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Nitrile-Promoted Rh-Catalyzed Intermolecular Hydroacylation of Olefins with Salicylaldehyde

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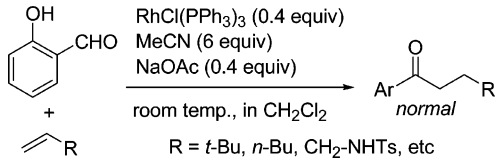
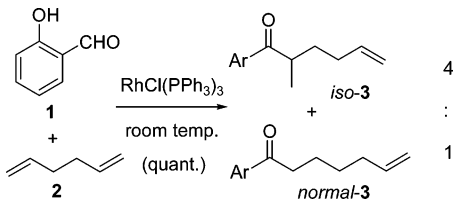


Rh-catalyzed intermolecular hydroacylation between salicylaldehyde and alkenylnitriles proceeded at room temperature to preferentially give normal-hydroacylated products. Addition of CH_3CN and NaOAc accelerated the Rh-catalyzed hydroacylation of monoolefins to exclusively produce the normal-hydroacylated products under mild reaction conditions. Plausible mechanisms for the regioselections are also described.

Introduction

Rhodium-catalyzed intermolecular hydroacylations have independently been reported by the Jun[1] and the Miura groups.[2] They reported that chelation of aldehyde-imine, or that of salicylaldehyde to the Rh-metal, suppressed the decarbonylation and promoted the intermolecular hydroacylation. However, their Rh-catalyzed hydroacylation reactions required rigorous reaction conditions of refluxing in toluene. Recently, we have discovered that Rh-catalyzed intermolecular hydroacylation between salicylaldehyde **1** and 1,4-penta- or 1,5-hexadienes proceeded under very mild conditions based on a "double-chelation" concept.[3] However, the Rh-catalyzed intermolecular hydroacylation was restricted to the 1,4-penta- or 1,5-hexadiene as an olefin (Scheme 1). Unfortunately, the intermolecular hydroacylation of monoolefins such as 1-hexene and 1-octene did not proceed well, except for the case of norbornenes.[3c] Also, the Willis group reported Rh-catalyzed intermolecular hydroacylation between β-sulfido aldehyde and α,β-unsaturated esters under mild reaction conditions (55 °C), but in general the olefin substrates were limited to α,β-unsaturated esters.[4,5] Herein, we report the Rh-catalyzed intermolecular hydroacylation of alkenylnitriles[6]

SCHEME 1



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(5) Recently, Willis and coworkers reported Rh-catalyzed intermolecular hydroacylation of monoolefins with β-sulfido aldehyde by using cationic Rh-complex having a P−O−P diphosphine ligand. See: Moxham, G. L.; Randell-Sly, H. E.; Brayshaw, S. K.; Woodward, R. L.; Weller, A. S.; Willis, M. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 7618−7622.

(6) Rh-catalyzed hydroformylation of alkenylnitriles. See: Lambers-Verstappen, M. M. H.; de Vries, J. G. *Adv. Synth. Catal.* **2003**, *345*, 478−482.

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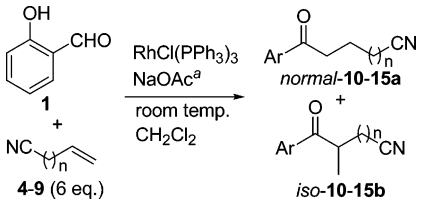
TABLE 1. Rh-Catalyzed Hydroacylation between Salicylaldehyde and Alkenylnitriles



entry	$RhCl(PPh_3)_3$ (equiv)	alkenylnitrile	products: yield % (ratio: *n*:*i*)
1	0.20	**4**: $n = 1$	**10**: 51 (5:1)
2	0.40	**4**: $n = 1$	**10**: 98 (5:1)
3	0.20	**5**: $n = 2$	**11**: 50 (>20:1)
4	0.40	**5**: $n = 2$	**11**: 94 (>20:1)
5	0.40	**5**: $n = 2$[b]	**11**: 63 (>20:1)
6	0.20	**6**: $n = 3$	**12**: 40 (>20:1)
7	0.40	**6**: $n = 3$	**12**: 93 (>20:1)
8	0.40	**7**: $n = 4$	**13**: 99 (>20:1)
9	0.40	**8**: $n = 8$	**14**: 70 (>20:1)
10	0.40	**9**: $n = 9$	**15**: 80 (>20:1)

[a] The same equivalents of NaOAc as that of Rh-complex was added, and the reaction was quenched in 5 h. [b] 1.5 equiv of 4-pentenenitrile **5** was used.

and also the effect of nitrile compounds on the Rh-catalyzed intermolecular hydroacylation of olefins.[7]

Results and Discussion

Rh-Catalyzed Hydroacylation between Salicylaldehyde and Alkenylnitriles. We envisaged that a nitrile functional group may coordinate to the Rh-complex because MeCN is capable of coordinating to the Rh-complex.[8] Thus, if alkenylnitriles that have an olefin and a nitrile functional group are used instead of 1,5-hexadiene, the Rh-catalyzed hydroacylation with salicylaldehyde may proceed via chelation of both alkenylnitrile and salicylaldehyde to the Rh-complex. We examined the hydroacylation between salicylaldehyde **1** (1.0 equiv) and various alkenylnitriles (6.0 equiv) at room temperature (20−30 °C) in the presence of $RhCl(PPh_3)_3$ and NaOAc. The results are summarized in Table 1.

The hydroacylation of allyl cyanide **4** with **1** proceeded to afford a hydroacylated product **10**. The isolated yield of **10** was 51% by use of 0.20 equiv of $RhCl(PPh_3)_3$ and NaOAc, and the yield increased to 98% by use of 0.40 equiv of the Rh-complex and NaOAc. The ^1H NMR spectrum of **10** showed the methylene proton signals at δ 3.22 (t, $J = 7.0$ Hz, 1.67H), as well as the methine proton signal at δ 3.86 (sestet, $J = 7.3$ Hz, 0.17H) and the methyl proton signal at δ 1.47 (d, $J = 7.3$ Hz, 0.5H), suggesting the product **10** was a mixture of normal-**10a** and iso-**10b** in a ratio of 5 to 1. The hydroacylation of 4-pentenenitrile **5** by use of 0.4 equiv of the Rh-complex also afforded the products **11a**,**b** in 94% yield; preferentially normal-**11a** was obtained as a major product (entry 4). It is noteworthy that the normal-product **11a** was obtained in preference to iso-**11b** because in the case of the corresponding hydroacylation of 1,5-hexadiene the iso-product was preferred.[3a,b] Even by the use of 1.5 equiv of 4-pentenenitrile **5**, the hydroacylation proceeded to give the product **11a** in 63% yield (entry 5). The hydroacylation of 5-hexenenitrile **6** gave the hydroacylated product **12a** in 93% yield, whereas that of 1,6-heptadiene could not proceed because of the long distance between the two olefins.[3a,b] However, when benzaldehyde or 2-cyanobenzaldehyde was used instead of **1**, the hydroacylation did not proceed at all. Furthermore, the hydroacylation of alkenylnitriles **7**−**9** bearing a longer distance between an olefin and a nitrile function proceeded smoothly to afford the products **13**−**15** in 70−99% yields.

TABLE 2. Rh-Catalyzed Hydroacylation between Salicylaldehyde and 1,5-Hexadiene in the Presence of MeCN[a]

entry	additive	solvent	time (h)	**3**: yield % (ratio: *n*:*i*)
1[b]		MeCN	72	39 (1:3)
2	NaOAc (0.2 equiv)	MeCN	72	59 (1:3)
3[b]	NaOAc (0.2 equiv)	CH_2Cl_2	4	>99 (1:5)
4	MeCN (6 equiv)	CH_2Cl_2	72	27 (1:9)
5	MeCN (6 equiv), NaOAc (0.2 equiv)	CH_2Cl_2	2	>99 (1:5)
6	adiponitrile (6 equiv), NaOAc (0.2 equiv)	CH_2Cl_2	2	>99 (1:5)

[a] The reaction was carried out at room temperature using $RhCl(PPh_3)_3$ (0.2 equiv) in CH_2Cl_2 (1.5 mL). [b] These reaction conditions have already been reported by us.

We reasoned that the alkenylnitriles may not chelate to the Rh-metal, but the nitrile group coordinates to the Rh-metal to effect the hydroacylation. That is to say, one nitrile coordinates to the Rh metal to change the property of the Rh-complex, and the newly formed Rh-complex catalyzes the hydroacylation of the other alkenylnitrile molecule with salicylaldehyde. This presumption arises from the fact that the normal-hydroacylated products **10**−**15** were obtained as a major product, whereas the iso-products were obtained in the case of the double-chelation-promoted hydroacylation of 1,5-hexadienes.[3a,b] Furthermore, the hydroacylation of **8** and **9** having a long distance between two functional groups proceeded smoothly. The chelation of **8** or **9** to the Rh-metal forms a large ring metallocycle, and this large ring might thermodynamically not be preferred.

Effect of Nitrile on the Rh-Catalyzed Hydroacylation of 1,5-Hexadiene. Next, we examined the additional effect of nitriles on the hydroacylation between salicylaldehyde **1** and 1,5-hexadiene **2**. The results are summarized in Table 2. The hydroacylation of **2** in MeCN as a solvent was sluggish and did not proceed efficiently even with the addition of NaOAc (entries 1 and 2).[3b,9] This drawback might be due to the low solubility of a mixture in MeCN solution. Interestingly, when MeCN (6.0 equiv) and NaOAc (0.20 equiv) were added to the CH_2Cl_2 solution, the hydroacylation of 1,5-hexadienes **2** was accelerated, completed within 2 h (entry 5), and the hydroacylated products were obtained in quantitative yield (entry 5). The addition of MeCN without a base was not advantageous (entry 4). Addition of adiponitrile instead of MeCN also worked well (entry 6). The ratio of iso- and normal-hydroacylated products was almost the same as that without nitriles; that is, the iso-hydroacylated product was preferentially formed.[3a,b]

(7) Ru- and Co-catalyzed intermolecular hydroacylations. (a) Lenges, C. P.; White, P. S.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 6955−6979. (b) Kondo, T.; Hiraishi, N.; Morisaki, Y.; Wada, K.; Watanabe, Y.; Mitsudo, T. *Organometallics* **1998**, *17*, 2131−2134 and references therein.

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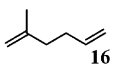
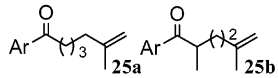
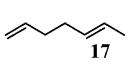
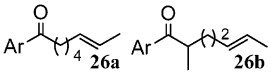
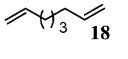
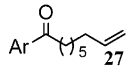
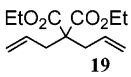
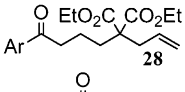
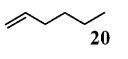
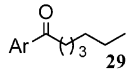
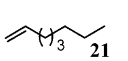
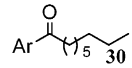
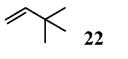
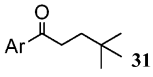
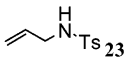
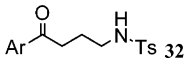
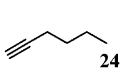
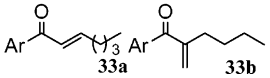
(9) Addition of NaOAc may deprotonate the phenolic hydroxyl group and accelerate the reaction.

TABLE 3. Rh-Catalyzed Hydroacylation between Salicylaldehyde and Various Olefins 16−24 in the Presence of MeCN

entry[a]	olefins	time (h)	products	yield% (ratio: *n*:*i*)
1[b]	 **16**	3	 **25a** **25b**	95 (1 :10)
2[b]	 **17**	7	 **26a** **26b**	82 (10 :1:1)[c]
3	 **18**	7	 **27**	73[d]
4	 **19**	6	 **28**	80[e]
5	 **20**	8	 **29**	86[d]
6	 **21**	8	 **30**	82[d]
7	 **22**	7	 **31**	82[e]
8	 **23**	2	 **32**	53[e]
9	 **24**	1	 **33a** **33b**	91 (1.1:1)

[a] The reaction was carried out at room temperature using $RhCl(PPh_3)_3$ (0.4 equiv), NaOAc (0.4 equiv), and MeCN (6 equiv) in CH_2Cl_2 solution. [b] 0.2 equiv of $RhCl(PPh_3)_3$ was used. [c] Isomer, which was acylated at the C_5-position of diene, was also formed. [d] The ratio was >20 (*n*):1 (*i*). [e] The iso-hydroacylated product was not detected.

Effect of Nitrile on the Rh-Catalyzed Hydroacylation of Various Olefins. Next, we checked the hydroacylation of various olefins **16**−**23** with **1** using $RhCl(PPh_3)_3$ (0.20 or 0.40 equiv) in the presence of NaOAc (0.40 equiv) and MeCN (6.0 equiv) in CH_2Cl_2 solution. Table 3 summarizes the results. The hydroacylation of 1,5-hexadienes **16** and **17** having a substituent proceeded in 3−7 h at room temperature to produce the hydroacylated products **25** and **26** in good yields (entries 1 and 2). The hydroacylation of **16** preferentially afforded the iso-hydroacylated product **25b** similarly to that in the absence of MeCN,[3a,b] but that of **17** dominantly gave the normal-hydroacylated product **26a**. The hydroacylation of **18** without MeCN gave the product in merely 10−15% yield. In contrast, that under the conditions of $RhCl(PPh_3)_3$ (0.40 equiv), NaOAc (0.40 equiv), and MeCN (6.0 equiv) in CH_2Cl_2 solution afforded the normal- and iso-hydroacylated products in a ratio of >20 to 1 in 73% yield (entry 3). The reaction was tolerant of an ester functional group. The hydroacylation of 1,6-diene **19** bearing a diester smoothly proceeded to give normal-products **28** in 80% yield. The iso-product was not detected at all (entry 4). The hydroacylation of **19** could not proceed by use of $RhCl(PPh_3)_3$ only; therefore, the addition of MeCN and NaOAc would enhance the reactivity. These results suggested that the hydroacylation of some 1,5- and 1,6-dienes in the presence of NaOAc and MeCN may proceed via the diene-mono-coordinated intermediate, but not via the diene-chelated intermediate.

Thus, we tested the hydroacylation of various monoolefins, which were not appropriate as the Rh-catalyzed-hydroacylation substrate before. As expected, the Rh-catalyzed hydroacylation between salicylaldehyde **1** and monoolefins such as 1-hexene and 1-octene smoothly proceeded to give the normal- and iso-hydroacylated products **29** and **30** in a ratio of >20 to 1, in 86% and 82% yields, respectively. The ratio of normal- and iso-products (>20:1) was almost the same as that of alkenylnitriles (entries 3−10 in Table 1) and that of 1,7-octadiene (entry 3 in Table 3). Therefore, these reactions might proceed via the same reaction pathway. The hydroacylation of 3,3-dimethylbut-1-ene **22**, which is a *tert*-butyl ethylene, also proceeded at room temperature, and the normal-hydroacylated product **31** was exclusively obtained in 82% yield (entry 7). Unfortunately, the hydroacylation of disubstituted olefins or internal olefins did not proceed, or proceeded just in trace amount. It should be noted that the reaction was tolerant of protected amine, and thus the hydroacylation of allyl amine **23** proceeded to give normal-hydroacylated product **32** in 53% yield (entry 8). Under the same reaction conditions, the hydroacylation of 1-hexyne **24** was completed within 1 h at room temperature, while the reported reaction conditions require 2 h and the rigorous condition of refluxing in toluene.[2]

Mechanistic Consideration of the Nitrile-Promoted Rh-Catalyzed Hydroacylation. The detailed reaction mechanism for the influence of nitriles is not clear. It has already been reported that nitrile could be exchanged for the phosphine ligand in the Rh-complex, or additionally coordinate to the transition metal-complex.[8] We measured a liquid-phase IR spectrum of $RhCl(PPh_3)_3$ (1.0 equiv), MeCN (1.0 equiv), and salicylaldehyde (1.0 equiv) in CH_2Cl_2 solution. The IR spectrum indicated an increase of the CN stretching frequency; that is, the absorption observed at 2256 cm^{-1} (ν_{CN}) in the free MeCN was shifted to absorption at 2356 cm^{-1} (ν_{CN}).[10] These results suggested that the use of MeCN as an outer ligand would change the property of the Rh-complex by coordination and might promote the hydroacylation reaction.

The regio-selectivity, that is, iso- and normal-selectivity of the products, could be explained on the basis of Rh-aldehyde-olefin intermediates, albeit the real intermediates might consist of nitrile, and the existence of the dinuclear Rh-complex may play some important roles.[11] The coordination of monoolefin and salicylaldehyde would afford two plausible intermediates (a) and (b), as shown in Figure 1. Transfer of the hydrogen from the Rh-complex to the coordinated olefin might produce alkylated Rh-intermediates (c) and (d). These intermediates (a−d) may be interchangeable. Reductive elimination from intermediate (c) affords the normal-hydroacylated product, whereas that from intermediate (d) gives the iso-hydroacylated product. Taking the thermodynamic stability of the intermediates into consideration, intermediates (a) and (c) seem to be more favorable than intermediates (b) and (d) because steric repulsion exists in intermediates (b) and (d). Thus, the Rh-catalyzed hydroacylation of monoolefins would preferentially afford the normal-hydroacylated products. On the other hand, the hydroacylation of 1,5-hexadiene afforded the iso-hydroacylated product as a major product. This may be attributed to the fact that the 1,5-hexadiene-chelated Rh-intermediates (e) and (f), which have only a minimal steric repulsion, may become thermodynamically

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(11) (a) Colebrooke, S. A.; Duckett, S. B.; Lohman, J. A. B. *Chem. Commun.* **2000**, 685−686. (b) Gridnev, I. D.; Higashi, N.; Asakura, K.; Imamoto, T. *J. Am. Chem. Soc.* **2000**, *122*, 7183−7194. (c) Aubry, D. A.; Bridges, N. N.; Ezell, K.; Stanley, G. G. *J. Am. Chem. Soc.* **2003**, *125*, 11180−11181.

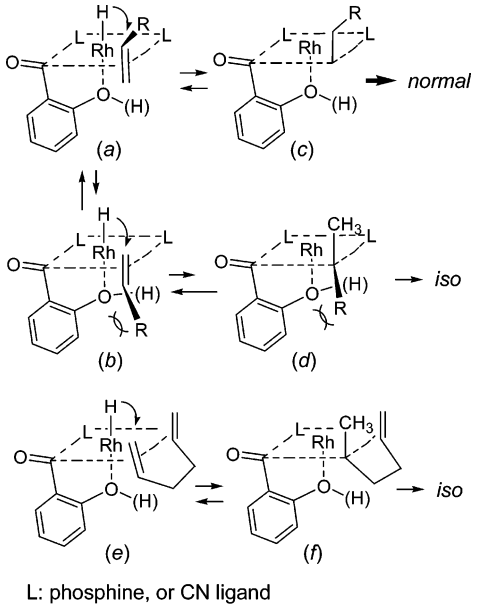

FIGURE 1. Plausible intermediates for the Rh-catalyzed hydroacylation.

stable, and the reductive elimination from the intermediate (f) would occur. Thus, the hydroacylation of 1,5-hexadienes **2** and **16** predominantly afforded the iso-hydroacylated products. However, the hydroacylation of 1,5-hexadiene **17** having a terminal substituent dominantly gave the normal-hydroacylated products **26a**; this result may be attributed to the fact that the terminal methyl group of 1,5-hexadiene would restrict the chelation of diene to the Rh-metal, and thus the reaction would proceed via a nonchelated mono-coordinated intermediate (c).

Conclusion

We have developed Rh-catalyzed intermolecular hydroacylation between salicylaldehyde and alkenylnitriles and, furthermore, disclosed that the addition of MeCN and NaOAc to the CH_2Cl_2 solution enhanced the Rh-catalyzed intermolecular hydroacylation. To the best of our knowledge, no additional effect of the CN ligand on transition metal-catalyzed reactions has been reported.[12] Under these conditions, the hydroacylation of monoolefins having a bulky substituent or a functional group smoothly proceeded at room temperature to give the normal-hydroacylated products,[13] albeit the reaction required a somewhat large loading of the Rh-catalyst. The effect of RCN in CH_2Cl_2 solution and its application to other metal-catalyzed reactions are under study in our group.

(12) Willis and coworkers reported that the Rh-catalyzed hydroacylation of 4-cyanostyrene with β-sulfido aldehyde was superior to that of styrene (ref 4). There may be two possibilities: one reason is the reactivity of 4-cyanostyrene by an electron-withdrawing group as reported, and the other reason may be coordination of the CN group to the Rh-metal to change the activity of the Rh-complex.

(13) Rh-catalyzed branch-selective hydroacylation of styrene. See: Hong, Y.-T.; Barchuk, A.; Krische, M. J. *Angew. Chem., Int. Ed.* **2006**, *45*, 6885−6888 and references therein.

Experimental Section

General Procedure for $RhCl(PPh_3)_3$-Catalyzed Hydroacylation between Salicylaldehydes and Alkenylnitriles. A solution of salicylaldehyde (0.50 mmol), alkenylnitrile (3.00 mmol), $RhCl(PPh_3)_3$ (184 mg, 0.20 mmol), and NaOAc (16 mg, 0.20 mmol) in CH_2Cl_2 (2.5 mL) was stirred at room temperature under an Ar atmosphere. After being stirred for 5−72 h, the solution was evaporated and diluted with ether. The precipitated Rh-complex was filtered off, and the filtrate was concentrated in vacuo to leave a residue. Purification by column chromatography on silica gel (EtOAc in hexane) gave the hydroacylated products as a mixture of iso- and normal-isomers.

General Procedure for $RhCl(PPh_3)_3$-Catalyzed Hydroacylation between Salicylaldehydes and Monoolefins in the Presence of MeCN and NaOAc. A solution of salicylaldehyde (0.50 mmol), monoolefin (3.00 mmol), $RhCl(PPh_3)_3$ (184 mg, 0.20 mmol), MeCN (0.16 mL, 3.00 mmol), and NaOAc (16 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature under an Ar atmosphere. After being stirred for 1−8 h, the solution was evaporated, and diluted with ether, and then the precipitated Rh-complex was filtered off. The filtrate was concentrated in vacuo, and the residue was purified by column chromatography on silica gel (EtOAc in hexane) to give the hydroacylated product.

1-(2-Hydroxyphenyl)nonan-1-one (30). A solution of salicylaldehyde (61 mg, 0.50 mmol), 1-octene (335 mg, 3.00 mmol), $RhCl(PPh_3)_3$ (184 mg, 0.20 mmol), MeCN (0.16 mL, 3.00 mmol), and NaOAc (16 mg, 0.20 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature under an Ar atmosphere. After being stirred for 8 h, the solution was evaporated, and diluted with ether. Next, the precipitated Rh-complex was filtered off, and the filtrate was concentrated in vacuo to leave a residue, which was purified by column chromatography on silica gel to give **30** (96 mg, 82%) as a colorless oil. IR (neat): 2930, 2860, 1642 cm^{-1}. ^1H NMR ($CDCl_3$): δ 12.40 (s, 1H), 7.77 (br d, J = 8 Hz, 1H), 7.46 (br t, J = 8 Hz, 1H), 6.98 (br d, J = 8 Hz, 1H), 6.89 (br t, J = 8 Hz, 1H), 2.98 (t, J = 7.6 Hz, 2H), 1.74 (quintet, J = 7.6 Hz, 2H), 1.28−1.41 (m, 10H), 0.88 (t, J = 6.6 Hz, 3H). EI-HRMS calcd for $C_{15}H_{22}O_2$ (M^+) 234.1620, found 234.1616.

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Supporting Information Available: Preparation of alkenylnitriles **8** and **9**, spectroscopic data, and copies of ^1H NMR or ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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