3-Iodopropyl Radical. Lack of 1,3 Iodine Transfer[1]

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Abstract: The decomposition of 0.010 *M* $(ICH_2CH_2CH_2CO_2-)_2$ in CCl_4 at 95.1° gave cyclopropane (9.4%), $ICH_2CH_2CH_2Cl$ (67.6%), $ICH_2CH_2CH_2I$ (16.1%), $(ICH_2CH_2CH_2-)_2$ (25.7%), $ICH_2CH_2CH_2CO_2CH_2CH_2CH_2I$ (15.8%), and C_2Cl_6 (24.2%). Decomposition of $(ICH_2CH_2CD_2CO_2-)_2$ under the same conditions gave $ICH_2CH_2CD_2Cl$ and $(ICH_2CH_2CD_2-)_2$; if the reaction mixture was treated with Ph_3SnH, $CH_3CH_2CD_2Cl$, $(CH_3CH_2CD_2-)_2$, and $CH_3CH_2CD_2CO_2CD_2CH_2CH_3$ were produced. Decomposition of $(ICD_2CH_2CH_2CO_2-)_2$ under the same conditions in $CHCl_3$ gave 22% $CH_3CH_2CD_2I$. The rate constant for decomposition of $(ICH_2CH_2CH_2CO_2-)_2$ in CCl_4 at 85° is 44% that of $(CH_3CH_2CH_2CO_2-)_2$. From these results it is argued that $ICH_2CH_2CH_2\cdot$ is not symmetrically bridged and that a 1,3-iodine shift cannot compete with trapping by CCl_4. The corresponding intermolecular iodine-transfer reaction has an activation energy >11 kcal/mol less than the intramolecular reaction; it is pointed out that this difference may indicate a preference for inversion in a radical displacement on iodine.

With the goals of probing the existence of a symmetrically 1,3-bridged iodopropyl radical as either an intermediate or a transition state and perhaps obtaining information relevant to the preferred stereochemistry[3] of a carbon radical displacement on iodine, and in view of interest in neighboring group assistance in radical reactions, we have determined the rate and products of the decomposition of 2,2-dideuterio-4-iodobutyryl peroxide.

Products of the decomposition of $(ICH_2CH_2CH_2CO_2-)_2$ in CCl_4 and the distribution of deuterium in those from $(ICH_2CH_2CD_2CO_2-)_2$ are described in Tables I and II, respectively. None of the products for which such an examination is meaningful show any detectable "scrambling" of the deuterium atoms, an observation which would lead to the conclusion that there is no "scrambling" in the 3-iodopropyl radical if the mechanism of formation of these products, particularly 1-chloro-3-iodopropane, is substantially the same as is usually ascribed[4] to those from unsubstituted peroxides. In support of the proposition that there is no significant difference in mechanism, the following may be cited. (a) A perturbing influence of the iodine on the mechanism may be manifested in a change in rate of decomposition. We have found (Table III) that the difference between $(ICH_2CH_2CH_2CO_2-)_2$ and $(CH_3CH_2CH_2CO_2-)_2$ is not large ($\Delta\Delta G^{\ddagger} = 0.6$ kcal/mol at 85°) and is opposite in direction from what would be anticipated were assistance by iodine important in the transition state of the rate-determining step. (b) Our distribution of products (Table I) is very similar to those reported for the decomposition of $(PhCH_2CH_2CH_2CH_2CO_2-)_2$[5e] and $(CH_3CH_2CH_2CH_2CH_2CH_2CO_2-)_2$[5g] in CCl_4. (c) The effect of solvent (benzene *vs.* CCl_4) on the rate of decomposition of $(ICH_2CH_2CH_2CO_2-)_2$ is "normal" (Table III and ref 5a,d, 8). (d) Several 0.010 *M* solutions of $(ICH_2CH_2CH_2CO_2-)_2$ in benzene–carbon tetrachloride mixtures were heated at 95.1°. Plots of [cyclopropane]/[$ICH_2CH_2CH_2Cl$] *vs.* the reciprocal of the CCl_4 concentration (molarity and mole fraction) were linear with a very small negative intercept. This study and similar ones involving the $ICH_2CH_2CH_2I/(PhCO_2-)_2$ system will be discussed in a subsequent paper concerned with the mechanism of formation of cyclopro-

Table I. Decomposition of 0.010 *M* $(ICH_2CH_2CH_2CO_2-)_2$ in CCl_4 at 95.1°

Product	Mol % yield[a,b]
Cyclopropane	9.4 ± 0.3
$ICH_2CH_2CH_2Cl$	62.9 ± 0.5
$ICH_2CH_2CH_2I$	16.1 ± 0.3
$ICH_2CH_2CH_2CH_2CH_2CH_2I$	25.7 ± 0.3
$ICH_2CH_2CH_2CO_2CH_2CH_2CH_2I$	15.8 ± 0.3
C_2Cl_6	24.2 ± 0.7

[a] Moles per mole of peroxide decomposed. Based on $(ICH_2CH_2CH_2CO_2-)_2$, mp 34.0–35.0°. An average of three analyses of each of three reaction mixtures. Uncertainties are average deviations. Products identified by comparison of spectra and vpc behavior with those of authentic samples. [b] It has been reported[22] that 4-iodobutyryl peroxide, mp 30–31°, gave γ-butyrolactone (66%), $ICH_2CH_2CH_2I$ (66%), CO_2 (92%), and cyclopropane (2–3%) when heated to 85° over 5 hr (~3 half-lives at 85°, Table III) in a flask attached to a tube at 225° and 0.002 mm of pressure.

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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] The discussion of Pryor and Smith [*J. Amer. Chem. Soc.*, **92**, 2731 (1970), footnote 7] illustrates the difficulty of describing the course of such reactions in terms of "retention" and "inversion."

[4] The $(RCO_2-)_2 + CCl_4$ reaction system behaves as would be expected were free $R\cdot$ a precursor of RCl.[5,6]

[5] (a) F. G. Edwards and F. R. Mayo, *J. Amer. Chem. Soc.*, 72, 1265 (1950); (b) M. S. Kharasch, F. Engelmann, and W. H. Urry, *ibid.*, **65**, 2428 (1943); (c) M. S. Kharasch, S. S. Kane, and H. C. Brown, *ibid.*, **63**, 526 (1941); (d) R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *ibid.*, 87, 3928 (1965); (e) D. F. DeTar and C. Weis, *ibid.*, 79, 3041 (1957); (f) D. F. DeTar and R. C. Lamb, *ibid.*, 81, 122 (1959); (g) D. F. DeTar and D. V. Wells, *ibid.*, 82, 5839 (1960); (h) R. Kaptein, J. A. DenHollander, D. Antheunis, and L. J. Oosterhoff, *J. Chem. Soc. D*, 1687 (1970).

[6] Had the work been designed for our present purposes and the appropriate control experiments performed, the reports[7] that decomposition of $(RCO_2-)_2$ in CCl_4 gave RCl with loss of configuration about the original carboxyl-bearing carbon would indicate that $R\cdot$ is "free," at least on some time scale and in relation to some chlorine donor (CCl_4 or, for example,[5e] chlorine in $R\cdot\ CO_2\ \cdot Cl$).

[7] (a) D. F. DeTar and C. Weis, *J. Amer. Chem. Soc.*, **79**, 3045 (1957); (b) F. D. Greene, C.-C. Chu, and J. Walia, *J. Org. Chem.*, **29**, 1285 (1964); (c) H. M. Walborsky and J.-C. Chen, *J. Amer. Chem. Soc.*, **93**, 671 (1971); (d) H. J. Dauben, Jr., and H.-T. Liang, unpublished results cited in H. J. Dauben, Jr., and L. L. McCoy, *ibid.*, **81**, 5404 (1959).

[8] (a) S. D. Ross and M. A. Fineman, *ibid.*, 73, 2176 (1951); (b) M. Levy, M. Steinberg, and M. Szwarc, *ibid.*, 76, 5978 (1954); (c) P. D. Bartlett, *Experientia, Suppl.*, 7, 275 (1957); (d) H. J. Shine, J. A. Waters, and D. M. Hoffman, *J. Amer. Chem. Soc.*, 85, 3613 (1963).

Table II. Decomposition of 0.010 M $(ICH_2CH_2CD_2CO_2-)_2$[a] in CCl_4 at 95.0°

Product isolated from reaction mixture	Distribution of deuterium	Product isolated from Ph_3SnH-treated reaction mixture	Distribution of deuterium[b]
1-Chloro-3-iodopropane	97.7 ± 0.1% α to Cl	1-Chloropropane	97.8 ± 0.1, 97.9 ± 0.1% α to Cl
1,6-Diiodohexane	95.8 ± 2% in methylenes	*n*-Hexane	97.6 ± 1.3% in methylenes
3-Iodopropyl 4-iodobutyrate	?	*n*-Propyl butyrate	94.5 ± 0.9, 96.1 ± 0.4% α to carbonyl; 96.6 ± 0.7, 96.3 ± 0.7% α to O

[a] 96.3 ± 1.3% D α to carbonyl, mp 33.5–35°, 99.5 wt % pure. [b] Multiple entries represent the results of independent reactions and analyses.

Table III. Decomposition of 4-Iodobutyryl and Other Peroxides

Peroxide	Concn, M	Solvent	Temp, °C	No. of half-lives followed	$k \times 10^5$, sec^{-1} [a]	Ref
$(ICH_2CH_2CH_2CO_2-)_2$	0.0101	CCl_4	62.5[b]		0.26	This work
$(ICH_2CH_2CH_2CO_2-)_2$[e]	0.0101	CCl_4	85.1	5	6.5 ± 0.2[c]	This work
$(ICH_2CH_2CH_2CO_2-)_2$[e]	0.0101	CCl_4	95.0	6.5	23.3 ± 0.3[c]	This work
$(ICH_2CH_2CD_2CO_2-)_2$[i]	0.0100	CCl_4	95.0	3.5	21.6[d]	This work
$(ICH_2CH_2CH_2CO_2-)_2$[k]	0.0100	Benzene	85.0	4.5	12.2 ± 0.7[c]	This work
$(ICH_2CH_2CO_2-)_2$	0.024	Benzene	62.5	?	23.9	*g*
$(CH_3CH_2CH_2CO_2-)_2$	0.0073	Benzene	62.5[b]		1.66	*h*
$(CH_3CH_2CH_2CO_2-)_2$	0.0073	Benzene	85.0	?	30.2	*h*
$(CH_3CH_2CH_2CO_2-)_2$[f]	0.0111	Benzene	85.1	5	27.8 ± 0.4[c]	This work
$(CH_3CH_2CH_2CO_2-)_2$[j]	0.0100	CCl_4	85.1	4.5	14.9 ± 0.2[c]	This work

[a] First-order rate constants determined by use of a weighted-least-squares treatment of [peroxide]–time data. Uncertainties are average deviations. [b] Extrapolated. [c] An average of four runs, each consisting typically of 12 "kinetic points." [d] Result of a single run consisting of five "kinetic points." [e] Mp 34.5–35.0°, 98.6 wt % pure. [f] 98 wt % pure. [g] J. E. Leffler and J. S. West, *J. Org. Chem.*, **27**, 4191 (1962). [h] J. Smid, A. Rembaum, and M. Szwarc, *J. Amer. Chem. Soc.*, **78**, 3315 (1956). [i] Mp 33.5–35°, 99.5 wt % pure. [j] 95 wt % pure. [k] Mp 34.5–35.0°, 99.9 wt % pure.

pane and the occurrence of a carbon radical displacement on carbon.

Our view is that a preponderance of evidence supports the position that the mechanisms of decomposition of $(ICH_2CH_2CH_2CO_2-)_2$ and $(RCO_2-)_2$ in CCl_4 are substantially the same and that free $R\cdot$ is the precursor of RCl.

Based upon the above discussion and our observation that decomposition of 0.010 M $(ICD_2CH_2CH_2CO_2-)_2$[9a] in $CHCl_3$[10] at 95.0° led to 1-iodopropane[9b] with no detectable "scrambling" of the deuterium, we will presume that 1-chloro-3-iodopropane is produced directly from free 3-iodopropyl radical. It would follow that the 3-iodopropyl radical is not symmetrically bridged[11] and that a 1,3-iodine shift cannot compete with trapping by CCl_4.

This conclusion may be compared to what would be expected for the corresponding intermolecular process. The data in Table II and those of Young[12] lead to

$$\frac{k(\cdot CD_2CH_2CH_2I \rightarrow ICD_2CH_2CH_2\cdot)}{k(\cdot CD_2CH_2CH_2I + CCl_4 \rightarrow ClCD_2CH_2CH_2I)} < 9 \times 10^{-2}\ M^{-1}\ (95°) \quad (1)$$

Based upon the undefinitive but consonant reports of activation parameters for $(CH_3\cdot + CCl_4 \rightarrow CH_3Cl)$,[13a] $(CH_3\cdot + PhCH_3 \rightarrow CH_4)$,[13c–g] and $(CH_3\cdot + CF_3I \rightarrow CH_3I)$,[13a] rate constants for $(RCH_2\cdot + CH_3I \rightarrow RCH_2I)$,[13h] $(RCH_2\cdot + CH_3CH_2I \rightarrow RCH_2I)$,[13h] $(RCH_2\cdot + CH_3CH_2CH_2CH_2I \rightarrow RCH_2I)$,[13h] and $(RCH_2\cdot + CH_3CH_2CH_2CH_2CH_2CH_2CH_2I \rightarrow RCH_2I)$,[13h] and $k(CH_3\cdot + CH_3I \rightarrow CH_3I + CH_3\cdot)/k(CH_3\cdot + PhCH_3 \rightarrow CH_4)$[13b] and $k(CH_3\cdot + CH_3CH_2CH_2I \rightarrow CH_3I)/k(CH_3\cdot + CCl_4 \rightarrow CH_3Cl)$,[13a] we estimate that

$$k(CH_3CH_2CH_2\cdot + ICH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2I + \cdot CH_2CH_2CH_3) \cong 3 \times 10^4\ M^{-1}\ sec^{-1}\ (95°)$$

and

$$\frac{k(CH_3CH_2CH_2\cdot + ICH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2I + \cdot CH_2CH_2CH_3)}{k(CH_3CH_2CH_2\cdot + CCl_4 \rightarrow CH_3CH_2CH_2Cl)} \cong 1 \times 10^2\ (95°) \quad (2)$$

We estimate[14,15] that

$$A(\cdot CD_2CH_2CH_2I \rightarrow ICD_2CH_2CH_2\cdot) \cong 10^{11.7}\ sec^{-1} \quad (3)$$

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[9] (a) Mp 34.0–35.0°; 92.1 ± 0.4% D α to I. (b) 22% yield; 93.0 ± 0.3% D α to I.

[10] A system wherein RH is produced is not subject to at least one of the possible complications in mechanism attendant upon RCl being the product of interest.[6]

[11] For a discussion of the question of bridging by iodine, see L. Kaplan, "Bridged Free Radicals," Marcel Dekker, New York, N. Y., 1972.

[12] S. Young, *Sci. Proc. Roy. Dublin Soc.*, **12**, 374 (1910): a determination of the density of CCl_4 between −20 and 280°.

[13] (a) D. M. Tomkinson and H. O. Pritchard, *J. Phys. Chem.*, 70, 1579 (1966); however, see ref 14, p 101; (b) F. W. Evans, R. J. Fox, and M. Szwarc, *J. Amer. Chem. Soc.*, 82, 6414 (1960); R. J. Fox, F. W. Evans, and M. Szwarc, *Trans. Faraday Soc.*, **57**, 1915 (1961); (c) I. B. Burkley and R. E. Rebbert, *J. Phys. Chem.*, **67**, 168 (1963); (d) M. F. R. Mulcahy, D. J. Williams, and J. R. Wilmshurst, *Aust. J. Chem.*, **17**, 1329 (1964); (e) A. F. Trotman-Dickenson and E. W. R. Steacie, *J. Chem. Phys.*, **19**, 329 (1951); (f) R. E. Rebbert and E. W. R. Steacie, *ibid.*, **21**, 1723 (1953); (g) M. Szwarc and J. S. Roberts, *Trans. Faraday Soc.*, **46**, 625 (1950); (g) I. B. Afanas'ev and E. D. Safronenko, *Zh. Org. Khim.*, **6**, 1537 (1970).

[14] S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968.

[15] S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

and[13a,14,16] that

$$A(\mathrm{CH_3CH_2CH_2\cdot} + \mathrm{ICH_2CH_2CH_3} \rightarrow \mathrm{CH_3CH_2CH_2I} + \cdot\mathrm{CH_2CH_2CH_3}) \cong 10^{(8.5\pm1.5)}\ M^{-1}\ \mathrm{sec}^{-1} \quad (4)$$

Combination of eq 1–4 yields

$$E(\cdot\mathrm{CD_2CH_2CH_2I} \rightarrow \mathrm{ICD_2CH_2CH_2\cdot}) - E(\mathrm{CH_3CH_2CH_2\cdot} + \mathrm{ICH_2CH_2CH_3} \rightarrow \mathrm{CH_3CH_2CH_2I} + \cdot\mathrm{CH_2CH_2CH_3}) > 11\ \mathrm{kcal/mol}$$

We define this difference as "strain" and artificially separate out a part associated solely with the C–I–C angle in the bridged 3-iodopropyl radical. If a significant portion of the "strain" can be so associated, and since there are constraints on the structure of the transition state peculiar to the intramolecular iodine-transfer reaction, our results provide incentive to pursue the possibility that an "inversion"[3] pathway is preferred for a carbon radical displacement on iodine.[17]

Experimental Section[19]

Infrared and nmr spectra were obtained on Perkin-Elmer Infracord and Varian 60- and 100-MHz spectrometers, respectively. Microanalyses were performed by Micro-Tech Laboratories, Skokie, Ill. 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 location and amount of deuterium in labeled compounds were determined by integration of the appropriate peaks in the nmr spectra.

The reactions described in Tables I, II, and III 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. Cyclopropane (Matheson), **1-iodopropane** (Baker reagent), **benzene** (Mallinckrodt analytical reagent), **1,3-diiodopropane** (Eastman reagent), **1,6-diiodohexane** (Baker reagent), and **hexachloroethane** (Mallinckrodt reagent) were used without further purification. Purified **hexane** was donated by Professor N. C. Yang. *n*-**Propyl butyrate** was prepared from butyryl chloride and 1-propanol. **Triphenyltin hydride** was prepared from triphenyltin chloride and lithium aluminum hydride.

Chloroform (Mallinckrodt reagent) was passed through a column of Woelm activity 1 basic alumina; 0.5 g of alumina per milliliter of chloroform was used and the first 30% of eluate was discarded. The ethanol content, monitored by use of vpc, decreased from 0.75% in the untreated chloroform to 0.006% in the treated reagent; no other peaks were visible, under conditions such that less than 0.001% of impurity would have been detectable, over the range of temperatures and times of interest (up to 2 hr at a column temperature of 200°). The solvent was purified on the same day as it was used and was stored in an amber bottle in a refrigerator until use.

Carbon tetrachloride (Mallinckrodt reagent) was distilled from phosphorus pentoxide under a nitrogen atmosphere on a foil-wrapped 60-cm platinum spinning band column. Fractions were subjected to vpc analysis on a 5-ft SE-30 column (injector temperature 205°, column temperature ambient, flow rate 60 ml/min), with sufficient sample injected so as to give a full scale peak on attenuation 64; all parts of the chromatogram except the region where CCl_4 eluted were monitored at attenuation 1. Each fraction retained showed no impurity at attenuation 1, either before the solvent peak or after the column temperature was programmed to 100° and held for 2 hr. A peak of area $\geq$0.002% that of the major peak would have been observed. The distilled CCl_4 was stored under nitrogen at 5–6° in amber screw-cap bottles until use.

1-Chloro-3-iodopropane, bp 68° (18 mm), was prepared by reaction of 1-bromo-3-chloropropane with sodium iodide in acetone. After distillation on a 60-cm platinum spinning band column, it was injected onto a 10-ft SE-30 (20% on Chromosorb W) vpc column (injector 225°, detector 275°, column 100°, flow rate 60 ml/min) and gave a full-scale peak at attenuation 16; no other peaks were visible at attenuation 1 during a period which was ten times the retention time of the main peak. Its nmr spectrum (CCl_4) consisted of cleanly separated triplets at τ 6.4 and 6.7 and a multiplet at τ 7.7 with relative areas of 1.0, 1.0, and 1.0.

n-**Butyryl Peroxide.**[20] Sodium peroxide (3.9 g, 0.050 mol) was suspended in 250 ml of anhydrous ether in a flask fitted with mechanical stirrer, dropping funnel, and thermometer and held at −5°. Freshly distilled butyryl chloride (10.6 g, 0.10 mol, bp 101–102°) was added over about 5 min to the stirred suspension. After the mixture had stirred for an additional 15 min, ice was added, the temperature being maintained at −5 to 0°, until further addition of ice produced no temperature change. The cooling bath was removed and stirring continued until the ice in the flask had melted. The organic layer was washed with saturated Na_2CO_3 solution, dried over $MgSO_4$, and stripped of solvent, first on a rotary evaporator and then by evacuation to 0.1 mm for 12 hr. The product (4.4 g, 51%) was a clear, colorless oil, which crystallized from petroleum ether in a Dry Ice–acetone bath to give needle-like crystals which melted below room temperature. Addition of ice to the mixture of butyryl chloride and sodium peroxide in ether too early gave product contaminated with butyric acid which could readily be removed by washing with Na_2CO_3 solution, yielding material of 98 wt% titrimetric purity. Its infrared spectrum (CCl_4) showed absorption at ~1780 and 1810 cm^{-1} and its nmr spectrum (CCl_4) consisted of cleanly separated multiplets at τ 7.7, 8.2, and 8.9 with relative areas of 2, 2, and 3, respectively.

3-Iodopropyl 4-Iodobutyrate. 3-Chloropropanol (9.5 g, 0.10 mol, Aldrich reagent) in 60 ml of anhydrous ether was added dropwise to a refluxing solution of 4-chlorobutyryl chloride (14.1 g, 0.10 mol, Aldrich technical grade) over a period of ~0.5 hr. The mixture was allowed to reflux overnight, after which the ether was removed on a rotary evaporator. Distillation of the residue gave 18.6 g (92%) of colorless oil, bp 93–94° (0.9 mm). This material (18.5 g, 0.092 mol) was added to a solution of 60 g (0.40 mol) of NaI in 200 ml of acetone. The solution was stirred under reflux for 18 hr and filtered. The filtrate was evaporated to a volume of ~20 ml on a rotary evaporator, and the residue slurried in 100 ml of ether. The solution phase was washed with 2 × 50 ml of 1 *M* $Na_2S_2O_3$, 2 × 100 ml of water, dried over $MgSO_4$, and evaporated on a rotary evaporator to give 30 g of yellow oil as residue. Several bulb-to-bulb distillations gave material whose nmr spectrum (CCl_4) indicated absorption at τ 5.7 (t), 6.6 (m), and 7.3–8.1 (m) with relative areas of 2, 4, and 6, respectively. *Anal.* Calcd for $C_7H_{12}O_2I_2$: C, 22.00; H, 3.17; I, 66.48. Found: C, 21.97, 22.22; H, 3.11, 3.27; I, 66.50, 66.48.

4-Iodobutyric Acid.[21] Anhydrous hydrogen iodide (Matheson) was bubbled through a fritted glass dispersion tube into 8.6 g (0.10 mol) of butyrolactone (Eastman reagent) contained in a test tube cooled so as to maintain the temperature at 40–50°. When the weight of the tube and contents had increased by 13.8 g, corresponding to absorption of 0.109 mol of HI, the tube was stoppered and heated at 90 ± 2° for 1.0 hr. After the reaction mixture had cooled to room temperature, it was dissolved in ether and washed until colorless with 10% $Na_2S_2O_3$ solution. It was then washed with water and saturated NaCl solution and dried over Na_2SO_4. Most of the solvent was removed under reduced pressure and the resulting colorless oil was crystallized from ether–pentane at −78°. The crystals were filtered and dried under vacuum to yield 19.3 g (90%) of white crystals, mp 37–38° (lit.[21] 37–38°), whose nmr spectrum (CCl_4) indicated absorption at τ −3.80 (s), 6.8 (t), and 7.3–8.2 (m) with relative areas of 1.0, 2.0, and 4.0, respectively.

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(16) W. G. Alcock and E. Whittle, *Trans. Faraday Soc.*, **61**, 244 (1965).

(17) There is no direct experimental evidence concerning the structure of $R_2I\cdot$ species. Preliminary analyses of matrix infrared spectra have led to assignments to bent $ClF_2\cdot$[18a] and linear $Cl_3\cdot$.[18b] A Raman spectrum has been tentatively assigned to linear $Br_3\cdot$.[18c] For a review of theoretical calculations, see C. A. Parr and D. G. Truhlar, *J. Phys. Chem.*, **75**, 1844 (1971).

(18) (a) G. Mamantov, E. J. Vasini, M. C. Moulton, D. G. Vickroy, and T. Maekawa, *J. Chem. Phys.*, **54**, 3419 (1971); (b) L. Y. Nelson and G. C. Pimentel, *ibid.*, **47**, 3671 (1967); (c) D. H. Boal and G. A. Ozin, *ibid.*, **55**, 3598 (1971).

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

(20) O. A. Reutov, G. M. Ostapchuk, and V. A. Remova, *Izv. Akad, Nauk SSSR*, 519 (1964); S. S. Ivanchev, A. I. Yurzhendo, and Yu. N. Anisimov, *Zh. Fiz. Khim.*, **39**, 1900 (1965).

(21) H. Oelschlager, P. Schmersahl, and W. Toporski, *Arch. Pharm. (Weinheim)*, **294**, 488 (1961).

4-Iodobutyryl Chloride.[22] Iodobutyric acid (11.0 g, 0.051 mol) was dissolved in 10 ml of thionyl chloride (Matheson Coleman and Bell reagent) and stirred for 2 hr at room temperature under a $CaCl_2$ drying tube. The reaction mixture was then heated for 15 min on a steam bath and allowed to cool. The excess $SOCl_2$ was removed under reduced pressure. Distillation of the residue gave 10.6 g (91%) of material, bp 44–48° (0.6 mm) [lit.[22] 65–70° (0.6 mm)], whose nmr spectrum (CCl_4) indicated absorption at τ [6.9 (t) and 7.0 (t)] and 7.9 (m) with relative areas of 4.0 and 2.0, respectively, and whose infrared spectrum (CCl_4) indicated absorption at $\sim$1795 cm^{-1}.

4-Iodobutyryl Peroxide. A solution of 1.6 g (0.0069 mol) of 4-iodobutyryl chloride in 50 ml of ether was placed in a flask equipped with dropping funnel, mechanical stirrer, and thermometer and cooled to -20 to $-14°$ in a carbon tetrachloride–Dry Ice bath. "30%" hydrogen peroxide (3.80 ml) was added dropwise over a period of $\sim$3 min, followed by a solution of 3.0 g of NaOH in 15 ml of water over a period of 20–30 min, at such a rate as to maintain the temperature of the reaction mixture below $-10°$. After addition was complete, the two-phase system was stirred for another 15 min and then allowed to warm to 0°. Sufficient water was added to dissolve the white precipitate and the ether layer was washed with water and allowed to stand over $MgSO_4$ in a dark refrigerator for $\sim$0.5 hr. The solvent was removed under reduced pressure in an ice bath, yielding white crystals which were dissolved in a minimum of ether ($\sim$3 ml). Petroleum ether (bp 30–60°) (50 ml) was added and the resulting solution cooled to -78°. The product crystallized in needles over a period of $\sim$1 hr, and filtration and drying under vacuum gave 1.09 g (74%) of white crystals, mp 34.5–35.5° (lit.[22] 30–31°). Its infrared spectrum (CCl_4) indicated absorption at $\sim$1785 (s) and 1800 (s) cm^{-1} and its nmr spectrum ($CDCl_3$) consisted of a triplet at τ 6.76 (J = 6 cps) and a complex multiplet from τ 7.25 to 8.10. After three recrystallizations from ether–petroleum ether at $-78°$, a white powder was obtained, mp 34.5–35.0°, whose titrimetric purity was 98.6 wt %.

Butyrolactone-*4,4-d_2*. Methyl hydrogen succinate[23] (21.0 g, 0.159 mol), mp 56–58°, was placed in a flask maintained under nitrogen and fitted with condenser, dropping funnel, and gas inlet tube. A 250-ml center cut of tetrahydrofuran which had been refluxed overnight over CaH_2 (Ventron) was distilled into the flask. Sodium borodeuteride (5.0 g, 0.12 mol, Merck Sharpe and Dohme, 98%) was added in small portions with stirring. When gas evolution had ceased, the solution was brought to reflux for 15 min and then cooled in an ice bath. Freshly distilled boron trifluoride etherate (16.1 g, 0.217 mol, Eastman reagent) was added slowly over a period of several hours at such a rate as to minimize gas evolution, while the temperature of the reaction mixture was maintained at 0°. The solution was stirred for 10 hr at 0°, poured over 200 g of ice mixed with 5 ml of concentrated aqueous HCl, and stirred until the ice had melted. The tetrahydrofuran was removed under reduced pressure and the resulting aqueous solution continuously extracted with CH_2Cl_2. After extraction was judged to be complete (no detectable butyrolactone in the aqueous phase under vpc conditions which would have permitted the detection of less than 1% of the theoretical amount of butyrolactone), the CH_2Cl_2 extract was concentrated under reduced pressure, and the residue distilled on a spinning band column, yielding 6.3 g (45%) of labeled butyrolactone, bp 75–76° (5 mm). Under vpc conditions such that the butyrolactone peak was full scale, no other peaks were observed; it was estimated that a peak whose area was 1% that of the major peak would have been readily observable. Unreacted methyl hydrogen succinate (5 g) was recovered from the pot residue of the distillation.

4-Iodobutyryl-*4,4,4′,4′-d_4* peroxide, prepared in 40% yield from butyrolactone-*4,4-d_2*, as is described above for unlabeled material, was a white powder, mp 34.0–35.0°.

Butyrolactone-*α,α-d_2*.[24] To 15 g (0.65 g-atom) of sodium in a flask equipped with a mechanical stirrer, dropping funnel, and Dewar condenser charged with Dry Ice–acetone was added 270 ml of ethanol (USP reagent). After metallic particles were no longer visible and gas evolution had ceased, diethyl malonate (109 g, 0.68 mol, redistilled Matheson Coleman and Bell practical grade, bp 92° (16 mm)) was added dropwise over a period of 0.5 hr with vigorous stirring. After all the malonic ester had been added, the slurry was stirred for 0.5 hr, and ethylene oxide (26.1 g, 0.593 mol, Eastman reagent) was added in a single portion. Stirring was continued for another 2.5 hr and the resulting white slurry filtered. The precipitate was slurried with 100 ml of ethanol and filtered. This procedure was repeated twice with ethanol and three times with ether, and the resulting solid was dried under vacuum over P_2O_5, yielding 62 g (60%) of white powder. To 36 g (0.2 mol) of this material and 16 g (0.12 mol) of barium oxide (Allied Chemical Co.) in a flask maintained under nitrogen and equipped with a reflux condenser surmounted by a distillation assembly was added 60 ml of D_2O (Merck Sharpe and Dohme, 99.7%). After 1 hr of reflux, material was allowed to distill from 70 to 101°. After 10 ml had distilled at 101°, the distillation was stopped and refluxing resumed. D_2O (40 ml) was added. Thionyl chloride (Matheson Coleman and Bell reagent) was then added in portions until the greyish precipitate in the flask had dissolved (50 ml needed). The temperature of the surrounding oil bath was then raised slowly to 160–175°, and all liquid volatile at that temperature was distilled off under a slow stream of dry nitrogen. The remaining oil was held at 160–175° bath temperature for 3.5 hr and then allowed to cool to room temperature. Acetone (200 ml, dried over Na_2CO_3) was then added and the resulting mixture filtered. The filtrate was concentrated under reduced pressure and the residue distilled under vacuum, yielding 10.0 g of butyrolactone-*α,α-d_2*, bp 76–78° (5 mm).

4-Iodobutyric-*α,α-d_2* Acid. Butyrolactone-*α,α-d_2* (9.3 g, 0.108 mol) was treated as was the unlabeled material, except that the crude product was washed with $NaHSO_3$ instead of $Na_2S_2O_3$ solution. The yield of white crystals of labeled iodobutyric acid was 18.8 g (81%), mp 36–38°.

4-Iodobutyryl-*α,α-d_2* Chloride. 4-Iodobutyric-*α,α-d_2* acid (18.8 g, 0.088 mol) was treated with 20 ml of $SOCl_2$ and 1 drop of dimethylformamide for 2.2 hr. The excess $SOCl_2$ was then removed under reduced pressure. Distillation of the residue gave 19.8 g (98%) of orange oil, bp 56° (0.5 mm).

4-Iodobutyryl-*α,α,α',α'-d_4* Peroxide. The same procedure was followed as was for the unlabeled peroxide. Twelve batches of $\sim$1.6 g each of labeled acid chloride gave a total of 13.3 g (73%) of white crystals, mp 33.5–35°.

Table III. Titrimetry. The method used was a modification of that of Silbert and Swern.[25] Several methods were tried; that found best was as follows. Acetic acid (15 ml) containing 0.005 wt % $FeCl_3 \cdot 6H_2O$ and a sealed ampoule containing 10 ml of peroxide-containing solution were placed in a flask under nitrogen. Aqueous NaI solution (2 ml), prepared by dissolving NaI in water at $\sim$50° and allowing the solution to cool and crystallize for 1–2 days, and which was stored in an amber bottle under nitrogen until use, was added. The flask was then covered with aluminum foil, shaken gently until the ampoule broke, and shaken mechanically for 20 min. Water (50 ml) was added, and the iodine was titrated to a starch end point with 0.01 M $Na_2S_2O_3$ (made up as needed by dilution of a Fisher Scientific 1.0000 M stock solution).

This method gave titers close to the theoretical on peroxides of high purity by other criteria (small melting range, absence of extraneous carbonyl bands in infrared spectrum) with an uncertainty of ±1% on titration of a 10-ml aliquot of 0.01 M peroxide solution. This was not sensitive to the total amount of peroxide solution present in the range of 5–25 ml of 0.01 M solution, nor to the length of the shaking period in the range 15–40 min. Reaction times shorter than 10 min gave low results, while periods of 1 hr or more apparently allowed some seepage of atmospheric oxygen into the flasks with air oxidation of iodide and resulting overtitration.

Table III. An approximately 0.01 M stock solution of peroxide was prepared in order to determine purity of the peroxide. Aliquots (10 ml) were then pipetted into 10-ml ampoules which were degassed, sealed under vacuum, and placed in the oil bath. At appropriate times they were removed from the bath, quenched in ice water, and stored in the dark until analyzed. The blank (pure solvent) titers in this analysis varied from 0.0 to 0.3 ml of 0.01 M $Na_2S_2O_3$ solution, as compared to Silbert and Swern's[25] finding of "less than 0.03 ml" of 0.1 M $Na_2S_2O_3$ solution for the same amount of organic solution.

Tables I and II. Effect of Initially Nonisothermal Conditions. When ampoules filled with liquid initially at room temperature are placed in a bath at an elevated temperature, a period of time ensues during which the temperature of the liquid in the ampoule is signifi-

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[22] D. C. Blomstrom, K. Herbig, and H. E. Simmons, *J. Org. Chem.*, **30**, 959 (1965).

[23] J. Cason, "Organic Syntheses," Collect. Vol. III, Wiley, New York, N. Y., 1955, p 169.

[24] Unlabeled material: W. Traube and E. Lehman, *Ber.*, **34**, 1971 (1901); A. Michael and N. Weiner, *J. Amer. Chem. Soc.*, **58**, 1002 (1936).

[25] L. S. Silbert and D. Swern, *ibid.*, **81**, 2364 (1959).

cantly different from that of the bath. In thermal reactions such as peroxide decomposition, a certain fraction of the peroxide will thus react at a temperature significantly different from the recorded bath temperature, the possible result being an ill-defined reaction system. From determinations of the temperature in the ampoule as a function of time and the rate constant for decomposition of the peroxide in question as a function of temperature (Table III) we found, for a bath temperature of 95°, that <1.6% of the peroxide decomposed before the reaction temperature reached 94°. This situation was deemed acceptable and reactions were run at 95°. Of course, a temperature low enough such that we need not have been concerned with the possibility of some nonisothermal decomposition could have been used. However, as will be discussed in a subsequent paper, we are also concerned with the mechanism of formation of cyclopropane, and its yield increases with increasing temperature. Since the present work is concerned with other aspects of the chemistry of the same transient intermediate as will be central to forthcoming discussions, we decided to maximize the overlap between the two studies and ran the present reactions under those conditions which were best for the production of cyclopropane but still permitted almost all of the reaction to occur under isothermal conditions.

Table I. Aliquots of a 250-ml solution of 1.1127 g (2.612 mmol) of 4-iodobutyryl peroxide in CCl_4 were placed in ampoules which were degassed and sealed at 0.1 mm and boiling nitrogen temperature. The ampoules were heated in the oil bath at 95.1 ± 0.05° for 15 hr (~12 half-lives) and then stored in a freezer until analyzed.

At the peroxide concentration deemed optimum for minimizing undesired side reactions in the study of iodine scrambling, the solutions were too dilute to be analyzed directly by use of vpc with thermal conductivity detection. Flame ionization detection had sufficient sensitivity to permit direct analysis, but the passage of the halides involved through the detector caused large and erratic changes in sensitivity. The method of vpc analysis, using toluene as an internal standard, was a two-step procedure. Cyclopropane was determined on a 0.5 in. × 10 ft SE-30 (30% on Chromosorb W) column (column temperature 80°, flow rate 60 ml/min). The solution was then concentrated by distillation to ~5% of its original volume and analyzed on a 0.25 in. × 5 ft SE-30 (20% on Chromosorb W) column (injector 220°, detector 260°, column programmed from ambient to 200°, helium flow rate 25 cc/min). Controls run on known mixtures indicated that our analytical procedure gave a recovery of >97% for all components except CCl_3CCl_3 (93%).

Table II. Decomposition of $(ICH_2CH_2CD_2CO_2-)_2$. Ampoules prepared as described earlier were kept at 95.0 ± 0.05° for 12 hr (~10 half-lives). Solvent and low boiling products were removed by distillation on a 60-cm platinum spinning band column and the residue was subjected to a bulb-to-bulb vacuum distillation. The distillate was subjected to preparative vpc on a 0.5-in. 30% SE-30 column and the products with retention times of 1,3-diiodopropane, 1-chloro-3-iodopropane, hexachloroethane, 1,6-diiodohexane, and 3-iodopropyl 4-iodobutyrate were collected and analyzed.

Table II. Treatment of Products with Ph_3SnH. 4-Iodobutyryl-*2,2,2′,2′-d_4* peroxide (2.1469 g, 4.992 mmol, 96.3 ± 1.3% deuterium α to the carbonyl group) was dissolved in 500 ml of carbon tetrachloride and the resulting solution divided into fifty 10-ml ampoules which were degassed, sealed, and heated for 15 hr at 95.0 ± 0.05°. Solvent was distilled from the combined solutions on a 60-cm platinum spinning band column. Benzene (250 ml) was added to the 10-ml residue and the resulting solution concentrated to ~2 ml. The residue was distilled under vacuum (ultimately 0.002 mm) into an ampoule at boiling nitrogen temperature containing 4.0 g (11.4 mmol) of triphenyltin hydride. The ampoule was sealed at boiling nitrogen temperature and then warmed to room temperature and shaken vigorously. The reaction started spontaneously, with considerable evolution of heat, and was moderated as needed by cooling under running water. When the evolution of heat ceased, the ampoule was tumbled mechanically overnight. The products of the reaction were subjected to bulb-to-bulb distillation and the distillate, ~2 ml of colorless liquid, was subjected to vpc on the preparative SE-30 column described previously. The products with retention times of 1-chloropropane, hexane, and *n*-propyl butyrate were collected and analyzed.

Decomposition of $(ICD_2CH_2CH_2CO_2-)_2$ in Chloroform. A solution of 1.0592 g (2.462 mmol) of the peroxide in 250 ml of chloroform was divided into 25 10-ml ampoules, which were degassed, sealed, and heated at 95.0 ± 0.05° for 15 hr as described for the similar reaction in CCl_4. The combined products were distilled through a 60-cm platinum spinning band column, with a reflux ratio of ≧20; each 25-ml fraction was monitored by use of vpc, under conditions such that 2% of the total amount of 1-iodopropane finally isolated could have been detected in any one fraction. When the volume of liquid in the pot had been reduced to ~3 ml, without any 1-iodopropane detected at the head, the pot residue was subjected to preparative vpc on the SE-30 column previously described. Material with the retention times of 1-iodopropane and 1,6-diiodohexane was collected and analyzed.

A Mechanistic Study of the Synthesis and Spectral Properties of *meso*-Tetraarylporphyrins[1]

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Abstract: We have prepared 11 new derivatives of *meso*-tetraphenylporphin which are substituted on the phenyl groups. Kinetic studies of the rate of porphyrin formation and of oxygen consumption lead us to conclude that oxygen oxidation is the rate-determining step under ordinary synthetic conditions. We have also determined the extinction coefficients and the relative fluorescence intensities of these compounds.

In recent years we have been involved in a mechanistic investigation of the Rothemund reaction,[3] which is the only high-yield synthesis known for porphyrins starting from simple precursors. Badger, Jones, and Laslett,[4] who were the first to consider the mechanism, proposed that the reaction proceeded through the formation of an α,γ-dihydroxyporphyrinogen (**1**) chiefly

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(2) National Institutes of Health Fellow, 1970–1971.

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