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Assessment of fluoroalkyltin compounds as fluorous Lewis acid catalysts

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The synthesis of a variety of organotin compounds with 1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyl groups is reported, together with an improved method for the corresponding distannoxane. Unique properties of this compound are disclosed in terms of fluorophilicity and activity as a Lewis acid catalyst in comparison with other mono-nuclear derivatives. A new criterion for obtaining high solubility in fluorocarbon solvents is presented. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: fluoroalkyltin; Lewis acid catalyst; fluorous biphase technology

INTRODUCTION

Much attention has been paid to organotin compounds with fluorinated organic groups. For instance, perfluorophenyltin halides, which are more acidic than conventional alkyltin halides due to the strong electron-withdrawing power of the perfluorophenyl group, serve as unique Lewis acids in various reactions.[1–5] In addition, organotin derivatives with 1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyl ($C_6F_{13}C_2H_4$, Rf) groups play extremely versatile roles within the context of rapidly expanding fluorous technology. The C_6F_{13} moiety endows the molecule with fluorophilicity, and the C_2H_4 spacer insulates the electronic effect of the fluoroalkyl moiety on the central metal.[6,7] Curran and co-workers have prepared the relevant organotin reagents and utilized them for reactions under fluorous conditions: tin hydride for radical reactions,[8–12] aryltins for Migaita–Kosugi–Stille coupling,[13] allyltin for allylation of aldehydes,[14] and tin oxide for acylation.[15] Likewise, we have developed a unique Lewis acid, fluoroalkyldistannoxane ($ClRf_2SnOSnRf_2Cl)_2$ (**1**), that is capable of catalyzing highly atom-efficient (trans)esterification under fluorous biphasic conditions, i.e. 100% yields of esters can be achieved using equimolar amounts of reactants.[16–18] Of further significance is the perfect recovery of the catalyst simply by separating the fluorous layer from the organic layer, owing to the high fluorophilicity of the catalyst. Thus, we were interested in elucidating the relationship between the fluorophilicity and the structure of the compounds. In this paper, a variety of fluorous organotin compounds, Rf_nSnPh_{4-n} (**2**), Rf_nSnCl_{4-n} (**3**), $Rf_nSn(C_6F_5)_{4-n}$ (**4**) and Rf_4Sn (**5**), have been prepared and an improved procedure for the synthesis of **1** has been established in order to compare the fluorophilicity of these compounds from the viewpoint of fluorous Lewis acid catalysts (it has been reported[19] that Rf_2SnCl_2 exhibited marginal anti-tumour activity).

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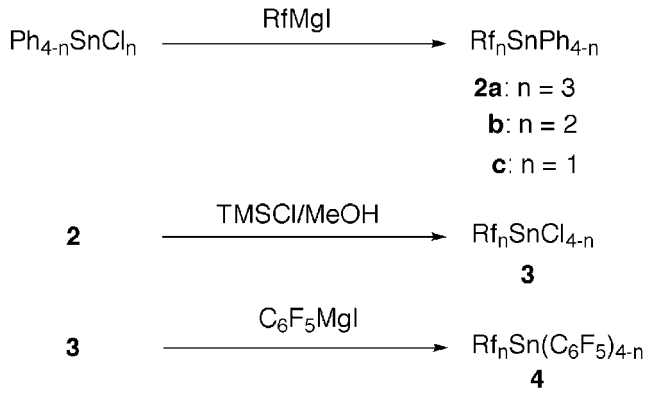
RESULTS AND DISCUSSION

Synthesis

The procedures for **2**, **3** and **4** are shown in Scheme 1. The first step is to attach the fluoroalkyl group(s) to phenyltin chlorides by the Grignard method, a protocol employed by Curran and co-workers[12,15] and Gielen and co-workers[19] previously. These compounds were easily obtained by column chromatography in high yields and pure form. Then, these compounds were converted to the corresponding chlorides **3**. The phenyl group could be cleaved through bubbling HCl gas into a CCl_4 solution of **2**, but handling of HCl gas is not operationally convenient. Alternatively, an *in situ* HCl generation method[20] served to effect more practical chlorination in satisfactory yields (chlorine in methanol solution was also employed: see Ref. 19). Thus, to a CCl_4 solution of **2a** or **2b** was added dry methanol (five equivalents) and trimethylchlorosilane (TMSCl) (1.5 equivalents) at 0 °C and the solution was stirred overnight at room temperature. The desired chlorides **3a** and **3b**[19] were obtained in 92 and 94% yields, respectively. However, this method was not applicable to prepare **3c**: this compound was obtained by treating **2c** with



Scheme 1.

concentrated aqueous HCl solution but in only 39% yield after distillation because of instability of this compound. Finally, **3a** and **3b** were transformed to **4a** and **4b** in reasonable yields by treating with C_6F_5MgI. When **3c** was subjected to the same reaction, $RfSn(C_6F_5)_3$ was not obtained in pure form. On the basis of NMR spectra of the products, the desired compound was suggested to be formed as a major component (~90% pure) but was contaminated by an ill-identified by-product, which was presumed to be $RfSnCl(C_6F_5)_2$, and all attempts at purification failed.

Previously, we have presented a procedure for **1** by reaction of $(Rf_2SnO)_n$ with aqueous HCl

$$\frac{4}{n}(Rf_2SnO)_n + 4HCl \longrightarrow \underset{\mathbf{1}}{(ClRf_2SnOSnRf_2Cl)_2} \qquad (1)$$

and described that the more practical route by use of $(Rf_2SnO)_n$ and **3b** (Eqn (2)) was not successful.[21]

$$\frac{2}{n}(Rf_2SnO)_n + 2Rf_2SnCl_2 \longrightarrow \mathbf{1} \qquad (2)$$

Since the reaction in Eqn (1) suffered some problems arising from difficulty in adjusting the amount of aqueous HCl, we examined the conditions for perform reaction (**2**) in high yield with reliable reproducibility. It transpired that the key point was the neutrality of $(Rf_2SnO)_n$. This compound is prepared by alkaline hydrolysis of **3b** but it cannot be purified due to its poor solubility in solvents. Thus, it is subjected to reaction (**2**) after washing with water. If the washing is insufficient, then no reaction occurs. Great care has to be taken that the washing should be repeated until the water becomes completely neutral. Then, heating the oxide thus obtained with an equimolar amount of **3b** in refluxing acetone or toluene afforded a quantitative yield of **1**. This procedure is much more convenient because the ratio of the reactants can be adjusted accurately by weight and the reaction is totally reproducible.

Rf_4Sn (**5**)[19] was prepared by the standard Grignard method:

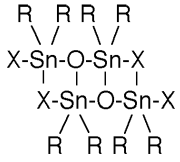
$$SnCl_4 + 4RfMgI \longrightarrow \underset{\mathbf{5}}{Rf_4Sn} \qquad (3)$$

The reaction proceeded slowly to provide a 60% yield after 4 days.

Solubility

As expected, the fluoroalkyltin compounds are soluble in FC-72 (perfluorohexanes) (Table 1). Compounds **1** and **3** possess fair to good solubility (we reported the solubility of **1** in FC-72 to be 41 g l^{-1},[21] but the correct value is as given in Table 1) and the replacement of chlorine in **3** with the perfluorophenyl group results in a dramatic increase of the solubility. In particular, oily **4a** and **5** seem to be miscible with FC-72 in any ratio; however, there is an upper limit (though very high) to the solubility for **4b**, notwithstanding that it is also oily (~500 g L^{-1}). Apparently, the Rf group is more effective than the perfluorophenyl group for increasing fluorophilicity. Then, partition of these compounds between FC-72 and conventional organic solvents was determined (Table 2). All of them exhibited a high preference for FC-72. In accordance with their solubility in FC-72, the partition coefficients of **4** are larger than those of **3**. Quite reasonably, the value decreases with decreasing number of the Rf group in both series of **3** and **4**, although virtually no difference was observed between **5** and **4a**.

Remarkably, the partition coefficients of distannoxane **1** are the same as or higher than those of **4**. This is a rather surprising outcome, because the solubility of **1** in FC-72 is much lower than **4**. A notion that the solubility in fluorocarbon solvents increases as the fluorine content in the molecule increases is generally accepted, and it was suggested that the total fluorine content of transition-metal complexes should be higher than 60% for sufficient fluorous compatibility.[22] However, as shown in Table 2, the fluorine content of **1** is smaller than **4a,b**, and **5**. This implies that the solubility is not governed solely by the fluorine content. It is well established that the distannoxanes possess a dimeric formulation,[23] and that this also holds for **1** is evident from the ^{119}Sn NMR spectrum, which gives rise to two signals diagnostic of the ladder structure **A**:



A

Table 1. Solubility of fluorous tin compounds in FC-72

Compound	Solubility (g l^{-1})
1	153
3a	59
3b	32
5	Freely miscible
4a	Freely miscible
4b	~500

Table 2. Partition of fluorous tin compounds between FC-72 and organic solvent

Compound	F content (%)	Organic solvent	Partition (FC-72/organic solvent)
1	57.68	Toluene	~100 : 0
		Benzene	~100 : 0
		Hexane	~100 : 0
		CH_2Cl_2	~99 : 1
		MeOH	98 : 2
		Acetone	97 : 3
		THF	96 : 4
3a	61.98	Toluene	92 : 8
		Benzene	88 : 12
		CH_2Cl_2	88 : 12
		THF	73 : 27
3b	55.89	Toluene	82 : 18
		Benzene	83 : 17
		CH_2Cl_2	71 : 29
		THF	68 : 32
5	65.55	Toluene	99 : 1
		Benzene	98 : 2
		CH_2Cl_2	97 : 3
		MeOH	98 : 2
		THF	97 : 3
4a	62.99	Toluene	99 : 1
		Benzene	98 : 2
		CH_2Cl_2	99 : 1
		MeOH	98 : 2
		THF	97 : 3
4b	59.63	Toluene	92 : 8
		Benzene	90 : 10
		CH_2Cl_2	89 : 11
		MeOH	96 : 4
		THF	88 : 12

The space-filling model of **1** illustrates the effective coverage of the stannoxane core with Rf groups, which leads to a double-layered structure, like an egg, with the fluorophilic surface (Fig. 1). It is concluded, therefore, that the coverage of the molecular surface with fluorine is another important aspect that should be considered for increasing the fluorophilicity.

Catalytic activity

The activity as Lewis acid catalyst was assessed for acylation of 2-phenylethanol:

$$Ph(CH_2)_2OH \xrightarrow{Ac_2O} Ph(CH_2)_2OAc \qquad (4)$$

The reaction was conducted in homogeneous 1,1,1-trifluorotoluene (benzotrifluoride, BTF) solution to render the conditions as identical as possible. The results are summarized in Table 3. Remarkably, a quantitative yield was obtained with **1** even by use of an equimolar amount of Ac_2O at room temperature (entry 1). On the other hand, the yields were much lower with **4a,b** and **5** under the same conditions (entries 2–4), yet the use of five equivalents of Ac_2O afforded quantitative yields. Nevertheless, a control experiment (entry 5) clearly shows that the activity is inherent even in these less-active compounds to some degree. Obviously, the distannoxane catalyst is more active than the mono-nuclear tin compounds **4** and **5**. The cooperative effect of the proximately located tin atoms proposed for the normal distannoxane catalysts[23] is supposed to work in **1** as well.

In conclusion, incorporation of 1*H*, 1*H*, 2*H*, 2*H*-perfluorooctyl groups on tin has proved to be effective for endowment of fluorophilicity. In particular, the unique structural feature of the corresponding distannoxane gives rise to a superb preference for partition in FC-72 and high catalytic activity. A new criterion for increasing the solubility in fluorous solvents can be drawn from these results: not only is the fluorine content important, but also the design of the molecular structure is of great significance.

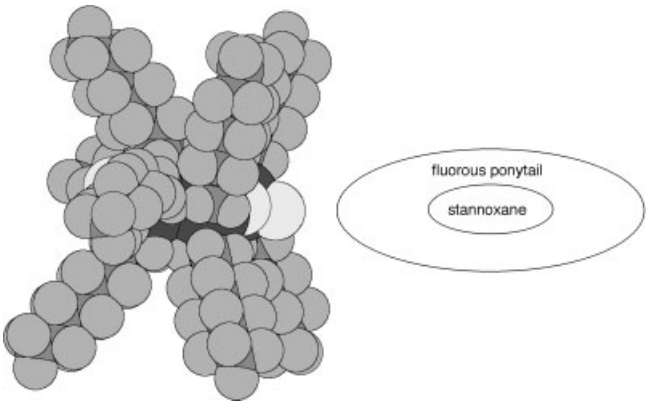


Figure 1. The space-filling model and double-layered structure of **1**.

Table 3. Acylation of 2-phenylethanol catalyzed by fluorous tin catalysts[a]

Entry	Catalyst	Yield of ester (%)
1	**1**	>99
2	**4a**	54(>99)[b]
3	**4b**	60(>99)[b]
4	**5**	40
5	None	15

[a] One equivalent of Ac_2O used.
[b] Five equivalents of Ac_2O used.

EXPERIMENTAL

General comments

Solvents were dried over sodium diphenyl ketyl [tetrahydrofuran (THF), Et_2O], CaH_2 (CCl_4) or $Mg(OMe)_2$ (MeOH) and distilled under argon prior to use. The reactions were carried out under argon. The fluorous compounds obtained are oily, unless noted otherwise. NMR spectra were run at room temperature on a Jeol Lambda 300 instrument.

Solubility (representative)

To FC-72 (10 ml) was added **3a** (1.0 g), and the mixture was stirred well. After filtration, the filtrate was evaporated and 590 mg of **3a** was recovered.

Partition (representative)

To a two-layered mixture of FC-72 (5 ml) and toluene (5 ml) was added **3a** (100 mg). This mixture was stirred vigorously, and two layers were separated. After evaporation, 92 mg of **3a** was recovered from the FC-72 layer, and 8 mg of **3a** was recovered from toluene.

Preparation of $RfSnPh_3$ (2c)

A flask containing magnesium turnings (0.24 g, 10 mmol) was heated by flame *in vacuo*. Dry Et_2O was added and the mixture was stirred at ambient temperature. An Et_2O solution (20 ml) of $C_6F_{13}C_2H_4I$ (4.26 g, 9 mmol) was added slowly at 0 °C. After the mixture had been stirred at ambient temperature for 3 h, Et_2O (20 ml) was added. To this mixture was slowly added Ph_2SnCl_2 (1.93 g, 5 mmol) in THF (10 ml) and the mixture was stirred at ambient temperature for 24 h. Water (30 ml) was added and the mixture was filtered through a Celite pad. The pad was washed with hexane. The combined filtrates were extracted with ethyl acetate and the organic layer was washed with water and brine. Drying ($MgSO_4$) and evaporation afforded a crude product, which was subjected to column chromatography on silica gel (hexane) to give pure **2c** (3.31 g, 95%). ^{1}H NMR δ 1.59 (t, 2H, $^2J_{Sn-H} = 56$ Hz), 2.35 (t, 2H, $J_{F-H} = 18$ Hz, $^3J_{Sn-H} = 95$ Hz), 7.38–7.61 (m, 15H); ^{119}Sn NMR δ −97.4; ^{19}F NMR δ −82.00 (m, 3F), −117.76 (m, 2F), −123.25 (m, 2F), −124.16 (m, 2F), −124.35 (m, 2F), −127.39 (m, 2F). Anal. Found: C, 44.69; H, 2.85. Calc. for $C_{26}H_{19}F_{13}Sn$: C, 44.80; H, 2.75%.

Preparation of Rf_3SnCl (3a)

To a CCl_4 solution (15 ml) containing **2a** (6.18 g, 5 mmol) and dry MeOH (1.0 ml, 25 mmol) was added TMSCl (0.95 ml, 7.5 mmol) at 0 °C and the solution was stirred at ambient temperature overnight. The reaction mixture was evaporated and the residue was subjected to column chromatography on silica gel (hexane) to give pure **3a** (5.49 g, 92%). ^{1}H NMR δ 1.51 (t, 6H, $^2J_{Sn-H} = 39$ Hz), 2.47 (t, 6H, $J_{F-H} = 17$ Hz, $^3J_{Sn-H} = 107$ Hz); ^{119}Sn NMR δ−67.1; ^{19}F NMR δ−82.05 (m, 9F), −117.29 (m, 6F), −123.19 (m, 6F), −124.18 (m, 6F), −124.72 (m, 6F), −127.47 (m, 6F). Anal. Found: C, 24.06; H, 0.85. Calc. for $C_{24}H_{12}ClF_{39}Sn$: C, 24.11; H, 1.01%.

Preparation of Rf_2SnCl_2 (3b)[19]

The analogous procedure employed for **3a** but employing **2b** (4.83 g, 5 mmol) and TMSCl (1.45 ml, 11.5 mmol) and recrystallization of the crude product afforded pure **3b** (4.15 g, 94%) as a white solid; m.p. 90–92 °C. ^{1}H NMR δ 1.96 (t, 4H, $^2J_{Sn-H} = 64$ Hz), 2.62 (t, 4H, $J_{F-H} = 16$ Hz, $^3J_{Sn-H} = 111$ Hz); ^{119}Sn NMR δ−42.7; ^{19}F NMR δ−82.00 (m, 6F), −116.71 (m, 4F), −123.10 (m, 4F), −124.10 (m, 4F), −124.56 (m, 4F), −127.39 (m, 4F). Anal. Found: C, 21.75; H, 0.70. Calc. for $C_{16}H_8Cl_2F_{26}Sn$: C, 21.74; H, 0.91%.

Preparation of $RfSnCl_3$ (3c)

A concentrated HCl solution (15 ml) of **2c** (3.48 g, 5 mmol) was heated at 80 °C overnight. The reaction mixture was washed with $CHCl_3$ (15 ml × 3) and the organic layer was washed with concentrated HCl (15 ml × 2). All the HCl layer was combined and evaporated. The residue was distilled with Kugel rohr (140 °C/5.0 × 10^{-4} Torr) to give pure **3c** (1.11 g, 39%). ^{1}H NMR δ 2.35 (t, 2H, $^2J_{Sn-H} = 90$ Hz), 2.66 (t, 2H, $J_{F-H} = 16$ Hz, $^3J_{Sn-H} = 152$ Hz); ^{119}Sn NMR δ−3.2; ^{19}F NMR δ−81.04 (m, 3F), −115.47 (m, 2F), −122.11 (m, 2F), −123.15 (m, 2F), −123.53 (m, 2F), −126.46 (m, 2F). Anal. Found: C, 16.67; H, 0.66. Calc. for $C_8H_4Cl_3F_{13}Sn$: C, 16.79; H, 0.70%.

Preparation of $Rf_3SnC_6F_5$ (4a)

Magnesium turnings (0.22 g, 9 mmol) and THF (20 ml) were charged in a flame-dried flask. C_6F_5Br (1.85 g, 7.5 mmol) in THF (20 ml) was slowly added at 0 °C. After the mixture had been stirred at ambient temperature for 3 h, THF (20 ml) was added. A THF solution (20 ml) of **3a** (5.97 g, 5 mmol) was added slowly and the mixture was stirred at ambient temperature for 24 h. Water (30 ml) was added and the mixture was filtered through a Celite pad. The pad was washed with hexane. The combined filtrates were extracted with ethyl acetate and the organic layer was washed with water and brine. Drying ($MgSO_4$) and evaporation afforded a crude product, which was subjected to column chromatography on silica gel (hexane) to give pure **4a** (5.8 g, 88%). ^{1}H NMR δ 1.83 (t, 6H, $^2J_{Sn-H} = 65$ Hz), 2.44 (t, 6H, $J_{F-H} = 17$ Hz, $^3J_{Sn-H} = 99$ Hz); ^{119}Sn NMR δ − 11.0; ^{19}F NMR δ − 81.14 (m, 9F), −116.36 (m, 6F), −122.28 (m, 6F), −123.26 (m, 6F), −123.81 (m, 6F), −126.63 (m, 6F), −121.82 ($C_6F_5\delta_o$), −148.34 ($C_6F_5\delta_p$), −158.23 ($C_6F_5\delta_m$). Anal. Found: C, 27.00; H, 0.69. Calc. for $C_{30}H_{16}F_{44}Sn$: C, 27.15; H, 0.91%.

Preparation of $Rf_2Sn(C_6F_5)_2$ (4b)

The analogous procedure employed for **4a** but employing magnesium turnings (0.36 g, 15 mmol), C_6F_5Br (3.0 g, 12.5 mmol), and **3b** (4.41 g, 5 mmol) afforded pure **4b** (4.47 g, 78%). ^{1}H NMR δ 1.83 (t, 4H, $^2J_{Sn-H} = 49$ Hz), 2.44 (t, 4H, $J_{F-H} = 16$ Hz, $^3J_{Sn-H} = 107$ Hz); ^{119}Sn NMR δ − 57.5; ^{19}F NMR δ − 81.13 (m, 6F), −116.34 (m, 4F), −122.25 (m, 4F), −123.23 (m, 4F), −123.78 (m, 4F), −126.46 (m, 4F), −121.80 ($C_6F_5\delta_o$), −148.36 ($C_6F_5\delta_p$); −158.27 ($C_6F_5\delta_m$). Anal. Found: C, 29.02; H, 0.48. Calc. for $C_{28}H_8F_{36}Sn$: C, 29.32; H, 0.70%.

Preparation of Rf_4Sn (5)[19]

Magnesium turnings (0.73 g, 30 mmol) were stirred at ambient temperature for 1 h in Et_2O (30 ml). An Et_2O solution (30 ml) of $C_6F_{13}C_2H_2I$ (11.85 g, 25 mmol) was slowly added at 0 °C. After the mixture had been stirred at this temperature for 3 h, Et_2O (30 ml) was added. $SnCl_4$ (1.3 g, 5 mmol) in THF (20 ml) was added and the mixture was heated at reflux for 4 days. Water (30 ml) was added and the mixture was filtered through a Celite pad. The pad was washed with hexane. The combined filtrates were extracted with ethyl acetate and the organic layer was washed with water and brine. Drying ($MgSO_4$) and evaporation afforded a crude product, which was subjected to column chromatography on silica gel (hexane) to give pure **5** (4.51 g, 60%). ^{1}H NMR δ 1.13 (t, 8H, $^2J_{Sn-H} = 52$ Hz), 2.29 (t, 8H, $J_{F-H} = 17$ Hz); ^{119}Sn NMR δ 8.1; ^{19}F NMR δ − 83.98 (m, 12F), −119.27 (m, 8F), −124.27 (m, 8F), −125.34 (m, 8F), −126.15 (m, 8F), −128.89 (m, 8F). Anal. Found: C, 25.59; H, 1.10. Calc. for $C_{32}H_{16}F_{52}Sn$: C, 25.50; H, 1.07%.

Improved method for synthesis of $(ClRf_2SnOSnRf_2Cl)_2$ (1)

To a THF solution (70 ml) of **3b** (8.82 g, 10 mmol) was added 4M NaOH solution (7.5 ml, 30 mmol) and the solution was stirred at ambient temperature for 6 h. The solution was evaporated and acetone (20 ml) was added to the residue. Heating with a heatgun resulted in a homogeneous solution. Upon addition of water (40 ml), a viscous oil separated on the bottom of the flask. After decanting the water, the residue was pumped *in vacuo*. The resulting oil was washed with water and pumped again. This was repeated until the water became pH 7. Then, the oil was washed with CH_2Cl_2 and pumped to give a white solid of $(Rf_2SnO)_n$ (7.2 g, 88%).[15] When the oil did not solidify, the oil was dissolved in a small amount of FC-72 and evaporation of this solution under reduced pressure afforded a solid.

An acetone solution (25 ml) of $(Rf_2SnO)_n$ (8.29 g, 10 mmol) and **3b** (8.83 g, 10 ml) was heated under reflux for 8 h. The solution was evaporated and the residue was recrystallized form 2 : 1 FC-72/hexane to give **1** (16.2 g, 95%).[21]

Acylation of 2-phenylethanol by fluorous tin catalysts (representative)

A BTF solution (5 ml) of 2-phenylethanol (122.2 mg, 1 mmol), Ac_2O (102.1 mg, 1 mmol) and **1** (17.1 mg, 0.01 mmol) was stirred for 22 h. Aqueous workup of the reaction mixture followed by gas–liquid chromatography analysis of the product revealed the formation of the desired ester in >99% yield. Other reactions were carried out similarly and the results are summarized in Table 3.

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