Ortho-Substituted Benzaldehydes.—For benzaldehydes substituted in the ortho position, a similar correlation could not be shown as there is no reliable set of ortho-substituent constants.[14,15] A correlation does exist, however, for values of K_{OH} for six benzaldehydes substituted in only one of the ortho positions, with the pK_a values[16] for the analogous substituted benzoic acids with a slope of -1.36 and correlation coefficient 0.984 (Figure 2). This correlation is limited to compounds with only one ortho position substituted, as the two compounds with substitution at both ortho positions deviate markedly. 2,4,6-Trimethylbenzaldehyde also deviates from the plot, as there was no indication of addition up to 1 M base, while the pK_a value for the corresponding acid is 3.44. A similar deviation of di-ortho substitution was noted when correlating the rate constants for the attack of diphenyldiazomethane on ortho-substituted benzoic acids in ethanol, with the pK_a's of the acids.[17]

Acknowledgment.—Discussions with W. P. Jencks and R. P. Bell are gratefully acknowledged.

[14] J. Shorter in "Advances in Free Energy Relationships," N. B. Chapman and J. Shorter, Ed., Plenum Press, London, 1972, p 72.

[15] M. Charton, *Progr. Phys. Org. Chem.*, **8**, 235 (1971).

[16] J. F. J. Dippy and S. R. C. Hughes, *Tetrahedron*, **19**, 1527 (1963).

[17] N. B. Chapman, J. Shorter, and J. H. P. Utley, *J. Chem. Soc.*, 1824 (1962).

Free-Radical Addition of Iodoperfluoroalkanes to Terminal Alkadienes. Relative Reactivity as a Function of Chain Length and Reaction Conditions[1,2]

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Terminal alkadienes, $CH_2{=}CH(CH_2)_nCH{=}CH_2$ (n = 1-4, 1 to 4), gave mono- and bisadducts from iodoperfluoroalkanes (R_FI) in high yield. 1,6-Heptadiene (**3**) was unusual in preferentially cyclizing under conditions which favored linear adducts from the other dienes. For **3** the ratio of linear to cyclic adducts was dependent on R_FI concentration, as predicted from kinetic analysis of the reaction scheme. Relative reactivities on an equivalent double-bond basis for alkadienes against either 1-hexene or 1-heptene were the following: **1**, 0.935; **2**, 0.805; **3**, 1.08-1.42, depending on reaction conditions; **4**, 0.945. Thus, only **3** reacted significantly faster than an alkene on the basis of available reaction sites, and this appears to be related to cyclization of **3**. The overall results are interpreted as being dependent on radical intermediate conformations. The absence of significant amounts of cyclization products from **2** or **4**, or of isomeric adducts of the structure $ICH_2CHR_F(CH_2)_nCH{=}CH_2$ (n = 1-4), has been confirmed for azonitrile-initiated reactions.

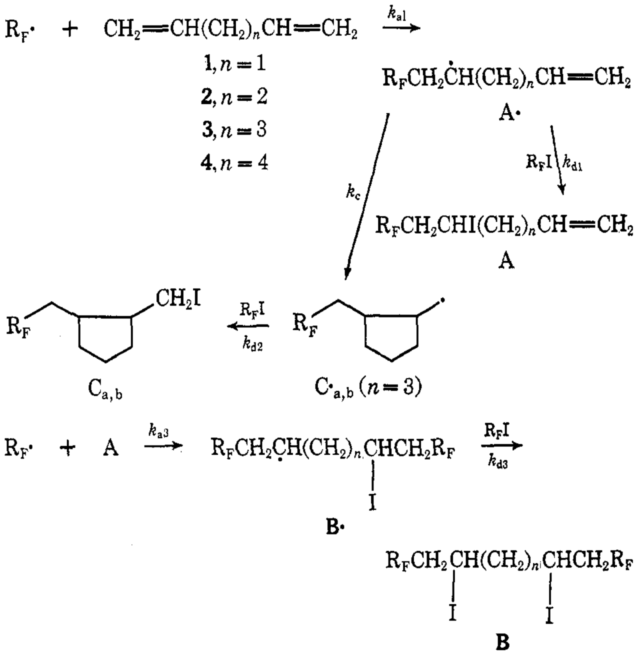
In previous work[3-5] it was found that 1,6-heptadiene (**3**) and substituted 1,6-heptadienes cyclized to *five-membered* ring compounds during the addition of free radicals from perfluoroalkyl iodides (R_FI), carbon tetrachloride, chloroform, and the like. 1,5-Hexadiene (**2**) or 1,7-octadiene (**4**) did not cyclize under free-radical conditions, however, but gave open-chain adducts in excellent yield. By contrast, R_FI and 1,3-butadiene reacted poorly, probably because an unstable product was formed.[6] (Styrene gave an adduct of analogous structure which also was exceedingly sensitive to heat, light, and air.)[7,8] As part of a continuing study of R_FI reactions it seemed worthwhile to determine the relative reactivity of terminal alkadienes, and to look more carefully into the matter of their propensity to cyclize.[9] Quantitative comparison with norbornadiene, which also cyclized with great ease,[10] was desired. It was felt that these data would shed some further light on the nature of these interesting free-radical processes.

Results

Reactions of R_FI with alkadienes **1-4** are outlined in Chart I. The yield of monoadduct A, bisadduct B, or cis and trans cyclic adducts $C_{a,b}$ varied with reaction conditions.

CHART I

REACTION OF R_FI WITH DIENES



[1] Presented in part at the Fourth European Symposium on Fluorine Chemistry at Ljubjlana, Yugoslavia, September 1972.

[2] See paragraph at end of paper regarding supplementary material.

[3] N. O. Brace, *J. Amer. Chem. Soc.*, **86**, 523 (1964).

[4] N. O. Brace, *J. Org. Chem.*, **31**, 2879 (1966).

[5] N. O. Brace, *ibid.*, **32**, 2711 (1967).

[6] N. O. Brace, U. S. Patent 3,145,222, assigned to E. I. du Pont de Nemours and Co., Aug 18, 1964.

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

[8] N. O. Brace, unpublished observations.

[9] E. S. Huyser, "Free Radical Chain Reactions," Wiley-Interscience, New York, N. Y., 1970, pp 182-185. Cyclizations of 1,7-octadiene and of 1,5-hexadiene during addition of CCl_4 are reported, but neither references to the original literature nor supporting evidence were given.

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

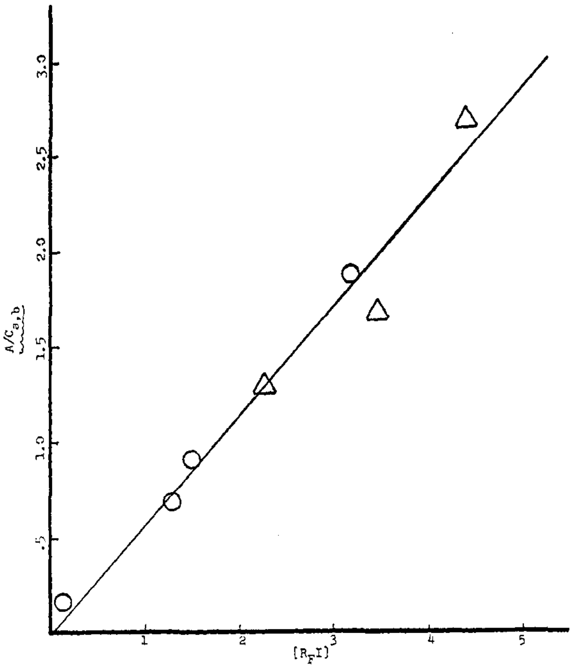


Figure 1.—Dependence of $A/C_{a,b}$ on R_FI concentration: △, mol/l. of $CF_3CF_2CF_2I$ and **3**; ○, **5**, **3**, and **6** (see Table I.)

Kinetic analysis of the reaction scheme given in Chart I, as employed by Carlsson and Ingold[11] or by Kochi and Powers[12] in somewhat analogous systems, predicts that the A to $C_{a,b}$ ratio should be proportional to R_FI concentration.

$$\frac{A}{C_{a,b}} = \frac{k_{d1}}{k_c}[R_FI]$$

The available data are consistent with this prediction, which assumes that k_{d1} and k_{d2} are of comparable value.[13] The A to $C_{a,b}$ ratio from reaction of R_FI with 1,6-heptadiene (**3**) at 70° (extrapolated to zero time) in seven sets of experiments are recorded in Table I and plotted in Figure 1. Reactions were all initiated by azobis-2-methylpropionitrile (ABN), but under different conditions. The data for runs using $CF_3CF_2CF_2CF_2I$ (**5**) were obtained in competitive experiments in which 1-hexene (**6**) was also present; details are given below.

Table I

Effect of R_FI Concentration on $A/C_{a,b}$ at 70°

$CF_3(CF_2)_nI$		Mol of	
n	mol/l.	$A/C_{a,b}$	Source of data
2	2.29^a	1.3	Ref 4
2	3.50^a	1.7	Ref 4
2	4.44^a	2.7	Ref 4
3	0.140	0.18	Table VII, runs 6–8
3	1.32	0.70	Table VII, runs 1–4
3	1.47	0.92	Table X, part 3
3	3.21	1.9	Table X, part 1

[a] $CF_3CF_2CF_2I$ and **3** only were present.

A second pathway to $C_{a,b}$ also exists, as a slow isomerization of A to $C_{a,b}$ occurs during reaction and subsequent to the addition of R_FI.[4] This can be seen from Figure 2. Under these reaction conditions (with excess diene) little B was formed, but $C_{a,b}$ continued to increase after all the R_FI was gone (41% of R_FI had reacted in 1 hr and 99.7% in 4 hr). It is significant that the trans isomer of C was formed about five or six times faster than cis C. Isomerization of A to $C_{a,b}$ and radical rearrangements of related compounds have been independently observed.[5]

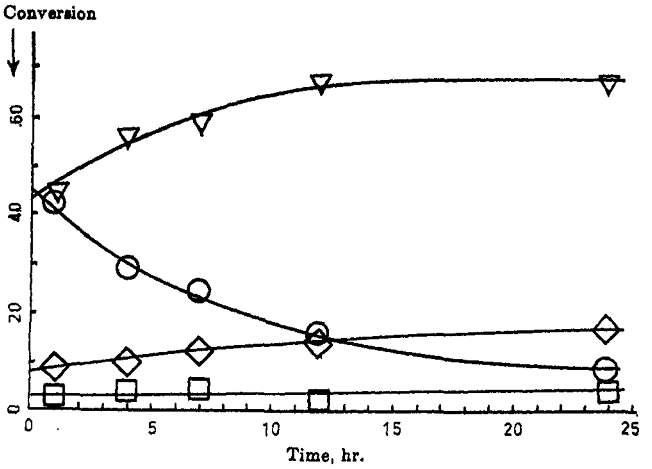


Figure 2.—Reaction of 1-iodoperfluoropropane and **3** at 70° (ref 4): $CF_3CF_2CF_2I$, 5.00 mmol; **3**, 10.00 mmol; ABN, 0.100 mmol. ▽, trans C_b; ○, monoadduct A; ◇, cis C_a; □, bis adduct B.

It was interesting to observe the effect of R_FI/diene ratio on mono- and bisadducts from reaction of **5** with these alkadienes. As shown in Table II, the highest A/B ratios were found with **1**, **2**, and **4** when an excess of diene was present; with **3**, however, *cyclization* to $C_{a,b}$ was the predominant reaction. Even in the presence of an excess of R_FI much of **3** cyclized, while the other dienes gave mostly B. As previously reported[4] for **2** and **4**, it is now found that also with **1** linear adducts are obtained under all conditions. Careful examination of product mixtures from all these dienes by gas–liquid partition chromatography (glpc) showed two or three impurities at the 1–2% level. In reaction mixtures of **4** there were found two additional products which appeared at the retention times anticipated for cyclic isomers.

Table II

Effect of Reactant Ratio on Mono- and Bisadducts from $CF_3CF_2CF_2CF_2I$ (**5**) and Alkadienes[a]

Diene	Mol of **5**/diene	Convn of diene or **5**, %	Mol of A/B
1	0.250	86	12.7
	4.00	76	0.410
2	0.250	76	11.5
	2.00^b	96	0.60^b
	2.50	95	0.25
3	0.250	81	*c*
	2.00	83	1.54^d
4	0.250	82	16.1
	0.500	44	10.1
	2.00^b	97	0.67^b
	2.10	95	0.672

[a] All reactions were done at 70.0° in a sealed tube, using ABN as initiator; see Table III for details. [b] See ref 4. [c] Reaction gave 1.5% of A, less than 2% of B, and 80% of $C_{a,b}$. [d] There was formed also 35.2% of $C_{a,b}$.

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(11) D. J. Carlsson and K. U. Ingold, *J. Amer. Chem. Soc.*, **90**, 7047 (1968).

(12) J. K. Kochi and J. W. Powers, *ibid.*, **92**, 137 (1970).

(13) It has been shown that cyclization in this system is not reversible[11] as ring opening of the cyclopentylmethyl radical does not occur.[14]

(14) R. C. Lamb, P. W. Ayers, and M. K. Toney, *J. Amer. Chem. Soc.*, **85**, 3483 (1963).

Table III

Preparation of Adducts from $CF_3CF_2CF_2CF_2I$ (**5**) and Terminal Alkadienes at 70°[a]

					Yield, %			Physical constants			
								A		B	
Diene	Mol	**5**/diene	ABN, mmol	Time, hr	A	B	C	Bp, °C (mm)	$n^{25}D$	Bp, °C (mm)	$n^{25}D$
1	0.100	0.250	2.00	16	74	12		68 (11)	1.3967	82 (0.10)	1.4050
1	0.0250	4.99	1.00	8.5	22.1	53.5					
2	0.200	0.250	1.82	9.5	65	11[b]		85 (12)	1.4010	79 (0.30)	1.4350
2	0.0200	2.50	2.00	6	20	79.2					
3	0.200	0.250	0.92	4	1	(2)	80[c]	90 (8)	1.4065		
3	0.100	2.00	0.92	1	28.9	18.8	35.2			108 (0.25)	1.4091
3	0.0250	2.00	0.50	16[d]	30.8	8.06	34.1				
4	0.200	0.250	1.00	18	72	(10)		57 (0.25)	1.4090		
4	0.200	0.500	2.00	16	38	(7.6)					
4[e]	0.0500	2.00	1.00	18	21	76		50 (0.25)[e]	1.4080[e]	115 (0.20)[e]	1.4100[e]
4	0.105	2.10	1.50	9	38.2	52.9					

[a] Satisfactory analytical data (±0.4% for C, H, F, or I) were reported for all new compounds listed in the table. [b] Moles times two since 2 mol of **5** used, limiting reactant. [c] C (n = 3), bp 69° (0.75 mm), $n^{25}D$ 1.4186. [d] Reaction temperature was 130°. [e] Reference 4.

The amount was too small, however, to warrant trapping for identification. The other isomers are probably of the type $ICH_2CHR_F(CH_2)_nCH{=}CH_2$ (n = 1, 2, or 4), as previously indicated for the addition of CF_3I to 1-heptene[15] (**7**) and now confirmed by others[16,17] for R_FI additions in similar cases. The amount of these isomers varied with reaction conditions, as it has been shown[17] that the linear adduct is favored by kinetic control. Rearrangement to the branched isomer has been demonstrated in one case.[17]

Details for the preparation of adducts, their physical properties, and analytical data are given in Tables III and IV. Characteristic infrared and nmr spectral properties are listed in the Experimental Section. The nmr spectrum of $C_4F_9CH_2CHI(CH_2)_3CH{=}CH_2$, A ($n$ = 3) is presented as Figure 3;[2] significant features of the linear adduct structure are clearly evident from the spectrum. The nmr spectrum of the 1-hexene adduct $C_4F_9CH_2CHI(CH_2)_3CH_3$ appears as Figure 4.[2] Spectral evidence is in full accord with the postulated structure. In both instances proton resonances for CHI at δ 4.4 and for R_FCH_2 at δ 2.8 have the correct areas and splitting patterns.

Relative Reactivities.—A reference olefin, 1-hexene (**6**) or 1-heptene (**7**), competing for **5** with another unsaturated compound, gave valid results when the reaction was conducted and the products analyzed as previously described.[15] Two different reference olefins were required to avoid overlapping of peaks in glpc analysis of **1–4**. This technique was recently applied to the determination of relative reactivities of a series of cyclic olefins.[18] It was not sufficient merely to follow the disappearance of olefin, as a small change in concentration was difficult to determine accurately; and as shown above, several products may be formed from the same starting material. Because of the disparate nature of the reactants and products, correction factors varied with composition of a mixture. Factors were therefore determined for more than one mixture of **3**, and in every case for a standard mixture similar in composition to unknown samples. Quantitative aspects of radical additions to olefins have been critically reviewed by Cadogan and Sadler.[19]

The method was applied to reaction of **5** with several pairs of alkenes (Tables V and VI).[2] 1-Hexene (**6**) against 1-heptene (**7**) gave initial and final reactivity ratios of **6**/**7** of 1.03 ± 0.02. The reactivity ratio for norbornene (**8**) against **7** was redetermined using the technique of this study; the two values (1.0[15] and 1.00) were identical. Norbornadiene (**9**) against **7** gave **9**/**7** of 1.83 ± 0.01. The diene series **1–4** was compared against either **6** or **7** for different reaction times and reactant ratios, particularly with **2** and **3** to ascertain what effect these variables might have on reactivity ratios. These data are collected in Tables VI[2] and VII, and summarized in Table VIII. Results for **3** are given separately because of their unique nature.

Discussion

Chart I summarizes the various reaction steps to be discussed. Termination reactions of the usual kind are assumed to account for the radical chain. These would result in the coupling of R_F radicals, of A·, B·, and $C_{a,b}$· radicals and probably in allylic termination reactions as previously observed.[4,10,15]

Relative reactivity $\bar{P}$ of two alkenes toward addition of R_F radicals is given by the usual equation[19,20]

$$\bar{P} = \frac{\log\ ([M_1]_0/[M_1]_f)}{\log\ ([M_2]_0/[M_2]_f)} = \frac{k_{a1}}{k_{a2}}$$

for competitive reactions, where $[M_1]_0$ and $[M_1]_f$ are initial and final concentrations of olefin M_1, and $[M_2]_0$ and $[M_2]_f$ are initial and final concentrations of M_2. It was advantageous, for analytical reasons, to substitute for $[M_1]_f$ the equivalent quantity ($[M_1]_0$ − [products]) in determining $\bar{P}$, as has been done by others.[17,19]

As summarized in Table VIII, 1,5-hexadiene appears to be significantly less reactive than the other dienes, but the difference in the remaining compounds is not great. The variation of adduct formation with time (extent of conversion) shown in Figure 2 was observed in reactions of **3** with R_FI at different reactant ratios. The reactivity ratio, however, varied only slightly as a function of R_FI conversion or $A/C_{a,b}$

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[15] N. O. Brace, *J. Org. Chem.*, **28**, 3093 (1963).

[16] M. Capka and V. Chvalovsky, *Collect. Czech. Chem. Commun.*, **33**, 2872 (1968).

[17] R. N. Haszeldine, D. W. Keen, and A. E. Tipping, *J. Chem. Soc. C*, 414 (1970).

[18] N. O. Brace, *J. Org. Chem.*, **37**, 2429 (1972).

[19] J. I. G. Cadogan and I. H. Sadler, *J. Chem. Soc. B*, 1191 (1966).

[20] E. S. Huyser, "Free Radical Chain Reactions," Wiley-Interscience, New York, N. Y., 1970, p 61.

TABLE VII

COMPETITION REACTIONS OF $CF_3CF_2CF_2CF_2I$ (**5**) WITH 1,6-HEPTADIENE AND 1-HEXENE

			Alkene$_1$ 1,6-Heptadiene (**3**)					Alkene$_2$ 1-Hexene (**6**)				
			mmol					mmol				
Run no.	Time, hr	**5**, initial mmol	Reactant	A	B	C	Convn % of **5**	Reactant	Product	Convn % of **5**	$\frac{A}{C_{a,b}}$	$\frac{k_1}{k_2}$
1	0.083	4.8800[a]	10.025	0.2133		0.3386	11.31	9.944	0.2676	5.48	0.630	2.145
2	0.167	4.8800	10.025	0.9628	0.0382	1.8248	57.90	9.944	1.4124	28.94	0.5488	2.162
3	0.33	4.8800	10.025	0.6900	0.0384	1.601	47.70	9.944	1.173	24.04	0.4596	2.105
4	1.00	4.8800	10.025	0.7197	0.0589	2.238	61.80	9.944	1.525	31.24	0.3479	2.196
5	1.00	4.8800	10.025	0.6731	0.0473	2.370	63.30	9.944	1.508	30.90	0.3090	2.185
											Mean	2.159
												± 0.040
6	1.16	1.2236[b]	10.1466	0.0793		0.4861	45.76	10.379	0.2657	21.71	0.1520	2.359
7	4.16	1.2236	10.1466	0.0509		0.6826	59.95	10.379	0.2713	22.17	0.07457	2.836
8	7.00	1.2236	10.1466	0.0504		0.6392	52.24	10.379	0.2306	18.85	0.0788	3.134[c]

[a] $[R_FI] = 1.32$. [b] $[R_FI] = 0.140$. [c] Owing to a decrease in adducts from both alkenes, this value is uncertain. See, however, Table X for a similar value from another experiment.

TABLE VIII

RELATIVE REACTIVITY OF ALKENES AND DIENES WITH $CF_3CF_2CF_2CF_2I$ (**5**) AT 70°

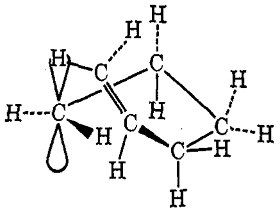
Olefin pair	$\bar{P}$	$\bar{P}$/ double bonds
6/7	1.03 ± 0.02	1.03 ± 0.02
8/7	0.996 ± 0.005	0.996 ± 0.005
9/7	1.83 ± 0.01	0.965 ± 0.01
1/7	1.87 ± 0.05	0.935 ± 0.05
2/7	1.61 ± 0.03	0.805 ± 0.03
3/6	2.16 ± 0.04[a]	1.08 ± 0.04[a]
3/6	2.84[b]	1.42[b]
4/6	1.89 ± 0.01	0.945 ± 0.01

[a] At moles of **5/3** = 0.4868. [b] At **5/3** = 0.1206.

ratio (Table VII, runs 1–5). At a low **5/3** reactant ratio of 0.1206 which greatly increased cyclization, $\bar{P}$ increased substantially to at least 2.84 (runs 6–8).

Reactivity ratio $\bar{P}_{\text{diene/alkene}}$ for a diene competing against an olefin should be twice as large as for an alkene, since there is twice the probability that an R_F radical will attack a diene at the same concentration as an alkene.

The reactivity ratio on a *per double bond basis* for dienes **1**–**4** and **9** shows that only **3** reacted significantly faster than the reference olefin. Models show that effective overlap of the adduct radical A· ($n = 3$) with the π electrons of the terminal double bond is quite possible in at least two staggered conformations. It seems significant that **3** reacted fastest under conditions where cyclization was enhanced. This may mean that rate of radical addition to **3** is increased by overlap to the π bond. While the amount of acceleration was not great, it was clearly present in **3** and not in **2** or in **4**. Indeed, it has been recently shown that the 5-hexenyl radical generated at low temperature readily rearranges to the cyclopentylmethyl radical[21–24] and that the esr spectrum of the 5-hexenyl radical exhibits large temperature-dependent changes.[23] The broadening of the β-proton triplets is attributed to coiling of the radical into conformation **10**, in which the terminal unsaturated linkage lies over the radical center.[24] This same conformation had been previously postulated by Lamb, Ayers, and Toney[14] as a possible common precursor to cyclization products.[25]



10

As pointed out by Capon and Rees,[26] cyclization of radical A· ($n = 3$) occurs by a path having a transition state closer in energy to the *open-chain* radical than to the more stable product radical. If overlap with the π electron cloud lowers the activation energy for radical cyclization, this may also reduce the energy required for the R_F· radical to open the original double bond. Hence, the two steps become effectively coupled.

$\bar{P}$ for **4** approached the statistical value of two. Cyclization, if it occurred, was only a minor reaction. It is suggested that entropy of bringing the two ends of the molecule in close proximity is too great to allow such a conformation to affect either the rate of addition of R_F radical or displacement on R_FI. This may also explain the lack of cyclization of **4**.

A folded conformation of an alkadiene would offer a certain amount of steric hindrance to the approach of an R_F radical in the rate-determining step. For **1** there is a greater probability that the two ends of the molecule will sweep past each other than for the larger dienes. A model of **1**, however, shows that nonbonded repulsion of hydrogens on carbons one and five may be sufficient to restrain such motion and maintain the molecule in a more open conformation. Thus, rate of attack by R_F radical would be less affected.

2 has more degrees of freedom than **1** and attack by the R_F radical may be hindered by proximity of the other terminal double bond. This cannot be due merely to the presence of a four carbon chain residue, since addition to 1-hexene was actually slightly faster than to 1-heptene (Table VIII). Examination of models of **2** shows that there are several staggered conformations which have the terminal double bonds in close proximity. Approach of the R_F radical is

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[21] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, **91**, 3940 (1969).

[22] R. A. Sheldon and J. K. Kochi, *ibid.*, **92**, 4395 (1970).

[23] D. J. Edge and J. K. Kochi, *ibid.*, **94**, 7695 (1972).

[24] It was also indicated that such a coiled conformation was not observed for the 3-butenyl radical, although it is known to cyclize.

[25] N. O. Brace, *J. Polym. Sci., Part A-1*, **8**, 2091 (1970).

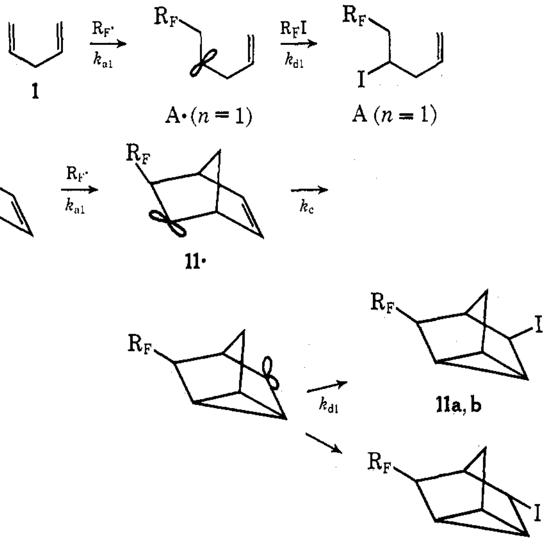
[26] B. Capon and C. W. Rees, *Proc. Chem. Soc., London*, **61**, 221, 261 (1964).

thought to occur best in the plane perpendicular to the nodal plane[25] and partial blockage of the bulky R_F radical in this orientation could be responsible for the slowing of rate.

The significant difference between the dienes **1** and **9**, both of which are 1,5 dienes, is that the adduct radical **11**· from **9** has the required geometry for facile overlap and cyclization while A· (n = 1) radical does not. This is because addition to **1** occurs predominantly at the end of the double bond and overlap and cyclization would have to form a strained four-membered ring (Chart II).

Chart II

Radical Intermediates in Addition of R_FI to 1 and to Norbornadiene (9)



While **9** cyclized completely it did not react faster than an alkene or even norbornene (**8**) on an equivalent double bond basis (Table VIII). A similar result was reported by Trecker and Henry[27] for relative reactivity of **8** and **9** toward carbon tetrachloride. **9** reacted just twice as fast as **8**, and **9** also cyclized completely to a nortricyclene derivative.

Experimental Section

Sources of Materials and Methods.—Dienes **1-3** and 1-hexene (**6**) came from Chemical Samples Co.; **4** was obtained from Cities Service Co. and was redistilled, bp 117°, n^{25}D 1.4191. **5** was obtained from Thiokol Chemical Co., **7** and **9** from Aldrich Chemical Co., and **8** from Columbia Organic Chemicals Co. The remaining compounds were standard laboratory grade. Glpc analyses of all samples were performed using replicate injections of 1-2 μl on a 6 ft × 0.25 in. column packed with SE-30 silicone oil (10%) on 60-80 mesh Chromosorb W unless otherwise indicated. The column was temperature programmed from 60 to 175° at 20° per minute; the injector was at 150° and the detector at 250°. Helium carrier gas flow of 27 ml/min was used. A Sargent Welch gas chromatograph was fitted with a thermal conductivity detector. Table IX lists the times and weight factors determined for prepared mixtures, using n-octane (**12**), chlorobenzene (**13**), or o-xylene (**14**) as reference compound. In some cases the reference compound was present during reaction.

Infrared spectra were recorded using a Perkin-Elmer Model 337 grating spectrophotometer. Nmr spectra were obtained on a Varian A-60 or T-60 spectrometer. Distillations were performed in a Nester/Faust 2-ft platinum spinning band column (column A).

Competitive Reaction of 6 and 7 with 5.—A mixture was weighed into a tightly capped vial, transferring known volumes of liquids in order of increasing volatility by graduated pipet, starting with chlorobenzene (0.3549 g), **7** (0.9569 g, 9.745 mmol), **6** (0.8339 g, 9.7085 mmol), and **5** (1.9502 g, 5.6371 mmol); a portion (0.3779 g) was removed to prepare a standard mixture (listed in Table IX), and to the remainder (3.7180 g) was added ABN (0.0475 g, 0.288 mmol). The reaction mixture was distributed by capillary pipet while cold into five ampoules made from 8-mm tubing which were evacuated and filled with nitrogen three times at −78° and sealed by hand torch. Four of the ampoules were heated for periods of time at 70.0° as given in Table V. The fifth was opened and analyzed to show that adducts **15** and **16** were not formed during analysis by glpc. The reaction samples were transferred to tightly capped vials and kept cold. Similar techniques were used in the experiments summarized in Tables V, VI, and VII.

Reaction of 5 and 6 to Give 1,1,1,2,2,3,3,4,4-Nonafluoro-6-iododecane (15).—**5** (17.30 g, 0.0500 mol), **6** (4.20 g, 0.0500 mol), and ABN (0.0820 g, 0.500 mmol) were charged to a Fischer-Porter pressure tube, evacuated, and filled three times with nitrogen, sealed and heated for 8 hr at 70°. Distillation gave **15**, bp 81° (10 mm), n^{25}D 1.3942, 15.64 g (72.7%); an oil residue, 0.60 g; and recovered starting materials, 2.40 g; ir ν_{CH} 2950, 2930, 2870, 2860 cm^{-1}; δ_{CH} 1460, 1425, 1375, 1350 cm^{-1}; ν_{CF} 1250-1200, 1130, and bands at 1080, 1020, 1010, 930, 880, 840 (d), 770, 735, 720, and 690 cm^{-1}; nmr (CCl_4) δ 0.90 (3 protons, m, CH_3), 1.1-2.2 [6 protons, $(CH_2)_3$], 2.82 (2 protons, t of d, J_{HF} = 18, J_{HH} = 6 Hz, $CF_2\mathbf{CH_2}CHI$), 4.4 (1 proton, 5 lines, J = 12, 6, 6 Hz, $CH_2\mathbf{CHI}CH_2$). The spectrum (Figure 4) conformed to the postulated structure of **15**, and not to an isomeric substance.

Anal. Calcd for $C_{10}H_{12}F_9I$: C, 27.92; H, 2.81; F, 39.76; I, 29.50. Found: C, 27.97; H, 2.77; F, 39.19; I, 29.47.

Reaction of 5 and 7 to Give 1,1,1,2,2,3,3,4,4-Nonafluoro-6-iodoundecane (16).—**5** (17.3 g, 0.0500 mol), **7** (9.82 g, 0.100 mol), and ABN (0.164 g, 1.00 mmol) were charged to a pressure tube and treated as above. After 18 hr at 70° the filtered liquid (26.82 g) gave **16**, bp 95° (10 mm), n^{25}D 1.3982, 17.20 g (77%); an oil residue, 0.57 g; and recovered starting materials, 6.39 g; ir was essentially identical with that of **15**. The nmr spectrum also resembled closely that of **16**, and not that of an isomeric substance.

Anal. Calcd for $C_{11}H_{14}F_9I$: C, 29.75; H, 3.18; F, 38.50; I, 28.57. Found: C, 29.73; H, 3.20; F, 38.22; I, 28.63.

Reaction of 5 with 1 to Give 4-Iodo-6,6,7,7,8,8,9,9,9-Nonafluoro-1-nonene [18 (A, n = 1)].—**5** (8.65 g, 0.0250 mol), **1** (6.81 g, 0.100 mol), and ABN (0.328 g, 2.00 mmol) were processed as above. After 16 hr at 70° the product mixture (16.0 g) gave unreacted **1**, bp 31°, 4.16 g; **18**, bp 68-69° (11 mm), n^{25}D 1.3967, 7.67 g, 74% conversion based on **5**; and an oil residue which glpc showed to contain 11.4% of **18**, an isomer (3.7%) and 49.7% of **19** (B, n = 1). Two higher retention time compounds (14.2 and 21.0%) also were present; ir (**18**) $\nu_{CH=}$ 3080; ν_{CH} 2980, 2920; $\nu_{C=C}$ 1640; ν_{CH} 1430, 1350; ν_{CF} 1250-1200, 1140; bands at 1020, 990, 925, 880, 775, 745, 740, 730, 690, and 515 cm^{-1}. Bands at 990 and 925 cm^{-1} are characteristic for this type of compound; nmr (CCl_4) δ 2.3-3.3 (4 protons, two m, $CF_2\mathbf{CH_2}CHICH_2$), δ 4.3 (1 proton, 5 line, J = 13 and 6 Hz, $CH_2\mathbf{CHI}CH_2$), 4.9-6.2 (3 protons, m, $\mathbf{CH{=}CH_2}$).

Reaction of 5 with 1 to Give 1,1,1,2,2,3,3,4,4,10,10,11,11,12,12,13,13,13-Octadecafluoro-6,8-diiodotridecane [19 (B, n = 1)].—**5** (34.56 g, 0.100 mol), **1** (1.70 g, 0.0250 mol), and ABN (0.164 g, 1.00 mmol) were treated as above, and heated at 70° for 8 hr. **5** (11.11 g) and trap liquid (8.68 g) were recovered: **18**, bp 64° (9.0 mm), n^{25}D 1.3970, 1.80 g (98.7% by glpc); a mixture of **18** and **19**, bp 57-81° (0.15 mm), 1.62 g (29.5% **18** and 70.5% **19** by glpc); **19**, bp 82° (0.10 mm), n^{25}D 1.4050, 9.04 g (99.5% by glpc); a residue, 0.9 g; ir (**19**), similar to that of (B, n = 4);[4] nmr (CCl_4) δ 2.2 (2 protons, t, J = 6 Hz, $CHI\mathbf{CH_2}CHI$), 2.2-3.5 [4 protons, m, $(CF_2\mathbf{CH_2}CHI)_2$], 4.4, [2 protons, m, $(\mathbf{CHI})_2$].

Reaction of 5 and 3 at 130° to Give 20 (A, n = 3), **21** (B, n = 3), **and 22a,b** (C, n = 3), **Using Di-*tert*-butyl Peroxide Initiator.**—**5** (16.4 g, 0.0500 mol), **3** (2.40 g, 0.0250 mol), and di-*tert*-butyl peroxide (0.0685 g, 0.500 mmol) were charged to a pressure tube and processed as above. After 16 hr at 130-132° the light yellow liquid (18.3 g) was distilled to give **20**, bp 89-90° (8 mm), n^{25}D 1.4065, 2.31 g, 97.3% **20** and 1.39% **22a,b** by glpc; a mixture, bp 96-105° (8 mm) and 60-55° (0.15 mm), 2.77 g; **22a,b**, bp 50° (0.12 mm), n^{25}D 1.4185, 3.49 g, 3.0% **20** and 97.0% **22a,b** by glpc; a solid residue of **21**, 4.70 g; and recovered **3** and **5** in trap, 5.37 g. Glpc analysis was done using a 6 ft × 0.25 in. Apiezon N (10%)

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[27] D. J. Trecker and J. P. Henry, *J. Amer. Chem. Soc.*, **85**, 3204 (1963).

column at 150°. There was a shoulder on the peak for **20**: ir **20** $\nu_{CH=}$ 3080; ν_{CH} 2980; 2930, 2850 (d); $\nu_{C=C}$ 1640; bands at 1025, 932, 880, 735, and 725 cm^{-1}; nmr (**20**, Figure 3), δ 1.3–1.9 (4 protons, m, CH_2 of C_4, C_5), 2.1 (2 protons, q, J = 13, 6 Hz, $CH_2CH_2CH{=}$), 2.75 (t of d, J_{HF} = 20 Hz, CF_2CH_2CH), 4.4 (1 proton, 5 line, J = 12 and 6 Hz, CH_2CHICH_2); nmr (**21**) δ 1.8 (6 protons, t of d, J_{HF} = 20, J = 8 Hz, CF_2CH_2CHI), 4.4 [2 protons, m, $(CHI)_2$].

Reaction of 5 and 8 to Give *endo*-2-Iodo-*exo*-3-perfluorobutylnorbornane (17).—**5** (17.3 g, 0.0500 mol), **8** (4.70 g, 0.0500 mol), and ABN (0.164 g, 1.00 mmol) were processed as above and heated for 3 hr at 70.0°. Distillation gave **17**: bp 79–82° (3.5 mm), 16.7 g (76%), a single peak by glpc; ir (KBr plates) δ_{CH} 1480, 1460, 1355, 1320; ν_{CF} 1250–1200, 1130; bands at 1030, 1020, 1010, 970, 945, 925, 910, 875, 855, 790, 760, 740, 735, 685, and 650 cm^{-1}; nmr was identical with the published spectrum of perfluoropropyl homolog.[10]

Anal. Calcd for $C_{11}H_{10}F_9I$: C, 30.02; H, 2.29; I, 28.84. Found: C, 30.2; H, 2.10; I, 28.2.

Reaction of 5 and 9 to Give 5-Perfluorobutyl-*exo*- and -*endo*-7-iodonortricyclene ($11_{a,b}$).—**5** (6.93 g, 0.0200 mol), **9** (0.921 g, 0.0100 mol), ABN (0.0328 g, 0.200 mmol), and 2-butanone (10 ml) were treated as above. After 16 hr at 70° the reaction mixture was analyzed by glpc (6-ft Apiezon N column, temperature-programmed 7°/min from 110° to 180°); adducts were found at 5.75 (3.19%), 9.5 (3.26%), and $11_{a,b}$ at 10.2 and 11.2 min (48.5 and 45.0% relative areas). The small amount of the first set of peaks precluded isolation. Distillation afforded $11_{a,b}$: bp 75–78° (1.5 mm), 3.56 g (81.3%); ir (KBr plates) ν_{CH} 3040, 3020, 3000, 2980, 2955; no bands at 1600–1900; δ_{CH} 1475, 1355, 1320, 1300; ν_{CF} 1250–1150; and bands at 1050, 1035, 1025, 980, 950, 910, 900, 880, 870, 820, 740, 730, 720, 700, and 650 cm^{-1}; nmr δ 1.0–2.68 (6 protons, m, ring protons), 3.2, (1 proton, t, J_{HF} = 17 Hz, CF_2CH-; δ 3.82 (0.9 proton, s, CHI), 4.25 (0.06 proton, s, CHI). That the perfluorobutyl group was exo was indicated by the absence of coupling of proton on C-5 to adjacent protons at a 90° dihedral angle.

Anal. Calcd for $C_{11}H_8F_9I$: C, 30.16; H, 1.84; F, 39.03; I, 28.97. Found: C, 30.4; H, 1.8; I, 27.7.

Competitive Addition of 5 to 6 and 3.—A 50 ml, three-necked, pear-shaped flask fitted with a nitrogen inlet, a Dry Ice filled condenser, and a liquid sampling tube extending to the bottom of the flask, was charged with materials as listed in Table X. The flask was partly immersed in an oil bath kept at 70° and at intervals indicated in Table X, a sample (approximately 0.010 g) was removed by suction through the sample tube. The liquid in the sample tube below the "Teflon-Varibor" valve was flushed back into the reaction by external nitrogen. Samples thus obtained from three different experiments were kept in a refrigerator and analyzed by glpc as described below.

A mixture of reaction products was weighed and weight/area factors were determined from replicate analysis as indicated in Table XI.[2] Results from these experiments were mainly used as guidance for more quantitative work, as given in Table VII.

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Registry No.—**1**, 591-93-5; **18**, 40735-20-4; **19**, 40735-21-5; **2**, 592-42-7; A (n = 2), 40735-22-6; B (n = 2), 40735-23-7; **3**, 3070-53-9; **20**, 40735-24-8; **21**, 40735-25-9; **22a** (cis), 40735-26-0; **22b** (trans), 40735-27-1; **4**, 3710-30-3; A (n = 4), 13105-45-8; B (n = 4), 40735-29-3; **5**, 423-39-2; **6**, 592-41-6; **7**, 592-76-7; **8**, 498-66-8; **9**, 121-46-0; **11a**, 40735-30-6; **11b**, 40735-31-7; **15**, 40735-32-8; **16**, 40735-33-9; **17**, 40735-34-0.

Supplementary Material Available.—Tables IV, V, VI, IX, X and XI and Figures 3 and 4 will appear immediately following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JOC-73-3167.

Reactions of Alkyl Phenyl Selenide with Benzoyl Peroxide

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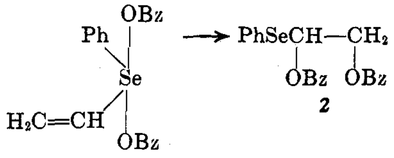
Benzoyl peroxide readily reacts with alkyl phenyl selenides in CCl_4 solution at room temperature to yield stable tetravalent selenium coordination compounds: alkylphenyldibenzoyloxyselenuranes (**4**). When refluxed in CCl_4, **4** decomposed into α-benzoyloxyalkyl phenyl selenides (**5**) and benzoic acid. Benzoyl peroxide further reacts with **5** to form stable selenium(IV) compounds: α-benzoyloxyalkylphenyldibenzoyloxyselenuranes (**9**). Upon heating, they decomposed into additional α-benzoyloxylation products (**10**). It is suggested that the reaction involves the initial decomposition of **4** into ion pairs and attack of the benzoate ion on the α hydrogen, producing a selenium-stabilized carbonium ion. Subsequently, the benzoyloxy moiety on the selenium rearranges the α position of the alkyl group and yields the benzoyloxylation product (**5a**).

Recently, we found that free-radical initiators such as benzoyl peroxide did not initiate the polymerization of phenylvinyl selenide. This failure was attributed to the addition of benzoyl peroxide on the selenium atom to give a tetravalent selenium(IV) compound (**1**).[1] Similar tetravalent selenium compounds have been known in the literature for some time.[2] Foster isolated diphenylselenium diacetate from the reaction of diphenylselenium oxide with acetic anhydride.[3] Stable

$PhSeCH{=}CH_2 + (BzO)_2 \longrightarrow$



$\longrightarrow \underset{\displaystyle OBz}{PhSeCH}-\underset{\displaystyle OBz}{CH_2}$ (1)

1

2

cyclic tetravalent selenium compounds were also prepared by the intramolecular reactions between selenium oxide and carboxylic acid.[4-6] More recently Reich

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