°. After recrystallization from ligroin the m.p. was 72.2–73.5°. (Found: C, 52.84; H, 3.77; Cl, 8.52; Sn, 27.53. $C_{19}H_{15}ClO_2Sn$ calcd.: C, 53.13; H, 3.53; Cl, 8.25; Sn, 27.64%.)

Diphenyltin dibenzoate. A solution of 1.21 g (3.5 mmoles) diphenyltin dichloride in 10 ml ligroin was added to a solution of 2.00 g (7.0 mmoles) trimethyltin benzoate in 30 ml ligroin. The solvent was removed under vacuum until crystallization began. Cooling resulted in 1.32 g (73%) of diphenyltin dibenzoate, m.p. 115–119°. Two recrystallizations from ligroin with a minimum of heating afforded small white crystals, m.p. 116–118.5°; lit.[20] 116–117°. (Found: C, 60.64; H, 4.12; Sn, 23.10. $C_{26}H_{20}O_4Sn$ calcd.: C, 60.62; H, 3.92; Sn, 23.04%.)

Dimethyltin chloride acetate. A solution of 1.07 g (4.9 mmoles) dimethyltin dichloride and 2.00 g (4.9 mmoles) triphenyltin acetate in 21 ml chloroform was concentrated and cooled to room temperature. This procedure yielded 0.91 g (77%) of dimethyltin chloride acetate, m.p. 182–184°; lit.[9] 185–186°. The IR and NMR spectra of this product were superimposable with the corresponding spectra of authentic dimethyltin chloride acetate; $J(^{119}Sn\text{–}C\text{–}H)$ 75.5 Hz; $\tau(Sn\text{–}CH_3)$ 8.90; $\tau(OOCCH_3)$ 7.88.

Dimethyltin diacetate. The NMR spectrum of a freshly prepared solution containing 0.53 g (2.45 mmoles) dimethyltin dichloride and 2.00 g (4.9 mmoles) triphenyltin acetate in 15 ml chloroform showed a chemical shift and coupling constant of the $(CH_3)_2Sn$ moiety corresponding to dimethyltin diacetate[21,22]. However, after evaporation of some solvent and cooling in the freezer, 0.12 g of crude dimethyltin chloride acetate was obtained, m.p. 178–179°; lit.[9] 185–186°. Vacuum distillation of the filtrate afforded a mixture of dimethyltin diacetate and triphenyltin chloride.

Reaction of dimethyltin dichloride with triphenyltin benzoate. A solution of 0.46 g (2.1 mmoles) dimethyltin dichloride and 2.00 g (4.25 mmoles) triphenyltin benzoate in 10 ml chloroform/hexane (1/3, v/v) was stirred until all solids dissolved. The solvent was removed under vacuum until crystallization began. This procedure yielded 0.99 g of white crystals, m.p. 88–115°. The filtrate was evaporated and recrystallized from chloroform/hexane (1/1, v/v) to yield 0.23 g of colorless crystals, m.p. 88–130°. Both crops were shown, by NMR spectroscopy, to be a mixture of dimethyltin dibenzoate and triphenyltin chloride. Attempts to separate the two products by vacuum sublimation were not successful.

RESULTS AND DISCUSSION

Typical results of the NMR studies are shown in Table 1, where data for the pure compounds are also included for comparison. From Table 1 it is seen that, for a mixture of R_2SnCl_2 and R_3SnCl in a 1/1 mole ratio, there was no significant change in the chemical shifts and tin–methyl coupling constants of the respective species compared to the individual compounds. However, the NMR spectrum of a solution containing $(CH_3)_2SnCl_2$ and $(CH_3)_3Sn(OOCC_6H_5)$ in a 1/1 mole ratio showed values for τ and J associated with five-coordinate dimethyltin halide chelates[4,9–11]. When the mole ratio of reactants was increased to 1/2, respectively, the τ and J values corresponded to six-coordinate dimethyltin bis(chelates)[11,21,22]. Moreover, the values observed for the latter system were practically identical with those of a solution containing R_3SnCl and $R_2Sn(OOCR'')_2$ in a 1/1 mole mixture, also shown in Table 1.

These results indicate that triorganotin carboxylates react with diorganotin dichlorides according to the following equations:

$$R_2SnCl_2 + R'_3Sn(OOCR'') \rightarrow R_2SnCl(OOCR'') + R'_3SnCl \qquad (2)$$

$$R_2SnCl_2 + 2\,R'_3Sn(OOCR'') \rightarrow R_2Sn(OOCR'')_2 + 2\,R'_3SnCl \qquad (3)$$

Reaction (2) occurs when $R_2SnCl_2/R'_3Sn(OOCR'')$ is in a 1/1 mole ratio while reaction (3) occurs when $R_2SnCl_2/R'_3Sn(OOCR'')$ is in a 1/2 mole ratio. Both reactions were essentially complete within seconds after mixing as shown by the immediate change in the chemical shift and coupling constant of the dimethyltin species.

Large scale reactions in which the products were isolated confirm the above reaction sequence. In addition, diorganotin chloride carboxylates were found to react with triorganotin carboxylates according to equation (4),

$$R_2SnCl(OOCR'')+R'_3Sn(OOCR'') \rightarrow R_2Sn(OOCR'')_2+R'_3SnCl \qquad (4)$$

The various systems studied and the compounds obtained are listed in Table 2.

TABLE 2

RESULTS OF EXCHANGE REACTIONS

R	R'	R''	moles $R'_3Sn(OOCR'')$/ moles R_2SnCl_2	Products
CH_3	CH_3	C_6H_5	1	$(CH_3)_2Sn(OOCC_6H_5)_2$
CH_3	CH_3	$ClCH_2$	1	$(CH_3)_2SnCl(OOCCH_2Cl)$
CH_3	n-C_4H_9	C_6H_5	1	$(CH_3)_2Sn(OOCC_6H_5)_2$
CH_3	C_6H_5	CH_3	1	$(CH_3)_2SnCl(OOCCH_3)$
C_6H_5	CH_3	C_6H_5	1	$(C_6H_5)_2SnCl(OOCC_6H_5)$
CH_3	CH_3	C_6H_5	2	$(CH_3)_2Sn(OOCC_6H_5)_2$
CH_3	CH_3	$ClCH_2$	2	$(CH_3)_2Sn(OOCCH_2Cl)_2$
CH_3	C_6H_5	CH_3	2	$(CH_3)_2Sn(OOCCH_3)_2$[a]
CH_3	C_6H_5	C_6H_5	2	$(CH_3)_2Sn(OOCC_6H_5)_2$[a]
C_6H_5	CH_3	C_6H_5	2	$(C_6H_5)_2Sn(OOCC_6H_5)_2$

[a] Unable to separate completely from triphenyltin chloride.

The results of the analysis of the new compounds listed in Table 2 are described in the experimental section. The properties of products which are known compounds agreed with reported data except for the cases of $(CH_3)_2Sn(OOCCH_3)_2$ and $(CH_3)_2Sn(OOCC_6H_5)_2$ prepared by the reactions of dimethyltin dichloride with triphenyltin acetate and triphenyltin benzoate, respectively. It was not possible to completely separate triphenyltin chloride from these two products. Otherwise, the IR spectra of the various products confirmed the absence of starting materials or impurities.

Although the NMR studies of solutions containing dimethyltin dichloride and various triorganotin benzoates in a 1/1 mole ratio indicated the existence of a five-coordinate dimethyltin species in solution, all attempts to isolate $(CH_3)_2SnCl(OOCC_6H_5)$ were unsuccessful. Reactions of dimethyltin chloride with either trimethyl- or tri-n-butyltin benzoate according to equation (2) afforded impure dimethyltin dibenzoate only.

Attempts to reverse equations (2–4) by addition of a large excess of R'_3SnCl to either $R_2SnCl(OOCR'')$ or to $R_2Sn(OOCR'')_2$ showed no evidence for reaction. In the investigation of an analogous reaction between dimethyl- and trimethylsilicon moieties, shown in equation (5), an equilibrium constant of 1.9×10^3 was found[23].

$$(CH_3)_2SiCl_2+2\,(CH_3)_3Si(OCH_3) \rightarrow (CH_3)_2Si(OCH_3)_2+2\,(CH_3)_3SiCl \qquad (5)$$

The failure to observe a reverse reaction in the organotin system suggests that

TABLE 3

RELEVANT INFRARED FREQUENCIES OF $(CH_3)_2SnCl_n(OOCR)_{2-n}$
In cm^{-1}.

$n=0$; $R=CH_2Cl$		$n=1$; $R=CH_2Cl$		$n=1$; $R=CH_3$[a]		$n=0$; $R=C_6H_5$		Assignments
KBr disk	$CHCl_3$ 5% soln.	KBr disk	$CHCl_3$ 3% soln.	KBr disk	$CHCl_3$ 1% soln.	KBr disk	$CHCl_3$ 2% soln.	
						1602 s	1608 s	ν(CC)
1611 s	1633 vs (br)	1583 vs (br)	1632 s	1564 vs	1596 s	1560 s	1568 s	Asym. CO_2 str.
						1547 s		
						1492 w	1493 w	ν(CC)
1406 s	1410 s	1410 s	1408 s	1410 s	1405 s	1406 s (sh)		CH_2 scissor
1376 vs (br)	1361 vs	1397 s (br)	1371 s	1455 s	1383 vs	1371 vs	1358 vs	Sym. CO_2 str.
				1413 m				
931 vw	934 w	937 vw	947 vw (sh)			939 vw		CH_2 rock
783 s	[b]	789 s	[b]					CCl str.
669 m (sh)	[b]	678 w	[b]	685 m	[b]	680 m	[b]	CO_2 scissor
588 m	580 w	578 w	565 w	578 m	528 m	589 vw	572 vw	Asym. SnC_2 str.
533 w	525 w	524 w	523 w	528 w	527 w	539 vw (sh)	526 vw	Sym. SnC_2 str.
		330 m[c]		326 s[c]	348 m			SnCl str.
					320 s			

[a] Data taken from ref. 11. [b] Region masked by solvent. [c] Nujol mull between CsBr plates; this work.

the equilibrium constants of equations (2–4) are also large. Hence, with the possible exception of dialkyltin chloride benzoate, these reactions afford a convenient method for the synthesis of diorganotin halide carboxylates and diorganotin dicarboxylates.

IR spectra

The principal bands in the IR spectra of the new compounds prepared are shown in Tables 3 and 4. The preparation of diphenyltin dibenzoate has been recently reported[20], however, no spectral data was given. Assignments of infrared bands were made in analogy to published studies[24–32] and by comparison with the spectra of the respective sodium carboxylates.

TABLE 4

RELEVANT INFRARED FREQUENCIES OF DIPHENYLTIN BENZOATES
In cm^{-1}.

$(C_6H_5)_2Sn(OOCC_6H_5)_2$		$(C_6H_5)_2SnCl(OOCC_6H_5)$		Assignments
KBr disk	$CHCl_3$ satd. soln.	KBr disk	$CHCl_3$ 2.5% soln.	
1596 vs	1605 s	1598 s	1601 m	ν(CC)
1546 vs (br)	1567 s	1547 s	1547 s	Asym. CO_2 str.
1497 s	1493 s	1495 w	1493 w	φ semicircle str.
1483 s	1482 w	1481 m	1481 m	ν(CC)
1392 vs (br)	1361 vs	1377 s	1388 s (br)	Sym. CO_2 str.
1307 m	1305 m	1308 w	1306 w	ν(CC)
1071 m	1070 w	1070 m	1073 w	β(CH)
717 vs	[a]	718 vs	[a]	φ(CC)
688 vs	[a]	689 s	[a]	Sym. CO_2 deform.
531 w	521 vw		523 vw	CO_2 rock
		317 m[b]		Sn–Cl str.

[a] Region masked by solvent. [b] Nujol mull between CsBr plates.

Inspection of Tables 3 and 4 shows that the asymmetric COO stretching vibrations increase while the symmetric COO stretching vibrations decrease in going from the solid to solution. The direction of the shifts and the positions of the frequencies observed signify a structural rearrangement involving bridging carboxyl groups in the solid state and chelated carboxyl groups in solution, similar to that observed for dialkyltin diacetates[21,22]. The only exception is the case of $(C_6H_5)_2SnCl(OOCC_6H_5)$, which shows the same position for the asymmetric frequency and an increase in the symmetric frequency in going from the solid to solution. This suggests a different structure for diphenyltin chloride benzoate in solution compared to the other organotin carboxylates studied.

The presence of two bands due to the SnC_2 asymmetric and symmetric stretching vibrations in the IR spectra of the dimethyltin compounds (Table 3) indicates that the C–Sn–C moiety is not linear. These observations are in agreement with the results of studies of dimethyltin bis(chelates)[4,10,11,21,22,33] and dimethyltin halide chelates[4,9–11].

ACKNOWLEDGEMENTS

We thank the City University of New York for financial assistance (to A.D.C.) and M & T Chemicals, Inc. for a gift of organotin compounds.

REFERENCES

1 A. K. Sawyer and H. G. Kuivila, *Chem. Ind. (London)*, (1961) 260.
2 D. L. Alleston and A. G. Davies, *J. Chem. Soc.*, (1962) 2050.
3 A. G. Davies and P. G. Harrison, *J. Chem. Soc., C*, (1967) 298.
4 K. Kawakami and R. Okawara, *J. Organometal. Chem.*, 6 (1966) 249.
5 A. H. Westlake and D. F. Martin, *J. Inorg. Nucl. Chem.*, 27 (1965) 1579.
6 A. K. Sawyer, J. E. Brown and E. L. Hanson, *J. Organometal. Chem.*, 3 (1965) 464.
7 W. P. Neumann and J. Pedain, *Tetrahedron Lett.*, (1964) 2461.
8 K. Kawakami, T. Saito and R. Okawara, *J. Organometal. Chem.*, 8 (1967) 377.
9 Y. Maeda, C. R. Dillard and R. Okawara, unpublished observations.
10 K. Komura, T. Tanaka and R. Okawara, *Inorg. Chim. Acta*, 2 (1968) 321.
11 M. Honda, M. Komura, Y. Kawasaki, T. Tanaka and R. Okawara, *J. Inorg. Nucl. Chem.*, 30 (1968) 3231.
12 R. Okawara and E. G. Rochow, *J. Amer. Chem. Soc.*, 82 (1960) 3285.
13 M. Wada, M. Shindo and R. Okawara, *J. Organometal. Chem.*, 1 (1963) 95.
14 H. Rubin, M. S. Thesis, Brooklyn College, 1965.
15 P. B. Simons and W. A. G. Graham, *J. Organometal. Chem.*, 10 (1967) 457.
16 M. Frankel, D. Gertner, D. Wagner and A. Zilkha, *J. Organometal. Chem.*, 9 (1967) 83.
17 R. Okawara, D. E. Webster and E. G. Rochow, *J. Amer. Chem. Soc.*, 82 (1960) 3287.
18 R. Okawara and M. Wada, *J. Organometal. Chem.*, 1 (1963) 81.
19 A. Saitow, E. G. Rochow and D. Seyferth, *J. Org. Chem.*, 23 (1958) 116.
20 W. T. Reichle, *J. Organometal. Chem.*, 18 (1969) 105.
21 Y. Maeda, C. R. Dillard and R. Okawara, *Inorg. Nucl. Chem. Lett.*, 2 (1966) 197.
22 Y. Maeda and R. Okawara, *J. Organometal. Chem.*, 10 (1967) 247.
23 K. Moedritzer and J. R. Van Wazer, *Inorg. Chem.*, 6 (1967) 93.
24 C. R. Dillard and L. May, *J. Mol. Spectrosc.*, 14 (1964) 250.
25 Y. Kawasaki, M. Hori and K. Uenaka, *Bull. Chem. Soc. Jap.*, 40 (1967) 2463.
26 D. H. Lohmann, *J. Organometal. Chem.*, 4 (1965) 382.
27 J. H. S. Green, W. Kynaston and A. S. Lindsey, *Spectrochim. Acta*, 17 (1961) 486.
28 D. H. Whiffen, *J. Chem. Soc.*, (1965) 1350.
29 A. R. Katritzky and P. Simons, *J. Chem. Soc.*, (1959) 2051.
30 A. R. Katritzky and N. A. Coats, *J. Chem. Soc.*, (1959) 2062.
31 A. R. Katritzky and R. A. Jones, *J. Chem. Soc.*, (1959) 3674.
32 R. Okawara and H. Sato, *J. Inorg. Nucl. Chem.*, 16 (1961) 204.
33 J. Otera, Y. Kawasaki and T. Tanaka, *Inorg. Chim. Acta*, 1 (1967) 294.