

Generation of Cycloheptyne during the Solvolysis of Cyclohexylidenemethyliodonium Salt in the Presence of Base

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Solvolysis of 4-methylcyclohexylidenemethyl(phenyl)iodonium tetrafluoroborate (**1**) and its *R* isomer (69% ee) was carried out in 2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP) in the presence of bases such as acetate, pyridine, triethylamine, and alkoxide. The reaction is much faster in TFE than in HFP. Products in TFE include solely un-rearranged (racemized) enol ether **2** together with iodobenzene, while the main product in HFP is ring-expanded (partially racemized) 1-alkoxycycloheptene **3**. Results show that **2** is formed via α -elimination with alkylidenecarbene as an intermediate, while the reaction in HFP to give **3** involves a cycloheptyne intermediate that is mostly derived from an intermediate cyclohept-1-enyl cation via the E1-type pathway.

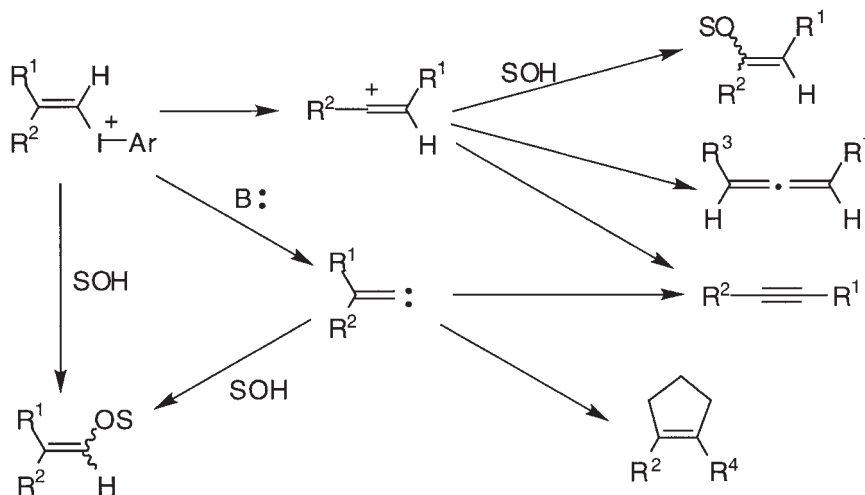
Solvolysis of primary alkenyl iodonium salts takes place via the rearrangement with β -alkyl participation as well as via the S_N2 -type substitutions with σ^* and π^* attacks to avoid the unstable primary vinyl cation (Scheme 1).^{1–10} The intermediate secondary vinyl cations formed by the 1,2-alkyl shift provide both substitution and elimination products.^{2,8} In the presence of an added base, the α -elimination predominates to give an alkylidenecarbene which leads to intramolecular or intermolecular insertion depending on the reaction conditions.^{2–4,6,11–15} The intramolecular insertion involves 1,2-shift of hydrogen, phenyl, or alkyl group to afford an alkyne.^{2–4,6,11–16} This type of rearrangement of cycloalkylidenecarbenes has been used as one of the methods of generation of cycloalkynes.¹⁷

The chirality probe approach using an optically active 4-methylcyclohexylidenemethyl(phenyl)iodonium tetrafluoroborate (**1**) showed that a symmetric primary vinyl cation is not involved during the reaction (Scheme 2).^{4,10} In this case, the cycloheptenyl cation **I**₁ formed by rearrangement leads only to a substitution product in nucleophilic alcoholic solvents. In-

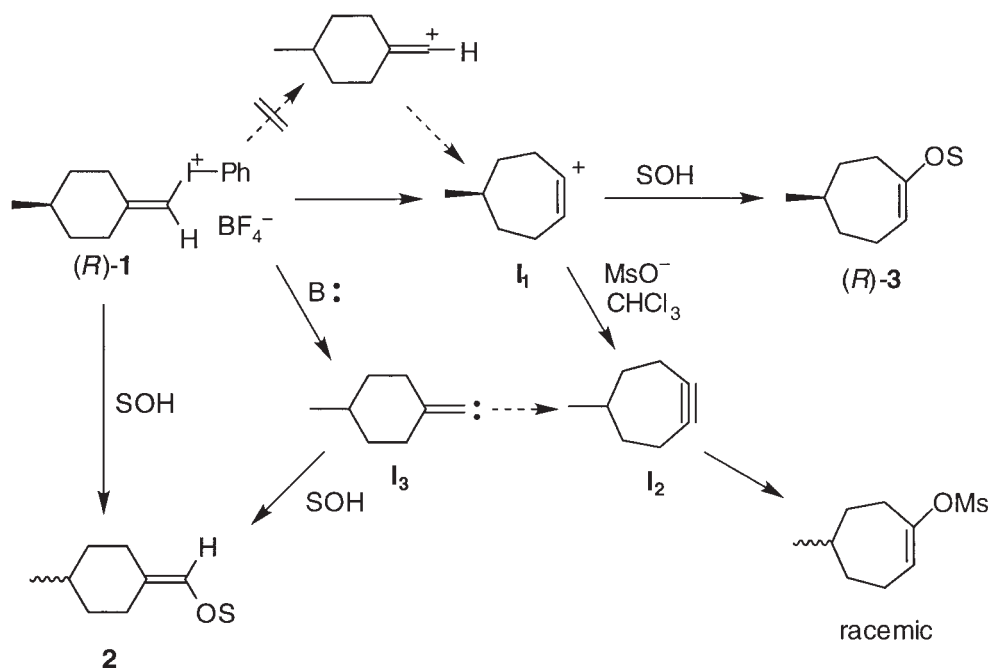
termediary formation of cycloheptyne **I**₂ was not usually observed under the solvolysis conditions, but one set of delicately balanced basic/nucleophilic conditions involving methanesulfonate in chloroform led to the cycloheptyne intermediate (**I**₂).⁵ There is some hope that the basic reactivity of the reaction medium can be controlled to induce the E1-type elimination (rather than nucleophilic S_N1 -type trapping) of the intermediate cycloheptenyl cation **I**₁. The basicity/nucleophilicity must be mild enough to allow rearrangement to **I**₁, but not so strong as to allow the α -elimination or the S_N2 -type substitutions of the substrate **1** itself. The present paper describes successful manipulations of solvolysis conditions to obtain cycloheptyne **I**₂ from cyclohexylidenemethyliodonium salt **1**. There is also some possibility of access to cycloheptyne **I**₂ from **1** via base-induced α -elimination–carbene rearrangement.

Results

Reactions of **1** with bases were carried out at 55–60 °C in poorly nucleophilic solvolytic media, i.e., fluoro alcohols,



Scheme 1.



Scheme 2.

Table 1. Reactions of **1** in Fluoro Alcohols Containing Base^{a)}

Entry	Solvent	Base ^{b)}	Time/h	Yield/%				
				2 ^{c)}	3 ^{c)}	4	PhI	Other
1 ^{d)}	TFE	none	9	0	75 (69) ^{e)}	0	84	—
2	TFE	CF ₃ CO ₂ Na	4	19 (0)	58 (66) ^{e)}	0	90	—
3	TFE	CH ₃ CO ₂ Na	1	99	0	0	100	—
4	TFE	pyridine	1	93	0	0	100	—
5	TFE	Et ₃ N	1	84 (0)	0	0	68	—
6	TFE	RONa	1	99	0	0	92	—
7 ^{f)}	TFE	RONa	1	76	0	0	82	<1 (5)
8 ^{d)}	HFP	none	20	0	41 (69) ^{e)}	0	60	—
9	HFP	CH ₃ CO ₂ Na	20	4	30	7	66	2 ^{g)}
10	HFP	Et ₃ N	8	6	43	20	74	—
11	HFP	RONa (0.01)	23	7	38	15	67	—
12	HFP	RONa	20	7 (0)	43 (13)	15	70	—
13	HFP	RONa (0.2)	10	6	36	18	65	—
14 ^{f)}	HFP	RONa	22	5	28	20	62	<1 (5)
15 ^{h)}	HFP	RONa	20	6 (0)	26 (16)	<1	65	25 (6)

a) The initial concentration of **1** was 5×10^{-3} mol dm⁻³, and reactions were carried out at 55–60 °C. b) The concentration was 0.1 mol dm⁻³ unless noted otherwise in parentheses, where the concentration are given in mol dm⁻³. c) The values in parentheses are the enantiomeric excess (ee) of the product obtained from 69% ee of (*R*)-**1**. The *R* isomer of **3** is in excess. d) The data has been reported previously.⁴ e) 4-Methylcycloheptanone. f) Cyclohexene (0.1 mol dm⁻³) was added. g) Yield of 5-methylcyclohept-1-enyl acetate. h) α -Pyrone (0.1 mol dm⁻³) was added.

2,2,2-trifluoroethanol (TFE) and 1,1,1,3,3,3-hexafluoropropan-2-ol (HFP), and the mixed solvents. Products include both unrearranged and rearranged enol derivatives, **2** and **3**, and 5-methylcycloheptene (**4**) as well as iodobenzene (Eq. 1). For some runs, optically active (*R*)-**1** (69% ee) was used as the substrate. Effects of added cyclohexene and α -pyrone were also examined for possible intermediates (Eqs. 2 and 3). Product yields were determined by gas chromatography and are summarized in Tables 1 and 2. Trapping experiments were further carried out on a preparative scale for cycloheptyne **I**₂ with tet-

raphenylcyclopentadienone (TPCD) (Eq. 4); the results are given in Table 3.

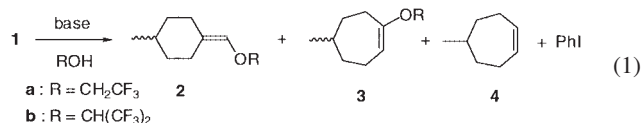


Table 2. Reactions of **1** in Mixed Alcohols Containing Sodium Alkoxide^{a)}

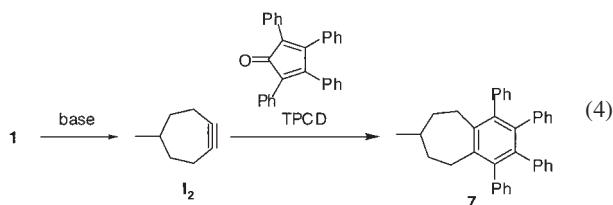
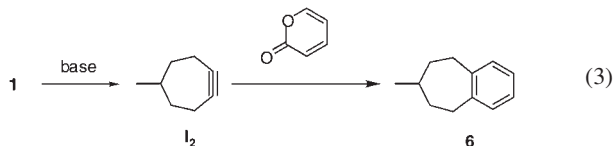
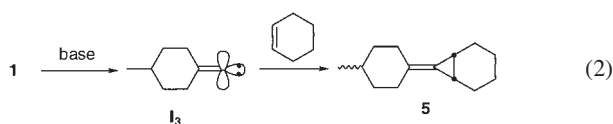
Entry	TFE/HFP	Time/h	Yield/%					PhI
			2a	3a	2b	3b	4	
6	100/0	1	99	— ^{b)}	0	0	0	92
16	70/30	1	94	— ^{b)}	0	0	6	97
17	50/50	3	76	— ^{b)}	3	4	16	100
18	30/70	7	34	— ^{b)}	<1	16	28	72
19	10/90	20	9	— ^{b)}	6	36	20	93
12	0/100	20	0	— ^{b)}	7	43	15	70

a) [**1**] = 5×10^{-3} mol dm⁻³, [alkoxide] = 0.1 mol dm⁻³, and at 55–60 °C. b) **3a** is not observed as an appreciable product.

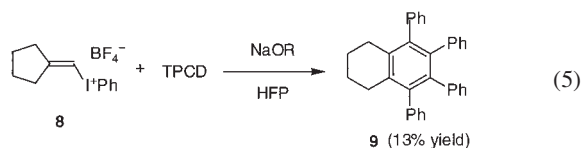
Table 3. Isolated Yields of **7** in the Reaction of **1** in the Presence of TPCD^{a)}

Entry	Solvent	Base	[Base]/mol dm ⁻³	Yield of 7 /%
20	CHCl ₃ ^{b)}	Et ₃ N	0.05	8
21	TFE/CHCl ₃ (9/1) ^{c)}	Et ₃ N	0.1	2
22	TFE/CHCl ₃ (9/1) ^{c)}	RONa	0.1	3
23	HFP	Et ₃ N	0.02	58
24	HFP	Et ₃ N	0.1	62
25	HFP	RONa	0.1	67
26	HFP/TFE (1/1)	RONa	0.1	26
27	HFP/TFE (9/1)	RONa	0.1	45
28	HFP/CHCl ₃ (1/9)	RONa	0.1	46

a) [**1**] = 1×10^{-2} mol dm⁻³, [TPCD] = 2×10^{-2} mol dm⁻³, and at 55–60 °C. b) At room temperature. c) Chloroform (10% (v/v)) was added to dissolve TPCD in solution.



The trapping experiment with TPCD was also applied to the reaction of cyclopentylidenemethyl(phenyl)iodonium tetrafluoroborate (**8**) in HFP in the presence of alkoxide; adduct **9** was isolated in 13% yield (Eq. 5).

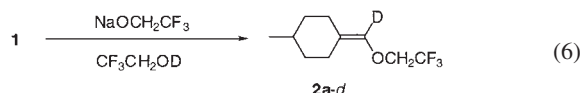


Discussion

Solvolyses of **1** in un-buffered TFE and HFP gave solely the rearranged ring-expanded product **3**, keeping the original opti-

cal purity when the optically active substrate was used (Entries 1 and 8). These and other observations show that the symmetric primary vinyl cation intermediate is avoided because of its instability.^{4,10} In contrast, reactions of **1** with base gave different results between the two fluoro solvents, TFE and HFP. Only the un-rearranged product **2a** was obtained in TFE, while the rearranged ones were the major products in HFP.

Reactions in TFE. The un-rearranged substitution product **2a** was obtained with accompanying iodobenzene in TFE in the presence of a range of bases from acetate to alkoxide (Entries 3–6), and it lost completely the optical purity of (*R*)-**1** (Entry 5). The reaction of **1** in a deuterium solvent TFE-*O*-*d* containing sodium alkoxide afforded the α -deuterated product **2a-d** (Eq. 6).



These results are consistent with the intermediary formation of alkylidenecarbene **I**₃ via α -elimination. However, the attempted trapping of **I**₃ with cyclohexene only gave a trace amount of the cyclopropylidene adduct **5** (Eq. 2) (Entry 7). Alcohol TFE must more effectively react with carbene **I**₃ to give the OH insertion product.

A poorly basic trifluoroacetate ($\text{p}K_a = 0.23$ in aqueous solution) gave 19% of **2a** and 58% of **3** (only the hydrolysis product, 4-methylcycloheptanone (**3C**), was isolated here) in TFE; the former was completely racemized while the latter kept mostly the original ee of (*R*)-**1** (Entry 2). This result shows that the rearrangement still occurs via participation which is followed by trapping of the resulting chiral cation **I**₁ to give

optically active **3**, while the competing α -elimination gives the un-rearranged and racemized **2a**.

Although the ring expansion of cycloalkylenecarbene has been used as one of the general routes to cycloalkynes,¹⁷ such rearrangement does not seem to take place in TFE. So, the reactions of **1** with bases were examined in still less reactive alcohol HFP.

Reactions in HFP. The base reaction in HFP is much slower than that in TFE, and preferentially gives the rearranged products, **3b** and **4**, together with some un-rearranged enol ether **2b** (Entries 9–13). The products obtained from (*R*)-**1** of 69% ee with alkoxide as a base include extensively racemized but still optically active **3b** (13% ee) and completely racemized un-rearranged product **2b** (Entry 12). The racemization of **2b** must occur via the intermediate carbene **I**₃, while that of **3b** must be due to formation of cycloheptyne **I**₂. Formation of **I**₂ is in fact confirmed by trapping experiments as described below. Nonetheless, the remaining optical purity of **3b** cannot be ascribed to the cycloheptyne route. The rearranged chiral cation **I**₁ is a most likely intermediate to afford the optically active **3b**. Thus, cycloheptyne **I**₂ can in principle be derived from cation **I**₁ as well as from carbene **I**₃. An attempted trapping with cyclohexene of **I**₃ was not successful in HFP (Entry 14), and the carbene route to **I**₂ could not be a major one if it operated as a minor route leading to **2b**. If cycloheptyne **I**₂ were formed from carbene **I**₃ in HFP, cyclohexene could have trapped **I**₃; **I**₃ was trapped by cyclohexene in chloroform before the rearrangement to **I**₂ occurred.^{4,5}

The reaction of optically active (*R*)-**1** was also examined in the presence of α -pyrone as a trapping agent (Entry 15). Although the trapping was not complete (25% adduct **6**, Eq. 3), the ee of the remaining **3b** increased to 16% (26% yield). This modest increase in ee corresponds to the increased fraction of optically active **3b**, which is formed independently of the cycloheptyne intermediate **I**₂, i.e., via the direct reaction with **I**₁.

The reaction of **1** with alkoxide was monitored by ¹H NMR in a deuterium solvent, HFP-*O-d*/CDCl₃ (1/10, v/v). Progress of the reaction can be monitored by formation of iodobenzene as well as by the substrate decrease (Fig. 1). Loss of the vinylic proton (δ = 6.49 ppm) of **1** was somewhat faster than the decrease in the other signals of **1**. That is, a deuterium is incorporated at the vinylic position to give deuterated **1-d**. The hydrogen–deuterium isotope exchange takes place during the reaction. This implies that iodonium ylide **I**₄ is formed reversibly as a precursor for carbene **I**₃ and that the rate-determining step for the α -elimination is departure of iodobenzene (Scheme 3). This is rather unexpected in view of the high leaving ability of the iodonio group,^{18–20} but it can be rationalized by reprotonation with acidic HFP (pK_a = 9.3).²¹ The reversibility of the deprotonation retards the formation of alkylidenecarbene, and makes formation of the rearranged cation **I**₁ via participation of a more favorable reaction.

Finally, unexpected formation of a considerable amount of the reduction product **4** was observed in basic HFP, accompanied with formation of **3b** (Table 1). It is noted that **4** was not detected in the reactions in neutral HFP or TFE where the corresponding enol ether **3** is formed directly from cation **I**₁ but not via **I**₂. This product **4** may be derived actually from cycloheptyne **I**₂ via reduction. Very suggestive results have been

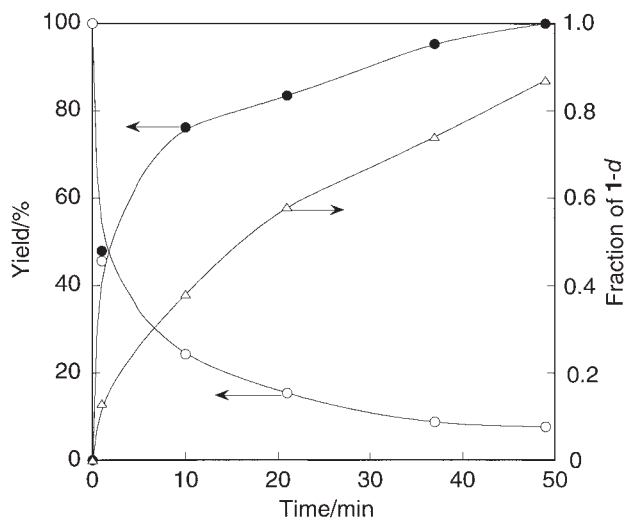
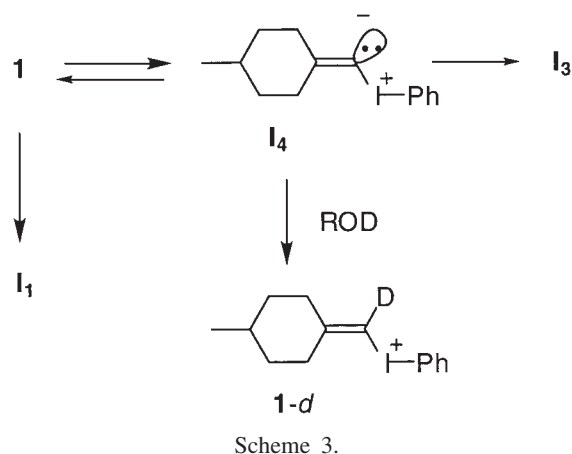
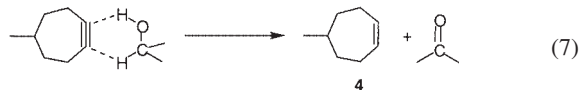


Fig. 1. Reaction of **1** (0.007 mol dm⁻³) in CDCl₃/HFP-*O-d* (10/1 v/v) containing sodium alkoxide (0.02 mol dm⁻³) at 297 K, monitored by ¹H NMR: **1** + **1-d** (○), PhI (●), and **1-d**/(**1** + **1-d**) (△).



reported of reduction of a seven-membered cycloalkyne with methanol.²² A higher yield of **4** was obtained in a mixed TFE–HFP solvent at the ratio 30/70 or 10/90 than in pure HFP (Entries 18 and 19), and TFE is a better reductant. An alternative possibility of hydride transfer from hexafluoro-2-propoxide to cation **I**₁ is less likely. If this were the case, a better yield of **4** would not be found in the mixed solvent. A probable mechanism is the concerted one as proposed for the methanol reduction²² and depicted in Eq. 7.



Formation of Cycloalkyne. Formation of cycloheptyne **I**₂ was examined by trapping with a very efficient trapping agent TPCD (Eq. 4 and Table 3). Higher yields of adduct **7** were obtained in HFP, and the highest yield was achieved with alkoxide in HFP (Entry 25). The attempted TPCD trapping in TFE gave very poor results (Entries 21 and 22) as expected from the product studies. That in chloroform gave a small amount (8%) of the TPCD adduct **7** (Entry 20). Under these conditions, al-

kyliidenecarbene **I**₃ is effectively generated to give **5** in the presence of cyclohexene.^{4,5} Partial rearrangement of carbene **I**₃ to cycloheptyne **I**₂ seems to occur in basic chloroform, but it is obviously not efficient. When 10% (v/v) of HFP was added to the chloroform reaction, the yield of adduct **7** was considerably improved (Entry 28). The cationic elimination route to **I**₂ must show up owing to the retardation of the reaction with base by acidic HFP.

Generation of a smaller ring alkyne, cyclohexyne, via ring expansion of cyclopentylidenemethyliodonium salt **8** was examined in the presence of TPCD (Eq. 5) under the best conditions for cycloheptyne formation. However, the isolated yield of the adduct **9** was only 13%. The rearrangement of **8** to cyclohex-1-enyl cation must occur less readily than that of **1** to **I**₁ owing to the higher strain of the smaller ring vinyl cation. So, the E1-type route to cyclohexyne from **8** should be less efficient. Although the rearrangement of cyclopentylidenecarbene is known as one of the well-studied routes for generation of cyclohexyne,^{17,23} the carbene route to cycloalkyne via α -elimination is again not effective owing to inefficient 1,2-alkyl shift of alkylidenecarbene.²⁴ It is noteworthy that β -elimination of cyclohex-1-enyliodonium salt with a mild base affords cyclohexyne in an excellent yield.²⁵

Reactions in Mixed Solvents. Rates of the reaction in TFE and HFP are contrastingly different. Bases accelerate very much the reaction in TFE, while they affect only slightly the rate of reaction in HFP, as the reaction times given in Table 1 imply. In the mixed solvents of TFE and HFP, the rate of reaction in the presence of alkoxide decreases with increasing fraction of HFP as is reflected in the reaction times of 1–20 h (Table 2). The proportion of the rearranged product **3** to the un-rearranged product **2** also increases with fraction of HFP. Acetate ($pK_a = 4.76$ in aqueous solution) works as a perfect base for α -elimination in TFE, while alkoxide of HFP ($pK_a = 9.3$) does not. The effective solvation by the acidic solvent may strongly reduce the basicity in HFP, but a more important factor to retard α -elimination in HFP would be the acidity itself of the solvent. Protonation of the intermediate ylide **I**₄ must be greatly accelerated in HFP, and this makes the deprotonation reversible as observed in HFP-CDCl₃. Thus, the overall rate of reaction in HFP is diminished to make the β -alkyl participation leading to the rearranged cation **I**₁ the main reaction. The fraction of rearrangement increases sharply above 50% content of HFP. It is noteworthy that TFE adduct **3a** was not clearly observed even in the presence of a large amount of TFE in a mixed solvent when a considerable formation of **3b** was apparent. Although TFE ($pK_a = 12.4$) is obviously more basic and nucleophilic than HFP, predominant alkoxide present in a mixed solvent should be that of HFP, and it must also be the more reactive nucleophile toward **I**₁ or **I**₂.

Conclusion

In HFP solution containing alkoxide, cycloheptyne **I**₂ is effectively generated from cyclohexylidenemethyliodonium salt **1** mainly via cycloheptynyl cation **I**₁, if the route via carbene **I**₃ is not completely excluded. Poor nucleophilicity and mild basicity of the HFP alkoxide and high acidity of the HFP solvent retard generation of alkylidenecarbene **I**₃ by way of efficient reprotonation of intermediate iodonium ylide **I**₄. This allows

β -alkyl participation leading to cation **I**₁ which now can be deprotonated with the mild base to give **I**₂. The 1,2-alkyl shift within alkylidenecarbene is not efficient.

Experimental

Proton and ¹³C NMR spectra were measured on a JEOL ECA-600 spectrometer; the samples were solutions in CDCl₃. ¹H NMR spectra were recorded using the residual CHCl₃ as an internal reference (7.24 ppm) and ¹³C NMR using CDCl₃ as an internal reference (77.00 ppm). Melting points were measured on a Yanaco micro-melting-point apparatus and are uncorrected. Mass spectrometers JEOL JMS-AX505HA, JEOL JMS-T100LC, and JEOL automass system II were used for MS and GC-MS. GC was conducted on a gas chromatograph with DB-1 (i.d. 0.25 mm $\times$ 30 m) or Chirasil-DEX-CB (i.d. 0.25 mm $\times$ 25 m). 4-Methylcyclohexylidenemethyl(phenyl)iodonium tetrafluoroborate (**1**) and the optically active (*R*)-**1** were prepared in the same way as before.⁴ Tetraphenylcyclopentadienone (TCI), α -pyrone (Aldrich), and cyclohexene (TCI) were used without further purification. HFP and TFE were distilled over molecular sieves 4A just before use for the reaction.

Cyclopentylidenemethyl(phenyl)iodonium Tetrafluoroborate (8). To a solution of trimethylsilylmethylenecyclopentane (0.86 g, 5.6 mmol), and PhIO (2.46 g, 11 mmol) in dichloromethane (20 mL) was added Et₂O $\cdot$ BF₃ (1.45 mL, 11 mmol) dropwise at 0 °C. After stirring for 80 min at 0 °C, a saturated aqueous sodium tetrafluoroborate solution was added to the reaction mixture. The mixture was stirred vigorously for 30 min, and extracted with dichloromethane. The organic layer was concentrated in vacuo to give an oil. Crystallization of the crude mixture from dichloromethane–ether–hexane gave the title compound (0.12 g, 0.3 mmol, 6%) as a white solid: mp 130–131 °C; ¹H NMR (600 MHz, CDCl₃) δ 7.91 (2H, d, *J* = 7.9 Hz), 7.62 (1H, t, *J* = 7.9 Hz), 7.48 (2H, t, *J* = 7.9 Hz), 6.70 (1H, s), 2.71 (2H, t, *J* = 6.9 Hz), 2.68 (2H, t, *J* = 6.9 Hz), 1.93 (2H, quint, *J* = 6.9 Hz), 1.85 (2H, quint, *J* = 6.9 Hz); ¹³C NMR (CDCl₃) δ 171.64, 134.62, 132.49, 132.46, 109.68, 88.26, 37.77, 36.12, 27.94, 25.74; HRMS (ESI) Calcd for C₁₂H₁₄I (M – BF₄) 285.0140, Found 285.0177.

Standard Procedure for Reaction of 1 in Fluoro Alcohol. A sodium alkoxide solution was prepared by dissolving a piece of sodium metal in the alcohol. The tetrafluoroborate salt of **1** (2 mg) was dissolved in 1 mL of fluoro alcohol containing a required amount of a base and kept in a sealed tube at 55–60 °C for a specified time. To the mixture were added water and 5 μ mol of tetradecane as an ether solution. The products were extracted with ether and washed with water. The yields of the products were determined by gas chromatography with tetradecane as an internal standard. The GC retention times of **4**, **2a**, **2b**, **3b**, PhI, and **3C** were 2.8, 7.5, 6.3, 6.9, 6.4, and 7.9 min, respectively, at the column (DB-1) temperature of 64 °C. The enantiomeric excess (ee) of the product from (*R*)-**1** of 69% ee was determined with a chiral GC column (DEX-CB). Preparation of the authentic samples of **2a**, (*R*)-**3C**, and 5-methylcyclohept-1-enyl acetate were described in the previous report,⁴ and they were used for the identification of these products. Selected data for **2b**: ¹H NMR (CDCl₃) δ 5.90 (1H, s), 4.15 (1H, sept, *J* = 5.8 Hz), 2.77 (1H, m), 2.02 (1H, m), 1.88 (3H, td, *J* = 13.1, 4.1 Hz), 1.75–1.63 (4H, m), 1.51–1.46 (2H, m), 0.88 (3H, d, *J* = 6.2 Hz); MS (EI) *m/z* (relative intensity, %) 276 (M⁺, 17), 220 (11), 93 (100); HRMS (EI) Calcd for C₁₁H₁₄F₆O (M) 276.0949, Found 276.0969; GC (DB-1, 64

°C) 6.3 min, Chiral GC (DEX-CB, 80 °C) 14.7 min and 16.6 min. Selected data for **3b**: $^1\text{H NMR}$ (CDCl_3) δ 5.10 (1H, m), 4.57 (1H, sept, $J = 5.8$ Hz), 2.38 (1H, m), 2.26 (1H, m), 2.12 (1H, m), 1.97 (1H, m), 1.76–1.60 (3H, m), 1.14 (1H, qd, $J = 11.7$, 2.1 Hz), 1.04 (1H, qd, $J = 11.7$, 1.4 Hz), 0.90 (3H, d, $J = 6.9$ Hz); MS (EI) m/z (relative intensity, %) 276 (M^+ , 2), 233 (20), 220 (13), 93 (33), 68 (100); HRMS (EI) Calcd for $\text{C}_{11}\text{H}_{14}\text{F}_6\text{O}$ (M) 276.0949, Found 276.0907; GC (DB-1, 64 °C) 6.9 min, Chiral GC (DEX-CB, 80 °C), 14.4 min (*R*-isomer) and 15.3 min (*S*-isomer). The absolute stereochemistry of **3b** was confirmed by the conversion to **3C**⁴ under acidic aqueous conditions. 5-Methylcycloheptene (**4**) has identical spectroscopic properties to those reported in the literature.²⁶ MS (EI) m/z (relative intensity, %) 110 (M^+ , 20), 95 (50), 82 (83), 67 (100); the reported value 110 (M^+ , 40), 95 (60), 82 (90), 67 (100).

Reaction in the Presence of α -Pyrone. The standard procedure for the reaction was applied to **1** (2 mg) in the presence of α -pyrone (8 μL) in HFP (1 mL) containing sodium alkoxide (0.1 mol dm^{-3}). The mixture was analyzed by GC (DB-1) after ether extraction. The retention time of the benzo adduct **6** was 16.2 min, when the column temperature was maintained at 64 °C during the initial 10 min and then raised up at the rate of 10 °C min^{-1} . Selected data for **6**: $^1\text{H NMR}$ (CDCl_3) δ 7.07 (s, 4H), 2.81 (td, $J = 14.4$, 1.4 Hz, 2H), 2.72 (ddd, $J = 14.4$, 7.6, 1.4 Hz, 2H), 1.90–1.85 (m, 3H), 1.80–1.74 (m, 2H), 0.91 (d, $J = 6.9$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl_3) δ 143.19, 128.74, 125.97, 36.27, 36.19, 35.04, 23.71; MS (EI) m/z (relative intensity, %) 160 (M^+ , 62), 104 (100); HRMS (EI) Calcd for $\text{C}_{12}\text{H}_{16}$ (M) 160.1252, Found 160.1260.

Reaction in the Presence of Cyclohexene. The reaction of **1** in fluoro alcohol containing base was carried out in the presence of cyclohexene (0.1 mol dm^{-3}), and the products were analyzed by GC. The authentic sample of cyclopropylidene product **5** was prepared according to the method reported previously.^{4,5}

Reaction in Fluoro Alcohol-*O-d*. The reaction of **1** was carried out in TFE-*O-d* or HFP-*O-d* containing sodium alkoxide. The deuterium incorporation of **2a** at the olefinic position was determined as 95% D by comparison of the peak areas due to the olefinic proton at $\delta = 5.80$ and the methylene proton at $\delta = 2.76$. In GC-MS analysis, **2a** has peaks at $m/z = 209$ and 208 in 64 and 6% relative intensities in comparison with 8 and 61% for those of the normal product. The HFP product **2b** has peaks at $m/z = 277$ and 276 in 33 and 4% relative intensities in comparison with 1 and 17% for those of the normal product. The rearranged product **3b** has a very small molecular peak: the normal product **3b** has a peak at $m/z = 276$ only in a 2% intensity while that obtained in HFP-*O-d* has a peak at $m/z = 277$ in a 2% intensity.

A Typical Procedure for Reaction of **1 in the Presence of TPCD.** A solution containing **1** (100 mg, 2.5×10^{-4} mol), TPCD (192 mg, 5×10^{-4} mol), and triethylamine (0.35 mL, 2.5×10^{-3} mol) in HFP (25 mL) was refluxed till the TLC spot of **1** disappeared, and then the solvent was removed by distillation. The residue was purified by chromatography (SiO_2 , eluent: 40% chloroform in hexane) to give the adduct **7** (72 mg, 62% yield), which had identical spectroscopic properties to those reported previously.⁵ A similar procedure was also applied to **8** to give **9**. **9**: mp 264–266 °C; $^1\text{H NMR}$ (CDCl_3) δ 7.16–7.13 (m, 4H), 7.08–7.06 (m, 6H), 6.80–6.74 (m, 10H), 2.52 (m, 4H), 1.70 (m, 4H); $^{13}\text{C NMR}$ (CDCl_3) δ 140.78, 140.62, 140.54, 138.44, 134.55, 131.26, 130.28, 127.45, 126.38, 125.89, 124.97, 29.66, 23.11; MS (EI) m/z (relative intensity, %) 436 (M^+ , 100); HRMS

(EI) Calcd for $\text{C}_{34}\text{H}_{26}$ (M) 436.2191, Found 436.2189.

Reaction of **1 in Chloroform Containing $(\text{CF}_3)_2\text{CHOD}$ and $(\text{CF}_3)_2\text{CHONa}$.** To a solution of **1** (8×10^{-3} mol dm^{-3}) in CDCl_3 (0.5 mL) was added the $(\text{CF}_3)_2\text{CHOD}$ solution (0.05 mL) containing sodium alkoxide (0.2 mol dm^{-3}), which was prepared by adding sodium to the alcohol. The reaction was monitored at 297 K by $^1\text{H NMR}$. On addition of alkoxide, an immediate shift of the NMR signals of **1** was apparent: before the addition of alkoxide; δ 7.90 (2H, d), 7.61 (1H, t), 7.47 (2H, t), 6.65 (1H, s), 2.75–2.66 (2H, m), 2.47–2.34 (2H, m), 1.90 (1H, m), 1.84 (m, 1H), 1.62 (1H, m), 1.15–1.00 (2H, m), 0.91 (3H, d); after the addition, δ 7.80 (2H, d), 7.70 (1H, t), 7.51 (2H, t), 6.49 (1H, s), 2.70–2.60 (2H, m), 2.48–2.36 (2H, m), 1.94 (1H, m), 1.87 (m, 1H), 1.65 (1H, m), 1.15–1.00 (2H, m), 0.93 (3H, d). The peak area at 6.49 ppm due to the vinylic proton of **1** decreased more rapidly than the other peak areas due to **1**. The yield of iodobenzene was determined by the comparison of the peak area due to the phenyl group (7.09 ppm) and the residual CHCl_3 as an internal standard. The total yield of **1** and deuterated **1** (**1-d**) was determined by the peak area at 7.80 ppm, and the protium content at the vinylic position of **1** was determined by the peak area at 6.49 ppm.

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