NOTES

The Reaction of Dialkyltin Dichlorides with α-Nitroso-β-naphthol

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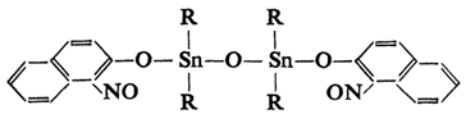
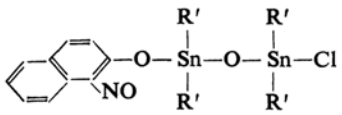
Dialkyltin dichlorides react with 8-hydroxyquinoline at the mole ratio of 1:2 to give dialkyltin bis(8-hydroxyquinolinates),[1,2] and with 2,2'-bipyridyl and 1,10-phenanthroline at the mole ratio of 1:1 to give dialkyltin(2,2'-bipyridyl) dichlorides and dialkyltin(1,10-phenanthroline) dichlorides[2,3] respectively. From these facts, bidentate ligand molecules, KeH, with protonating hydrogen had been expected to react with dialkyltin dichlorides to give the compounds of the R_2SnKe_2 type, compounds which might have the chelate structure containing a hexa-coordinated tin atom.

Such an expectation does not, however, seem to be true in the case of α-nitroso-β-naphthol, which reacted with dimethyltin dichloride under similar conditions to give tetramethyl-1,3-bis(α-nitroso-β-naphthoxy)distannoxane, $[(C_{10}H_6NO_2)(CH_3)_2Sn]_2O$ (Ia), but not dimethyltin bis(α-nitroso-β-naphtholate), $(CH_3)_2Sn(C_{10}H_6NO_2)_2$. Diethyltin dichloride also gave the corresponding distannoxane (Ib). On the other hand, under similar conditions, di-*n*-propyltin and di-*n*-butyltin dichlorides gave tetraalkyl-1-(α-nitroso-β-naphthoxy)-3-chlorodistannoxanes, $(C_{10}H_6NO_2)R'_2SnOSnR'_2Cl$ (II).



(Ia) $R=CH_3$
(Ib) $R=C_2H_5$



(IIa) $R'=n\text{-}C_3H_7$
(IIb) $R'=n\text{-}C_4H_9$

The infrared spectra of these distannoxanes I and II in the potassium bromide region are shown in Fig. 1, together with that of α-nitroso-β-naphthol. It was previously found by the present authors and by others that a

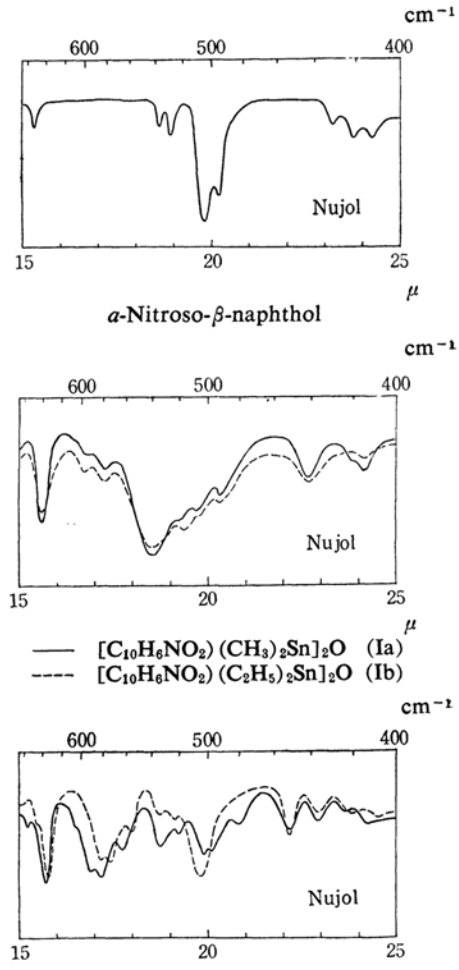
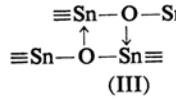


Fig. 1. Infrared spectra of α-nitroso-β-naphthol and its distannoxane derivatives.

1) D. Blake, G. E. Coates and J. M. Tate, *J. Chem. Soc.*, **1961**, 756.
2) T. Tanaka, M. Komura, Y. Kawasaki and R. Okawara, *J. Organometal. Chem.*, **1**, 484 (1964).
3) D. L. Alleston and A. G. Davies, *J. Chem. Soc.*, **1962**, 2050.

broad band near 600 cm^{-1} would be associated with the Sn–O–Sn stretching vibration in dimeric distannoxanes (III).[4,5] Although this



(III)

characteristic band has here been observed in the two compounds shown in I, the Sn–O–Sn stretching vibration in the compounds of II was observed at a lower frequency and with a different shape. Considering these spectra, the association of the latter two compounds in the solid state may be different from that of the former. The presence of the chelate structure in these compounds is, however, not yet obvious from the results of the present investigation.

Experimental

Materials.—Dialkyltin dichlorides supplied by the Nitto Kasei Company were purified either by sublimation or by recrystallization from ligroin or petroleum ether. α-Nitroso-β-naphthol was obtained commercially and checked with the melting point.

The Reaction of Dialkyltin Dichlorides with α-Nitroso-β-naphthol.—Into a solution of 1.0 g. (0.006 mol.) of α-nitroso-β-naphthol and 0.66 g. (0.003 mol.) of dimethyltin dichloride in 25 ml. of methanol, 6 ml. of 1 N ammonium hydroxide in methanol was slowly stirred in over a period of about one hour. During an additional three hours of stirring, a yellow precipitate gradually appeared, and the solution changed from dark green to brown. The precipitate was then filtered off, repeatedly washed with benzene, and dried under reduced pressure. Yield, 90%. M. p.>230°C. Found: C, 44.09; H, 3.73; Sn, 35.84. Calcd. for $[(C_{10}H_6NO_2)(CH_3)_2Sn]_2O$: C, 43.82; H, 3.68; Sn, 36.08%. This compound Ia was also obtained in almost the same yield by the reaction of dimethyltin dichloride with α-nitroso-β-naphthol at the mole ratio of 1 : 1. Similarly, diethyltin dichloride reacted with α-nitroso-β-naphthol to give a yellowish green precipitate. Recrystallization from a methanol-chloroform mixture (volume ratio 2 : 1) gave a dark brown crystalline compound (Ib). Yield, 70%. M. p. 163°C. Found: C, 47.04; H, 4.47; Sn, 32.92. Calcd. for $[(C_{10}H_6NO_2)(C_2H_5)_2Sn]_2O$: C, 47.11; H, 4.52; Sn, 33.25%. By a similar procedure with di-*n*-propyltin dichloride, a yellowish brown precipitate was obtained. Recrystallization from a dichloromethane-ligroin mixture gave a dark brown crystalline material (IIa). Yield, 40%. M. p. 159~160°C. Found: C, 41.60; H, 5.41; Sn, 37.61. Calcd. for $(C_{10}H_6NO_2)(C_3H_7)_2SnOSn(C_3H_7)_2Cl$: C, 41.72; H, 5.41; Sn, 37.48%. Di-*n*-butyltin dichloride gave a yellowish precipitate, which was recrystallized from methanol (IIb). Yield, 50%. M. p. 140~141°C. Found: C, 45.22; H, 6.04; Sn, 34.39. Calcd. for $(C_{10}H_6NO_2)(C_4H_9)_2SnOSn(C_4H_9)_2Cl$: C, 45.29; H, 6.14; Sn, 34.43%. The same compound was also prepared by the neutralization of the mixture of tetra-*n*-butyl-1,3-dichlorodistannoxane, $[(C_4H_9)_2ClSn]_2O$, and α-nitroso-β-naphthol at the mole ratio of 1 : 2 in methanol with 1 N ammonium hydroxide. This compound was identified by mixed melting point determination with the compound derived from di-*n*-butyltin dichloride.

Even when di-*n*-propyl and di-*n*-butyltin dichlorides were treated with a large excess of α-nitroso-β-naphthol and then neutralized, only the corresponding compounds of type II were obtained, not the compounds of type I.

Infrared Spectra.—The infrared spectra were taken in mulls in Nujol by a Hitachi EPI-2G grating infrared spectrophotometer.

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4) R. Okawara and M. Wada, *J. Organometal. Chem.*, **1**, 81 (1963); M. P. Brown, R. Okawara and E. G. Rochow, *Spectrochim. Acta*, **16**, 595 (1960).
5) R. C. Poller, *J. Inorg. Nucl. Chem.*, **24**, 593 (1962).