

PREPARATION AND PROPERTIES OF DIALKYL TIN NITRATE DERIVATIVES

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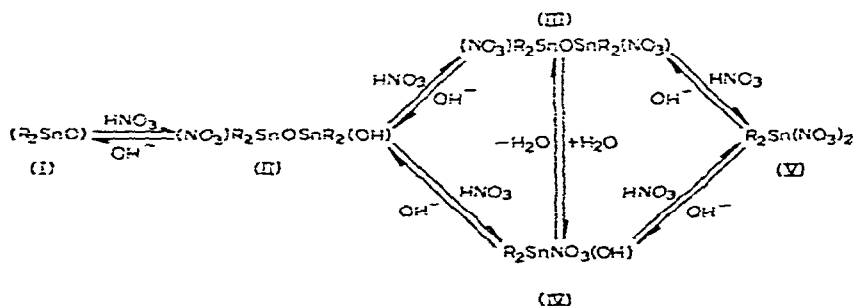
INTRODUCTION

Among the partial hydrolysis product of dialkyltin halides^{1,2} or pseudo-halides^{1,3} there are at least two types of fairly stable dimeric compounds which correspond to formulas (II) or (III). We have reported⁴ additional stable compounds, the dialkyltin hydroxide nitrates ($R = CH_3, C_2H_5$) having formula (IV) prepared by the reaction of dialkyltin oxides with nitric acid. This paper will report the preparation and properties of some dialkyltin nitrate derivatives, and will make clear their relationships. The important results obtained are given in the following reaction scheme.

EXPERIMENTAL

Preparation of dialkyltin nitrate hydroxide (IV) and dialkyltin dinitrate (V)

Di-n-propyltin hydroxide nitrate and its monohydrate. Di-n-propyltin oxide (10.0 g, 0.045 mole) was dissolved in a slight excess of nitric acid (0.053 mole) in acetone. The clear solution was evaporated at room temperature to give large crystals of $(n-C_3H_7)_2SnNO_3(OH) \cdot H_2O$, which were recrystallized from acetone containing a small amount of nitric acid, m.p. 183° (decomp.). (Found: C, 24.27; H, 5.82; N, 4.75; Sn, 39.30. $C_6H_{17}NO_5Sn$ calcd.: C, 23.87; H, 5.68; N, 4.64; Sn, 39.32 %.) The monohydrate was dehydrated in a desiccator over calcium chloride for several days to give $(n-C_3H_7)_2SnNO_3(OH)$. This change was followed by measuring the decrease in weight of the sample, and also by noting the disappearance of the band at 1640 cm^{-1} due to the bending vibration of the coordinated water molecule. M.p. 183° (decomp.). (Found: C, 24.97; H, 5.28; N, 4.90. $C_6H_{15}NO_4Sn$ calcd.: C, 25.38; H, 5.33; N, 4.93 %.)



Di-n-butyltin hydroxide nitrate (IV), di-n-butyltin dinitrate (V) and its dihydrate. Di-n-butyltin hydroxide nitrate, $(n\text{-C}_4\text{H}_9)_2\text{SnNO}_3(\text{OH})$ was obtained by the reaction of dibutyltin oxide (I) with an equivalent amount of nitric acid in benzene. M.p. $92.5\text{--}95^\circ$. (Found: C, 30.85; H, 6.21; Sn, 38.16. $\text{C}_8\text{H}_{18}\text{NO}_4\text{Sn}$ calcd.: C, 30.80; H, 6.14; Sn, 38.05 %.) When (I) was reacted with an equivalent amount of nitric acid in acetone the product was contaminated with $(n\text{-Bu})_2\text{Sn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ and unreacted (I). The X-ray powder pattern of the product was identical with that of the compound prepared in benzene, but the melting point range was wide and tin analysis of the products from several runs were not in agreement with the calculated value. When (I) was dissolved in acetone containing two equivalents of nitric acid, crystals of $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ were obtained, m.p. $83\text{--}87^\circ$. (Found: C, 24.63; H, 5.91; N, 6.96; Sn, 30.30. $\text{C}_8\text{H}_{22}\text{N}_2\text{O}_8\text{Sn}$ calcd.: C, 24.45; H, 5.64; N, 7.13; Sn, 30.21 %.) The X-ray diffraction pattern of this compound was clearly distinguishable from that of (IV). When this method was tried for the methyl, ethyl or n-propyl compounds, only $\text{R}_2\text{SnNO}_3(\text{OH})$ or the corresponding monohydrate was obtained even when an excess of nitric acid was used. On heating $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ under reduced pressure, $(n\text{-C}_4\text{H}_9)_2\text{Sn}(\text{NO}_3)_2$ (V) was obtained, m.p. $83\text{--}87^\circ$. (Found: Sn, 33.39. $\text{C}_8\text{H}_{18}\text{N}_2\text{O}_6\text{Sn}$ calcd.: Sn, 33.25 %.)

Preparation of tetraalkyl-1,3-dinitratodistannoxanes, (III)

In general, compounds (III) can be obtained by dehydrating compounds (IV) on heating under reduced pressure. The n-propyl and the n-butyl compounds are obtained more easily (10 mm Hg, 100° , 80° , respectively) compared to the methyl and the ethyl compounds (10 mm Hg, 200°). Properties of the products are summarized in Table I. All of these compounds were easily hydrolysed by atmospheric moisture.

TABLE I

TETRAALKYL-1,3-DINITRATODISTANNOXANES, (III)

R	M.p. ($^\circ\text{C}$)	% C Found (calcd.)	% H Found (calcd.)	% N Found (calcd.)	% Sn Found (calcd.)
CH_3	> 250				54.51 (54.26)
C_2H_5	214 (dec.)	19.34 (19.49)	4.05 (4.08)	5.33 (5.68)	48.34 (48.69)
$n\text{-C}_3\text{H}_7^a$	183 (dec.)	26.22 (26.22)	5.13 (5.13)	5.10 (5.10)	42.90 (43.18)
$n\text{-C}_4\text{H}_9$	92.5-95	32.52 (31.72)	6.02 (5.99)	4.26 (4.62)	39.05 (39.18)

^a The results of ebulliometric molecular weight determination in benzene are as follows: 1160, 1022 and 1052 at concentrations $[w(\text{sample})/w(\text{solvent})]$ 0.00666, 0.0101 and 0.02 respectively. Calcd. for $[\text{NO}_3(\text{n-Pr})_2\text{SnOSn}(\text{n-Pr})_2\text{NO}_3]_2$: 1100.

Preparation of tetraalkyl-1-nitrato-3-hydroxy distannoxanes, (II)

Dialkyltin hydroxide nitrate (IV) ($\text{R} = n\text{-C}_3\text{H}_7$, $n\text{-C}_4\text{H}_9$) was dissolved in aqueous acetone and titrated with NaOH. A typical titration curve is shown in Fig. 1. To prepare compounds (II), a slight excess of NaOH solution equivalent to a half mole

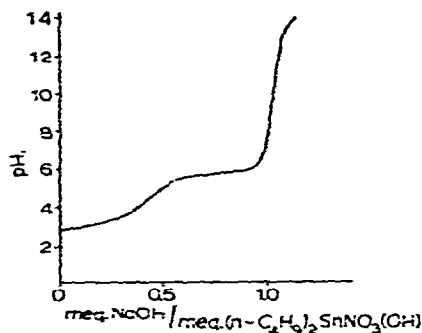


Fig. 1. Titration curve of $(n\text{-C}_4\text{H}_9)_2\text{SnNO}_3(\text{OH})$ with sodium hydroxide solution. When almost half equivalent of base was added, precipitation began to occur.

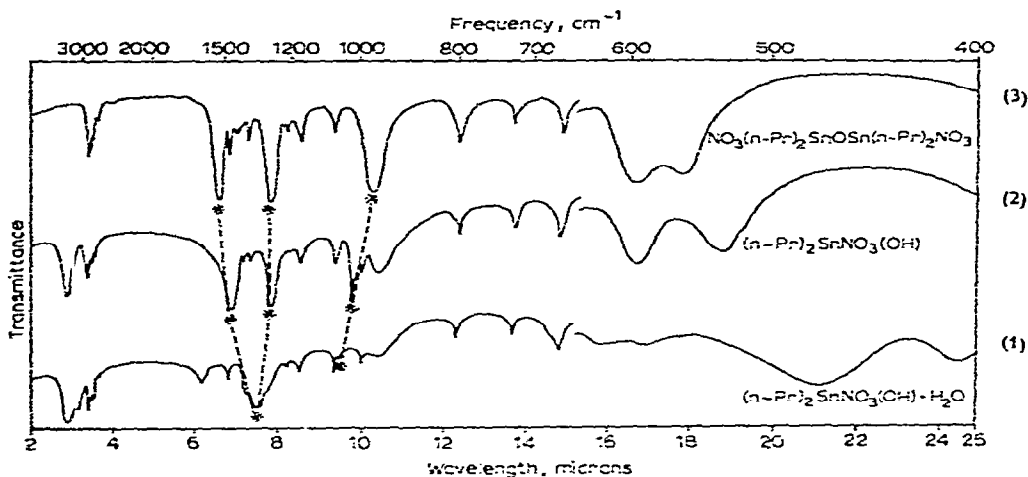


Fig. 2. Infrared spectra of tetra-*n*-propyl-1,3-dinitratodistannoxane, di-*n*-propyltin nitrate hydroxide and its monohydrate in Nujol or hexachlorobutadiene mulls. * NO_3 stretching vibration band.

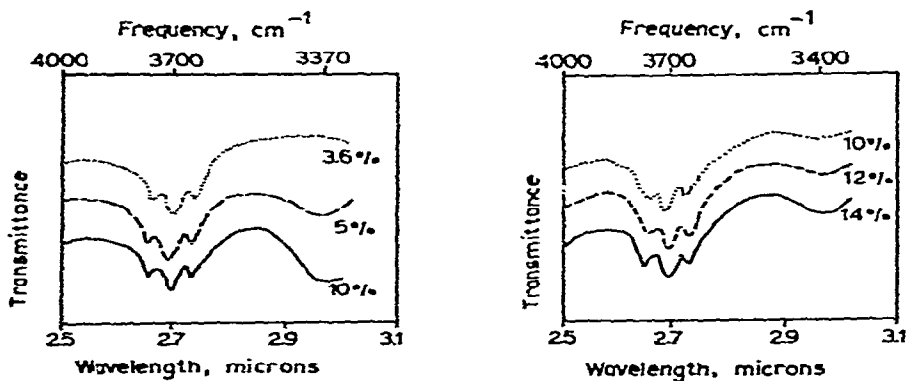


Fig. 3. Infrared spectra of $(n\text{-C}_4\text{H}_9)_2\text{SnNO}_3(\text{OH})$ in chloroform solution.

Fig. 4. Infrared spectra of $\text{Cl}(n\text{-C}_3\text{H}_7)_2\text{SnOSn}(n\text{-C}_3\text{H}_7)_2\text{Cl}$ in moist chloroform solution.

of (IV) was added to an aqueous acetone solution of (IV) to give a small amount of white precipitate (probably dialkyltin oxide). The filtrates, on evaporation, gave precipitates of $\text{NO}_3\text{R}_2\text{SnOSnR}_2\text{OH}$. $\text{R} = n\text{-C}_3\text{H}_7$; m.p. $221\text{--}222.5^\circ$ (decomp.) (Found: C, 28.63; H, 5.71; N, 2.81; Sn, 46.80. $\text{C}_{12}\text{H}_{29}\text{NO}_5\text{Sn}_2$ calcd.: C, 28.55; H, 5.79; N, 2.78; Sn, 47.03 %.) $\text{R} = n\text{-C}_4\text{H}_9$; m.p. $210\text{--}213^\circ$. (Found: Sn, 42.50. $\text{C}_{16}\text{H}_{37}\text{NO}_5\text{Sn}_2$ calcd.: Sn, 42.33 %).

Infrared spectra

The spectra in the solid state were obtained as mulls in nujol or hexachlorobutadiene. The spectra of the solutions were obtained using polyethylene or teflon film to protect the plates. Spectra are shown in Fig. 2 and 3. The positions and the tentative assignments of the relevant absorption bands are listed in Tables 2 and 3.

TABLE 2

RELEVANT INFRARED VIBRATIONAL FREQUENCIES OF TETRAALKYL-1,3-DINITRATODISTANNOXANES, (III)

Positions of bands in cm^{-1} .

$\text{R} = \text{CH}_3$	$\text{R} = \text{C}_2\text{H}_5$	$\text{R} = n\text{-C}_3\text{H}_7$	$\text{R} = n\text{-C}_4\text{H}_9$	Assignment
1524 s	1520 s	1520 s	1526 s } 1502 s }	NO_3 str.
1318 sh } 1280 s }	1283 s	1273 s	1276 s	NO_3 str.
989 s } 980 s }	985 s } 960 sh }	975 s	975 s	NO_3 str.
609 s	601 s	600 s	596 s	Sn-O str.
574 s	576 s	564 s	564 s	Sn-O str.

TABLE 3

RELEVANT INFRARED VIBRATIONAL FREQUENCIES OF DIALKYL TIN NITRATE HYDRONIDES, $\text{R}_2\text{SnNO}_3(\text{OH})$, (IV)

Positions of bands (in cm^{-1}).

$\text{R} = \text{CH}_3^3$ solid state	$\text{R} = \text{C}_2\text{H}_5^3$ solid state	$\text{R} = n\text{-C}_3\text{H}_7$ solid state	$\text{R} = n\text{-C}_4\text{H}_9$ solid state	CHCl_3 solution	Assignment
3390 s	3344 s	3430 s	3460 s	3700 m	O-H str.
1506 s	1493 s	1478 s	1479 s	1520 s	NO_3 str.
1287 s	1290 s	1280 s	1290 sh } 1278 s }	1280 s	NO_3 str.
994 s	994 s	1016 m	1017 m	975 s	NO_3 str.
530 s	517 s } 510 s }	597 s	586 s	594 s	Sn-O str.
403 s	413 s } 398 sh }	530 s	520 s	568 s	Sn-O str.

Titration of H_2O by Karl-Fischer reagent

Dialkyltin compounds having Sn-O bonds were titrated by Karl-Fischer reagent according to the method developed by Kushlefsky and Ross⁵. The results were as follows:

	Found	Calcd.	
	%	%	
$(n\text{-C}_3\text{H}_7)_2\text{Sn}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	8.5	9.2	$(2\text{H}_2\text{O})$
$(n\text{-C}_3\text{H}_7)_2\text{SnNO}_3(\text{OH}) \cdot \text{H}_2\text{O}$	11.8	11.9	$(2\text{H}_2\text{O})$
$(\text{C}_2\text{H}_5)_2\text{SnNO}_3(\text{OH})$	6.0	7.1	(H_2O)
$\text{Cl}(n\text{-C}_3\text{H}_7)_2\text{SnOSn}(n\text{-C}_3\text{H}_7)_2\text{Cl}$	4.3	3.6	(H_2O)

DISCUSSION

Qualitative estimation of the strength of coordination of NO_3 group to tin

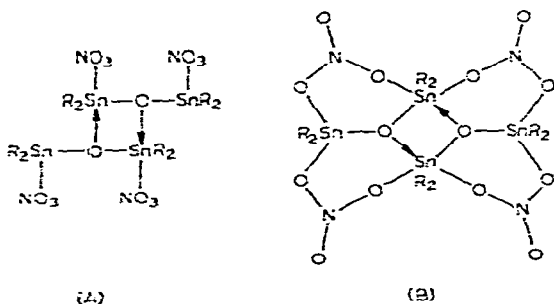
The infrared spectra of $(n\text{-Pr})_2\text{SnNO}_3(\text{OH}) \cdot \text{H}_2\text{O}$ (curve 1), $(n\text{-Pr})_2\text{SnNO}_3(\text{OH})$ (curve 2) and $\text{NO}_3(n\text{-Pr})_2\text{SnOSn}(n\text{-Pr})_2\text{NO}_3$ (curve 3) are shown in Fig. 2. In curve (1) the band at 1330 cm^{-1} is ascribed to the degenerate stretching of the NO_3 group having D_{3h} symmetry⁶ and a very weak band at 1040 cm^{-1} is ascribed to the infrared forbidden symmetric stretching mode. The appearance of the forbidden NO_3 symmetric stretching frequency may be due to the deformation of the ion in the molecular field of the crystals⁷.

On the other hand in the spectra of the other two compounds the degeneracy of the asymmetric frequency is removed and bands at $1480\text{--}1520$ and $\sim 1280\text{ cm}^{-1}$ are observed. Also the bands at $\sim 1040\text{ cm}^{-1}$ is much stronger. These changes suggest that the NO_3 group has C_{2v} symmetry in the latter cases⁶. Therefore the hydrate may contain an ionic nitrate as represented by the formula, $[(n\text{-Pr})_2\text{Sn}(\text{OH}) \cdot \text{H}_2\text{O}]^+\text{NO}_3^-$, while in $(n\text{-Pr})_2\text{SnNO}_3(\text{OH})$ and $\text{NO}_3(n\text{-Pr})_2\text{SnOSn}(n\text{-Pr})_2\text{NO}_3$, the NO_3 groups are coordinated to tin.

It can be seen in Fig. 2 that the degree of distortion of the NO_3 group as it assumes C_{2v} symmetry is reflected in the frequency shifts of the NO_3 stretching bands in going from the hydrate to the distannoxane. This suggests that the relative strengths of coordination of the NO_3 groups decrease in the order $\text{NO}_3\text{R}_2\text{SnOSnR}_2\text{NO}_3 > \text{R}_2\text{SnNO}_3(\text{OH}) > \text{R}_2\text{SnNO}_3(\text{OH}) \cdot \text{H}_2\text{O}$.

Structure of tetraalkyl-1,3-dinitratodistannoxane

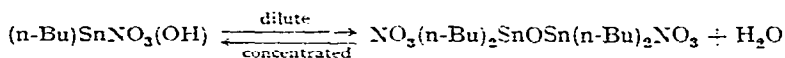
The relevant infrared frequencies of these compounds shown in Table 2 were selected by comparing the spectra with those of the corresponding halides. Molecular weight determinations in benzene show that the propyl compound is dimeric. The infrared spectra of these distannoxanes show a broad band near 600 cm^{-1} , which is the characteristic Sn-O-Sn stretching vibration of dimeric distannoxanes^{1,2,8}. These compounds must have a dimeric structure represented by (A) or (B) below.



In structure (A), there are two kinds of tin atoms, consequently there may be two different kinds of NO_3 groups on tin. In the cases of $(\text{R}_2\text{SnNCS})_2\text{O}^3$ and $[(\text{CH}_3)_3\text{SiOR}_2\text{Sn}]_2\text{O}^9$, the presence of two kinds of substituents have been confirmed by means of infrared spectra. On the other hand, the data of Table 2 indicate that only one kind of NO_3 group is present, although there are slight differences when the alkyl groups are methyl, ethyl and butyl. Accordingly structure (B) should be considered. In this structure the bridging NO_3 group would enhance the tendency toward dimerization. Considering that the molecular weight was measured in hot benzene, dimerization in the case of these compounds is strong by comparison with tetramethyl-1,3-bis(trimethylsiloxy)distannoxane which is monomeric in hot CHCl_3 and dimeric at room temperature¹⁰.

Structure of dialkyltin hydroxide nitrates $\text{R}_2\text{SnNO}_3(\text{OH})$, (IV)

The possible structures of the methyl and ethyl compounds have been discussed in the previous report⁴, in which OH-bridging structures were proposed. However, the structure of the propyl and butyl compounds seems different because, as shown in Table 3, in these compounds the positions of the infrared absorptions due to the Sn-O stretching vibrations appear at much higher frequencies than those of the methyl and ethyl compounds. Also given in Table 3 is data from the spectrum of $(n\text{-C}_4\text{H}_9)_2\text{SnNO}_3(\text{OH})$ in chloroform solution. The frequencies due to the NO_3 vibrations and Sn-O vibrations are quite similar to those of $\text{NO}_3\text{R}_2\text{SnOSnR}_2\text{NO}_3$ listed in Table 2. In addition a band at 3700 cm^{-1} due to free water is observed. This was confirmed by comparison with the spectrum of moist CHCl_3 . Spectra in the $3000\text{--}4000\text{ cm}^{-1}$ region of solutions of various concentrations are shown in Fig. 3. With increasing concentration, an additional OH band appears at 3370 cm^{-1} , which was not observed in the spectrum of moist CHCl_3 . This new band is considered to be associated with the coordinated OH stretching vibration of $(n\text{-C}_4\text{H}_9)_2\text{SnNO}_3(\text{OH})$ in solution. Therefore it is suggested that in a dilute solution, two molecules of $(n\text{-Bu})_2\text{SnNO}_3(\text{OH})$ may produce one molecule of H_2O and $\text{NO}_3(n\text{-Bu})_2\text{SnOSn}(n\text{-Bu})_2\text{NO}_3$, but in concentrated solution, some sort of equilibrium exists:



To confirm this equilibrium, solution spectra of $(n\text{-Bu})_2\text{SnNO}_3(\text{OH})$ in various solvents were measured. In cyclohexane, the NO_3 stretching frequencies were found near 1540 , 1275 and 960 cm^{-1} and the spectra resembled those of $\text{NO}_3(n\text{-Bu})_2\text{SnOSn}(n\text{-Bu})_2\text{NO}_3$. On the other hand, in polar solvents, acetone or nitrobenzene, the corresponding bands were found at about 1460 and 1275 cm^{-1} , but the third band, which is weak, could not be observed. These two bands resembled those of $(n\text{-Bu})_2\text{SnNO}_3(\text{OH})$ in the solid state. In addition, in polar solvents the coordinated OH stretching frequency was observed at near 3400 cm^{-1} . Thus in polar solvents, $(n\text{-Bu})_2\text{SnNO}_3(\text{OH})$ is the predominant species, while in non-polar solvents $\text{NO}_3(n\text{-Bu})_2\text{SnOSn}(n\text{-Bu})_2\text{NO}_3$ predominates.

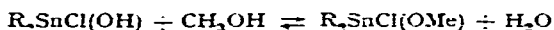
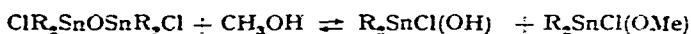
These results resemble those reported by Friebe *et al.*¹¹ and Kriegsmann *et al.*¹² who studied the behaviour of triphenyltin hydroxide in divergent solvents by means of infrared spectroscopy and found that $(\text{C}_6\text{H}_5)_3\text{SnOH}$ is in equilibrium with $(\text{C}_6\text{H}_5)_3\text{SnOSn}(\text{C}_6\text{H}_5)_3$ in solution.

Existence of R₂SnCl(OH) in solution

The facts described above suggest that distannoxane derivatives XR₂SnOSnR₂X (X = halogen, pseudohalogen) might be changed into R₂SnX(OH) in solutions containing H₂O.



Infrared studies confirm this and the results are shown in Fig. 4, where it is seen that moderately concentrated solutions of Cl(n-Pr)₂SnOSn(n-Pr)₂Cl in moist chloroform have a weak absorption band at ~ 3400 cm⁻¹ due to the coordinated OH stretching vibration. The existence of R₂SnCl(OH) in solution is further confirmed by the fact that distannoxane derivatives are titrated by Karl-Fischer method losing one molecule of H₂O from ClR₂SnOSnR₂Cl as was described in the experimental section. The following reactions between the distannoxane and the methanol in the Karl-Fischer reagent may have occurred as described by Gilman and Miller about organic silanols and silanediols¹³:



The assumption of the presence of R₂SnCl(OH) in solution makes clear the reason why, by refluxing equimolar amounts of R₂SnCl₂ and R₂SnO in a *wet* solvent, distannoxane XR₂SnOSnR₂X can be obtained smoothly².

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SUMMARY

Several series of dialkyltin (R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉) nitrate derivatives: dialkyltin nitrate hydroxides (IV), tetraalkyl-1,3-dinitratodistannoxanes (III), tetraalkyl-1-nitrato-3-hydroxydistannoxanes (II) and dibutyltin dinitrate (V) were prepared. The structures of (III) and (IV) are suggested. The existence of R₂SnX(OH) where X is NO₃ and Cl is indicated and discussed.

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