Regio-, Diastereo-, and Chemoselectivities in the Dioxirane Oxidation of Acyclic and Cyclic Allylic Alcohols by Methyl(trifluoromethyl)dioxirane (TFD): A Comparison with Dimethyldioxirane

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The solvent-dependent shift in the regioselectivity of the geraniol epoxidation by methyl(trifluoromethyl)dioxirane (TFD) reveals that as for the less reactive dimethyldioxirane (DMD), hydrogen bonding stabilizes the transition state of the epoxidation. In protic media, the hydrogen bonding is exerted intermolecularly by the solvent, whereas in unpolar, non-hydrogen-bonding solvents intramolecular assistance through the adjacent hydroxy functionality comes into the play and the attack on the allylic alcohol moiety is favored. For chiral allylic alcohols, additional steric interactions control the π-facial selectivity in the conformationally fixed transition state. Analogous to DMD, the preferred dihedral angle in the hydrogen-bonded transition state of the TFD epoxidation constitutes approximately 130°, but contrary to DMD and for synthetic purposes important, the allylic alcohols and derivatives **1** and **3−5** investigated here are chemoselectively epoxidized by TFD without formation of the corresponding enones.

Introduction

After a decade of mechanistic studies on the reactivity of dioxiranes,[1] recent work has been focused on the selectivity of these useful oxidants.[2] Special attention was paid to the π-facial selectivity of dimethyldioxirane (DMD) in epoxidations[3][4][5], since such oxygen-transfer reactions constitute a valuable tool in the diastereoselective synthesis.[6] Recent results have demonstrated that DMD displays slightly higher diastereoselectivities as epoxidizing agent than *m*CPBA when purely steric factors control the π-facial preference.[3b][5] Moreover, in analogy to peracids, also for DMD the transition state of the epoxidation is stabilized by hydrogen bonding with OH[3][4] and NH_2[7] functionalities. This appreciable diastereoselectivity-directing stabilization may either take place intermolecularly by a protic solvent or intramolecularly by an allylic hydroxy or amino group. Besides the stereoselectivity, the transition state stabilization through hydrogen bonding is further substantiated by kinetic competition experiments on the solvent-dependent regioselectivity of the geraniol epoxidation.[4a][4b] These selectivity trends reveal that hydrogen bonding is weaker for DMD than for *m*CPBA.[8]

In competition with such hydroxy-directed diastereoselective epoxidations, also allylic oxidation to the corresponding enone has been observed for a variety of allylic alcohols in the DMD oxidations. Especially cyclic substrates and vinylsilanes show a pronounced tendency towards competitive allylic oxidation instead of the expected epoxidation.

In the present study we have examined the oxidation of acyclic allylic alcohols **1** and the cyclic substrates **3−5** by methyl(trifluoromethyl)dioxirane (TFD). Two questions were of interest: on one hand, how sensitive is the more reactive TFD (compared to DMD) towards stabilization effects through hydrogen bonding by testing its regioselectivity and π-facial diastereoselectivity in the epoxidation; on the other hand, how chemoselective is the more reactive TFD (compared to DMD) as reflected in the extent of enone formation versus epoxidation. The results described herein unequivocally display that the more reactive TFD is definitely less regioselective, about as diastereoselective, but significantly more chemoselective than DMD.

Results and Discussion

All TFD epoxidation of geraniol **1a** and its derivatives **1b−d** were performed as with DMD[4a][4b] to only 30% conversion in order to prevent any bisepoxide formation. As shown in Table 1, geraniol (**1a**) is preferentially epoxidized by TFD at the 6,7 position, but the regioselectivity decreases (entries 1−3) from that in the most polar MeOH/TFA (9:1) to the least polar CCl_4/TFA (9:1) medium (TFA stands for 1,1,1-trifluoroacetone). In contrast, the geraniol methyl ether (**1b**) shows no detectable solvent effect (entries 4 to 6). For the trimethylsilyl ether (**1c**) and acetate (**1d**)

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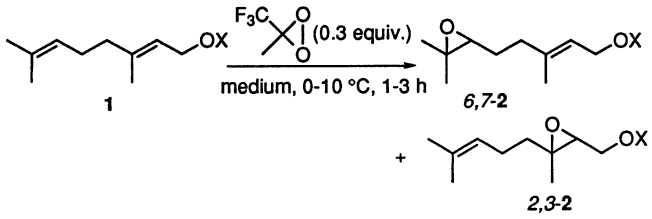
Table 1. Solvent effects on the regioselectivity in the TFD epoxidation of geraniol (**1a**) and derivatives **1b–d**



entry	substrate	X	medium[a]	conversion[b] [%]	*6,7*/*2,3* TFD	distribution[c] DMD[d]
1	**1a**	H	MeOH/TFA (9:1)	21	73:27	88:12
2	**1a**	H	TFA	22	68:32	74:26
3	**1a**	H	CCl_4/TFA (9:1)	25	57:43	51:49
4	**1b**	Me	MeOH/TFA (9:1)	31	68:32	88:12
5	**1b**	Me	TFA	32	73:27	88:12
6	**1b**	Me	CCl_4/TFA (9:1)	32	71:29	87:13
7	**1c**	$SiMe_3$	TFA	33	70:30	85:15
8	**1d**	Ac	TFA	30	83:17	96:4

[a] TFA = 1,1,1-trifluoroacetone. – [b] Mass balances >90%. – [c] Determined by ^{1}H-NMR analysis directly on the crude product mixture (error ±5% of the stated values). – [d] Ref.[4b], values given for identical solvent mixtures with acetone instead of TFA.

of geraniol, again the 6,7 regioisomer is favored (entries 7 and 8).

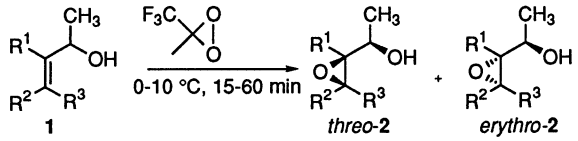
The π-facial diastereoselectivity was tested for the set of methyl-substituted, acyclic allylic alcohols **1e–i** (Table 2). The substrates **1e** and (*E*)-**1g** without methyl substituents in the *gem*- or *cis*- positions react rather unselectively to yield nearly 50:50 diastereoselectivities, irrespective of the solvent used (Table 2, entries 1, 4, and 5). For the *gem*-disubstituted substrate **1f** with 1,2-allylic ($A^{1,2}$) strain, the *threo* selectivity is enhanced in the CCl_4/TFA (9:1) compared to TFA (entries 2 and 3). Still higher diastereoselectivities were obtained for the substrates (*Z*)-**1g** (entries 6 and 7) and **1h** (entries 8 and 9) with $A^{1,3}$ strain, which again increased in the unpolar CCl_4/TFA (9:1) mixture. For the derivative **1i** with both $A^{1,2}$ and $A^{1,3}$ strain, the diastereoselectivities are the highest of the substrates examined herein (entries 10 and 11).

Unexpected was the fact that the *trans*-disubstituted substrate (*E*)-**1g** was cleanly epoxidized by TFD without allylic oxidation, whereas with DMD as much as 10% of the corresponding enone was obtained.[4b] This encouraged us to probe more deliberately such allylic oxidations of TFD with cyclic allylic alcohols.[4a] The results in Table 3 show that for TFD exclusively epoxidation takes place with increased *cis* diastereoselectivities in the oxygen transfer for the parent 2-cyclohexenol (**3**) and for isophorol (**4**) in the less polar medium (entries 1–4). Even for the substrate **5** (enty 5), which is the most susceptible one towards allylic oxidation (DMD gave 57% enone[4a]), no allylic oxidation was observed. Noteworthy, the DMD oxidation of substrate **5** yields quite similar epoxide/enone ratios in 4:1 trifluoroacetone/acetone as in pure acetone (cf. footnotes e and g in Table 3).

Regioselectivity

The regioselectivity data (Table 1) for geraniol (**1a**) and its oxygen-functionalized derivatives **1b–d** express clearly the hydroxy-directing effects in the TFD epoxidations. Analogous to DMD, in all solvent systems the terminal *6,7* rather than the *2,3* double bond is preferentially epoxidized. Although both double bonds are trisubstituted, the nucleophilicity of the *2,3* double bond is significantly lowered by the inductively electron-accepting hydroxy group. As to the solvent effects, methanol (entry 1) stabilizes both dipolar transition states to the same extent, so that intramolecular hydrogen bonding by the allylic hydroxy functionality does not come into play and the regioisomeric product distribution is merely a function of the relative nucleophilicity of the two double bonds. In contrast, in the least polar and non-protic medium 9:1 CCl_4 and trifluoroacetone (entry 3), external hydrogen bonding is absent and the dipolar transition state to afford the *2,3*-epoxide is assisted through intramolecular hydrogen bonding by the allylic hydroxy functionality. The observed small but definite shift to more *2,3*-epoxide provides evidence for the conformationally preferred six-membered-ring, hydrogen-bonded transition state (Figure 1). Thus, the unfavorable π nucleophilicity of the *2,3* double bond is counteracted by the favorable hydroxy-group assistance. The stabilization is, however, less pronounced for TFD than for DMD, as manifested by the smaller solvent-induced shift in the regioselectivity for the former (compare last two columns in Table 1).

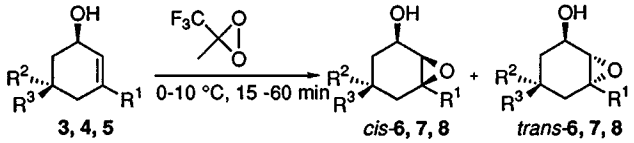
Table 2. Solvent effects on the diastereoselectivities in the dioxirane epoxidation of allylic alcohols **1**



entry	substrate	R^1	R^2	R^3	medium[a]	m.b.[b] [%]	conv. [%][c,d]	*threo*/*erythro* TFD	selectivity[d] DMD[e]
1	**1e**	H	H	H	B	90	>95	55:45	50:50
2	**1f**	Me	H	H	A	99	>95	53:47	60:40
3	**1f**	Me	H	H	B	92	>95	62:38	70:30
4	(*E*)-**1g**	H	Me	H	A	97	>95	48:52	53:47[f]
5	(*E*)-**1g**	H	Me	H	B	87	76	43:57	56:44[f]
6	(*Z*)-**1g**	H	H	Me	A	98	95	77:23	67:33
7	(*Z*)-**1g**	H	H	Me	B	68	93	88:12	85:15
8	**1h**	H	Me	Me	A	95	>95	76:24	76:24
9	**1h**	H	Me	Me	B	82	>95	82:18	82:18
10	**1i**	Me	H	Me	A	99	>95	85:15	87:13
11	**1i**	Me	H	Me	B	84	60	90:10	91:9

[a] A: 1,1,1-trifluoroacetone (TFA), B: CCl_4/TFA (9:1). – [b] Mass balance. – [c] Yield >95% in all cases. – [d] Determined by ^{1}H-NMR analysis of characteristic signals (error ±5% of the stated values). – [e] Ref.[4b], values given for identical solvent mixtures with acetone instead of TFA. – [f] Epoxide/enone ratio ca. 90:10.

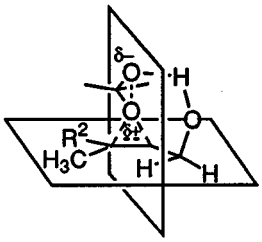
Table 3. Diastereoselectivities in the dioxirane epoxidations of cyclic allylic alcohols **3**–**5**



entry		R^1	R^2	R^3	medium[a]	m.b.[b] [%]	conv.[c,d] [%]	*cis*/*trans* TFD	selectivity[d] DMD[e]
1	**3**	H	H	H	A	85	70	57:43	43:57 [52:48]
2	**3**	H	H	H	B	96	78	70:30	66:34 [61:39]
3	**4**	Me	Me	Me	A	100	84	88:12	83:17 [77:23]
4	**4**	Me	Me	Me	B	92	70	94: 6	96: 4 [92: 8]
5	**5**	H	H	*t*Bu	A	99	80	73:27[f]	60:40[f] [44:56][g]

[a] A: 1,1,1-trifluoroacetone (TFA), B: CCl_4/TFA (9:1); for DMD, acetone instead of TFA applies (cf. ref.[4a]). – [b] Mass balance. – [c] Yield >95% in all cases. – [d] Determined by ^{1}H-NMR analysis of characteristic signals (error ±5% of the stated values). – [e] For DMD also appreciable amounts of enone were obtained, cf. ref.[4b], the epoxide/enone ratio (chemoselectivity) is given in brackets. – [f] Relative configuration with respect to the hydroxy group. – [g] The epoxide/enone ratio is the same (within the experimental error) for pure acetone and for an 4:1 mixture of TFA/acetone.

Figure 1. Stabilization of the *spiro* transition state through intramolecular hydrogen bonding



The assistance through intramolecular hydrogen bonding by the allylic hydroxy group is further substantiated by the regioselective epoxidation of the methyl ether **1b**. In this case, no allylic hydroxy proton is available to assist intramolecularly in the epoxidation of the less nucleophilic *2,3* double bond. Hence, the ratio of *6,7*- to *2,3*-epoxides is within the experimental error the same in all three solvents employed (Table 1, entries 4–6) and the regioselectivity is similar to that for geraniol (**1a**) in methanol as cosolvent (entry 1). Moreover, the corresponding trimethylsilyl ether **1c** with similar electronic properties as the methyl ether **1b** (enty 7) yields a regioselectivity identical to that for the methyl ether **1b** (entry 5). The acetate **1d** (entry 8), however, shows a more pronounced 6,7 regioselectivity, which is due to the stronger deactivation of the 2,3 double bond by the

higher inductive electron-withdrawal of the acetoxy functionality.

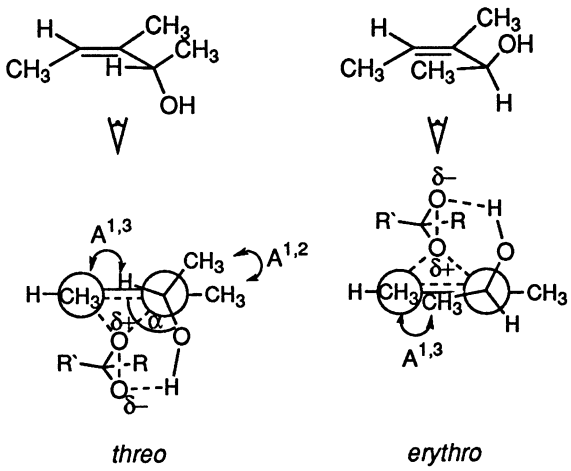
Noteworthy is the fact that the preference for the 6,7 double-bond epoxidation is generally less pronounced for TFD than for DMD (compare the last two columns in Table 1), i.e. TFD as the more reactive oxidant responds less sensitively to the relative nucleophilicity of the two double bonds. Only in the CCl_4 solvent mixture (Table 1, entry 3) shows TFD a slightly higher propensity towards 6,7 epoxidation than DMD. In this non-polar medium, the intramolecular stabilization by the allylic hydroxy functionality is coming fully into play and the inversion of the general trend reflects the more pronounced hydrogen bonding for DMD as compared to TFD.

Diastereoselectivity

As a consequence of stabilization effects through intramolecular hydrogen bonding, the diastereoselectivity should also be directed in the TFD epoxidation of chiral allylic alcohols by the hydroxy group, as already demonstrated for DMD[4]. Indeed, for TFD a similar solvent dependence of the *threo*/*erythro* diastereoselectivity is observed in the epoxidation of the acyclic substrates **1e−i** as for DMD (compare the last two columns in Table 2). The substrates **1e** and (*E*)-**1g** without any allylic strain[9] (entries 1, 4, and 5), do not display any diastereoselectivity nor solvent effects in the dioxirane epoxidations. Therefore, the lack of allylic strain provides no steric differentiation of the two π faces irrespective whether a hydrogen-bonded stabilization operates in the transition state. For the substrate **1f** with only $A^{1,2}$ strain (entries 2 and 3) and for the derivatives (*Z*)-**1g** and **1h** with only $A^{1,3}$ strain (entries 6−9), the diastereoselectivities are always significantly higher in the unpolar 9:1 TFA/CCl_4 solvent mixture (entries 3, 7, and 9) than in the more polar TFA (entries 2, 6, and 8). As suggested in Figure 1, in the non-polar solvent mixture the transition state geometry is best fixed by intramolecular hydrogen bonding with the allylic hydroxy group and, hence, the better the π-facial control. Notably, as for DMD, also for TFD (compare last two columns in Table 2), $A^{1,3}$ strain in the *cis*-substituted substrates (*Z*)-**1g** (entry 7) and **1h** (entry 9) is more effective in dictating the *threo* selectivity than the $A^{1,2}$ strain in the *gem*-substituted derivative **1f** (entry 3). This is unequivocally demonstrated by the stereochemical probe,[10] namely the chiral allylic alcohol **1i** (entry 11) with both $A^{1,2}$ and $A^{1,3}$ strain, which displays the highest *threo* diastereoselectivity of all the acyclic substrates (Table 2) examined here.

For convenience, the two possible diastereomeric transition states of the oxygen transfer for the stereochemical probe **1i** are exhibited in Figure 2. Since with both TFD and DMD the same *threo* selectivity is observed (entry 11), the same C=C−C−O dihedral angle (α ca. 130°)[4a][4b] applies. Consequently, it is not surprising that $A^{1,3}$ dominates over $A^{1,2}$ strain. In fact, a slight synergistic effect operates since the preference for the *threo* attack is significantly larger for substrate **1i** with both $A^{1,3}$ and $A^{1,2}$ strain (entry 11) than for derivative **1h** with only $A^{1,3}$ (entry 9) or **1f** with only $A^{1,2}$ strain (entry 3).

Figure 2. Diastereomeric transition states in the epoxidation of allylic aclcohol **1i**



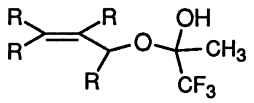
Furthermore, also the diastereoselectivity data for the epoxidation of the cyclic allylic alcohols **3**−**5** (Table 3) by TFD is in good accord with the results for DMD.[4a][4b] Therefore, also these stereochemical results substantiate the conclusions derived from the acyclic systems (Figure 2) in regard to the suggested transition-state geometry.

Chemoselectivity

As stated initially, our interest in the cyclic substrates **3**−**5** was to test the chemoselectivity of the more reactive TFD in terms of enone formation by CH insertion versus epoxidation. In this context, the finding was unexpected that for TFD all three substrates were exclusively epoxidized without even traces of enone (Table 3). Analogous to the enone formation in the oxidation of allylic alcohols by $VO(acac)_2$/tBuOOH as oxidant,[11] a convincing mechanistic rationale is yet to be given for the unusual DMD reactivity.

In view of the higher propensity of TFA versus acetone to form hydrates with water, we suspected that the allylic alcohol was converted to the corresponding hemiacetal structure **9** in the TFA medium and thereby the substrate was deactivated towards allylic CH oxidation to the enone. This is akin to the lack of CH bond oxidation in acetates and also acetyl derivatives of allylic alcohols.[3b][4a][4b][12] However, that this explanation does not apply is convincingly demonstrated by the control experiment (cf. footnotes e and g in Table 3) with substrate **5**, in which the epoxide/enone ratio was for DMD the same (within the experimental error) in the 4:1 TFA/acetone mixture as in pure acetone. Hence, even though TFD is the more reactive oxidant than DMD, it is also significantly more chemoselective in terms of epoxidation versus allylic oxidation.

This apparent violation of the reactivity-selectivity principle (RSP) is remarkable since the regioselectivity of the geraniol epoxidation (Table 1) followed the expected reac-



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tivity trend, i.e. the more reactive TFD is also the less regioselective. Presumably, for competitive epoxidations with similar transition states, as is unquestionably the case in the regioselectivity for geraniol (**1a**), the RSP is obeyed and many cases have been reported.[13] Nevertheless, for processes with different transition states, as must be undoubtedly the case for the competitive allylic oxidation versus epoxidation, the RSP fails.

Conclusion

In conclusion, our present study on the regioselectivity and diastereoselectivity of TFD oxidations for a variety of substrates manifests that also for this highly reactive dioxirane, intramolecular stabilization through hydrogen bonding operates in the epoxidation of allylic alcohols. The geometry of the postulated six-membered-ring cyclic transition state is similar to the one postulated for DMD, as derived from the diastereoselectivities displayed by the chiral allylic alcohols. Furthermore, the more nucleophilic double bond is preferentially epoxidized, provided no hydroxy-directing effect counteracts this nucleophilicity trend. These facts also imply that as for DMD,[14] the epoxidation by TFD proceeds by an oxenoid attack of the dioxirane on the double bond to form a partially polarized transition state. Of synthetic importance is the fact that TFD possesses a much higher chemoselectivity than DMD, since none of the allylic alcohols **1** and **3**−**5** were oxidized to the corresponding enone, which would have been hardly anticipated.

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Experimental Section

General Aspects: ^{1}H- and ^{13}C-NMR spectra were recorded with a Bruker AC 200 and AC 250 spectrometer by using $CDCl_3$ as internal standard. Potassium iodide starch paper (Merck) was used for the peroxide tests. − Methyl(trifluoromethyl)dioxirane (TFD)[15] and dimethyldioxirane (DMD)[16] were prepared according to the described literature procedure, whereby essentially ketone-free solutions were obtained by the extraction procedure. The starting materials **1b**[17], **1c**[18], and **1d**[19] were prepared according to literature procedures, **1f**−**i**[4a] and **3**−**5**[4b] were made as earlier described. The product ratios were determined by comparison of the spectral data with those given in the literature for *2,3*-**2a**[4a], *6,7*-**2a**[4a], *2,3*-**2b**[22], *6,7*-**2b**[17], *2,3*-**2c**[21], *2,3*-**2d**[22], *6,7*-**2d**[22], **2e**−**i**[4a], **3**[4b], **4**[4b], and **5**[4b] or by independent preparation according to literature procedures. The commercial compounds **1a** and **1e** were used as received, solvents were purified and dried by reported standard methods. The hitherto unknown epoxide *6,7*-**2c** was fully characterized.

General Procedure for the Epoxidations of Alkenes by Methyl(trifluoromethyl)dioxirane: The alkene **1**, **3**, **4**, or **5** was dissolved in an organic solvent (cf. Table 1−3) and 0.3−1.1 equiv. of methyl(trifluoromethyl)dioxirane (0.2−0.45 M solution in acetone) was rapidly added at 0−10°C. The solution was stirred at this temperature until the peroxide test (KI/HOAc) was negative. The solvent was removed (20°C, 20−100 Torr) to afford a mixture of the corresponding epoxides in high purity and the product mixture analyzed by ^{1}H NMR spectroscopy. The quantitative results are summarized in Tables 1−3.

2,2-Dimethyl-3-[3-methyl-5-trimethylsilyloxy-(E)-pent-3-enyl]oxirane (*6,7*-**2c**): A 0.08-M solution of dimethyldioxirane (5.45 ml, 0.44 mmol) in 1,1,1-trifluoroacetone was added to 300 mg (1.33 mmol) alkene. The solution was stirred at ca. 20°C for 15 min and the solvent was removed (20°C, 20 Torr) to yield, at a conversion of 35%, 312 mg of a colorless oil. The two regioisomers were separated by low-temperature (−10°C) column chromatography on silica gel with petroleum ether/Et_2O (4:1) as eluent to yield 100 mg (32%) of the regioisomerically pure epoxide *6,7*-**2c**. − ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.12 (s, 9 H), 1.25 (s, 3 H), 1.30 (s, 3 H), 1.66 (s, 3 H), 1.59−1.71 (m, 2 H), 2.03−2.27 (m, 2 H), 2.71 (dd, J_1 = 6.4, J_2 = 6.0 Hz, 1 H), 4.15 (d, J = 6.4 Hz, 2 H), 5.36 (mdd, J_1 = 6.7, J_2 = 6.4 Hz, 1 H). − ^{13}C NMR (63 MHz, $CDCl_3$): δ = 0.0 (3× q) 16.3 (q), 18.7 (q), 24.8 (q), 27.1 (t), 36.1 (t), 58.4 (s), 59.3 (t), 64.0 (d), 124.3 (d), 136.7 (s). − IR (CCl_4): $\tilde{\nu}$ = 2940, 1440, 1370, 1240, 1110, 1060, 870, 840 cm^{-1}. − calcd. $C_{13}H_{26}OSi$ (242.4): C 64.41, H 10.81; found: C 63.91, H 11.08.

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