Lead Tetraacetate Induced Addition Reaction of Difluorodiiodomethane to Alkenes and Alkynes. Synthesis of Fluorinated Telechelic Compounds

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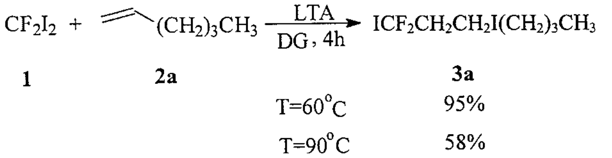
Received 2 May 1997; revised 18 June 1997

Lead tetraacetate (LTA) can smoothly induce the addition reaction of difluorodiiodomethane (**1**) with electron-rich alkenes at 60 °C in diglyme to give monoadducts ($RCHICH_2CF_2I$) and diadducts $(RCHICH_2)_2CF_2$. The similar, clean reaction of fluoroolefins, such as tetrafluoroethene, hexafluoropropene, with **1** occurs only in acetic acid. However, non-fluorinated β-iodo-α,β-unsaturated carboxylic esters are obtained when **1** reacts with alkynes in alcohol. The iododifluoromethyl radical generated by possible pathways from **1** with LTA is discussed.

The addition reaction of perfluoroalkyl halides (R_FX) to alkenes or alkynes is one of the most important methods for synthesizing commercial fluorocarbon intermediates and products.[1] Such a process is traditionally accomplished by photochemical,[2] thermal,[3] electrolytic[4] and free radical initiation.[5] In recent years great progress has been achieved in this field. For example, many metals, transition metals, inorganic reductants, such as Cu,[6] Zn,[7] Mg,[8] Ni,[9] Fe,[10] Pd,[11,12] Pt,[13] $Fe_3(CO)_{12}$,[14] $Na_2S_2O_4$,[15] thiourea dioxide[16] were successfully applied to this reaction. Some redox systems, e.g. $(NH_4)_2S_2O_8/HCO_2Na$,[17] $CrCl_3/Fe$,[18] Co(II)/Zn[19] were also reported to efficiently induce addition reactions to electron-rich olefins as well as electron-deficient ones. However, all these new initiators are in essence considered to be reductive systems because the key initiation step is a single electron-transfer (SET) from the reductant to the R_FX molecule resulting in the formation of perfluoroalkyl radical, $R_F\bullet$.[20] To the best of our knowledge, oxidants have not been used to initiate the same addition reaction although it is known that lead tetraacetate, cobalt triacetate or managanese triacetate could induce the addition of acetic acid to alkenes.[21-23] The only exception was that in 1988 we found that lead tetraacetate (LTA) and lead dioxide could catalyze the addition reaction of perfluoroalkyl iodides to alkenes giving the adducts in high yields.[24]

In order to extend the utilization of LTA as a catalyst, we herein present the reaction results of difluorodiiodomethane with alkenes and alkynes. The reasons why difluorodiiodomethane was chosen as the substrate were as follows. First, this compound, as a simple analog of perfluoroalkyl iodides, has been much less developed probably due to its difficult preparation, but now is readily available due to improvements in its synthesis.[25] Secondly, this compound is a difluorocarbene or difluoroiodomethyl radical source; its reaction with alkenes would afford the fluorinated telechelic compounds, which are important for synthesizing uniquely fluorinated polymers.[26] Finally, it was found in our previous reports that there are some differences in the reactivity with alkenes between difluorodiiodomethane and perfluoroalkyl iodides. For example, although difluorodiiodomethane, like perfluoroalkyl iodides,[7,10-12,15] could smoothly react with terminal electron-rich olefins to give the monoadducts, $RCHICH_2CF_2I$, in the presence of zinc,[27] iron,[27] Pd(0) [of $PdCl_2(PPh_3)_2$],[28] $Na_2S_2O_4$.[29] However, for electron-deficient alkenes, iron powder was the only choice.[27] For internal olefins, such as cyclohexene, palladium dichloride complex gave the monoadducts in high yields.[28] If the diadducts, $(RCHICH_2)_2CF_2$, rather than monoadducts, were desirable, the sulfinato–dehalogenation system (e.g. $Na_2S_2O_4/NaHCO_3$) was preferable.[29] Nevertheless, all of these four reductive species were shown to be unable to induce the addition of difluorodiiodomethane to alkynes, polyfluoroalkylethenes and perfluoroethenes. This limitation promoted us to seek new initiators. We were fortunate to find that LTA can serve this purpose.

It was found that LTA is a good initiator for the addition of difluorodiiodomethane (**1**) to alkenes **2**. For example, when **1** reacted with hex-1-ene in a molar ratio of 1:3 in the presence of a catalytic amount (5 mol %) of LTA in diglyme (DG) at 60 °C for 4 hours, it yielded the monoadduct **3a** in very high yield (95 %); if the reaction was carried out at 90 °C, the yield of the adduct was dramatically reduced (58 %), probably due to the decomposition of **1** at this temperature.

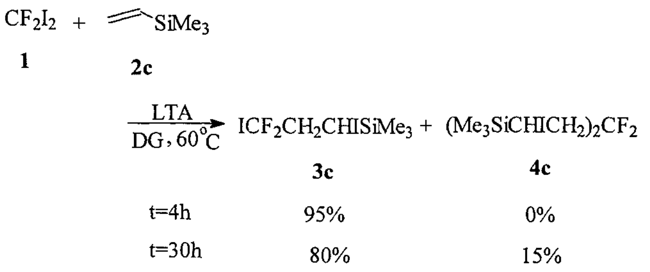


With allyl alcohol **2b**, under similar conditions, the yield of monoadduct **3b** was also excellent. If the reaction time was lengthened from 4 hours to 20 hours, the diadduct **4b** was obtained in addition to the major monoadduct **3b**. When increasing the amount of LTA to one equivalent and heating the mixture for 30 hours at the same temperature (60 °C), the yield ratio of monoadduct to diadduct did not change significantly (62 % versus 30 %).

$$\underset{\mathbf{1}}{CF_2I_2} + \underset{\mathbf{2b}}{CH_2{=}CHCH_2OH} \xrightarrow[DG,\ 60^{\circ}C]{LTA} \underset{\mathbf{3b}}{ICF_2CH_2CHICH_2OH} + \underset{\mathbf{4b}}{(HOCH_2CHICH_2)_2CF_2}$$

	3b	4b
t=4h	93%	0%
t=20h	68%	25%

Similar results were obtained with trimethylsilylethene (**2c**).

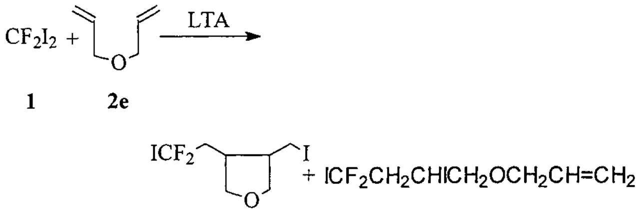


	3c	4c
t=4h	95%	0%
t=30h	80%	15%

However, with allyl ethyl ether (**2d**), only monoadduct **3d** was obtained even when the reactants were kept at 60 °C for 30 hours.

$$\underset{\mathbf{1}}{CF_2I_2} + \underset{\mathbf{2d}}{CH_2{=}CHCH_2OC_2H_5} \xrightarrow[60^\circ C, 30h]{LTA, DG} \underset{\mathbf{3d}}{ICF_2CH_2CHICH_2OC_2H_5}$$

Both the cyclic (tetrahydrofuran derivative) and acyclic addition products were formed from **1** with diallyl ether (**2e**) under similar conditions.

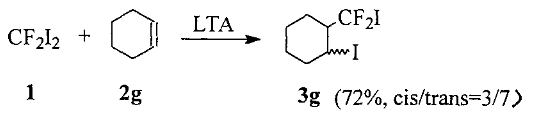


3e (75%) 3e' (15%)

Treatment of the simplest olefin, ethene (**2f**) with **1** in DG at 70 °C in an autoclave for 7 hours gave only the diadduct in high yield (86%).

$$\underset{\mathbf{1}}{CF_2I_2} + \underset{\mathbf{2f}}{CH_2{=}CH_2} \xrightarrow{LTA} \underset{\mathbf{4f}}{ICH_2CH_2CF_2CH_2CH_2I}$$

Cyclohexene, unlike the above olefins used, reacted with **1** to give a *cis*/*trans* mixture of the adduct **3g** with lower conversion (46 %).



3g (72%, cis/trans=3/7)

The data collected in Table 1 seem to show that both reaction temperature and time have some influence on the products and yields. The suitable temperature is 60–70 °C. The formation of the diadduct requires longer time if the monoadducts can further react with alkenes. The monoadducts are always the major products even in the presence of an equivalent of LTA and under longer reaction times.

The suitable solvent used was DG, although other solvents such as CH_3CN, MeOH, EtOH and DMF could also be employed with similar results as shown in Table 2.

The success of the LTA induced addition of **1** with the electron-rich alkenes **2** encouraged us to extend it to fluoroolefins. It is known that per(poly)fluoroalkylethenes do not easily react with perfluoroalkyl iodides.[30] When using $Na_2S_2O_4$ as an initiator, only a low yield of the adduct was obtained from $Cl(CF_2)_4CH{=}CH_2$ and $Cl(CF_2)_2I$.[30] We failed to get any positive results from the reaction of **1** with $X(CF_2)_4CH{=}CH_2$ (X=Cl, **5**) in the presence of zinc, iron, $Pd(Ph_3P)_4$ [of $PdCl_2(PPh_3)_2$]; with the first two catalysts, the products were HCF_2I and $CF_2{=}CF_2$. Although **5** could react with **1** in the presence of a catalytic amount of LTA in DG at 70 °C for 24 hours, the conversion of **1** was only 40 % and the products were too complicated to be purified. Varying the solvent, such as CH_3CN, EtOH, MeOH, DMF, or THF instead of DG and increasing the amounts of LTA to one equivalent did not improve the situation. Finally, it was found that HOAc is the solvent of choice, which can give a clean reaction of **1** with **5** or **6** in the presence of 5 mol% LTA at 70 °C for 7 hours.

$$\underset{\mathbf{1}}{CF_2I_2} + CH_2{=}CH(CF_2)_4X \xrightarrow[70^\circ C, 7h]{LTA,\ HOAc} ICF_2CH_2CHI(CF_2)_4X$$

1	**5** (X=Cl)	**7** (80%)
	6 (X=Br)	**8** (78%)

Acetic acid was also critical for the successful reaction of **1** with fluorinated olefins in the presence of LTA. For example, vinylidene fluoride (**9**) reacted with **1** in an autoclave in the presence of 10 mol% of LTA in HOAc at 70 °C for 14 hours giving the monoadduct **10** in very high yield. Similar to the case with **2a**, at 100 °C for the same period the yield decreased to 48 %.

$$\underset{\mathbf{1}}{CF_2I_2} + \underset{\mathbf{9}}{CH_2{=}CF_2} \xrightarrow[HOAc,\ 14h]{LTA} \underset{\mathbf{10}}{ICF_2CH_2CF_2I}$$

	10
70°C	92%
100°C	48%

Judging from the signals of ^{19}F NMR spectroscopy at $\delta = 14.6$ and -39.3 (from TFA), a small amount of diadduct (< 1 %) $ICF_2CH_2CF_2CH_2CF_2I$ seemed to be present. Treatment of **10** with K_2CO_3 in CH_3CN at 60 °C for 4 hours gave tetrafluoroallene (**11**) directly in high yield.

$$\underset{\mathbf{10}}{ICF_2CH_2CF_2I} + K_2CO_3 \xrightarrow[60^\circ C,\ 4h]{CH_3CN} \underset{\mathbf{11}\ (82\%)}{CF_2{=}C{=}CF_2}$$

Due to simple synthetic procedures and high yields of both **10** and **11**, this seems to be a better approach to prepare the interesting compound **11** as compared with that from CF_2Br_2. There were two methods for synthesizing **11** from CF_2Br_2:

Table 1. The Reaction of **1** with Alkenes **2** in the Presence of LTA in DG[a]

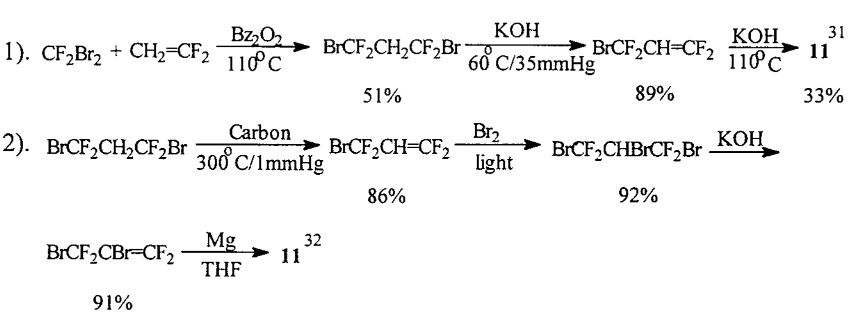
Entry	2	R	Temp (°C)	Time (h)	Conv. (%)	Products[b] (%)
1	**a**	Bu	60	4	100	**3a** (95)
2			95	2	100	(58)
3	**b**	CH_2OH	60	4	100	**3b** (93)
4			60	20	100	**3b** (68) + **4b** (25)
5[c]			60	30	100	**3b** (62) + **4b** (30)
6	**c**	$SiMe_3$	60	4	100	**3c** (95)
7			60	30	100	**3b** (80) + **4c** (15)
8	**d**	CH_2OEt	60	30	100	**3d** (92)
9	**e**	$CH_2OCH_2CH{=}CH_2$	60	4	100	**3e** (75) + **3e'** (15)
10			60	24	100	**3e** (75) + **3e'** (15)
11	**f**	H	65	7	100	**4f** (86)
12	**g**	$(CH_2)_4$	75	12	46	**3g** (72)

[a] **1**: **2**: LTA = 1:3:0.05, unless otherwise stated.
[b] Isolated yields based on **1**.
[c] **1**: **2**: LTA = 1:3:1.

Table 2. The Influence of Solvent on the Reaction of **1** and **2** in the Presence of LTA[a]

Entry	2	Solvent	Temp (°C)	Time (h)	Conv. (%)	Products[b] (%)
1	**2c**	DG	60	4	100	**3c** (97)
2	**2c**	DMF	70	5	100	**3c** (93)
3	**2c**	CH_3CN	70	5	100	**3c** (92)
4	**2e**	DG	60	4	100	**3e** (79) + **3e'** (20)
5	**2e**	EtOH	70	4	100	**3e** (71) + **3e'** (23)
6	**2e**	CH_3OH	55	5	100	**3e** (78) + **3e'** (15)
7	**2g**	DMF	70	14	42	**3g** (71)
8	**2g**	CH_3OH	55	14	48	**3g** (74)
9	**2g**	CH_3CN	70	13	47	**3g** (72)

[a] **1**: **2**: LTA = 1:3:0.05.
[b] Determined by ^{19}F NMR based on **1**.



$$1).\ CF_2Br_2 + CH_2{=}CF_2 \xrightarrow[110^\circ C]{Bz_2O_2} BrCF_2CH_2CF_2Br \xrightarrow[60^\circ C/35mmHg]{KOH} BrCF_2CH{=}CF_2 \xrightarrow[110^\circ C]{KOH} 11^{31}$$

51% 89% 33%

$$2).\ BrCF_2CH_2CF_2Br \xrightarrow[300^\circ C/1mmHg]{Carbon} BrCF_2CH{=}CF_2 \xrightarrow[light]{Br_2} BrCF_2CHBrCF_2Br \xrightarrow{KOH}$$

86% 92%

$$BrCF_2CBr{=}CF_2 \xrightarrow[THF]{Mg} 11^{32}$$

91%

Tetrafluoroethene (TFE, **12**) was originally thought to telomerize with **1** to give oddnumber telomers, $ICF_2(CF_2CF_2)_nI$, which, like $I(CF_2CF_2)_nI$, $FOC(CF_2CF)_nCOF$, $I(CH_2CH_2)_mC_nF_{2n}(CH_2CH_2)_mI$, might be useful in industry.[26,33] However, it was found that neither thermal nor peroxide initiated telomerization of TFE with **1** could afford the telomers. For example, heating **1** with TFE (molar ratio of 1:1) in an autoclave at 70 °C for 15 hours no reaction occurred; whereas at 90 °C for 10 hours no addition or telomerization products could be detected. The decomposition of **1** resulted in only TFE and iodine residue.

$$CF_2I_2 + CF_2{=}CF_2 \longrightarrow ICF_2CF_2CF_2I$$

1 12 13 (90%)

The thermal behavior of **1** is similar to that of 1,2-diiodotetrafluoroethane, ICF_2CF_2I,[34] the latter, nevertheless, starts to degrade from 190 °C indicating that both C–I bonds of **1** are much weaker then those in ICF_2CF_2I.

However, TFE (**12**), like vinylidene difluoride, could smoothly react with **1** in HOAc in an autoclave in the presence of catalytic amounts of LTA at 70 °C for 20 hours giving the monoadduct **13** in high yield.

$$CF_2I_2 + CF_2{=}CF_2 \longrightarrow ICF_2CF_2CF_2I$$

1 12 13 (90%)

Long-chain telomers, $ICF_2(CF_2CF_2)_nI$, $n \geq 2$ have not been observed even using an excess of **12** (**1**/**12** = 1:3), although 2–3% of diadduct, $ICF_2CF_2CF_2CF_2CF_2I$

(^{19}F NMR: $\delta = -14.6$, ICF_2; 36.6, $ICF_2CF_2CF_2$; 43.0, $-CF_2CF_2CF_2-$) was detected by ^{19}F NMR spectroscopy, when the same reaction was carried out for 50 hours.

Similarly, hexafluoropropene (**14**), perfluorovinyl ether (**16**) could undergo the same addition reactions with **1** to afford the corresponding monoadducts with lower conversions.

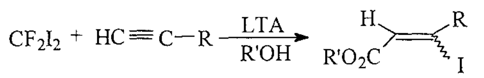
$$\underset{\mathbf{1}}{CF_2I_2} + \underset{\mathbf{14}}{CF_2{=}CFCF_3} \xrightarrow[70^\circ C, 30h]{LTA} \underset{\mathbf{15}}{ICF_2CF_2CFICF_3}$$

Conv.: 49%
Yield: 85%

$$\underset{\mathbf{1}}{CF_2I_2} + \underset{\mathbf{16}}{CF_2{=}CFO(CF_2)_3CFCl_2} \xrightarrow[70^\circ C, 32h]{LTA} \underset{\mathbf{17}}{ICF_2CF_2CFIO(CF_2)_3CFCl_2}$$

Conv.: 73%
Yield: 91%

When we turned our attention to the reaction with alkynes, to our surprise, no anticipated iododifluoromethylated adducts were observed. For example, **1** was allowed to react with hex-1-yne (**18a**) in ethanol in the presence of LTA (5 mol%) at 80 °C for 24 hours. The only product identified on the basis of ^{1}H NMR, MS and elemental analyses was ethyl 3-iodohept-2-enoate (**19aa**).



1 **18** **19**

R		R^1	
a	Bu	**a**	Et
b	n-C_5H_{11}	**b**	Me
c	Ph	**c**	Bu
d	CH_2OMe		

The configuration of Z/E isomers was assigned on the basis of chemical shift of the vinyl proton.

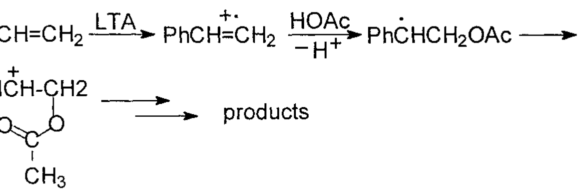
An attempt to use DG, CH_3CN, HOAc, DMF, or THF as a solvent instead of alcohol resulted in not only lower conversions of **1** (e.g. in DG 40% conversion of **1** in the reaction with **18a** at 70 °C for 12 h) but also the formation of a complicated mixture.

Hept-1-yne (**18b**), phenylacetylene (**18c**) and 3-methoxyprop-1-yne (**18d**) reacted with **1** in various alcohols in a similar fashion. The results are listed in Table 3.

The corresponding acids of **19** have been prepared by treating **1** with alkynes with aqueous hydrogen peroxide in acetone.[35] Both β-iodo-α,β-unsaturated carboxylic acids and esters are important intermediates in organic synthesis owing to the presence of three functional groups.[36]

Regarding the reaction mechanism, it is known that LTA is a typical oxidant ($E_{red} \approx 1.6$ V in perchloric acid),[22] which can oxidize a variety of organic compounds including unactivated aromatic C–H bonds.[22] An alkyl radical produced by thermal decomposition of the lead(IV) carboxylate in the addition reaction of acetic acid with alkenes in the presence of LTA was first suggested by Kochi in 1965.[37] It was also reported to involve the competing radical and ionic paths.[23]

However, Thomas and co-workers proposed that the first step of the reaction involves a direct electron transfer[23] from alkene (e.g. styrene) to LTA to generate the alkene radical cation which is expected to be attacked by nucleophile to give benzylic radical, oxidation of which would then give the products.



In order to demonstrate that methyl radicals might not be involved in our reaction, we used lead dioxide and DG instead of LTA and HOAc. It was found that hex-1-ene (**2a**) did react with **1** to give the desired adduct, **3a**.

$$CF_2I_2 + \underset{\mathbf{2a}}{CH_2{=}CH(CH_2)_3} \xrightarrow[DG, 80^\circ C]{PbO_2} \underset{\mathbf{3a}}{ICF_2CH_2CHI(CH_2)_3CH_3}$$

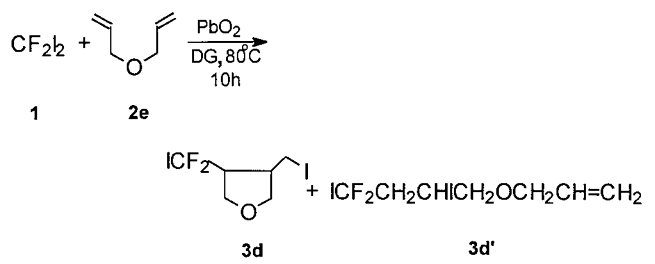
	Conv.	Yield
10h	30%	-
16h	45%	93%

The cyclic and acyclic products were also obtained when **1** was reacted with **2e** under similar conditions.

Table 3. The Reaction of **1** with Alkyne in the Presence of LTA[a]

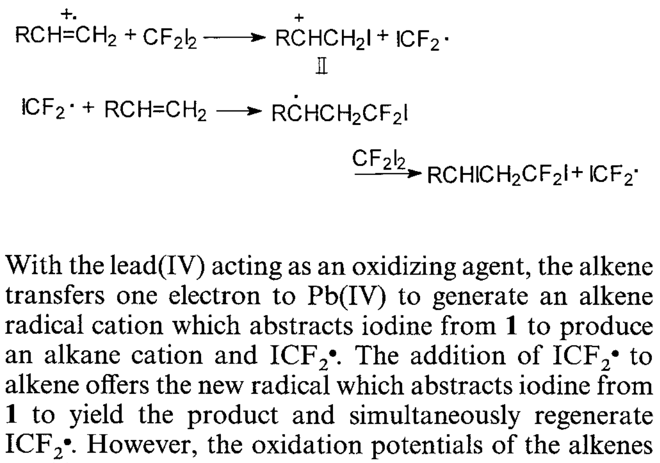
Entry	Alkyne	Solvent	Temp (°C)	Time (h)	Conv. (%)	Product	Yield[b] (%)	Ratio E/Z
1	**18a**	EtOH	80	20	80	**19aa**	78	90:10
2		MeOH	60	25	80	**19ab**	80	89:11
3		BuOH	80	24	78	**19ac**	72	87:13
4	**18b**	EtOH	80	20	80	**19ba**	76	92:8
5	**18c**	EtOH	80	25	78	**19ca**	67	86:14
6	**18d**	EtOH	80	20	83	**19da**	70	72:28
7		MeOH	60	23	81	**19db**	64	70:30

[a] **1**: **18**: LTA = 1:2:0.05.
[b] Isolated yields based on the conversion of **1**.



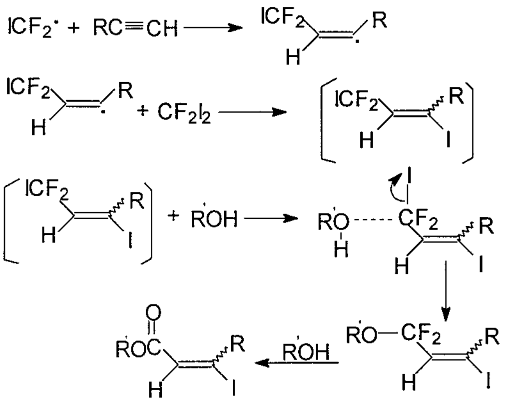
Conv.: 80%, Yield: 95%, 3d:3d'=4:1

The conversions of **1** in these reactions were not as high as those in HOAc, probably due to the poor solubility of PbO_2 in DG. The results possibly indicate not only the exclusion of the necessity of methyl radical initiation, but also the presence of free radical intermediates through electron transfer mechanism on the bases of the formation of both cyclic and acyclic products from **2e**.[38] But what is the initiation step and how can the iododifluoromethyl radical be produced by the strong oxidant, LTA? It would be possible that similar to the initiation mechanism proposed by Thomas et al. in the reaction of styrene with HOAc in the presence of LTA, the mechanism of the reaction of **1** with alkenes may also involve the transient radical cation intermediate as follows.


$$RCH{=}CH_2 \xrightarrow{\text{Lead(IV)}} \overset{+\cdot}{RCH{=}CH_2}\ \text{I} + Pb(III)$$
$$\overset{+\cdot}{RCH{=}CH_2} + CF_2I_2 \longrightarrow \overset{+}{R}CHCH_2I + ICF_2\cdot\quad \text{II}$$
$$ICF_2\cdot + RCH{=}CH_2 \longrightarrow R\dot{C}HCH_2CF_2I \xrightarrow{CF_2I_2} RCHICH_2CF_2I + ICF_2\cdot$$

With the lead(IV) acting as an oxidizing agent, the alkene transfers one electron to Pb(IV) to generate an alkene radical cation which abstracts iodine from **1** to produce an alkane cation and $ICF_2\bullet$. The addition of $ICF_2\bullet$ to alkene offers the new radical which abstracts iodine from **1** to yield the product and simultaneously regenerate $ICF_2\bullet$. However, the oxidation potentials of the alkenes used here seem too high (e.g. ethene, E°_{ox}, 2.90; but-1-ene, E°_{ox}, 2.79 V vs $Ag^+/AgNO_3$)[39] to generate the alkene radical cation by LTA, although the polar solvent can certainly compensate for this unfavorableness to some extent. It is also uncertain if **1** could be oxidized by LTA, although it is known that the R_FI (E°_{ox} = ca 1.68 V vs. SCE.) were able to give radical cation under electrochemical oxidation conditions.[40] Therefore, it apparently needs more work to elucidate the reaction mechanism. For the electron-deficient fluorinated olefins, due to their clean reactions with **1** only in HOAc, a simple methyl radical initiation path is most likely.

The radical $ICF_2\bullet$ however generated adds to alkyne, and subsequent iodine abstraction leads to the formation of the adduct, which readily undergoes alcoholysis to the non-fluorinated β-iodo-α,β-unsaturated carboxylic ester.



Further mechanistic studies on the addition reactions by LTA and by other oxidants are in progress.

Boiling (melting) points are uncorrected. IR spectra were recorded on a Shimadzu IR-440 spectrometer. ^{19}F NMR spectra were obtained on a Varian EM-360 spectrometer (60 MHz) using TFA as an external standard, downfield shifts being designated as negative. ^1H NMR spectra were carried out on a FX-90Q (90 MHz) instrument with TMS as an internal standard. Mass spectra were measured on a Finnigan GC-MS-4021 mass spectrometer. All reactions were routinely monitored with the aid of TLC or ^{19}F NMR spectroscopy.

Reaction of 1 with Electron-Rich Alkenes 2 in the Presence of LTA; General Procedure:

Under N_2, a mixture of CF_2I_2 (**1**, 1.5 g, 5 mmol), alkene (15 mmol) and LTA (5 mol %) in DG (5 mL) was placed in a 25-mL two-necked flask equipped with a magnetic stirrer, a thermometer and reflux condenser (for ethene, a 100-mL stainless autoclave was used as a container). Then the mixture was heated to 60 °C for 4–7 h. When the reaction was over, the solution was poured into H_2O (5 mL) and extracted with Et_2O (3 × 20 mL). The extracts were washed with H_2O, dried ($MgSO_4$), and evaporated in vacuo. The crude product was subjected to column chromatography to give **3**.

1,1-Difluoro-1,3-diiodoheptane (**3a**):[29] yellow oil.

IR (film): ν = 2900, 1160, 1060, 900 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 1.00 (t, J = 6 Hz, 3 H), 1.20–2.20 (m, 6 H), 2.80–3.50 (m, 2 H), 4.30 (m, 1 H).

^{19}F NMR ($CDCl_3$): δ = −41.3 (m, 2 F).

MS: m/z (%) = 388 (M^+, 6.00), 133 ($m^+ - HI - I$, 100.00).

4,4-Difluoro-2,4-diiodobutan-1-ol (**3b**): yellow oil.

IR (film): ν = 3300, 1700, 1420, 1040, 980, 900, 760 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 3.13–3.80 (m, 3 H), 4.05 (d, J = 8 Hz, 2 H), 4.40–4.70 (m, 1 H).

^{19}F NMR ($CDCl_3$): δ = −40.3 (m, 2 F).

MS: m/z (%) = 362 (M^+, 1.24), 187 (100.00), 127 (I^+, 21.91).

HRMS: $C_4H_6F_2I_2O$, Calcd: 361.8476, Found: 361.8455.

4,4-Difluoro-2,6-diiodoheptane-1,7-diol (**4b**): yellow oil.

IR (film): ν = 3300, 2900, 1700, 1420, 1360, 1020 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 2.50–3.20 (m, 4 H), 3.56 (s, 2 H), 3.95 (d, J = 8 Hz, 4 H), 4.30–4.63 (m, 2 H).

^{19}F NMR ($CDCl_3$): δ = 18.20 (m, 2 F).

MS: m/z (%) = 420 (M^+, 1.57), 293 ($M^+ - I$, 6.15), 255 (84.17), 127 (45.95), 85 (100.00).

HRMS: $C_7H_{12}F_2I_2O$, Calcd: 419.8895, Found: 419.8891.

1,1-Difluoro-1,3-diiodo-3-trimethylsilylpropane (**3c**): yellow liquid.

IR (film): ν = 2950, 1410, 1340, 1260, 1180, 1080, 980, 840 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 0.23 (s, 9 H), 2.60–3.23 (m, 3 H).

^{19}F NMR ($CDCl_3$): δ = −42.2 (m, 2 F).

MS: m/z (%) = 404 (M^+, 5.63), 277 (M^+-I, 4.78), 185 (100.00).

Anal. Calcd for: $C_4H_6F_2I_2O$, C: 17.82, H: 2.97, Found: C: 18.11, H: 3.04.

3,3-Difluoro-1,5-diiodo-1,5-trimethylsilylpentane (**4c**):[29] yellow oil.

IR (film): $\nu = 1250, 1180, 1075\ cm^{-1}$.

^1H NMR ($CDCl_3$): $\delta = 0.20$ (s, 18H), 1.26–2.70 (m, 4H), 3.5 (t, $J = 7$ Hz, 2H).

^{19}F NMR ($CDCl_3$): $\delta = 16.30$ (m, 2F).

MS: m/z (%) = 504 (M^+, 1.98), 377 (M^+-1, 2.88), 77 (53.11), 73 (100.00).

4-Ethoxy-1,1-difluoro-1,3-diiodobutane (**3d**): yellow liquid.

IR (film): $\nu = 3000, 2900, 1100, 980\ cm^{-1}$.

^1H NMR ($CDCl_3$): $\delta = 1.20$ (t, $J = 6$ Hz, 3H), 2.80–3.23 (m, 3H), 3.40–3.66 (m, 4H), 4.23 (m, 1H).

^{19}F NMR ($CDCl_3$): $\delta = -42.6$ (m, 2F).

MS: m/z (%) = 391 (M^++1, 0.24), 390 (M^+, 2.10), 345 ($M^+-C_2H_5O$, 11.20), 217 ($M^+-HI-C_2H_5O$, 100.00), 215 (75.29).

Anal. Calcd for: $C_6H_{10}F_2I_2O$, C: 18.46, H: 2.56, Found: C: 18.72, H: 2.60.

3-(2,2-Difluoro-2-iodoethyl)-4-(iodomethyl)tetrahydrofuran (**3e**): mp 68–69 °C.

IR (film): $\nu = 2850, 2700, 1425, 1240, 1210, 1175, 1045, 1015, 910, 880\ cm^{-1}$.

^1H NMR ($CDCl_3$): $\delta = 2.10$–4.40 (m, 10H).

^{19}F NMR ($CDCl_3$): $\delta = -40.0$ (m, 2F).

MS: m/z (%) = 402 (M^+, 0.04), 275 (M^+-I, 43.10), 127 (I^+, 69.00), 99 (100.00).

Anal. Calcd for: $C_7H_{10}F_2I_2O$, C: 20.90, H: 2.49, Found: C: 20.80, H: 2.38.

4-Allyloxy-1,1-diiodo-1,3-diiodobutane (**3e′**): yellow liquid.

IR (film): $\nu = 2850, 1710, 1420, 1350, 1220, 1060, 980, 860, 760\ cm^{-1}$.

^1H NMR ($CDCl_3$): $\delta = 2.80$–3.43 (m, 2H), 3.56–3.76 (m, 3H), 4.00 (m, 1H), 4.13–4.33 (m, 1H), 5.10–5.30 (m, 2H), 5.63–6.03 (m, 1H).

^{19}F NMR ($CDCl_3$): $\delta = -41.6$ (m, 2F).

MS: m/z (%) = 402 (M^+, 1.36), 345 ($M^+-CH_2{=}CHCH_2O$, 40.34), 217 ($ICF_2CH_2CH{=}CH^+$, 100), 215 (54.85).

Anal. Calcd for: $C_7H_{10}F_2I_2O$, C: 20.90, H: 2.49, Found: C: 20.85, H: 2.35.

3,3-Difluoro-1,5-difluoropentane (**4f**): mp 63–65 °C.

IR (film): $\nu = 1020$–$1200\ cm^{-1}$.

^1H NMR ($CDCl_3$): $\delta = 2.17$–2.83 (m, 4H), 3.17 (t, $J = 8$ Hz, 4H).

^{19}F NMR ($CDCl_3$): $\delta = 23.7$ (m, 2F).

MS: m/z (%) = 360 (M^+, 2.45), 233 (M^+-I, 100), 213 (M^+-I-HF, 18.95), 85 (21.58), 77 (26.35).

Anal. Calcd for: $C_5H_8F_2I_2$, C: 16.67, H: 2.22, Found: C: 16.26, H: 2.13.

1-Difluoroiodomethyl-2-iodocyclohexane (**3g**):[28] liquid.

IR (film): $\nu = 2920, 2860, 1715, 1450, 1360, 1330, 1300, 1240\ cm^{-1}$.

^1H NMR ($CDCl_3$): $\delta = 2.20$–2.70 (m, 9H), 4.63–4.93 (*trans*, m, 0.7H), 5.20 (*cis*, m, 0.3H).

^{19}F NMR ($CDCl_3$): $\delta = -34.0$ (*trans*, m, 2F), -26.2 (*cis*, m, 0.3F).

MS: m/z (%) = 387 (M^++1, 0.36), 386 (M^+, 4.58), 259 (M^+-I, 35.12), 131 (M^+-HI-I, 100).

LTA Induced Reaction of 1 with Per(poly)fluoroalkyl Ethenes; Typical Procedure:

To HOAc (10 mL), were added CF_2I_2 (**1**, 1.5 g, 5 mmol), **5** (10 mmol) and LTA (5 mol %). The stirring solution was heated to 70 °C for 7 h. The mixture was then poured into H_2O (10 mL) and extracted with Et_2O (3 × 20 mL). The extracts were washed with satd aq $NaHCO_3$, dil HCl, brine, dried ($MgSO_4$), and evaporated in vacuo. The crude product was subjected to column chromatography to give **7**.

2H,2H,3H-Perfluoro-7-chloro-1,3-diiodoheptane (**7**): liquid.

IR (film): $\nu = 1420, 1260, 1200, 1140, 1080, 1000, 920, 840, 740, 520\ cm^{-1}$.

^1H NMR ($CDCl_3$): $\delta = 2.66$–2.74 (m, 2H), 4.20–4.80 (m, 1H).

^{19}F NMR ($CDCl_3$): $\delta = -39.95$ (m, 2F), -9.6 (s, 2F), 27.0 (m, 2F), 39.0 (s, 2F), 42.0 (s, 2F).

MS: m/z (%) = 439 (M^+-I, 100), 441 (32.00), 213 (26.98), 177 (42.82), 127 (29.25), 85 (44.63), 77 (39.75).

HRMS: $C_7H_3ClF_{10}I_2$, Calcd: 565.7853, Found: 565.7845.

2H,2H,3H-Perfluoro-7-bromo-1,3-diiodoheptane (**8**): liquid.

IR (film): $\nu = 1420, 1370, 1300, 1270, 1060$–$1160, 985, 920, 760, 700, 640\ cm^{-1}$.

^1H NMR ($CDCl_3$): $\delta = 2.73$–3.73 (m, 2H), 4.30–4.70 (m, 1H).

^{19}F NMR ($CDCl_3$): $\delta = -39.6$ (m, 2F), -17.6 (s, 2F), 24.2 (m, 2F).

MS: m/z (%) = 511 (M^+, 25.79), 509 (26.57), 383 (29.26), 335 (55.40), 302 (57.88), 177 (100), 131 (86.84), 129 (89.01), 127 (81.48), 77 (81.74).

HRMS: $C_5H_3BrF_6I_2$, Calcd: 509.7412, Found: 509.7407.

LTA Induced Reaction of 1 with Fluoroethenes; General Procedure:

A mixture of HOAc (10 mL), LTA (10 mol %), CF_2I_2 (**1**, 3 g, 10 mmol) and fluoroethene was charged into a 100-mL autoclave. The contents were then heated at 60–70 °C for 14 h. After usual workup the product was obtained.

1,1,3,3-Tetrafluoro-1,3-diiodopropane (**10**): bp 62–64 °C/30 Torr.

IR (film): $\nu = 1420, 1360, 1340, 1150$–$1200, 1120, 1070, 980\ cm^{-1}$.

^1H NMR ($CDCl_3$): $\delta = 3.90$ (m, 2H).

^{19}F NMR ($CDCl_3$): $\delta = -38.8$ (m, 4F).

MS: m/z (%) = 368 (M^+, 1.36), 241 (M^+-I, 100), 177 (ICF_2^+, 52.40), 127 (9.81).

HRMS: $C_3H_2F_4I_2$, Calcd: 367.8182, Found: 367.8221.

Tetrafluoroallene (11):[31]

Into a three-necked 25 mL-flask equipped with a magnetic stirrer, a dropping funnel and reflux condenser connected to a dry ice trap was added K_2CO_3 (2.8 g, 20 mmol) and CH_3CN (10 mL). On heating at 60 °C, **10** (5.5 g, 15 mmol) was added dropwise over 4 h. The gas was collected in the trap (1.4 g, 82 %); bp −37.0 °C.

^{19}F NMR ($CDCl_3$): $\delta = 14.0$ (s, 4F).

Perfluoro-1,3-diiodopropane (**13**): bp 40 °C/30 Torr.

IR (film): $\nu = 1245, 1160$–$1200, 1120, 1060, 940, 905\ cm^{-1}$.

^{19}F NMR ($CDCl_3$): $\delta = -17.3$ (s, 4F), 28.0 (s, 2F).

MS: m/z (%) = 404 (M^+, 10.38), 277 (M^+-I, 100), 177 (ICF_2^+, 43.60), 149 (34.73), 43 (68.16).

HRMS: $C_3F_6I_2$, Calcd: 403.7994, Found: 403.7966.

Perfluoro-1,3-diiodobutane (**15**): bp 65 °C/30 Torr.

IR (film): $\nu = 1270, 1220, 1150, 1110, 1080, 900\ cm^{-1}$.

^{19}F NMR ($CDCl_3$): $\delta = -21.0$ (s, 2F), -5.0 (s, 3F), 19.5 (s, 2F), 67.7 (s, 1F).

MS: m/z (%) = 327 (M^+-I, 3.29), 254 (24.50), 128 (42.39), 73 (48.19), 69 (48.94), 55 (54.23), 45 (39.40), 44 (98.45), 43 (100).

HRMS: $C_4F_8I_2$, Calcd: 326.89 ($M+-I$), Found: 326.8956.

Perfluoro [1,1-dichloro-4-(1,3-diiodopropoxy)]butane (**17**): liquid.

IR (film): $\nu = 1330, 1090$–$1210, 1045, 900, 840\ cm^{-1}$.

^{19}F NMR ($CDCl_3$): $\delta = -20.5$ (m, 2F), -9.5 (s, 1F), 26.0 (m, 2F), 38.0 (s, 2F), 45.0 (s, 2F).

MS: m/z (%) = 654 (M^++2, 3.10), 652 (M^+-1, 4.80), 385 (11.12), 277 (28.23), 253 (70.99), 251 (100), 177 (31.44), 85 (51.77).

Anal. Calcd for: $C_7F_{12}ClI_2O$, C: 12.86, F: 34.92, Found: C, 12.65, F: 35.59.

Reaction of 1 with Alkynes in the Presence of LTA; General Procedure:

Under a N_2, a mixture of CF_2I_2 (**1**, 1.5 g, 5 mmol), alkyne (10 mmol), LTA (5 mol%) and ROH (5 mL) was charged into a two-necked flasked equipped with a thermometer, magnetic stirrer and a reflux condenser. Then the mixture was heated at 80 °C for 20–25 h. After the reaction was over, the solution was poured into H_2O (5 mL) and extracted with Et_2O (3 × 20 mL). The extracts were washed with H_2O, dried ($MgSO_4$), and evaporated in vacuo. The crude product was subjected to column chromatography to give **19**.

Ethyl (E/Z)-3-Iodohept-2-enoate (**19aa**): liquid.

IR (film): ν = 3400, 3000, 1720, 1620, 1180, 1120, 860 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = (*E*): 0.93 (t, *J* = 7 Hz, 3 H), 1.13–1.48 (m, 7 H), 3.06 (t, *J* = 7 Hz, 2 H), 4.06 (q, *J* = 7 Hz, 2 H), 6.53 (s, 1 H); (*Z*): 0.93 (t, *J* = 7 Hz, 3 H), 1.13–1.48 (m, 7 H), 2.70 (t, *J* = 7 Hz, 2 H), 4.06 (q, *J* = 7 Hz, 2 H), 6.24 (s, 1 H).

MS: *m*/*z* (%) = 237 (M^+ – EtO, 25.49), 155 (M^+ – I, 34.57), 81 (M^+ – HI–COOEt, 60.44), 57 ($C_4H_9^+$, 100.00), 55 (67.42), 43 ($C_3H_7^+$, 78.97).

Anal. Calcd for: $C_9H_{15}IO_2$, C: 38.30, H: 5.32, Found: C: 38.09, H: 5.37.

Methyl (E/Z)-3-Iodohept-2-enoate (**19ab**): liquid.

IR (film): ν = 2950, 2860, 1720, 1610, 1420, 1340, 1320, 1180, 1120, 980 cm^{-1}.

^1H NMR ($CDCl_3$): δ = (*E*): 0.96 (t, *J* = 7 Hz, 3 H), 1.13–1.63 (m, 4 H), 3.03 (t, *J* = 7 Hz, 2 H), 3.60 (s, 3 H), 6.53 (s, 1 H); (*Z*): 0.96 (t, *J* = 7 Hz, 3 H), 1.13–1.63 (m, 4 H), 2.66 (t, *J* = 7 Hz, 2 H), 3.65 (s, 3 H), 6.26 (s, 1 H).

MS: *m*/*z* (%) = 268 (M^+, 11.35), 141 (M^+ – I, 34.57), 81 (85.24), 69 (100.00).

HRMS: $C_8H_{13}IO_2$, Calcd: 267.9960, Found: 268.0007.

Butyl (E/Z)-3-Iodohept-2-enoate (**19ac**): liquid.

IR (film): ν = 2950, 1860, 1720, 1620, 2460, 1180 cm^{-1}.

^1H NMR ($CDCl_3$): δ = (*E*): 0.93–1.66 (m, 14 H), 3.19 (t, *J* = 7 Hz, 2 H), 4.09 (t, *J* = 7 Hz, 2 H), 6.59 (s, 1 H); (*Z*): 0.93–1.66 (m, 14 H), 2.69 (t, *J* = 7 Hz, 2 H), 4.13 (t, *J* = 7 Hz, 2 H), 6.23 (s, 1 H).

MS: *m*/*z* (%) = 312 (M^+ + 2, 0.65), 311 (M^+ + 1, 0.45), 310 (M^+, 31.90), 254 (51.22), 255 (43.00), 237 (82.47), 127 (97.83), 81 (100.00).

HRMS: $C_{11}H_{19}IO_2$, Calcd: 183.1385 (M^+ – I), Found: 183.1365.

Ethyl (E/Z)-3-Iodooct-2-enoate (**19ba**): liquid.

IR (film): ν = 2900, 1720, 1620, 1460, 1370, 1160, 1020, 880 cm^{-1}.

^1H NMR ($CDCl_3$): δ = (*E*): 0.85 (t, *J* = 7 Hz, 3 H), 1.13–1.56 (m, 9 H), 3.03 (t, *J* = 7 Hz, 2 H), 4.03 (q, *J* = 7 Hz, 2 H), 6.50 (s, 1 H); (*Z*): 0.86 (t, *J* = 7 Hz, 1.13–1.56 (m, 9 H), 2.72 (t, *J* = 7 Hz, 2 H), 4.03 (q, *J* = 7 Hz, 2 H), 6.22 (s, 1 H).

MS: *m*/*z* (%) = 251 (2.16), 205 (35.77), 91 (100.00).

Anal. Calcd for: $C_{10}H_{17}IO_2$, C: 40.54, H: 5.74, Found: C: 40.49, H: 5.86.

Ethyl (E/Z)-3-Iodo-3-phenylprop-2-enoate (**19ca**): liquid.

IR (film): ν = 3000, 1720, 1600, 1440, 1180, 1020, 960, 860 cm^{-1}.

^1H NMR ($CDCl_3$): δ = (*E*): 0.90 (t, *J* = 7 Hz, 3 H), 3.80 (q, *J* = 7 Hz, 2 H), 6.66 (s, 1 H), 7.16 (m, 5 H); (*Z*): 1.20 (t, *J* = 7 Hz, 3 H), 4.10 (q, *J* = 7 Hz, 2 H), 6.46 (s, 2 H), 7.16 (m, 5 H).

MS: *m*/*z* (%) = 304 (M^+ + 2, 6.73), 303 (M^+ + 1, 48.41), 302 (M^+, 89.80), 257 ($M^+ - C_2H_5O$, 31.11), 175 (M^+ – I, 100.00), 147 (M^+ – I – CO, 27.67), 102 ($M^+ - ICO_2Et$, 35.43).

HRMS: $C_{11}H_{11}IO_2$, Calcd: 301.9804, Found: 301.9839.

Ethyl (E/Z)-3-Iodo-4-methoxybut-2-enoate (**19da**): liquid.

IR (film): ν = 3000, 2900, 2850, 1720, 1620, 1450, 1370, 1330, 1200, 1100, 1040 cm^{-1}.

^1H NMR ($CDCl_3$): δ = (*E*): 1.30 (t, *J* = 7 Hz, 3 H), 3.30 (s, 3 H), 4.13–4.26 (m, 4 H), 6.63 (s, 1 H); (*Z*): 1.30 (t, *J* = 7 Hz, 3 H), 3.30 (s, 3 H), 3.85 (s, 2 H), 4.20 (q, *J* = 7 Hz, 2 H), 6.32 (s, 1 H).

MS: *m*/*z* (%) = 272 (M^+ + 2, 0.89), 271 (M^+ + 1, 8.30), 2.70 (M^+, 100.00), 143 (M^+ – I, 64.54), 98 ($M^+ - I - CH_2OCH_3$, 66.93).

HRMS: $C_7H_{11}IO_3$, Calcd: 269.9753, Found: 269.9760.

Methyl (E/Z)-3-Iodo-4-methoxybut-2-enoate (**19db**): liquid.

IR (film): ν = 3000, 2950, 2850, 1730, 1640, 1440, 1300, 1200, 1170, 1000, 920 cm^{-1}.

^1H NMR ($CDCl_3$): δ = (*E*): 3.44 (s, 3 H), 3.77 (s, 3 H), 4.14 (s, 2 H), 6.67 (s, 1 H); (*Z*): 3.44 (s, 3 H), 3.81 (s, 3 H), 3.84 (s, 2 H), 6.33 (s, 1 H).

MS: *m*/*z* (%) = 257 (M^+ + 1, 15.84), 256 (M^+, 100.00), 129 (M^+ – I, 80.13), 101 (M^+ – I – CO, 61.15).

HRMS: $C_6H_9IO_3$, Calcd: 255.9597, Found: 255.9603.

The authors thank Professors W.-Y. Huang and X.-K. Jiang for their encouragement. Financial support of this work by the National Natural Science Foundation of China is gratefully acknowledged.

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