(12) G. Levin, C. Sutphen, and M. Swarc, *J. Am. Chem. Soc.*, **94**, 2652 (1972).

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$$2(Py^{+}TCNQ^{-}\cdot) + O_2 \rightleftarrows Py^{+}O_2^{-}\cdot + Py^{+}TCNQ^{-}\cdot TCNQ^{0}$$

$$Py^{+}TCNQ^{-}\cdot + Py^{+}O_2^{-}\cdot \rightarrow Py^{+}DCTC^{-} + Py^{+-}OCN$$

It was shown to be thermodynamically unfavorable by calculation of K_{eq} for the first step, reduction of O_2 by $TCNQ^{-}\cdot$.[11,15] K_{eq} is approximately 10^{-18}.

(15) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems", Marcel Dekker, New York, N.Y., 1970, pp 497–505.

(16) It should also be noted that oxidation of $TCNQ^{-}\cdot$ by Py^{+} as a source of $TCNQ^{0}$, a process observed by Ashwell and co-workers in bipyridyl tetracyano-*p*-quinodimethane salts,[17] does not appear to be operative here. It cannot account for $TCNQ^{2-}$ formation and no dihydropyridine derivatives nor their degradation products are observed.

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Syntheses with *F*-Alkyl Radicals from *F*-Alkyl Iodides: Amine and Amine Salt Induced Addition to Alkenes[1]

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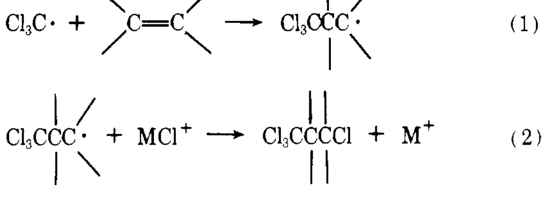
Free radical induced reactions of 1-iodo-*F*-alkanes (R_FI) with diallyl ether, *N*-methyldiallylamine, and 1-heptene, using an amine or amine salt as initiator at 120–140 °C, are described. Copper(I) or copper(II) ions appear to inhibit the reaction, while copper ion and an amine or amine salt in no case gave faster reaction than amine or amine salt alone. These results are contrasted with CCl_4 additions which are strongly accelerated by this initiating system. The best initiator found for R_FI addition was benzyltriethylammonium chloride, which gave 94% conversion of diallyl ether to adducts at 135 °C in 3 h. An azonitrile initiator would be preferred, however, for most R_FI additions which can be carried out at 50–110 °C.

Free radical addition of *F*-alkyl iodides (R_FI) to unsaturated compounds is by now a well-known process.[2] Azonitrile initiators, peroxides, and of course heat and irradiation have been used to initiate these reactions. Other polyhalogenated substances such as CCl_4 also add to double bonds and one of the best methods employs a metal salt–amine system of initiation.[3,4] Monomers such as acrylate esters, which telomerize with CCl_4, gave simple 1:1 adducts in high yield when metal salts, an amine, and amine hydrochloride are used. This was attributed to more efficient transfer from a metal complex according to the simplified mechanism, in which M^{+} represents a metal ion, e.g., Cu^{+} or Fe^{2+}.[3b] The amine salt apparently catalyzes the chain transfer step 2, making it faster than direct transfer on CCl_4.[3b] Carbon tetrachloride and 1,6-heptadiene gave a five-membered ring cyclization product, confirming the free radical nature of the process.[5] Peroxides[6] or other free radical generating systems[7] have subsequently been used in similar additions of CCl_4 to diallyl ether[6] or for the telomerization of diallylamine derivatives.[7–9] For reactions of R_FI initiated by copper salts or amines, the nature of the process is not clear, as copper(II) iodide does not appear to exist. Thus, Burton and Kehoe[10] in a study of several polyhalogenated compounds refluxed 1-octene and 1-iodo-*F*-propane with copper(I) chloride (1%) and 2-aminoethanol (50 mol %) and isolated both adduct and dehydrohalogenated product in modest yield.[11] Jaeger[12] heated a mixture of R_FI and various alkenes with a catalytic amount of copper or other metal salt and an amine at 140–180 °C. However, at these temperatures thermally induced addition of R_FI is likely to occur.[13,14]



(1)

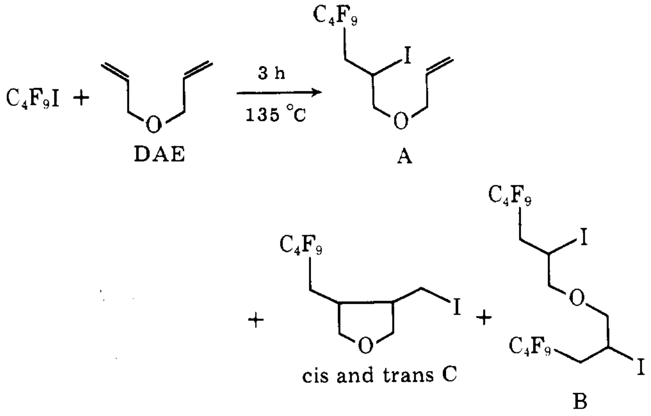
(2)

$$M^{+} + Cl_3C—Cl \longrightarrow MCl^{+} + Cl_3C\cdot \qquad (3)$$

It is the purpose of this paper to describe new and more efficient methods for the initiation of free radical additions of R_FI, involving amines and amine derivatives. The role of amine and copper salt in reactions of CCl_4 will be contrasted with reactions of R_FI. Preparation and stereochemistry of cyclization products from R_FI and diallyl ether will be described in some detail.

Results and Discussion

Reaction of 1-iodo-*F*-butane with diallyl ether (DAE) was chosen for initial study because the free radical nature of the process could be readily proved by the structure of the prod-



DAE

A

cis and trans C

B

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Table I. Copper/Amine or Amine Salt Induced Addition of 1-Iodo-*F*-butane to Diallyl Ether[a]

expt	mole ratio DAE:R_FI	catalyst system mol % on DAE CuCl	amine	conversion to adducts, % A	B	C	total
1	1.016	none	none	5.20		25.1	30.3
2[b]	0.961	none	none	4.23		19.9	24.1
3[b]	0.961	4.04	none	2.86		13.4	16.2
4	0.961	2.02	0.44[c]	4.59	0.27	28.3	33.2
5[b,d]	0.923	none	3.75[c]	6.9		46.5	53.4
6	0.842	4.14	5.15[e]	9.52	0.65	37.5	47.7
7[f]	0.869	3.75[g]	4.81[e]	3.50	0.02	8.4	12.0
8[b]	0.929	none	3.79[h]	7.27	3.13	65.0	75.4
9[b]	1.046	none	15.1[h]	4.21	1.62	62.4	68.2
10[f]	0.860	none	4.28[h]	5.50	1.62	69.0	76.1
11[f]	0.869	none	6.32[i]	5.16	3.51	67.2	75.9

[a] All experiments run in a sealed tube, with a magnet bar stirring, heated in constant temperature bath at 135 °C for 3 h. Conversion (mole of adduct/mol of limiting reactant) was determined by gas chromatography. [b] Alumina (0.30 g) added. [c] 2-Aminoethanol. [d] 1-Iodo-*F*-hexane used and heated at 130 °C for only 2 h. [e] Diethylamine hydrochloride. [f] Acetonitrile (2 mol) used as solvent. [g] $CuCl_2$ dihydrate. [h] Piperidine. [i] Et_3N.

ucts and because it was possible to run these reactions under controlled and reproducible conditions.

Table I lists experiments in which amines or an amine salt and copper ion catalyzed formation of linear adduct A, cis and trans cyclic adducts C, and a linear bis adduct B. In the absence of catalysts some thermal reaction (24–30%) occurred at 135 °C in 3 h. 2-Aminoethanol, diethylammonium hydrochloride, and acetonitrile solvent were used, in separate runs, to demonstrate that, unlike CCl_4 additions which are strongly catalyzed by this system,[3] free radical addition of 1-iodo-*F*-butane is not accelerated by either copper(I) or -(II) ions. Thus, the thermal reaction was actually suppressed by either cuprous chloride alone or cupric chloride and an amine salt in homogeneous solution (runs 3 and 7), and copper(II) more so than copper(I) ion. For free radical additions of CCl_4 the cupric salt was more effective than the cuprous salt as a catalyst.[3] Primary, secondary, and tertiary amines catalyzed the reaction at 135 °C. It is clear from these results, therefore, that it is the amine and not the copper salt or a copper–ammine complex which is responsible for initiating the chain reaction.

The reaction was extended to 1-heptene and 1-iodo-*F*-butane and as much as 72% of $CF_3(CF_2)_3CH_2CHI(CH_2)_4CH_3$ (D) was formed in 17 h at 125 °C, using 7.68% of pyridine. A lower temperature limit of 110 °C was found, and above 140 °C, appreciable decomposition occurred. Reaction of 1-heptene and 1-iodo-*F*-butane catalyzed by triethylamine is graphically presented in Figure 1. Other experiments are listed in Table VI (Experimental Section).

Diallylcyanamide and a 1-iodo-*F*-alkane mixture reacted exothermically at 135 °C in the presence of copper(I) chloride and 2-aminoethanol. The adduct was identical to that obtained by azonitrile-initiated reaction at 70 °C, in quantitative yield.[15]

Initiation by Charge-Transfer Complexes. An exothermic reaction occurred upon mixing of mole amounts of 1-iodo-*F*-hexane and *N*-methyldiallylamine (NMDA) at room temperature, giving an unstable charge-transfer complex. Such complexes from simple amines and R_FI have been recently carefully investigated.[16] However, such a charge transfer complex cannot be responsible for the addition of R_FI to the double bond of alkenes, since only at higher temperature and long reaction time was any insolable addition product formed. As shown previously[15] addition of R_FI to diallylamine did not occur at 70 °C. Using an azonitrile as initiator, addition took place but the adduct reacted further with another molecule of amine (acting as a nucleophile) to give an amine salt. Reaction of 1-iodo-*F*-hexane and NMDA at 100–110 °C gave a solid salt very similar to that obtained (in quantitative yield at 70 °C) with azonitrile initiator having infrared bands expected for the salt group R_4N^+ at 2700–2500 cm^{-1}.

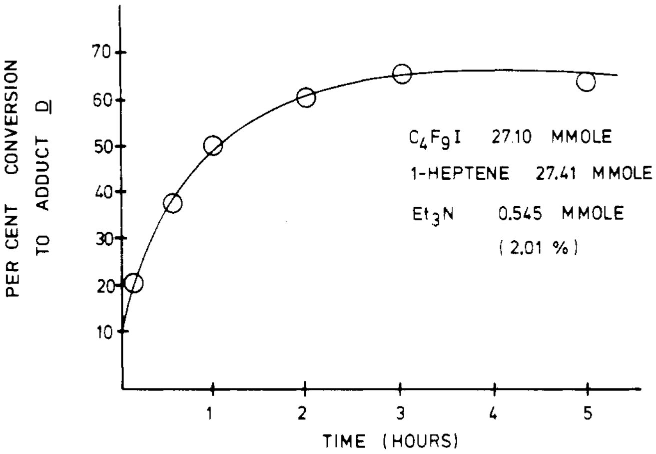
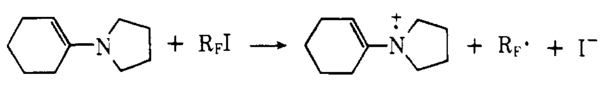


Figure 1. Triethylamine-catalyzed addition of 1-iodo-*F*-butane to 1-heptene.

A charge transfer complex between R_FI, an enamine, and HI was recently isolated by Cantacuzene, Wakselman, and Dorme, who observed rapid, room temperature addition of R_FI to the double bond of enamines, without initiator or UV irradiation.[17] Formation of a radical cation was suggested as an initiation step:



The complex was implicated in the free radical chain addition of R_FI to ynamines, but no complex formation occurred with an ammonium salt such as $MeEt_3N^+I^-$.

Quaternary Ammonium Salt Induced Reaction. In all cases in which an amine was used as initiator or as reactant, a solid amine salt was formed, possibly by reactions such as: (1) alkylation of the amine with some of the adduct formed by thermally induced reaction; (2) dehydrohalogenation of the adduct; and (3) dealkylation of another amine salt. Could it be true that thermolysis of an amine salt gives free radicals which initiate the addition reaction?

It was found that indeed quaternary ammonium salts such as benzyltriethylammonium chloride (BTEA) or tetrabutylammonium iodide (TBAI) did initiate reaction at 135 °C.

Table II. Quaternary Ammonium Salt Induced Addition of 1-Iodo-*F*-butane to Diallyl Ether[a]

expt	mole ratio DAE / R_FI	catalyst system, mol % on DAE	conversion to adducts, % A	B	C	total
12	0.802	BTEA,[b] 5.93	13.1	4.8	60.4	78.3
13	2.088	BTEA, 4.32	16.2	0.69	77.2	94.1
14[c]	1.156	BTEA, 4.03	9.56	1.26	60.8	72.4[d]
15	2.088	TBAI,[e] 4.29	7.46	0.63	67.5	75.6
16	1.89	BTEA, 3.29	13.5	0.74	73.2	87.4

[a] All experiments run in sealed tube, with magnet bar stirring; heated in constant temperature bath at 135 °C for 3 h. [b] BTEA is benzyltriethylammonium chloride. [c] 1-Iodo-*F*-hexane used instead of 1-iodo-*F*-butane. [d] The product was also distilled, giving 69% of theory of adducts. [e] TBAI is tetrabutylammonium iodide.

Table III. Reaction of 1-Iodo-*F*-butane and 1-Heptene Induced by Quaternary Ammonium Salts[a]

expt.	mole ratio hept/R_FI	catalyst system, mol % on 1-heptene	temp, °C	time, h	conversion % of D
17	1.802	BTEA, 2.58	120	3	37.6
18	1.207	TCAC,[b] 3.19	120	16	50.6[c]
19	1.802	TBAI, 2.25	135	5.5	82.2[d]
20	1.207	TCAC,[b] 3.19	135	3	67.4

[a] All experiments run as in Table II, except where noted. [b] TCAC is tricaprylmethylammonium chloride. [c] Impurities appeared at 6.0 and 7.3 min retention time, 2.68%. [d] Impurities (2.88 and 4.34%) and a dark brown solid also.

Optimization of reaction conditions and structure of salt has not yet been done but the few experiments showed the value of these initiators (Table II).

At a 2:1 reactant ratio using BTEA there was nearly quantitative conversion of 1-iodo-*F*-butane to adducts A, B, and C and recovery of unreacted DAE. Less than 3% of 1-iodo-*F*-butane remained unreacted, about 3% of 1-hydryl-*F*-butane was formed, and adduct peaks comprised at least 94% of theory. At 0.8 to 1.16 mole ratio (using a lower level of BTEA) adducts totaled 87.4% of theory. At the higher reactant ratios yield of bisadduct B was markedly reduced, as expected from previous work.[18] Clearly, reactant ratio had an important effect on distribution and amount of products formed.

Toluene was not observed from reactions employing BTEA but about 2–4% of (presumably) dehydrohalogenation or coupling products were detected. During the reaction a solid was formed which weighed slightly more than the added BTEA and its NMR spectrum and analysis indicated it to be triethylammonium iodide. The absence of a benzyl group was definitely established.

Reaction of 1-iodo-*F*-butane with 1-heptene induced by quaternary salt gave as much as 82.2% of theory of adduct D, together with 2.9 and 4.3% of side products (Table III). This was significantly more than the 65% conversion achieved using Et_3N as initiator under these conditions (see Figure 1).

$$CF_3(CF_2)_3I + CH_2{=}CH(CH_2)_4CH_3 \xrightarrow[135\ °C]{BTEA} CF_3(CF_2)_3CH_2CHI(CH_2)_4CH_3$$

D

Reaction Mechanism. It has been previously shown that quaternary salts such as BTEA undergo dissociation on photolysis into radicals and ions.[19–21] Though conditions previously studied were quite different from those we have used, thermal generation of free radicals is consistent with our results and with the known thermal instability of quaternary ammonium salts.[22] Accordingly, a reaction sequence is postulated, using BTEA and 1-heptene as typical substances (Scheme I). In this sequence abstraction of hydrogen atoms by the triethylammonium cation–radical (eq 6) is given, rather than alternative paths such as addition to the alkene, since the isolated products included triethylammonium iodide. There is also precedence for involving the amine cation–radical in a scheme such as this.[17] Benzyl radicals are assumed to initiate the chain reaction, although other species might also be involved such as the 3-heptenyl radical (eq 6 and 7). In 1851 Hofmann had already studied the relative ease of cleavage of groups from quaternary ammonium compounds.[23] Formation of a dark colored gum would be consistent with the unstable nature of benzyl iodide or of 3-iodo-1-heptene. The absence of toluene in the reaction product mixture would indicate coupling rather than H abstraction as the fate for part of the benzyl radicals.

In those reactions in which a free amine was used as initiator it is postulated that thermal reaction first produced a small amount of adduct D for example. The quaternary salt formed by reaction with an amine then dissociated into free radicals. Alternatively, the amine dehydrohalogenated the adduct into the alkene, forming at the same time an amine salt, which

Scheme I. Thermolysis of Quaternary Ammonium Salts: Radical Chain Initiation

initiation

$$C_6H_5CH_2NEt_3{}^+Cl^- \rightarrow C_6H_5CH_2\cdot + Et_3N^{+}\cdot + Cl^- \quad (1)$$

$$C_6H_5CH_2\cdot + R_FI \rightarrow C_6H_5CH_2I + R_F\cdot \quad (2)$$

propagation

$$R_F\cdot + CH_2{=}CH(CH_2)_4CH_3 \rightarrow R_FCH_2\dot{C}H(CH_2)_4CH_3 \quad (3)$$

$$R_FCH_2\dot{C}H(CH_2)_4CH_3 + R_FI \rightarrow R_FCH_2CHI(CH_2)_4CH_3 + R_F\cdot \quad (4)$$

$$R_F\cdot + CH_2{=}CH(CH_2)_4CH_3 \rightarrow R_FH + CH_2{=}CH\dot{C}H(CH_3)_3CH_3 \quad (5)$$

$$Et_3N^{+}\cdot + CH_2{=}CHCH_2(CH_2)_3CH_3 \rightarrow Et_3NH^+Cl^- + CH_2{=}CH\dot{C}H(CH_2)_3CH_3 \quad (6)$$

$$CH_2{=}CH\dot{C}H(CH_2)_3CH_3 + R_FI \rightarrow CH_2{=}CHCHI(CH_2)_3CH_3 + R_F\cdot \quad (7)$$

termination

$$2C_6H_5CH_2\cdot \rightarrow C_6H_5CH_2CH_2C_6H_5 \quad (8)$$

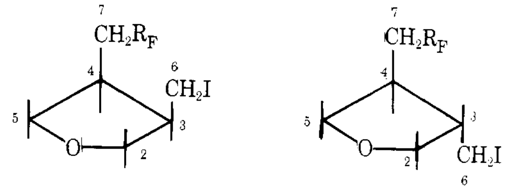
$$2R_F\cdot \rightarrow R_F{-}R_F \quad (9)$$

homolyzed. The process is evidently a chain reaction, as shown by the large number of starting molecules that are converted to product from a small amount of amine. Reaction is initiated more rapidly by a quaternary salt possibly because free radicals are generated immediately, and also because the salt (e.g., BTEA) is more labile. Higher yield of product and less unwanted side reactions result from use of a nonbasic salt instead of a basic amine.

The requirement of an initiation temperature above 120 °C, however, would not be suitable for labile adducts or reactants. Initiation at a lower temperature by an azonitrile or peroxide initiator in these cases would be preferred. Conversely, when a higher reaction temperature is required because of the nature of the reactants (i.e., high melting) or to induce reaction to occur, the quaternary salt might be more appropriate. Additionally, removal of the salt at the end of the reaction is not difficult and the toxicity of the substances introduced in the reaction system might not be as serious as for azonitrile initiators.

Isolation and Identification of Cyclization Products from 1-Iodo-*F*-alkanes and Diallyl Ether. Previously, the cyclic products from 1-iodo-*F*-propane and DAE were not separated, but chemical evidence indicated a substituted tetrahydrofuran structure.[18] Fortunately, in this new work, pure, crystalline, cyclic adducts C could be isolated (in which R_F was *F*-butyl, *F*-hexyl, or *F*-octyl). An NMR study of the mixture of isomers formed in the reaction showed that the cis isomer predominated, just as found previously for cyclization of 1,6-heptadiene.[18] Use was made of ^{13}C-NMR spectra and correlation with structure for analogous cis and trans isomers of 3,4-diethyl-1-methylpyrrolidine.[24,25] Hawthorne, Johns, and Willing found that the trans isomer gave ^{13}C chemical shifts for each carbon atom which was downfield from the corresponding carbons in the cis isomer. By means of these shift parameters it was possible to estimate the composition of a mixture of the two isomers. NMR spectral data for isomers of (*F*-alkyl)methyl-3-iodomethyltetrahydrofuran (where R_F is butyl, hexyl, or octyl) are listed in Table IV. Once the pure cis C isomers were isolated and identified the proton NMR spectra also became amenable to interpretation. The proton resonances were not well resolved in these isomers, however, and cis and trans isomers could not be distinguished from each other by this means.

Table IV. Carbon-13 NMR Spectral Data (ppm) for *cis*- and *trans*-4-(*F*-Alkyl)methyl-3-iodomethyltetrahydrofuran (cis and trans C)



cis-C

trans-C

carbon no.	cis isomer	trans isomer
C-2	73.37	73.73
C-3	45.09	47.83
C-4	35.69	39.24
C-5	71.65	73.35
C-6	2.34	6.30
C-7	28.26[a]	33.78[a]

[a] A triplet from F–C–C coupling.

Experimental Section

Source of Materials and Physical Measurements. *F*-Alkyl iodides were obtained from Ciba-Geigy Corp., Ardsley, N.Y. as a gift from Dr. E. K. Kleiner. The physical constants were those previously given.[26] Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer and NMR spectra were obtained at 100 MHz, through the courtesy of Dr. Ronald Rodebaugh, who also obtained the ^{13}C spectra reported herein. Gas chromatographic analyses were performed using a Sergent-Welch thermal conductivity instrument fitted with dual 6-ft by 0.25 in. columns, packed with silicone oil SE 30, 10% on Chromosorb WA. Satisfactory analyses were obtained for all new substances reported (see Table VII).

1-Iodo-*F*-butane and Diallyl Ether. A 15-mL glass pressure tube reactor fitted with a Teflon needle valve and magnet stirring bar was charged with 1-iodo-*F*-butane (9.00 g, 26.0 mmol), diallyl ether (DAE, 2.37 g, 24.1 mmol), and piperidine (0.077 g, 0.9149 mmol, 3.79% on DAE). The tube was cooled to −78 °C and evacuated and filled with nitrogen three times. The tube was heated while being stirred in an oil bath at 135 ± 0.1 °C for 3 h. The reaction mixture turned brown in color in 10 min and formed precipitated solid on the sides of the reactor tube. When cool the product was removed (11.22 g, 98% recovery of materials). GC analysis, using a known mixture to give weight/area factors (see below), showed 7.27% of adduct A, 65.0% of cyclic adducts C (cis/trans = 2.2/1), and 3.13% of B. Distillation gave a yellow oil, bp 92–115 °C (9 mm), $[n]^{25}_D$ 1.4115, 7.06 g (61.1% conversion), and a dark gum residue, 1.77 g. The sample became crystalline at 0 °C and solid (1.98 g) was collected on a Hirsch funnel. Recrystallization of 0.4045 g from 3 mL of ligroine (60–70 °C) gave 0.2446 g of *cis*-C, mp 36.5–37.8 °C.

GC Analysis of a Known Mixture and Reaction Product from 1-Iodo-*F*-butane and DAE. 1-Iodo-*F*-butane (0.6987 g, 2.0196 mmol), DAE (0.0875 g, 0.8917 mmol), *n*-decane (0.1106 g), and the purified adduct mixture above (0.1696 g, 0.3819 mmol) were mixed. GC analysis was done using a flow rate of helium of 26 mL/min and the temperature programmed from 80 to 180 °C, at 20 °C/min. Cyclic isomers C were not resolved from each other but were determined by a separate run at 140 °C isothermal column temperature. Replicate analyses were averaged. 1-Iodo-*F*-butane, retention time 1.7 min, 46.82% area, 0.3304 response factor relative to *n*-decane; DAE, retention time 2.8 min, 17.77%, 1.0014 response factor relative to *n*-decane; *n*-decane, retention time 7.9 min, 22.43%, 1.00 response factor; A, 9.2 min, 9.29%, 0.3774 response factor; *cis*- and *trans*-C, 11.2 min retention time, 12.05%, 0.3774 response factor; B, 17.4 min retention time (from another sample, 0.46 response factor from previous work).

Reaction product from above gave C_4F_9H, 1.1 min retention time, 2.94% relative area, 1.6 mmol, using response factor of 0.5 estimated from previous work; 1-iodo-*F*-butane, 14.85%, 6.01 mmol; DAE, 9.84%, 4.424 mmol; *n*-decane, 9.84%; A, 6.36%, 1.757 mmol; C, 56.86%, 15.71 mmol; B, 2.98%, 0.0378 mmol.

Recovery of Triethylammonium Iodide from BTEA-Initiated Reaction of 1-Iodo-*F*-butane and DAE. The crystalline solid from part of the product mixture was collected, rinsed with toluene, and air dried. The solid was immediately soluble in water and gave a positive test for iodide ion with silver nitrate solution. NMR analysis showed that the benzyl group was not present, but the sample had a spectrum consistent for triethylammonium iodide.

Anal. Calcd for $C_6H_{16}HI$: C, 31.45; H, 7.04; N, 6.11; I, 55.39. Found: C, 33.30; H, 7.07; N, 5.8; I, 52.5.

Reaction of 1-Iodo-*F*-butane and Pyrrolidine. A 50-mL round-bottom flask, fitted with a total reflux distilling head connected to a dry ice cooled trap, an addition funnel, and a magnet stirring bar, heated in an oil bath was charged with 1-iodo-*F*-butane (8.65 g, 0.0250 mol). Pyrrolidine (7.11 g, 0.100 mol) was added slowly during 45 min at 48–66 °C (bath temperature 69 °C) and became dark red in color during 2 h of refluxing at 73–93 °C (bath temperature 77–110 °C). Liquid slowly distilled, bp 43–58 °C, 5.1 g, during 1 h, leaving a dark gum residue (8.1 g). The trap liquid (2.6 g, 47% conversion) was 1-hydryl-*F*-butane; the methine proton was seen as a triplet of triplets centered at 6.0 ppm in the NMR spectrum taken at 0 °C. The gum residue was insoluble in water and soluble in acetone or ethanol, and in hot ligroine; thus, it was not a simple salt of pyrrolidine. Total recovery was 15.8 g, 100%.

Reaction of 1-Iodo-*F*-butane with Diallylamine. 1-Iodo-*F*-butane (8.65 g, 0.0250 mol) and diallylamine (4.85 g, 0.0500 mol) were heated at 70 °C for 4.5 h and the liquid remained colorless. Distillation of the cold liquid (14.1 g) in a 2-ft platinum spinning band column first at 110 mm of mercury and then at 85 mm gave a mixture of 1-iodo-*F*-butane and diallylamine, bp 44–51 °C (85 mm), $[n]^{25}_D$ 1.3868, 3.50 g; and bp 49 °C (80–72 mm), pot temperature 52–65 °C, $[n]^{25}_D$ 1.4358, 4.00 g. A brown residue of 0.2 g remained. The cold trap contained 5.6 g of starting materials (95% recovery).

1-Iodo-*F*-hexane and DAE with 2-Aminoethanol Initiation:

Table V. Reaction of 1-Iodo-*F*-hexane and *N*-Methyldiallylamine

reaction time, h	total elapsed time, h	temp, °C	recovery (%) of $C_6F_{13}I$	recovery (%) of NMDA[a]	conversion (%) to adduct	conversion (%) to salt	remarks
21	21	70.0	99	99	0.52		colorless liquid
4	4	90.0	90	88	2.0	8	light yellow liquid
3	7	100.0	72	65	10.3	25	two layers, fuming
3	10	110.0	19.7	22.4	15	65	dark red liquid and solid

[a] NMDA is *N*-methyldiallylamine.

Table VI. Reaction of 1-Iodo-*F*-butane and 1-Heptene Catalyzed by Amines

expt	mol ratio 1-heptene/R_FI	catalyst, mol % on 1-heptene	temp, °C	time, h	conversion % of D
12	0.988	Et_3N 2.01	110	3	1.01
13	0.988	Et_3N, 2.01	120	3	41.7
14	0.782	none, none	125	4	21.0
15	0.816	pyr, 4.96	125	4	49.1
16	0.816	pyr, 7.68	125	4	56.1
17	0.816	pyr, 7.68	125	17	71.8
18	0.751	$BuNH_2$, 8.44	125	5.5	59.1[a]
19	0.988	none, none	135	3	10.8
20	0.988	Et_3N, 2.01	135	10 min	22.1
21	0.988	Et_3N, 2.01	135	0.5	38.0
22	0.988	Et_3N, 2.01	135	1.0	48.6
23	0.988	Et_3N, 2.01	135	2.0	58.5
24	0.988	Et_3N, 2.01	135	3.0	64.9
25	0.988	Et_3N, 2.01	135	5.0	62.5
26	0.816	pyr, 4.96	135	3	40.8
27	0.751	$BuNH_2$, 8.44	135	2	53.0[b]
28	0.751	$BuNH_2$, 8.44	135	2.5	59.7[c]
29	0.768	pyr, 7.68	140	3	54.1

[a] 1.49% of side product formed also. [b] 1.42% of side product. [c] 2.81% of side product formed also.

Isolation of *cis*-C ($R_F = C_6F_{13}$). Iodo-*F*-hexane (24.12 g, 54.08 mmol), DAE (4.90 g, 49.9 mmol), aminoethanol (0.1144 g, 1.874 mmol, 3.75% on DAE), alumina (0.30 g), and *n*-octane (1.5694 g, GC reference liquid) were heated at 130 °C for 2 h. GC analysis gave 1-hydryl-*F*-hexane (1.83 g, 10.6%), 1-iodo-*F*-hexane (7.92 g, 32.87% recovery), DAE (1.837 g, 37.49% recovery), A (1.83 g, 6.74%), and isomers of C (12.64 g, 46.6% conversion). Distillation gave a mixture of 1-iodo-*F*-hexane and DAE, bp 46–54 °C (107 mm), 10.51 g, and trap liquid, 1.85 g; an adduct mixture, bp 122–142 °C (9 mm), 15.12 g (55.61% conversion), and a brown residue, 1.35 g (total, 97.9%). A portion of the adduct mixture (6.82 g) was recrystallized from ligroine (20 mL). Fractions, 4.007 g, mp 58–60 °C, 0.413 g and 0.693 g, mp 55–56 °C, were recovered. A second recrystallization of 4.007 g gave pure *cis*-C from ^{13}C NMR spectrum analysis, 2.062 g, mp 59.5–61 °C.

1-Iodo-*F*-hexane and DAE with BTEA Initiation. 1-Iodo-*F*-hexane (24.462 g, 54.848 mmol. 94.8% pure), DAE (6.2215 g, 63.39 mmol), BTEA (0.5031 g, 2.209 mmol, 3.48% on DAE), and *n*-decane (0.5603 g) were heated 3 h at 135 °C and while warm a sample was removed for GC analysis. White and some dark crystals of triethylammonium iodide (0.60 g) were rinsed out of the reactor tube with acetone. Distillation in a variable T/O head gave recovered 1-iodo-*F*-hexane and DAE, bp 59 °C, 0.81 g, and trap liquid, 5.69 g; an adduct mixture, bp 128–143 °C (10 mm), 20.54 g (68.89%); and dark brown residue, 2.42 g. GC analysis gave 1-hydryl-*F*-hexane, 1.6 min retention time, 1.41 g; 1-iodo-*F*-hexane, 2.6 min, 2.98 g; DAE, 3.2 min, 2.13 g; *n*-decane, 6.6 min, (0.5603 g); unknown, 7.8 min, 0.2548 g; unknown, 8.3 min, 0.2228 g; A, 8.7 min, 2.376 g, 9.56% conversion; C, 10.8 min, 18.15 g, 60.82% conversion; and B, 18.8 min, 0.3774 g, 1.26% conversion. GC run isothermally at 145 °C gave 13.33% at 30.0 min and 86.66% at 32.6 min. The distilled fraction gave 16.56% at 30.0 min and 83.43% at 32.6 min.

Reaction of 1-Iodo-*F*-hexane with *N*-Methyldiallylamine without Added Catalyst at 70–110 °C. A reactor tube was charged with 1-iodo-*F*-hexane (5.30 g, 11.88 mmol. 99%), *N*-methyldiallylamine (NMDA, 1.2251 g, 11.02 mmol), and *n*-decane (0.8030 g, GC reference liquid). Noticeable heat was produced as the two reactants were mixed and the temperature rose from 20 to 28 °C in 3 min. The tube was cooled to −78 °C, evacuated, filled three times with nitrogen, and sealed. After heating at 70.0 °C for 21 h, the nearly colorless liquid (7.0748 g, 96.5% recovery) contained no trace of solid. GC analysis gave almost 100% recovery of starting materials. GC response factors were: 1-iodo-*F*-hexane, 0.3751; NMDA, 0.9904; the monoadducts were assumed to be the same as previous, similar compounds. Further heating gave the results listed in Table V.

Reaction with Azonitrile Initiator at 70.0 °C. As above 1-iodo-*F*-hexane (9.51 g, 21.3 mmol), NMDA (0.9472 g, 8.519 mmol), and azobis(isobutyronitrile) (0.0565 g, 0.400 mmol) were heated at 70.0 °C for 16 h. Within 15 min the reaction mixture had become dark brown in color, and after a few hours very viscous. The brown, semisolid mass was sampled and the remainder dissolved out of the reactor tube with acetone and evaporated off. An infrared spectrum showed bands for R_4N^+ at 2700–2500, CF bands at 1250–1100, and bands at 710, 690, 670, 665, and 635 cm^{-1}.

1-Iodo-*F*-octane and DAE: Isolation of *cis*-C ($R_F = C_8F_{17}$). 1-Iodo-*F*-octane (14.2 g, 25.0 mmol), DAE (2.45 g, 25.0 mmol), copper(I) chloride (0.1000 g, 1.01 mmol), piperidine (0.35 g, 4.1 mmol, 16.4% on DAE), and alumina (0.36 g) were heated at 135 °C for 25 min. The light green suspension became quickly dark and while still warm was poured into a flask (15.16 g, loss of 2.29 g). A black tar remained in the reactor tube which dissolved only when heated with concentrated sulfuric acid. Distillation gave adduct mixture, bp 103–116 °C (0.30 mm), 10.95 g, mp 67–78 °C (68% conversion to adducts). A dark black tar remained in the pot flask (1.74 g). GC analysis showed a ratio of linear to cyclic adducts of 3.62/96.3. A portion of the product (2.32 g) was recrystallized from ligroine (bp 60–70 °C) and gave *cis*-C, 1.63 g, mp 81–82.5 °C; repeated recrystallization gave mp 81.5–83 °C. Integrated areas from ^{13}C NMR spectrum showed that 80% of cis and 20% of trans isomer were present. In mixtures of very similar compounds of this type the accuracy of analysis was estimated to be ±2%.

1-Iodo-*F*-octane and DAE with Azonitrile Initiator. 1-Iodo-*F*-octane(10.92 g, 20.00 mmol), DAE (3.92 g, 40.0 mmol), and azobis(isobutyronitrile) (0.0500 g, 0.305 mmol, 1.5% on 1-iodo-*F*-octane) were heated for 20 h at 70 °C. The colorless solid was dissolved out

Table VII. Analyses of Cyclization Products C from *F*-Alkyl Iodides and Diallyl Ether

		calcd				Found			
isomer	R_F	C	H	F	I	C	H	F	I
cis-C	C_4F_9	27.04	2.27	38.5	28.6	27.6	2.21	39.8	26.8
cis-C	C_6F_{13}	26.28	1.85	45.4	23.3	26.7	1.85	46.7	23.4
cis-C[a]	C_8F_{17}	26.10	1.57	50.2	19.7	26.07	1.76	50.2	19.3

[a] Mixture of 80/20 *cis*-C/*trans*-C.

of the reactor tube with boiling ligroine (50 mL), and solid adduct fractions 7.89 g, mp 82–83.2 °C, 1.78 and 0.277 g, mp 79–80 °C, were obtained. The filtrate gave a mixture containing a little of A (infrared bands at 3090 and 990 cm^{-1}) and *cis*- and *trans*-C, 2.41 g. The total recovery was quantitative.

Reaction of 1-Iodo-*F*-butane and 1-Heptene. 1-Iodo-*F*-butane (4.4056 g, 12.73 mmol), 1-heptene (0.9538 g, 9.7138 mmol), pyridine (0.0590 g, 0.746 mmol), and *n*-octane (0.4822 g) were mixed. A 0.80-g portion was heated at 125 °C for 17 h as above. GC analysis gave average areas as follows: 1-iodo-*F*-butane, 23.39%, 5.824 mmol, 45.74% recovery; 1-heptene, 10.54%, 2.597 mmol, 26.73% recovery; *n*-octane, 18.34%; and adduct D, 47.50%, 6.973 mmol, 71.78% conversion.[27] Total recovery was 98.4%. A known mixture gave response factors relative to *n*-octane: 1-iodo-*F*-butane, 0.3052; 1-heptene, 0.9923; and adduct D, 0.4033. Additional experiments are listed in Table VI. Only 1.11% reaction occurred in 3 h at 110 °C, 41.7% at 120 °C and 65% at 135 °C, using 2.01% of triethylamine as catalyst.

1-Iodo-*F*-Alkanes and Diallylcyanamide. A 1-iodo-*F*-alkane mixture (C_6, C_8, C_{10} 1:2:1 mole ratio, 31.34 g, 57.40 mmol), 2-aminoethanol (0.1524 g, 3.12 mmol), and copper(I) chloride (0.2343 g, 3.465 mmol) were charged to a 100 mL, round-bottom flask, fitted with a nitrogen inlet, dropping funnel, and reflux condenser, and heated in an oil bath while stirring by a magnet bar. At 132 °C bath temperature diallylcyanamide (DAC, 6.35 g, 52.0 mmol) was added dropwise during 8 min of reaction time. After 3 min an exotherm raised the temperature inside the flask from 130 to 136 °C (bath temperature 130 °C), and a clear brown slowly refluxing solution was formed. After 0.5 h a sample showed unreacted DAC was present (IR bands at 3080, 1100, and 1650 cm^{-1}) and a brown gum had formed on the sides of the flask. The bath temperature was raised to 140 °C and in 1 h a sample showed only a little DAC remained; an additional 0.0380 g (0.622 mmol) of 2-aminoethanol was added and in 0.5 h refluxing had ceased and no DAC was present. An NMR spectrum was very similar to that of the product prepared from 1-iodo-F-hexane and DAC using azonitrile initiator at 70 °C in quantitative yield, mp 68–70 °C.[15] Spectral properties and elemental analyses were unchanged by recrystallization.

Anal. Calcd for $C_{13}H_{10}F_{13}N_2I$: C, 27.48; H, 1.77; F, 43.47; N, 4.93; I, 22.34. Found: C, 27.39; H, 1.79; F, 43.18; N, 4.08; I, 22.26.

Registry No.—A, 68344-71-8; B, 68344-72-9; *cis*-C ($R_F = C_4F_9$), 68344-73-0; *trans*-C ($R_F = C_4F_9$), 68344-74-1; *cis*-C ($R_F = C_6F_{13}$), 68344-75-2; *cis*-C ($R_F = C_8F_{17}$), 68344-76-3; *trans*-C ($R_F = C_8F_{17}$), 68344-77-4; D, 40735-33-9; 1-iodo-*F*-butane, 423-39-2; diallyl ether, 557-40-4; triethylammonium iodide, 4636-73-1; pyrrolidine, 123-75-1; diallylamine, 124-02-7; 1-iodo-*F*-hexane, 355-43-1; 2-aminoethanol, 141-43-5; BTEA, 56-37-1; *N*-methyldiallylamine, 2424-01-3; azobis(isobutyronitrile), 78-67-1; 1-iodo-*F*-octane, 507-63-1; 1-heptene, 592-76-7; 1-iodo-*F*-decane, 463-62-1.

References and Notes

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