Reaction of Trifluoromethyl Ketones. V.[1] Dehydration of Trifluoromethylated Homoallyl Alcohols: Synthesis of Trifluoromethylated Dienes[2]

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1-(Trifluoromethyl)homoallyl alcohols, which were obtained by the ene reaction of trifluoromethyl ketones with olefins, were dehydrated with $POCl_3$–pyridine or other acyl halide–organic base mixtures to trifluoromethylated dienes. Dehydration of the homoallyl alcohols from hexafluoroacetone afforded only one kind of products, while those from other trifluoromethyl ketones were dehydrated to the *E*-isomers of conjugated dienes as major products with small amounts of regio- and stereoisomers. Treatment of the homoallyl alcohols from inner olefins with phosphorus oxychloride in pyridine gave the conjugated dienes stereoselectively. The saturated (trifluoromethyl)-carbinols which were obtained by hydrogenation of trifluoromethylated homoallyl alcohols were very difficult to dehydrate. This fact shows that the formation of a conjugated double bond or the presence of an allylic hydrogen facilitates the dehydration.

Keywords dehydration; *E*2 mechanism; homoallyl alcohol; ene-reaction product; trifluoromethyl; diene; phosphorus oxychloride; pyridine; stereospecific

The ene reaction of trifluoromethyl ketones has been investigated, and this reaction was found to be very useful for the synthesis of trifluoromethylated homoallyl alcohols.[3-5] We are now engaged in the derivatization of these homoallyl alcohols to various kinds of trifluoromethylated compounds. In the previous paper, we reported the cyclization of the homoallyl alcohols to 2-(trifluoromethyl)tetrahydrofurans.[1] This paper is concerned with the dehydration of the trifluoromethylated homoallyl alcohols to trifluoromethylated dienes.

First, bis-(trifluoromethyl)homoallyl alcohols (**1a**—**e**), obtained by the ene reaction of hexafluoroacetone with terminal olefins, were treated with phosphorus oxychloride in pyridine to give the corresponding dienes (Table I). In these cases, the *E*-configuration of the starting materials was retained and the conjugated dienes were formed. The yields from **1c** and **1d** were rather low compared with that from the homoallyl alcohol (**1a**) substituted with a phenyl group, and formation of tarry substances was observed. The acetyl compound (**1e**) was more reactive than the above compounds and formation of tarry substances was appreciable even at 60 °C, while at room temperature, the recovery of the starting material became fairly large. Treatment of this compound with methanesulfonyl (mesyl) chloride and triethylamine at 0 °C gave a satisfactory yield of the diene (**2e**).

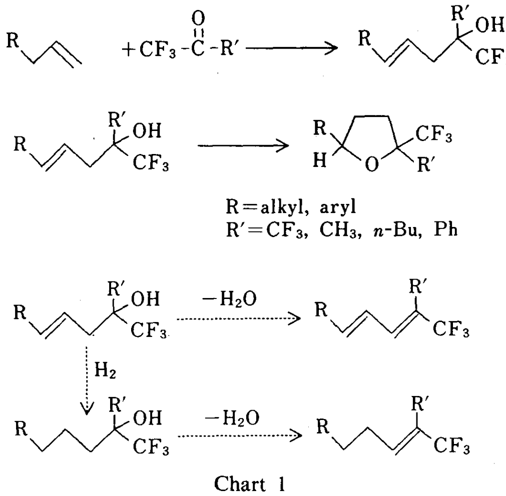
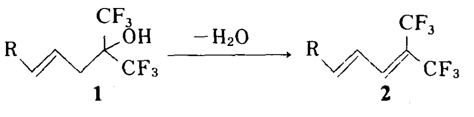


Chart 1

The homoallyl alcohol obtained by the reaction of trifluoroacetone with allylbenzene was expected to be dehydrated in two directions to give conjugated dienes or an isolated 1,4-diene. In the former case, two stereoisomers could be produced. Actually, treatment of 1,1,1-trifluoro-2-methyl-5-phenyl-4-pentenol (**4a**) with phosphorus oxychloride and pyridine gave the conjugated and the isolated dienes in a ratio of 92 : 8 in the total yield of 76%. The ratio of stereoisomers (1*E*,3*E*) : (1*E*,3*Z*) of the conjugated dienes was 9 : 2, but formation of the (1*Z*,3*E*) isomer was not observed. This result shows that isomerization of the old double bond did not occur during the dehydration reaction and that the *E*-configuration at the new double bond is more stable than the *Z*-configuration, possibly because a trifluoromethyl group is larger than a methyl group (see Table II).

Dehydration of 1,1,1-trifluoro-2-phenyl-4-decen-2-ol (**4b**) with phosphorus oxychloride and pyridine gave a much lower yield of a diene (**5b**) than that of **4a**. This shows that the vinylogous benzylic proton of **4a** is much more reactive than the allylic one of **4b**. The (*E*)/(*Z*) ratio

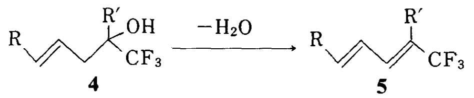
TABLE I. Dehydration of Bis(trifluoromethyl) Homoallyl Alcohols



	R	Condition	Yield[a] (%)
1a	C_6H_5	$POCl_3$, Py., 110 °C, 65 h	81
1b	C_6H_5S	$POCl_3$, Py., 110 °C, 65 h	90
1c	*n*-C_5H_{11}	$POCl_3$, Py., 100 °C, 57 h	21
1d	*n*-C_7H_{15}	$POCl_3$, Py., 100 °C, 65 h	48
1e	CH_3CO	$POCl_3$, Py., 60 °C, 2 h	31
		$POCl_3$, Py., r.t., 4.5 h	22[b]
		MsCl, Et_3N, 0 °C, 1 h	65[c]

a) Isolation yield. *b*) **1e** was recovered in 60% yield. *c*) 7,7,7-Trifluoro-6-mesyloxy-6-(trifluoromethyl)-3-hepten-2-one (**3**) was obtained in 10% yield with recovery of **1e** (8%). Py.: pyridine.

TABLE II. Dehydration of Mono(trifluoromethyl) Homoallyl Alcohols



4 **5**

	Starting mat. R	R′	Condition	Yield[a] (%)	Ratio[b] (*E*/*Z*)
4a	C_6H_5	CH_3	$POCl_3$, Py., 75 °C, 24 h	70[c]	9:2
4b	n-C_5H_{11}	C_6H_5	$POCl_3$, Py., 110 °C, 65 h	40[d]	7:2
		C_6H_5	$SOCl_2$, Py., r.t., 38 h	11[e]	3:1
4c	n-C_3H_7	C_6H_5	$POCl_3$, Py., 90 °C, 24 h	16[f]	3:1
4d	n-C_3H_7	n-C_4H_9	$POCl_3$, Py., 80 °C, 55 h	31[g]	2:1
		n-C_4H_9	$SOCl_2$, Py., r.t., 25 h	31[h]	2:1

a) Total yield of isomers. *b*) The newly formed double bond ratio estimated from the GLC and/or ^{19}F-NMR data. *c*) 1-Phenyl-4-(trifluoromethyl)-1,4-pentadiene (**6**) was formed in 6% yield. *d*) 2-Chloro-1,1,1-trifluoro-2-phenyl-4-decene (**7**) was formed in 9% yield as estimated by GLC. *e*) **7** was formed in 21% yield as estimated by GLC. *f*) Estimated by GLC. *g*) The starting material (18%) was recovered. 5-(Trifluoromethyl)-4,7-undecadienes [**8**, 11%, (4*E*,7*E*):(4*Z*,7*E*) = 1:1] were formed. *h*) The starting material (16%) was recovered.

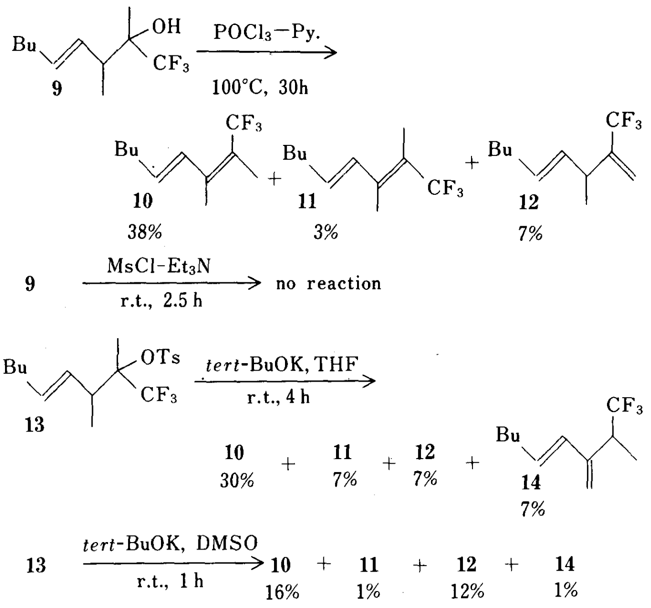


Chart 2

concerning the new double bond of **5b** is 7:2, which is smaller than that of **5a**. This may be explained by the fact that a phenyl group is larger than a methyl group, and that the steric requirement of a trifluoromethyl group is larger than that of a planar benzene ring. Treatment of **4b** with thionyl chloride and pyridine gave 2-chloro-1,1,1-trifluoro-2-phenyl-4-decene (**7**) in 21% yield besides **5b** in 11% yield. In this case, substitution reaction occurred preferentially to elimination. Therefore, the α-phenyl group facilitated the substitution reaction rather than the elimination reaction. The reaction of 1,1,1-trifluoro-2-phenyl-4-octen-2-ol (**4c**) with phosphorus oxychloride gave a similar result to that of **4b**. Dehydration of 5-(trifluoromethyl)-7-decen-5-ol (**4d**) with phosphorus oxychloride and pyridine gave 7-(trifluoromethyl)-4,6-undecadiene [**5d**, (4*E*,6*E*) : (4*E*,6*Z*) = 2:1] with formation of a small amount of 5-(trifluoromethyl)-4,7-undecadiene (**8**). The ratio of isomers of **5d** shows that the steric requirement of a trifluoromethyl group is a little larger than that of a linear butyl group. Treatment of **4d** with thionyl chloride in pyridine gave the dienes in a similar ratio to that in the reaction with phosphorus oxychloride, but no chloro compounds were isolated. This fact supports the hypothesis that the α-phenyl group facilitates the substitution in the reaction of **4b** (Table II).

In the previous paper,[4] we reported the stereospecific ene reaction of trifluoroacetone with 2-octene to give (2*R**,3*R**,4*E*)-1,1,1-trifluoro-2,3-dimethyl-4-nonen-2-ol (**9**). Treatment of **9** with phosphorus oxychloride in pyridine gave 38% of (2*Z*,4*E*)-1,1,1-trifluoro-2,3-dimethyl-2,4-nonadiene (**10**) together with 3% of the (2*E*,4*E*)-isomer (**11**), and a small amount of 1,1,1-trifluoro-3-methyl-2-methylene-4-nonene (**12**). Compound **10** is expected to be less stable than the (2*E*,4*E*)-isomer (**11**), since a trifluoromethyl group is much larger than a methyl group. However, **10** was obtained as a major product. This result shows that the elimination reaction of homoallyl alcohols with phosphorus oxychloride in pyridine proceeds mainly through the *E*2 mechanism. Treatment of **9** with MsCl in pyridine resulted in the recovery of the starting material. This result is in marked contrast to the result with **1e**, which gave the diene (**2e**) in a good yield (see Chart 2).

Compound **9** was converted to a tosyl ester (**13**) and treated with potassium *tert*-butoxide in tetrahydrofuran (THF) to give **10**, **11** and **12**, together with another isomer, 1,1,1-trifluoro-2-methyl-3-methylene-4-nonene (**14**). The ratio of **10**:**11** was smaller than that in the reaction of **9** with phosphorus oxychloride. Formation of the latter two products suggests that the *E*1cB mechanism might participate to a small extent.

The ene reaction product (**15**) from trifluoroacetone and cyclohexene was dehydrated stereospecifically to (*Z*)-3-[methyl(trifluoromethyl)methylene]cyclohexene (**16**) in 28% yield, with very small amounts of 2-(3-cyclohexenyl)-3,3,3-trifluoropropene (**17**) and another isomer. Treatment of the tosyl ester (**18**) of **15** with potassium *tert*-butoxide in THF gave a much lower yield of **16** together with small amounts of other isomers (see Chart 3).

Treatment of (5*R**,6*R**)-6-methyl-5-(trifluoromethyl)-7-dodecen-5-ol (**19**) with phosphorus oxychloride in pyridine gave (5*Z*,7*E*)-6-methyl-5-(trifluoromethyl)-5,7-dodecadiene (**20**) in 15% yield together with (4*Z*,7*E*)-6-methyl-5-(trifluoromethyl)- 4,7-dodecadiene (**21**) and (4*E*,7*E*)-isomer (**22**) in 12 and 5% yields, respectively. This result further supports the proposed *E*2 mechanism. Namely, **19** has one proton at the 6-position and the elimination reaction gives only one isomer (**20**), while it has two protons at the 4-position and the reaction gives two isomers (**21** and **22**). Predominant formation of **21** suggests that the steric requirement of a trifluoromethyl group is smaller than that of a 2-(3-octenyl) group. An elimination reaction of the tosyl ester (**23**) of **19** with potassium *tert*-butoxide gave **20**, **21** and the (5*E*,7*E*)-isomer (**24**) of **20** in 10%, 2% and 2% yields, respectively. Formation of **24** supports participation of the *E*1cB mechanism in the elimination of the tosyl ester as shown above (see Chart 3).

Reaction of (2*R**,3*S**,4*E*)-1,1,1-trifluoro-3-methyl-2-phenyl-4-nonen-2-ol (**25**) with phosphorus oxychloride in pyridine gave (2*Z*,4*E*)-1,1,1-trifluoro-3-methyl-2-phenyl-2,4-nonadiene (**26**), 2-butyl-3-chloro-4-methyl-1-phenyl-1-(trifluoromethyl)cyclobutane (**27**, two diastereomers) and

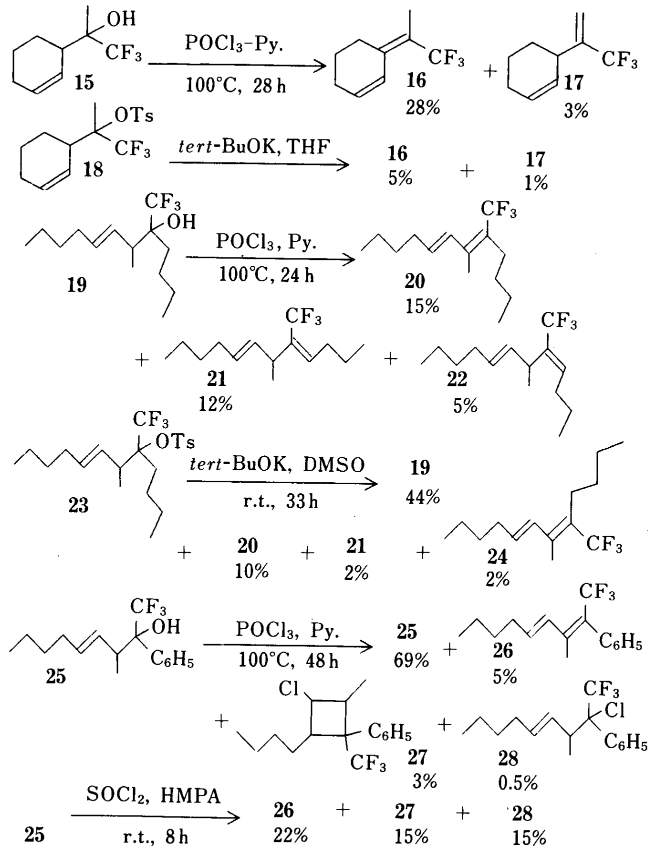


Chart 3

2-chloro-1,1,1-trifluoro-3-methyl-2-phenyl-4-nonene (**28**, two diastereomers), but the (2*E*,4*E*)-isomer of **26** was not isolated. This result suggests that the elimination proceeded through the *E*2 mechanism and that the phenyl group stabilized a carbenium ion, which gave the chloro compound (**28**) through *S*$_N$1 reaction and the intramolecular cyclization product (**27**). These two products were each obtained as two diastereomers, supporting the participation of a planar carbenium ion. A similar reaction of **25** with thionyl chloride in hexamethylphosphoramide (HMPA) gave **26**, **27** and **28** in an approximate ratio of 2 : 1 : 1 (see Chart 3).

Finally, the dehydration of α-(trifluoromethyl) alcohols, which were obtained by hydrogenation of the α-(trifluoromethyl) homoallyl alcohols, was examined. The dehydration of bis(trifluoromethyl) alcohols was unsuccessful. Treatment of 1,1,1-trifluoro-2-(trifluoromethyl)-6-oxo-2-heptanol (**29**) with phosphorus oxychloride in pyridine resulted in the formation of a complex mixture of products with recovery of most of the starting materials. The sulfonate ester of **29** was completely hydrolyzed by treatment under basic conditions. For example, treatment of the tosyl ester (**30**) with diazabicycloundecene (DBU) resulted in the formation of **29**. On the other hand, mono(trifluoromethyl)alcohol was dehydrated to the olefinic compound much more slowly than in the case of corresponding homoallyl alcohols. Thus, 1,1,1-trifluoro-2-methyl-2-decanol (**31**) was dehydrated by thionyl chloride in pyridine to (2*E*)- (**32**) and (2*Z*)-1,1,1-trifluoro-2-methyl-2-decene (**34**), and 2-(trifluoromethyl)-1-decene (**33**) in the ratio of 8 : 1 : 2. This order is that expected based on the *E*2 mechanism. In this reaction, no chloro compounds were isolated, possibly due to the absence of the α-phenyl group. Treatment of the tosyl ester (**35**) of **31** with potassium *tert*-butoxide gave only the *exo*-methylene compound (**33**), probably because of the large steric effect of the *tert*-butoxide ion and absence of a double bond, which activates the α-methylene proton (see Chart 4).

In conclusion, some trifluoromethylated dienes were obtained by dehydration of trifluoromethylated homoallyl alcohols formed by the ene reaction of trifluoromethyl ketones. The bis(trifluoromethyl)homoallyl alcohols obtained by the ene reaction of hexafluoroacetone were dehydrated with phosphorus oxychloride and pyridine to give bis(trifluoromethyl)dienes as sole products. Mono(trifluoromethyl)homoallyl alcohols obtained by the ene reaction of monotrifluoromethyl ketones and terminal olefins were dehydrated mainly to (trifluoromethyl)dienes with (*E*)-configuration at the double bond substituted with a trifluoromethyl group, while those from inner olefins gave dienes of (*Z*)-configuration. These results can be explained by the *E*2 mechanism. Namely, the former gave comparatively stable isomers, while the latter had only one proton and inevitably gave unstable isomers. Elimination reaction of tosyl esters seemed to proceed through the *E*1cB mechanism to a small extent. Elimination reaction of bis(trifluoromethyl)carbinols obtained by hydrogenation of the homoallyl alcohols was unsuccessful even through sulfonate esters. Elimination of (trifluoromethyl)carbinols proceeded much more slowly than that of allyl(trifluoromethyl)carbinols.

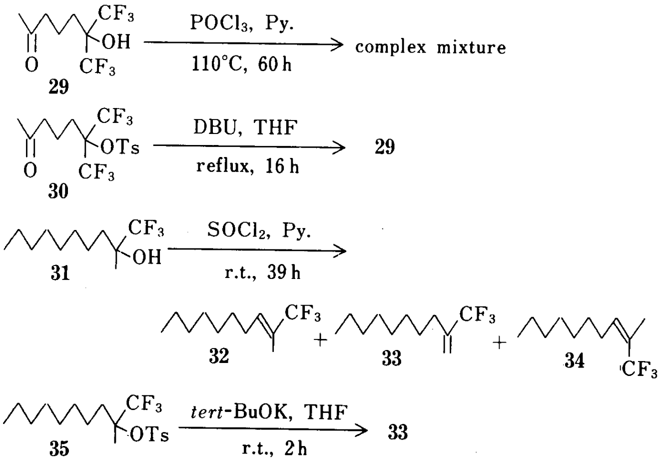


Chart 4

Experimental

Trifluoromethyl homoallyl alcohols were synthesized according to the literature.[3-5] ^{1}H-Nuclear magnetic resonance (^{1}H-NMR) spectra were obtained on JNM-FX90Q and JNM-GX400 spectrometers. ^{19}F-NMR spectra were recorded on a JNM-FX90Q spectrometer, using benzotrifluoride as an internal standard (upper field taken as plus). Preparative gas liquid chromatography (GLC) was performed on a Hitachi 163 apparatus; column 15% SE-30, L = 1 m, i.d. = 4 mm; carrier He, 30 ml/min, unless otherwise stated. The ratio of the products was estimated from the peak areas in GLC (without correction for sensitivity, since the structures of these compounds resembled each other) and the intensities of peaks in the ^{19}F-NMR spectra. The ratio estimated by GLC was approximately same as that by ^{19}F-NMR.

5,5,5-Trifluoro-1-phenyl-4-(trifluoromethyl)-1,3-pentadiene (2a) Phosphorus oxychloride (1.08 g, 7.0 mmol) was added to a solution of

1,1,1-trifluoro-5-phenyl-2-(trifluoromethyl)-4-penten-2-ol (**1a**, 2.0 g, 7.0 mmol) in pyridine (2.6 ml) at 0 °C. The mixture was stirred at 110 °C for 65 h. Ice-water was added to the cooled reaction mixture. After being stirred for 5 h, the mixture was extracted with ether. The ether layer was washed with dilute HCl, aqueous $NaHCO_3$ and brine, and dried over $MgSO_4$. After evaporation of the solvent, the residue was distilled under vacuum to give **2a** as a colorless oil (1.52 g, 81%). bp 95—108 °C (5 mmHg, bulb-to-bulb distillation). Mass spectrum (MS) *m/z*: 266 (M^+). High resolution mass spectrum (HRMS) Calcd for $C_{12}H_8F_6$: 266.053. Found: 266.053. ^1H-NMR ($CDCl_3$) δ: 7.00—7.09 (1H, m), 7.11—7.21 (2H, m), 7.36—7.43 (3H, m), 7.48—7.54 (2H, m). ^{19}F-NMR ($CDCl_3$): −5.18 (q, $J=6.8$ Hz), 0.52 (q, $J=6.8$ Hz).

5,5,5-Trifluoro-1-phenylthio-4-(trifluoromethyl)-1,3-pentadiene (2b) Phosphorus oxychloride (1.35 g, 8.8 mmol) was added to a solution of 1,1,1-trifluoro-5-phenylthio-2-(trifluoromethyl)-4-penten-2-ol (**1b**, 2.80 g, 8.9 mmol) in pyridine (3.3 ml) at 0 °C, and the mixture was stirred at 110 °C for 65 h. After a similar work-up to that in the case of **2a**, the residue was distilled under vacuum to give **2b** as a slightly yellow oil (2.37 g, 90%). bp 94—95 °C (3 mmHg, bulb-to-bulb distillation). MS *m/z*: 298 (M^+). HRMS Calcd for $C_{12}H_8F_6S$: 298.025. Found: 298.025. ^1H-NMR ($CDCl_3$) δ: 6.45 (1H, dd, $J=11.9$, 14.7 Hz), 6.98 (1H, d, $J=11.9$ Hz), 7.15 (1H, d, $J=14.7$ Hz), 7.34—7.52 (5H, m). ^{19}F-NMR ($CDCl_3$): −4.85 (q, $J=6.8$ Hz), 0.21 (q, $J=6.8$ Hz).

1,1,1-Trifluoro-2-(trifluoromethyl)-2,4-decadiene (2c) Phosphorus oxychloride (185 mg, 1.2 mmol) was added to a solution of 1,1,1-trifluoro-2-(trifluoromethyl)-4-decen-2-ol (**1c**, 278 mg, 1.0 mmol) in pyridine (1 ml) at 0 °C, and the mixture was stirred at 100 °C for 57 h. After work-up as above, the residue was separated on an SiO_2 column in hexane solution to give **2c** as a colorless oil (54 mg, 21%). MS *m/z*: 260 (M^+). HRMS Calcd for $C_{11}H_{14}F_6$: 260.100. Found: 260.099. ^1H-NMR ($CDCl_3$) δ: 0.90 (3H, t, $J=7.0$ Hz), 1.25—1.40 (4H, m), 1.40—1.55 (2H, m), 2.26 (2H, td, $J=7.2$, 7.2 Hz), 6.35 (1H, dt, $J=14.5$, 7.2 Hz), 6.51 (1H, dd, $J=14.4$, 11.6 Hz), 7.00 (1H, d, $J=11.6$ Hz). ^{19}F-NMR ($CDCl_3$): −4.90 (q, $J=6.7$ Hz), 0.62 (q, $J=6.7$ Hz).

1,1,1-Trifluoro-2-(trifluoromethyl)-2,4-dodecadiene (2d) Phosphorus oxychloride (459 mg, 3 mmol) was added to a solution of 1,1,1-trifluoro-2-(trifluoromethyl)-4-dodecen-2-ol (**1d**, 612 mg, 2 mmol) in pyridine (1 ml) at 0 °C, and the mixture was stirred at 100 °C for 65 h. After work-up as above, the extract was separated on an SiO_2 column in hexane solution to give **2d** as a colorless oil (276 mg, 48%). MS *m/z*: 288 (M^+). HRMS Calcd for $C_{13}H_{18}F_6$: 288.131. Found: 288.131. ^1H-NMR ($CDCl_3$) δ: 0.89 (3H, t, $J=6.2$ Hz), 1.08—1.68 (10H, m), 2.08—2.42 (2H, m), 6.07—6.77 (2H, m), 7.02 (1H, d, $J=10.2$ Hz). ^{19}F-NMR ($CDCl_3$): −4.91 (q, $J=6.9$ Hz), 0.63 (q, $J=6.9$ Hz).

1,1,1-Trifluoro-2-(trifluoromethyl)-6-oxo-4-hepten-2-ol (1e) A solution of benzoyl chloride (2.109 g, 15 mmol) in Et_2O (10 ml) was added to a solution of 4-penten-2-ol (861 mg, 10 mmol) and pyridine (1.185 g, 15 mmol) in Et_2O (10 ml) at 0 °C. After being stirred at room temperature for 24 h, the mixture was poured into ice-water and extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was purified on an SiO_2 column in hexane–CH_2Cl_2 (4 : 1) to give 4-penten-2-yl benzoate as a colorless oil (1.603 g, 84%). MS *m/z*: 190 (M^+). HRMS Calcd for $C_{12}H_{14}O_2$: 190.099. Found: 190.100. ^1H-NMR ($CDCl_3$) δ: 1.35 (3H, d, $J=6.4$ Hz), 2.24—2.64 (2H, m), 4.98—5.43 (2H, m), 5.60—6.12 (1H, m), 7.30—7.69 (3H, m), 7.95—8.18 (2H, m).

A solution of the above benzoate (1.86 g, 9.8 mmol) and hexafluoroacetone (2 ml) in dry benzene (20 ml) was heated at 150 °C for 48 h in a stainless steel tube. The cooled reaction mixture was extracted with Et_2O. The organic layer was washed with water, dried over $MgSO_4$ and concentrated under vacuum. The residue was purified on an SiO_2 column in hexane–CH_2Cl_2 (1 : 1) to give 6-benzoyloxy-1,1,1-trifluoro-2-(trifluoromethyl)-4-hepten-2-ol as a colorless oil (3.01 g, 86%). MS *m/z*: 356 (M^+). HRMS Calcd for $C_{15}H_{14}F_6O_3$: 356.085. Found: 356.084. ^1H-NMR ($CDCl_3$) δ: 1.43 (3H, d, $J=6.4$ Hz), 2.60—2.80 (2H, m), 5.32—5.68 (1H, m), 5.68—6.00 (2H, m), 7.26—7.71 (3H, m), 7.86—8.14 (2H, m). ^{19}F-NMR ($CDCl_3$): 13.65—14.15 (m).

A solution of the above ester (356 mg, 1 mmol) and NaOH (90 mg, 2.2 mmol) in H_2O (4 ml) was refluxed for 1 h. The mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and concentrated under vacuum. The residue was distilled under vacuum to give 7,7,7-trifluoro-6-(trifluoromethyl)-3-heptene-2,6-diol as a colorless oil (234 mg, 93%). bp 90—100 °C (20 mmHg, bulb-to-bulb distillation). MS *m/z*: 252. HRMS Calcd for $C_8H_{10}F_6O_2$: 252.059. Found: 252.059. ^1H-NMR ($CDCl_3$) δ: 1.29 (3H, d, $J=6.4$ Hz), 2.46 (2H, br s), 2.51—2.74 (2H, m), 4.33 (1H, qd, $J=6.4$, 6.0 Hz), 5.37—5.94 (2H, m). ^{19}F-NMR ($CDCl_3$): 13.30—14.20 (m).

Jones' reagent (CrO_3–H_2SO_4, 2.5 ml) was added to a solution of the above diol (321 mg, 1.3 mmol) in acetone (5 ml) at 0 °C until the color of the solution became dark green, and the mixture was stirred at 0 °C for 3.5 h. The mixture was poured into ice water and extracted with CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ and brine, and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified on an SiO_2 column in CH_2Cl_2–Et_2O (10 : 1) to give **1e** as colorless needles (264 mg, 83%). mp 51—54 °C. bp 100 °C (12 mmHg, bulb-to-bulb distillation). MS *m/z*: 250 (M^+). HRMS Calcd for $C_8H_8F_6O_2$: 250.043. Found: 250.042. ^1H-NMR ($CDCl_3$) δ: 2.29 (3H, s), 2.88 (2H, d, $J=7.2$ Hz), 4.75 (1H, s), 6.21 (1H, d, $J=15.8$ Hz), 6.86 (1H, dt, $J=15.8$, 7.2 Hz). ^{19}F-NMR ($CDCl_3$): 13.87 (s).

7,7,7-Trifluoro-6-(trifluoromethyl)-3,5-heptadien-2-one (2e) (a): Phosphorus oxychloride (153 mg, 1 mmol) was added to a solution of 1,1,1-trifluoro-2-(trifluoromethyl)-6-oxo-4-hepten-2-ol (**1e**, 250 mg, 1.0 mmol) in pyridine (1 ml) at 0 °C, and the mixture was stirred at 60 °C for 2 h. After work-up as above, the residue was distilled to give **2e** as a pale yellow oil (71 mg, 31%). bp 80 °C (30 mmHg, bulb-to-bulb distillation). MS *m/z* 232 (M^+). HRMS Calcd for $C_8H_6F_6O$: 232.032. Found: 232.032. ^1H-NMR ($CDCl_3$) δ: 2.38 (3H, s), 6.53 (1H, d, $J=14.9$ Hz), 7.10 (1H, d, $J=11.9$ Hz), 7.45 (1H, dd, $J=14.9$, 11.9 Hz). ^{19}F-NMR ($CDCl_3$): −5.14 (q, $J=6.8$ Hz), 1.48 (q, $J=6.8$ Hz).

(b): Phosphorus oxychloride (220 mg, 1.4 mmol) was added to a solution of **1e** (252 mg, 1.0 mmol) in pyridine (0.5 ml) at 0 °C, and the mixture was stirred at room temperature for 4.5 h. After work-up as above, the residue was separated on an SiO_2 column in CH_2Cl_2 to give **2e** (51 mg, 22%) and **1e** (152 mg, 60%).

(c): Methanesulfonyl chloride (137 mg, 1.2 mmol) was added to a solution of **1e** (250 mg, 1.0 mmol) in triethylamine (150 mg, 1.5 mmol) at 0 °C, and this mixture was stirred for 1 h at the same temperature. The reaction mixture was poured into ice-water and extracted with ether. The ether layer was washed with dilute HCl, aqueous $NaHCO_3$ and brine, and dried over $MgSO_4$. The solvent removed, and the residue was separated on an SiO_2 column in hexane–CH_2Cl_2 (2 : 1) to give **2e** (151 mg, 65%), 7,7,7-trifluoro-6-mesyloxy-6-(trifluoromethyl)-3-hepten-2-one (**3**, 33 mg, 10%) and **1e** (20 mg, 8%). **3**: A colorless oil. MS *m/z*: 328 (M^+), 249 (M − Ms), 232 (M − MsOH). HRMS Calcd for $C_8H_6F_6O$ (M − MsOH): 232.032. Found: 232.033. ^1H-NMR ($CDCl_3$) δ: 2.29 (3H, s), 3.27 (3H, s), 3.41 (2H, d, $J=7.0$ Hz), 6.27 (1H, d, $J=15.8$ Hz), 6.81 (1H, dt, $J=15.8$, 7.0 Hz). ^{19}F-NMR ($CDCl_3$): 10.37 (s).

Dehydration of 1,1,1-Trifluoro-2-methyl-5-phenyl-4-penten-2-ol (5a) Phosphorus oxychloride (337 mg, 2.2 mmol) was added to a solution of **4a** (504 mg, 2.2 mmol) in pyridine (1 ml) at 0 °C, and this mixture was stirred at 75 °C for 24 h. After a usual work-up, the residue was applied to an SiO_2 column in hexane to give a mixture of diene compounds (356 mg, 76%) and **4a** (20 mg, 4%). Analysis of the mixture of dienes by ^{19}F-NMR and GLC showed that it contained (1*E*,3*E*)-5,5,5-trifluoro-4-methyl-1-phenyl-1,3-pentadiene [(1*E*,3*E*)-**5a**, 75 parts], (1*E*,3*Z*)-**5a** (17 parts) and 1-phenyl-4-(trifluoromethyl)-1,4-pentadiene (**6**, 8 parts). This mixture was separated by a preparative GLC at 110 °C to give **5a** (a mixture of diastereomers) and **6**. **5a**: A colorless oil. MS *m/z*: 212 (M^+). HRMS Calcd for $C_{12}H_{11}F_3$: 212.081. Found: 212.081. The ^1H-NMR spectrum was recorded on a JNM-GX400 and the signals of both isomers were assigned. (1*E*,3*E*)-**5a**: ^1H-NMR ($CDCl_3$) δ: 1.98 (3H, s), 6.70 (1H, d, $J=10.8$ Hz), 6.79 (1H, d, $J=15.6$ Hz), 6.94 (1H, dd, $J=15.6$, 10.8 Hz), 7.26—7.47 (5H, m). ^{19}F-NMR ($CDCl_3$): 6.17 (s). (1*E*,3*Z*)-**5a**: ^1H-NMR ($CDCl_3$) δ: 1.98 (3H, s), 6.37 (1H, d, $J=11.5$ Hz), 6.64 (1H, d, $J=15.5$ Hz), 7.14 (1H, ddq, $J=15.5$, 11.5, 2.0 Hz), 7.26—7.47 (5H, m). ^{19}F-NMR ($CDCl_3$): 1.90 (d, $J=2.0$ Hz). **6**: A colorless oil. MS *m/z*: 212 (M^+). HRMS Calcd for $C_{12}H_{11}F_3$: 212.081. Found: 212.080. ^1H-NMR ($CDCl_3$) δ: 3.10 (2H, d, $J=6.6$ Hz). 5.39 (1H, q, $J=1.3$ Hz), 5.73 (1H, q, $J=1.1$ Hz), 6.17 (1H, td, $J=6.6$, 15.7 Hz), 6.48 (1H, d, $J=15.7$ Hz), 7.15—7.48 (5H, m). ^{19}F-NMR ($CDCl_3$): 6.08 (s).

1,1,1-Trifluoro-2-phenyl-2,4-decadiene (5b) (a): Phosphorus oxychloride (530 mg, 3.5 mmol) was added to a solution of 1,1,1-trifluoro-2-phenyl-4-decen-2-ol (**4b**, 789 mg, 2.76 mmol) in pyridine (1 ml) at 0 °C, and this mixture was stirred at 110 °C for 55 h. After a usual work-up, the residue was separated on an SiO_2 column in hexane to give a colorless oil (365 mg), which was found to contain a mixture of dienes (80%) and 2-chloro-1,1,1-trifluoro-2-phenyl-4-decene (**7**, 20%) based on the peak areas in GLC-MS. [Yield: total dienes, 40%; **7**, 9%.] This mixture was separated by preparative GLC (column diethylene glycol succinate (DEGS), L = 2 m, i.d. = 4 mm; temperature 120 °C) to give (2*E*,4*E*)- and (2*Z*,4*E*)-**5b**, and **7**. (2*E*,4*E*)-**5b**: A colorless oil. MS *m/z*: 268 (M^+). HRMS Calcd for $C_{16}H_{19}F_3$: 268.144. Found: 268.144. ^1H-NMR ($CDCl_3$) δ: 0.86 (3H, t, $J=$

6.8 Hz), 1.05—1.53 (6H, m), 1.89—2.21 (2H, m), 5.77—6.27 (2H, m), 6.82 (1H, d, $J=10.2$ Hz), 7.18—7.52 (5H, m). ^{19}F-NMR ($CDCl_3$): 1.86 (s). (2*Z*,4*E*)-**5b**: A colorless oil. MS *m*/*z*: 268 (M^+). HRMS Calcd for $C_{16}H_{19}F_3$: 268.144. Found: 268.143. ^{1}H-NMR ($CDCl_3$) δ: 0.90 (3H, t, $J=6.6$ Hz), 1.17—1.65 (6H, m), 2.04—2.35 (2H, m), 6.02 (1H, dt, $J=13.0$, 6.8 Hz), 6.35—6.87 (2H, m), 7.26—7.45 (5H, m). ^{19}F-NMR ($CDCl_3$): -6.38 (s). The peak ratio on ^{19}F-NMR showed that the ratio of (2*E*,4*E*) : (2*Z*,4*E*) was 7 : 2. **7**: A colorless oil. MS *m*/*z*: 304 (M^+). HRMS Calcd for $C_{16}H_{20}ClF_3$: 304.121. Found: 304.120. ^{1}H-NMR ($CDCl_3$) δ: 0.83 (3H, t, $J=7.2$ Hz), 1.07—1.34 (6H, m), 1.84—1.98 (2H, m), 2.99 (1H, dd, $J=15.0$, 7.0 Hz), 3.26 (1H, dd, $J=15.0$, 6.7 Hz). 5.20 (1H, dt, $J=15.2$, 6.7 Hz), 5.58 (1H, dt, $J=15.2$, 7.0 Hz), 7.33—7.45 (3H, m), 7.60—7.67 (2H, m). ^{19}F-NMR ($CDCl_3$): 12.74 (s).

(b): Compound **4b** (143 mg, 0.5 mmol), thionyl chloride (95 mg, 0.8 mmol) and pyridine (0.5 ml) were mixed in this order under ice-cooling, and the mixture was stirred at room temperature for 38 h. After a usual work-up, the residue was purified on an SiO_2 column in hexane to give a colorless oil (48.4 mg). Analysis of this oil by GLC-MS showed that it contained **5b** and 2-chloro-1,1,1-trifluoro-2-phenyl-4-decene (**7**) in 31% and 66% yields based on peak areas. (Total yields were 11% and 21%, respectively.)

1,1,1-Trifluoro-2-phenyl-2,4-octadiene (5c) Phosphorus oxychloride (98 mg, 0.64 mmol) was added to a solution of 1,1,1-trifluoro-2-phenyl-4-octen-2-ol (**4c**, 166 mg, 0.64 mmol) in pyridine (0.5 ml) at 0 °C, and the mixture was stirred at 90 °C for 24 h. After a usual work-up, the residue was separated on an SiO_2 column in hexane to give a mixture of (2*E*,4*E*)- and (2*Z*,4*E*)-**5c** (25 mg, 16%) and **4c** (84 mg, 51%). The mixture was estimated to contain the (2*E*,4*E*)- and (2*Z*,4*E*)-isomers in the ratio of 3 : 1 based on the ^{19}F-NMR and GLC results. The mixture was separated by preparative GLC at 140 °C. (2*E*,4*E*)-**5c**: A colorless oil. MS *m*/*z*: 240 (M^+). HRMS Calcd for $C_{14}H_{15}F_3$: 240.113. Found: 240.112. ^{1}H-NMR ($CDCl_3$) δ: 0.87 (3H, t, $J=7.3$ Hz), 1.38 (2H, qt, $J=7.3$, 7.3 Hz), 2.04 (2H, td, $J=7.3$, 7.0 Hz), 5.96 (1H, dd, $J=15.5$, 10.8 Hz), 6.08 (1H, dt, $J=15.5$, 7.0 Hz), 6.82 (1H, dq, $J=10.8$, 1.5 Hz), 7.25—7.46 (5H, m). ^{19}F-NMR ($CDCl_3$): 1.90 (s). (2*Z*,4*E*)-**5c**: A colorless oil. MS *m*/*z*: 240 (M^+). HRMS Calcd for $C_{14}H_{15}F_3$: 240.113. Found: 240.113. ^{1}H-NMR ($CDCl_3$) δ: 0.95 (3H, t, $J=7.3$ Hz), 1.48 (2H, qt, $J=7.3$, 7.3 Hz), 2.20 (2H, td, $J=7.3$, 7.3 Hz), 6.04 (1H, td, $J=7.3$, 14.7 Hz), 6.50 (1H, d, $J=11.5$ Hz), 6.67 (1H, dd, $J=14.7$, 11.5 Hz), 7.28—7.43 (5H, m). ^{19}F-NMR ($CDCl_3$): -6.36 (s).

7-(Trifluoromethyl)-4,6-undecadiene (5d) (a): Phosphorus oxychloride (119 mg, 0.78 mmol) was added to a solution of 5-(trifluoromethyl)-7-undecen-5-ol (**4d**, 185 mg, 0.78 mmol) in pyridine (1 ml) at 0 °C, and the mixture was stirred at 80 °C for 55 h. After a usual work-up, the residue was separated on an SiO_2 column in hexane to give a mixture of diene compounds (71 mg, 41%) and **4d** (33 mg, 18%). Analysis of this mixture of dienes by ^{19}F-NMR and GLC showed that it contained four isomers; (4*E*,6*E*)-**5d**, (4*E*,6*Z*)-**5d**, (4*Z*,7*E*)-5-(trifluoromethyl)-4,7-undecadiene [(4*Z*,7*E*)-**8**], and (4*E*,7*E*)-**8** in a ratio of 4 : 2 : 1 : 1. This mixture was separated by preparative GLC at 110 °C to give (4*E*,6*E*)-**5d**, (4*E*,6*Z*)-**5d** and a mixture of **8**. (4*E*,6*E*)-**5d**: A colorless oil. MS *m*/*z*: 220 (M^+). HRMS Calcd for $C_{12}H_{19}F_3$: 220.144. Found: 220.144. ^{1}H-NMR ($CDCl_3$) δ: 0.93 (6H, t, $J=7.5$ Hz), 1.36 (2H, qt, $J=7.5$, 7.5 Hz), 1.42—1.51 (4H, m), 2.15 (2H, td, $J=7.5$, 7.5 Hz), 2.20—2.28 (2H, m), 5.97 (1H, td, $J=7.5$, 15.0 Hz), 6.22 (1H, dd, $J=15.0$, 11.0 Hz), 6.51 (1H, d, $J=11.0$ Hz). ^{19}F-NMR ($CDCl_3$): 3.75 (s). (4*E*,6*Z*)-**5d**: A colorless oil. MS *m*/*z*: 220 (M^+). HRMS Calcd for $C_{12}H_{19}F_3$: 220.144. Found: 220.144. ^{1}H-NMR ($CDCl_3$) δ: 0.91 (3H, t, $J=7.3$ Hz), 0.92 (3H, t, $J=7.3$ Hz), 1.33 (2H, qt, $J=7.3$, 7.3 Hz), 1.39—1.49 (4H, m), 2.12 (2H, td, $J=7.3$, 7.3 Hz), 2.17 (2H, td, $J=7.3$, 7.3 Hz), 5.84 (1H, td, $J=7.3$, 15.0 Hz), 6.17 (1H, d, $J=11.6$ Hz), 6.43 (1H, dd, $J=15.0$, 11.6 Hz). ^{19}F-NMR ($CDCl_3$): -3.55 (br s). A mixture of **8**: A colorless oil. MS *m*/*z*: 220 (M^+). HRMS Calcd for $C_{12}H_{19}F_3$: 220.144. Found: 220.144. ^{1}H-NMR ($CDCl_3$) δ: 0.87 (3H, t, $J=7.3$ Hz), 0.89 (3H, t, $J=7.3$ Hz), 0.92 (3H, t, $J=7.3$ Hz), 0.93 (3H, t, $J=7.3$ Hz), 1.32—1.49 (8H, m), 1.98 (4H, td, $J=7.3$, 7.0 Hz), 2.05—2.16 (2H, m), 2.17—2.27 (2H, m), 2.82 (2H, d, $J=6.4$ Hz), 2.88 (2H, d, $J=6.4$ Hz), 5.34 (2H, td, $J=7.0$, 15.0 Hz), 5.48 (2H, td, $J=6.4$, 15.0 Hz), 5.68 (1H, t, $J=8.0$ Hz), 6.13 (1H, tq, $J=7.5$, 1.8 Hz). ^{19}F-NMR ($CDCl_3$): -2.84 (br s), 4.52 (br s), ratio 1 : 1.

(b): Thionyl chloride (84 mg, 0.7 mmol) was added to a solution of **4d** (120 mg, 0.5 mmol) in pyridine (0.5 ml) at 0 °C, and the mixture was stirred at room temperature for 25 h. After a usual work-up, the residue was separated on an SiO_2 column in hexane to give a mixture of the dienes having the same composition as above (a) (47 mg, 43%) and **4d** (20 mg, 16%).

(2*Z*,4*E*)- (10) and (2*E*,4*E*)-1,1,1-Trifluoro-2,3-dimethyl-2,4-nonadienes (11), and (4*E*)-3-Methyl-2-(trifluoromethyl)-1,4-nonadiene (12) (a): A mixture of phosphorus oxychloride (153 mg, 1.0 mmol), (2*R**,3*R**,4*E*)-1,1,1-trifluoro-2,3-dimethyl-4-nonen-2-ol (**9**, 218 mg, 0.97 mmol) and pyridine (80 mg, 1 mmol) was heated at 100 °C for 30 h. After a usual work-up, the residue was separated on an SiO_2 column in hexane to give a mixture of dienes (100 mg, 50%). This mixture was estimated to contain **10** (75%), **11** (6%) and **12** (14%) based on ^{19}F-NMR. This was separated by preparative GLC at 80 °C to give a mixture of diastereoisomers (**10** and **11**) and **12**. **10**: A colorless oil. MS *m*/*z*: 206 (M^+). HRMS Calcd for $C_{11}H_{17}F_3$: 206.128. Found: 206.128. ^{1}H-NMR ($CDCl_3$) δ: 0.86 (3H, t, $J=5.7$ Hz), 1.02—1.72 (4H, m), 1.83 (6H, s), 1.94—2.29 (2H, m), 5.90 (1H, dt, $J=16.0$, 7.4 Hz), 6.54 (1H, d, $J=16.0$ Hz). ^{19}F-NMR ($CDCl_3$): -6.09 (s). These ^{1}H- and ^{19}F-NMR signals are attributed to **10**. The nuclear Overhauser effect (NOE) in the ^{1}H-NMR indicated an association between the 3-methyl and 5-position protons. ^{19}F-NMR showed another small signal at -4.66 (s), which was attributed to **11**. **12**: A colorless oil. MS *m*/*z*: 206 (M^+). HRMS Calcd for $C_{11}H_{17}F_3$: 206.128. Found: 206.128. ^{1}H-NMR ($CDCl_3$) δ: 0.89 (3H, t, $J=7.0$ Hz), 1.21 (3H, t, $J=7.0$ Hz), 1.24—1.39 (4H, m), 2.01 (2H, td, $J=6.5$, 7.0 Hz), 3.06 (1H, qd, $J=7.0$, 7.0 Hz), 5.35 (1H, q, $J=1.3$ Hz), 5.37 (1H, dd, $J=7.0$, 15.0 Hz), 5.49 (1H, td, $J=6.5$; 15.0 Hz), 5.69 (1H, q, $J=1.5$ Hz). ^{19}F-NMR ($CDCl_3$): 4.03 (s).

(b): Compound **9** (224 mg, 1 mmol), triethylamine (0.2 ml, 1.5 mmol) and MsCl (143 mg, 1.3 mmol) were added to CH_2Cl_2 (2 ml) at 0 °C under stirring in this order, and the mixture was stirred at this temperature for 1 h and at room temperature for 2.5 h, but no products were observed thin layer chromatography (TLC) or GLC.

(2*R,3*R**,4*E*)-1,1,1-Trifluoro-2,3-dimethyl-2-tosyloxy-4-undecene (13)** A solution of **9** (672 mg, 3 mmol) in THF (5 ml) was added to a suspension of 60% NaH (180 mg, 4.5 mmol) in THF (5 ml) under stirring at 0 °C. This mixture was stirred at room temperature for 10 min, then it was cooled to 0 °C. A solution of TsCl (640 mg, 3.4 mmol) in THF (3 ml) was added at this temperature under stirring and stirring was continued at room temperature for 7 h. The reaction mixture was poured into ice-water and extracted with ether. The ether layer was washed with dilute HCl, saturated $NaHCO_3$ and brine, and dried over $MgSO_4$. After evaporation of the solvent, the residue was purified on an SiO_2 column in hexane–CH_2Cl_2 (3 : 1) to give **13** as a colorless oil (978 mg, 86%). MS *m*/*z*: 378 (M^+). HRMS Calcd for $C_{18}H_{25}F_3O_3S$: 378.148. Found: 378.148. ^{1}H-NMR ($CDCl_3$) δ: 0.73—1.01 (3H, m), 1.01—1.48 (7H, m), 1.79 (3H, s), 1.86—2.19 (2H, m), 2.43 (3H, s), 2.55—3.16 (1H, m), 5.10—5.80 (2H, m), 7.32 (2H, d, $J=8.2$ Hz), 7.79 (2H, d, $J=8.2$ Hz). ^{19}F-NMR ($CDCl_3$): 12.49 (s).

Elimination Reaction of 13 (a): A solution of **13** (756 mg, 2 mmol) in THF (1.5 ml) was added to a suspension of *tert*-BuOK (336 mg, 3 mmol) in THF (0.5 ml) at 0 °C, and the mixture was stirred at room temperature for 4 h. The reaction mixture was poured into ice-water, and extracted with ether. The ether layer was washed with dilute HCl, saturated $NaHCO_3$ and brine, and dried over $MgSO_4$. After evaporation of the solvent, the residue was separated on an SiO_2 column in hexane to give a mixture of diene compounds (205 mg, 50%). Analysis of this mixture by ^{19}F-NMR and GLC showed that it contained **10**, **11**, **12** and 1,1,1-trifluoro-2-methyl-3-methylene-4-nonene (**14**) in a ratio of 4.5 : 1 : 1 : 1. These isomers were separated by preparative GLC at 60 °C. **14**: A colorless oil. MS *m*/*z*: 206 (M^+). HRMS Calcd for $C_{11}H_{17}F_3$: 206.128. Found: 206.129. ^{1}H-NMR ($CDCl_3$) δ: 0.90 (3H, t, $J=7.2$ Hz), 1.25—1.45 (4H, m), 1.30 (3H, d, $J=7.0$ Hz), 2.12 (2H, td, $J=7.0$, 7.0 Hz), 3.17 (1H, qq, $J=7.0$, 8.8 Hz), 5.11 (1H, s), 5.21 (1H, s), 5.76 (1H, td, $J=7.0$, 15.9 Hz), 6.04 (1H, d, $J=15.9$ Hz). ^{19}F-NMR ($CDCl_3$): 8.00 (d, $J=8.8$ Hz).

(b): A solution of **13** (134 mg, 0.35 mmol) in dimethyl sulfoxide (DMSO) (0.5 ml) was added to a solution of *tert*-BuOK (39 mg, 0.35 mmol) in DMSO (0.5 ml) at 0 °C, and the mixture was stirred at room temperature for 1 h. After work-up as above, the residue was separated on an SiO_2 column in hexane to give a mixture of dienes (24 mg, 31%) and **13** (14 mg, 10%). Analysis of the mixture of dienes by ^{19}F-NMR and GLC showed that it consisted of **10**, **11**, **12** and **14** in a ratio of 10 : 1 : 8 : 1.

3-[Methyl(trifluoromethyl)methylene]cyclohexene (16) A mixture of 2-(3-cyclohexenyl)-1,1,1-trifluoro-2-propanol (**15**, 975 mg, 5 mmol), $POCl_3$ (1.0 g, 6.5 mmol) and pyridine (1 ml) was stirred at 100 °C for 28 h. After a usual work-up, the residue was purified on an SiO_2 column in pentane to give a mixture of diene compounds (275 mg, 31%), which was found to contain 90% of **16**, and 4% and 3% of other isomers based on ^{19}F-NMR and GLC. From this mixture, **16** was isolated by preparative GLC at 60 °C. **16**: A colorless oil. bp 80 °C (35 mmHg, bulb-to-bulb distillation). MS *m*/*z*: 176 (M^+). HRMS Calcd for $C_9H_{11}F_3$: 176.081. Found: 176.081. ^{1}H-NMR ($CDCl_3$) δ: 1.66—1.80 (2H, m), 1.83 (3H, s), 2.10—2.19 (2H, m), 2.34—2.40 (2H, m), 6.01 (1H, td, $J=4.5$, 10.4 Hz), 6.59 (1H, dq, $J=$ 10.4, 2.4 Hz). ^{19}F-NMR ($CDCl_3$) −5.57 (q, $J=2.4$ Hz). The NOE in the ^{1}H-NMR showed an association between the methyl protons and 4-methylene protons, which indicated that the configuration of the double bond was (*Z*). Another isomer (1% yield) was estimated to be 2-(3-cyclohexenyl)-3,3,3-trifluoropropene (**17**) based on the MS [*m*/*z*: 176 (M^{+})] and ^{19}F-NMR results.

2-(3-Cyclohexenyl)-1,1,1-trifluoro-2-propyl *p*-Toluenesulfonate (18) A solution of **15** (388 mg, 2 mmol) in THF (2 ml) was added to a suspension of NaH (60%, 120 mg, 3 mmol) in THF (4 ml) at 0 °C, and at the same temperature, a solution of TsCl (428 mg, 2.2 mmol) in THF (4 ml) was then added to the mixture. The reaction mixture was stirred at room temperature for 19 h. After a usual work-up, the residue was purified on an SiO_2 column in CH_2Cl_2–hexane (1 : 4) to give **18** as a colorless oil (571 mg, 82%). MS *m*/*z*: 176 (M−TsOH). HRMS Calcd for $C_9H_{11}F_3$ (M−TsOH): 176.081. Found: 176.083. ^{1}H-NMR ($CDCl_3$) δ: 1.11—2.08 (6H, m), 1.69 (3H, s), 2.31 (3H, s), 2.67—2.93 (1H, m), 5.52—6.03 (2H, m), 7.25 (2H, d, $J=8.2$ Hz), 7.73 (2H, d, $J=8.2$ Hz). ^{19}F-NMR ($CDCl_3$): 13.43 (s).

Elimination Reaction of 18 with a Base A solution of **18** (174 mg, 0.5 mmol) and *tert*-BuOK (67 mg, 0.6 mmol) in THF (1 ml) was stirred at room temperature for 18 h. After a usual work-up, the residue was purified on an SiO_2 column in pentane to give a mixture of dienes (6 mg, 7%), which was found to contain 70% of **16**, based on GLC.

6-Methyl-5-(trifluoromethyl)-5,7-dodecadiene (20) and Isomers A mixture of (5*R**,6*R**)-6-methyl-5-(trifluoromethyl)-7-dodecen-5-ol (**19**, 798 mg, 3 mmol), $POCl_3$ (765 mg, 5 mmol) and pyridine (3 ml) was stirred at 100 °C for 24 h. After a usual work-up, the residue was separated on an SiO_2 column in hexane to give a mixture of dienes (237 mg, 32%) and **19** (323 mg, 40%). Analysis of the mixture of dienes by ^{19}F-NMR and GLC showed that it contained **20**, (4*Z*,7*E*)-6-methyl-5-(trifluoromethyl)-4,7-dodecadiene (**21**) and (4*E*,7*E*)-6-methyl-5-(trifluoromethyl)-4,7-dodecadiene (**22**) in a ratio of 8 : 6 : 3. These isomers were isolated by preparative GLC at 110 °C. **20**: A colorless oil. MS *m*/*z*: 248 (M^{+}). HRMS Calcd for $C_{14}H_{23}F_3$: 248.175. Found: 248.175. ^{1}H-NMR ($CDCl_3$) δ: 0.91 (3H, t, $J=7.0$ Hz), 0.92 (3H, t, $J=7.0$ Hz), 1.29—1.45 (8H, m), 1.91 (3H, q, $J=$ 2.4 Hz), 2.15 (2H, td, $J=7.0$, 7.0 Hz), 2.25 (2H, t, $J=7.9$ Hz), 5.92 (1H, td, $J=7.0$, 15.3 Hz), 6.56 (1H, br d, $J=15.3$ Hz). ^{19}F-NMR ($CDCl_3$): −7.49 (br s). **21**: A colorless oil. MS *m*/*z*: 248 (M^{+}). HRMS Calcd for $C_{14}H_{23}F_3$: 248.175. Found: 248.174. ^{1}H-NMR ($CDCl_3$) δ: 0.89 (3H, t, $J=$ 7.0 Hz), 0.91 (3H, t, $J=7.0$ Hz), 1.15 (3H, d, $J=6.7$ Hz), 1.25—1.49 (6H, m), 1.97—2.05 (2H, m), 2.19—2.28 (2H, m), 3.04 (1H, dq, $J=7.0$, 7.0 Hz), 5.31—5.50 (2H, m), 5.69 (1H, t, $J=7.8$ Hz). ^{19}F-NMR ($CDCl_3$): −4.07 (s). **22**: A colorless oil. MS *m*/*z*: 248 (M^{+}). HRMS Calcd for $C_{14}H_{23}F_3$: 248.175. Found: 248.174. ^{1}H-NMR ($CDCl_3$) δ: 0.89 (3H, t, $J=7.0$ Hz), 0.91 (3H, t, $J=7.0$ Hz), 1.23 (3H, d, $J=7.2$ Hz), 1.25—1.49 (6H, m), 1.97—2.05 (2H, m), 2.09—2.19 (2H, m), 3.28 (1H, dq, $J=7.0$, 7.0 Hz), 5.31—5.50 (2H, m), 6.06 (1H, tq, $J=7.5$, 1.8 Hz). ^{19}F-NMR ($CDCl_3$): 1.42 (s).

6-Methyl-5-(trifluoromethyl)-7-dodecen-5-yl *p*-Toluenesulfonate (23) A solution of **19** (798 mg, 3 mmol) in THF (5 ml) was added to a suspension of NaH (60%, 240 mg, 6 mmol) in THF (5 ml) at 0 °C. The mixture was stirred at room temperature for 10 min, then cooled to 0 °C, and TsCl (712 mg, 3.7 mmol) was added. The mixture was stirred at room temperature for 4 h and worked up as usual to give **23** as a viscous oil (1.39 g), which decomposed on an SiO_2 column and therefore was used without further purification. MS *m*/*z*: 248 (M−TsOH). HRMS Calcd for $C_{14}H_{23}F_3$ (M−TsOH): 248.175. Found: 248.175. ^{1}H-NMR ($CDCl_3$) δ: 0.63—0.94 (6H, m), 0.94—1.57 (11H, m), 1.74—2.06 (2H, m), 2.06—2.51 (2H, m), 2.37 (3H, s), 2.71—3.03 (1H, m), 5.08—5.66 (2H, m), 7.14 (2H, d, $J=7.5$ Hz), 7.77 (2H, d, $J=7.5$ Hz). ^{19}F-NMR ($CDCl_3$): 6.57 (s).

Elimination Reaction of 23 A solution of **23** (163 mg, 0.4 mmol) and *tert*-BuOK (57 mg, 0.5 mmol) in DMSO (0.5 ml) was stirred at room temperature for 33 h. After a usual work-up, the residue was separated on an SiO_2 column in hexane to give a mixture of diene compounds (35 mg, 14%) and **19** (42 mg, 44%). Analysis of the mixture of dienes by ^{19}F-NMR and GLC showed that it contained **20**, **21** and (5*E*,7*E*)-6-methyl-5-(trifluoromethyl)-5,7-dodecadiene (**24**) in proportions of 44%, 12% and 12% based on the peak areas in GLC. This mixture was separated by preparative GLC at 110 °C. **24**: A colorless oil. MS *m*/*z*: 248 (M^{+}). HRMS Calcd for $C_{14}H_{23}F_3$: 248.175. Found: 248.175. ^{1}H-NMR ($CDCl_3$) δ: 0.92 (6H, t, $J=7.2$ Hz), 1.28—1.46 (8H, m), 1.96 (3H, q, $J=2.4$ Hz), 2.19 (2H, td, $J=7.0$, 7.0 Hz), 2.29 (2H, t, $J=7.5$ Hz), 6.00 (1H, td, $J=7.0$, 15.5 Hz), 6.39 (1H, d, $J=15.5$ Hz). ^{19}F-NMR ($CDCl_3$): −5.93 (s). The NOE in the ^{1}H-NMR showed an association between the 4-methylene protons and 7-methine proton. This result shows that **24** has (5*E*) configuration.

(2*Z*,4*E*)-1,1,1-Trifluoro-3-methyl-2-phenyl-2,4-nonadiene (26) (a): A solution of (2*R**,3*S**,4*E*)-1,1,1-trifluoro-3-methyl-2-phenyl-4-nonen-2-ol (**25**, 1.115 g, 4 mmol) and $POCl_3$ (974 mg, 6 mmol) in pyridine (3 ml) was stirred at 100 °C for 48 h. After a usual work-up, the residue was separated on an SiO_2 column in hexane to give a non-polar oil (137 mg) and **25** (772 mg, 69%). This non-polar oil was found to contain twelve components based on ^{19}F-NMR and GLC, and was separated by preparative GLC (column DEGS (15%), L = 2 m, i.d. = 4 mm) at 130 °C. Five components, **26**, two diastereomers of 2-butyl-3-chloro-4-methyl-1-phenyl-1-(trifluoromethyl)cyclobutane (**27**) and two diastereomers of 2-chloro-1,1,1-trifluoro-3-methyl-2-phenyl-4-nonene (**28**) (peak area %, **26**: 37%, **27**: 22%, and **28**: 3%), were isolated and identified by MS and NMR. **26**: the first fraction on GLC. A colorless oil. MS *m*/*z*: 268 (M^{+}). HRMS Calcd for $C_{16}H_{19}F_3$: 268.144. Found: 268.143. ^{1}H-NMR ($CDCl_3$) δ: 0.93 (3H, t, $J=7.2$ Hz), 1.32—1.50 (4H, m), 1.72 (3H, q, $J=2.2$ Hz), 2.23 (2H, td, $J=6.9$, 6.9 Hz), 6.08 (1H, td, $J=6.9$, 15.2 Hz), 6.76 (1H, br d, $J=$ 15.2 Hz), 7.15 (2H, d, $J=7.9$ Hz), 7.20—7.30 (3H, m). ^{19}F-NMR ($CDCl_3$): −9.46 (m). NOE showed associations between 2-phenyl and 3-methyl, 3-methyl and 5-methine, and 4-methine and 6-methylene protons. This result shows that the configuration of **26** is (2*Z*,4*E*). One isomer of **27**: The second fraction in GLC. A colorless oil. MS *m*/*z*: 304 (M^{+}). HRMS Calcd for $C_{16}H_{20}ClF_3$: 304.121. Found: 304.120. ^{1}H-NMR ($CDCl_3$) δ: 0.90 (3H, t, $J=7.2$ Hz), 1.17—1.32 (3H, m), 1.46 (3H, dd, $J=6.7$, 1.5 Hz), 1.77 (1H, dd, $J=7.0$, 10.4 Hz), 1.82—1.91 (1H, m), 3.06 (1H, ddd, $J=10.4$, 6.0, 2.5 Hz), 7.30—7.40 (5H, m). ^{19}F-NMR ($CDCl_3$): 0.19 (s). The other isomer of **27**: The fourth fraction on GLC. A colorless oil. MS *m*/*z*: 304 (M^{+}). HRMS Calcd for $C_{16}H_{20}ClF_3$: 304.121. Found: 304.120. ^{1}H-NMR ($CDCl_3$) δ: 0.98 (3H, t, $J=7.3$ Hz), 1.31—1.60 (3H, m), 1.45 (3H, d, $J=$ 7.0 Hz), 1.62—1.80 (2H, m), 1.91 (1H, dd, $J=10.5$, 10.5 Hz), 1.96—2.07 (1H, m), 2.07—2.17 (1H, m), 4.21 (1H, ddd, $J=10.5$, 10.5, 2.4 Hz), 7.28—7.42 (5H, m). ^{19}F-NMR ($CDCl_3$): −5.21 (s). One isomer of **28**: The fifth fraction on GLC. A colorless oil. MS *m*/*z*: 304 (M^{+}). HRMS Calcd for $C_{16}H_{20}ClF_3$: 304.121. Found: 304.120. ^{1}H-NMR ($CDCl_3$) δ: 0.93 (3H, t, $J=7.2$ Hz), 1.31 (3H, d, $J=6.4$ Hz), 1.33—1.52 (4H, m), 2.24 (2H, td, $J=7.1$, 7.1 Hz), 4.72 (1H, q, $J=6.9$ Hz), 5.69 (1H, d, $J=16.2$ Hz), 5.78 (1H, dt, $J=16.2$, 6.7 Hz), 7.28—7.42 (3H, m), 7.46—7.55 (2H, m). ^{19}F-NMR ($CDCl_3$): 1.68 (s). The other isomer of **28**: The third fraction on GLC. A colorless oil. MS *m*/*z*: 304 (M^{+}). HRMS Calcd for $C_{16}H_{20}ClF_3$: 304.121. Found: 304.121. ^{1}H-NMR ($CDCl_3$) δ: 0.85 (3H, d, $J=6.7$ Hz), 0.91 (3H, t, $J=7.2$ Hz), 1.25—1.43 (4H, m), 1.99—2.11 (2H, m), 3.22—3.34 (1H, m), 5.55—5.67 (2H, m), 7.33—7.45 (3H, m), 7.65—7.75 (2H, m). ^{19}F-NMR ($CDCl_3$): 6.51 (s).

(b): A solution of **25** (81 mg, 0.28 mmol) and $SOCl_2$ (70 mg, 0.6 mmol) in HMPA (0.5 ml) was stirred at room temperature for 8 h. After a usual work-up, the residue was purified on an SiO_2 column in hexane to give a colorless oil (61 mg), which was found to contain **26**, **27** and **28** (35%, 19% and 19%, respectively, based on the peak areas on GLC).

1,1,1-Trifluoro-2-(trifluoromethyl)-6-oxo-2-heptanol (29) A solution of **1e** (125 mg, 0.5 mmol) in MeOH (5 ml) was stirred in the presence of 5% Pd–C (7 mg) in an atmosphere of hydrogen until 11 ml of hydrogen had been absorbed. The catalyst was filtered off, and the filtrate was concentrated under vacuum and purified on an SiO_2 column in CH_2Cl_2 to give **29** as colorless needles (103 mg, 81%). mp 61—62 °C. MS *m*/*z*: 252 (M^{+}). HRMS Calcd for $C_8H_{10}F_6O_2$: 252.058. Found: 252.058. ^{1}H-NMR ($CDCl_3$) δ: 1.67—2.11 (4H, m), 2.20 (3H, s), 2.60 (2H, t, $J=5.5$ Hz), 5.37 (1H, s). ^{19}F-NMR ($CDCl_3$): 14.45 (s).

1,1,1-Trifluoro-2-(trifluoromethyl)-6-oxo-2-heptyl *p*-Toluenesulfonate (30) A solution of TsCl (356 mg, 1.9 mmol) in THF (3 ml) was added to a mixture of **29** (420 mg, 1.67 mmol) and 50% NaH (120 mg, 2.5 mmol) in THF (3 ml) at 0 °C. The mixture was refluxed for 1 h and worked up as a usual manner. The residue was separated on an SiO_2 column in CH_2Cl_2–hexane (1 : 3 to 1 : 1) to give **30** as a colorless oil (307 mg, 45%) and **29** (95 mg, 23%). **30**: MS *m*/*z*: 406 (M^{+}). HRMS Calcd for $C_{15}H_{16}F_6O_4S$: 406.067. Found: 406.068. ^{1}H-NMR ($CDCl_3$) δ: 1.71—2.12 (2H, m), 2.16 (3H, s), 2.34—2.73 (4H, m), 2.45 (3H, s), 7.37 (2H, d, $J=8.3$ Hz), 7.82 (2H, d, $J=8.3$ Hz). ^{19}F-NMR ($CDCl_3$): 10.34 (s).

Attempted Dehydration of 30 A solution of **30** (105 mg, 0.26 mmol) and DBU (105 mg, 0.7 mmol) in THF (1 ml) was refluxed for 16 h. Analysis of the reaction mixture by TLC showed that only hydrolysis of **30** to **29** had occurred. No dehydration products were observed.

1,1,1-Trifluoro-2-methyl-2-decanol (31) A solution of 1,1,1-trifluoro-2-methyl-4-decen-2-ol (1.12 g, 5 mmol) in MeOH (5 ml) was stirred in the presence of 5% Pd–C (10 mg) in an atmosphere of hydrogen, until 115 ml of hydrogen had been absorbed. The catalyst was filtered off, and the filtrate was concentrated under vacuum to give **31** as a colorless oil (1.17 g, quantitative). MS *m*/*z*: 208 (M−H_2O). HRMS Calcd for $C_{11}H_{19}F_3$

(M$-$H$_2$O): 208.144. Found: 208.143. ^{1}H-NMR (CDCl$_3$) δ: 0.88 (3H, t, $J=5.9$ Hz), 1.04—1.75 (17H, m), 1.83 (1H, s). ^{19}F-NMR (CDCl$_3$): 20.34.

Dehydration of 31 A solution of **31** (113 mg, 0.5 mmol) and thionyl chloride (120 mg, 1 mmol) in pyridine (0.5 ml) was stirred at room temperature for 39 h. After a usual work-up, the residue was separated on an SiO$_2$ column in hexane to give a mixture of olefinic compounds (40 mg, 39%) and **31** (19 mg, 17%). The mixture of olefinic compounds was found to contain three kinds of trifluoromethyl compounds in a ratio of 8 : 2 : 1 based on the peak ratio in ^{19}F-NMR. Analysis of the 400 MHz ^{1}H-NMR spectrum showed that the major product was (*E*)-1,1,1-trifluoro-2-methyl-2-decene (**32**), the second one, 2-(trifluoromethyl)-1-decene (**33**), and the third one, (*Z*)-1,1,1-trifluoro-2-methyl-2-decene (**34**). **32**: MS *m*/*z*: 208 (M$^+$). HRMS Calcd for C$_{11}$H$_{19}$F$_3$: 208.144. Found: 208.144. ^{1}H-NMR (CDCl$_3$) δ: 0.89 (3H, t, $J=6.9$ Hz), 1.20—1.37 (10H, m), 1.75 (3H, s), 2.09 (2H, td, $J=7.5$, 7.5 Hz), 6.07 (1H, tq, $J=7.5$, 1.5 Hz). Small peaks assigned to **34** were observed at 1.83 (q, $J=1.4$ Hz) and 5.68 (t, $J=7.6$ Hz). ^{19}F-NMR (CDCl$_3$): 6.61 (**32**, d, $J=1.5$ Hz), 5.88 (**33**, s) and -1.30 (**34**, br s) in a ratio of 8 : 2 : 1. The peak at 5.88 was assigned to **33**. The full data of **33** will be presented later.

2-(Trifluoromethyl)-2-decyl *p*-Toluenesulfonate (35) A solution of TsCl (356 mg, 1.9 mmol) in THF (3 ml) was added to a mixture of **31** (343 mg, 1.5 mmol) and 50% NaH (100 mg, 2 mmol) in THF (3 ml) at 0 °C under stirring. After being stirred at room temperature for 9 h, the mixture was worked up as usual. The residue was purified on an SiO$_2$ column in CH$_2$Cl$_2$–hexane (1 : 2) to give **35** as a colorless oil (468 mg, 82%). MS *m*/*z*: 208 (M$-$TsOH). HRMS Calcd for C$_{11}$H$_{19}$F$_3$: 208.144. Found: 208.144. ^{1}H-NMR (CDCl$_3$) δ: 0.89 (3H, t, $J=6.0$ Hz), 1.10—1.60 (12H, m), 1.78 (3H, s), 1.85—2.10 (2H, m), 2.44 (3H, s), 7.32 (2H, d, $J=8.1$ Hz), 7.79 (2H, d, $J=8.1$ Hz). ^{19}F-NMR (CDCl$_3$): 17.10 (s).

2-(Trifluoromethyl)-1-decene (33) A mixture of **35** (76 mg, 0.2 mmol) and potassium *tert*-butoxide (56 mg, 0.5 mmol) in THF (1 ml) was stirred at room temperature for 2 h. A usual work-up gave **33** as a colorless oil (36 mg, 87%). MS *m*/*z*: 208 (M$^+$). HRMS Calcd for C$_{11}$H$_{19}$F$_3$: 208.144. Found: 208.144. ^{1}H-NMR (CDCl$_3$) δ: 0.84 (3H, t, $J=6.9$ Hz), 0.97—1.80 (12H, m), 2.18 (2H, t, $J=7.6$ Hz), 5.29 (1H, q, $J=1.4$ Hz), 5.64 (1H, s). ^{19}F-NMR (CDCl$_3$): 5.88 (s).

References and Notes

1) Part IV: T. Nagai, T. Miki, and I. Kumadaki, *Chem. Pharm. Bull.*, **35**, 3620 (1987).
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