

3-Iodopropyl Radical. Closure to Cyclopropane¹Robert F. Drury^{2a} and Leonard Kaplan^{*2b}

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Abstract: From quantitative analyses of the products of the decomposition of $\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}-\text{Bz}_2\text{O}_2$ (111.0°) and $(\text{ICH}_2\text{CH}_2\text{CH}_2\text{CO}_2^-)_2$ (95.1°) in several benzene- CCl_4 solutions it was determined that $k(\text{ICH}_2\text{CH}_2\text{CH}_2\cdot \rightarrow \text{cyclopropane} + \text{I}\cdot)/k(\text{ICH}_2\text{CH}_2\text{CH}_2\cdot + \text{CCl}_4 \rightarrow \text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl} + \cdot\text{CCl}_3) = 2.2\text{--}4.0 M$ and $k(\text{Ph}\cdot + \text{ICH}_2\text{CH}_2\text{CH}_2\text{I} \rightarrow \text{PhI} + \text{cyclopropane} + \text{I}\cdot)/k(\text{Ph}\cdot + \text{ICH}_2\text{CH}_2\text{CH}_2\text{I} \rightarrow \text{PhI} + \text{ICH}_2\text{CH}_2\text{CH}_2\cdot) < 0.17$ in benzene at 111.0°. From these results and other arguments, it is concluded that >80% of the cyclopropane produced in these reactions is derived from $\text{ICH}_2\text{CH}_2\text{CH}_2\cdot$, with high probability *via* a unimolecular carbon radical displacement on carbon with a rate constant of $\sim 2 \times 10^3 \text{ sec}^{-1}$ at 111°.

The occurrence of a carbon radical displacement on formally saturated carbon^{3,4} or of an other-than- β radical elimination from a carbon radical⁴ has not been demonstrated. We have reported several reactions⁵ which can be viewed in terms either of these events or of other mechanisms which also involve processes or intermediate species which are unprecedented in free radical chemistry.⁶

We wish to report observations which are relevant to the mechanism of formation of cyclopropane in the $\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}-\text{Bz}_2\text{O}_2$ ^{5a} and $(\text{ICH}_2\text{CH}_2\text{CH}_2\text{CO}_2^-)_2$ ^{4a,5b} systems. Our approach was directed primarily toward the question of the degree to which cyclopropane is formed from the 3-iodopropyl radical *via* a radical displacement on carbon. The principal method of radical generation was that introduced by us earlier,^{5a} reaction of a reactive radical (phenyl or methyl) with an organic iodide. In order to determine the extent to which the cyclopropane is formed from a precursor which can be trapped as $\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}$ by CCl_4 , we have determined the products of the reaction of $\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}$ with Bz_2O_2 in the presence of varied concentrations of CCl_4 . These results and those of a less complete study of the decomposition of $(\text{ICH}_2\text{CH}_2\text{CH}_2\text{CO}_2^-)_2$ under the same conditions of concentration and temperature as used previously^{5b} are summarized in Tables I and II, respectively, and in Figure 1.

Analysis of Results

The scheme composed of reactions 1–8 was examined

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(2) (a) National Science Foundation Predoctoral Fellow, 1966–1970; National Institutes of Health Predoctoral Fellow, 1970–1971; (b) Alfred P. Sloan Foundation Fellow, 1968–1970.

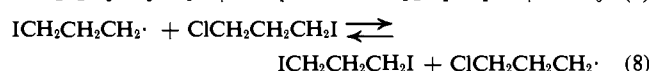
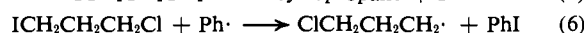
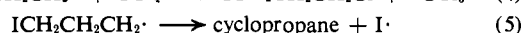
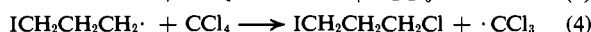
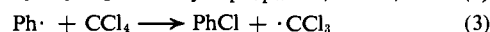
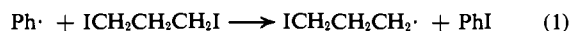
(3) (a) One of the reasonable formulations of the reaction between BrCCl_3 and a highly strained 1,2-diphenylcyclopropane [B. B. Jarvis, *J. Org. Chem.*, **35**, 924 (1970)] involves such a step and is sufficiently plausible so as to merit study of the mechanism and a more detailed investigation of the structure of the products. (b) Polymerizations under free radical conditions of bicyclobutanes to yield polymers containing 1,3-substituted cyclobutane units have been reported: H. K. Hall, Jr., E. P. Blanchard, Jr., S. C. Cherkofsky, J. B. Sieja, and W. A. Sheppard, *J. Amer. Chem. Soc.*, **93**, 110 (1971); H. K. Hall, Jr., C. D. Smith, E. P. Blanchard, Jr., S. C. Cherkofsky, and J. B. Sieja, *ibid.*, **93**, 121 (1971).

(4) For recent investigations, see (a) D. C. Blomstrom, K. Herbig, and H. E. Simmons, *J. Org. Chem.*, **30**, 959 (1965); (b) W. S. Trahanovsky and M. P. Doyle, *ibid.*, **32**, 146 (1967).

(5) (a) L. Kaplan, *J. Amer. Chem. Soc.*, **89**, 1753 (1967); (b) *ibid.*, **89**, 4566 (1967); (c) *J. Org. Chem.*, **32**, 4059 (1967); (d) *Chem. Commun.*, 754 (1968); (e) R. F. Drury and L. Kaplan, *J. Amer. Chem. Soc.*, **94**, 3982 (1972).

(6) See the discussion in ref 5a and 5b.

for conformity to the data in Table I. Our principal goals are the determination of k_5/k_4 and k_2/k_1 .



Application of the steady-state approximation to the behavior of $\text{ICH}_2\text{CH}_2\text{CH}_2\cdot$ and $\text{ClCH}_2\text{CH}_2\text{CH}_2\cdot$, with the exclusion of reactions 8 and with recognition of the near-constancy of $[\text{CCl}_4]$ throughout each reaction (Table I), leads to eq 9. If the values of k_1 , k_2 , k_4 , and

$$\frac{[\text{cyclopropane}]}{[\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}] + [\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}]} = \frac{k_5}{k_4} \left(1 + \frac{k_2}{k_1} \right) \frac{1}{[\text{CCl}_4]} + \frac{k_2}{k_1} \quad (9)$$

k_5 for a particular solution are taken to be the averages of the values, weighted according to the relative mole fractions of CCl_4 and benzene in that solution, CCl_4 and benzene, eq 10³ is obtained from eq 9. We

$$\frac{[\text{cyclopropane}]}{[\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}] + [\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}]} = \frac{\frac{k_2^{\text{B}}}{k_1^{\text{B}}} \left(\frac{k_2^{\text{C}}}{k_2^{\text{B}}} - 1.088 + \frac{9.97}{[\text{CCl}_4]} \right)}{\frac{k_1^{\text{C}}}{k_1^{\text{B}}} - 1.088 + \frac{9.97}{[\text{CCl}_4]}} + \frac{\frac{1}{[\text{CCl}_4]} \left(\frac{k_5^{\text{B}}}{k_4^{\text{B}}} \right) \left(\frac{k_5^{\text{C}}}{k_5^{\text{B}}} - 1.088 + \frac{9.97}{[\text{CCl}_4]} \right)}{\frac{k_4^{\text{C}}}{k_4^{\text{B}}} - 1.088 + \frac{9.97}{[\text{CCl}_4]}} \times \left[1 + \frac{\frac{k_2^{\text{B}}}{k_1^{\text{B}}} \left(\frac{k_2^{\text{C}}}{k_2^{\text{B}}} - 1.088 + \frac{9.97}{[\text{CCl}_4]} \right)}{\frac{k_1^{\text{C}}}{k_1^{\text{B}}} - 1.088 + \frac{9.97}{[\text{CCl}_4]}} \right] \quad (10)$$

(7) All analyses of data are based upon and imply the use of molarity as the specification of the relative quantity of CCl_4 .

(8) Superscripts C and B refer to solvents CCl_4 and benzene, respectively. The molar volumes of CCl_4 and benzene at 111° were obtained from the data of S. Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910).

Table I. Reaction of 1,3-Diiodopropane and Benzoyl Peroxide in Benzene-CCl₄ Solutions at 111.0°

Solution	1	2	3	4	5	6	7	8	9	10
Reactants, mmol										
Bz ₂ O ₂	0.3951	0.3976	0.3992	0.3996	0.3988	0.3980	0.3988	0.3984	0.3980	0.3984
ICH ₂ CH ₂ CH ₂ I	1.7459	1.7706	1.7500	1.7523	1.7486	1.7530	1.7374	1.7516	1.7563	1.7486
CCl ₄	3.127	4.139	5.022	6.136	7.248	8.378	10.632	15.281	17.207	19.153
Benzene	19.887	18.279	17.201	15.960	14.919	13.778	11.258	6.629	4.538	2.217
Total liquid volume at 111.0°, ml	2.60	2.60	2.59	2.59	2.60	2.60	2.58	2.65	2.63	2.61
Products, mmol ^a										
Cyclopropane	0.239 ± 0.002	0.216 ± 0.002	0.208 ± 0.002	0.1924 ± 0.0020	0.1744 ± 0.0016	0.1600 ± 0.0019	0.1394 ± 0.0017	0.1060 ± 0.0016	0.0939 ± 0.0014	0.0830 ± 0.0014
ClCH ₂ CH ₂ CH ₂ Cl	0.0021 ± 0.0003	0.0021 ± 0.0002	0.0054 ± 0.0008	0.0076 ± 0.0005	0.0080 ± 0.0007	0.0102 ± 0.0007	0.0139 ± 0.0008	0.0184 ± 0.0014	0.0203 ± 0.0007	0.0210 ± 0.0012
ICH ₂ CH ₂ CH ₂ Cl	0.111 ± 0.002	0.149 ± 0.005	0.168 ± 0.005	0.199 ± 0.007	0.218 ± 0.007	0.235 ± 0.007	0.271 ± 0.012	0.326 ± 0.017	0.317 ± 0.011	0.336 ± 0.013
ICH ₂ CH ₂ CH ₂ I	1.21 ± 0.05	1.33 ± 0.05	1.27 ± 0.06	1.31 ± 0.05	1.32 ± 0.06	1.32 ± 0.06	1.33 ± 0.05	1.29 ± 0.05	1.29 ± 0.08	1.32 ± 0.08
Unknown 1 ^{b,c}	0.0093 ± 0.0007	0.0096 ± 0.0014	0.0081 ± 0.0006	0.0064 ± 0.0005	0.0059 ± 0.0005	0.0048 ± 0.0002	0.0032 ± 0.0004	0.0015 ± 0.0002	0.0011 ± 0.0002	0.0008 ± 0.0001
Unknown 2 ^d		~0.003	~0.006	~0.008	~0.009	~0.012	~0.016	~0.02	~0.02	~0.03
Unknown 3 ^e	0.0031 ± 0.0004	0.0031 ± 0.0005	0.0033 ± 0.0003	0.0036 ± 0.0005	0.0025 ± 0.0002	0.0026 ± 0.0003	0.0027 ± 0.0005	0.0025 ± 0.0002	0.0025 ± 0.0004	0.0016 ± 0.0002
PhCl	0.0096 ± 0.0009	0.0135 ± 0.0005	0.017 ± 0.001	0.0205 ± 0.0007	0.023 ± 0.001	0.028 ± 0.001	0.033 ± 0.001	0.047 ± 0.002	0.051 ± 0.002	0.057 ± 0.003
PhI	0.59 ± 0.02	0.66 ± 0.02	0.65 ± 0.02	0.68 ± 0.02	0.66 ± 0.02	0.66 ± 0.02	0.67 ± 0.02	0.67 ± 0.02	0.66 ± 0.03	0.67 ± 0.03
PhCO ₂ Ph	0.011 ± 0.001	0.0101 ± 0.0009	0.0097 ± 0.0007	0.0097 ± 0.0006	0.0098 ± 0.0011	0.0098 ± 0.0007	0.010 ± 0.002	0.0082 ± 0.0005	0.0081 ± 0.0005	0.0075 ± 0.0006
Unknown 4 ^{e,f}	0.020 ± 0.002	0.021 ± 0.003	0.022 ± 0.002	0.022 ± 0.002	0.023 ± 0.003	0.021 ± 0.002	0.018 ± 0.001	0.0135 ± 0.0008	0.0137 ± 0.0009	0.0127 ± 0.0009
CHCl ₃	0.024 ± 0.002	0.029 ± 0.003	0.035 ± 0.002	0.040 ± 0.002	0.042 ± 0.002	0.044 ± 0.003	0.050 ± 0.003	0.057 ± 0.005	0.060 ± 0.003	0.061 ± 0.003
C ₂ Cl ₆	0.020 ± 0.001	0.030 ± 0.001	0.040 ± 0.002	0.050 ± 0.002	0.057 ± 0.003	0.066 ± 0.004	0.083 ± 0.003	0.114 ± 0.005	0.121 ± 0.006	0.135 ± 0.007
Material balance, %										
Iodine	90 ± 3	98 ± 3	96 ± 3	100 ± 3	101 ± 3	101 ± 3	103 ± 3	103 ± 3	101 ± 5	104 ± 5
C ₃ H ₆	90 ± 3	97 ± 3	95 ± 3	98 ± 3	99 ± 3	99 ± 3	101 ± 3	100 ± 3	98 ± 5	101 ± 5

^a Uncertainties are standard deviations and include errors (typically *ca.* seven determinations) of the relative molal responses of the vpc detector. Results are typically the average of *ca.* eight analyses.

^b Vpc retention time same as that of PhCH₂CH₂CH₂I, whose relative molal detector response was used in computing the yield. ^c The nmr spectrum of a mixture of unknowns 1 and 4 was the same as that of a mixture of PhCH₂CH₂CH₂I and biphenyl. ^d Mass and nmr [τ (CCl₄) 6.67 (d), 6.56 (br s), 5.0-5.6 (m), with relative areas of 1, 2, and 2, respectively] spectra and vpc retention time are the same as those of a product of the reaction of CH₂=CHCH₂I and Bz₂O₂ in CCl₄ at 111.2°. Relative molal response of the vpc detector taken to be relative molecular weight, with the structure assumed to be CCl₃CH₂CHClCH₂CCl₃. ^e Vpc retention time same as that of CH₃CH₂CH₂I, whose relative molal detector response was used in computing the yield. ^f Vpc retention time same as that of biphenyl, whose relative molal detector response was used in computing the yield.

Table II. Decomposition of $(\text{ICH}_2\text{CH}_2\text{CH}_2\text{CO}_2^-)_2$ in Benzene- CCl_4 Solutions at 95.1°

Solution	1	2	3	4	5
Reactants, mmol					
$(\text{ICH}_2\text{CH}_2\text{CH}_2\text{CO}_2^-)_2$	1.010	1.004	0.571	0.5042	0.5181
CCl_4	1028	519.4	126.1	91.57	65.25
Benzene		552.3	420.4	452.9	483.4
Total liquid volume at 95.1°, ml	110.0	109.6	54.8	54.2	54.3
Products, mol % ^{a,b}					
Cyclopropane	10.8 ± 0.9	21.3 ± 1.2	31.6 ± 1.3	35.8 ± 1.1	41.4 ± 1.8
$\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}$	68.1 ± 3.0	55.7 ± 2.9	37.1 ± 1.0	31.1 ± 0.9	25.2 ± 0.6
$\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}$	15.5 ± 1.0	23.9 ± 2.9	35.5 ± 1.5	41.7 ± 2.1	45.7 ± 2.0
C_2Cl_6	21.8 ± 1.4	17.3 ± 1.3	10.4 ± 0.3	7.3 ± 0.7	5.5 ± 0.3
Cyclopropane/ $\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}$	0.158 ± 0.011	0.383 ± 0.010	0.852 ± 0.029	1.15 ± 0.03	1.64 ± 0.07

^a Based on moles per mole of peroxide decomposed. Uncertainties are standard deviations and include errors (typically *ca.* seven determinations) of the relative molal responses of the vpc detector. Results are typically the average of a total of *ca.* six analyses of three separate runs. ^b Also produced were $\text{ICH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$ and $\text{ICH}_2\text{CH}_2\text{CH}_2\text{COCH}_2\text{CH}_2\text{CH}_2\text{I}$ in per cent yields whose average deviations were 0.02 and 0.04, respectively, of the average yields from all five solutions. The yield of $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}$ was <2%.

examined the range of k_2^B/k_1^B and of k_5^B/k_4^B for which eq 10 could be fit⁹ to the $[\text{cyclopropane}]/([\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}] + [\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}])$ vs. $[\text{CCl}_4]^{-1}$ data of Table I¹⁰ by means of independent variation of k_1^C/k_1^B , k_2^C/k_2^B , k_4^C/k_4^B , and k_5^C/k_5^B , each within the range 0.01 to 100.¹¹ k_5^B/k_4^B was found to be greater than

(9) Here and in subsequent analyses, in making the inherently subjective determination of acceptable vs. unacceptable fit, *i.e.*, in formulating an operational definition of "fit," we have deliberately underestimated the precision of our data.

(10) A weighted least-squares analysis of the data in Table I leads to

$$\frac{[\text{cyclopropane}]}{[\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}] + [\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}]} = \frac{(2.49 \pm 0.05)}{[\text{CCl}_4]} - (0.114 \pm 0.018)$$

at 111.0°, where the uncertainties are standard deviations. Similarly, the data in Table II yield at 95.1°

$$\frac{[\text{cyclopropane}]}{[\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}] + [\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}]} = \frac{(2.06 \pm 0.03)}{[\text{CCl}_4]} - (0.056 \pm 0.007)$$

(11) Studies of the solvent effect of CCl_4 vs. benzene on volumes of activation,¹² enthalpies and entropies of activation,¹³ rate constants,¹⁴ relative reactivities,¹⁵ and heats of solution¹⁶ in radical processes have been reported. Reports of rate constants for dimerization of I[•] in CCl_4 and benzene¹⁷ and of equilibrium constants of complex formation between I₂ and benzene¹⁸ provide no cause for concern over whether k_5 in particular might vary with solvent even beyond our extreme limits.

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$$1 - \frac{\left\{ \frac{d(\text{cyclopropane})}{d([\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}] + [\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}])} \right\}_{\text{eq 1-7}}}{\left\{ \frac{d(\text{cyclopropane})}{d([\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}] + [\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}])} \right\}_{\text{eq 1-8}}} = \frac{k_7[\text{CCl}_4]/k_4 - \left(\frac{k_5}{k_4} + [\text{CCl}_4] \right) \frac{k_{-8}k_6}{k_8k_1}}{\frac{k_5k_1k_{-8}k_6}{k_4k_2k_8k_1} + \frac{k_7[\text{CCl}_4]}{k_4} \left[1 + \left(1 + \frac{k_1}{k_2} \right) \frac{k_5}{k_8[\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}]} + \frac{k_4[\text{CCl}_4]}{k_8[\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}]} \right] + \frac{k_{-8}[\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}]}{k_8[\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}]} \left[\frac{k_5}{k_4} \left(1 + \frac{k_1}{k_2} \right) + [\text{CCl}_4] \right]} \quad (11)$$

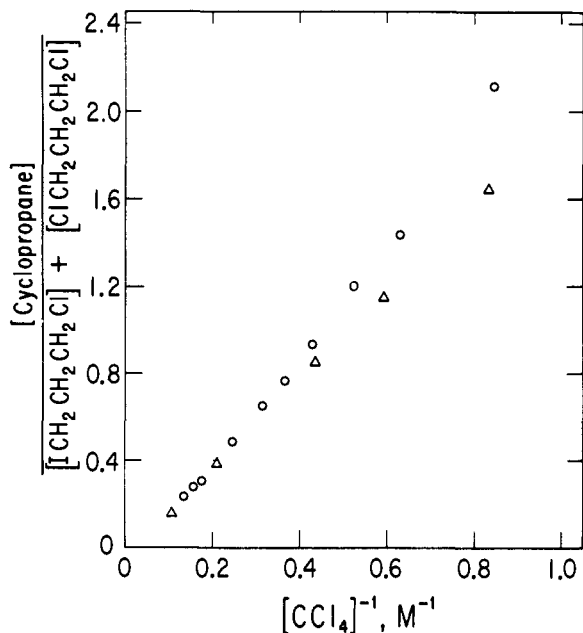


Figure 1. Product ratios from the decomposition of $\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}-\text{Bz}_2\text{O}_2$ at 111.0° (circles) and $(\text{ICH}_2\text{CH}_2\text{CH}_2\text{CO}_2^-)_2$ at 95.1° (triangles) in several benzene- CCl_4 solutions.

would have on the limiting values of $k_2^{\text{B}}/k_1^{\text{B}}$ and $k_5^{\text{B}}/k_4^{\text{B}}$ consistent with compatibility of reactions 1-8 with the data in Table I. It was found that application of this correction, in either a maximally¹⁹ positive²⁰ or negative²² sense, could not expand the limits of $k_2^{\text{B}}/k_1^{\text{B}}$ or $k_5^{\text{B}}/k_4^{\text{B}}$; they were either unchanged or contracted.

Discussion of Results

Based upon our analysis of the data in Table I, we

(19) The limits placed on the various parameters in eq 11 in the direction(s) which would produce the maximum positive (negative) error were not those which appeared to be most reasonable, but those against which we could argue strongly, but not definitively.

(20) The correction is more positive the smaller are k_{-8}/k_8 , k_6/k_1 , k_4/k_8 , and $[\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}]$ and the larger are k_7/k_4 and $[\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}]$. $[\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}] = [\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}]_{\text{final}}$, $[\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}] = [\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}]_{\text{final}}$, and, based upon reports of the effects of γ halogens on the stability, reactivity, and ease of formation of radicals,²¹ $k_{-8}/k_8 \geq 2$, $k_6/k_1 \geq 0.11$, $k_4/k_8 \geq 0.001$, and $k_7/k_4 \leq 10$ were used.

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(22) The correction is more negative the smaller are k_7k_8/k_4k_{-8} and $[\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}]$ and the larger are k_6/k_1 and $[\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}]$. Based as in ref 20, $k_6/k_1 \leq 1$, $[\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}] = [\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}]_{\text{final}}$, $k_7k_8/k_4k_{-8} \geq 0.01$, and $[\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}] = [\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}]_{\text{final}}$ were used.

conclude that $k_5^{\text{B}}/k_4^{\text{B}} = 2.2-4.0 M$ and that $k_2^{\text{B}}/k_1^{\text{B}} < 0.17$ at 111° . Based upon that analysis, upon the data in Table II, obtained independently for another system which involves $\text{ICH}_2\text{CH}_2\text{CH}_2\cdot$ as a precursor of $\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}$,^{5a} and the comparison (ref 10 and Figure 1) between them and those of Table I, we conclude that the parameters $k_5^{\text{B}}/k_4^{\text{B}}$ and $k_2^{\text{B}}/k_1^{\text{B}}$ represent, in actuality, the ratios of overall rate constants of the correspondingly labeled reactions.²³ Therefore, $>80\%$ of the cyclopropane is produced from a species, considered to be the 3-iodopropyl radical, derived from both $\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}-\text{Bz}_2\text{O}_2$ and $(\text{ICH}_2\text{CH}_2\text{CH}_2\text{CO}_2^-)_2$ and trappable as $\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}$ by CCl_4 .

Evidence that the 3-iodopropyl radical is on the reaction path to cyclopropane does not specify a mechanism by which the radical is converted to cyclopropane. A unimolecular single- or multistep process would constitute a carbon radical displacement on carbon, with a rate constant of $\sim 2 \times 10^3 \text{ sec}^{-1}$ at 111° .²⁴ We believe alternatives involving attack by a second radical on a 3-iodopropyl radical of either "conventional"^{25,26a} (an unprecedented homodisproportionation) or ir-

(23) Our experimentally determined value of k_5/k_4 is not inconsistent with the value obtained from an extrapolation of S. W. Benson's [*J. Chem. Phys.*, **34**, 521 (1961)] estimate of k_5 [gas phase, based upon the unjustified assumption that $D(\text{ICH}_2\text{CH}_2\text{CH}_2-\text{H}) = D(\text{CH}_3\text{CH}_2-\text{H})$, i.e., that there is no extraordinary stabilization of the 3-iodopropyl radical] and our estimate of k_4 which is based upon the unjustified assumption that $k_4 \cong k(\text{CH}_3\text{CH}_2\text{CH}_2\cdot + \text{CCl}_4)$.^{5b} Since Benson's and our assumptions are similar, the result that the calculated and experimental values of k_5/k_4 do not disagree seriously is not relevant to their validity.

(24) If $k_4 \cong 800 M^{-1} \text{ sec}^{-1}$ at 111° ; see ref 23.

(25) (a) This mechanism would require that the $(\text{R}\cdot + \text{ICH}_2\text{CH}_2\text{CH}_2\cdot \rightarrow \text{RI} + \text{cyclopropane})$ reaction compete successfully with the "almost-diffusion-controlled" coupling reaction. (b) The amounts of $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{I}$ (which need not arise exclusively *via* radical coupling) and $\text{ICH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{I}$ produced are <3 and $<2\%$, respectively, that of cyclopropane. (c) The contribution to a significant degree of a cyclopropane-producing step bimolecular in radicals would change the form of the dependence of $[\text{cyclopropane}]/([\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}] + [\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}])$ on $[\text{CCl}_4]$. (d) The competitive occurrence of such a step in the $(\text{ICH}_2\text{CH}_2\text{CH}_2\text{CO}_2^-)_2$ system, even with a diffusion-controlled rate, would require that the effective steady-state concentration of $\text{R}\cdot$ be at least $\sim 10^{-4}([\text{ICH}_2\text{CH}_2\text{CH}_2\text{CO}_2^-]_{\text{initial}})$ (based upon our estimate of k_5 ; see below). (e) The $\text{ICH}_2\text{CH}_2\text{CH}_2\text{I}-\text{Bz}_2\text{O}_2$ and $(\text{ICH}_2\text{CH}_2\text{CH}_2\text{CO}_2^-)_2$ systems, wherein the effective steady-state concentration of each $\text{R}\cdot$ would differ, showed very similar variations of $[\text{cyclopropane}]/([\text{ICH}_2\text{CH}_2\text{CH}_2\text{Cl}] + [\text{ClCH}_2\text{CH}_2\text{CH}_2\text{Cl}])$ with $[\text{CCl}_4]$.

(26) (a) This process may be classified as a carbon radical displacement on carbon, assisted by external $\text{R}\cdot$ with the leaving group being RI rather than $\text{I}\cdot$, i.e., general radical catalysis^{26b} of the displacement. An analogous process, a general acid catalyzed conversion of an α,ω -diol to a cyclic ether, would be classified as an intramolecular nucleophilic displacement. (b) Such terminology, normally confined to "acid-base chemistry," should prove to be of significant assistance in the conceptualization and categorization and, hence, in the design of experiments in free radical chemistry. For recent work based on the concept of a free radical buffer system, see R. Hiatt and S. W. Benson, *Int. J. Chem. Kinet.*, **4**, 151, 479 (1972), and R. Hiatt and S. W. Benson, *J. Amer. Chem. Soc.*, **94**, 25 (1972).

reversibly produced,^{5e} symmetrically bridged²⁷ limiting structure to be unlikely.

Experimental Section²⁸

Infrared and nmr spectra were obtained on Perkin-Elmer Infracord and Varian 60-MHz spectrometers, respectively. Vpc analyses were performed on Varian Aerograph thermal conductivity instruments; in all cases appropriate corrections were made for the varied response of the detector. Each product was identified by comparison of retention time and spectra of collected material with those of an authentic sample.

The reactions described in Tables I and II were run in a covered oil bath (P. M. Tamson, 12-gal. capacity, stirred by circulating pump, temperature controlled by adjustable mercury-column-actuated relays and coiled immersion heater).

Materials. Reagent grades benzene (Mallinckrodt), 1,3-dichloropropane (Aldrich), chlorobenzene (Fisher), iodobenzene (Matheson Coleman and Bell), 1,3-diiodopropane (Eastman), benzoic acid (Baker and Adamson), biphenyl (Eastman), phenyl benzoate (Eastman), and hexachloroethane (Mallinckrodt) were used without further purification.

Benzoyl peroxide (Lucidol) was recrystallized twice from chloroform-ethanol in *vacuo*, yielding white needles, mp 106–107°, which were stored in a freezer.

Carbon tetrachloride was distilled from phosphorus pentoxide on a platinum spinning band column (Nester and Faust), with column and pot protected from light by a wrapping of aluminum foil. Fractions were taken at reflux ratio >20 until a small low-boiling impurity (presumably chloroform) was no longer observed when 10 μ l of the solution was analyzed on a 10-ft SE-30 (20% on acid-washed DMCS-treated Chromosorb W 20–80) vpc column (column temperature 30°, He flow rate 60 ml/min, injector temperature 210°, detector temperature 325°) on attenuation 1, conditions such that the major peak was full scale on attenuation 64. The main fraction was collected at a lower (>10) reflux ratio and was stored under nitrogen in an amber bottle in a freezer.

1-Chloro-3-iodopropane. In a system maintained under nitrogen, a solution of NaI (16.0 g, 0.10 mol, Mallinckrodt reagent) in 100 ml of acetone was added to a solution of 15.7 g (0.10 mol) of BrCH₂CH₂CH₂Cl in 100 ml of acetone. The resulting solution was stirred for 2 hr at room temperature, the product mixture was filtered, and the filtrate was concentrated on a rotary evaporator until ~20 ml of liquid remained. Ether (100 ml) was added, the resulting mixture filtered, and the filtrate concentrated on a rotary evaporator until ~10 ml of liquid remained. Distillation on a 60-cm platinum spinning band column yielded 15.8 g (77%), bp 68° (18 mm) (lit.²⁹ 60.8° (15 mm)), of material whose nmr spectrum (CCl₄) consisted of absorption at τ 6.41 (t, $J = 6$ cps), 6.71 (t, $J = 6$ cps), and 7.79 (quintet) with relative areas of 1.0, 1.0, and 1.0, respectively. Injection of a 1- μ l sample onto a 10-ft SE-30 (20% on Chromosorb W) vpc column (injector temperature 225°, detector temperature 275°, column temperature 100°, He flow rate 60 ml/min) gave a full-scale peak on attenuation 16, and no other visible peaks at an attenuation of 1 over a run which was ten times the retention time of the main peak.

3-Iodopropylbenzene, prepared³⁰ from 3-chloropropylbenzene and NaI, had bp 71.5–73° (0.25 mm) (lit.³⁰ 105–105.5° (3 mm)). Its nmr spectrum (CCl₄) consisted of absorption at τ 2.7–3.1 (m), 6.9 (t), 7.2–7.5 (m), and 7.7–8.2 (m), with relative areas of 5.0, 2.0, 2.0, and 2.0, respectively.

Table I. Benzoyl peroxide, ICH₂CH₂CH₂I, benzene, and CCl₄ were sealed into 9-in. 5-mm OD nmr tubes (Wilmad) and the tubes were heated at 111.0 \pm 0.05° for 12 hr, conditions under which the liquid/vapor volume ratio was typically ~9.

The quantity of cyclopropane in the liquid phase of the product mixture was determined by integration of the appropriate peaks in the nmr spectrum. The tubes were shaken for 10–15 min prior to

(27) (a) See ref 25c–e. (b) This mechanism would involve the concurrent existence of two 3-iodopropyl radicals, with "conventional" and symmetrically-bridged structures, the former being trapped to a significant extent by CCl₄, but not by R· and the latter by R· but not^{5e} by CCl₄.

(28) For greater detail, see the Ph.D. Thesis of R. F. Drury, University of Chicago, 1972.

(29) H. B. Hass and H. C. Huffman, *J. Amer. Chem. Soc.*, **63**, 1233 (1941).

(30) A. Iliceto, A. Fava, and A. Simeone, *Gazz. Chim. Ital.*, **90**, 660 (1960).

insertion into the spectrometer probe, which was maintained at room temperature in order to avoid temperature, and hence [cyclopropane], gradients. Four analyses were performed, each on a different day. The four results were combined as a weighted average, the weights assigned being equal to the inverse of the square of the standard deviation from the mean of the ~15 integrations which comprised each analysis, with a corresponding standard deviation. The Bunsen coefficients (the volume, at STP, of a substance which will dissolve in a unit volume of solution when the equilibrium partial pressure of the substance above the solution is 1 atm) of cyclopropane in benzene, CCl₄, and a benzene–CCl₄ mixture were determined by use of a modified atmospheric pressure hydrogenation apparatus in order that each result could be corrected for the small amount of cyclopropane in the vapor phase. Results are in Table III.

Table III. Solubility of Cyclopropane and Propane in Benzene and CCl₄, 25.0 \pm 0.3°

Compd	Solvent	Bunsen coefficient ^a
Cyclopropane	Benzene	32.8 \pm 0.4 ^{b,c}
Cyclopropane	CCl ₄	37.7 \pm 0.1 ^d
Cyclopropane	Benzene–CCl ₄ , 50/50 (v/v)	35.0
Propane	Benzene	14.5 \pm 0.2 ^{b,e}

^a Uncertainties are average deviations. ^b An average of four determinations. ^c E. S. Thomsen and J. C. Gjaldbaek, *Dan. Tidsskr. Farm.*, **37**, 9 (1963), reported 33.2 at 25°. ^d An average of three determinations. ^e E. S. Thomsen and J. C. Gjaldbaek, *Acta Chem. Scand.*, **17**, 134 (1963), reported 14.7 at 25°.

All other products were analyzed on an SE-30 (20% on acid-washed, DMCS-treated Chromosorb W 20–80) vpc column (He flow rate 60 ml/min, injector temperature 230°, detector temperature 275°, column ambient until elution of solvent, then programmed to 100° and held isothermal until elution of ICH₂CH₂CH₂I, then programmed to 200° and held isothermal).

In order to confirm our acceptable material balances, an experiment which might have been indicative of the failure of some product(s) to emerge from the vpc was performed. It was shown that a reaction mixture could be transferred quantitatively (–0.01 wt % residue) by distillation (ultimately 200° (0.01 mm)) and that the material with the highest vpc retention time comprised the same fraction (<0.4% decrease) of the reaction mixture both before and after distillation. If the distillation were stopped prematurely, leaving a residue of 0.53 wt %, the fraction of the distillate comprised by the material with the highest retention time decreased by 34%. If the order of boiling points of the less volatile products is roughly that of their retention times on an SE-30 vpc column, these results indicate the absence of any product with a retention time greater than the highest observed; this contrasts with what might be concluded from a significant distillation residue being accompanied by no reduction in the amount of observed material of high retention time.

In order to investigate the possibility of reversal of the formation of cyclopropane and iodine, a CCl₄ solution 0.01002 *M* [$>10^3$ times the concentration which could have been present (visual detection) during the course of the Table I reactions] in iodine and ~0.19 *M* (more than double the highest final concentration of cyclopropane in Table I) in cyclopropane was heated at 111.1 \pm 0.1° for 12 hr. Titration with 0.01000 *M* Na₂S₂O₃ solution (prepared from Fisher Scientific 1.000 *M* solution and standardized against a solution of iodine in CCl₄) indicated that 1.9% of the iodine had been destroyed. Similarly, analysis of a benzene solution, 0.01005 *M* in iodine and ~0.19 *M* in cyclopropane, which had been heated for 15 hr indicated that the cyclopropane was responsible for the destruction of 1.7% of the iodine.

Table II. Solutions of 4-iodobutyl peroxide^{5e} (titrimetric purity 99.9 wt %) in benzene–CCl₄ were sealed into 5-ml ampoules which were then heated at 95.1 \pm 0.05° for 15 hr. All products were analyzed on a 10-ft SE-30 (20% on acid-washed DMCS-treated Chromosorb W 20–80) vpc column (He flow rate 37 ml/min; injector temperature 230°; detector temperature 275°; column ambient until elution of solvent, then programmed to 90° and held isothermal until elution of ICH₂CH₂CH₂Cl, then programmed to 200° and held isothermal).