Re-investigation of the Coupling Reaction of 2-Aryl-1,1-dibromo-3,3,3-trifluoropropenes. Preparation of Perfluoroalkylated [3]Cumulenes

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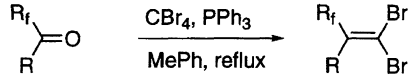
(Received December 2, 1998)

The coupling reaction of perfluoroalkylated 2-aryl-1,1-dibromoalkenes using zinc and copper(I) bromide gave stereoisomeric mixtures of [3]cumulenes and [4]radialenes. The ratio of [3]cumulenes and [4]radialenes mainly depended upon the reaction temperature and the electronic character of the aryl group. When the coupling reaction was carried out at −40 °C, (*E*)- and (*Z*)-[3]cumulenes were obtained in good selectivity and only trace amounts of [4]radialenes were detected by a ^{19}F NMR analysis. On the other hand, a similar reaction at −60 °C afforded a considerable amount of [4]radialene isomers. When the *cis*-[3]cumulenes were heated at an appropriate temperature, selective isomerization to *trans*-[3]cumulenes occurred.

The cumulated butatriene carbon framework is not only an important unit for the construction of highly conjugated π-systems,[1] but also a certain kind of 1,2,3-butatrienes ([3]cumulenes) have been reported to have interesting amphoteric multistage redox properties.[2] During our continuous investigation of the electrolysis using a sulfur/graphite electrode, we were also interested in the reaction of [3]cumulenes with polysulfide anions generated from the electrode.[3] In order to help the product analysis, we required stereoisomerically pure trifluoromethylated [3]cumulenes. Among the reported syntheses of such cumulenes,[4] Burton's method[5] has attracted our interest due to easy accessibility, although they reported the formation of stereoisomeric mixtures (*E*/*Z* = 1/2). *trans*-[3]Cumulenes bearing two alkyl groups at the cumulene terminal positions were first stereoselectively synthesized by Negishi et al.[6] in the coupling reaction of 1-iodoalkynes with thexylborane; then the generation of 1,2,3-butatrienes having *cis* phenyl groups at 1- and 4-positions was reported in the reaction of 1-alkynyl sulfides with organocupurates.[7] Facile thermal and photochemical isomerization and dimerization of [3]cumulenes are also well known in solution and in a solid,[8] and these reactions have made the preparation of stereochemically pure [3]cumulenes rather difficult. Probably due to the difficulty to monitor the progress of these reactions, however, detailed studies on the generation and thermal behavior of [3]cumulenes are rare. Thus, we started a re-investigation of Burton's coupling reaction and the thermal behavior of the [3]cumulenes in order to prepare trifluoroalkyl-substituted [3]cumulenes stereoselectively.

Results and Discussion

Preparation of 2-Aryl-1,1-dibromo-3,3,3-trifluoropropenes. 1,1-Dibromo-3,3,3-trifluoropropenes **2a—e** and **2h** were prepared according to a modified literature procedure (Eq. 1).[9] 2,2,2-Trifluoroacetophenone derivatives **1** were obtained from the corresponding aryl Grignard reagents and trifluoroacetic acid.[10] Then, the trifluoroacetyl derivatives **1** were treated with carbon tetrabromide and triphenylphosphine to give the aimed products **2** in good yields (74—84% from trifluoroacetic acid). Similarly, tridecafluorohexyl derivative **2i** was prepared from tridecafluoroheptanophenone **1i** in 81% yield.

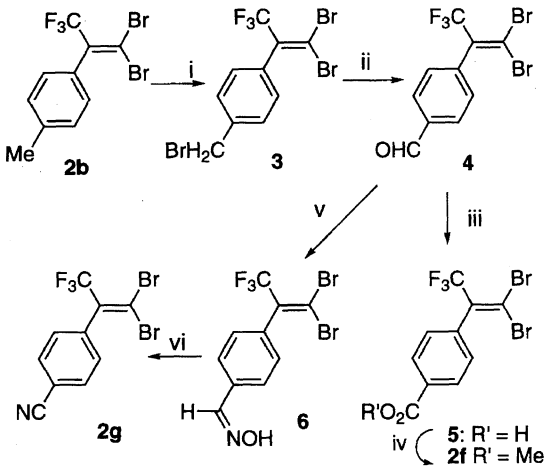


(1)

1a: $R_f = CF_3$, R = Ph
1b: $R_f = CF_3$, R = 4-MeC_6H_4
1c: $R_f = CF_3$, R = 4-ClC_6H_4
1d: $R_f = CF_3$, R = 4-$MeOC_6H_4$
1e: $R_f = CF_3$, R = 4-PhC_6H_4
1h: $R_f = CF_3$, R = *c*-C_6H_{11}
1i: R_f = *n*-C_6F_{13}, R = Ph

2

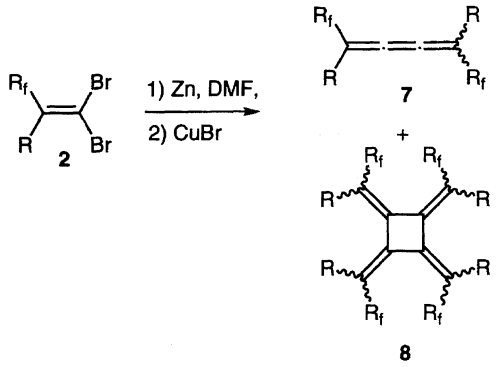
1,1-Dibromo-3,3,3-trifluoropropenes with electron-deficient aryl groups, such as *p*-cyanophenyl and *p*-methoxycarbonylphenyl, were first attempted starting from 2,2,2-trifluoro-4′-methylacetophenone (**1b**). The oxidation of **1b** with $KMnO_4$ followed by methylation with diazomethane gave methyl 4-(trifluoroacetyl)benzoate (**1f**) in moderate yield. The Wittig reaction of **1f** with CBr_4 and PPh_3 in toluene, however, gave a complex mixture involving the desired dibromide **2f** and the corresponding monobromides. Repeated chromatography of the mixture gave **2f** only in low yield. Next, the preparation from 1,1-dibromo-3,3,3-trifluoro-2-*p*-tolylpropene **2b** via aldehyde **4** was examined (Scheme 1). The treatment of **2b** with *N*-bromosuccinimide (NBS) in refluxing carbon tetrachloride gave tribromide **3** in fairly good yield accompanied by a small amount of the corresponding



Scheme 1. Preparaion of **2f** and **2g**. Reagents and conditions: i) NBS, CCl_4, AIBN, refl. ii) $C_6H_{12}N_4$, $CHCl_3$, reflux; H_2O/AcOH (1/1), reflux. iii) $NaClO_2$, H_2O_2, Na_2HPO_4, r.t. iv) CH_2N_2, Et_2O, r.t. v) NH_2OH·HCl, pyridine, r.t. vi) MsCl, pyridine, r.t.

tetrabromide. This crude mixture was subject to the next Sommelet reaction.[11] The crude tribromide **3** was heated with hexamethylenetetramine in chloroform to give the corresponding iminium salt as a powdery solid and the contaminants, such as **2b** and the tetrabromide remained intact in the chloroform solution. The powdery salt was then decomposed in aqueous acetic acid (1/1) at reflux to afford the aldehyde **4** in 50% yield from **2b**. When the decomposition was carried out in water, the yield of **4** was greatly decreased.[11] The oxidation of **4** with sodium chlorite in hydrogen peroxide followed by esterification with diazomethane provided the methyl ester **2f** in 85% yield (2 steps). The cyano derivative **2g** was prepared in 97% yield from the aldehyde **4** in two steps: oximation with hydroxylamine in pyridine followed by dehydration with mesyl chloride and pyridine.

Coupling Reaction of 2-Aryl-1,1-dibromo-3,3,3-trifluoropropene. At first, the coupling reaction of 1,1-dibromo-3,3,3-trifluoro-2-phenylpropene (**2a**) was carried out under a slightly modified procedure.[5] The dibromide **2a** and one equivalent of Zn dust in dry DMF was sonicated at room temperature. After the disappearance of Zn, the mixture was cooled to −45 °C by a Dry Ice–MeCN bath and purified copper(I) bromide (8 mol%) was added. The mixture was stirred at the same temperature for 30 min and then allowed to warm to room temperature. A ^{19}F analysis of the reaction mixture revealed that (*E*)- and (*Z*)-1,1,1,6,6,6-hexafluoro-2,5-diphenyl-2,3,4-hexatrienes (*E*-**7a** and *Z*-**7a**) were formed in a ratio of ca. 1/2[12] and some other compounds containing CF_3 groups existed (Eq. 2). The latter materials were proved to be (*E*)- and (*Z*)-1-bromo-3,3,3-trifluoro-2-phenylpropenes (**11a**) and four isomers of [4]radialene **8a**.[13] The isomeric ratio of **8a** was near to the statistic ratio (I : II : III : IV = 2 : 2 : 10 : 5).[13] Based on the integral of CF_3-absorbing region (from −80 to −50 ppm), the relative yields of **7a** and **8a** were 77 and 11%, respectively. The isolated yields of **7a** and **8a** were 45 and 5%, respectively. Since Burton et al. did not report on the formation of [4]radialenes,[5] the reaction was examined in the presence of $Hg(OAc)_2$. However, a similar result to that mentioned above was obtained.



(2)

The distinctive difference between our conditions and Burton's was the activation method of zinc and the reaction temperatures (−50——45 °C vs. −40 °C). Thus, we examined the temperature effect in the absence of $HgCl_2$. Because aqueous quenching of the intermediate zinc reagent **10a** generated at various temperatures (15—60 °C) gave a similar ratio (*E*/*Z* = ca. 3/2—6/5) of the corresponding monobromides **11a**, the coupling stage using copper(I) bromide was examined at various temperatures (Table 1). The lower was the temperature, the more were the [4]radialenes formed.

Takai et al. reported that Pb impurities in commercially available zinc powder prepared by distillation affected the bismetallation of *gem*-dihalides.[14] We turned our attention to the effects of metals which might be contaminated in the reaction (Table 2), and commercially available zinc dust prepared from electrolysis was used in the following experiments. Similar amounts of [4]radialenes as in the cases of distilled zinc were produced in the absence of an additive, and a slightly preferable formation of [4]radialenes was observed in the presence of $PdCl_2$ and $Rh_2(OAc)_4$ (Runs 8 and 9); also, no obvious change in the sense of isomeric ratios of the [3]cumulenes and [4]radialenes was observed in all cases.

Table 1. Coupling Reaction of **2a** Using Distilled Zinc Dust at Different Temperatures[a]

Run	Temp	**7a**		**8a**	
	°C	Yield/%[b]	*E*/*Z*[c]	Yield/%[d]	I/II/III/IV[c]
1	−60 — −55	54	44/56	28	10/13/40/37
2	−55 — −50	57	43/57	19	10/12/40/30
3	−45 — −40	66	32/68	5	11/10/61/18
4	−40 — −35	56	32/68	3	15/14/57/14
5	−35 — −30	55	31/69	2	12/5/53/30

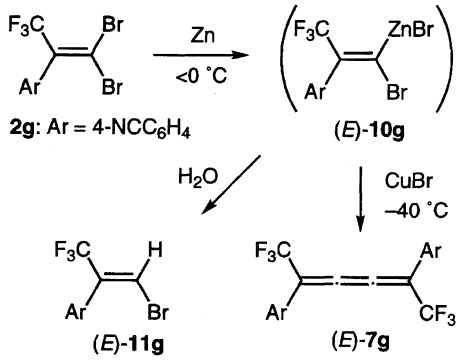
a) The values obtained in three experiments were averaged. b) Combined isolated yield of **7a**. c) Ratios were calculated by ^{19}F NMR spectra of the reaction mixture using benzotrifluoride as an internal standard. d) Yields were estimated by the ^{19}F NMR spectra of the chromatographed materials assuming that all compounds should have been derived only from the Ph(CF_3)-C=C moiety.

Table 2. Coupling Reaction of **2a** Using Electrolytic Zinc Dust in the Presence of an Additive

Run	Temp	Additive	**7a**		**8a**	
	°C	(mol%)	Yield/%[a]	E/Z[a]	Yield/%[a]	I/II/III/IV[a]
1	−45	None	74	30/70	10	10/8/61/20
2[b]	−45	CuI (13)[c]	74	34/66	13	9/6/49/36
3	−40	None	50	30/70	3	28/8/52/12
4[d]	−40	None	49	35/65	2	9/17/61/13
5	−40	$PbBr_2$ (2)[e]	76	29/71	3	21/14/51/14
6	−40	$OsCl_3$ (1)[e]	67	31/69	3	10/10/64/16
7	−40	$CuCl_2$ (1)[f]	62	38/62	3	15/15/58/12
8	−40	$PdCl_2$ (1)[f]	48	36/64	7	9/7/53/31
9	−40	$Rh_2(OAc)_4$ (1)[f]	40	37/63	6	11/7/49/33

a) The yields and ratios were estimated by the ^{19}F NMR spectra of the reaction mixture using benzotrifluoride as an internal standard. b) The distilled zinc dust was used. c) Copper(I) iodide was used instead of CuBr. d) The reaction was carried out in the dark. e) The additive was added with zinc dust. f) The additive was added with CuBr.

Other dibromopropenes **2** were subject to a coupling reaction under our conditions (Table 3). Similar *E*/*Z* selectivity and preference of *Z*-isomers were realized, except for the cyano derivative **2g**. The coupling reaction of the cyclohexyl derivative **2h** afforded a complex mixture, from which [3]radialenes **9** in addition to the [3]cumulenes **7h** and [4]radialenes **8h** were obtained in impure form by repeated column chromatography and GPC. The dibromopropenes with an electron-donating group tended to give [4]radialenes. Fair amounts of [4]radialenes **8** were obtained in the cases of *p*-methoxyphenyl and 4-biphenylyl derivatives **2d** and **2e** (Runs 3 and 4), while the methoxycarbonyl and cyano derivatives **2f** and **2g** did not give any [4]radialene (Runs 5 and 7). In the latter cases, no activation of zinc was required. Because the reaction of **2g** under the normal conditions afforded an intractable mixture, probably derived from the further reduction with zinc, preparation of the intermediate zinc reagent was performed at 0 °C and the coupling reaction was quenched below 0 °C. Under these conditions, a predominant formation of (*E*)-**7g** was observed. When the intermediate zinc reagent **10g** was quenched with water, (*E*)-monobromide **11g** was formed in 93% selectivity (Scheme 2). The selective insertion of zinc to the carbon–bromine bond *cis* to the trifluoromethyl group was not surprising, and was rationalized by chelation with the neighboring trifluoromethyl



Scheme 2. Reaction of **2g**.

Table 3. Coupling Reaction of **2** Using Distilled Zinc Dust

Run	**2**	Temp	**7**		**8**	
		°C	Yield/%[a]	E/Z[b]	Yield/%[a]	I/II/III/IV[b]
1	**2b**	−45	71 (80)	(31/69)	(6)	(9/16/57/17)
2	**2c**	−45	44 (66)	(28/72)	(6)	(8/13/53/26)
3	**2d**	−45	54 (74)	(31/69)	(14)	(13/9/59/19)
4	**2e**	−45	54 (62)	34/66 (29/71)	(32)	(12/26/45/17)
5	**2f**	−45	61	(38/62)	(0)[c]	—
6	**2g**	−45	—[d]	—	—[d]	—
7[e]	**2g**	−40	57	96/4 (99/1)	(0)[c]	—
8	**2h**	−45	7[f] (18)	(37/63)	11 (17)	(3/30/59/8)
9	**2i**	−45	72	40/60 (42/58)	—[g]	—

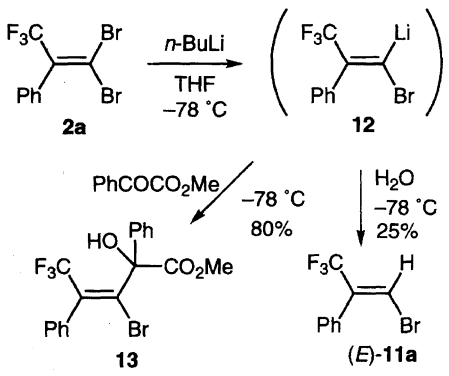
a) Combined isolated yield. The yield in the parentheses was estimated by the ^{19}F NMR spectra of the reaction mixture assuming that all compounds should have been derived only from the $Ar(CF_3)C{=}C$ moiety. b) The ratio was calculated by the ^{19}F NMR analysis of the chromatographed material. The ratio in the parentheses was estimated by the ^{19}F NMR spectra of the reaction mixture assuming that all compounds should have been derived only from the $Ar(CF_3)C{=}C$ moiety. c) Formation of radialenes was not observed. d) A complex mixture was formed and the products could not be identified. e) Preparation of the intermediate zinc reagent was carried out at −5—0 °C. f) Contaminated with unidentified compounds. g) Formation of radialenes could not be determined.

group. Non-stereoselective formation of the zinc intermediates observed in other cases would be the consequence of equilibrium via alkylidene carbene–metal complexes.

The directing ability of fluorine and trifluoromethyl groups has been investigated in the *ortho*-metallation of fluorinated aromatic compounds.[15] Thus, a lithium–bromine exchange reaction of **2a** was examined (Scheme 3). The treatment of **2a** with *n*-BuLi in THF at −78 °C brought about a smooth and highly selective formation of lithiated E-isomer **12** (lithium and CF_3 are *cis*), which was confirmed by quenching with water and methyl benzoylformate to give (*E*)-**11a** and **13** in high stereoselectivity (>95%).[16] The structure of **13** was unambiguously determined by an X-ray analysis. We attempted a coupling reaction by using stereochemically pure **12**. Thus, the lithio derivative **12** was transmetallated with $ZnBr_2$ at −78 °C, and then DMF followed by CuBr was added at −40 °C. However, the isomeric ratio of **7a** was *E*/*Z* = 1/3, though the monobromide **11a** obtained by quenching the intermediate was only *trans*.

The *E*/*Z* isomerization of cumulenes would be facilitated even at low temperatures by electron transfer from the intermediate zinc or copper reagents, and that the *E*-cumulenes would selectively precipitate out from the reaction mixtures in the reaction of **2g**, because reduction potentials of cumulenes were fairly high (from −0.06 V for **7f** to −0.62 V for **7d** vs. Ag/AgI)[17] and precipitation of the cumulenes was observed in all experiments. Thus, the coupling reaction of **2e** was conducted in the presence of pure (*E*)-**7a** or (*Z*)-**7a** at −40 °C. From a NMR analysis of both reaction mixtures, however, the added cumulenes (*E*)-**7a** and (*Z*)-**7a** remained completely intact and isomeric mixtures (*E*/*Z* = ca. 1/2) of cumulenes **7e** were formed in 63—65% yield in addition to [4]radialenes (3%). No reaction between **7a** and **2e** giving mixed radialenes was observed, either.[18]

Rearrangement of the Cumulene. Next, isomerization from (*Z*)-**7a** to (*E*)-**7a** was examined, since the thermal and photo isomerization of [3]cumulenes are well known.[8,19] Selective isomerization to (*E*)-hexa-2,3,4-dienedioates in a solid was also reported at the measurement of melting points.[20] In fact, *E*/*Z* isomerization was realized on two-dimensional TLC in the cases of phenyl, *p*-tolyl, and *p*-methoxyphenyl substituted cumulenes **7a**, **7b**, and **7d**. When both pure (*E*)- and (*Z*)-**7a** were dissolved in $CDCl_3$ at room temperature, they isomerized to the equilibrium mixtures of *E*/*Z* = ca. 2/1 after 3 d. On the other hand, upon heating at 150 °C without solvent, (*Z*)-**7a** first selectively isomerized to (*E*)-**7a** within 1 h and then reached to the equilibrium (*E*/*Z* = 7/3) after the formation of the [4]radialenes was recognized (Table 4). The maximum selectivity of (*E*)-**7a** at 150 °C was 88% (1 h). At a lower temperature, where only (*E*)-**7a** was still solid (130 °C), the maximum selectivity became 95%. Thus, the best isomerization time of other cumulenes **7** was examined between the melting points of *E*- and *Z*-cumulenes (Table 5). In the cases of diaryl cumulenes, *E*-isomers were obtained in >94% selectivity.



Scheme 3. Reaction of lithiated **2a**.

Consideration on the Coupling Reaction of 2. Although it is rather difficult to describe the mechanism of the coupling reaction at this moment, possible reaction pathways are illustrated in Scheme 4. Burton et al. reported smooth transmetallation of the zinc reagent with CuBr and interruption of the dimeric intermediate corresponding to **15** with HCl.[5] At low temperature (< −40 °C), the lifetime of the dimeric copper reagent **15** would be fairly long, even though β-elimination of CuBr was thought to be an easy process. Thus, the dimer **15** would undergo the insertion of another carbenoid to form trimeric **16**, the CuBr loss of which would be slower than that of **15**, because ring closures are generally much slower than β-elimination in acyclic systems. The trimeric **16** would undergo the insertion of **14** to give tetrameric **17** rather than the elimination of CuBr leading [3]-

Table 4. Thermal Isomerization of the Cumulene **7a** at 150 °C without Solvent

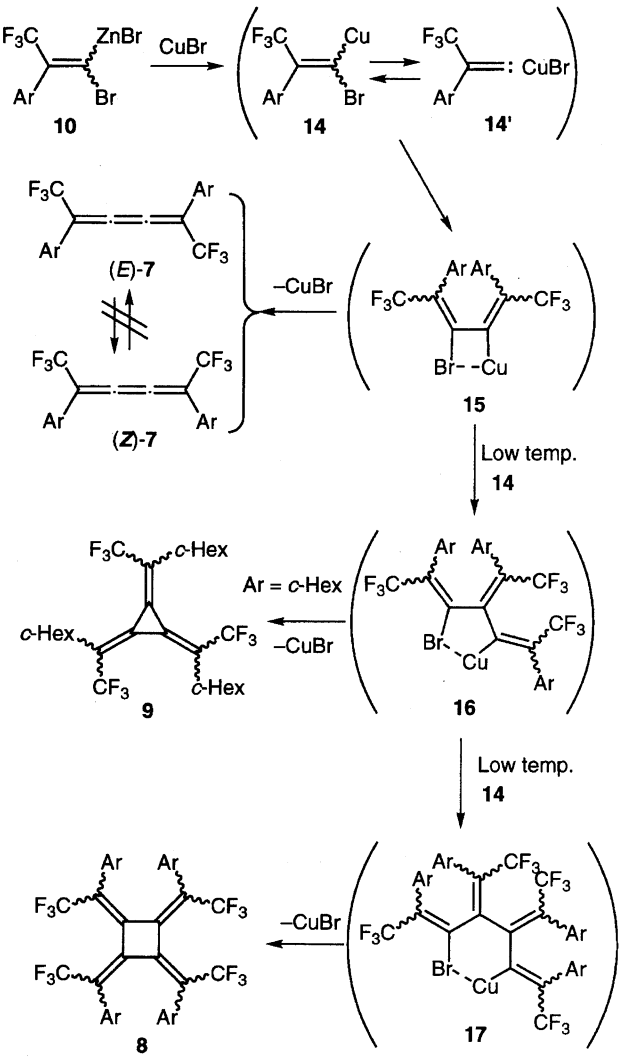
Time	Cumulene **7a**		Radialene **8a**	
	Ratio/%[a]	*E*/*Z*	Ratio/%[a]	I/II/III/IV
0	100	0/100	0	—
10 min	100	64/36	0	—
30 min	100	74/26	0	—
1 h	100	88/12	0	—
2 h	93	70/30	7	ca. 10/30/40/20
4 h	79	70/30	11	ca. 10/35/45/10
8 h	48	70/30	32	6/57/30/7
24 h	9	40/60	47	3/58/29/10

a) The ratio was estimated by the ^{19}F NMR spectra of the reaction mixture assuming that all compounds should have been derived only from the $Ar(CF_3)C{=}C$ moiety.

Table 5. Thermal Isomerization of Cumulenes **7**

Run	**7**		Mp/°C		Temp	Time	Ratio
		E/*Z*	*E*	*Z*	°C	min	*E*/*Z*
1	**7a**	0/100	147—149	104—107	130	60	95/5
2	**7b**	0/100	161—163	131—133	150	10	94/6
3	**7c**	12/88	165—167	121—123	150	10	99/1
4	**7d**	21/79	172—173	99—101	150	10	98/2
5	**7e**	48/52	242—244	—[a]	200	30	95/5
6	**7f**	10/90	188—189	152—154	170	30	> 99/ < 1
7	**7h**	0/100	—[a]	66—73	170	60	2/1
8	**7i**	0/100	108—110	32—34	90	720	99/1

a) The isomer could not be obtained in the pure state.



Scheme 4. Possible pathways for the reaction of **2**.

radialenes, except in the case of **3h**. The tetramer **17** would then decomposed to the [4]radialenes **8**. This pathway would be supported by the following fact. The dibromides **2** bearing electron-deficient aryl groups, such as cyanophenyl and methoxycarbonylphenyl, gave no [4]radialenes. The carbanionoid form **14** of these compounds would be more important than the carbenoid form **14′**. Thus, the insertion process giving radialenes would be suppressed. The insertion of the carbenoid **14** to tetramer **17** would probably be disfavored due to a steric hindrance. The high *E*-selectivity observed in the case of **2g** remains unclear, although there is a possibility that this might be related to the stereoselective formation of (*E*)-**10**.

Conclusion

In the coupling reaction of perfluoroalkylated 2-aryl-1,1-dibromoalkenes **2** using zinc and copper(I) bromide, stereoisomeric mixtures of [3]cumulenes and [4]radialenes were obtained and the ratio between [3]cumulenes and [4]-radialenes mainly depended upon the reaction temperature. At −40 °C, (*E*)- and (*Z*)-[3]cumulenes were obtained in good selectivity and only trace amounts of [4]radialenes were formed, except for the cases of **2f** and **2g** bearing electron-withdrawing aryl groups. In the cases of **2f** and **2g**, the formation of [4]radialenes could not be detected, even in the reaction mixtures. However, the lower was the temperature, the more were the [4]radialenes formed. At −60 °C, the reaction of **2a** afforded a considerable amount (28%) of [4]-radialene isomers. The isomeric ratio of cumulenes were around $E/Z = 1/2$ under various reaction conditions, except for the case of **2g**. In the latter case, an exclusive formation of *E*-**7g** was realized. When the *cis*-[3]cumulenes **7** were heated in neat below the melting points of the corresponding *trans*-[3]cumulenes **7**, selective isomerization occurred and *trans*-[3]cumulenes **7** were obtained in > 94% selectivity.

Experimental

General Details. The melting points are uncorrected. Unless otherwise specified, NMR spectra were obtained with a JEOL GSX-270 or JMN-400 spectrometer at ambient temperature by using $CDCl_3$ as a solvent and tetramethylsilane and $CFCl_3$ as internal standards for ^1H, ^{13}C, and ^{19}F. In NMR spectra, asterisks (*) denote the changeable assignment. Mass spectra and high resolution mass spectra were measured with a Hitachi M80B-LCAPI spectrometer under the following ionizing conditions: EI (electron impact, 20 eV; 70 eV for HRMS; high boiling perfluorokerosine as a standard) and CI (chemical ionization, 70 eV, isobutane as CI gas). Column chromatography and TLC analysis were carried out using BM-127ZH (Fuji-Davison) and Kieselgel 60 F_{254} (Merck), respectively. Ether and THF were freshly distilled from sodium benzophenone ketyl. Dichloromethane, benzene, toluene, and triethylamine were distilled from CaH_2 under an inert atmosphere. Distilled zinc was purchased from Wako Chemical Co. and electrolytic zinc was purchased from Merck Co. Both forms of zinc dust were treated according to the literature.[21] Copper(I) bromide was recryatallized from a sat. KBr aqueous solution, dried in vacuo, and stored under N_2.[21] Other commercially available materials were used without further purification.

Preparation of Perfluoroalkanoyl Compounds. 2,2,2-Trifluoroacetophenone (**1a**) was purchased from Tokyo Kasei Co. 2,2,3,3,4,4,5,5,6,6,7,7,7-Tridecafluoroheptanophenone (**1i**) was prepared from methyl benzoate and tridecafluorohexyl iodide according to the literature procedure.[22] 2,2,2-Trifluoro-4′-methylacetophenone (**1b**; bp 89—91 °C/40 mmHg, 1 mmHg = 133.322 Pa), 4′-chloro-2,2,2-trifluoroacetophenone (**1d**; bp 97 °C/42 mmHg), 2,2,2-trifluoro-4′-methoxyacetophenone (**1c**; bp 118—120 °C/35 mmHg), and 2,2,2-trifluoro-4′-phenylacetophenone (**1e**; bp 135—140 °C/2 mmHg; mp 47—48 °C) were prepared in respective yields of 80, 83, 90, and 81% from trifluoroacetic acid and the corresponding Grignard reagents according to the modified method of the literature,[10] as follows.

General Procedure. A 1-l, three-necked, round-bottomed flask equipped with a stirring bar, a reflux condenser, and a 250-ml pressure-equalized dropping funnel was arranged for conducting a reaction in an atmosphere of nitrogen by fitting into the top of the condenser a T-tube attached to a low-pressure supply of nitrogen and to a bubbler. The flask was dried by warming with a soft flame or heat gun as a slow stream of nitrogen was passed through the system. Magnesium turnings (10.68 g, 0.44 g atom) and 100 ml of anhydrous diethyl ether were put in the cooled flask and bromine (31.96 g, 10.32 ml, 0.2 mol) was placed in the dropping funnel. The

flask was immersed in an ice bath and bromine was slowly added with stirring (ca. 30 min). Trifluoroacetic acid (45.6 g, 30.8 ml, 0.4 mol) and 80 ml of anhydrous ether were added through the dropping funnel at room temperature (ca. 1.5 h). Vigorous evolution of hydrogen occurred. The viscous solution of the trifluoroacetate was diluted with 120 ml of dry ether and then cooled with an ice-salt bath (around −15 °C). The Grignard reagent prepared from 0.5 mol of the corresponding bromide and magnesium turnings (13.37 g, 0.55 g atom) in ether or THF (200 ml) was transferred in the dropping funnel by a cannula and added to the trifluoroacetate solution over a two-hour period at the temperature. The mixture was stirred overnight at room temperature, refluxed for 1 h, and then poured onto a mixture of ice (100 ml), water (200 ml), and excess of concentrated hydrochloric acid (100 ml). The layers were separated and the aqueous phase was extracted with ether (2×100 ml). The combined ether extracts were washed with water (2×100 ml), a saturated sodium hydrogencarbonate solution (2×100 ml), and brine (100 ml), and then dried over magnesium sulfate. The solvent was removed by distillation and the residue was put in a 100-ml flask equipped with a vigreux column and a semi-micro distillation apparatus, and distilled under a reduced pressure. The yields mentioned above were based on the amount of trifluoroacetic acid.

Methyl 4-(Trifluoroacetyl)benzoate (1f). To a stirred mixture of **1b** (7.53 g, 40.0 mmol) and sodium dichromate (52.0 g, 216 mmol) in 140 ml of water was added dropwise 86.8 ml of concd sulfuric acid for 15 min. The mixture was refluxed for 4 h and then cooled to room temperature. The reaction mixture was diluted with 200 ml of water and extracted with EtOAc (3×100 ml). The organic phase was washed with brine (100 ml), dried over Na_2SO_4, and concentrated. The residue was dissolved in 200 ml of hot $CHCl_3$ and filtered through a Celite pad which was washed with hot $CHCl_3$. The filtrate was concentrated to ca. 70 ml and cooled in a freezer. The precipitates were collected by filtration to give 3.06 g of 4-(trifluoroacetyl)benzoic acid as pale green leaflets. Another crop (0.28 g) was obtained by concentrating of the mother liquor to ca. 20 ml followed by adding hexane (30 ml). The combined yield was 3.34 g (15.3 mmol, 38%). Mp 135—138 °C (sublimation); ^{1}H NMR δ = 8.0 (1H, very broad, CO_2H), 8.17 (2H, m, H^3 and H^5), and 8.27 (2H, m, H^2 and H^6); ^{13}C NMR δ = 116.5 (q, J = 291 Hz, CF_3), 130.1 (q, J = 2 Hz, C^3 and C^5), 130.7 (C^2 and C^6), 134.0 (C^1), 135.0 (C^4), 169.9 (CO_2H), and 180.2 (q, J = 36 Hz, $COCF_3$); ^{19}F NMR δ = −72.43 (s); IR (KBr) 3500—2400s, 1724vs, 1694vs, 1290s, 1210vs, 1186vs, 1154vs, and 952s cm^{-1}; MS *m/z* (rel intensity) 218 (M^+; 4), 201 (2), 149 (100), and 121 (19). To an ice-cooled solution of the acid (3.30 g, 15.1 mmol) in ether (50 ml) was added a solution of diazomethane prepared from 12.9 g (60 mmol) of *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide.[2] The resulting yellow solution was stirred for 10 min at the temperature, and then excess diazomethane was destroyed by adding acetic acid. The mixture was dried over $MgSO_4$ and concentrated. The residue was chromatographed on silica gel (20—50% EtOAc/hexane) to give 2.20 g (9.48 mmol, 67%) of **1f** [R_f = 0.1 (20% EtOAc/hexane)] as a mixture of **1f** and its hydrate. Further purification by distillation with a Kugelrohr apparatus (100—110 °C/15 mmHg) gave pure **1f** as colorless crystals: Mp 37—39 °C; ^{1}H NMR δ = 3.98 (3H, s, CO_2Me), 8.13 (2H, m, H^3 and H^5), and 8.19 (2H, m, H^2 and H^6); ^{13}C NMR δ = 52.7 (OMe), 116.4 (q, J = 291 Hz, CF_3), 130.0 (q, J = 3 Hz, C^3 and C^5), 130.1 (C^2 and C^6), 133.0 (C^1), 135.9 (C^4), 165.6 (CO_2), and 180.1 (q, J = 36 Hz, $COCF_3$); ^{19}F NMR δ = −72.18 (s); IR (KBr) 1728vs, 1694vs, 1288vs, and 1172vs cm^{-1}; MS *m/z* (rel intensity) 232 (M^+; 5), 201 (26), 163 (100), 135 (16), and 104 (11).

Preparation of 2-Aryl-1,1-dibromo-3,3,3-trifluoropropenes. General Procedure. A 1-l flask with three necks was equipped with a Teflon®-coated magnetic follower, a septum, a N_2 tee, triphenylphosphine (115.6 g, 0.441 mol), and anhydrous toluene (400 ml). The stream of nitrogen was increased, and then carbon tetrabromide (73.37 g, 0.221 mol) was added all at once. The solution immediately changed from colorless to yellow, and finally to an orange suspension. After stirring for 30 min at room temperature, a trifluoroacetyl compound (0.201 mol) and 3×15 ml of dry toluene were added via a cannula. The mixture was stirred for 30 min and then refluxed for 1 h. After cooling, water (500 ml) was added with stirring. The organic phase was separated and the aqueous phase was extracted with toluene (2×200 ml). The combined organic phase was washed with water (200 ml), sat $NaHCO_3$ (2×200 ml), and brine (200 ml), dried over Na_2SO_4, filtered, and concentrated to a volume of 100 ml. After the resulting suspension was treated with 300 ml of 5% EtOAc/hexane, the suspension was filtered through a silica-gel pad (10 i.d.×5 cm), which was washed with 5% EtOAc/hexane (500 ml). The filtrate was concentrated by a rotary evaporator and the residue was put in a 200-ml round-bottomed flask fitted with a Vigreux column (10 cm) and a semi-micro distillation apparatus. Several drops of forerun were collected and the product was distilled under reduced pressure.

1,1-Dibromo-3,3,3-trifluoro-2-phenylpropene (2a): Yield 90%; bp 140 °C/50 mmHg (lit,[5] 94—104 °C/11 mmHg).

1,1-Dibromo-3,3,3-trifluoro-2-*p*-tolylpropene (2b): Yield 95%; bp 114—116 °C/12 mmHg; ^{1}H NMR δ = 2.37 (3H, s, Me), 7.10 (2H, m, $H^{3'}$ and $H^{5'}$), and 7.22 (2H, m, $H^{2'}$ and $H^{6'}$); ^{13}C NMR δ = 21.4 (Me), 101.3 (q, J = 4 Hz, C^1), 122.0 (q, J = 277 Hz, C^3F_3), 128.5 ($C^{3'}$ and $C^{5'}$), 129.4 ($C^{2'}$ and $C^{6'}$), 132.5 ($C^{1'}$), 137.6 (q, J = 32 Hz, C^2), and 139.4 ($C^{4'}$); ^{19}F NMR δ = −59.03 (s); IR (neat) 1612s, 1584s, 1514s, 1294vs, 1200vs, 1174vs, and 1134vs cm^{-1}; MS *m/z* (rel intensity) 346 [M^+ ($^{81}Br_2$); 38], 344 [M^+ ($^{81}Br^{79}Br$); 76], 342 [M^+ ($^{79}Br_2$); 40], 184 (52), 115 (43), 82 (94), and 80 (100). Anal. Calcd for $C_{10}H_7Br_2F_3$: C, 34.92; H, 2.05%. Found: C, 35.26; H, 2.16%.

1,1-Dibromo-3,3,3-trifluoro-2-(*p*-methoxyphenyl)propene (2c): Yield 93%; bp 135—137 °C/12 mmHg, colorless crystals, mp 45—47 °C; ^{1}H NMR δ = 3.82 (3H, s, Me), 6.93 (2H, m, $H^{3'}$ and $H^{5'}$), and 7.14 (2H, m, $H^{2'}$ and $H^{6'}$); ^{13}C NMR δ = 55.2 (Me), 101.5 (q, J = 3 Hz, C^1), 114.1 ($C^{3'}$ and $C^{5'}$), 121.9 (q, J = 277 Hz, C^3F_3), 127.6 ($C^{1'}$), 130.1 ($C^{2'}$ and $C^{6'}$), 137.3 (q, J = 33 Hz, C^2), and 160.2 ($C^{4'}$); ^{19}F NMR δ = −59.05 (s); IR (KBr) 1610s, 1584s, 1514vs, 1290vs, 1252vs, 1204s, 1170vs, and 1128vs cm^{-1}; MS *m/z* (rel intensity) 362 [M^+($^{81}Br_2$); 50], 360 [M^+($^{81}Br^{79}Br$); 100], 358 [M^+($^{79}Br_2$); 51], 212 (15), 210 (16), 200 (66), and 157 (17). Anal. Calcd for $C_{10}H_7Br_2F_3O$: C, 33.37; H, 1.96%. Found: C, 33.38; H, 2.02%.

1,1-Dibromo-2-*p*-chlorophenyl-3,3,3-trifluoropropene (2d): Yield 94%; bp 123 °C/12 mmHg; ^{1}H NMR δ = 7.18 (2H, m, $H^{2'}$ and $H^{6'}$) and 7.40 (2H, m, $H^{3'}$ and $H^{5'}$); ^{13}C NMR δ = 102.3 (q, J = 4 Hz, C^1), 121.7 (q, J = 277 Hz, C^3F_3), 129.2 ($C^{3'}$ and $C^{5'}$),* 130.1 ($C^{2'}$ and $C^{6'}$),* 133.8 ($C^{1'}$), 135.6 ($C^{4'}$), and 136.5 (q, J = 33 Hz, C^2); ^{19}F NMR δ = −59.00 (s); IR (neat) 1580s, 1492s, 1296vs, 1202vs, 1178vs, 1136vs, and 1092s cm^{-1}; MS *m/z* (rel intensity) 368 [M^+ ($^{81}Br_2{}^{37}Cl$); 12], 366 [M^+ ($^{81}Br_2{}^{35}Cl$ and $^{81}Br^{79}Br^{37}Cl$); 61], 364 [M^+ ($^{81}Br^{79}Br^{35}Cl$ and $^{79}Br_2{}^{37}Cl$); 100], 362 [M^+ ($^{79}Br_2{}^{35}Cl$); 42], 248 (13), 216 (17), 204 (41), and 169 (39). Anal. Calcd for $C_9H_4Br_2ClF_3$: C, 29.67; H, 1.11%. Found: C, 29.94; H, 1.21%.

2-(4-Biphenylyl)-1,1-dibromo-3,3,3-trifluoropropene (2e). In

this case, the work-up procedure was modified as follows: Silica gel (60 g) was added to the toluene extracts derived from 21.93 g (87.6 mmol) of **1e**, and then the toluene was removed by a rotary evaporator. The residue was sprinkled onto a silica-gel column (6 i.d.×20 cm) and eluted with hexane (500 ml) and 5% EtOAc (1000 ml). The eluate was concentrated to leave 34.16 g (84.1 mmol, 96%) of the title compound as pale-yellow crystals. Recrystallization from hexane (ca. 50 ml) gave 30.51 g (75.1 mmol, 86%) of analytically pure **2e** as very pale-yellow rods. An additional crop (1.97 g) was obtained by recrystallization of the residue from the mother liquor. The combined yield was 32.48 (80.0 mmol, 91%). **2e**: Mp 89—90 °C; ^{1}H NMR δ = 7.27 (2H, m, H$^{2'}$ and H$^{6'}$), 7.34 (1H, m, H$^{4''}$), 7.42 (2H, m, H$^{3''}$ and H$^{5''}$), 7.57 (2H, m, H$^{2''}$ and H$^{6''}$), and 7.61 (2H, m, H$^{3'}$ and H$^{5'}$); ^{13}C NMR δ = 101.7 (q, J = 3 Hz, C^1), 121.9 (q, J = 277 Hz, C^{3}F$_3$), 127.1 (C$^{3'}$ and C$^{5'}$),* 127.4 (C$^{2''}$ and C$^{6''}$),* 127.8 (C$^{4''}$), 128.9 (C$^{2'}$ and C$^{6'}$),* 129.1 (C$^{3'}$ and C$^{5'}$),* 134.3 (C$^{1'}$), 137.3 (q, J = 32 Hz, C^2), 140.0 (C$^{4'}$), and 142.2 (C$^{1''}$); ^{19}F NMR δ = −58.84 (s); IR (KBr) 1580m, 1488m, 1296vs, 1206vs, 1190vs, 1176vs, and 1124vs cm^{-1}; MS *m/z* (rel intensity) 408 [M$^+$ (^{81}Br$_2$); 50], 406 [M$^+$ (^{81}Br^{79}Br); 100], 404 [M$^+$ (^{79}Br$_2$); 52], 326 (6), 256 (12), and 246 (90). Anal. Calcd for $C_{15}H_9Br_2F_3$: C, 44.37; H, 2.23%. Found: C, 44.48; H, 2.37%.

4-(2,2-Dibromo-1-trifluoromethylvinyl)benzaldehyde (4). 1,1-Dibromo-3,3,3-trifluoro-2-*p*-tolylpropene (**2b**; 10.32 g, 30 mmol), *N*-bromosuccinimide (NBS, 5.85 g, 33.0 mmol), 2,2′-azobisisobutyronitrile (AIBN, 100 mg), and CCl_4 (100 ml) were placed in a 200-ml round-bottomed flask equipped with a magnetic stirring bar, a reflux condenser, and a $CaCl_2$ drying tube and the mixture was refluxed overnight. After the mixture was cooled to room temperature, carbon tetrachloride was thoroughly removed by a closed-circuit type evaporator. After the resulting syrup was treated with toluene (50 ml), the white solid of succinimide was filtered off. The solid was washed with toluene (2×20 ml). The combined filtrate was washed with water (5×30 ml) and brine (30 ml), dried over Na_2SO_4, and concentrated in a 200-ml round-bottomed flask to give 13.30 g of the crude product. ^{1}H NMR and GLC analyses revealed that the material consisted of the staring material **2b**, 1,1-dibromo-2-*p*-(bromomethyl)phenyl-3,3,3-trifluoropropene (**3**), and 1,1-dibromo-2-*p*-(dibromomethyl)phenyl-3,3,3-trifluoropropene (**3′**) in a molar ratio of 13 : 70 : 17. The crude material was used in the next step without purification.

3: ^{1}H NMR δ = 4.49 (2H, s, CH_2Br), 7.21 (2H, m, H$^{2'}$ and H$^{6'}$), and 7.45 (2H, m, H$^{3'}$ and H$^{5'}$).

3′: ^{1}H NMR δ = 6.65 (1H, s, $CHBr_2$), 7.23 (2H, m, H$^{2'}$ and H$^{6'}$), and 7.62 (2H, m, H$^{3'}$ and H$^{5'}$).

The flask containing the above mixture was equipped with a magnetic stirring bar, a reflux condenser, and a $CaCl_2$ drying tube. Hexamethylenetetramine (4.21 g, 30.0 mmol) and chloroform (60 ml) were added and the mixture was refluxed. After 2 h, the reflux condenser was replaced by a distilling head and about 50 ml of the solvent was distilled off. The mixture was cooled to room temperature, 100 ml of ether was added with stirring, and then the suspension was filtered. The white precipitates were washed with ether (2×20 ml), transferred to a 200-ml round-bottomed flask, and then dried in vacuo to give 12.65 g (75% from **2b**) of the iminium salt. (GLC analysis of the mother liquor shows that **3** was completely consumed and that **2b** and the tetrabromide **3′** were almost intact.) The flask was equipped with a magnetic stirring bar and a reflux condenser. After water (50 ml) and acetic acid (50 ml) were added, the mixture was refluxed for 1 h. After almost all of the solvent was removed by a rotary evaporator, brine (100 ml) and EtOAc (100 ml) were added. The organic phase was separated and the aqueous phase was extracted with EtOAc (2×50 ml). The combined organic phase was washed sequentially with water (50 ml), saturated aq-$NaHCO_3$ (3×30 ml), water (30 ml), and brine (30 ml), dried over Na_2SO_4, and concentrated. The residue was chromatographed on a short silica-gel column [5 i.d.×20 cm; 10% EtOAc/hexane; R_f = 0.3 (10% EtOAc/hexane)] to give 5.35 g (50% from **2b**) of the title compound **4** as a pale yellow oil. This material could be used in the next step. Distillation by a Kugelrohr apparatus gave pure **4** as a colorless oil: bp 135—140 °C/12 mmHg (oven temp); ^{1}H NMR δ = 7.43 (2H, m, H^3 and H^5), 7.95 (2H, m, H^2 and H^6), and 10.06 (1H, s, CHO); ^{13}C NMR δ = 102.5 (q, J = 3 Hz, C$^{1'}$), 121.5 (q, J = 277 Hz, C$^{3'}$F$_3$), 129.6 (C^3 and C^5),* 130.0 (C^2 and C^6),* 136.6 (q, J = 33 Hz, C$^{2'}$), 136.7 (C^1), 141.0 (C^4), and 191.3 (CHO); ^{19}F NMR δ = −58.78 (s); IR (neat) 2836m, 2744m, 1708vs, 1608s, 1296vs, 1202vs, 1178vs, and 1136vs cm^{-1}; MS *m/z* (rel intensity) 360 [M$^+$ (^{81}Br$_2$); 44], 359 [M$^+$−1 (^{81}Br$_2$); 58], 358 [M$^+$ (^{81}Br^{79}Br); 98], 357 [M$^+$−1 (^{81}Br^{79}Br); 100], 356 [M$^+$ (^{79}Br$_2$), 52], 355 [M$^+$−1 (^{79}Br$_2$); 51], 229 (16), 197 (23), and 169 (72).

4-(2,2-Dibromo-1-trifluoromethylvinyl)benzoic Acid (5). The aldehyde **4** (3.58 g, 10.0 mmol), disodium hydrogenphosphate dodecahydrate (358 mg, 1.0 mmol), water (4 ml), acetonitrile (10 ml), and 30% hydrogen peroxide (1.1 ml) were placed in a 100-ml round-bottomed flask equipped with a magnetic stirring bar and a dropping funnel. The mixture was cooled with an ice bath and sodium chlorite ($NaClO_2$, 1.60 g, 14 mmol) in water (14 ml) was added from the dropping funnel with stirring for ca. 30 min. After the mixture was stirred overnight, 5% HCl (40 ml) was added. The mixture was extracted with ether (3×50 ml) and the ethereal solution was washed with brine (30 ml). After the ethereal solution was dried over Na_2SO_4, the solvent was removed to give 3.76 g of crude **5** as a white solid. Recrystallization from ether/hexane gave 3.30 g (88%) of **5** as colorless crystals: mp 187—188 °C; ^{1}H NMR δ = 7.38 (2H, m, H^3 and H^5), 8.19 (2H, m, H^2 and H^6), and 10.45 (1H, broad, CO_2H); ^{13}C NMR δ = 102.4 (q, J = 3 Hz, C$^{1'}$), 121.6 (q, J = 276 Hz, C$^{3'}$F$_3$), 129.0 (C^3 and C^5),* 130.2 (C^1), 130.7 (C^2 and C^6),* 136.7 (q, J = 32 Hz, C$^{2'}$), 140.7 (C^4), and 171.5 (CO_2H); ^{19}F NMR δ = −58.81 (s); IR (KBr) 3300—2300vs, 1694vs, 1428s, 1298vs, 1206vs, 1184vs, and 1134vs cm^{-1}; MS *m/z* (rel intensity) 376 [M$^+$ (^{81}Br$_2$); 51], 374 [M$^+$ (^{81}Br^{79}Br); 100], 372 [M$^+$ (^{79}Br$_2$); 53], 357 [M$^+$−OH (^{81}Br^{79}Br); 15], 293 (9), 229 (16), and 170 (31). Anal. Calcd for $C_{10}H_4Br_2F_3O_2$: C, 32.12; H, 1.35%. Found: C, 32.22; H, 1.44%.

Methyl 4-(2,2-Dibromo-1-trifluoromethylvinyl)benzoate (2f). The acid **5** (15.68 g, 41.9 mmol) and ether (140 ml) were placed in a 500-ml round-bottomed flask equipped with a magnetic stirring bar and the flask was immersed in an ice bath. Ethereal diazomethane solution previously prepared from *N*-nitroso-*p*-toluenesulfonamide (20.4 g, 95.3 mmol) was slowly added until color of the mixture became yellow. After the mixture was stirred for 10 min, acetic acid was added to destroy excess diazomethane. The mixture was washed with sat $NaHCO_3$ (3×100 ml) and brine (100 ml), dried over $MgSO_4$, and concentrated to give **2f** in an almost quantitative amount. Distillation with a Kugelrohr apparatus gave 15.70 g (97%) of the title compound **2f** as colorless crystals: Bp 130—135 °C/2 mmHg; mp 57—58 °C; ^{1}H NMR δ = 3.94 (3H, s, CO_2Me), 7.33 (2H, m, H^3 and H^5), and 8.10 (2H, m, H^2 and H^6); ^{13}C NMR δ = 52.3 (Me), 102.2 (q, J = 4 Hz, C$^{1'}$), 121.6 (q, J = 277 Hz, C$^{3'}$F$_3$), 128.8 (C^3 and C^5),* 130.0 (C^2 and C^6),* 131.0 (C^1), 136.8 (q, J = 33 Hz, C$^{2'}$), 139.7 (C^4), and 166.3 (CO_2); ^{19}F NMR δ = −58.85 (s); IR (KBr) 1714vs, 1442m, 1292vs, 1184vs, 1176vs, and 1138vs cm^{-1}; MS *m/z* (rel intensity) 390 [M$^+$ (^{81}Br$_2$); 31], 388 [M$^+$ (^{81}Br^{79}Br); 61], 386 [M$^+$ (^{79}Br$_2$); 32], 359 [M$^+$−OMe (^{81}Br$_2$);

50], 357 [M^+−OMe ($^{81}Br^{79}Br$); 100], 355 [M^+−OMe ($^{79}Br_2$); 54], 197 (11), and 169 (37).

4-(2,2-Dibromo-1-trifluoromethylvinyl)benzonitrile (2g). The aldehyde (**4**; 5.20 g, 14.5 mmol) and hydroxylamine hydrochloride (1.21 g, 17.4 mmol) were weighed in a 200-ml round-bottomed flask. Dry pyridine (15 ml) was added at room temperature and the mixture was stirred. Progress of the reaction was monitored by TLC [R_f: 0.7 for **4**, 0.5 for (*E*)-**6**, and 0.25 for (*Z*)-**6** (EtOAc/hexane = 20/80)]. Within 1 h, the reaction completed. Water (50 ml) and EtOAc (90 ml) were added. The organic phase was separated and the aqueous phase was extracted with EtOAc (3×60 ml). The combined organic phase was washed with water (2×50 ml) and brine (50 ml), dried over Na_2SO_4, and concentrated in a 500-ml round-bottomed flask to give 5.40 g (99%) of almost pure *N*-[4-(2,2-dibromo-1-trifluoromethylvinyl)benzylidene]hydroxylamine (**6**) as a mixture of stereo isomers (*E*/*Z* = 19/1). Although further purification and separation of the stereo isomers could be done by column chromatography on silica gel, the crude material was used in the next step, even if a trace amount of pyridine remained.

(*E*)-**6**: Mp 73—75 °C; ^{1}H NMR δ = 7.26 (2H, m, H^3 and H^5), 7.64 (2H, m, H^2 and H^6), 8.06 (1H, broad, OH), and 8.16 (1H, s, CH=N); ^{13}C NMR δ = 102.0 (q, *J* = 3 Hz, C^1), 121.7 (q, *J* = 277 Hz, $C^{3'}F_3$), 127.3 (C^3 and C^5),* 129.2 (C^2 and C^6),* 133.1 (C^1), 136.8 (C^4), 137.0 (q, *J* = 33 Hz, $C^{2'}$), and 149.5 (CH=N); ^{19}F NMR δ = −58.90 (s); IR (KBr) 3336vs, 1300vs, 1202vs, 1186vs, and 1130vs cm^{-1}; MS *m/z* (rel intensity) 375 [M^+ ($^{81}Br_2$); 50], 373 [M^+ ($^{81}Br^{79}Br$); 100], 371 [M^+ ($^{79}Br_2$); 53], 355 (21), 330 (26), and 169 (37).

(*Z*)-**6**: Mp 112—113 °C, ^{1}H NMR δ = 7.31 (2H, m, H^3 and H^5), 7.44 (1H, s, CH=N), 8.02 (2H, m, H^2 and H^6), and 10.1 (1H, broad, OH); ^{13}C NMR δ = 102.1 (q, *J* = 3 Hz, C^1), 121.7 (q, *J* = 277 Hz, $C^{3'}F_3$), 128.9 (C^3 and C^5),* 131.0 (C^1), 131.2 (C^2 and C^6),* 136.9 (C^4), 136.9 (q, *J* = 33 Hz, $C^{2'}$), and 145.8 (CH=N); ^{19}F NMR δ = −58.80 (s); IR (KBr) 3300—2700vs, 1584m, 1298vs, 1208vs, 1164vs, and 1130vs cm^{-1}.

A magnetic stirring bar and dry pyridine (30 ml) were added in a flask containing **6**, the flask was capped with a rubber septum and a N_2 balloon, and then the flask was immersed in an ice bath. Freshly distilled methanesulfonyl chloride (5.73 g, 3.86 ml, 17.6 mmol) was added by a syringe for 5 min with stirring. After the addition, the bath was removed and the mixture was stirred at room temperature. Pyridinium salts gradually precipitated. Progress of the reaction was monitored by TLC [R_f: 0.65 for **2g** (EtOAc/hexane = 20/80)]. After completion (within 1 h), water (300 ml) and ether (150 ml) were added. The organic phase was separated and the aqueous phase was extracted with ether (3×70 ml). The combined ethereal phase was washed sequentially with 2.5% aq-HCl (3×100 ml), water (100 ml), saturated aq-$NaHCO_3$ (100 ml), and brine (100 ml); dried over Na_2SO_4; filtered through a silica gel column (5 i.d.×7 cm) which was washed with ether (300 ml); and concentrated to leave 4.99 g (98%) of almost pure **2g** as pale yellow crystals. Recrystallization from ether/hexane gives 4.12 g (81%) of the title compound as colorless crystals: Mp 89—90 °C; ^{1}H NMR δ = 7.38 (2H, m, H^3 and H^5) and 7.74 (2H, m, H^2 and H^6); ^{13}C NMR δ = 103.1 (q, *J* = 3 Hz, $C^{1'}$), 113.5 (C^1), 117.9 (CN), 121.4 (q, *J* = 276 Hz, $C^{3'}F_3$), 129.7 (C^2 and C^6),* 132.6 (C^3 and C^5),* 136.0 (q, *J* = 33 Hz, $C^{2'}$), and 139.7 (C^4); ^{19}F NMR δ = −58.76 (s); IR (KBr) 2232s, 1612m, 1590m, 1298vs, 1204vs, 1164vs, and 1152vs cm^{-1}; MS *m/z* (rel intensity) 357 [M^+ ($^{81}Br_2$), 50]; 355 [M^+ ($^{81}Br^{79}Br$); 100], 353 [M^+ ($^{79}Br_2$); 52], 276 (27), 274 (27), 256 (17), 254 (17), and 195 (56). Anal. Calcd for $C_{10}H_4Br_2F_3N$: C, 33.84; H, 1.14; N, 3.95%. Found: C, 33.84; H, 1.24; N, 3.98%.

1,1-Dibromo-2-cyclohexyl-3,3,3-trifluoropropene (2h): Contaminated with ca. 5% of the monobromides; yield 70%; colorless oil; 128 °C/31 mmHg; ^{1}H NMR δ = 1.10—1.35 (3H, m), 1.15—1.90 (7H, m), and 2.97 (1H, m); ^{19}F NMR δ = −56.93 (br); ^{13}C NMR δ = 25.5, 26.7, 29.0, 97.6 (q, *J* = 5 Hz, C^1), 122.9 (q, *J* = 279 Hz, CF_3), and 139.6 (q, *J* = 29 Hz, C^2); IR (neat) 1570s, 1452s, 1274vs, 1241s, 1170vs, 1134vs, and 1103s cm^{-1}; MS *m/z* (rel intensity) 338 [M^+ ($^{81}Br_2$); 22], 336 [M^+ ($^{81}Br^{79}Br$); 42], 334 [M^+ ($^{79}Br_2$); 24], 282 (37), 280 (78), 278 (38), 201 (88), 199 (100), and 175 (82). Anal. Calcd for $C_9H_{11}Br_2F_3$: C, 32.17; H, 3.30%. Found: C, 32.70; H, 3.27%.

1,1-Dibromo-3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-2-phenyloctene (2i): Yield 81%; colorless oil; bp 100 °C/0.5 mmHg (oven temperature); ^{1}H NMR δ = 7.22 (2H, m, *meta*) and 7.41 (3H, m, *ortho* and *para*); ^{19}F NMR δ = −81.28 (3F, t, *J* = 10 Hz, F^8), −103.48 (2F, m, F^3), −118.76 (2F, m, F^4), −122.37 (2F, m, F^6), −123.24 (2F, m, F^5), and −126.64 (2F, m, F^7); IR (neat) 1580m, 1484m, 1448m, 1364vs, 1242vs, 1214vs, 1144vs, 1124vs, and 1075s cm^{-1}; MS *m/z* (rel intensity) 582 [M^+ ($^{81}Br_2$); 50], 580 [M^+ ($^{81}Br^{79}Br$); 100], 578 [M^+ ($^{79}Br_2$); 50], and 505 (5). Anal. Calcd for $C_{14}H_5Br_2F_{13}$: C, 28.99; H, 0.89%. Found: C, 29.62; H, 0.87%.

Coupling Reaction of 2. General Procedure. Zinc dust (327 mg, 5 mmol, activated with dil HCl) and dibromide **2** (5 mmol) was put in a 30-ml flask equipped with a Teflon®-coated stirring bar and three-way stopcock with a septum and N_2 balloon. The flask was flushed with nitrogen and then dry DMF (4 ml) was added. The suspension was sonicated (28 KHz, 150 W). Zinc dust disappeared after about 1—1.5 h; at this point the mixture became an orange-brown solution. The mixture was cooled at the indicated temperature; then, CuBr (55 mg, 0.38 mmol) was added, the mixture was stirred at the temperature for at least 30 min, at which it was warmed to room temperature over 2—4 h. The reaction was quenched with water and the mixture was filtered through a Celite pad, which was thoroughly washed with chloroform or ether. The aqueous filtrate was extracted with ether and the combined organic phase was concentrated. In the cases of **2e** and **2g**, recrystallization was performed and the mother liquor was subject to chromatographic purification. In other cases, the obtained material was directly chromatographed on silica gel. A broad yellow band was collected as three fractions. The first and third fractions consisted of almost pure (*E*)- and (*Z*)-**7**, respectively.

1,1,1,6,6,6-Hexafluoro-2,5-diphenyl-2,3,4-hexatriene (7a). (*E*)-**7a**: R_f = 0.5 (hexane); yellow needles, mp 147—149 °C (lit,[5] 140—141 °C); ^{1}H NMR δ = 7.40 (6H, m, $H^{3'}$, $H^{4'}$, and $H^{5'}$) and 7.68 (4H, m, $H^{2'}$ and $H^{6'}$); ^{13}C NMR δ = 115.7 (q, *J* = 35 Hz, C^2 and C^5), 121.9 (q, *J* = 274 Hz, C^1F_3 and C^6F_3), 127.9 ($C^{2'}$ and $C^{6'}$), 129.1 ($C^{3'}$ and $C^{5'}$), 130.3 ($C^{4'}$), 131.1 ($C^{1'}$), and 156.9 (m, C^3 and C^4); ^{19}F NMR δ = −59.64 (s); IR (KBr) 1448s, 1308vs, 1190vs, 1164vs, 1154vs, and 1124vs cm^{-1} (The cumulene stretching around 2050 cm^{-1} was too weak to be identified.); MS *m/z* (rel intensity) 340 (M^+; 100), 271 (9), 251 (21), and 202 (35).

(*Z*)-**7a**: R_f = 0.35 (hexane); yellow prismatic crystals, mp 104—107 °C (lit,[5] 104—107 °C); ^{1}H NMR δ = 7.42 (6H, m, $H^{3'}$, $H^{4'}$, and $H^{5'}$) and 7.65 (4H, m, $H^{2'}$ and $H^{6'}$); ^{13}C NMR δ = 115.9 (q, *J* = 36 Hz, C^2 and C^5), 121.7 (q, *J* = 275 Hz, C^1F_3 and C^6F_3), 128.1 ($C^{2'}$ and $C^{6'}$), 129.1 ($C^{3'}$ and $C^{5'}$), 130.3 ($C^{4'}$), 131.4 ($C^{1'}$), and 157.6 (m, C^3 and C^4); ^{19}F NMR δ = −60.03 (s); IR (KBr) 2056w, 1494m, 1320vs, 1296vs, 1258vs, 1186vs, 1168vs, 1138vs, and 1122vs cm^{-1}.

1,1,1,6,6,6-Hexafluoro-2,5-di-*p*-tolyl-2,3,4-hexatriene (7b). (*E*)-**7b**: R_f = 0.7 (hexane); yellow needles, mp 161—163 °C; ^{1}H NMR δ = 2.38 (6H, s, Me), 7.22 (4H, m, $H^{3'}$ and $H^{5'}$), and

7.56 (4H, m, $H^{2'}$ and $H^{6'}$); ^{13}C NMR δ = 21.4 (Me), 115.1 (q, J = 34 Hz, C^2 and C^5), 122.2 (q, J = 274 Hz, C^1F_3 and C^6F_3), 127.9 ($C^{2'}$ and $C^{6'}$), 128.7($C^{1'}$), 129.9 ($C^{3'}$ and $C^{5'}$), 140.8 ($C^{4'}$), and 155.6 (m, C^3 and C^4); ^{19}F NMR δ = −59.73 (s); IR (KBr) 1608m, 1306vs, 1184vs, 1162vs, and 1118vs cm^{-1}; MS *m/z* (rel intensity) 369 (M^++1; 23), 368 (M^+; 100), 284 (13), and 230 (12). Anal. Calcd for $C_{20}H_{14}F_6$: C, 65.22; H, 3.83%. Found: C, 65.45; H, 4.10%.

(*Z*)-**7b**: R_f = 0.55 (hexane); yellow prismatic crystals, mp 131—133 °C; ^{1}H NMR δ = 2.37 (6H, s), 7.22 (6H, m, $H^{3'}$ and $H^{5'}$), and 7.52 (4H, m, $H^{2'}$ and $H^{6'}$); ^{13}C NMR δ = 21.3 (Me), 115.4 (q, J = 35 Hz, C^2 and C^5), 121.9 (q, J = 275 Hz, C^1F_3 and C^6F_3), 128.1 ($C^{2'}$ and $C^{6'}$), 129.0 ($C^{1'}$), 129.9 ($C^{3'}$ and $C^{5'}$), 140.8 ($C^{4'}$), and 156.3 (m, C^3 and C^4); ^{19}F NMR δ = −60.08 (s); IR (KBr) 2056m, 1606s, 1322vs, 1298vs, 1256vs, 1168vs, 1138vs, and 1122vs cm^{-1}. Anal. Calcd for $C_{20}H_{14}F_6$: C, 65.22; H, 3.83%. Found: C, 65.25; H, 4.21%.

1,1,1,6,6,6-Hexafluoro-2,5-di-*p*-methoxyphenyl-2,3,4-hexatriene (7c). (*E*)-**7c**: R_f = 0.5 (5% EtOAc/hexane); yellow needles, mp 165—167 °C; ^{1}H NMR δ = 3.86 (6H, s, Me), 6.95 (4H, m, $H^{3'}$ and $H^{5'}$), and 7.61 (4H, m, $H^{2'}$ and $H^{6'}$); ^{13}C NMR δ = 55.4 (OMe), 113.5 (q, J = 34 Hz, C^2 and C^5), 114.6 ($C^{3'}$ and $C^{5'}$), 122.2 (q, J = 274 Hz, C^1F_3 and C^6F_3), 124.1 ($C^{1'}$), 129.4 ($C^{2'}$ and $C^{6'}$), 153.4 (m, C^3 and C^4), and 161.1 ($C^{4'}$); ^{19}F NMR δ = −59.59 (s); IR (KBr) 2056vw, 1604s, 1514s, 1306vs, 1258vs, 1190vs, 1122vs, and 1158vs cm^{-1}; MS *m/z* (rel intensity) 401 (M^++1; 22), 400 (M^+; 100), 385 (39), and 149 (10). Anal. Calcd for $C_{20}H_{14}F_6O_2$: C, 60.01; H, 3.52%. Found: C, 59.99; H, 3.74%.

(*Z*)-**7c**: R_f = 0.25 (5% EtOAc/hexane); orange rods, mp 121—123 °C; ^{1}H NMR δ = 3.86 (6H, s, Me), 6.97 (4H, m, $H^{3'}$ and $H^{5'}$), and 7.59 (4H, m, $H^{2'}$ and $H^{6'}$); ^{13}C NMR δ = 55.5 (OMe), 113.8 (q, J = 35 Hz, C^2 and C^5), 114.7 ($C^{3'}$ and $C^{5'}$), 122.0 (q, J = 275 Hz, C^1F_3 and C^6F_3), 124.3 ($C^{1'}$), 129.6 ($C^{2'}$ and $C^{6'}$), 154.2 (m, C^3 and C^4), and 161.0 ($C^{4'}$); ^{19}F NMR δ = −59.95 (s); IR (KBr) 2056w, 1600vs, 1514s, 1300vs, 1268vs, 1158vs, and 1118vs cm^{-1}. Anal. Calcd for $C_{20}H_{14}F_6O_2$: C, 60.01; H, 3.52%. Found: C, 60.15; H, 3.76%.

2,5-Di-(*p*-chlorophenyl)-1,1,1,6,6,6-hexafluoro-2,3,4-hexatriene (7d). (*E*)-**7d**: R_f = 0.85 (hexane); yellow leaflets, mp 172—173 °C; ^{1}H NMR δ = 7.42 (4H, m, $H^{3'}$ and $H^{5'}$) and 7.60 (4H, m, $H^{2'}$ and $H^{6'}$); ^{13}C NMR δ = 115.0 (q, J = 35 Hz, C^2 and C^5), 121.7 (q, J = 275 Hz, C^1F_3 and C^6F_3), 129.1 ($C^{2'}$ and $C^{6'}$), 129.4 ($C^{1'}$), 129.5 ($C^{3'}$ and $C^{5'}$), 136.9 ($C^{4'}$), and 156.4 (m, C^3 and C^4); ^{19}F NMR δ = −59.86 (s); IR (KBr) 1588m, 1496m, 1304s, 1192vs, 1170vs, 1130vs, and 1094vs cm^{-1}; MS *m/z* (rel intensity) 412 [M^+ ($^{37}Cl_2$); 13], 410 [M^+ ($^{37}Cl^{35}Cl$); 66], 408 [M^+ ($^{35}Cl_2$); 100], 338 (12), 304 (38), and 270 (18). Anal. Calcd for $C_{18}H_8Cl_2F_6$: C, 52.84; H, 1.97%. Found: C, 52.66; H; 2.14%.

(*Z*)-**7d**: R_f = 0.7 (hexane); yellow plates, mp 99—101 °C; ^{1}H NMR δ = 7.44 (4H, m, $H^{3'}$ and $H^{5'}$) and 7.56 (4H, m, $H^{2'}$ and $H^{6'}$); ^{13}C NMR δ = 115.3 (q, J = 35 Hz, C^2 and C^5), 121.4 (q, J = 275 Hz, C^1F_3 and C^6F_3), 129.1 ($C^{2'}$ and $C^{6'}$), 129.6 ($C^{3'}$ and $C^{5'}$), 129.8 ($C^{1'}$), 136.9 ($C^{4'}$), and 157.3 (m, C^3 and C^4); ^{19}F NMR δ = −60.21 (s); IR (KBr) 2060w, 1584s, 1494s, 1322s, 1296vs, 1248s, 1168vs, and 1124vs cm^{-1}. Anal. Calcd for $C_{18}H_8Cl_2F_6$: C, 52.84; H, 1.97%. Found: C, 52.60; H; 2.13%.

2,5-Di-4-biphenylyl-1,1,1,6,6,6-hexafluoro-2,3,4-hexatriene (7e). (*E*)-**7e**: R_f = 0.55 (5% EtOAc/hexane); yellow needles, mp 242—243 °C; ^{1}H NMR δ = 7.39 (2H, m, $H^{4''}$), 7.48 (4H, m, $H^{3''}$ and $H^{5''}$), 7.64 (4H, m, $H^{2''}$ and $H^{6''}$), 7.69 (4H, m, $H^{3'}$ and $H^{5'}$), and 7.77 (4H, m, $H^{2'}$ and $H^{6'}$); ^{13}C NMR (50 °C) δ = 115.3 (q, J = 35 Hz, C^2 and C^5), 122.1 (q, J = 274 Hz, C^1F_3 and C^6F_3), 127.1 ($C^{2''}$ and $C^{6''}$), 127.7 ($C^{3'}$ and $C^{5'}$), 128.2 ($C^{4''}$), 128.5 (br, $C^{2'}$ and $C^{6'}$), 129.0 ($C^{3''}$ and $C^{5''}$), 130.3 ($C^{1'}$), 139.8 ($C^{4'}$), 143.1 ($C^{1''}$), and 155.9 (m, C^3 and C^4); ^{19}F NMR δ = −59.50 (s); IR (KBr) 1604m, 1488m, 1300s, 1182vs, and 1130vs cm^{-1}; MS *m/z* (rel intensity) 492 (M^+; 100), 454 (8), 354 (41), and 91 (56). Anal. Calcd for $C_{30}H_{18}F_6$: C, 73.17; H, 3.68%. Found: C, 73.57; H, 4.11%.

(*Z*)-**7e**: ^{1}H NMR (50 °C) δ = 7.38 (2H, m, $H^{4''}$), 7.46 (4H, m, $H^{3''}$ and $H^{5''}$), 7.62 (4H, m, $H^{2''}$ and $H^{6''}$), 7.69 (4H, m, $H^{3'}$ and $H^{5'}$), and 7.76 (4H, m, $H^{2'}$ and $H^{6'}$); ^{13}C NMR (50 °C) δ = 115.6 (q, J = 34 Hz, C^2 and C^5), 121.8 (q, J = 275 Hz, C^1F_3 and C^6F_3), 127.1 ($C^{2''}$ and $C^{6''}$), 127.8 ($C^{3'}$ and $C^{5'}$), 128.2 ($C^{4''}$), 128.7 (br, $C^{2'}$ and $C^{6'}$), 129.0 ($C^{3''}$ and $C^{5''}$), 130.7 ($C^{1'}$), 139.8 ($C^{4'}$), 143.1 ($C^{1''}$), and 156.6 (m, C^3 and C^4); ^{19}F NMR δ = −59.88 (s).

1,1,1,6,6,6-Hexafluoro-2,5-di-*p*-methoxycarbonylphenyl-2,3,4-hexatriene (7f). (*E*)-**7f**: R_f = 0.5 (10% EtOAc/hexane); yellow needles, mp 188—189 °C; ^{1}H NMR δ = 3.95 (6H, s, Me), 7.74 (4H, m, $H^{2'}$ and $H^{6'}$), and 8.09 (4H, m, $H^{3'}$ and $H^{5'}$); ^{13}C NMR δ = 52.4 (Me), 116.3 (q, J = 35 Hz, C^2 and C^5), 121.5 (q, J = 275 Hz, C^1F_3 and C^6F_3), 127.9 ($C^{2'}$ and $C^{6'}$), 130.2 ($C^{3'}$ and $C^{5'}$), 131.6 ($C^{1'}$),* 134.7 ($C^{4'}$),* 158.3 (m, C^3 and C^4), and 166.0 (CO_2); ^{19}F NMR δ = −59.72 (s); IR (KBr) 1724vs, 1288vs, 1188vs, 1170vs, and 1124vs cm^{-1}; MS *m/z* (rel intensity) 457 (M^++1; 24), 456 (M^+; 100), and 425 (52).

(*Z*)-**7f**: R_f = 0.3 (10% EtOAc/hexane); yellow needles, mp 152—154 °C; ^{1}H NMR δ = 3.96 (6H, s, Me), 7.76 (4H, m, $H^{2'}$ and $H^{6'}$), and 8.10 (4H, m, $H^{3'}$ and $H^{5'}$); ^{13}C NMR δ = 52.5 (Me), 117.0 (q, J = 35 Hz, C^2 and C^5), 121.2 (q, J = 276 Hz, C^1F_3 and C^6F_3), 128.2 ($C^{2'}$ and $C^{6'}$), 130.2 ($C^{3'}$ and $C^{5'}$), 131.6 ($C^{1'}$),* 135.2 ($C^{4'}$),* 159.1 (m, C^3 and C^4), and 166.0 (CO_2); ^{19}F NMR δ = −60.08 (s); IR (KBr) 1726vs, 1324m, 1286vs, 1170vs, and 1128vs cm^{-1}. Anal. Calcd for $C_{22}H_{14}F_6O_4$: C, 57.90; H, 3.09%. Found: C, 58.04; H, 3.19%.

2,5-Di-*p*-cyanophenyl-1,1,1,6,6,6-hexafluoro-2,3,4-hexatriene (7g). (*E*)-**7g**: R_f = 0.45 (10% EtOAc/hexane); yellow plates, mp 225—235 °C (decomp); ^{1}H NMR δ = 7.76 (4H, m, Ar) and 7.78 (4H, m, Ar); ^{13}C NMR δ = 114.2 (*C*CN), 116.5 (q, J = 40 Hz, C^2 and C^5), 117.8 (CN), 121.2 (q, J = 276 Hz, CF_3), 128.5 ($C^{2'}$ and $C^{6'}$), 132.8 ($C^{3'}$ and $C^{5'}$), 134.5 ($C^{1'}$), and 156.0 (m, C^3 and C^4); ^{19}F NMR δ = −59.82 (s); IR (KBr) 2227s, 1305vs, 1198s, 1165vs, 1143vs, 941s, 854s, and 840s cm^{-1}; MS *m/z* (rel intensity) 390 (M^+; 100), 371 (4), 352 (8), 321 (10), 301 (23), and 252 (30).

(*Z*)-**7g**: R_f = 0.35 (10% EtOAc/hexane); ^{1}H NMR δ = 7.76 (4H, m, Ar) and 7.78 (4H, m, Ar); ^{19}F NMR δ = −60.13 (s).

2,5-Dicyclohexyl-1,1,1,6,6,6-hexafluoro-2,3,4-butatriene (7h). (*E*)-**7h**: White syrup; ^{1}H NMR δ = 1.10—1.45 (5H, m), 1.60—2.05 (5H, m), and 2.39 (1H, m); ^{19}F NMR δ = −63.62 (s); ^{13}C NMR δ = 25.6, 26.0, 32.3, 39.5, 121.1 (q, J = 33 Hz, C^2 and C^5), 122.1 (q, J = 274 Hz, CF_3), and 163.2 (m, C^3 and C^4).

(*Z*)-**7h**: Colorless needles; mp 66—73 °C (partially decomp); ^{1}H NMR δ = 1.10—1.45 (5H, m), 1.60—2.05 (5H, m), and 2.41 (1H, m); ^{19}F NMR δ = −63.90 (s); ^{13}C NMR δ = 25.7, 26.0, 32.8, 39.2, 121.0 (q, J = 32 Hz, C^2 and C^5), 121.9 (q, J = 275 Hz, CF_3), and 163.1 (m, C^3 and C^4); IR (KBr) 2936vs, 2860s, 2086vw, 1298vs, 1262vs, 1168vs, 1112vs, and 986s cm^{-1}; MS *m/z* (rel intensity) 352 (M^+; 34), 284 (48), 242 (58), 189 (74), and 176 (100).

1,1,1,2,2,3,3,4,4,5,5,6,6,11,11,12,12,13,13,14,14,15,15,16,16,16-Hexafluoro-7,10-phenyl-7,8,9-hexadecatriene (7i). (*E*)-**7i**: Mp 108—110 °C; ^{1}H NMR δ = 7.41 (3H, m, *meta* and *para*) and 7.65 (2H, m, *ortho*); ^{19}F NMR δ = −81.26 (6F, t, J = 10 Hz, F^1 and F^{16}), −103.53 (4F, m, F^6 and F^{11}), −120.26 (4F, m, F^5 and F^{12}), −121.94 (4F, m, F^3 and F^{14}), −123.20 (4F, m, F^4 and F^{13}), and −126.60 (4F,

m, F^2 and F^{15}); IR (KBr) 1364s, 1278s, 1244vs, 1200vs, 1154vs, 1138vs, 1122s, and 1068s cm^{-1}; MS *m/z* (rel intensity). Anal. Calcd for $C_{28}H_{10}F_{26}$: C, 40.02; H, 1.20%. Found: C, 39.55; H, 1.07%.

(*Z*)-**7i**: Mp 32—34 °C; ^{1}H NMR δ = 7.43 (3H, m, *meta* and *para*) and 7.63 (2H, m, *ortho*); ^{19}F NMR δ = −81.39 (6F, t, J = 10 Hz, F^1 and F^{16}), −104.15 (4F, m, F^6 and F^{11}), −120.61 (4F, m, F^5 and F^{12}), −122.09 (4F, m, F^3 and F^{14}), −123.36 (4F, m, F^4 and F^{13}), and −126.74 (4F, m, F^2 and F^{15}); IR (KBr) 2052w, 1364s, 1240vs, 1206vs, 1144vs, 1122s, and 1072s cm^{-1}. Anal. Calcd for $C_{28}H_{10}F_{26}$: C, 40.02; H, 1.20%. Found: C, 39.68; H, 1.26%.

Lithiation of 2a Followed by Quenching with Methyl Benzoylformate. To a stirred solution of **2a** (3.299 g, 10 mmol) in dry THF (20 ml) was added a hexane solution of *n*-BuLi (1.63 M; 7.36 ml, 12 mmol) at −78 °C. After the mixture was stirred for 30 min at the temperature, methyl benzoylformate (1.71 ml, 12 mmol) was added. After 1 h, the reaction was quenched by adding sat. NH_4Cl solution (10 ml) and water (20 ml), and the mixture was extracted with ether (3×30 ml). The ethereal extract was washed with water and brine, dried over $MgSO_4$, and concentrated. The residue was chromatographed on silica gel to give 3.314 g of methyl 3-bromo-5,5,5-trifluoro-2-hydroxy-2,4-diphenyl-3-pentenoate (**13**) as colorless crystals: R_f 0.35 (20% EtOAc/hexane); mp 136—137 °C (ether/hexane); ^{1}H NMR δ = 3.85 (3H, s, OMe), 4.41 (1H, s, OH), 7.24 (2H, m, Ar), 7.3—7.45 (6H, m, Ar), and 7.58 (2H, m, Ar); ^{13}C NMR δ = 53.7 (OMe), 83.0 (C^2), 121.5 (q, J = 276 Hz, C^5), 126.5 (Ar), 128.0 (Ar), 128.5 (Ar), 128.6 (Ar), 128.7 (Ar), 128.7 (Ar), 135.3 (q, J = 33 Hz, C^4), 137.8 (q, J = 2 Hz, *ipso* C of 4-Ph), 138.6 (q, J = 4 Hz, C^3), 140.9 (*ipso* C of 2-Ph), and 172.5 (CO_2); ^{19}F NMR δ = −57.07 (s); IR (KBr) 3488vs, 1746vs, 1736vs, 1294vs, 1258vs, 1206vs, 1174vs, 1122vs, and 700vs cm^{-1}; MS *m/z* (rel intensity) 357 [M^+ (^{81}Br)−CO_2Me; 81], 355 [M^+ (^{81}Br)−CO_2Me; 81], 337 (34), 335 (33), 317 (36), 279 (38), 277 (41), and 105 (100). Anal. Calcd for $C_{18}H_{14}BrF_3O_3$; C, 52.07; H, 3.40%. Found: C, 52.10; H, 3.35%.

X-Ray Analysis. A colorless prismatic crystal of **13** having approximate dimensions of 0.45×0.45×0.25 mm was mounted on a glass fiber. All measurements were made on a Rigaku AFC5R diffractometer with graphite monochromated Cu $K\alpha$ radiation and a 12 kW rotating anode generator. Cell constants and an orientation matrix for data collection, obtained from a least-squares refinement using the setting angles of 25 carefully centered reflections in the range $50.45 < 2\theta < 52.00°$, corresponded to a triclinic cell with dimensions: a = 11.938(3), b = 14.487(2), c = 11.217(3) Å, α = 109.66(1)°, β = 105.26(2)°, γ = 85.02(2)°, and V = 1761.8(7) Å^3. For Z = 2 and FW = 830.41, the calculated density is 1.565 g cm^{-3}. Based on packing considerations, a statistical analysis of the intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $P\bar{1}$ (#2). The data were collected at a temperature of 25 ± 1 °C using the ω scan technique to a maximum 2θ value of 122.9°. Omega scans of several intense reflections, made prior to data collection, had an average width at half-height of 0.18° with a taking-off angle of 6.0° min^{-1} (in omega). The weak reflections [$I < 10.0\sigma(I)$] were rescanned (maximum of 2 rescans) and the counts were accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. The ratio of the peak counting time to the background counting time was 2 : 1. The diameter of the incident beam collimator was 0.5 mm and the crystal to detector distance was 25.8 cm. Of the collected 5757 reflections, 5456 were unique (R_{int} = 0.027). An empirical correction for the absorption was made based on azimuthal (Ψ) scans of three reflections.[23] The structure was solved by the direct method using the MITHRIL program.[24] The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined isotropically. Calculations were carried out on a VAX station 3200 computer with TEXSAN programs[25] which used the atomic scattering factors taken from "International Tables for X-Ray Crystallography".[26] The final cycle of full-matrix least-squares refinement yields R = 0.046, R_w = 0.055 and goodness-of-fit = 1.93 for 3995 observed reflections [$I > 3.00\sigma(I)$] and 451 variable parameters. The final atomic parameters are deposited as Document No. 72021 at the Office of the Editor of Bull. Chem. Soc. Jpn. The ORTEP drawing of **13** was shown in Fig. 1.

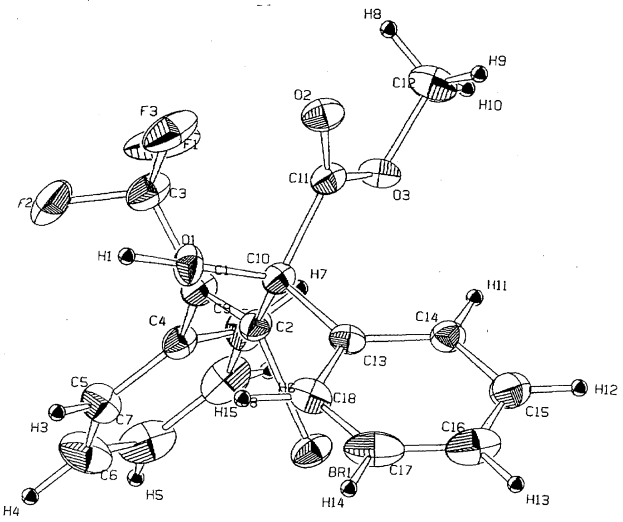


Fig. 1. ORTEP drawig of **13**.

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