Effect of Methyl Substituents on the Double Bond Involved in the Formation of Tetrahydropyrans from Hydroxy Allylic Acetates

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Synopsis. Substitutive cyclization of allylic acetates by an internal secondary hydroxyl group under acidic conditions to yield 2,6-disubstituted tetrahydropyrans has been investigated. The reaction is influenced by the substitution type of the double bond.

Methyl sarcophytoate (**1**), isolated from the Okinawan soft coral *Sarcophyton glaucum*,[1] and four other members belong to biscembranoids (tetraterpenoids).[2] Biogenetically, they are considered to be formed by Diels–Alder reaction of two cembranes.[1,2] During the course of our synthetic studies of biscembranoids,[2] we discovered that treatment of each of the C28-epimeric allylic alcohols **2** with $BF_3{\cdot}OEt_2$ afforded the 2,6-disubstituted tetrahydropyran **3** as the sole product (Fig. 1).[3] It is clear that the reaction occurred via allylic substitution by the C32-oxygen atom concomitant with the acetonide migration. 2,6-Disubstituted tetrahydropyran units and 2,5-disubstituted tetrahydrofuran units are widely found in many natural products and a variety of synthetic methods of such units have been investigated.[4] Some example employing π-orbital-activated substitution reactions are cyclization of hydroxy propargyl sulfonates,[5a] palladium-catalyzed cyclization of hydroxy allylic acetates,[5b] acid-catalyzed cyclization of hydroxy vinyl epoxides,[5c] palladium-catalyzed cyclization of hydroxy epoxy unsaturated esters,[5d] cyclization of a hydroxy furylmethyl sulfonate,[5e] acid-catalyzed cyclization of allyloxy allylic acetates,[5f] Mitsunobu cyclization of diols substituted with heterocycles,[5g] and acid-catalyzed cyclization of hydroxy *p*-methoxystyrylmethyl alcohol.[5h] We expected that substitutive cyclization of allylic acetates by an internal secondry hydroxyl group under acidic conditions would provide cyclic ethers possessing diequatorial substituents on both the carbons adjacent to the oxygen. We wish to describe here our preliminary results concerning the effect of the methyl substituents on the double bond involved in the formation of 2,6-disubstitued tetrahydropyrans from hydroxy allylic acetates.

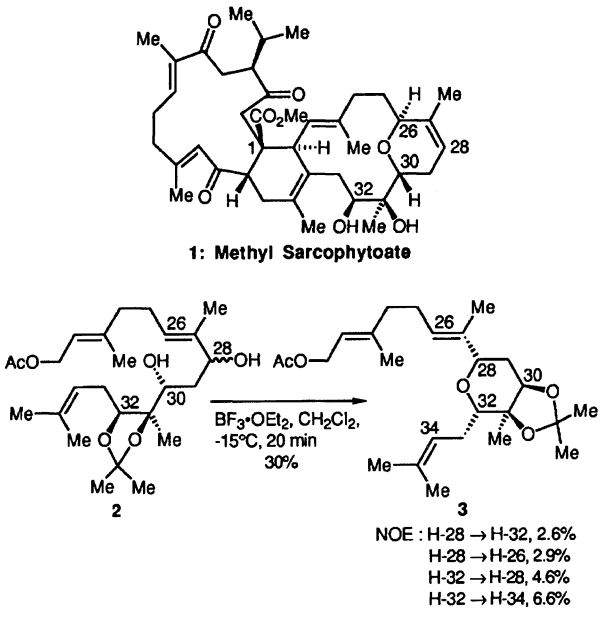


Fig. 1.

Results and Discussion

Preparation of the model compounds was straightforward (Fig. 2). Aldehyde **4**[6] underwent addition reaction with vinyl Grignard reagents or vinyllithium reagent to afford allylic alcohols **5a**—**5e**. Acetylation of **5a**—**5e** followed by desilylation provided allylic acetates **6a**—**6e**. The diastereoisomeric ratio of **6a**—**6e** are almost 1 : 1 judging from the ^{1}H NMR analyses of the corresponding naphthoyl esters **7a**—**7e**. Both **6c** and **6d** are a 1 : 3 mixture of *E* and *Z* isomers.

We examined a number of conditions to achieve cyclization. In the cases of the monosubstituted olefin **6a** and the 1,1-disubstituted olefin **6b**, all attempts

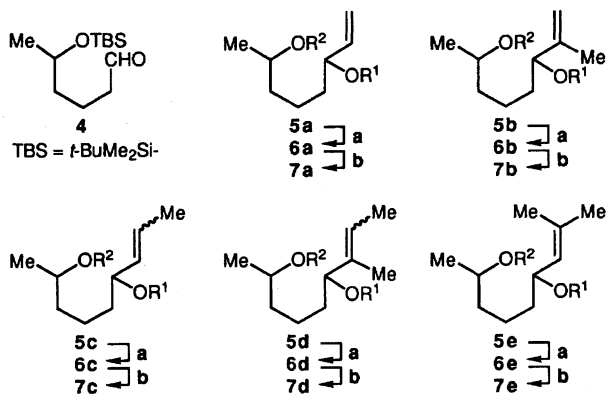
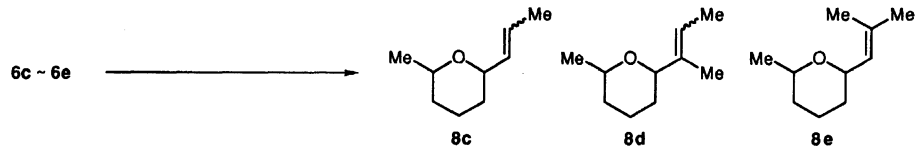


Fig. 2.

Table 1. Cyclization of **6c**—**6e**



8c 8d 8e

Entry	Substrate	Conditions				Product	Product ratio[a]		
		Acid (equiv)	Solvent	Temp (°C)	Time		2,6-*cis* : 2,6-*trans*	*E* : *Z*	
								2,6-*cis*	2,6-*trans*
1	**6c**	BF_3·OEt_2 (1.1)	CH_2Cl_2	−78—0	2.5 h	Decomposition			
2	**6c**	BF_3·OEt_2 (1.1)	CH_3CN	−20—25	1.0 h	No reaction			
3	**6c**	BF_3·OEt_2 (1.1)	DMF	0—70	4.5 h	Decomposition			
4	**6c**	CSA (1.1)	CH_3CN	25	22 h	**8c**	1 : 1	3 : 1	3 : 1
5	**6c**	CSA (1.1)	CH_3CN	25	14 d	**8c**	10 : 1	3 : 1	1 : 1
6	**6d**	BF_3·OEt_2 (1.1)	CH_2Cl_2 or CH_3CN	0	0.5 h	Decomposition			
7	**6d**	CSA (1.1)	CH_3CN	25	4 h	**8d**	2 : 1	3 : 1	1 : 1
8	**6d**	CSA (1.1)	CH_3CN	25	5 d	**8d**	1 : 0	3 : 1	
9	**6d**	CSA (0.1)	CH_3CN	25	4 h	**8d**	3 : 1	3 : 1	1 : 1
10	**6e**	BF_3·OEt_2 (1.1)	CH_2Cl_2 or CH_3CN	0	1.5 h	Decomposition			
11	**6e**	CSA (1.1)	CH_3CN	25	0.5 h	**8e**	1 : 0		
12	**6e**	CSA (0.1)	CH_3CN	25	0.5 h	**8e**	1 : 0		

a) Product ratio was based on the ^{1}H NMR (270 MHz) analysis of the crude product.

were completely unsuccessful, giving either recovered starting material or decomposition, depending on the conditions employed [acids: BF_3·OEt_2, $TiCl_4$, $SnCl_4$, Et_2AlCl, $EtAlCl_2$, $AlCl_3$, camphorsulfonic acid (CSA); solvents: CH_2Cl_2, CH_3CN, DMF; various reaction temperatures and times]. In sharp contrast, detailed in Table 1, when the 1,2-disubstituted olefin **6c** was treated with 1.1 equiv of CSA in acetonitrile at 25 °C for 22 h, tetrahydropyran **8c** was obtained as a 1 : 1 mixture of the 2,6-*cis* and the 2,6-*trans* isomers (**8c-*cis*** and **8c-*trans***, respectively) in almost quantitative yield (Entry 4).[7] The *E*: *Z* ratio of the olefin geometry changed from 1 : 3 in **6c** to 3 : 1 in **8c**. Prolonged (25 °C, 14 d) exposure of **6c** in the same conditions produced a 10 : 1 mixture of **8c-*cis*** and **8c-*trans*** (Entry 5) and the *E*: *Z* ratio of **8c-*cis*** and **8c-*trans*** was 3 : 1 and 1 : 1, respectively.[8] We next examined cyclization of the trisubstituted olefins **6d** and **6e** (Entries 6—12). In the case of **6d**, a 2 : 1 mixture of the 2,6-*cis* and the 2,6-*trans* isomers, **8d-*cis*** and **8d-*trans***, was obtained under the conditions of 1.1 equiv of CSA in acetonitrile at 25 °C for 4 h (Entry 7); the *E*: *Z* ratio of **8d-*cis*** and **8d-*trans*** was 3 : 1 and 1 : 1, respectively. After five days, **8d-*cis*** became the only product (*E*: *Z* = 3 : 1) (Entry 8). A 3 : 1 mixture of **8d-*cis*** and **8d-*trans*** was obtained when **6d** was treated with a catalytic amount (0.1 equiv) of CSA (Entry 9). In the case of **6e**, the reaction proceeded rapidly under the same conditions (Entries 11 and 12). It is noteworthy that the 2,6-*cis* isomer **8e-*cis*** was the sole product.[9] The stereochemical assignment of **8c-*cis***—**8e-*cis*** was confirmed by the ^{1}H NMR *J* analyses and the NOE measurements (see Experimental). On the contrary, the conformation of **8c-*trans*** and **8d-*trans*** could not be determined because of their conformational flexibilities.

Solvolysis reactions of allylic chlorides and allylic *p*-nitrobenzoates have been shown to proceed via allylic cations in 0.5% aqueous formic acid at 44.6 °C[10] and in 80% aqueous acetone at 25 °C,[11] respectively. The relative rates of these unimolecular hydrolyses are the following (Fig. 3). Ab initio MO calculations of methyl-substituted allylic cations have been investigated and the stability data are in good accordance with the above solvolysis experiments.[12] Our own results are consistent with all these previous data. Namely, cyclization proceeds in a S_N1 fashion including allylic cations, whose stabilities govern the reactivity of allylic acetates, the rate of cyclization, and the rate for establishing equilibrium. Sequential substitution of the olefinic hydrogens by methyl groups facilitates the formation of tetrahydropyrans and substitution of the terminal position is more crucial than that of the internal position.

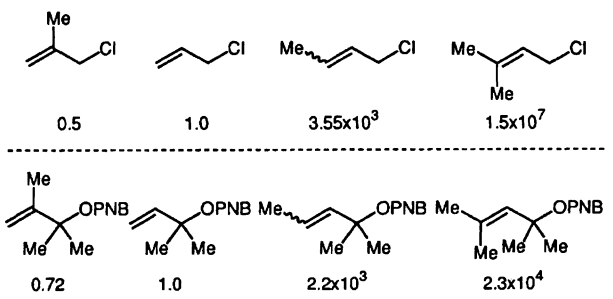


Fig. 3.

Experimental

IR spectra were recorded on a BIO RAD DIGILAB FTS-65 spectrometer and ^{1}H NMR spectra on a JEOL GSX270 spectrometer in $CDCl_3$ using TMS as internal standard unless otherwise noted. Mass spectra were recorded on a JEOL JMS-DX302 mass spectrometer. Silica-gel TLC and column chromatography were performed on a Merck TLC 60F-254 and a Fuji-Davison BW-820MH, respectively.

General Procedure. Preparation of 5a—5d: To a solution of **4** (198 mg, 0.860 mmol) in dry THF (4 ml) at −90 °C was added a Grignard reagent [prepared from the corresponding allylic bromide (8.60 mmol) and Mg (4.30 mmol) in dry THF (10 ml) at 25 °C for 1.5 h] and the mixture was stirred at −90 °C for 0.5—1.0 h. Saturated aqueous NH_4Cl was added and the mixture was extracted with $CHCl_3$. The extracts were washed with saturated aqueous NaCl, dried and concentrated. The residue was chromatographed on silica gel with hexane–ethyl acetate to afford **5a—5d** (67% for **5a**, 72% for **5b**, 82% for **5c**, 68% for **5d**) as colorless syrups.

Preparation of 5e: To a solution of 1-bromo-2-methyl-1-propene (0.227 ml, 2.21 mmol) in dry THF (5.1 ml) was added at −78 °C 1.61 M *t*-BuLi in pentane (2.76 ml, 4.44 mmol) (1 M=1 mol dm^{-3}). After 10 min at −78 °C, the mixture was cooled to −90 °C and to this was added a solution of **4** (225 mg, 1.11 mmol) in dry THF (2.55 ml). After 1 h at −90 °C, the reaction mixture was worked up as described for the preparation of **5a—5d** to afford **5e** (139 mg, 44%) as a colorless syrup.

Preparation of 6a—6e: To a solution of **5a—5e** (0.750 mmol) in dry CH_2Cl_2 (4.0 ml) were added acetic anhydride (2.25 mmol), triethylamine (3.00 mmol), and 4-dimethylaminopyridine (0.0750 mmol). After 0.5 h at 25 °C, the reaction mixture was poured into water and this was extracted with ethyl acetate. The extracts were washed with saturated aqueous NaCl, dried, and concentrated. The residue was dissolved in THF (2.5 ml) and to this was added 1 M tetrabutylammonium fluoride in THF (2.25 mmol). After 15 h at 35 °C, the mixture was worked up as described above for acetylation and the residue was chromatographed on silica gel with hexane–ethyl acetate to afford **6a—6e** (80—94%) as colorless syrups.

Preparation of 7a—7e: Treatment of a solution of **6a—6e** in dry pyridine with 1-naphthoyl chloride (1.5 equiv) at 25 °C for 1 h afforded **7a—7e** (95—100%) as colorless syrups.

Cyclizaiton of 6c—6e: All reactions in Table 1 were carried out by adding an acid to a solution of **6** in solvent (0.25 M for **6**). Each reaction was stopped when **6** disappeared on TLC or after the indicated time. After addition of saturated aqueous $NaHCO_3$, the mixtuer was extracted with pentane and the extracts were washed with saturated aqueous NaCl, dried, and concentrated under reduced pressure below 0 °C to afford **8c—8e** quantitatively.

6-Acetoxy-7-octen-2-ol (6a): 87% yield; IR ($CHCl_3$) 1723 cm^{-1}; ^{1}H NMR ($CHCl_3$=7.26) δ=1.18 (3H, d, J=6.0 Hz, Me), 1.30—1.70 (6H, m, 3×CH_2), 2.07 (3H, s, OAc), 3.79 (1H, br m, C*H*OH), 5.10—5.30 (3H, m, CH=C*H*$_2$ and C*H*OAc), 5.77 (1H, ddd, J=17.0, 10.0, and 6.0 Hz, C*H*=CH$_2$). HRMS, Found: m/z 187.1342 (M^++1). Calcd for $C_{10}H_{19}O_3$: M+1, 187.1334.

6-Acetoxy-7-methyl-7-octen-2-ol (6b): 80% yield; IR ($CHCl_3$) 1729 cm^{-1}; ^{1}H NMR δ=1.19 (3H, d, J=6.0 Hz, Me), 1.25—1.70 (6H, m, 3×CH_2), 1.72 (3H, br s, C*Me*=CH$_2$), 2.07 (3H, s, OAc), 3.79 (1H, br m, C*H*OH), 4.88 and 4.95 (each 1H, each br s, C=C*H*$_2$), 5.17 (1H, t, J=6.0 Hz, C*H*OAc). HRMS, Found: m/z 201.1482 (M^++1). Calcd for $C_{11}H_{21}O_3$: M+1, 201.1491.

6-Acetoxy-7-nonen-2-ol (6c): 94% yield; IR ($CHCl_3$) 1726 cm^{-1}; ^{1}H NMR of *Z*-isomer: δ=1.19 (3H, d, J=6.2 Hz, Me), 1.25—1.80 (9H, m, 3×CH_2 and CH=CH*Me*), 2.03 (3H, s, OAc), 3.79 (1H, br m, C*H*OH), 5.32 (1H, ddq, J=11.0, 9.2, and 2.0 Hz, C*H*=CHMe), 5.57 (1H, m, C*H*OAc), 5.65 (1H, dq, J=11.0 and 7.0 Hz, CH=C*H*Me). ^{1}H NMR of *E*-isomer: δ=1.19 (3H, d, J=6.2 Hz, Me), 1.25—1.80 (9H, m, 3×CH_2 and CH=CH*Me*), 2.04 (3H, s, OAc), 3.79 (1H, br m, C*H*OH), 5.19 (1H, ddd, J=7.6, 7.6, and 7.6 Hz, C*H*OAc), 5.41 (1H, ddq, J=15.2, 7.6, and 1.6 Hz, C*H*=CHMe), 5.72 (1H, dq, J=15.2 and 6.4 Hz, CH=C*H*Me). HRMS (*EZ* mixture), Found: m/z 200.1389 (M^+). Calcd for $C_{11}H_{20}O_3$: M, 200.1413.

6-Acetoxy-7-methyl-7-nonen-2-ol (6d): 93% yield; IR ($CHCl_3$) 1725 cm^{-1}; ^{1}H NMR of *Z*-isomer: δ=1.19 (3H, d, J=6.0 Hz, Me), 1.25—1.80 (12H, m, 3×CH_2 and C*Me*=CH*Me*), 2.04 (3H, s, OAc), 3.79 (1H, br m, C*H*OH), 5.39 (1H, br q, J=6.0 Hz, C=C*H*Me), 5.64 (1H, t, J=7.0 Hz, C*H*OAc). ^{1}H NMR of *E*-isomer: δ=1.18 (3H, d, J=6.0 Hz, Me), 1.25—1.80 (12H, m, 3×CH_2 and C*Me*=CH*Me*), 2.04 (3H, s, OAc), 3.79 (1H, br m, C*H*OH), 5.13 (1H, t, J=7.0 Hz, C*H*OAc), 5.52 (1H, br q, J=6.0 Hz, C=C*H*Me). HRMS (*EZ* mixture), Found: m/z 215.1665 (M^++1). Calcd for $C_{12}H_{23}O_3$: M+1, 215.1647.

6-Acetoxy-8-methyl-7-nonen-2-ol (6e): 89% yield; IR ($CHCl_3$) 1724 cm^{-1}; ^{1}H NMR ($CHCl_3$=7.26) δ=1.18 (3H, d, J=6.0 Hz, Me), 1.25—1.70 (6H, m, 3×CH_2), 1.72 (6H, br s, CH=C*Me*$_2$), 2.02 (3H, s, OAc), 3.79 (1H, br m, C*H*OH), 5.09 (1H, d with a small long-range coupling, J=9.0 Hz, C*H*=CMe$_2$), 5.48 (1H, dt, J=9.0 and 6.0 Hz, C*H*OAc). HRMS, Found: m/z 214.1578 (M^+). Calcd for $C_{12}H_{22}O_3$: M, 214.1569.

2-Methyl-6-(1-propenyl)tetrahydropyran (8c): 8c-*cis*: ^{1}H NMR of *E* isomer: δ=1.19 (3H, d, J=6.2 Hz, Me), 1.20—1.90 (9H, m, 3×CH_2 and CH=CH*Me*), 3.48 (1H, ddq, J=11.0, 6.2, and 2.0 Hz, C*H*Me), 3.77 (1H, ddd, J=10.2, 6.2, and 1.0 Hz, C*H*CH=CHMe), 5.51 (1H, ddq, J=16.0, 6.2, and 1.4 Hz, C*H*=CHMe), 5.69 (1H, dq, J=16.0 and 6.0 Hz, CH=C*H*Me) (NOE: H-2→H-6, 6.8%). ^{1}H NMR of *Z* isomer: δ=4.17 (1H, ddd, J=10.2, 8.0, and 1.0 Hz, C*H*CH=CHMe).

8c-*trans*: ^{1}H NMR of *E* isomer: δ=1.17 (3H, d, J=6.2 Hz, Me), 1.20—1.90 (9H, m, 3×CH_2 and CH=CH*Me*), 3.91 (1H, ddq, J=7.0, 6.2, and 3.0 Hz, C*H*Me), 4.28 (1H, br m, C*H*CH=CHMe), 5.40—5.75 (2H, m, C*H*=C*H*Me). ^{1}H NMR of *Z* isomer: δ=4.64 (1H, m, C*H*CH=CHMe). HRMS (**8c** mixture), Found: m/z 140.1181 (M^+). Calcd for $C_9H_{16}O$: M, 140.1201.

2-Methyl-6-(1-methyl-1-propenyl)tetrahydropyran (8d): 8d-cis ^{1}H NMR of *E* isomer: δ=1.18 (3H, d, J=6.0 Hz, CH*Me*), 1.20—1.90 (12H, m, 3×CH_2 and C*Me*=CH*Me*), 3.49 (1H, ddq, J=11.0, 6.0, and 2.0 Hz, C*H*Me), 3.68 (1H, br d, J=11.0 and 0.0 Hz, C*H*CMe=CHMe), 5.52 (1H, q with a small long-range coupling, J=7.0 Hz, CMe=C*H*Me) (NOE: H-2→H-6, 2.6%). ^{1}H NMR of *Z* isomer: δ=1.17 (3H, d, J=6.0 Hz, CH*Me*), 4.23 (1H, dd, J=10.0 and 2.0 Hz, C*H*CMe=CHMe), 5.28 (1H, q with a small long-range coupling, J=6.0 Hz,

CMe=C*H*Me) (NOE: H-2→H-6, 1.6%).

8d-*trans*: ^{1}H NMR δ=1.21 and 1.31 (total 3H, each d, J=6.0 Hz, CH*Me*), 3.91 (0.5H, m), 4.07 (0.5H, m,), 4.20 (0.5H, m), 4.56 (0.5H, dd, J=10.8 and 2.2 Hz). HRMS (**8d** mixture), Found: m/z 154.1340 (M^+). Calcd for $C_{10}H_{18}O$: M, 154.1358.

2-Methyl-6-(2-methyl-1-propenyl)tetrahydropyran (8e): 8e-cis: ^{1}H NMR δ=1.18 (3H, d, J=6.0 Hz, Me), 1.20—1.90 (6H, m, 3×CH_2), 1.68 and 1.72 (each 3H, each br s, CH=C*Me*$_2$), 3.48 (1H, ddq, J=11.0, 6.0, and 2.0 Hz, C*H*Me), 4.04 (1H, ddd, J=11.0, 8.0, and 2.0 Hz, C*H*CH=CMe$_2$), 5.19 (1H, d with a small long-range coupling, J=8.0 Hz, C*H*=CMe$_2$) (NOE: H-6→H-2, 5.7%; H-6→CH=C*Me*, 3.9%). HRMS, Found: m/z 154.1368 (M^+). Calcd for $C_{10}H_{18}O$: M, 154.1358.

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6) Aldehyde **4** was prepared from 1,5-pentanediol by the following six-step sequence: 1) PvCl, Et_3N, CH_2Cl_2, 0 °C, 1 h, 50%; 2) PCC, MS 4AP, CH_2Cl_2, 25 °C, 0.5 h; 3) MeMgBr, ether, 0 °C, 0.5 h, 70% (2 steps); 4) TBSCl, imidazole, CH_2Cl_2, 25 °C, 1 h, 92%; 5) DIBAL, CH_2Cl_2, −78 °C, 0.5 h, 99%; 6) DMSO, $(COCl)_2$, CH_2Cl_2, −78 °C, 0.5 h, then Et_3N, −78 to 0 °C, 0.5 h, 100%. Aldehyde **4** has been previously prepared in different routes, see: C. Lüthy, P. Konstantin, and K. G. Untch, *J. Am. Chem. Soc.*, **100**, 6211 (1978); B. Ernst and B. Wagner, *Helv. Chim. Acta*, **72**, 165 (1989).

7) Although we could not obtain the exact yield of all cyclization reactions of this study because of the volatility of the cyclization products, the reaction proceeded quantitatively, judging from TLC and the ^{1}H NMR spectra of the crude reaction products.

8) Compound **8c** has been previously prepared by either Pd-mediated cyclization of a hydroxy alkene or $AgNO_3$-mediated cyclization of a hydroxy allene, see: S. Arseniyadis and J. Sartoretti, *Tetrahedron Lett.*, **26**, 729 (1985); M. F. Semmelhack, C. R. Kim, W. Dobler, and M. Meier, *Tetrahedron Lett.*, **30**, 4925 (1989).

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