

The first step is rapid with a small value for K and hence

$$-\frac{d[\text{Fe}(\text{CN})_6^{3-}]}{dt} = K k_2 [\text{Fe}(\text{CN})_6^{3-}] [\text{OH}^-] [\text{CH}_3\text{COCOO}^-]$$

The free radical formed in step (2) is rapidly oxidised in alkaline medium to acetic (step 3) and oxalic acid (step 4) anions.

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Synthesis of Trimethylantimony(V) Dicarboxylates, Amides & Oximates

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Trimethylantimony dicarboxylates, amides and oximates have been prepared by a metathetical reaction of trimethylantimony(V) dibromide with the corresponding carboxylic acid, succinimide, benzimidazole or an oxime. The compounds have been characterised on the basis of analytical, IR and conductance data. Insecticidal and bactericidal behaviour of some representative compounds have also been examined.

IN contrast to a large number of studies on triarylantimony dicarboxylates, very few corresponding trialkylantimony(V) derivatives have been studied¹⁻⁵. Moreover, no trialkylantimony(V) diamide or oximate has so far been reported^{6,7}. We have recently reported synthesis, reactions and biocidal activities of a number of triarylantimony(V) dicarboxylates⁸, amides⁶, oximates⁷. We report here the preparation and biocidal activities of a number of trimethylantimony(V) dicarboxylates, amides and oximates.

Reaction of a benzene solution of trimethylantimony dibromide with two equivalents of an acid, succinimide, a benzimidazole or an oxime in the presence of triethylamine yields the corresponding trimethylantimony(V) derivatives (Eq. 1).

All the reactions proceed under mild conditions and are generally quantitative. The new derivatives are stable under aerobic conditions and monomeric in freezing benzene. Molar conductance values of 10⁻³M solutions of the complexes in acetonitrile range between 15 and 19 ohm⁻¹ cm² mol⁻¹ at 30° indicating their non-ionic character⁹.

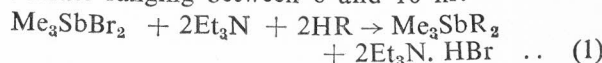
These products were soluble in organic solvents such as acetone, chloroform, and benzene, but insoluble in water.

The infrared spectra were recorded in KBr/nujol in the region 4000-400 cm⁻¹ on a Perkin-Elmer spectrophotometer. All the carboxylates and succinimide derivatives show a medium to very strong band around 1650 cm⁻¹ due to "ester-like" CO-group. The νC = N in trimethylantimony dioximates is observed at ~ 1600 cm⁻¹ as a weak to medium intensity band.

The PMR spectrum (recorded on a Bruker 60 instrument at the University of Guelph, Ontario, Canada) of Me₃Sb (OOCCH₂Ph)₂ shows a multiplet centered at 7.20 δ (due to Ph, 10H) and two singlets at 3.43 δ (due to -CH₂, 4H) and 1.73 δ (due to Me, 9H). The Me singlet remains unaffected even at -60°C which excludes the presence of non-equivalent methyl groups provided the exchange rates of the bonding groups are low enough. Thus the, most likely structure for these compounds is the trigonal-bipyramidal one, where two unidentate groups bond to Sb from the apical directions and the methyl groups occupy the equatorial positions.

Insecticidal activity -- A few representative compounds at two concentrations (0.1% and 0.5% in acetone) were employed against the adult cockroaches with the help of microsyringe in 3/4 abdominal segment¹⁰.

The control was done with parathion. The mean knock-down values for parathion and acetone were 4 and 40 hr respectively. It was observed that the values for the compounds VI, VIII and X are quite moderate ranging between 8 and 10 hr.



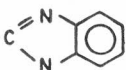
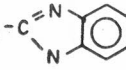
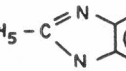
- I, R = OOCCH₂C₆H₅
- II, R = OOCCH=CHC₆H₅
- III, R = OOCCH=CHCH₃
- IV, R = OOH
- V, R = OOCCH₂CH(CH₃)₂
- VI, R = N $\begin{matrix} \text{CO}-\text{CH}_2 \\ | \\ \text{CO}-\text{CH}_2 \end{matrix}$
- VII, R = H-C $\begin{matrix} \text{N} \\ / \quad \backslash \\ \text{C} \quad \text{C} \\ \backslash \quad / \\ \text{N} \end{matrix}$ 
- VIII, R = CH₃-C $\begin{matrix} \text{N} \\ / \quad \backslash \\ \text{C} \quad \text{C} \\ \backslash \quad / \\ \text{N} \end{matrix}$ 
- IX, R = C₂H₅-C $\begin{matrix} \text{N} \\ / \quad \backslash \\ \text{C} \quad \text{C} \\ \backslash \quad / \\ \text{N} \end{matrix}$ 
- X, R = ON = C $\begin{matrix} \text{CH}_3 \\ | \\ \text{C} \\ | \\ \text{CH}_3 \end{matrix}$
- XI, R = ON = C $\begin{matrix} \text{CH}_3 \\ | \\ \text{C} \\ | \\ \text{C}_2\text{H}_5 \end{matrix}$
- XII, R = ON = C $\begin{matrix} \text{CH}_3 \\ | \\ \text{C} \\ | \\ \text{C}_6\text{H}_4\text{NO}_2(p) \end{matrix}$

TABLE 1 — ANALYTICAL AND m.p. DATA OF TRIMETHYLANTIMONY DICARBOXYLATES, IMIDES AND OXIMATES

Sl. No. (see Eq. 1)	m.p. (°C)	Found (Calc.), %		
		C	H	N
I	63	52.00 (52.20)	5.15 (5.30)	—
II	120	54.18 (54.69)	4.84 (5.02)	—
III	58–60	39.04 (39.20)	5.42 (5.68)	—
IV	63–65	23.12 (23.27)	4.08 (4.31)	—
V	165–68	45.22 (45.36)	7.68 (7.86)	—
VI	116–17	36.22 (36.39)	4.70 (4.72)	7.71 (7.720)
VII	115	50.50 (50.90)	4.66 (4.77)	13.84 (13.97)
VIII	80	53.00 (53.17)	5.28 (5.40)	12.96 (13.06)
IX	141	55.10 (55.16)	5.80 (5.95)	11.96 (12.15)
X	147	33.98 (34.75)	6.56 (6.80)	8.89 (9.01)
XI	220(d)	38.58 (38.96)	7.28 (7.43)	8.08 (8.26)
XII	112	43.06 (43.28)	4.72 (4.77)	10.56 (10.63)

Antibacterial activity — The method developed by Varma and Imam¹¹ was employed for the determination of antibacterial spectrum of the compounds of Table 1 against the two organisms; *Bacillus subtilis* and *Sorsena-lutea*. The compounds VII and XI act as strong inhibitors against these two organisms.

Trimethylantimony dibromide was prepared by adding bromine (1 mol) to an ethereal solution of Me₃Sb (1 mol) at 0°C (ref. 12).

A typical experiment is described below, other details are given in Table 1.

Trimethylantimony dibromide (4 mmol), the ligand (carboxylic acid, succinimide, benzimidazole or oxime) (8 mmol) and Et₃N (2 ml) were stirred together in benzene (25 ml) at room temperature for 2 hr. The reaction mixture was refluxed (~ 1 hr) to ensure completion of the reaction, Et₃N.HBr was filtered off and the filtrate on concentration *in vacuo* afforded the product which was recrystallised from pet. ether (40–60°C) or acetonitrile/pet. ether. Often oily product was obtained which solidified on scratching with a glass rod and cooling.

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Cu(II) & Ni(II) Complexes with a Tetradentate Schiff Base Derived from 2-Hydroxynaphthaldehyde & Ethylenediamine

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Copper(II) and nickel(II) complexes of a tetradentate schiff base derived from 2-hydroxynaphthaldehyde and ethylenediamine have been obtained as crystalline solids. Analytical, magnetic moment, UV-visible, infrared, molar conductance and mass spectral data are presented in support of the structures of the complexes.

MUCH work has been reported on the transition metal complexes of tetradentate schiff bases derived from suitably substituted aromatic carbonyl compounds and a number of diamines, such as ethylenediamine and propylenediamine¹⁻⁶. However very little work appears to have been done on the metal complexes of polynuclear aromatic schiff bases. One of the available works⁷ suggests the formation of N,N'-ethylenebis-(2-hydroxy-1-naphthalaldiminato)copper(II) and N,N'-trimethylenebis-(2-hydroxy-1-naphthalaldiminato)copper(II) complexes during an attempted preparation of copper(II) mixed chelates from dibasic schiff base, glycine-hydroxynaphthaldehyde, copper acetate and appropriate diamine (ethylenediamine and trimethylenediamine respectively). We now report the direct preparation of N,N'-[bis(1-naphthalyl)ethylenediminato]copper(II), (1) and N,N'-[bis(1-naphthalyl)ethylenediminato]nickel(II), (2) complexes from the pre-formed schiff base and their characterisation based on analytical and spectral (UV-visible, IR and mass) data.

The schiff base was prepared by condensing ethylenediamine with 2-hydroxy-1-naphthaldehyde in 1:2 molar ratio in ethyl alcohol under refluxing condition (30 min) and crystallised from DMF as shining yellow plates, m.p. 283° [Found : C, 78.5; H, 5.5; N, 8.1. C₂₄H₂₀O₂N₂ requires C, 78.2; H, 5.5; N, 7.6%]; MS; *m/e* 368 (M⁺).

Copper(II) complex (1) was prepared by refluxing (1 hr) a mixture of the schiff base and cupric acetate monohydrate in ethanol at pH 6-7 (adjusted

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