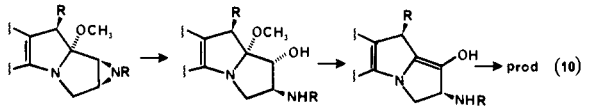
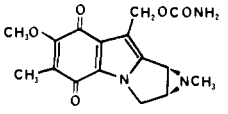
Stevens and co-workers[12] have proposed the mechanism of eq 10. Here a stereospecific trans aziridine ring opening occurs as



(10)

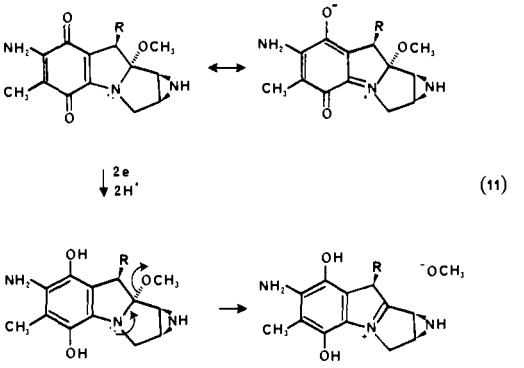
the first step and the elimination follows initially involving the hydrogen at C1. This mechanism was invoked specifically to explain deuterium incorporation at C1 during mitomycin C solvolysis in deuterated acetic acid, but it obviously also accounts for the lack of stereospecificity in the aziridine hydrolysis. We feel that this mechanism is not accommodated by the present results for the hydrolysis reaction, and our NMR experiments in fact establish that during D_2O hydrolysis no exchange occurs. Cheng and Remers[30] have prepared the mitosene MA with an intact aziridine ring from *N*-methylmitomycin A and find it hydrolyzes also to give a 3:1 cis:trans ratio very similar to that found with the mitomycin itself. As noted by these authors, the Stevens



MA

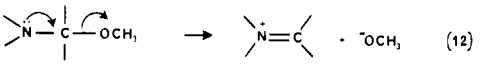
mechanism is not possible starting from MA. A unimolecular reaction of this mitosene, however, does explain the results.

Reductive Activation. A parallelism does exist between the acid activation and the reductive activation.[11] The aziridinomitosene MA was prepared by the hydrogenation of the mitomycin in ethyl acetate followed after a short reaction time by reoxidation. This is strong evidence that elimination precedes the aziridine ring opening under reductive conditions as well, with the important differences that under the conditions employed in the synthesis the aziridine solvolysis of the eliminated product is slower than the initial elimination. In terms of the mechanism of the acid hydrolysis the "activation" afforded by reduction can be quite easily understood. In the oxidized mitomycin the nitrogen lone pair is strongly conjugated with the quinone ring. The system can be



(11)

regarded as a homoconjugated amide. This nitrogen lone pair is required to stabilize the carbocation center at C10 which forms during hydrolysis. The conjugation with the quinone ring works against this so that the departing alcohol must be converted to an excellent leaving group by protonation for the hydrolysis to occur. In the reduced hydroquinone form, however, the conjugation with the aromatic ring is greatly reduced, and the nitrogen electron pair becomes much more available to initiate the elimination. A comparison here is with α-amino ethers and amide acetals, species which are very reactive toward C–O cleavage even in the absence of acid, readily expelling the alcoxide as an anion.[31]


(12)

We propose therefore that mitomycin reduction triggers the loss of alcoxide which initiates the elimination and the entire reaction sequence. The double bond produced by the elimination is now conjugated with a very electron rich aromatic ring, so that as proposed by Iyers and Szybalski[5] the subsequent aziridine ring opening should also be significantly accelerated in the reduced form.

Supplementary Material Available: Tables of first-order rate constants (4 pages). Ordering information is given on any current masthead page.

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Ultrasound-Promoted Selective Perfluoroalkylation on the Desired Position of Organic Molecules

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Abstract: Perfluoroalkylzinc iodides or bromides which were prepared from perfluoroalkyl iodides or bromides and zinc powder in *N,N*-dimethylformamide or tetrahydrofuran with ultrasonic irradiation were found to behave as potential perfluoroalkylating reagents for the preparation of a wide variety of perfluoroalkylated compounds. Especially, the ultrasound-promoted asymmetric induction with perfluoroalkyl group on the asymmetrical carbon was achieved by the reaction of perfluoroalkyl halides with optically active enamines in the presence of zinc powder and a catalytic amount of dichlorobis(π-cyclopentadienyl)titanium.

The utility of organometallic reagents has been generally recognized to be useful in organic synthesis.[1] However, very little synthetic application of perfluoroalkylmetallic reagents has been studied,[2-8] probably due to their low stability or low reactivity. For example, perfluoroalkylmagnesium or lithium compounds readily decompose into perfluoroolefins and magnesium or lithium halides,[9] and they are not used practically to introduce the per-

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Table I. Preparation of α-Perfluoroalkylated Carbinols

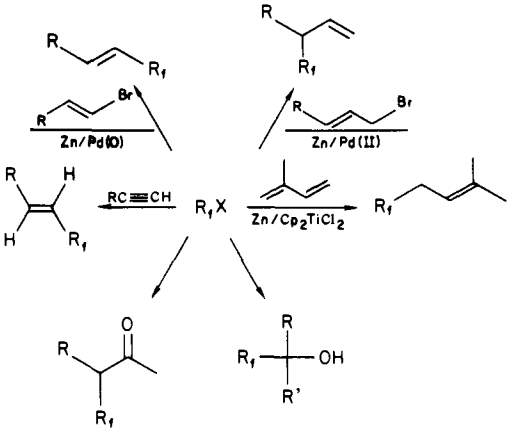
reactants		products[a]	reaction time, h	yield, %	bp, °C (mmHg)
RC(O)R′	R_fX				
PhCHO	CF_3I	$PhCH(CF_3)OH$	0.5	72	105–108 (16)
	CF_3Br		3	56	[105 (17)][c]
	C_2F_5I	$PhCH(C_2F_5)OH$[b]	0.5	67	115–118 (14)
	n-C_3F_7I	$PhCH(C_3F_7{}^n)OH$[b]	0.5	58	86–88 (15)
	i-C_3F_7I	$PhCH(C_3F_7{}^i)OH$[b]	0.5	56	120–123 (104)
	n-C_4F_9I	$PhCH(C_4F_9{}^n)OH$[b]	0.5	61	81–83 (36)
	n-C_4F_9Br		3	49	
	n-$C_6F_{13}I$	$PhCH(C_6F_{13}{}^n)OH$[b]	0.5	66	86–88 (18)
	n-$C_8F_{17}I$	$PhCH(C_8F_{17}{}^n)OH$[b]	0.5	58	87–89 (6)
	n-$C_8F_{17}Br$		2	32	
$C_5H_{11}CHO$	CF_3I	$C_5H_{11}CH(CF_3)OH$[b]	0.5	61	96–97 (18)
	CF_3Br		3	47	
	C_2F_5I	$C_5H_{11}CH(C_2F_5)OH$[b]	1	54	91–93 (15)
	n-C_4F_9I	$C_5H_{11}CH(C_4F_9{}^n)OH$[b]	0.5	71	86–88 (11)
	n-C_4F_9Br		2	52	
	n-$C_8F_{17}I$	$C_5H_{11}CH(C_8F_{17}{}^n)OH$[b]	0.5	62	91–93 (4)
MeCH=CHCHO	CF_3I	$MeCH{=}CHCH(CF_3)OH$[b]	0.5	62	92–95 (105)
	CF_3Br		3	41	
	C_2F_5I	$MeCH{=}CHCH(C_2F_5)OH$[b]	0.5	40	88–91 (58)
	n-C_4F_9Br	$MeCH{=}CHCH(C_4F_9{}^n)OH$[b]	2	58	82–84 (25)
PhCH=CHCHO	CF_3I	$PhCh{=}CHCH(CF_3)OH$[b]	0.5	69	86–88 (5)
	CF_3Br		3	45	
	C_2F_5I	$PhCH{=}CHCH(C_2F_5)OH$[b]	1	48	93–95 (6)
	n-C_3F_7I	$PhCH{=}CHCH(C_3F_7{}^n)OH$[b]	0.5	60	95–98 (3)
PhC(O)Me	CF_3I	$PhC(CF_3)(Me)OH$	1.5	13	81–83 (3)
	CF_3I/Cp_2TiCl_2		3	36	
	CF_3Br/Cp_2TiCl_2		3	33	
	n-C_4F_9I	$PhC(C_4F_9{}^n)(Me)OH$[b]	2	12	102–105 (2)
	n-C_4F_9I/Cp_2TiCl_2		3	38	
$CH_2{=}CHCH_2C(O)Me$	CF_3I	$CH_2{=}CHCH_2C(CF_3)(Me)OH$[b]	1.5	18	94–97 (65)
	CF_3I/Cp_2TiCl_2		3	41	
	CF_3Br/Cp_2TiCl_2		3	36	

[a] The structures were also confirmed by spectral data. [b] New compound. The microanalysis was in satisfactory agreement with the calculated values (C, H, N; ±0.4%). [c] Value given in the literature.

fluoroalkyl groups into the organic molecules. In fact, reported introduction of perfluoroalkyl groups on an organic molecule so far is limited to (1) indirect routes such as a halogen exchange of CCl_3 with HF–$SbCl_5$[10] or fluorination of CO_2H by SF_4,[11] (2) the radical addition of perfluoroalkyl iodides to olefins,[12-17] (3) the Ullman-type reaction for the synthesis of fluorinated aromatic compounds,[5,6,8] and (4) cationic perfluoroalkylation with perfluoroalkylphenyliodonium sulfonates.[18-20]

Therefore, in the field of fluorine chemistry, it is a challenge to use a new type of technical method to introduce perfluoroalkyl groups on the organic molecules. Ultrasound provides a solution of this problem and our recent communications indicated its considerable potentially in the selective introduction of perfluoroalkyl groups into a desired position of organic molecules.[21-24] The ultrasonic technique was reported by Luche and his co-workers

Scheme I



on the formation of the organometallic compounds,[25-31] and then several reports on the ultrasound-promoted reactions appeared in the literature.[30-42]

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Table II. Perfluoroalkylation on the Vinyllic Position

substrate	R_fX	product[a]	reaction time, h	yield, %	bp, °C [(mmHg)] (mp, °C)
(*E*)-PhCH=CHBr	CF_3I	(*E*)-PhCH=CHCF$_3$	1	65	70–72 (25)
	CF_3Br		3	53	[64 (18)][c]
	C_2F_5I	(*E*)-PhCH=CHC$_2$F$_5$	1	47	76–78 (21)
	n-C_3F_7I	(*E*)-PhCH=CHC$_3$F$_7$[b]	1	66	78–80 (24)
	i-C_3F_7I	(*E*)-PhCH=CHC$_3$F$_7$[b]	1	72	75–77 (24)
	n-C_4F_9I	(*E*)-PhCH=CHC$_4$F$_9$[b]	1	62	76–78 (23)
	n-C_4F_9Br		3	32	
(*E*)-4-MeC_6H_4CH=CHBr	CF_3I	(*E*)-4-MeC_6H_4CH=CHCF$_3$	1	67	(59–60) (59)[c]
	CF_3Br		3	41	
	n-C_3F_7I	(*E*)-4-MeC_6H_4CH=CHC$_3$F$_7$[b]	1	68	(71–73)

[a] The structures were determined by means of IR, NMR, and mass spectral data. [b] New compounds. The microanalysis was in satisfactory agreement with the calculated values. [c] Fuchikami, T.; Yatabe, M.; Ojima, I. *Synthesis* **1981**, 365.

Table III. Perfluoroalkylation on the Allylic Position

R_fX	substrate	product	reaction time, h	yield, %	bp, °C (mmHg)
CF_3I	PhCH=CHCH$_2$Br	Ph(CF_3)CHCH=CH$_2$[b]	1	51	81–83 (25)
CF_3Br			3	36	
C_2F_5I		Ph(C_2F_5)CHCH=CH$_2$[b]	1	42	86–89 (18)
n-C_3F_7I		Ph(C_3F_7[n])CHCH=CH$_2$[b]	1	71	86–88 (21)
i-C_3F_7I		Ph(C_3F_7[i])CHCH=CH$_2$[b]	1	78	80–82 (21)
n-C_4F_9I	MeCH=CHCH$_2$Br	Me(C_4F_9[n])CHCH=CH$_2$[b]	1	68	81–84
n-C_4F_9Br			3	37	
n-$C_6F_{13}I$		Me(C_6F_{13}[n])CHCH=CH$_2$[b]	1	56	131–134

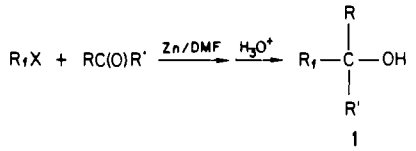
[a] Structures were determined by means of IR, NMR, and mass spectral data. [b] New compounds. The microanalysis was in satisfactory agreement with the calculated values (C, H, N; ±0.4%).

Perfluoroalkylzinc iodides or bromides produced from perfluoroalkyl iodides or bromides by ultrasonically dispersed zinc in *N*,*N*-dimethylformamide, which are much more stable than the corresponding magnesium compounds, have a marked effect on the synthetic application of perfluorooorganometallic reagents.

This work describes the synthetic utilization of the ultrasound-promoted perfluoroalkylzinc iodides which are useful reagents with unusual properties for synthetic work as shown in Scheme I.

Results and Discussion

Perfluoroalkylation of Aldehydes and Ketones Giving α-(Perfluoroalkyl) Alcohols. Few practical methods to introduce a perfluoroalkyl group onto the carbonyl group have been developed.[43,44] For our ultrasound-promoted perfluoroalkylation, we found that it is very susceptible to the Barbier-type reaction with carbonyl compounds, affording α-perfluoroalkylated alcohols in good yields (Table I).



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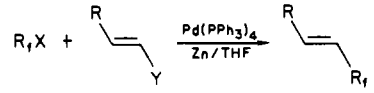
In particular, a wide variety of aldehydes was converted into the α-trifluoromethylated alcohols even in the CF_3Br–Zn system. However, the low reactivity of organozinc compounds to ketones prevented the perfluoroalkylation of the carbonyl group of ketones in good yield. In the ketone system, bis[π-cyclopentadienyl]titanium(II), produced from the reduction of titanocene dichloride with zinc under ultrasound,[45-50] was a very useful catalyst for the perfluoroalkylation. The titanocene dichloride/Zn system was used in the reaction of acetophenone and trifluoromethyl iodide or bromide, furnishing α-trifluoromethyl alcohol in 36% or 33% yield, respectively. This fact suggests that bis[π-cyclopentadienyl]titanium(II) is a useful Lewis acid to activate the carbonyl group.

In these systems, technical grade *N*,*N*-dimethylformamide or dimethyl sulfoxide dried over molecular sieves (4A) can be used, though the former was preferred.

Perfluoroalkylation of Vinylic and Allylic Halides. On consideration of the affinity of Grignard reagents for a halogen atom on the carbon–carbon double bond, perfluoroalkylzinc iodides or bromides were expected to react with vinylic halides in the presence of some kinds of catalysts.

Perfluoroalkylation on the vinylic position was achieved by using tetrakis(triphenylphosphine)palladium as a catalyst (Table II).[51-53]



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X=I, Br

When palladium(II) chloride was used in this system, the reduction of Pd(II) to Pd(0) according to the following equation

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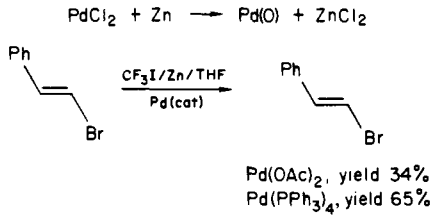
Table IV

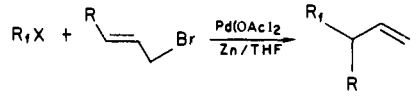
catalyst	yield,[a] %	catalyst	yield,[a] %
$Pd(OAc)_2$	63	$PdCl_2(PPh_3)_2$	51
$PdCl_2$	34	$PdCl_2(PhCN)_2$	23

[a] Yields were determined by ^{19}F NMR, using $PhCF_3$ as reference.

was confirmed experimentally, decreasing the yield for the cross-coupling reaction.



Palladium-catalyzed perfluoroalkylation of allylic halides with perfluoroalkylzinc iodies or bromides, which were formed in situ from perfluoroalkyl iodies or bromides and zinc powder in tetrahydrofuran, proceeded smoothly. The perfluoroalkyl group was introduced regioselectively (>95%) at the γ-position of the allylic derivative, **3**, as shown Table III.

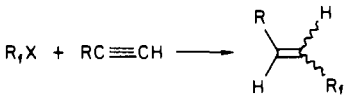


3

Various kinds of palladium compounds were examined as a catalyst in the case between trifluoromethylzinc iodide and cinnamyl bromide, which resulted as shown in Table IV. Thus, $Pd(OAc)_2$ was found to be the most suitable catalyst.

Hydroperfluoroalkylation of Alkynes and Dienes. The light- or thermo-induced free radical addition of perfluoroalkyl iodides to alkynes has been reported by several authors, though regio- and stereochemical information about the product is limited.[54-57]

Ultrasound-promoted hydro(perfluoroalkyl)ation of alkynes with perfluoroalkylcuprates, which was formed in situ from perfluoroalkyl iodides or bromides and zinc in the presence of copper(I) iodide in tetrahydrofuran, proceeded smoothly as shown Table V. The above hydro(perfluoroalkyl)ation of alkynes is regioselective, but not stereoselective.



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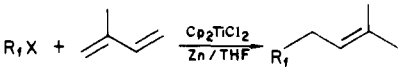
Various kinds of copper compounds, such as CuI, CuCl, $CuCl_2$, CuBr, and CuF_2, were examined as a copper metal source in this system. As a result, copper(I) iodide was found to be the most effective for this purpose.[58] In this system, copper metal produced from the reduction of copper(I) iodide with ultrasonically dispersed zinc powder seemed to enhance the perfluoroalkylation.

Similarly, we found that bis[π-cyclopentadienyl]titanium(II),[59] when produced in situ by the reduction of titanocene dichloride with ultrasonically dispersed zinc, and accompanied by ultrasonic irradiation, greatly enhanced the bis[π-cyclopentadienyl]titanium(II)-catalyzed hydro(perfluoroalkyl)ation of an alkadiene such as isoprene (Table VI).

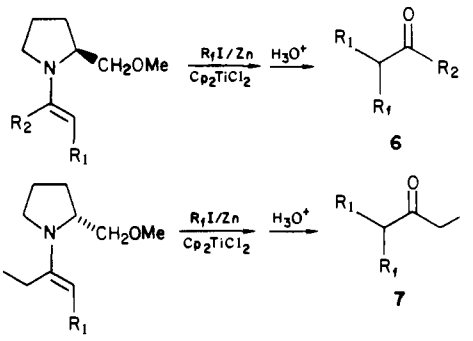


5

Perfluoroalkylation with the Asymmetric Induction. The next ultrasonically synthetic application is asymmetric induction with the introduction of perfluoroalkyl group on the desired position of a molecule. Recently, Wakselman and co-workers[60-64] reported the reaction of perfluoroalkyl iodide with an enamine under UV irradiation in an inert solvent. However, no stereochemical information was revealed. Until now, no reports of an asymmetric induction with the introduction of perfluoroalkyl group into the molecule have been published except for the synthesis of an optically active carbinol by the addition of perfluoroethyllithium on a complexed aldehyde.[65]

In our ultrasound-promoted perfluoroalkylation, it is possible to introduce the perfluoroalkyl group with asymmetric induction into a molecule by the dichlorobis[π-cyclopentadienyl]titanium-catalyzed reaction of perfluoroalkylzinc halides with an optically active enamin.

Our favorite chiral enamines are prepared from (*S*)-proline or (*S*)-glutamic acid by the reported route[66] and then purified with column chromatography on silica. The perfluoroalkylation with asymmetric induction was examined by using several types of catalyst, e.g., L_2PdCl_2, L_2NiCl_2, $(PPh_3)_4Pd$, $Ni(acac)_2$, etc., and found that the best results are obtained with Cp_2TiCl_2. Furthermore, the experimental results, that no reaction occurred in the presence of $TiCl_4$ or $TiCl_3$, support that the actual catalyst is bis[π-cyclopentadienyl]titanium(II), which is formed from Cp_2TiCl_2 and Zn powder with ultrasound. However, details of the catalytic system and the mechanism are not yet known.



Optical purities of the products were determined by ^{19}F NMR and/or ^1H NMR with both chiral NMR shift reagent and silver perfluoroalkylate, which have been developed by our group.[67]

We have prepared a number of optically active ketones with the perfluoroalkyl group in this way; however, these absolute configurations have no explanation at the present time and still await detailed studies.

The present asymmetrical approach is considered to be a convenient process for preparing optically active perfluorinated compounds, and it offers a possibility for the asymmetric induction in fluorine chemistry.

With respect to these results, we believe that the presently reported procedures provide an available and selective introduction of perfluoroalkyl groups on a desired position of organic molecules

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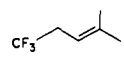
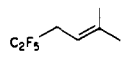
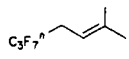
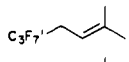
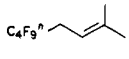
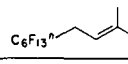
Table V. Hydroperfluoroalkylation of Alkynyl Compounds

R_fX	substrate	product	yield, %	bp, °C [(mmHg)]	Z/E ratio[c]
CF_3I	PhC≡CH	CF_3CH=$CHPh$	65	71–73 (25)	72/28
CF_3Br			47	[64 (18)][d]	68/32
CF_3I	BuC≡CH	CF_3CH=$CHBu$[b]	71	78–81 (56)	76/24
CF_3Br			39		71/29
CF_3I	$HOCH_2C$≡CH	CF_3CH=$CHCH_2OH$	61	126–129	68/32
CF_3Br			43	[128][e]	65/35
C_2F_5I		C_2F_5CH=$CHCH_2OH$[b]	46	141–143	67/33
i-C_3F_7I	PhC≡CH	i-C_3F_7CH=$CHPh$[b]	52	75–78 (12)	69/31
i-C_3F_7I	$HOCH_2C$≡CH	i-C_3F_7CH=$CHCH_2OH$[b]	65	54–55 (34)	67/33
n-C_3F_7I	BuC≡CH	n-C_3F_7CH=$CHBu$[b]	59	82–85 (27)	74/26
n-C_3F_7I	$HOCH_2C$≡CH	n-C_3F_7CH=$CHCH_2OH$[b]	66	65–67 (58)	70/30
n-C_4F_9I		n-C_4F_9CH=$CHCH_2OH$[b]	74	59–62 (32)	73/27
n-C_4F_9Br			51		64/36
n-$C_6F_{13}I$		n-$C_6H_{13}CH$=$CHCH_2OH$[b]	55	71–73 (29)	75/25
n-$C_8F_{17}I$		n-$C_8F_{17}CH$=$CHCH_2OH$[b]	58	84–86 (18)	77/23
n-$C_8F_{17}Br$			32		71/29

[a] The structures were also confirmed by spectral data. [b] New compound. The microanalysis was in satisfactory agreement with the calculated values. [c] Stereochemistry was determined from the relative intensities of ^{19}F NMR signals. [d] Fuchikami, T.; Yatabe, M.; Ojima, I. *Synthesis* **1981**, 365. [e] McBee, E. T.; Pierce, O. R.; Smith, D. D. *J. Am. Chem. Soc.* **1954**, *76*, 3725.

Table VI. Hydroperfluoroalkylation of Isoprene

R_fX	product[a] R_f	yield, %	bp, °C (mmHg)
CF_3I		56	102–105
CF_3Br		41	
C_2F_5I		52	126–128
n-C_3F_7I		57	160–163
i-C_3F_7I		74	158–160
n-C_4F_9I		61	61–63 (28)
n-C_4F_9Br		43	
n-$C_6F_{13}I$		52	74–76 (23)

[a] Structures of those products are established from spectral data. For the new compound the microanalysis was in satisfactory agreement with the calculated values (C, H, N; 0.4%).

and that the ultrasonic irradiation is a more advantageous technical way than other ways in fluorine chemistry.

Experimental Section

General Procedures. All reactions were carried out with an ultrasonic laboratory cleaner (32 KHz, 35W; 45 KHz, 100 W) in quartz vessel. Commercially available zinc powder (Wako's 1st grade) was used. Solvents, e.g., THF and DMF, were dried over molecular sieves (4A). Infrared spectra were obtained by using a Jasco A-102 spectrometer and KBr pellets. The ^1H (internal Me_4Si) and ^{19}F (external CF_3CO_2H) NMR spectra were recorded by using a Varian EM-390 spectrometer. Mass spectra were obtained by using a Hitachi M-52 spectrometer at 20 eV. The NMR, IR, etc. data for some of perfluoroalkylated compounds illustrated in the tables are discussed in the literature.[23] Perfluoroalkylzinc reagents were used without the purification, after checking the production of them in situ by ^{19}F NMR. Yields were those of the products actually isolated. The purity of products was determined by GLC and/or GLPC (>95%).

2,2,2-Trifluoro-1-phenylethanol. A flask containing zinc powder (1.30 g, 0.02 g-atom), trifluoromethyl iodide (3.0 g, 20 mmol), and benzaldehyde (1.06 g, 10 mmol) in *N,N*-dimethylformamide (30 ml) and then equipped with a dry ice–acetone reflux condenser was irradiated in the water bath of an ultrasonic laboratory cleaner for 1 h. Then, the solution was poured into a 2% HCl solution and an oily material extracted with diethyl ether. After the ethereal solution was dried over magnesium sulfate, the solvent was removed. Distillation gave a 2,2,2-trifluoro-1-phenylethanol in a yield of 72% (1.27 g), bp 105–108 °C (16 mmHg). ^{19}F NMR (CCl_4) δ −0.3 (CF_3, d, $J_{CF_3\text{-}H}$ = 5.6 Hz) from external CF_3CO_2H. ^1H NMR (CCl_4) δ 5.00 (CH, q), 6.22 (OH), and 7.50 (Ar–H). Mass: M^+ 176

1-Trifluoromethyl-1-phenylethanol. A flask containing commercially available zinc powder (1.30 g, 0.02 g-atom), dichloro[π-cyclopentadienyl]titanium (0.25 g, 1 mmol), trifluoromethyl bromide (2.24 g, 15 mmol), and methyl phenyl ketone (1.20 g, 10 mmol) in *N,N*-dimethylformamide (25 mL) and equipped with a dry ice–acetone reflux condenser was irradiated in the water bath of an ultrasound laboratory cleaner for 3 h and then worked up as usual. Distillation gave 1-trifluoromethyl-1-phenylethanol in a yield of 33%, bp 81–83 °C (3 mmHg). ^{19}F NMR (CCl_4) δ 0.6 (CF_3). ^1H ($CDCl_3$) δ 1.45 (CH_3), 4.0 (OH), 7.4 (Ar–H).

4,4,4-Trifluoro-1-phenyl-1-butene. A flask, equipped with a dry ice–actone reflux condenser, containing zinc powder 1.30 g, 0.02 g-atom), trifluoromethyl iodide (2.5 g, 25 mmol), cinnamyl bromide (1.97 g, 10 mmol), and palladium acetate (0.11 g, 0.5 mmol) in tetrahydrofuran (25 mL) is irradiated in the water bath of an ultrasound laboratory cleaner for 1 h. Then, the solution was poured into water and oily material was extracted with diethyl ether. After the ethereal solution was dried over magnesium sulfate, the solvent was removed. Distillation gave 4,4,4-trifluoro-1-phenyl-1-butene in 63% yield, bp 81–83 °C (25 mmHg). ^{19}F NMR ($CDCl_3$) δ −0.2 (CF_3, d, $J_{CF_3\text{-}CH}$ = 6.6 Hz). ^1H NMR ($CDCl_3$) δ 4.72 (CH, d q, $J_{CH\text{-}CH}$ = 8.6 Hz), 5.81 (CH=, d q, $J_{CH\text{-}CH}$ 13 Hz), 6.9 (CH=, d), 7.50 (Ar–H). Mass: M^+ 186

Table VII. Physical Properties of Optically Active Compounds with the Perfluoroalkyl Group

compound no.	R_fX	R_1	R_2	yield, %	optical purity	α_D % ee (neat: l = 1)	bp, °C (mmHg)
6	CF_3I	C_2H_5	CH_3	38	62	−11.3	65–68 (140)
	CF_3Br	C_2H_5	CH_3	46	76	−13.9	
	C_2F_5I	C_2H_5	CH_3	51	54	−16.5	70–73 (105)
	n-C_3F_7I	C_2H_5	CH_3	48	59	−13.1	72–75 (80)
	n-C_4F_9Br	C_2H_5	CH_3	58	64	−14.6	86–88 (72)
	n-$C_6F_{13}I$			57	68	+9.8	96–98 (0.5)
	n-$C_8F_{17}I$	C_2H_5	CH_3	56	72	−8.6	89–91 (15)
7	CF_3I	C_2H_5	CH_3	31	67	+12.2	62–64 (137)
	C_2F_5I	C_2H_5	CH_3	42	59	+18.0	74–76 (108)

[a] Structures of these products are established from spectral data. For the new compound the microanalysis was in satisfactory agreement with the calculated values (C, H, N; ±0.4%).

(*E*)-3,3,3-Trifluoro-1-phenylpropene. In the above reaction, zinc powder (1.30 g, 0.02 g-atom), trifluoromethyl bromide (3.0 g, 20 mmol), *trans*-β-bromostyrene (1.83 g, 10 mmol), and tetrakis(triphenylphosphine)palladium (0.23 g, 0.2 mmol) in tetrahydrofuran (25 mL) were used. Distillation gave (*E*)-3,3,3-trifluoro-1-phenylpropene in 42% yield, bp 70–72 °C (25 mmHg).

3,3,3-Trifluoro-1-phenylpropene from Phenylacetylene. A flask, equipped with a dry ice–acetone reflux condenser, containing commercially available zinc powder (1.30 g, 0.02 g-atom) and copper(I) iodide (0.72 g), trifluoromethyl bromide (3.0 g, 20 mmol), and phenylacetylene (1.02 g, 10 mmol) in tetrahydrofuran (30 mL), is irradiated for 2 h in the water bath of an ultrasound laboratory cleaner. Then, the solution was poured into a 2% HCl solution and an oily material was extracted with diethyl ether. After the ethereal solution was dried over magnesium sulfate, the solvent was removed. Distillation gave 3,3,3-trifluoro-1-phenylpropene in a yield of 55% (1.11 g), bp 71–73 °C (25 mmHg).

5,5,5-Trifluoro-2-methyl-2-pentene. In the above reaction, zinc powder (1.30 g, 0.02 g-atom), dichlorobis[π-cyclopentadienyl]titanium (0.25 g, 1 mmol), trifluoromethyl iodide (2.25 g, 12 mmol) and isoprene (3.06 g, 45 mmol) in tetrahydrofuran (30 mL) were used. Distillation gave 5,5,5-trifluoro-2-methyl-2-pentene in 56% yield, bp 102–105 °C. ^{19}F NMR ($CDCl_3$) δ 0.5 (CF_3, t, $J_{CF_3-CH_2}$ = 5.2 Hz). ^1H NMR ($CDCl_3$) δ 2.06, 2.09 ($CH_3 \times 2$), 4.48 (CH=), 2.70 (CH_2, d q, J_{CH_2-CH} = 3 Hz)

(−)-2-(Trifluoromethyl)pentan-3-one. A flask equipped with a dry ice–acetone reflux condenser, containing zinc powder (2.60 g, 0.04 g-atom), trifluoromethyl iodide (4.3 g, 22 mmol), optically active enamine (**6**, $R_1 = C_2H_5$, $R_2 = CH_3$ 5.5 g, 30 mmol), and dichlorobis[π-cyclopentadienyl]titanium (0.5 g, 2 mmol) in *N*,*N*-dimethylformamide (30 mL), was irradiated in the water bath (50–60 °C) of an ultrasound laboratory cleaner (45 kHz, 100 W) for 3 h. Then, the solution was poured into a 40% H_2SO_4 solution and an oily material was extracted with diethyl ether. After the ethereal solution was dried over magnesium sulfate, the solvent was removed. Distillation gave (−)-2-trifluoromethylpentan-3-one, bp 65–68 °C (140 mmHg).

A Theoretical Evaluation of the Mechanism of Acetylene Formation in the Reactions of Atomic Carbon with Hydrocarbons

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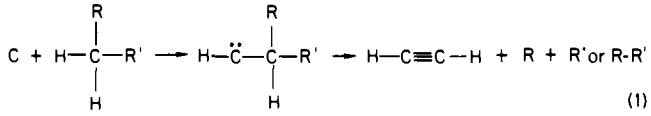
Abstract: A study has been made of the C_2H_4 potential energy surface, for the reaction of atomic C with CH_4, in which energies are calculated at the MP3/6-31G** level and zero-point energies are included at the 3-21G basis set level. The reaction of $C(^3P)$ with CH_4 on the lowest triplet surface and the reaction of $C(^1D)$ on the two lowest singlet surfaces have been followed. The observed acetylene formation from nucleogenic carbon atoms and methane is calculated to occur via the formation of the $^1A''$ excited singlet state of ethylidene from $C(^1D)$ which sequentially eliminates two hydrogen atoms. Several other pathways to acetylene were found to be unimportant due to high barriers or to rapid vibrational deexcitation to ethylene.

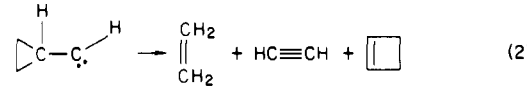
Of the many interesting reactions that have been reported for atomic carbon,[1] perhaps the most intriging is the formation of acetylene in the reaction of carbon atoms with compounds containing C–H bonds. In the case of ^{11}C atoms produced by nuclear reaction,[1d,e] this process must involve the reaction of a single atom of carbon. There are not sufficient atoms of ^{11}C generated to allow dimerization to C_2 and subsequent hydrogen abstraction to give C_2H_2, a process that is important when C_2 is generated directly in a carbon arc.[1a]

The mechanism most often proposed[2] for the production of C_2H_2 in the reaction of C_1 with saturated hydrocarbons involves initial insertion of C_1 into a CH bond generating a carbene which subsequently cleaves to C_2H_2 and other fragments as shown in eq 1. This mechanistic interpretation is weakened by the fact that



(1)

carbenes, when generated by conventional methods, generally do not cleave the two bonds β to the carbene carbon to give C_2H_2 but undergo 1,2 migration to give an olefin.[3] A notable exception is the cyclopropyl carbene, which cleaves and rearranges as shown in eq 2.[4,5] In this case, relief of ring strain undoubtably provides a thermodynamic driving force. Thus, such β-cleavages of



(2)

carbenes are possible and may occur in the highly exothermic reactions of atomic carbon. It is of interest that a study of the reaction of ^{11}C atoms with saturated hydrocarbons showed that cyclopropane gave the highest yield of $H^{11}C{=}CH$.[6]

Another factor which must be considered in the process shown in eq 1 is the electronic state of the reacting carbon and of the resultant carbene. Carbon atoms may react in any of three states: $C(^3P)$ (ΔH_f = 171 kcal/mol), $C(^1D)$ (ΔH_f = 201 kcal/mol), and $C(^1S)$ (ΔH_f = 232 kcal/mol). However, it has been proposed that $C(^3P)$ and $C(^1D)$ rather than $C(^1S)$ serve as acetylene precursors in these systems[2,7] and that $C(^1S)$ is rather unreactive in general.[8] Consequently, we have considered three electronic surfaces on which carbon can insert into the C–H bond. The triplet surface,

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