carried out. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated to give a residue which was subjected to silica gel chromatography using 9:1 petroleum ether/ethyl acetate as the eluent.

Procedure B. The procedure is similar to A with the difference that a catalytic amount of concentrated hydrochloric acid was used instead of Bu_4NF in THF (2 mL).

Procedure C. The procedure is similar to A except that the reaction mixture was diluted with moist THF (10 mL) instead of dry THF (10 mL).

Procedure D. The procedure is similar to B with the differences that 5 equiv of **1** (10 mmol) was employed instead of 2 equiv of **1** (2 mmol) and 5:2:3 petroleum ether/ethyl acetate/acetone was used as the eluent for chromatography.

Ethyl 2-(trifluoromethyl)-4-oxobutanoate (5a): ^{1}H NMR (CCl_4) δ 1.20 (t, J = 7 Hz, 3 H), 2.7–3.83 (m, 3 H),[18] 4.20 (q, J = 7 Hz, 2 H), 9.7 (s, 1 H); ^{19}F NMR (CCl_4) δ –9.0 (d, J_{H-F} = 6.6 Hz); IR (neat) 1750 (broad s), 2870 (m); MS m/e (relative intensity) 199 (M + 1, 75), 179 (2), 170 (15), 153 (100), 102 (38), 45 (38). Anal. Calcd for $C_7H_9O_3F_3$: C, 42.42; H, 4.55; F, 28.78. Found: C, 41.95; H, 4.59; F, 28.77.

Ethyl 2-(trifluoromethyl)-4-oxopentanoate (5b): ^{1}H NMR (CCl_4) δ 1.10 (t, J = 7 Hz, 3 H), 1.95 (s, 3 H), 2.75–3.90 (m, 3 H), 4.23 (q, J = 7 Hz, 2 H); ^{19}F NMR (CCl_4) δ –9.0 (d, J_{H-F} = 6.6 Hz); IR (neat) 1755 (s), 1730 (s); MS m/e (relative intensity) 213 (M + 1, 86), 197 (4), 167 (64), 147 (33), 43 (100). Anal. Calcd for $C_8H_{11}O_3F_3$: C, 45.28; H, 5.19; F, 26.88. Found: C, 45.29; H, 5.21; F, 26.85.

Ethyl 2-(trifluoromethyl)-4-oxohex-5-enoate (5c): ^{1}H NMR (CCl_4) δ 1.25 (t, J = 7 Hz, 3 H), 2.70–3.90 (m, 3 H), 4.24 (q, J = 7 Hz, 2 H),5.76–6.10 (m, 1 H), 6.2–6.50 (m, 2 H); ^{19}F NMR (CCl_4) δ –9.0 (d, J_{H-F} = 6.6 Hz); IR (neat) 1750 (s), 1690 (s), 1620 (s); MS m/z (relative intensity) 225 (M + 1, 72), 192 (26), 180 (100), 159 (20). Anal. Calcd for $C_9H_{11}O_3F_3$: C, 48.21; H, 4.91; F, 25.45. Found: C, 48.26; H, 4.93; F, 25.57.

Ethyl 6-methyl-2-(trifluoromethyl)-4-oxohex-5-enoate (5d): ^{1}H NMR (CCl_4) δ 1.25 (t, J = 7 Hz, 3 H), 1.85 (s, 3 H), 2.05 (s, 3 H), 2.40–3.72 (m, 3 H), 4.20 (q, J = 7 Hz, 2 H), 6.05 (s, 1 H); ^{19}F NMR (CCl_4) δ –9.0 (d, J_{H-F} = 6.6 Hz); IR (neat) 1750 (s), 698 (s), 1620 (s); MS m/z (relative intensity) 252 (M, 10), 207 (21), 117 (20), 109 (14), 84 (100), 96 (12), 55 (40). Anal. Calcd for $C_{11}H_{15}O_3F_3$: C, 52.35; H, 5.95; F, 22.62. Found: C, 51.85; H, 5.93; F, 22.67.

Ethyl 4-phenyl-2-(trifluoromethyl)-4-oxobutanoate (5e): ^{1}H NMR (CCl_4) δ 1.15 (t, J = 7 Hz, 3 H), 2.75–3.85 (m, 3 H), 4.10 (q, J = 7 Hz, 2 H), 7.10–7.50 (m, 3 H), 7.58–7.95 (m, 2 H); ^{19}F NMR (CCl_4) δ –9.0 (d, J_{H-F} = 6.6 Hz); IR (neat) 1750 (s) 1695 (s); MS m/z (relative intensity) 275 (M + 1, 1), 229 (11), 209 (4), 105 (100), 77 (17). Anal. Calcd for $C_{13}H_{13}O_3F_3$: C, 56.93; H, 4.74; F, 20.80. Found: C, 56.47; H, 4.46; F, 20.40.

Ethyl 4-(4′-methoxyphenyl)-2-(trifluoromethyl)-4-oxobutanoate (5f): ^{1}H NMR (CCl_4) δ 1.25 (t, J = 7 Hz, 3 H), 2.75–3.85 (m, 3 H), 3.80 (s, 3 H), 4.20 (q, J = 7 Hz, 2 H), 6.82 (d, J = 8.5 Hz, 2 H), 7.85 (d, J = 8.5 Hz, 2 H); ^{19}F NMR (CCl_4) δ –9.0 (d, J_{H-F} = 6.6 Hz); IR (neat) 1750 (s), 1680 (s); MS m/z (relative intensity) 304 (M, 11), 239 (2), 259 (17), 135 (100), 92 (7), 63 (2). Anal. Calcd for $C_{14}H_{15}O_4F_3$: C, 55.26; H, 4.93; F, 18.75. Found: C, 55.37; H, 5.25; F, 18.75.

Ethyl 6-phenyl-2-(trifluoromethyl)-4-oxohex-5-enoate (5g): mp 65–67 °C; ^{1}H NMR (CCl_4) δ 1.16 (t, J = 7 Hz, 3 H), 2.58–3.80 (m, 3 H), 4.10 (q, J = 7 Hz, 2 H), 6.55 (d, J = 16.8 Hz, 1 H) 7.10–7.65 (m, 6 H); ^{19}F NMR (CCl_4) δ –9.1 (d, J_{H-F} = 6.6 Hz); IR (KCl) 1740 (s), 1685 (s), 1660 (m), 1615 (m); MS m/z (relative intensity) 300 (M, 9), 255 (16), 144 (17), 132 (12), 131 (100), 103 (32), 77 (17), 51 (7). Anal. Calcd for $C_{15}H_{15}O_3F_3$: C, 60.00; H, 5.00; F, 19.00. Found: C, 59.58; H, 4.89; F, 19.25.

25-Ethoxy-3α,6α-dihydroxy-24-(trifluoromethyl)-26,27-dinor-5β-cholestane-22,25-dione (5h): mp 85–87 °C; ^{1}H NMR (CD_3COCD_3) δ 0.72 (s, 3 H, 18-H_3), 0.95 (s, 3 H, 19-H_3), 3.30 (broad s, 2 H, 2 OH), 4.20 (q, J = 7 Hz, 2 H), 2.50–4.25 (m, 5 H, 23-H_2, 24-H, 3-H, and 6-H); ^{19}F NMR (CD_3COCD_3) δ –9.4 (d, J_{H-F} = 6.8 Hz), –9.3 (d, J_{H-F} = 6.8 Hz), IR (KCl) 1750 (s), 1720 (s), 3100–3650 (s); MS m/z (relative intensity) 517 (M + 1, 5), 498 (M – H_2O, 14), 480 (M – $2H_2O$, 18), 465 (6), 435 (5), 273 (11), 255 (21), 231 (21), 226 (20), 213 (37), 169 (43), 95 (100), 81 (64). Anal. Calcd for $C_{28}H_{43}O_5F_3$: C, 65.12; H, 8.33; F, 11.05. Found: C, 65.62; H, 8.24; F, 11.50.

Quench of the Anion 6 (R = *p*-MeOPh) with Deuterium Oxide. The cyclopropanation reaction of **3f** (2 mmol) with **1** (4 mmol) was performed as described above. The resulting reaction mixture was diluted with THF (15 mL) and treated successively with Bu_4NF in THF (1 M, 2 mL)[19] and deuterium oxide (1 mL); 1% aqueous HCl solution (30 mL) was then added, and the remaining workup was the same as described in the general procedure. The product was identified as ethyl 2-deuterio-4-(4′-methoxyphenyl)-2-(trifluoromethyl)-4-oxobutanoate (**7**): ^{1}H NMR (CCl_4) δ 1.25 (t, J = 7 Hz, 3 H), 3.12 and 3.60 (2 d, AB system, J = 18 Hz, 2 H), 3.78 (s, 3 H), 4.20 (q, J = 7 Hz, 2 H), 6.82 (d, J = 8.5 Hz, 2 H), 7.85 (d, J = 8.5 Hz, 2 H); ^{19}F NMR (CCl_4) δ –9.0 (s); MS m/z (relative intensity) 305 (M, 6), 260 (7), 239 (1), 135 (100), 92 (7), 69 (2), 64 (6).

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[18] For compound **5a–g**, the signals appearing in the range of 2.5–3.9 ppm have similar absorption patterns and can be assigned to the protons on C-2 (1 H) and C-3 (2 H) carbons which constitute the ABM portion of a complicated $ABMX_3$ system (X = F).

[19] Commercial Bu_4NF in THF usually contains a small amount of water. To avoid incomplete deuteration, the reagent employed in this procedure was freshly prepared with careful drying.

Effect of Cation, Temperature, and Solvent on the Stereoselectivity of the Horner–Emmons Reaction of Trimethyl Phosphonoacetate with Aldehydes

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It is known that the E/Z ratio of olefinic products formed in the Horner–Emmons reaction of dialkyl 2-phosphonopropionates and 2-phosphonopropionitriles with aldehydes increases as the metal cation is changed from K^+ to Na^+ to Li^+ and as the reaction temperature is increased.[1] This effect has been attributed to an increase in the "reversibility factor" (e.g., k_{-E}/k'_E in Scheme I) for more coordinating cations and at higher temperatures.[1a,2,3] It has been assumed that the same effects operate in the Horner–Emmons reaction of dialkyl 2-phosphonoacetates with aldehydes and the effects of metal cation and reaction temperature on the E/Z ratio have been reported for an isolated example.[4] However, no effect on the E/Z ratio by a change of solvent from tetrahydrofuran (THF) to 1,2-dimethoxyethane (DME) has been reported. We report here a study of the effects of the metal cation, reaction

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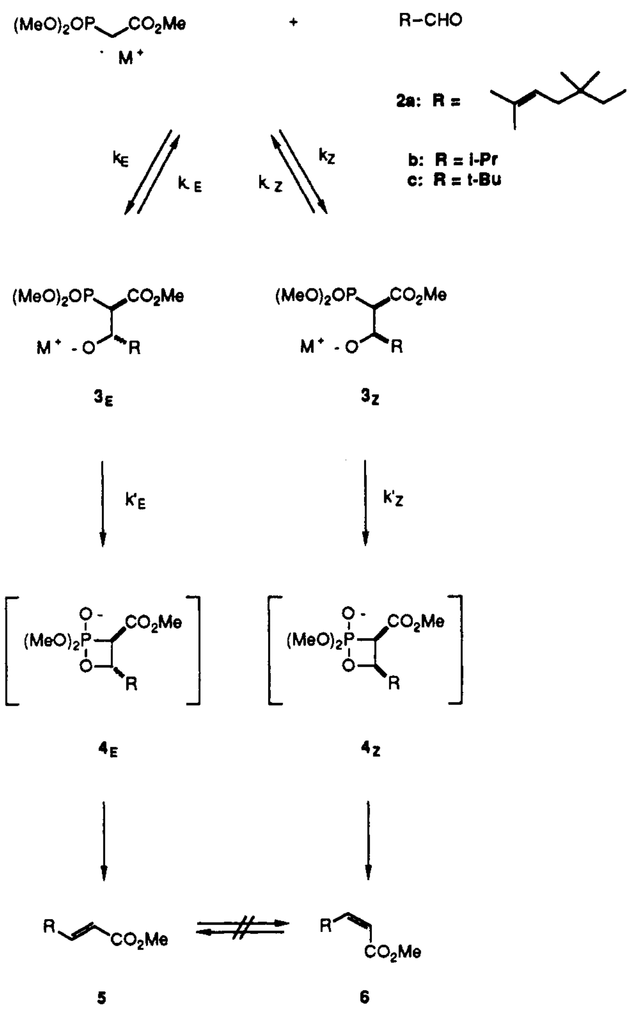
0022-3263/90/1955-3386$02.50/0

Scheme I



temperature, and solvent on the *E*/*Z* ratio of product unsaturated esters formed in the reaction of trimethyl phosphonoacetate anion with three aldehydes (**2a**,[5] **2b**, **2c**) of varying α-substitution patterns.

Results and Discussion

The aldehydes studied were chosen to cover the full range in degree of α-substitution (α-mono, di-, and trisubstituted acetaldehydes). The product mixtures were analyzed by ^{1}H NMR (250 MHz) to determine product ratios. Isolated yields were typically 95–100% for reactions with aldehyde **2a**, but isolated yields for reactions with **2b** and **2c** were typically lower (60% for **2b** and 75% for **2c**), because of the volatility of the products. Although prolonged concentration (under aspirtor pressure) of product mixtures resulted in diminished isolated yields, no changes in the *E*/*Z* ratios were observed. Stereochemical data are summarized in Table I.

Of the four variables studied, the one having the greatest effect on the *E*/*Z* ratio is the alkyl substitution pattern on the aldehyde. Although reactions with **2a** and **2b** follow somewhat similar trends, reactions involving **2c** resulted in the formation of the *E* unsaturated ester exclusively, regardless of the metal cation, reaction temperature, or solvent. Since the products of the Horner–Emmons reaction do not undergo *E*/*Z* isomerization under the reaction conditions,[6] the stereospecificity of the reaction with **2c** can be attributed to a much greater propensity for the formation of **3E**/**4E** than for **3Z**/**4Z** under any reaction conditions, probably because of steric crowding in **3Z** and/or **4Z** or a kinetic preference for the formation of **3E**. For the reactions with **2a** and **2b**, however, significant effects of metal cation, reaction temperature, and solvent were observed (Table I).

Table I. *E*/*Z* Ratios for the Reaction of Trimethyl Phosphonoacetate Anion with Aldehydes 2a, 2b, and 2c[a]

entry	aldehyde	cation	temperature (°C)	product ratio (*E*/*Z*) THF	product ratio (*E*/*Z*) DME
1	**2a**	Li$^+$	−78	1.4/1	7.5/1
2	**2a**	Li$^+$	23	12/1	20/1
3	**2a**	Na$^+$	−78	6.7/1	6.7/1
4	**2a**	Na$^+$	23	7.5/1	9/1
5	**2a**	K$^+$	−78	4.8/1	4.8/1
6	**2a**	K$^+$	23	4.8/1	4.8/1
7	**2b**	Li$^+$	−78	1/3	1/1
8	**2b**	Li$^+$	23	5.3/1	12/1
9	**2b**	Na$^+$	−78	1/1	1/1
10	**2b**	Na$^+$	23	4.3/1	5/1
11	**2b**	K$^+$	−78	1/1	1/1
12	**2b**	K$^+$	23	4/1	4/1
13	**2c**	Li$^+$	−78	>50/1	>50/1
14	**2c**	Li$^+$	23	>50/1	>50/1
15	**2c**	Na$^+$	−78	>50/1	>50/1
16	**2c**	Na$^+$	23	>50/1	>50/1
17	**2c**	K$^+$	−78	>50/1	>50/1
18	**2c**	K$^+$	23	>50/1	>50/1

[a] In all reactions with aldehyde **2c**, only the *E* unsaturated ester was observed within the limits of detection.

In general, the variable that has the smallest effect on the *E*/*Z* ratio is the metal cation. This effect, in which the use of the lithium cation at room temperature offers the best *E* selectivity, can be attributed to a higher degree of association of Li$^+$ to the alkoxides **3E** and **3Z** at room temperature, resulting in a decrease in the rate of nucleophilic attack of the oxygen at phosphorus to give **4**[3] and a corresponding increase in the reversibility of the reaction. Furthermore, it appears that the magnitude of the cation effect is dependent not only on the reaction temperature but also on the solvent used.

The effect of reaction temperature, the largest of the effects studied, is a 5- to 6-fold increase in the amount of minor (*Z*) isomer formed in reactions with **2a** and **2b** when the temperature is decreased from room temperature to −78 °C and lithium is the cation. This effect is of greatest magnitude when the lithium cation is used and diminishes when the cation is sodium or potassium. The effect could be due to increased solvation of the lithium alkoxide intermediate **3**, which is favored at lower temperatures because of the substantial negative entropy change associated with the solvation process.[7] Because of the decrease in the reversibility of the reaction at lower temperatures,[1a] the product ratios resemble the kinetic ratios at low temperatures rather than the thermodynamic ratios resembled at room temperature. Furthermore, the magnitude of the effect is essentially the same in THF or DME.

The most interesting and unexpected effect is that of the solvent. This effect, like the temperature effect, is most pronounced when the lithium cation is used and diminishes greatly when the cation is sodium or potassium. Also, the magnitude of the solvent effect is relatively invariant with reaction temperature. Changing the solvent from DME

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[5] Aldehyde **2a** was prepared in two steps in 71% overall yield by addition of (3-methyl-2-butenyl)magnesium chloride to 3-methyl-2-butenal to give 3,3,6-trimethylhepta-2,5-dien-4-ol, which was converted to **2a** by an anion-accelerated oxy-Cope rearrangement.

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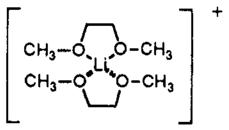
to THF appears to have the same effect as a decrease in temperature, which causes a decrease in the E/Z ratio due to increased solvation of alkoxide intermediate **3** at lower temperatures. However, an increase in the E/Z ratio would be expected when the solvent was changed from DME to THF because of the greater ability of DME to solvate cations by the formation of a bidentate chelate (structure **7**). In some cases, the larger dielectric constant and dipole moment[8,9] of THF allow it to be superior to DME in cation solvating ability due to the formation of a stable THF solvate, as is the case for Grignard reagents.[10] Alternatively, the change in E/Z ratio could be a result of a change in the kinetic ratio of alkoxides **3E**/**3Z** by the change of solvent. But since the intermediate alkoxide **3** cannot be isolated or observed, the occurrence of such phenomena cannot be rigorously corroborated. To lend some support, the reaction was carried out in two other nonchelating solvents, ether and benzene, under conditions that produced a large solvent effect (aldehyde **2a**, lithium cation, room temperature). The E/Z ratio for these reactions was 20/1, the same ratio observed when DME was used as the solvent.



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In summary, we have described the effects of metal cation, reaction temperature, and solvent on the E/Z ratio of unsaturated esters resulting from the Horner–Emmons reaction of trimethyl phosphonoacetate with three aldehyde of varying degrees of alkyl substitution. Although none of these effects alone are very large, the combination of the effects allows for a rather large effect on the stereoselectivity of the reaction. Hence, it is possible to obtain either the E or Z unsaturated ester as the major product in the reaction without changing the nature of the phosphonate reagent,[11] but by judicious choice of metal cation, reaction temperature and solvent, providing that the inherent E/Z selectivity of the aldehyde in the reaction permits (e.g., aldehyde **2b**).

Experimental Section

General. Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. Ether, tetrahydrofuran (THF), and 1,2-dimethoxyethane (DME) were distilled from sodium/benzophenone ketyl immediately prior to use. Benzene and pentane were distilled from CaH_2 prior to use. All reactions were conducted under an atmosphere of dry argon in oven-dried glassware. NaH and KH were rinsed free of mineral oil with pentane under an atmosphere of dry argon and then dried in vacuo and stored in a glovebox under a nitrogen atmosphere. IR spectra were measured as films on NaCl plates. ^{1}H and ^{13}C NMR spectra were measured as solutions in $CDCl_3$ at 250 MHz and 125 MHz, respectively. J values are in hertz.

General Procedure for Horner–Emmons Reactions. Lithium Cation. To a stirring solution of 275 mg (1.50 mmol, 245 μL) of trimethyl phosphonoacetate in 2.5 mL of dry solvent, cooled to 0 °C, was added dropwise 650 μL (1.38 mmol) of a 2.11 M solution of n-butyllithium in hexanes. After 10 min, the reaction mixture was brought to the desired temperature and 1.25 mmol of aldehyde was added dropwise. After being stirred for 1.5 h, the mixture was quenched by the addition of 3 mL of water. The mixture was diluted with 5 mL of ether, the organic layer was washed with saturated brine, dried ($MgSO_4$), and filtered, and the solvents were removed with a rotary evaporator to give the product as a colorless liquid.

Sodium and Potassium Cation. To a stirring suspension of 1.38 mmol of NaH or KH in 2.5 mL of dry solvent was added dropwise 275 mg (1.50 mmol, 245 μL) of trimethyl phosphonoacetate. The mixture (a slurry in the case of sodium anion) was brought to the desired temperature and 1.25 mmol of aldehyde was added dropwise. After being stirred for 1.5 h, the mixture was worked up as above.

Spectral Data for New Compounds (5a and 6a). (*E*)-Methyl 5,5,8-trimethylnona-2,7-dienoate (5a): bp 55–56 °C, 0.01 mm (with Z isomer). IR: 1735 cm^{-1}. ^{1}H NMR: δ 0.89 (s, 6), 1.59 (s, 3), 1.72 (s, 3), 1.90 (d, 2, J = 7.6), 2.09 (dd, 2, J = 1.3, 7.9), 3.73 (s, 3), 5.17 (m, 1), 5.81 (dt, 1, J = 1.3, 15.5), 6.99 (dt, 1, J = 7.9, 15.5). ^{13}C NMR: δ 17.904, 26.054, 26.867 (2 C), 35.054, 40.227, 44.488, 51.341, 120.491, 122.787, 133.434, 147.201, 166.931. Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.43; H, 10.69.

(*Z*)-Methyl 5,5,8-trimethylnona-2,7-dienoate (6a): bp 55–56 °C, 0.01 mm (with E isomer). IR: 1735 cm^{-1}. ^{1}H NMR: δ 0.90 (s, 6), 1.59 (s, 3), 1.72 (s, 3), 1.93, (d, 2, J = 7.6), 2.60 (dd, 2, J = 1.7, 7.7), 3.71 (s, 3), 5.18 (m, 1), 5.90 (dt, 1, J = 1.7, 11.7), 6.32 (dt, 1, J = 7.7, 11.7). ^{13}C NMR: δ 17.881, 26.054, 26.652 (2 C), 34.975, 40.163, 40.270, 50.910, 120.383, 120.800, 133.193, 147.964, 166.887. Anal. Calcd. for $C_{13}H_{22}O_2$: C, 74.24; H, 10.54. Found: C, 74.63; H, 10.76.

(E)-Methyl 4-methyl-2-pentenoate (**5b**), (Z)-methyl 4-methyl-2-pentenoate (**6b**), and (E)-methyl 4,4-dimethyl-2-pentenoate (**5c**) exhibited spectral data identical with those previously reported.[12,13]

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Palladium(0)-Catalyzed Reaction of (*Z*)-2-Butene-1,4-diyl Bis(methyl carbonate) and (*Z*)-2-Butene-1,4-diyl Diacetate with Bifunctional Nitrogen Nucleophiles

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Allylic monoacetates and monocarbonates are extensively used in palladium(0)-catalyzed allylation of nucleophiles, which provides a useful method in organic synthesis.[1] On the other hand, there are few reports on palladium(0)-catalyzed reaction of bifunctional allylic diacetates and dicarbonates with nucleophiles featuring their bifunctionality.[2] We now report that the palladium(0)-catalyzed reaction of (Z)-2-butene-1,4-diyl bis(methyl carbonate) (**1**) and (Z)-2-butene-1,4-diyl diacetate

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