1-Iodo-2-(perfluoroalkyl)cycloalkanes by the Free Radical Addition of Iodoperfluoroalkanes to Cyclohexane and Cyclopentene

Neal O. Brace

Contribution No. 342, Research and Development Division, Organic Chemicals Department, E. I. du Pont de Nemours and Company, Wilmington, Delaware

Received May 2, 1963

Iodoperfluoroalkanes and cyclohexene or cyclopentene gave adducts in up to 50% conversion (80–90% yield) by a short chain free radical process initiated by peroxides, azonitriles, or radiant energy. The *trans–cis* ratio of the nonplanar 1-iodo-2-(perfluoroalkyl)-cyclohexanes varied with the iodoperfluoroalkane being added, and with the initiation method. 1-Iodoperfluorobutane and cyclopentene gave only a *trans* adduct; cyclopentadiene gave no adduct at all. Trifluoriodomethane, 1-iodoperfluoropropane, and 2-iodoperfluoropropane gave adducts with cyclohexene in relative amounts of 0.05:1:2; the ratio of R_fI addition to abstraction (giving R_fH) was 6.56 for $CF_3CF_2CF_2I$ and only 1.73 for $(CF_3)_2CFI$. No CF_3H could be detected from CF_3I. Though formed at a greater rate, the adducts from 2-iodoperfluoropropane were unusually labile and were isolated in lower yield. This behavior was not typical for $(CF_3)_2CFI$; it reacted faster and more efficiently than $CF_3CF_2CF_2I$ with 1-heptene and norbornene.

Free radical addition of 1-iodoperfluoropropane to strained bicyclic olefins like norbornene or norbornadiene occurred with great facility when an azonitrile initiator was used.[1,2] In analogous reaction of cyclohexene or cyclopentene with tetrahalomethanes, however, there is also a serious competing process by which an allylic hydrogen is abstracted.[3] The ratio of addition to abstraction for cyclohexene and $BrCCl_3$ was found[4] to be only 1.2, while for 1-octene it was 43. Consequently, a chain of reasonable length, which depends on efficient propagation and transfer steps for its success, has been difficult to achieve with cyclic olefins.[3,4] Indeed, preliminary experiments showed that cyclohexene and 1-iodoperfluoropropane in *equimolar* amount gave only a 2 to 5% conversion to adducts[5] using the procedure[1] which gave excellent addition to β-pinene, norbornene, or vinyl acetate. Serious wastage of initiator must have occurred, since essentially all the olefin and 1-iodoperfluoropropane were recovered.

A more careful examination of the reaction system was therefore made in order to discover the reasons for the inefficient chain reaction with cyclohexene. We also wished to learn if this behavior was typical for iodoperfluoroalkanes (R_fI) having shorter or longer R_f groups and for both primary and secondary iodides. In order to ascertain optimum conditions, the effect of reaction variables—temperature, extent of reaction, reactant ratios, and initiator concentration—on yield and conversion to adducts was explored. The mode of generating the initiating radicals was also varied, since photochemical or X-ray initiation would not introduce extraneous initiator fragments unavoidably associated with peroxide or azonitrile catalysts. The relative rate of addition and the ratio of addition to abstraction as a function of the structure of the R_fI was determined for cyclohexene and for norbornene (which has no abstractable allylic hydrogen) and 1-heptene. The stereochemistry of the addition reaction was examined in detail, and evidence was obtained which provided a rational basis for discussion of this radical chain reaction. The reaction of R_fI with cyclopentene and with cyclopentadiene was also carried out, taking advantage of the techniques first developed for cyclohexene.

The n.m.r. spectra,[5] dipole moments, conformation equilibria, and some of the novel aspects of the chemistry of the adducts are being reported separately.

Results and Discussion

Synthesis of Adducts Using Azonitrile or Peroxide Initiators.—Iodoperfluoroalkanes having R_f groups varying from CF_3– to $CF_3(CF_2)n$– (n = 1, 2, 3, 6) and $(CF_3)_2CF$– gave widely differing amounts of *cis* and *trans* isomers of the family of 1-iodo-2-(perfluoroalkyl)-cyclohexanes. Results for azonitrile and peroxide-induced reactions are given in Table I. The lowest conversion and efficiency was shown by CF_3I and the highest by $CF_3(CF_2)_2I$, or higher homologs. The secondary iodide, $(CF_3)_2CFI$, gave a lower yield than did $CF_3(CF_2)_2I$. *In order to attain a 50% conversion at 90% yield of adducts, a severalfold excess of cyclohexene, 3–5 mole % (on R_fI) of initiator, and a sufficient length of time for the decomposition of the initiator must be employed.*

Gas–liquid chromatography (g.l.c.) was used to establish the amounts of the various products. The rate of reaction at 65° and isomer ratios are shown graphically for $CF_3(CF_2)_2I$ in Fig. 1 and for $(CF_3)_2$-CFI in Fig. 2. It is apparent that the *trans–cis* adduct ratio is dependent upon the structure of R_fI.

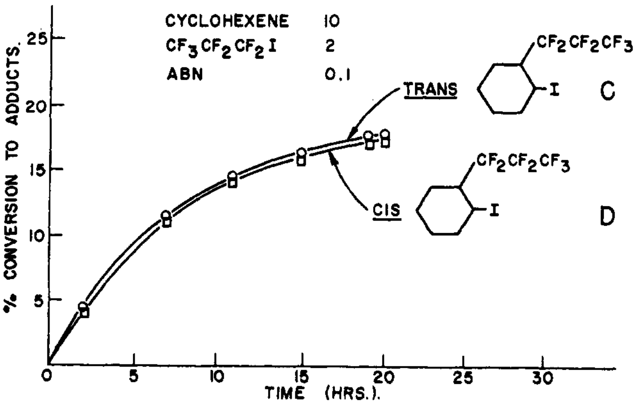

Fig. 1.—Rate of conversion to adducts from $CF_3CF_2CF_2I$ and cyclohexene at 65°.

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[1] N. O. Brace, *J. Org. Chem.*, **27**, 3027, 3033 (1962).

[2] N. O. Brace, Abstracts of the 142nd National Meeting of the American Chemical Society, Atlantic City, N. J., 1962, p. 95Q.

[3] For a review of the subject see C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 247.

[4] E. S. Huyser, *J. Org. Chem.*, **26**, 3261 (1961).

[5] N. O. Brace, *J. Am. Chem. Soc.*, **84**, 3020 (1962).

[6] N. O. Brace, to be published.

TABLE I

AZONITRILE OR PEROXIDE-INDUCED ADDITION OF R_fI TO CYCLOHEXENE

Expt. no.	R_fI	Mole	Cyclohexene,[a]/ R_fI, moles	Initiator, mole %	Temp., °C.	Time, hr.	Conversion, %[b]	Yield,[b] %	*trans*/*cis*	Reaction efficiency[c]
1	CF_3I[d]	0.25	5	ABN 4	80	20	7.0	90	1.81	1.7
2	CF_3I[d]	.25	8	ABN 4	80	15	8.0	90	1.95	2.0
3	CF_3CF_2I[d]	.40	8[e]	DTBP 10	130	15	40.0	. .	1.14	4.0
4	$(CF_3)_2CFI$	.5	4	ABN 6	68	22	16	70	2.5	2.7
5	$(CF_3)_2CFI$	.17	4	ABN 6	50	30	19	80	2.5	3.3
6	$(CF_3)_2CFI$	.15	4[e]	ABN 6.7	68	15	25	80	. . .	3.8
7	$(CF_3)_2CFI$	.25	8	ABN 12	68	21	50	80	2.7	4.2
8	$CF_3(CF_2)_2I$	.2	1	ABN[f] 1.2	53	11	*ca.* 7	95	. . .	4.2
9	$CF_3(CF_2)_2I$[d]	.1	1	DTBP 3.4	140	10	*ca.* 7	95	. . .	2.0
10	$CF_3(CF_2)_2I$	.15	4[e]	ABN 6.7	71	16	35	90	1.01	5.0
11	$CF_3(CF_2)_2I$	.4	5	ABN 6[g]	68	46	50[g]	87	1.01	7.9
12	$CF_3(CF_2)_2I$	.2	5[e]	ABN 3	50	22	50	90	1.01	16.1
13	$CF_3(CF_2)_3I$	.2	1[e]	ABN 5	72	13	21.5	90	. . .	4.2
14	$CF_3(CF_2)_3I$	.1	2[e]	ABN 5	75	10	27	90	1.07	5.2
15	$CF_3(CF_2)_6I$	.1	2[e]	ABN 5	75	12	31	88	1.05	6.1
16	$CF_3(CF_2)_6I$	.1	3[e]	ABN 5	75	22	35	88	1.1	7.0

[a] Treated with activated alumina under nitrogen to remove peroxide unless otherwise noted. [b] Conversion is mole of adducts per mole of R_fI charged times 100; yield is per cent of distilled adducts on R_fI used up. [c] Moles of adducts per mole of α,α-azobisisobutyronitrile[9] (ABN) or per mole of di-*t*-butyl peroxide (DTBP) charged. [d] Reaction in a 400-ml. sealed shaker tube. [e] Cyclohexene *not* treated to remove peroxide. [f] Either ABN or azobis-2,4-dimethylvaleronitrile[9] (AVN) were used. [g] One-half of the ABN was added after 23 hr. The conversion (by g.l.c.) was 23% after 23 hr.

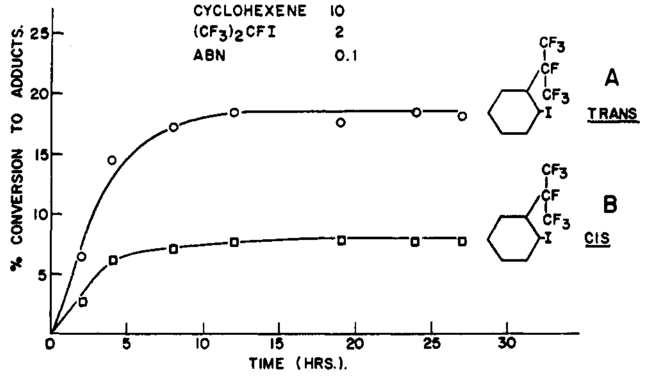
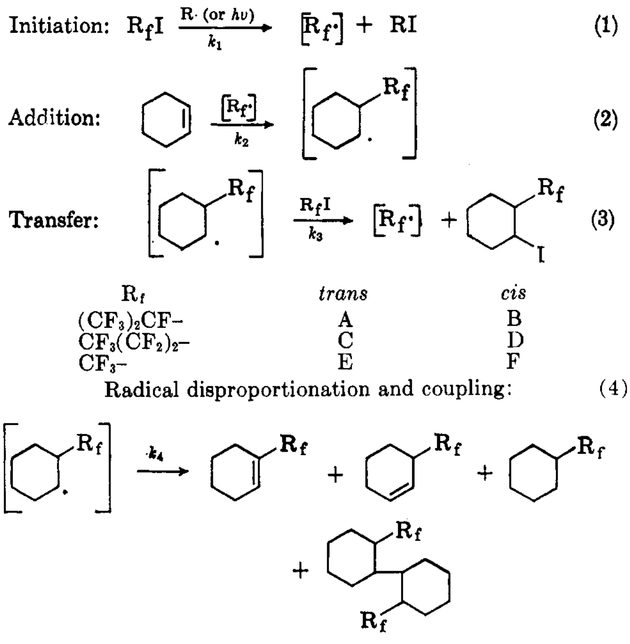


Fig. 2.—Rate of conversion to adducts from $(CF_3)_2CFI$ and cyclohexene at 65°.

Ratios for other R_fI are listed in Table I. Less efficient reaction resulted from replacing part of the excess cyclohexene with cyclohexane[7] or benzene. The conversion to adducts was cut in half. Evidently, the over-all rate of reaction is affected by the concentration of cyclohexene.[8] Peroxide-free cyclohexene gave a *slower* rate of addition and lower conversion to product than did untreated cyclohexene. In fact, $(CF_3)_2CFI$ and cyclohexene in sealed cylinders which contained some oxygen were found to react on standing at 25°. Reaction was apparently induced by peroxide formed *in situ*.

Side Reactions Which Caused Poor Efficiency.—In Chart I are summarized the successive steps (1 to 3) in the normal chain reaction sequence.[3] Steps 4 and

CHART I



$$\text{Hydrogen abstraction:}\quad [R_f\cdot] + RH \xrightarrow{k_5} R_fH + [R\cdot] \quad (5)$$

(RH is cyclohexene or other hydrogen-containing compounds.)

5 are side reactions which remove some of the adduct radicals or R_f radicals from the system and reduce the length of the repetitive chain process. A third cause of poor efficiency was decomposition of the adducts themselves. This resulted ultimately in hydrogen iodide being formed which itself is an efficient radical chain inhibitor. In some unknown manner small amounts of iodocyclohexane and cyclohexenyl iodide were also formed, probably through cyclohexenyl radical (from equation 5) abstraction and disproportionation reactions.

The reason for the poor efficiency observed with CF_3I was the slow rate of transfer (equation 3) rather

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[7] W. J. Kirkham and J. C. Robb, *Trans. Faraday Soc.*, **57** [10], 1757 (1961), observed a sevenfold reduction in the rate of $BrCCl_3$ telomerization of styrene when cyclohexane was used as solvent.

[8] In the case of $(CF_3)_2CFI$ and cyclohexene in cyclohexane solution a significant side reaction gave as much iodocyclohexane as *cis* and *trans* adducts, whereas only a trace of iodocyclohexane was obtained from $CF_3CF_2CF_2I$ and cyclohexene in cyclohexane. Hydrogen abstraction from cyclohexane by $(CF_3)_2CF\cdot$, or $(CH_3)_2\dot{C}CN$ occurred, since a mixture of ABN and $(CF_3)_2CFI$ in cyclohexane (no cyclohexene) gave iodocyclohexane in a facile, but short chain process. Kirkham and Robb[7] noted that no reaction occurred between $BrCCl_3$ and cyclohexane when photolyzed at 3650 Å.

than hydrogen abstraction. Some of the intermediate adduct radical was used up in coupling and disproportionation reactions. The amount of CF_3H obtained was too small to detect by mass spectrum analysis, in contrast to the large amount[4] of $HCCl_3$ given by CCl_3Br or CCl_4.[3,4]

With CF_3CF_2I, using di-*t*-butyl peroxide initiator, CF_3CF_2H again was a minor side product, but a significant amount of high-boiling residue was found. However, hydrogen abstraction was a major side reaction of $(CF_3)_2CF\cdot$, giving $(CF_3)_2CFH$ which was quantitatively determined by g.l.c. analysis. The ratio of adducts A and B to $(CF_3)_2CFH$ was about 2.0; for C and D to $CF_3CF_2CF_2H$, the ratio was 6.56. These results will be discussed later.

Inhibition of addition to cyclohexene by decomposition of the labile adducts A and B was demonstrated in three parallel experiments. As seen in Fig. 1, *cis* and *trans* adducts from $CF_3CF_2CF_2I$ continued to be formed up to 20 hours, whereas with $(CF_3)_2CFI$ (Fig. 2) adduct concentration leveled off after 12 hours of reaction. Initiator [azobisisobutyronitrile (ABN), half-life,[9] 4.6 hours. at 68°] is not completely decomposed during this time. *In a mixture of $(CF_3)_2CFI$ and $CF_3CF_2CF_2I$ with cyclohexene, formation of both sets of adducts ceased after 15 hours* (Fig. 3). Therefore, cyanoisopropyl radicals were being consumed by side reactions not giving addition. This is true in spite of the fact that twice as much of the adducts from $(CF_3)_2CFI$ as from $CF_3CF_2CF_2I$ was obtained. The total rate of conversion to products in separate experiments is compared directly in Fig. 4. At first a slower rate of reaction of $CF_3CF_2CF_2I$ was observed compared with $(CF_3)_2CFI$; after 8 hours the rate of C and D formation was faster and after 12 to 20 hours, the total amount of addition exceeded that obtained from $(CF_3)_2CFI$. Note also that chain initiation by azobisisobutyronitrile was still occurring after 20 hours in the presence of $CF_3CF_2CF_2I$ and its adducts.

Under these conditions $(CF_3)_2CFI$ and 1-heptene gave complete conversion to the adduct $(CF_3)_2CFCH_2CHI(CH_2)_4CH_3$ (G) in only one hour. Therefore, *$(CF_3)_2CFI$ itself is not responsible for inhibition of addition to cyclohexene.* The $(CF_3)_2CFI$ adduct A was unaffected by heating in cyclohexene at 71° for one hour, but with azobisisobutyronitrile present about 35% of A was converted to disproportionation and coupling products of equation 4. Hence, cyanoisopropyl radicals readily induce decomposition of this labile adduct, and hydrogen iodide and iodine are in some manner released. Proof for this was easily secured.

In preparative experiments with $(CF_3)_2CFI$ a solid hydroiodide salt precipitated during reaction; at the same time, adduct radical disproportionation and coupling products were obtained. The water-soluble salt was identified as tetramethyl-5-imino-2-pyrrolidone hydroiodide formed by cyclization[10,11] and partial hydrolysis[11] of the hydrogen iodide adduct of tetramethylsuccinonitrile, the coupling product from cyanoisopropyl radicals. In reactions of $CF_3CF_2CF_2I$ no precipitate of salt was observed; however, the adduct radical disproportionation and coupling product mixture was obtained, though in smaller amount.

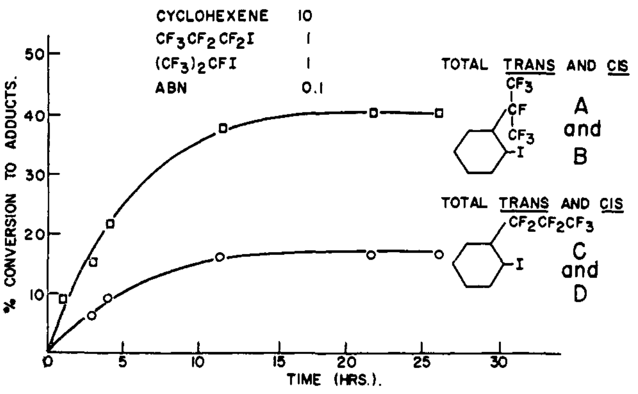


Fig. 3.—Relative rates of reaction of $CF_3CF_2CF_2I$ and $(CF_3)_2CFI$ with cyclohexene at 65°.

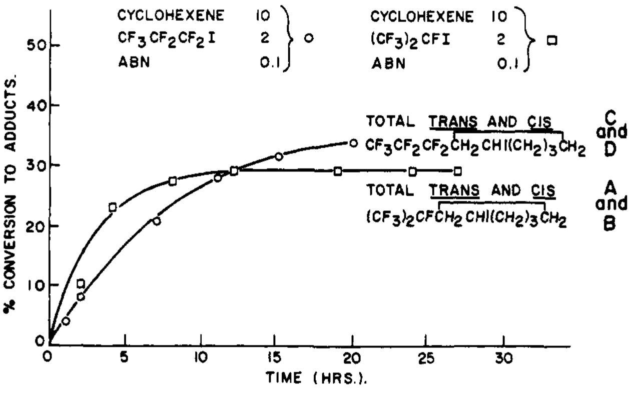
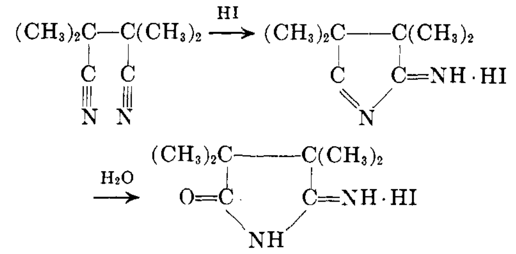


Fig. 4.—Rate of conversion to adducts at 65°; —o— of $CF_3CF_2CF_2I$ and cyclohexene; —□— of $(CF_3)_2CFI$ and cyclohexene.



$(CH_3)_2C(CN)—C(CH_3)_2CN \xrightarrow{HI}$ tetramethyl-5-imino-pyrrolidine ring $\xrightarrow{H_2O}$ $(CH_3)_2C—C(CH_3)_2$, $O=C$, $C=NH\cdot HI$, NH

In peroxide-induced reactions a significant amount of 1-cyclohexen-3-one was invariably obtained, which was also present in cyclohexene exposed to the air. It was, therefore, probably derived from the hydroperoxide.

Reaction Induced by Radiant Energy.—For the experiments listed in Table II, reaction was induced by sunlight passing through Pyrex glass, by ultraviolet light from mercury vapor in an internal quartz coil[12] or by X-rays from a gold target. It was anticipated that cleaner product could be obtained at the lower temperatures possible with irradiation, and, of course, initiator decomposition products would be absent. Unfortunately, photolysis[13] of the adducts also usually occurred,

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(9) C. G. Overberger, M. T. O'Shaughnessy, and H. Shalit, *J. Am. Chem. Soc.*, **71**, 2661 (1949). The half-life of AVN (see footnote *f* of Table I) is one hour at 68°.

(10) T. J. Dougherty, *ibid.*, **83**, 4849 (1961).

(11) A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 1493 (1950); *cf.* M. C. Ford and W. A. Waters, *J. Chem. Soc.*, 1857 (1951). Bickel and Waters previously observed the cyclization of TMSN to tetramethyl succinimide during alkaline hydrolysis. Acid hydrolysis, however, gave an intractable mixture.

(12) M. S. Kharasch and H. N. Friedlander, *J. Org. Chem.*, **14**, 239 (1949).

(13) G. V. D. Tiers, *ibid.*, **27**, 2261 (1962).

TABLE II

RADIATION-INDUCED ADDITION OF R_fI TO CYCLOHEXENE

Expt. no.	R_fI	Mole	Cyclohexene/ R_fI, moles	Temp., °C.	Time, hr.	Conversion,[a] %	Yield,[a] %	*trans/cis*
1[b]	CF_3I	0.05	35.2	20–40	11.7	35.4	*ca.* 50	1.4
2[c]	$(CF_3)_2CFI$	.1	4.0	25–30	168	26	46	1.5
3[b]	$(CF_3)_2CFI$	.08	5.0	2 2 2	10.5 22 50	9.3 14.0 18.6	. . .	2.54 2.16 2.1
4[b]	$CF_3(CF_2)_2I$	.22	4.55	−20 to 2	19.5	41[b]	72	0.82–0.92
5[c]	$CF_3(CF_2)_2I$	.20	5.0	25–35	96	39	77	0.87
6[d]	$CF_3(CF_2)_3I$	.10	5.0	47	35	32	70	1.0
7[d]	$CF_3(CF_2)_3I$	.14	4.5	48–60	126	49	68	1.04
8[e]	$CF_3(CF_2)_6I$	.1	3.0	25	3.5[f]	20	90	1.07
9[c]	$CF_3(CF_2)_6I$	.1	3.0	25	5.75[g]	41	75	1.10

[a] Conversion is moles of adducts per mole of R_fI charged times 100; yield is per cent of distilled adducts based on R_fI used up. [b] A cell having an internal quartz coil described by Kharasch and Friedlander[12] was used, mounted under a −70° condenser. Shielding of the portion of the coil not immersed in liquid gave cleaner reaction. [c] Pyrex heavy-walled tube sealed in *vacuo*, was placed outside in the sun in August. [d] A General Electric 275-watt sunlamp placed eight inches from the liquid in a Pyrex flask was used. [e] See Experimental. [f] 30,000 rads/min. calculated by Dr. F. W. Stacey from standard dosimetry methods. [g] 45,000 rads/min. calculated by Dr. F. W. Stacey.

TABLE III

PHYSICAL PROPERTIES OF 1-IODO-2(PERFLUOROALKYL)CYCLOHEXANES

$R_fCH_2CHI(CH_2)_3CH_2$ R_f	Isomer	B.p., °C. (mm.)	Retention time, min.		$n^{25}D$	d^{25}_4	ϵ	Ultraviolet, $\lambda_{max}^{CH_3OH}$ mμ	Analyses Calcd. C	H	F	I	Analyses Found C	H	F	I
CF_3—	*trans*-	76 (17)	13.9[a]		1.4803	. . .	. . .	. . .	30.23	3.62	20.5	45.64	30.3	3.6	20.0	45.8
	cis-	48 (2.5)	22.9[a]		1.4811	. . .	. . .	. . .					30.3	3.6	20.3	45.1
CF_3CF_2—	*trans*-	60 (6.0)	7.0[a]	18.0[b]	1.4512	1.766	517	265	29.29	3.07	28.96	38.69	29.3	3.0	29.1	38.9
	cis-	70 (6.0)	14.0[a]	28.2[b]	1.4527	1.780	512	260					29.4	3.0	29.1	39.0
$(CF_3)_2CF$—	*trans*-	48 (1.3)	9.2[a]	20.8[b]	1.4392	1.792	525	266	28.7	2.64	35.3	33.6	28.7	2.9	35.8	33.0
	cis-	50 (1.3)	12.5[a]	26.4[b]	1.4387	1.804	498	261					28.9	2.8	35.7	33.3
$CF_3(CF_2)_2$—	*trans*-	76 (8.0)	7.5[a]	19.0[b]	1.4311	1.772	516	265	28.7	2.64	35.3	33.6	28.8	2.7	35.3	33.8
	cis-	80 (8.0)	15.5[a]	28.6[b]	1.4331	1.784	533	261					28.8	2.7	35.2	33.8
$CF_3(CF_2)_3$—	*trans*-	80 (5)[e]	9.05[c]	8.8[d]	1.4170[e]	1.792[e]	. . .	. . .	28.05	2.59	39.94	29.64	28.3	2.4	39.1	29.8
	cis-	78 (3.3)[e]	13.1[c]	10.2[d]	1.4188[e]	1.801[e]	. . .	. . .					28.2	2.4	39.4	29.4
$CF_3(CF_2)_6$—	*trans*-	74 (0.7)[e]	15.0[c]	15.3[d]	1.3933[e]	. . .	. . .	. . .	27.0	1.74	49.3	21.95	27.2	1.8	49.0	22.1
	cis-	m.p. 45–46[e]	20.7[c]	20.1[d]	Solid	. . .	. . .	. . .					27.0	1.8	49.0	22.0

[a] One-meter tricresyl phosphate (20%) on firebrick column at 124° using helium carrier gas (1.5-p.s.i. applied pressure) at about 53 ml./min. [b] Two-meter polypropylene glycol (Perkin-Elmer "R") column at 150° using helium carrier gas (15-p.s.i. applied pressure) at about 46 ml./min. [c] Same column at 173°; helium at about 27 ml./min. [d] Three-meter "Apiezon" M on alkaline washed "Chromosorb" W (60–80 mesh) at 150° using helium (15-p.s.i. applied pressure) at about 65 ml./min. [e] Approximately 95% pure indicated isomer; remainder is the other isomer.

which limited the usefulness of this technique. Much iodine and decomposition products were obtained. As with azonitrile initiator, CF_3I and $(CF_3)_2CFI$ gave lower yields than did $CF_3CF_2CF_2I$. Free radical addition of $CF_3(CF_2)_6I$, induced by X-ray irradiation at room temperature, gave a moderate conversion in a few hours, and no free iodine. No advantage in yield or rate of reaction over azonitrile initiation could be realized. The *trans–cis* isomer ratios were lower for $(CF_3)_2CFI$ or $CF_3CF_2CF_2I$ addition than the values obtained with analogous azonitrile-initiated reactions. The ratio of C to D was quite close to the equilibrium ratio,[6] which indicated equilibration was occurring during reaction. This observation is consistent with the dependence of isomer ratio upon irradiation time and temperature.

Physical Properties and Separation of *cis* and *trans* Isomers.—The physical constants and analyses of the various adducts, including the retention times for g.l.c. columns and conditions we have used, are listed in Table III. For each pair of isomers the *trans* adduct had the lower boiling point (or retention time), refractive index (except for A and B), and density. The ultraviolet absorption maximum of the *trans* isomers having C_2F_5– or isomeric perfluoropropyl groups occurred at a slightly longer wave length (265 mμ) than the *cis* isomers (261 mμ). The absorption maximum of iodocyclohexane in ethanol was reported[14] to be 259 mμ while that of $CF_3CH_2CH_2I$[14] was 261 mμ. For comparison, the maximum for $(CF_3)_2CFI$ in methanol is 252 mμ (ε 189) and in isooctane, 278 mμ (ε 237). Preparative g.l.c. was required to separate cleanly *cis* and *trans* isomers, except for *cis*-1-iodo-2-(perfluoroheptyl)cyclohexane which was obtained as a crystalline solid. Not only were the isomers similar in volatility, but the thermal stability of A and B was not sufficient to permit fractional distillation under conditions adequate for their separation. Decomposition to iodine, HI, and tars occurred when the distillation flask was heated above 75°. By careful fractionation in an efficient spinning-band column the adducts from $CF_3(CF_2)_nI$ (n = 1, 2, 3) were separated to a great extent (95–99%).

Relative Reactivity of R_fI with Olefins.—By allowing an equimolar mixture of two R_fI to compete for an equivalent amount of cyclohexene, the relative reactivity was determined (see Fig. 3). In similar fashion 1-heptene and norbornene were employed as the olefin substrate. The data are in Table IV. *$(CF_3)_2CFI$ was invariably twice as reactive as $CF_3CF_2CF_2I$ even though the over-all rate of reaction varied considerably*

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(14) R. N. Haszeldine, *J. Chem. Soc.*, 1764 (1953).

TABLE IV

RELATIVE REACTIVITY OF R_fI WITH OLEFINS

Olefin	Ratio of addition (k_2) $CF_3CF_2CF_2I$/ CF_3I	Ratio of addition (k_2) $(CF_3)_2CFI$/ $CF_3CF_2CF_2I$	Ratio of addition to abstraction (k_2/k_5) $CF_3CF_2CF_2I$	Ratio of addition to abstraction (k_2/k_5) $(CF_3)_2CFI$
1-Heptene	$4^{a,b}$	$2^{b,c}$	104	192
Norbornene	$5^{a,b}$	$2^{b,d}$	$46^{b,d}$	$33^{b,d}$
Cyclohexene	18	2	6.56^{e}	$1.73^{e,f}$

[a] A mixture of 0.05 mole each of olefin, the two R_fI, 0.35 mole of cyclohexane, and 0.0025 mole of ABN was kept at 78° for ten hours. Total conversion was 83 to 89%. [b] Analysis was by g.l.c. using the "R" column at 150°, with 15 p.s.i. of helium pressure. [c] A mixture of 0.01 mole each of olefin, the two R_fI, 0.07 mole of cyclohexane, and 0.00025 mole of ABN was kept at 78° for 4 hours. Total conversion was 87%. [d] Amount of compound (0.01 mole) heated for 3 hr. at 65° using 0.0001 mole of ABN. Conversion was 96%. [e] After 21 hours of reaction at 65°. [f] k_2/k_5 was 2.05 after 4.5 hours.

with each olefin. However, with CF_3I and $CF_3CF_2CF_2I$ the same set of olefins gave quite different results; with cyclohexene $CF_3CF_2CF_2I$ gave eighteen times as much adduct as CF_3I, but with 1-heptene and with norbornene the discrimination was not so great (rate factor = 4 to 5). These ratios are consistent with results from a different series of reactions in which 1-heptene and norbornene or 1-heptene and cyclohexene were allowed to compete for $CF_3CF_2CF_2I$ (Table V).

TABLE V

RELATIVE REACTIVITY OF OLEFINS WITH $CF_3CF_2CF_2I$

Olefin mixture	Ratio of adducts	Total conversion, %
1-Heptene–norbornene	1/1	100
1-Heptene–cyclohexene	14/1	*ca.* 30

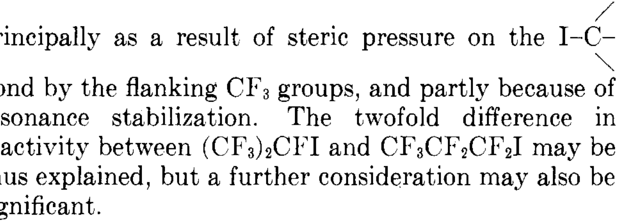
Norbornene and 1-heptene reacted at comparable rates, but cyclohexene was only 1/14 as reactive as 1-heptene. A strong retardation of addition to 1-heptene also was observed when cyclohexene was present. This we would now ascribe to chain-breaking reactions involving cyclohexene and its adducts. It is significant also that telomers of 1-heptene and norbornene were obtained only with CF_3I. The rate of transfer (k_3) was sufficiently low to permit addition of the adduct radical to another molecule of olefin before transfer occurred. Ordinarily, telomers of such reactive nonpolymerizable olefins with R_fI were not observed.

Ratio of Addition to Hydrogen Abstraction.—The much smaller ratio of addition to abstraction for $(CF_3)_2CF\cdot$ and cyclohexene ($k_2/k_5 = 1.73$) as compared with $CF_3CF_2CF_2\cdot$($k_2/k_5 = 6.56$) is especially striking when compared with the ratios observed for reaction with 1-heptene or norbornene (Table IV). For $(CF_3)_2CF\cdot$, $k_2/k_5 = 192$ after 7 hours of reaction with two moles of 1-heptene; for $CF_3CF_2CF_2\cdot$ it was 104, according to g.l.c. analysis of sealed reaction mixtures. *Thus, addition of $(CF_3)_2CFI$ to the open chain olefin was twice as efficient and rapid as the addition of $CF_3CF_2CF_2I$.* It is significant that with two moles of $(CF_3)_2CFI$ and only one mole of 1-heptene k_2/k_5 fell to 33.5. In the first case all of the R_fI was gone in less than an hour and the yield of adduct was 99%; in the second instance hydrogen abstraction by $(CF_3)_2CF$ continued on after all the olefin was used up, since the yield of adduct was still 99%. These results provide strong presumptive evidence for ascribing the lower k_2/k_5 value of $(CF_3)_2CF\cdot$ with cyclohexene to a greater steric retardation of k_2 with the bulkier R_fI. From the decrease in k_2/k_5 with time it appears that with cyclohexene also, hydrogen abstraction continues unabated after adduct concentration has reached a maximum (see Fig. 4). The much smaller difference in k_2/k_5 values of the two isomeric R_fI with norbornene is consistent with a considerably smaller steric retardation of k_2.

Theoretical Considerations.—It is interesting to consider the basis for the marked differences in addition and transfer rates of the various R_fI with cyclohexene and other olefins. A decrease in bond dissociation energy in the series $CF_3I > CF_3CF_2I > CF_3CF_2CF_2I > (CF_3)_2CFI$ may be postulated in accord with the known[3] variation of RX dissociation energies with alkyl structure. An increase in the resonance energy of $R_f\cdot$ with increasing size has been suggested[15,16] as the reason for the greater reactivity of $CF_3CF_2CF_2I$ over CF_3I in addition to ethylene or propargyl alcohol. Presumably this comes about because of a lower activation energy for addition, since the reaonance energy of $R_f\cdot$ can be contributed to the adduct radical in the addition step (equation 2, Chart I). In this connection it may be appropriate to reiterate the principle cited by Walling[17]: "... as one goes down a table of bond dissociation energies and radical stabilization, the radicals are formed with increasing ease. But they become progressively less reactive. This balance is often very important in determining the scope of a given type of chain reaction." Not only may R_f radicals differ in energy, but the adduct radicals with various olefins may have quite different stabilization energies. The competition between transfer and hydrogen abstraction or coupling reactions can be profoundly affected.

The greater reactivity of $(CF_3)_2CFI$ over $CF_3CF_2CF_2I$ may be attributed to a smaller bond dissociation energy, principally as a result of steric pressure on the $\text{I–C}\!<$ bond by the flanking CF_3 groups, and partly because of resonance stabilization. The twofold difference in reactivity between $(CF_3)_2CFI$ and $CF_3CF_2CF_2I$ may be thus explained, but a further consideration may also be significant.

In addition of a radical to an olefin, polar structures involving a dipole interaction between the radical and the π-electrons of the double bond can reduce the energy required to bring the two species together.[17,18]



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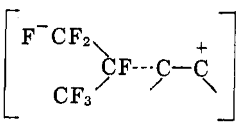
[15] F. E. Lawlor, Abstracts, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., 1955.

[16] J. D. Park, F. E. Rogers, and J. R. Lacher, *J. Org. Chem.*, **26**, 2089 (1961).

[17] C. Walling, *Chem. Eng. News*, **39**, 102 (1961).

[18] A. P. Stefani and M. Szwarc, *J. Am. Chem. Soc.*, **84**, 3661 (1962); (b) J. Gresser, A. Rajbenbach, and M. Szwarc, *ibid.*, **83**, 3005 (1961); (c) A. P. Stefani, L. Herk, and M. Szwarc, *ibid.*, **83**, 4732 (1961).

One would certainly expect that $(CF_3)_2CF\cdot$ would be better able to participate in a polar addition complex of the sort pictured than would $CF_3CF_2CF_2\cdot$ which has only two β-fluorines. The addition complex may actually involve additional resonance structures such as

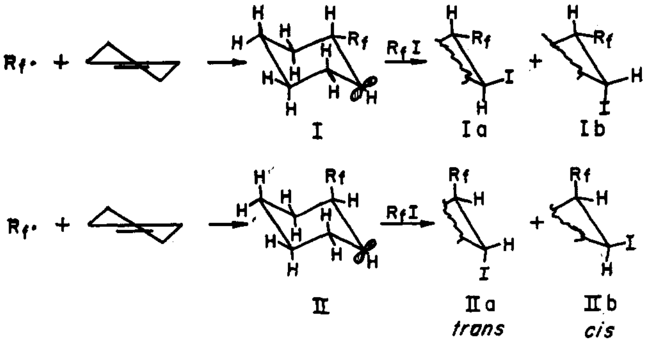


which can contribute to the over-all structure. In other words $(CF_3)_2CF\cdot$ is the more electrophilic radical. A similar argument may be given for $CF_3CF_2\cdot$ or $CF_3\cdot$ when compared with $CH_3\cdot$ or alkyl as has been done by Stefani and Szwarc.[18]

It is evident that selectivity of the olefin towards addition or hydrogen abstraction of $R_f\cdot$ is strongly influenced by the over-all reaction process. The marked difference in reactivity of cyclohexene and 1-heptene is a manifestation of the generally observed preference for addition of a radical to a more accessible terminal olefinic linkage.[3] In this respect the unusually low "methyl affinity" of cyclohexene in comparison with other olefins[18b] is quite consistent, as is the unusually high reactivity of norbornene which involves, of course, relief ring strain. The reduced selectivity of $CF_3\cdot$ (0.8) as compared with $CH_3\cdot$ (1.0 by definition)[18] is another indication that $R_f\cdot$ will be less discriminating in its reactions. In further studies this discrimination of addition of R_fI *vs.* abstraction by $R_f\cdot$ with various olefins will be explored.

Stereochemistry of the Addition Reaction.—The discovery[5] that the isomeric adducts A, B, C, and D assume different preferred conformations makes the stereochemical course of the reaction of great interest. There are evidently two contradictory steric considerations: (1) the bulky and electronegative iodine and perfluoroalkyl groups would prefer to be separated as far from each other as possible[1]; (2) in cyclohexane chair structures, axial hydrogens exert a crowding force on large axial substituents on the same side of the ring.[19]

One possible representation of the steric relationships which are involved during reaction is as follows.



It has been possible from a study of the n.m.r. spectra and dipole moments of the adducts to ascertain the preferred conformation of the 1,2-substituted cyclohexane rings.[5] These data are being reported in detail separately,[6] but the conclusions are summarized here.[20]

The *cis* isomers in the chair conformation have the R_f group (rather than the smaller iodo group) exclusively in the more open equatorial position. The *trans* isomers are faced with a disagreeable decision; either the two groups must be both equatorial and uncomfortably close to each other or they must both be subjected to repulsions by the four axial protons. For those *trans* isomers in which R_f is larger than CF_3– and linear, the preferred choice is to go into the diaxial conformation, with considerable bending away from the axial protons. This option appears to be closed to the adducts with $(CF_3)_2CF$– (which is branched at the bonding carbon) because of space limitations in the axial position. In both cases some distortion of the ring from a true chair structure is probable.[6]

The *trans* (a,a) conformers IIa from $CF_3(CF_2)_nI$ ($n = 1, 2, 3, 6$) have a higher energy content at 70° than the *cis* (a,e) conformers Ib, according to thermal equilibration studies.[6] Therefore, the slight preference for *trans* over *cis* in the preparative experiments must arise from kinetic control. The rate of transfer of adduct radical II with R_fI, giving *trans* isomer IIa, may be slightly faster than in the case of radical I, which gives *cis* isomer Ib, for steric reasons. The bulky R_f group of I is in a gauche position with respect to the incipient bond with R_fI; for II the groups are in an *anti* or *trans* position. In the transition state complex in radical transfer reactions of this type, a high degree of rigidity (because of low entropy value) has been postulated.[3,4,18]

The 3:1 preference for *trans* over *cis* isomer from $(CF_3)_2CFI$ is a more striking illustration of kinetic control, since *trans* (e,e) adduct is also slightly less stable[6] than the *cis* (e,a) conformer at 70°. Observe that the n.m.r. data indicate there is no detectable interconversion of *cis* conformers Ib and IIb or of *trans* conformers Ia and IIa (when R_f is greater than CF_3). Transfer of radical I from the more open equatorial side of the ring with $(CF_3)_2CFI$ might be expected to occur at a faster rate than from the axial side which may suffer from *axial* hydrogen opposition limiting the rate of transfer. A more sophisticated treatment must be deterred for the present.

In the case of CF_3I adducts, the fact that equilibration between conformations Ia and IIa (but not between Ib and IIb) is taking place above −90° may be decisive in giving a *trans–cis* ratio of 2.0. Transfer with CF_3I in the *anti* sense can occur with either radical I or II. The *cis* adduct exists to a detectable degree only in the (e,a) conformation Ib, derived from radical I. Therefore, Ib has only half the probability of being formed as Ia and IIa, other factors being equal.

Iodoperfluoroalkane Addition to Cyclopentane.—Free radical addition of 1-iodoperfluorobutane to cyclopentene by either light- or azonitrile-induced reaction gave *trans*-1-iodo-2-(perfluorobutyl)cyclopentane (M) in 40% conversion (80% yield). No evidence for an

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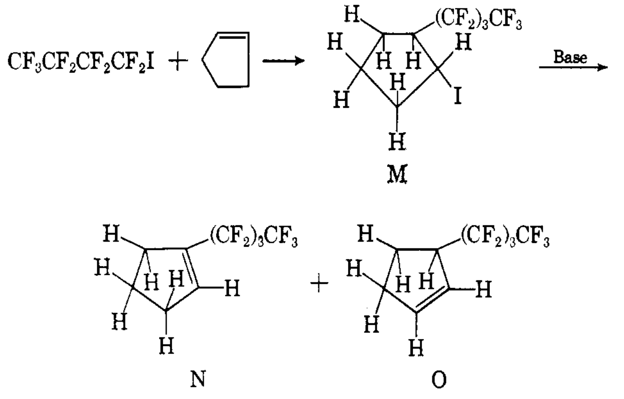
[19] For a recent excellent discussion see E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Company, Inc., New York, N. Y., 1962, p. 204.

[20] Adduct A prefers conformation Ia, and adduct B, conformation Ib according to n.m.r. spectra.[5] The *trans* adducts from $CF_3(CF_2)_nI$ ($n = 1, 2, 3, 6$), however, assume the diaxial conformation IIa even though the *cis* adducts prefer conformation Ib. Temperatures from 90° to −100° did not significantly affect the n.m.r. spectra of the *cis* or *trans* adducts from $CF_3(CF_2)_nI$ ($n = 1, 2, 3$) or from $(CF_3)_2CFI$, and the *cis* adduct from CF_3I. Just as found for iodocyclohexane, however, the mobile equilibrium of the two *trans* conformers of E ($Ia \rightleftharpoons IIa$) was arrested at −90° to −105°.[6]

isomeric adduct was obtained. The *trans* structure is consistent with the n.m.r. spectrum which has a low-field multiplet of four lines spaced 5 to 6 c.p.s. apart at −267 c.p.s. (relative to tetramethylsilane at 60 Mc.). The splitting is attributed to the proton on C-1 coupled with two protons (J = *ca.* 6 c.p.s.) on C-5 and with a proton on C-2 (J = *ca.* 5 c.p.s.). These are reasonable values for coupling constants of *trans*-oriented protons of cyclopentane rings.[21]



From an examination of models it is clear that a *cis* adduct would have considerable crowding of the R_f and iodo groups.

Elimination of HI by heating *M* with tri-*n*-butylamine gave an olefin mixture (94%) which consisted of the Δ^1-isomer N (18%) and the Δ^2-isomer O (82%) according to g.l.c. analysis and n.m.r. spectra. The relative amounts of N and O are reasonable for preferential *trans* elimination of hydrogen iodide, taking into consideration the dihedral angle of about 123° rather than the preferred 180° known to obtain for *trans* elimination in this system.[22,23] The corresponding *cis* adduct would be expected to give a preponderance of N by elimination of the more acidic *trans* proton attached to the carbon atom bearing the R_f group.[6]

The dipole moment of M (2.99 D.) was quite close to the value (3.09 D.) obtained for *endo*-2-iodo-3-*exo*-(perfluoropropyl)norbornane.[1,6] This further supports the *trans* structure, since the bond angles are quite similar to those found in the five-membered ring of the *trans*-norbornane derivative.

Radical addition to cyclopentadiene of 1-iodoperfluoropropane could not be effected, nor would the azonitrile-induced addition to 1-heptene occur in the presence of this reactive diene. It is probable that the perfluoropropyl radicals, therefore, add readily to the conjugated diene, but that transfer of the resonance-stabilized adduct radical with R_fI does not occur at a rate sufficient to maintain a chain reaction. Such a situation was observed for styrene[1] which gives a stable benzyl-type adduct radical.

Experimental

All experiments were carried out in an atmosphere of nitrogen. Gas-liquid chromatography of all compounds was done with a Perkin-Elmer vapor fractometer, Model 154-C. The columns and conditions used are listed in Table III. Except where specified, a reagent grade of cyclohexene was used (99.82 mole % minimum, Phillips Petroleum Co., treated with Woelm activated alumina, activity grade I, to remove peroxide). Iodotrifluoromethane, 1-iodoperfluoroethane, 1-iodoperfluoropropane, and 1-iodoperfluoroheptane were obtained from Columbia Organic Chemical Co. 1-Iodoperfluoroethane (b.p. 13°, 99.9% pure), 1-iodoperfluoropropane (colorless, b.p. 41°, n^{25}D 1.3250, 99.9% pure), and 1-iodoperfluoroheptane [b.p. 70° (70 mm.), n^{25}D 1.3270, containing about 10% of an isomeric impurity as shown by g.l.c.] were redistilled. 1-Iodoperfluorobutane was prepared from iodoperfluoroethane and tetrafluoroethylene[24] and redistilled, b.p. 67.8°; n^{25}D 1.3258 (98% pure). 2-Iodoperfluoropropane was prepared from perfluoropropylene and iodine pentafluoride,[25] b.p. 39.5°; n^{25}D 1.3263 (99.9% pure). 1-Heptene was obtained from the Humphrey-Wilkinson Co., and redistilled, b.p. 93°; n^{25}D 1.3975. Cyclopentene, from the Aldrich Chemical Co., was redistilled, b.p. 44°; n^{25}D 1.4190 (100% pure). Norbornene was redistilled, b.p. 94–95°, sublimable solid (99% pure). 1-Hydroperfluoropropane[26] (b.p. −17°) and 2-hydroperfluoropropane[26] (b.p. −18°) were a gift from S. Andreades. Experiments with CF_3I and CF_3CF_2I were carried out in Hastelloy C-lined steel 400-ml. shaker tubes.

***trans*-1-Iodo-2-(perfluoroisopropyl)cyclohexane (A) and *cis* Isomer B.** (a) **From Azobisisobutyronitrile-Initiated Reaction.**—Cyclohexene (54.7 g., 0.67 mole, 99.8 mole %), 2-iodoperfluoropropane (50.0 g., 0.17 mole), and azobisisobutyronitrile (1.6 g., 0.01 mole) were heated at 50° in an oil bath at constant temperature for 30 hr. in a flask fitted with a syringe port and having a −70° condenser. Samples removed showed by g.l.c. analysis a steady increase in product concentration up to 25 hr., and then a decrease; the ratio of A to B fell from 3.3 after 9 hr. to 2.7 after 17 hr. The conversion to A and B from g.l.c. analysis was 21%; the yield was 82%. The orange solution (101.2 g.) was cooled to 5° and filtered. 2-Hydroperfluoropropane and 2-iodoperfluoropropane were lost during filtration. The filtrate (96.2 g.) was fractionated in a 3-ft. platinum spinning band column (column A). 2-Iodoperfluoropropane (30.4 g.) cyclohexene (50 g.), and a mixture of A and B (with small amount of impurities), b.p. 36–43° (0.8 mm.) (12.5 g., 19.5% conversion), distilled, leaving a dark residue of 1.2 g. (10%). The adducts were kept dark and cold. Preparative g.l.c. was used for purification.

The solid obtained at 5° was rinsed with 25 ml. each of cyclohexene and dichloromethane. Azobisisobutyronitrile (ABN) (0.215 g.), m.p. 100–101° (undepressed by mixture with ABN), was obtained. Other substances were present in the filtrate.

(b) **Isolation and Identification of Tetramethyl-5-imino-2-pyrrolidone Hydroiodide.**—2-Iodoperfluoropropane (150.0 g., 0.5 mole), cyclohexene (164 g., 2.0 moles), and ABN (5.0 g., 0.03 mole) were heated for 22 hr. at 52–70°. Solid (0.335 g.) remained in the flask when the product mixture was decanted at 5°. The light sensitive solid was placed in a subliming tube and volatile material removed at 125° at 0.1 mm., leaving 0.23 g. of nonvolatile salt. It decomposed when heated in an open melting point tube. In a sealed capillary tube, however, the salt melted at 315° without evident decomposition. It was soluble in water, giving a precipitate of silver iodide by reaction with silver nitrate solution, and was recrystallized from acetone in the dark at 5°. A solution gradually darkened and formed tar. An infrared spectrum[27] (potassium bromide disk) showed a strong bonded NH band at 3.0 μ, carbonyl group bands at 5.60 and 6.15 μ, and several longer wave-length bands. These bands are analogous to those reported[28] for creatinine hydrochloride which also has an $HX\cdot HN{=}\overset{|}{C}{-}\overset{|}{N}HCO{-}$ grouping.

Anal. Calcd. for $C_8H_{14}N_2OI$: C, 34.18; H, 5.02; N, 9.97; I, 45.15. Found: C, 34.4; H, 5.7; N (Dumas), 9.5; I, 44.8.

(c) **Relative Rates of Allylic Hydrogen Abstraction and of Addition of 2-Iodoperfluoropropane or 1-Iodoperfluoropropane to Cyclohexene.**—Cyclohexene (4.2 g., 0.05 mole), 2-iodoperfluoro-

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[21] C. D. Jardestzky, *J. Am. Chem. Soc.*, **84**, 62 (1962).

[22] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Company, Inc., New York, N. Y., 1959, p. 472.

[23] (a) P. I. Abell and C. Chiao, *J. Am. Chem. Soc.*, **82**, 3610 (1960); (b) C. H. De Puy, R. D. Thurn, and G. F. Morris, *ibid.*, **84**, 1314 (1962).

[24] R. N. Haszeldine, *J. Chem. Soc.*, 2856 (1949); *ibid.*, 3761 (1953).

[25] M. Hauptschein and M. Braid, *J. Am. Chem. Soc.*, **83**, 2383 (1961).

[26] A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, p. 60.

[27] I am indebted to Dr. R. K. Miller for assistance in obtaining and interpreting the infrared spectrum.

[28] H. M. Randall, R. G. Fowler, N. Fuson, and J. R. Dangl, "Infrared Determination of Organic Structures," D. Van Nostrand and Company, Inc., Princeton, N. J., 1949, p. 229.

propane (3.0 g., 0.10 mole), and ABN (0.081 g., 0.0005 mole) were sealed in a 10-ml. stainless steel cylinder, filled with nitrogen, and heated at 73° for 20.5 hr. While inverted, the cylinder was sampled at 7.5 mm. allowing the liquid to expand at 25° into a 1-l. volume chamber which had been previously evacuated to 0.5 mm. A 25-ml. portion of the gas mixture was passed into the vapor fractometer. Relative areas of $(CF_3)_2CFH$, $(CF_3)_2CFI$ and of cyclohexene were determined for the original mixture, for samples taken at 4.5 and 20.5 hr., and two known weighed mixtures of these compounds. The amount of $(CF_3)_2CFH$ increased from about 12.2 to 16% conversion during this time, but the amount of $(CF_3)_2CFI$ converted to adducts could not be accurately determined by this technique, because of changes in weight/area factors with change in composition and low volatility of the adducts. However, the total product mixture at −50° was sampled with a cold syringe and the composition determined by g.l.c. analysis. The conversion to $(CF_3)_2CFH$ was 15.9%, to A, 19.3%, and to B, 8.2%; the amount of $(CF_3)_2CFI$ used up was 50%, and the ratio of addition to abstraction was, therefore, 1.73. The radical coupling products less volatile than B were not observed by this technique.

An identical procedure using 1-iodoperfluoropropane gave $CF_3CF_2CF_2H$ (8.2%), recovered $CF_3CF_2CF_2I$ (42%), and C and D (26 and 27.8%, respectively). The ratio of addition to abstraction was 6.56. The yield of adducts was 93% based on 1-iodoperfluoropropane used up. To determine product composition the g.l.c. weight/area factors were determined at two levels of conversion: $CF_3CF_2CF_2H$ (weight %, 1.66; weight/area, 0.70); $CF_3CF_2CF_2I$ (32.0; 2.16); cyclohexene (52.3; 0.78); C and D (13.48; 1.25); and $CF_3CF_2CF_2H$ (9.50; 0.79); $CF_3CF_2CF_2I$ (29.0; 1.98); cyclohexene (54.6; 0.85); and C and D adducts (6.82; 1.31). The 1-m. tricresyl phosphate column operated at 124° was used (see Table III). Similar results were obtained using $(CF_3)_2CFI$ and its products.

***trans*-1-Iodo-2-(perfluoropropyl)cyclohexane (C) and the *cis* isomer D. (a) ABN-Initiated Reaction.**—1-Iodoperfluoropropane (62.0 g., 0.20 mole), cyclohexene (Phillips, 99.8%, *not* treated with activated alumina; 82 g., 1.0 mole) and ABN (1.00 g., 0.008 mole) were heated at 50° for 22 hr. G.l.c. analysis showed a steady increase in conversion with time. The ratio of *trans* C to D *cis* isomers was constant at 1.01. Distillation of the slightly colored liquid in a 16-in. platinum spinning band column (column B) gave cuts: (1) 1-iodoperfluorpropane, b.p. 41°, $n^{25}D$ 1.3335 (21.5 g.); (2) cyclohexene, b.p. 50° (200 mm.), $n^{25}D$ 1.4418 (65 g.); (3) contained tetramethylsuccinonitrile (TMSN), C, and D, b.p. 40–42° (2.2 mm.) (2.2 g.); (4) a second impure fraction, b.p. 47–50° (2.0 mm.), $n^{25}D$ 1.4620, 7.3 g., which contained 79.4% of C, 10.5% of D, 1-cyclohexen-3-one (*ca.* 0.4 g.), and iodocyclohexane and/or 3-iodo-1-cyclohexene (*ca.* 0.1 g.); (5) C and D, b.p. 51–53° (2.0 mm.), $n^{25}D$ 1.4340, 28.9 g.; and hold-up in the column, $n^{25}D$ 1.4475, 1.5 g. There was no tarry residue. The hold-up contained C, D, and "dimeric" coupled products[6] with retention times of 27.4 (*ca.* 0.15 g.) and 39.3 min. (*ca.* 0.6 g.). The trap contained 2.5 g. of 1-iodoperfluoropropane and 1-hydroperfluoropropane mixture. The total conversion of C and D was 50% on 1-iodoperfluoropropane (90% yield). The conversion under other conditions is given in Table I; analytical data and physical properties are in Table III. C and D were separated by g.l.c. on a preparative scale. Fractionation in column A gave partial separation; cuts containing 80% of C and 20% of D, and 5% of C and 95% of D were obtained.

(b) Ultraviolet Light-Reduced Reaction at −20 to 0°.—A reaction vessel identical to that described by Kharasch and Friedlander[12] was used. 1-Iodoperfluoropropane (63.7 g., 0.215 mole) and cyclohexene (82.3 g., 1.0 mole, 99.82% not treated with alumina) was irradiated at −20°. In a few minutes, a dark deposit formed in the reactor and the liquid darkened. After 1 hr., a 23% conversion to C and D was attained; the ratio of C to D was 0.86. After 4 hr. at −15° to −13°, the conversion was 38%, and after 6 hr. at −13°, 51.0%. Further irradiation at 0° for 8 hr., (14 hr. total) gave no further increase of C and D, and, after 5.5 hr. at 0 to 2° (19.5 hr. total), a small decrease in C and D. The ratio of C/D also rose to 0.92. The total amount of (perfluoropropyl) cyclohexane and of 1- and 3-(perfluoropropyl)-1-cyclohexene was: after 1 hr., 1.5%, 4 hr., 2.0%; 6 hr., 2.7%; 14 hr., 3.4%; and 19.5 hr., 3.5%.

Distillation gave C and D (41% conversion, 72% yield on recovered 1-iodoperfluoropropane), the (perfluoropropyl)cyclohexane–cyclohexene mixture (which see) (1.2 g.), and iodocyclohexane and 3-iodo-1-cyclohexene as above not separated from C and D (1.55 g., 3.4% conversion, g.l.c. analysis). The residue was 1.3 g. of black tar. The darkly colored distilled C and D was treated with activated alumina and carbon to remove iodine.

***trans*-1-Iodo-2-(trifluoromethyl)cyclohexane (E) and *cis* Isomer F by ABN-Initiated Reaction.**—CF_3I (49.0 g., 0.25 mole), cyclohexene (162.0 g., 2.0 mmoles), and ABN (1.64 g., 0.01 mole) were shaken at 80° for 15 hr., and vented at 50° into a cold trap. The CF_3I which was collected (5.0 g., 95.3%) contained no CF_3H by mass spectra analysis. The liquid (211 g.) was cooled to −20°, sampled for g.l.c. analysis, filtered from 0.2 g. of tetramethylsuccinonitrile (TMSN) (m.p. 155–160°, crude), and distilled in column A using a liquid nitrogen cooled trap to collect CF_3I (39.5 g.). Cyclohexene, b.p. 50° (200 mm.) (156.0 g.) and a mixture of E and F and coupled products [b.p. 49–52° (2.5 mm.), $n^{25}D$ 1.4814 to 1.4828 (7.53 g.)] were obtained. The residue (1.4 g.) was a light-sensitive gum, soluble in dichloromethane. Analyses showed 24.0% iodine and mol wt. (ebulloscopic in acetone) of 280. The volatile products were redistilled, b.p. 66–75° (17 mm), without effecting a separation. The sample contained (weight %) 20% of CF_3I, 74% of cyclohexene, 0.8% of isomeric trifluorocyclohexenes, 1.8% (3.8 g.) of *trans* adduct E, 0.9% (1.9 g.) of *cis* adduct F, and 0.31% of TMSN (8% conversion to E and F).

Time-of-flight mass spectra analysis[29] of g.l.c. separated cuts showed the main components (80 to 90%) were E and F. The presence of cyclohexenyl iodide in one cut was confirmed, but it was only about 0.008% of the total material distilled. Preparative g.l.c. was used to separate the materials, which then were better than 99% pure isomer. The addition of CF_3I to cyclohexene, by reaction with a large amount of magnesium amalgam, has been recently reported.[30] The physical properties of the isomer mixture obtained in 43% yield agree well with the values for the pure isomers given in Table III.

***cis*- and *trans*-1-Iodo-2-(perfluoroethyl)cyclohexanes by Peroxide-Initiated Reaction.**—Cyclohexene (184 g., 2.0 moles) di-*t*-butyl peroxide (6.0 g., 0.04 mole) and iodopentafluoroethane (98.4 g., 0.4 mole) were shaken for 15 hr. at 130°. The product mixture was transferred while cold to a distilling flask and fractionated in column A. Low boiling liquid (26 g.) collected in the −70° trap and was analyzed by g.l.c. [2.5-m. "R" polypropylene glycol column, helium at 14 p.s.i., temperature programmed at the rate of 40°/min. from 25 to 100°], and time-of-flight mass spectrum analysis.[29] Compounds were eluted in the order: hydropentafluoroethane (2.8%), isobutylene (9.4), iodopentafluoroethane (85%), acetone (0.07), iodomethane (0.09), cyclohexane (0.02), *t*-butyl alcohol (0.18), cyclohexene (2.3), and benzene (0.16). There was less benzene and cyclohexane in the original cyclohexene than this.

The first fraction, b.p. 43° (160 mm.), 162.0 g., contained cyclohexene, acetone, *t*-butyl alcohol, and other substances. Fraction 2, b.p. 49–52° (5.0 mm.) (6.0 g.), contained about 1% of 1-(and 3)-(perfluoroethyl)cyclohexene, 55% of *trans*-1-iodo-2-(perfluoroethyl)cyclohexane, 22% of 1-cyclohexen-3-one, 5.5% of iodocyclohexane and 3-iodo-1-cyclohexene, and 3.4% of *cis*-1-iodo-2-(perfluoroethyl)cyclohexane. The side products were unequivocally identified by t.o.f. mass spectrum analysis[29] of g.l.c. separated components. The infrared spectrum also showed a strong carbonyl band at 5.99–6.02 μ (doublet) attributed to the unsaturated ketone. Subsequent fractions, b.p. 50° (5.2 mm. to 2.0 mm.), totaled 53.0 g. and contained 28.1 g. of *trans* and 24.5 g. of *cis* adduct (40% conversion; *trans–cis*, 1.15; total recovery 95%) according to g.l.c. analysis. The pot residue was 6.2 g. of a viscous dark liquid condensation product.

The dark adduct mixture was passed down activated alumina and carbon and the colorless material redistilled. Careful fractionation in column A afforded *trans* isomer, b.p. 58° (5.5 mm.) (96% pure), and *cis* isomer, b.p. 68° (5.5 mm.) (99% pure, g.l.c. analysis).

When less pure cyclohexene (2.0 moles, 98.6%) was used (see following experiment) the conversion fell to 14% of the adducts. When the amount of cyclohexene (99%) was reduced to 64 g. (0.8 mole), and 64 g. (0.8 mole) of benzene was added, the conversion to adducts was reduced to 15%.

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(29) Time-of-flight (t.o.f.) analyses were performed by Dr. D. O. Miller and Dr. F. Kitson, to whom I am indebted for assistance in obtaining and interpreting these data.

(30) E. T. McBee, R. D. Battershell, and H. P. Braendlin, *J. Org. Chem.*, **28**, 1131 (1963).

Crystalline *cis*-1-iodo-2-(perfluoroheptyl)cyclohexane by X-Ray-Induced Reaction.—Cyclohexene (24.6 g., 0.3 mole, 98.6% by g.l.c., containing 1.3% of methylcyclopentene by t.o.f. analysis) and 1-iodoperfluoroheptane (49.6 g., 0.1 mole, containing about 10% of an isomeric iodoperfluoroheptane by g.l.c.) was sealed under nitrogen in a 300-ml. steel tube fitted with a collar device for rotating in front of a gold target impinged upon by an electron beam from a Van de Graf accelerator.[31] After 3.5 hr. at 25° and 30,000 rads/min. dose rate, a sample (nearly colorless) showed about 20% conversion (90% yield) to adducts; after 5.75 hr. at 45,000 rads/min., the reaction mixture was sampled and distilled. There was evidence of decomposition, since white fumes and dark blue liquid was obtained. The recovery of 1-iodoperfluoroheptane was 28 g. (73%), and the yield of isomeric adducts was 23 g. (41% conversion). There was about 4 g. (10%) of $C_7F_{15}H$ formed and isolated as an azeotrope (with cyclohexene) which separated into two layers. The isomeric mixture of adducts partly solidified when cooled to 5° for 1 day. When placed on a cold Hirsch funnel, 0.8 g. of solid *cis* isomer was collected; 18.0 g. of liquid mixture was recovered. Recrystallization from dichloromethane at −70° gave 0.4 g. of *cis* isomer, m.p. (sinter 45°) 46–47° (g.l.c., 95% pure).

Preparative scale g.l.c. of the isomeric mixture gave the solid *cis* and the pure liquid *trans* isomer which distilled at b.p. 74° (0.7 mm.); $n^{25}{}_D$ 1.3933.

G.l.c. Separation of Isomeric Adducts.[32]—The most suitable conditions found for the separation of these sensitive materials by g.l.c. was as follows. A 12-ft. by 0.75-in. column packed with 20% of tricresyl phosphate on "Chromasorb" was heated to 150° while helium at 1550 ml./min. was used as a carrier gas to elute 1-ml. quantities of *trans* and *cis* adducts. The colorless material was transferred to ampoules without appreciable darkening, and kept dark and cold. An attempt to purify the product mixture using similar conditions with a polypropylene glycol column packing satisfactory for analysis failed because the liquid did not elute properly. Properties and analysis of adducts are listed in Table III.

Relative Rate of Reaction of CF_3I and $CF_3CF_2CF_2I$ with Cyclohexene.—Iodotrifluoromethane (3.92 g., 0.02 mole) was weighed in a small brass cylinder, and condensed into a 400-ml. steel shaker tube (with a Hastelloy C liner) in which had been placed 16.4 g. (0.20 mole) of cyclohexene, 5.92 g. (0.02 mole) of 1-iodoperfluoropropane, and 0.33 g. (0.002 mole) of ABN. The tube was heated to 80° for 20 hr. while shaking, cooled to 25°, vented, and the liquid product (23.0 g.) sampled for g.l.c. analysis (1-m. "TCP" column, 125°, 53 ml./min. of helium). The areas of the component peaks were converted to per cent conversion by calculation using the factors obtained from a similar mixture.[33] The products were a mixture of (perfluoroalkyl)cyclohexenes (R_f = CF_3 and C_3F_7-), *ca.* 2.5% conversion (on total R_fI); *trans* isomer C (1.77 g., 23.5%); *trans* isomer E (0.10 g., 1.75% based on CF_3I); *cis* isomer D (1.69 g., 22.3%); *cis* isomer F (0.06 g., 0.85%); TMSN (0.129 g., 47% on ABN); and coupled products (two peaks; *ca.* 2.3% on total R_fI). The disproportionation products were identified by comparison with the previously isolated compounds,[6] and are the sum of the mixture obtained. The ratio of adducts from $CF_3CF_2CF_2I$ to adducts from CF_3I was 17.6; the ratio of E to F was 2.06 and of C to D, 1.05. The efficiency of addition in total moles of adducts was 4.83. For comparison, with CF_3I and cyclohexene alone under similar conditions the efficiency was 2.67; with $CF_3CF_2CF_2I$ and cyclohexene, 7.91.

Distillation of 22.5 g. (94.3% of total) gave CF_3I (collected in the −70° trap, 1.3 g.); $CF_3CF_2CF_2I$ (0.83 g.); cyclohexene (14.0 g.); and a mixture of the two pairs of adducts, b.p. 56–66° (4.5–3.5 mm.); 3.57 g. (theory, 3.61 g.). The residue and hold-up was 0.56 g. G.l.c. analysis showed that the ratio of adducts in the distilled sample was 18.6 to 1 in close agreement with the results given above.

Relative Rate of Addition of $CF_3CF_2CF_2I$ and $(CF_3)_2CFI$ to Cyclohexene. (a) **At 65° with ABN Initiator.**—Cyclohexene (8.21 g., 0.10 mole), 1-iodoperfluoropropane (2.96 g., 0.01 mole), 2-iodoperfluoropropane (2.96 g., 0.01 mole), and ABN (0.164 g., 0.0010 mole) were heated at 65°. The per cent conversions to adducts obtained are plotted as a function of time in Fig. 3. At the conclusion of the experiment the product mixture was a light yellow color. After 11–20 hr. about 2–4% of (perfluoropropyl) cyclohexenes was present in the product mixture.

Precisely the same conditions were used with 1-iodoperfluoropropane or 2-iodoperfluoropropane *alone* in separate experiments. The rate of total product formation is plotted in Fig. 1, 2, and 4. There was no change in the isomer ratio with time in either case. There was no (perfluoropropyl)cyclohexene obtained from reaction of 1-iodoperfluoropropane, but a 2–3% conversion to a (perfluoroisopropyl)cyclohexene mixture occurred with 2-iodoperfluoropropane. A variable amount of R_fH was lost by the sampling technique, and no attempt was made to measure the quantity present.

Over-all reaction rates were also determined in cyclohexane solution. Cyclohexane (Spectro Grade, 5.89 g., 0.070 mole), 2-iodoperfluoropropane (2.96 g., 0.01 mole), cyclohexene (0.82 g., 0.01 mole), and ABN (0.082 g., 0.0005 mole) was heated at 65°, samples taken, and analyzed. The conversion to adducts attained 10.5% of A and 4.5% of B after 17 or 23 hr. For the same reaction time 9.0 % conversion [on $(CF_3)_2$ CFI] to iodocyclohexane was obtained and about 1% of (perfluoroisopropyl)cyclohexenes. The solution was slightly yellow and the crystalline hydriodide salt was formed.

1-Iodoperfluoropropane under these conditions gave a 15% conversion to C and D in 17 hr., 17% conversion in 24 hr., and 18.4% conversion in 29 hr. The (perfluoropropyl)cyclohexenes were formed after 21-hr. reaction time (about 1% conversion).

2-Iodoperfluoropropane, cyclohexane, and ABN (same amounts as before; no cyclohexene) gave iodocyclohexane as follows: 1 hr., 4.45% conversion [on $(CF_3)_2CFI$]; 2 hr., 6.73%; 3 hr., 9.79%; 4 hr., 12.0%; 5 hr., 16.0% (or 0.0013 mole). The amount of ABN decomposed during this time (half-life, 4 hr. at 74°) was *ca.* 0.00025 mole; therefore, about 6 moles of iodocyclohexane was produced for each mole of ABN decomposed.

(b) **At 130° with Di-*t*-butyl Peroxide Initiator.**—1-Iodoperfluoropropane (40 g., 0.135 mole), 2-iodoperfluoropropane (21.0 g., 0.71 mole), cyclohexene (not treated with alumina, 164 g. 2.00 moles), and di-*t*-butyl peroxide (6.0 g., 0.04 mole) were heated in a Hastelloy C-lined shaker tube at 130° for 15 hr. The ratio of adducts was ascertained before and after work up by g.l.c. analysis. The recovered iodoperfluoroalkane cuts (16.0 g.) contained a large number of components. The distilled *cis* and *trans* adducts (30.8 g., 40% total conversion) comprised: A, 33.2% conversion and B, 15.5% [from $(CF_3)_2CFI$]; and C, 21.3% and D, 18% conversion (from $CF_3CF_2CF_2I$). The ratio of adducts (A + B/C + D) was 0.653, whereas the ratio of reactants was 0.526; hence, the rate of adduct formation from 2-iodoperfluoropropane was 1.24 times greater. Because of the large number of volatile products obtained no estimate of the ratio of abstraction to addition could be made.

Azonitrile-Induced Isomerization and Disproportionation of A.—A mixture of 0.1951 g. (0.000516 mole) of A, 4.1 g. (0.0050 mole) of cyclohexene, and ABN (0.0827 g., 0.000504 mole) was heated in a bath at 71°. The relative amounts were estimated from the areas in comparison with cyclohexene. Initially only A (4.45% by weight) and cyclohexene (95.4% by weight) were present. After 1 hr. the composition was cyclohexene (93%), 1- and 3-(perfluoroisopropyl)1-cyclohexene[6] mixture (0.5%), A (2.8%), B (1.3%), TMSN (0.5%), and "coupled" product[6] (0.5%). After 3, 5, 10, or 22 hr., the composition was cyclohexene (95%), olefin mixture (0.5%), A (3.0%), TMSN, and "coupled" product (2.5%).

Relative Rates of Addition and Abstraction of $CF_3CF_2CF_2I$ or of $(CF_3)_2CFI$ with 1-Heptene.—1-Perfluoropropyl-2-iodoheptane (H) was prepared from 1-heptene (4.0 g., 0.04 mole), 1-iodoperfluoropropane (6.0 g., 0.02 mole), and ABN (0.03 g., 0.0002 mole) kept at 65° for 6 hr. in a 10-ml. steel cylinder, which was evacuated to 0.5 mm. at −70°. The liquid was sampled at −70° for g.l.c. analysis (2-m. "R" column; 150°; 15 p.s.i. of helium pressure) and distilled in column B, b.p. 86° (10 mm.); $n^{25}{}_D$ 1.4072, $d^{25}{}_D$ 1.5608; 6.5 g. (84% recovery). Moles of H/$CF_3CF_2CF_2H$ from area ratio × weight/area factor (1.2 for both substances) was 104/1. There was only 0.0022% of $CF_3CF_2CF_2I$ unreacted. A 99% yield of H was shown by g.l.c. analysis. Retention time was 19.4 min.

Anal. Calcd. for $C_{10}H_{14}F_7I$: C, 30.4; F, 33.7; H, 3.56; I, 32.2. Found: C, 30.5; F, 33.6; H, 3.8; I, 31.9.

1-Isoperfluoropropyl-2-iodo-heptane (G) was prepared under the conditions used previously, and also in cyclohexane solution.

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[31] The technique and equipment was that used by Dr. F. W. Stacey, to whom I am indebted for assistance.

[32] I am indebted to J. B. Robson for assistance.

[33] The weight/area factors for the product mixture were very similar to those given for adducts A to D in similar mixtures.

No further reaction occurred after 1 hr. at 65°, and all the 2-iodoperfluoropropane was used up (g.l.c. analysis of samples). Distillation in column B gave G, b.p. 78° (10 mm.); $n^{25}\text{D}$ 1.4075; 7.1 g. (90% recovery). Retention time was 14.6 min. Moles G/$(CF_3)_2CHF$ was 192; yield of G was better than 99%.

1-Heptene (1.95 g., 0.02 mole), 2-iodoperfluoropropane (11.4 g., 0.038 mole), and ABN (0.03 g., 0.0002 mole) under these conditions gave by distillation, G (6.8 g., 86% recovery), and $(CF_3)_2$-CFI (5.4 g.). G.l.c. analysis showed that $(CF_3)_2CFH$ (0.12 g., 2.1% conversion), G (99% conversion), and no 1-heptene were present. Moles of G/$(CF_3)_2CFH$ was 33.5.

Anal. Calcd. for $C_{10}H_{14}F_7I$: C, 30.5; F, 33.7; H, 3.56; I, 32.2. Found: C, 30.4; F, 33.3; H, 3.8; I, 31.9.

2-*endo*-Iodo-3-*exo*-trifluoromethylnorbornane (J) **and 2,2′-Bis-(3-iodo-3′-Trifluoromethylnorbornyl).**—Iodotrifluoromethane (9.8 g., 0.05 mole), norbornene (9.0 g., 0.1 mole), and ABN (1.0 g., 0.0061 mole) were kept at 80° for 15 hr. while shaking. Fractionation gave norbornene (1.65 g.), J [b.p. 87° (20 mm.) or 72° (6.0 mm.); $n^{25}\text{D}$ 1.4851; 10.2 g. (60%)], and 2,2′-bis(3-iodo-3′-trifluoromethylnorbornyl) [b.p. 106° (0.3 mm.); $n^{25}\text{D}$ 1.5238; 4.2 g. (22%)]. G.l.c. analysis showed that J contained about 5% of TMSN. The liquid was twice cooled to 5°, filtered from solid TMSN and passed over activated alumina. TMSN was reduced to 1.6%, but was not completely removed (high carbon analysis).

Anal. Calcd. for $C_8H_{10}F_3I$: C, 33.12; H, 3.47; F, 19.65; I, 43.75. Found: C, 33.8; H, 3.5; F, 19.8; I, 42.7.

Anal. Calcd. for $C_{15}H_{20}F_3I$: C, 46.9; H, 5.24; I, 33.0; mol. wt., 384.2. Found: C, 46.9; H, 5.1; I, 33.8; mol. wt. (ebulloscopic in acetone), 365.

1-Trifluoromethyl-2-iodoheptane (**K**) **and 1-Trifluoromethyl-4-iodo-8-pentylnonane.**—CF_3I (9.8 g., 0.05 mole), 1-heptene (10.0 g., 0.1 mole), and ABN (1.0 g., 0.0061 mole) were kept at 80° while shaking for 15 hr. Distillation in column B gave K, b.p. 72° (10 mm.); $n^{25}\text{D}$ 1.4398 (9.0 g., 68% yield) and CF_3CH_2-$CH[(CH_2)_4CH_3]CH_2CHI(CH_2)_4CH_3$, b.p. 94–96° (0.25 mm.); $n^{25}\text{D}$ 1.4597 (4.90 g., 25% yield). G.l.c. analysis of K showed that 5% of an isomeric substance was present. TMSN was removed by filtration and chromatography on alumina. The 2 to 1 telomer was redistilled in a sublimer cup, b.p. 80° (0.15 mm.).

Anal. Calcd. for $C_8H_{14}F_3I$: C, 32.7; H, 4.8; F, 19.4; I, 43.1. Found: C, 32.7; H, 4.8; F, 19.7; I, 42.6.

Anal. Calcd. for $C_{17}H_{28}F_3I$: C, 45.9; H, 7.2; F, 14.5; I, 32.3. Found: C, 46.1; H, 7.0; F, 13.9; I, 32.4.

Relative Rates of Reaction of Cyclohexene and 1-Heptene and of Norbornene and 1-Heptene with 1-Iodoperfluoropropane.—1-Heptene (1.04 g., 10.6 mmoles), cyclohexene (1.00 g., 12.3 mmoles), 1-iodoperfluoropropane (3.06 g., 10.3 mmoles), and AVN[9] (0.025 g., 0.1 mmole) were divided among 6 tubes sealed *in vacuo* at −70° and heated at 70 ± 1° in an oil bath for the period indicated. The amount of reaction was determined by g.l.c. analysis having previously obtained the characteristic retention times and weight/area factors. Less than 30% of the $CF_3CF_2CF_2I$ was used up in 4 hr. The ratio of H to C and D taken from the areas under the curves were at the times given: 0.25 hr., 14.0; 1.0 hr., 11.5; 2 hr., 10.1; 3 hr., 8.5. The ratios reflect the changing reactant composition, and the low over-all conversion the retarding effect of the cyclic olefin and its adducts on the radical-induced addition.

1-Heptene (0.98 g., 10.0 mmoles), norbornene (0.94 g., 10.0 mmoles), 1-iodoperfluoropropane (3.32 g., 11.2 mmoles), and AVN[9] (0.025 g., 0.1 mmole) were used as before. Almost complete reaction of 1-iodoperfluoropropane resulted. The ratio of H to the norbornene adduct[1] L taken from the areas under the curves were as follows: 0.25 hr., 0.98; 0.5 hr., 1.05; 1.0 hr., 1.05; 2 hr., 1.15; 3.0 hr., 1.10. Very little discriminaton between olefins was observed and no retardation of addition.

1-Iodoperfluoropropane and Cyclopentadiene.—1-Iodoperfluoropropane (29.6 g., 0.1 mole) and freshly distilled cyclopentadiene (6.6 g., 0.1 mole), kept at −70° (obtained by thermal cracking of cyclopentadiene dimer), and ABN (0.2 g., 0.0008 mole) were heated to reflux under nitrogen in a flask fitted with a −70° reflux condenser in an oil bath at 73–76° for 20 hr. (inside temperature 64–70°). The mixture turned green in color. G.l.c. analysis showed that none of the 1-iodoperfluoropropane was used up, but that about one-half of the cyclopentadiene was gone. Distillation gave 4.5 g. of viscous oil residue, but no volatile adducts.

1-Iodoperfluoropropane (35.2 g., 0.12 mole), cyclopentadiene (1.0 g., 0.015 mole), 1-heptene (10.0 g., 0.1 mole), and ABN (0.2 g., 0.0008 mole) were heated as before for 8 hr. at reflux temperature (52–53°). G. l.c. analysis showed that very little reaction had occurred. Distillation gave 27.4 g. of unchanged 1-iodoperfluoropropane and 8.2 g. of 1-heptene. There was a residue of 2.8 g. *Without cyclopentadiene, these reactants gave in 4 hr. an* 84% conversion to H.

***trans*-1-Iodo-2-(perfluorobutyl)cyclopentane** (**M**).—1-Iodoperfluorobutane (52.0 g., 0.15 mole), cyclopentene (34 g., 0.47 mole) and ABN (1.64 g., 0.01 mole) sealed in a heavy wall Pyrex glass tube *in vacuo* were heated at 75–82° for 7.5 hr. The red liquid (80.3 g.) was fractionated in column B. Cyclopentene and 1-iodoperfluorobutane codistilled, b.p. 36–39°; $n^{25}\text{D}$ 1.3929; 48.5 g. An intermediate cut, b.p. 54–82° (20 mm.), $n^{25}\text{D}$ 1.4030, 1.3 g., and (M), b.p. 86–88° (21 mm.), $n^{25}\text{D}$ 1.4045, 21.9 g. (38% conversion; about 75% yield on R_fI) distilled, leaving a hold-up of 0.95 g. and a residue of 1.1 g. The −70° trap contained 12.2 g. of 1-iodoperfluorobutane (total recovered, 24.6 g. from g.l.c. analysis). The product fractions were filtered from TMSN at 5° and redistilled. G.l.c. analysis (using a 2-m. "R" column; 150°; 27 ml./min. of helium) showed one substance (99.2%) at a retention time of 10.5 min. The ultraviolet spectrum in CH_3OH gave λ_{max} at 263 mμ (ε 461.2).

Anal. Calcd. for $C_9F_9H_8I$: C, 26.1; H, 1.95; I, 30.65. Found: C, 26.2; H, 2.0; I, 30.3.

The recovered mixture (48.3 g.) containing 13.6 g. (0.04 mole) of 1-iodoperfluorobutane and 35.3 g. (0.52 mole) of cyclopentene was placed in a heavy wall Pyrex glass tube as before. After a 31-hr. exposure to direct sunlight in August (ambient temperatures to 35°), the liquid (44.5 g.) was removed from a dark, solid deposit, filtered through activated carbon, and distilled. A mixture of cyclopentene and 1-iodoperfluorobutane (b.p. 41–45°; $n^{25}\text{D}$ 1.4013; 21.7 g.) and dark colored liquid M, b.p. 60–65° (10 to 5 mm.), 11.2 g. (42% conversion), was obtained. *Decomposition of material in the pot flask was observed. The trap liquid* (8.0 g.) was mostly 1-iodoperfluorobutane.

1-(Perfluorobutyl)-1-cyclopentene (**N**) **and 3-(Perfluorobutyl)-1-cyclopentene** (**O**).—M (5.0 g., 0.012 mole) and tri-*n*-butylamine (3.7 g., 0.020 mole) were heated in column B for 1 hr. at 150°, and then to 200° while taking off distillate, b.p. 126–130°; $n^{25}\text{D}$ 1.3401; 2.97 g. The column hold-up (0.60 g.) was pulled over by reducing the pressure. After washing with 10% hydrochloric acid and drying over magnesium sulfate the mixture of N and O (3.24 g., 94%) distilled, b.p. 124–126°; $n^{25}\text{D}$ 1.3386. An infrared spectrum showed a vinyl stretching band at 3.22 μ and bands at 6.10 and 10.05 μ.

Anal. Calcd. for $C_9H_7F_9$: C, 37.8; H, 2.5; F, 59.8. Found: C, 37.8; H, 2.4; F, 60.2.

G.l.c. analysis (using a 2-m. bis-2-methoxyethyl phthalate (20%) on 60–80 mesh "Chromasorb" column at 65°; 46 ml./min. of helium) showed two substances were present; 16.1% at 12.1 min. retention time and 83.3% at 14.65 min.

The proton n.m.r. spectrum, taken with a Varian Associates A-60 spectrometer at 60 Mc. with tetramethylsilane internal reference, gave vinyl proton resonances for two different olefins. There was a distorted three-line resonance of one vinyl proton (0.18 proton area) centered at −380 c.p.s., two vinyl proton resonances at −358 and −343 c.p.s. (0.79 and 0.70 proton area) and a broad proton resonance band of the $H{-}\overset{|}{C}{-}R_f$ at −240 to −180 c.p.s. (0.88 proton area). The vinyl proton resonance of the Δ^1 olefin was also at lower field than the two vinyl proton resonances for the Δ^2 olefin in the related Δ^1 and Δ^2-(perfluoropropyl)cyclohexene isomers.[6]