3-Iodopropyl Radical. Closure to Cyclopropane[1]

Robert F. Drury[2a] and Leonard Kaplan*[2b]

Contribution from the Department of Chemistry, University of Chicago, Chicago, Illinois 60637. *Received July 24, 1972*

Abstract: From quantitative analyses of the products of the decomposition of $ICH_2CH_2CH_2I$–Bz_2O_2 (111.0°) and $(ICH_2CH_2CH_2CO_2-)_2$ (95.1°) in several benzene–CCl_4 solutions it was determined that $k(ICH_2CH_2CH_2\cdot \rightarrow \text{cyclopropane} + I\cdot)/k(ICH_2CH_2CH_2\cdot + CCl_4 \rightarrow ICH_2CH_2CH_2Cl + \cdot CCl_3) = 2.2\text{–}4.0\ M$ and $k(Ph\cdot + ICH_2CH_2CH_2I \rightarrow PhI + \text{cyclopropane} + I\cdot)/k(Ph\cdot + ICH_2CH_2CH_2I \rightarrow PhI + ICH_2CH_2CH_2\cdot) < 0.17$ 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 $ICH_2CH_2CH_2\cdot$, with high probability *via* a unimolecular carbon radical displacement on carbon with a rate constant of $\sim 2 \times 10^3\ sec^{-1}$ 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 radical[4] has not been demonstrated. We have reported several reactions[5] 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 $ICH_2CH_2CH_2I$–Bz_2O_2[5a] and $(ICH_2CH_2CH_2CO_2-)_2$[4a,5e] 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 $ICH_2CH_2CH_2Cl$ by CCl_4, we have determined the products of the reaction of $ICH_2CH_2CH_2I$ 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 $(ICH_2CH_2CH_2CO_2-)_2$ under the same conditions of concentration and temperature as used previously[5e] are summarized in Tables I and II, respectively, and in Figure 1.

Analysis of Results

The scheme composed of reactions 1–8 was examined for conformity to the data in Table I. Our principal goals are the determination of k_5/k_4 and k_2/k_1.

$$Ph\cdot + ICH_2CH_2CH_2I \longrightarrow ICH_2CH_2CH_2\cdot + PhI \tag{1}$$

$$Ph\cdot + ICH_2CH_2CH_2I \longrightarrow \text{cyclopropane} + PhI + I\cdot \tag{2}$$

$$Ph\cdot + CCl_4 \longrightarrow PhCl + \cdot CCl_3 \tag{3}$$

$$ICH_2CH_2CH_2\cdot + CCl_4 \longrightarrow ICH_2CH_2CH_2Cl + \cdot CCl_3 \tag{4}$$

$$ICH_2CH_2CH_2\cdot \longrightarrow \text{cyclopropane} + I\cdot \tag{5}$$

$$ICH_2CH_2CH_2Cl + Ph\cdot \longrightarrow ClCH_2CH_2CH_2\cdot + PhI \tag{6}$$

$$ClCH_2CH_2CH_2\cdot + CCl_4 \longrightarrow ClCH_2CH_2CH_2Cl + \cdot CCl_3 \tag{7}$$

$$ICH_2CH_2CH_2\cdot + ClCH_2CH_2CH_2I \rightleftarrows ICH_2CH_2CH_2I + ClCH_2CH_2CH_2\cdot \tag{8}$$

Application of the steady-state approximation to the behavior of $ICH_2CH_2CH_2\cdot$ and $ClCH_2CH_2CH_2\cdot$, with the exclusion of reactions 8 and with recognition of the near-constancy of $[CCl_4]$[7] throughout each reaction (Table I), leads to eq 9. If the values of k_1, k_2, k_4, and

$$\frac{[\text{cyclopropane}]}{[ICH_2CH_2CH_2Cl] + [ClCH_2CH_2CH_2Cl]} = \frac{k_5}{k_4}\left(1 + \frac{k_2}{k_1}\right)\frac{1}{[CCl_4]} + \frac{k_2}{k_1} \tag{9}$$

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 10[8] is obtained from eq 9. We

$$\frac{[\text{cyclopropane}]}{[ICH_2CH_2CH_2Cl] + [ClCH_2CH_2CH_2Cl]} = \frac{\dfrac{k_2{}^{B}}{k_1{}^{B}}\left(\dfrac{k_2{}^{C}}{k_2{}^{B}} - 1.088 + \dfrac{9.97}{[CCl_4]}\right)}{\dfrac{k_1{}^{C}}{k_1{}^{B}} - 1.088 + \dfrac{9.97}{[CCl_4]}} + \frac{\dfrac{1}{[CCl_4]}\left(\dfrac{k_5{}^{B}}{k_4{}^{B}}\right)\left(\dfrac{k_5{}^{C}}{k_5{}^{B}} - 1.088 + \dfrac{9.97}{[CCl_4]}\right)}{\dfrac{k_4{}^{C}}{k_4{}^{B}} - 1.088 + \dfrac{9.97}{[CCl_4]}} \times \left[1 + \frac{\dfrac{k_2{}^{B}}{k_1{}^{B}}\left(\dfrac{k_2{}^{C}}{k_2{}^{B}} - 1.088 + \dfrac{9.97}{[CCl_4]}\right)}{\dfrac{k_1{}^{C}}{k_1{}^{B}} - 1.088 + \dfrac{9.97}{[CCl_4]}}\right] \tag{10}$$

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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).

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[6] See the discussion in ref 5a and 5b.

[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–CCl_4 Solutions at 111.0°

Solution	1	2	3	4	5	6	7	8	9	10
Reactants, mmol										
Bz_2O_2	0.3951	0.3976	0.3992	0.3996	0.3988	0.3980	0.3988	0.3984	0.3980	0.3984
$ICH_2CH_2CH_2I$	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
$ClCH_2CH_2CH_2Cl$	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
$ICH_2CH_2CH_2Cl$	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
$ICH_2CH_2CH_2I$	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
$PhCO_2Ph$	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[c,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_2Cl_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_3H_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 $PhCH_2CH_2CH_2I$, 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 $PhCH_2CH_2CH_2I$ and biphenyl. [d] Mass and nmr [$\tau(CCl_4)$ 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 $CH_2{=}CHCH_2I$ and Bz_2O_2 in CCl_4 at 111.2°. Relative molal response of the vpc detector taken to be relative molecular weight, with the structure assumed to be $CCl_3CH_2CHClCH_2CCl_3$. [e] Vpc retention time same as that of $CH_3CH_2CH_2I$, 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 $(ICH_2CH_2CH_2CO_2-)_2$ in Benzene–CCl_4 Solutions at 95.1°

Solution	1	2	3	4	5
Reactants, mmol					
$(ICH_2CH_2CH_2CO_2-)_2$	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
$ICH_2CH_2CH_2Cl$	68.1 ± 3.0	55.7 ± 2.9	37.1 ± 1.0	31.1 ± 0.9	25.2 ± 0.6
$ICH_2CH_2CH_2I$	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/ $ICH_2CH_2CH_2Cl$	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 $ICH_2CH_2CH_2CH_2CH_2CH_2I$ and $ICH_2CH_2CH_2OCOCH_2CH_2CH_2I$ inper cent yields whose average deviations were 0.02 and 0.04, respectively, of the average yields from all five solutions. The yield of $ClCH_2CH_2CH_2Cl$ 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 fit[9] to the [cyclopropane]/($[ICH_2CH_2CH_2Cl]$ + $[ClCH_2CH_2CH_2Cl]$) *vs.* $[CCl_4]^{-1}$ data of Table I[10] 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 2.2 *M* and less than an upper limit which decreased steadily from 4.0 to 3.0 *M* as $k_2{}^B/k_1{}^B$ increased within its range of 0.00–0.17.

Steady-state treatment of the above scheme including reactions 8 permitted an estimate of the fractional error resulting from use of eq 10, derived for reactions 1–7, for the calculation of the values of [cyclopropane]/($[ICH_2CH_2CH_2Cl]$ + $[ClCH_2CH_2CH_2Cl]$) to be expected from a scheme comprised of reactions 1–8. We examined quantitatively the effect which the correction (eq 11)

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[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

$$\frac{[\text{cyclopropane}]}{[ICH_2CH_2CH_2Cl] + [ClCH_2CH_2CH_2Cl]} = \frac{(2.49 \pm 0.05)}{[CCl_4]} - (0.114 \pm 0.018)$$

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

$$\frac{[\text{cyclopropane}]}{[ICH_2CH_2CH_2Cl] + [ClCH_2CH_2CH_2Cl]} = \frac{(2.06 \pm 0.03)}{[CCl_4]} - (0.056 \pm 0.007)$$

[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 solution[16] in radical processes have been reported. Reports of rate constants for dimerization of I· in CCl_4 and benzene[17] and of equilibrium constants of complex formation between I_2 and benzene[18] provide no cause for concern over whether k_6 in particular might vary with solvent even beyond our extreme limits.

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$$1 - \frac{\left\{\dfrac{\mathrm{d([cyclopropane])}}{\mathrm{d([ICH_2CH_2CH_2Cl] + [ClCH_2CH_2CH_2Cl])}}\right\}_{\mathrm{eq\ 1-7}}}{\left\{\dfrac{\mathrm{d([cyclopropane])}}{\mathrm{d([ICH_2CH_2CH_2Cl] + [ClCH_2CH_2CH_2Cl])}}\right\}_{\mathrm{eq\ 1-8}}} =$$

$$\frac{k_7[\mathrm{CCl_4}]/k_4 - \left(\dfrac{k_5}{k_4} + [\mathrm{CCl_4}]\right)\dfrac{k_{-8}k_6}{k_8k_1}}{\dfrac{k_5k_1k_{-8}k_6}{k_4k_2k_8k_1} + \dfrac{k_7[\mathrm{CCl_4}]}{k_4}\left[1 + \left(1 + \dfrac{k_1}{k_2}\right)\dfrac{k_5}{k_8[\mathrm{ICH_2CH_2CH_2Cl}]} + \dfrac{k_4[\mathrm{CCl_4}]}{k_8[\mathrm{ICH_2CH_2CH_2Cl}]}\right] + \dfrac{k_{-8}[\mathrm{ICH_2CH_2CH_2I}]}{k_8[\mathrm{ICH_2CH_2CH_2Cl}]}\left[\dfrac{k_5}{k_4}\left(1 + \dfrac{k_1}{k_2}\right) + [\mathrm{CCl_4}]\right]} \tag{11}$$

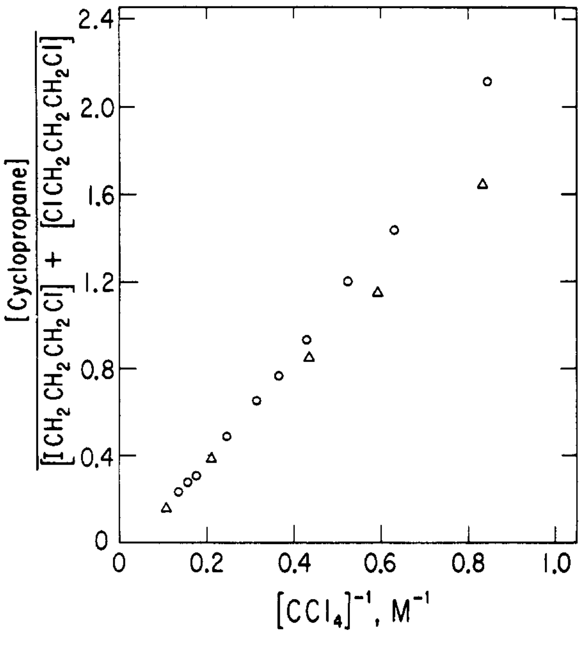

Figure 1. Product ratios from the decomposition of $ICH_2CH_2CH_2I$-Bz_2O_2 at 111.0° (circles) and $(ICH_2CH_2CH_2CO_2-)_2$ at 95.1° (triangles) in several benzene-CCl_4 solutions.

would have on the limiting values of k_2^B/k_1^B and k_5^B/k_4^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 maximally[19] positive [20] or negative[22] sense, could not expand the limits of k_2^B/k_1^B or k_5^B/k_4^B; they were either unchanged or contracted.

Discussion of Results

Based upon our analysis of the data in Table I, we conclude that $k_5^B/k_4^B = 2.2$–4.0 *M* and that $k_2^B/k_1^B < 0.17$ at 111°. Based upon that analysis, upon the data in Table II, obtained independently for another system which involves $ICH_2CH_2CH_2\cdot$ as a precursor of $ICH_2CH_2CH_2Cl$,[5e] and the comparison (ref 10 and Figure 1) between them and those of Table I, we conclude that the parameters k_5^B/k_4^B and k_2^B/k_1^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 $ICH_2CH_2CH_2I$-Bz_2O_2 and $(ICH_2CH_2CH_2CO_2-)_2$ and trappable as $ICH_2CH_2CH_2Cl$ 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 $\sim 2 \times 10^3$ 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-

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(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 $[ICH_2CH_2CH_2I]$ and the larger are k_7/k_4 and $[ICH_2CH_2CH_2Cl]$. $[ICH_2CH_2CH_2I] = [ICH_2CH_2CH_2I]_{final}$, $[ICH_2CH_2CH_2Cl] = [ICH_2CH_2CH_2Cl]_{final}$, and, based upon reports of the effects of γ halogens on the stability, reactivity, and ease of formation of radicals,[21] $k_{-8}/k_8 \geqq 2$, $k_6/k_1 \geqq 0.11$, $k_4/k_8 \geqq 0.001$, and $k_7/k_4 \leqq 10$ were used.

(21) (a) J. K. Kochi and D. M. Singleton, *J. Org. Chem.*, **33**, 1027 (1968); (b) P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, **91**, 582 (1969); (c) W. C. Danen and R. L. Winter, *ibid.*, **93**, 716 (1971); (d) L. Kaplan, "Bridged Free Radicals," Marcel Dekker, New York, N. Y., 1972, Chapters 5 and 7.

(22) The correction is more negative the smaller are k_7k_8/k_4k_{-8} and $[ICH_2CH_2CH_2I]$ and the larger are k_6/k_1 and $[ICH_2CH_2CH_2Cl]$. Based as in ref 20, $k_6/k_1 \leqq 1$, $[ICH_2CH_2CH_2I] = [ICH_2CH_2CH_2I]_{final}$, $k_7k_8/k_4k_{-8} \geqq 0.01$, and $[ICH_2CH_2CH_2Cl] = [ICH_2CH_2CH_2Cl]_{final}$ were used.

(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 $D(ICH_2CH_2CH_2{-}H) = D(CH_3CH_2{-}H)$, *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 $k_4 \cong k(CH_3CH_2CH_2\cdot + CCl_4)$.[5e] 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} sec^{-1} at 111°; see ref 23.

(25) (a) This mechanism would require that the ($R\cdot + ICH_2CH_2CH_2\cdot \rightarrow RI$ + cyclopropane) reaction compete successfully with the "almost-diffusion-controlled" coupling reaction. (b) The amounts of $PhCH_2CH_2CH_2I$ (which need not arise exclusively *via* radical coupling) and $ICH_2CH_2CH_2CH_2CH_2CH_2I$ 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 [cyclopropane]/($[ICH_2CH_2CH_2Cl] + [ClCH_2CH_2CH_2Cl]$) on $[CCl_4]$. (d) The competitive occurrence of such a step in the $(ICH_2CH_2CH_2CO_2-)_2$ system, even with a diffusion-controlled rate, would require that the effective steady-state concentration of $R\cdot$ be at least $\sim 10^{-4}[(ICH_2CH_2CH_2CO_2-)_2]_{initial}$ (based upon our estimate of k_5; see below). (e) The $ICH_2CH_2CH_2I$-Bz_2O_2 and $(ICH_2CH_2CH_2CO_2-)_2$ systems, wherein the effective steady-state concentration of each $R\cdot$ would differ, showed very similar variations of [cyclopropane]/($[ICH_2CH_2CH_2Cl] + [ClCH_2CH_2CH_2Cl]$) with $[CCl_4]$.

(26) (a) This process may be classified as a carbon radical displacement on carbon, assisted by external $R\cdot$ with the leaving group being RI rather than $I\cdot$, *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 bridged[27] limiting structure to be unlikely.

Experimental Section[28]

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 and dried *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 μl 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 $BrCH_2CH_2CH_2Cl$ 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 (CCl_4) 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-μl 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, prepared[30] from 3-chloropropylbenzene and NaI, had bp 71.5–73° (0.25 mm) (lit.[30] 105–105.5° (3 mm)). Its nmr spectrum (CCl_4) 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, $ICH_2CH_2CH_2I$, benzene, and CCl_4 were sealed into 9-in. 5-mm OD nmr tubes (Wilmad) and the tubes were heated at 111.0 ± 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 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, CCl_4, and a benzene–CCl_4 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 CCl_4, 25.0 ± 0.3°

Compd	Solvent	Bunsen coefficient[a]
Cyclopropane	Benzene	32.8 ± 0.4[b,c]
Cyclopropane	CCl_4	37.7 ± 0.1[d]
Cyclopropane	Benzene–CCl_4, 50/50 (v/v)	35.0
Propane	Benzene	14.5 ± 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 $ICH_2CH_2CH_2I$, 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 CCl_4 solution 0.01002 M [>10^2 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 ± 0.1° for 12 hr. Titration with 0.01000 M $Na_2S_2O_3$ solution (prepared from Fisher Scientific 1.000 M solution and standardized against a solution of iodine in CCl_4) 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-iodobutyryl peroxide[5e] (titrimetric purity 99.9 wt %) in benzene–CCl_4 were sealed into 5-ml ampoules which were then heated at 95.1 ± 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 $ICH_2CH_2CH_2Cl$, then programmed to 200° and held isothermal).

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[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 CCl_4 but not by R· and the latter by R· but not[5e] by CCl_4.

[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).