was prepared from 1-bromopropane, magnesium turnings, and **1** as described in the previous experiment. The exit line from the reaction flask was connected to a vessel containing 25 ml of bromine in 100 ml of chloroform to trap any by-product propene. After stirring for 15 hr at 25°, the mixture was cooled to 0° and hydrolyzed with an ice-cold solution of 10.7 g of ammonium chloride in 15 ml of water. The mixture was allowed to warm to room temperature, and the aqueous layer was extracted with two 100-ml portions of ethyl ether. The combined organic layers were washed with 50 ml of water, dried, and concentrated. Vacuum distillation of the residue yielded 8.2 g of liquid, bp 75–78° (18 mm). Redistillation afforded 6.9 g (49%) of colorless **4b**: bp 85° (20 mm); $n^{25}D$ 1.5233; d^{25}_4 0.8993; ultraviolet λ_{max}^{EtOH} 281 mμ (ε 17300); infrared $\lambda_{max}^{CCl_4}$ 3.25, 3.40, 5.54, 6.18, 6.88, 7.03, 7.25, 7.74, 8.06, 8.36, 9.47, 10.10, 11.11, and 11.60 μ; nmr signals (neat), multiplet between τ 3.13–3.64 (1 H), broad singlet at 4.37 (1 H), multiplet between 4.91–5.33 (2 H), triplet at 7.65 (J = 8.0 cps, 2 H), doublet at 8.44 (J = 1.0 cps, 3 H), multiplet between 8.54–8.94 (2 H), and triplet at 9.30 (J = 8.0 cps, 3 H). Glpc analysis (15% Dow 550, 50–175° at 10°/min) showed only one peak.

Anal. Calcd for $C_8H_{14}S$: C, 67.55; H, 9.91; S, 22.54. Found: C, 67.70; H, 9.80; S, 22.30.

Reduction of the excess bromine in the trapping solution with sodium bisulfite and subsequent glpc analysis showed the absence of 1,2-dibromopropane.

Reduction of Butadienyl Sulfide 4a.—A mixture of 32.0 g of 10% palladium-on-carbon catalyst in 100 ml of 95% ethyl alcohol was placed in a Parr hydrogenation apparatus and shaken at 39 psig until no further sorption of hydrogen was detected. A solution of 7.0 g (0.18 mole) of **4a** in 100 ml of ethyl alcohol was then carefully added to the activated catalyst. This mixture was shaken at 47 psig for 4 hr (final pressure 42.5 psig). The solution was filtered through Celite and the collected catalyst was washed with 100 ml of boiling ethyl alcohol. The filtrate was concentrated to *ca.* 60 ml and diluted with 60 ml of ethyl ether. The ether solution was washed with 10% sodium hydroxide and water, dried, and concentrated. Distillation of the residue afforded 4.2 g (13%) of colorless **1-phenylthio-2-methylbutane** (**6a**): bp 125° (17 mm); $n^{25}D$ 1.5362 (lit.[11] bp 99–101° (4.5 mm), $n^{20}D$ 1.5408). Glpc analysis (15% Dow 550, 100–225° at 10°/min) showed only one peak. The infrared and nmr spectra of this material were in excellent agreement with those of an authentic sample of **6a** having $n^{25}D$ 1.5369 which was prepared in this laboratory using the procedure described in footnote 11. Treatment of the spent catalyst with mineral acid resulted in the evolution of hydrogen sulfide. Thus, the low yield of **6a** could be attributed to desulfurization which accompanied reduction.

Reduction of Butadienyl Sulfide 4b.—A 5.4-g (0.038 mole) sample of **4b** was reduced as described in the previous experiment. Work-up and distillation yielded 1.3 g (23%) of colorless **1-*n*-propylthio-2-methylbutane** (**6b**): bp 170° (710 mm); $n^{25}D$ 1.4490. Glpc analysis (15% Dow 550, 120°) showed only one peak. The infrared and nmr spectra were in excellent agreement with those of an authentic sample of the previously unreported **6b**.

1-*n*-Propylthio-2-methylbutane (**6b**).—To a solution of 4.0 g (0.10 mole) of sodium hydroxide in 75 ml of water was slowly added 7.62 g (0.10 mole) of *n*-propyl mercaptan. The resulting solution was warmed to 50° and carefully treated with 15.1 g (0.10 mole) of optically active 1-bromo-2-methylbutane.[12] The mixture was vigorously stirred for 6 hr at 80–90°. The cooled mixture was diluted with water, and the organic layer was washed with 40 ml of 10% sodium hydroxide and two 50-ml portions of water. Distillation of the dried organic layer yielded 6.1 g (42%) of colorless **6b**: bp 174° (712 mm). Redistillation yielded an analytical sample: bp 178° (713 mm); $n^{25}D$ 1.4512; d^{25}_4 0.8422; infrared $\lambda_{max}^{CCl_4}$ 3.44, 6.85, 7.25, 7.48, 7.74, 7.82, and 8.11 μ; nmr signals (neat), multiplet between τ 7.50–7.87 (4 H), multiplet between 8.33–8.90 (major peaks separated by 7 cps, 8 H), and multiplet between 9.06–9.34 (6 H).

Anal. Calcd for $C_8H_{18}S$: C, 65.69; H, 12.39; S, 21.92. Found: C, 65.62; H, 12.16; S, 22.15.

(11) V. N. Ipatieff, H. Pines, and B. S. Friedman, *J. Am. Chem. Soc.*, **60**, 2731 (1938).

(12) This alkyl halide was prepared in moderate yield from active amyl alcohol: H. O. Jones, *J. Chem. Soc.*, 138 (1905).

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A Radical-Induced ε Elimination[1]

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We recently reported a radical-induced 1,3 elimination from a three-carbon acyclic skeleton and pointed out that all of the mechanisms we could envision for this reaction involved processes or intermediate species which are unprecedented in free-radical chemistry.[2] The determination of whether this reaction can yield larger rings is naturally of interest for both mechanistic and synthetic reasons.[3] We wish to report that cyclopentane can be produced by reaction of 1,5-diiodopentane with a peroxide.[4] Results are summarized in Table I.

TABLE I

REACTION OF 1,5-DIIODOPENTANE WITH *t*-BUTYL AND BENZOYL PEROXIDES

	Reactn conditions[a]		
	168°, 1 hr		115°, 70 min
Reactants, mmole			
$I(CH_2)_5I$	0.428	0.266	0.271
$(PhCO_2)_2$[b]			0.407
$(t\text{-}BuO)_2$[b]	0.439	0.440	
Products, mmole[c]			
Cyclopentane	0.023	0.024	0.012
Pentene	*d*	*d*	0.008
$CH_3(CH_2)_4I$	0.071	0.041	0.023
$CH_2{=}CH(CH_2)_3I$	Trace	Trace	0.003
$Ph(CH_2)_5I$	0.005		0.007
$Ph(CH_2)_4CH_3$	0.004	0.006	0.013
$I(CH_2)_5I$	0.10		
PhI	0.007	0.008	0.45
CH_3I	0.46	0.57	
$PhCH_3$	0.034	0.013	
CH_3COCH_3	0.54	0.57	
$(CH_3)_3COH$[e]	0.35	0.27	
$(CH_3)_2{=}CH_2$[e]	0.013	0.007	

[a] No significance should be attached to the reaction time with the exception that it is long enough so that no detectable reaction occurred on further heating. [b] No reaction occurred in the absence of peroxide. [c] In addition, we observed in the 115° run trace amounts of materials which had the same vpc retention times as (4-pentenyl)benzoate and (5-iodopentyl)-benzoate. [d] Undetermined. [e] The effect of reaction time on the isobutylene:*t*-butyl alcohol ratio was not studied.

All of the mechanisms mentioned in connection with our 1,3-diiodopropane → cyclopropane conversion,[2] in particular a carbon radical displacement on carbon, should be considered as possibilities for the present

(1) This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation and a Biomedical Sciences Support grant from the National Institutes of Health.

(2) L. Kaplan, *J. Am. Chem. Soc.*, **89**, 1753 (1967).

(3) See W. S. Trahanovsky and M. P. Doyle, *J. Org. Chem.*, **32**, 146 (1967), for a recent unsuccessful attempt to observe an ε elimination.

(4) This reaction was mentioned in passing in footnote 9 of our earlier communication.[2]

TABLE II
REACTION OF 1,5-DIIODOPENTANE, 5-IODO-1-PENTENE, AND CYCLOPENTYL IODIDE WITH *t*-BUTYL AND BENZOYL PEROXIDES

	Per cent yield[a]					
	Benzoyl peroxide, 70 min, 115°			*t*-Butyl peroxide, 1 hr, 168°		
Product	$I(CH_2)_5I$	Cyclopentyl iodide	$CH_2{=}CH(CH_2)_3I$	$I(CH_2)_5I$	Cyclopentyl iodide	$CH_2{=}CH(CH_2)_3I$
Cyclopentane	4.5	22		8.2	49	Trace
Cyclopentene		13			21	Trace
$Ph(CH_2)_3CH{=}CH_2$			4.4			1.4
Cyclopentyl benzoate		6.0	Trace			
Cyclopentylcyclopentane		0.3			Trace	
Cyclopentylbenzene		9.5			0.5	
Cyclopentyl iodide	Trace		Trace	Trace		Trace
$PhCO_2(CH_2)_3CH{=}CH_2$	Trace		Trace			

[a] By "trace" we mean an amount which corresponds to less than 10% of the lowest yield reported in this table.

reaction. In addition, there is a precedented route: 5-iodo-1-pentene, which is a very minor product, could yield the 5-penten-1-yl radical which could then cyclize to the cyclopentyl radical and go on to cyclopentane. In order to help us decide whether this possibility, or any other which involves the cyclopentyl radical, need be considered seriously, we have performed experiments designed to indicate the fates of 5-iodo-1-pentene and the cyclopentyl radical (generated from cyclopentyl iodide) under the reaction conditions.[5] Presented in Table II are the yields of those products derived from reaction of cyclopentyl iodide, 5-iodo-1-pentene, and 1,5-diiodopentane with benzoyl and di-*t*-butyl peroxides which we feel are pertinent to this question. We believe that the results obtained with 1,5-diiodopentane are sufficiently different from those obtained with cyclopentyl iodide and 5-iodo-1-pentene so as to enable us to conclude that it is unlikely that the products formed from 1,5-diiodopentane, particularly cyclopentane, result to a significant extent from reaction of either 5-iodo-1-pentene or the cyclopentyl radical.

Experimental Section

Reactions were run in sealed nmr tubes in benzene as solvent. Products for which numerical yields are reported have been identified by direct comparison with independently obtained samples. Yields were estimated by use of nmr spectroscopy and gas chromatographic analysis.

1,5-Diiodopentane, di-*t*-butyl peroxide, benzoyl peroxide, cyclopentane, cyclopentyl iodide, pentenes, 1-iodopentane, 1-phenylpentane, iodobenzene, methyl iodide, toluene, acetone, *t*-butyl alcohol, isobutylene, benzene, cyclopentene, cyclopentylcyclopentane, and cyclopentylbenzene were commercial materials.

5-Iodo-1-pentene[6] and (4-pentenyl)benzene[7] were prepared by literature procedures.

(4-Pentenyl) benzoate and cyclopentyl benzoate were prepared by reaction of the corresponding alcohols with benzoyl chloride in pyridine.

(5-Iodopentyl) benzoate and (5-iodopentyl)benzene were prepared by reaction of (5-bromopentyl) benzoate[8] and (5-bromopentyl)benzene,[9] respectively, with sodium iodide in acetone.

(5) In these circumstances one unfortunately cannot rigorously determine the expected fate of a given substance, were it formed during the reaction, by introducing that substance into the reaction mixture or by subjecting it to the "reaction conditions" since the mere presence of the material in an artificially created concentration or in the absence of other materials results in a perturbed system, particularly with regard to the probability of occurrence of various bimolecular steps. The difficulty is compounded by our poor material balances.

(6) T. D. Perrine, *J. Org. Chem.*, **18**, 1356 (1953).

(7) J. von Braun, *Ber.*, **45**, 1246 (1912).

(8) J. von Braun, *ibid.*, **46**, 1782 (1913).

(9) R. Huisgen, W. Rapp, I. Ugi, H. Walz, and I. Glogger, *Ann.*, **586**, 52 (1954).

The Structure of Phthalaldehydic Acid[1]

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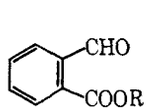
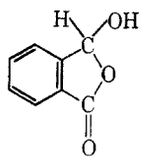
Because phthalaldehydic acid was known to give derivatives of either 2-carboxybenzaldehyde (I) or 3-hydroxyphthalide (II), its actual structure has been in doubt ever since it was first described.[2]



I, R = H
III, R = D



II

The failure of chemical techniques to ascertain the structure of phthalaldehydic acid led Buu-Hoi and Lin-Chen-Kin[3] to examine its ultraviolet spectrum. They concluded that the two forms I and II were in a solvent-dependent equilibrium and that, whereas II was the only form present in dioxane, water solutions contained a mixture of I and II. Later, three groups examined the infrared spectrum of phthalaldehydic acid in the solid state and in aqueous solution.[4-6] All agreed that in both cases the compound existed in the cyclized form II. Furthermore, it was shown that upon alkali treatment the lactol ring was opened, forming the anion of I.[6]

In view of the historical interest of this problem and because a recent article[7] has implicitly challenged the above results, we wish to present the results of a reinvestigation of the structure of phthalaldehydic acid by nuclear magnetic resonance.

The resonance of aldehyde protons occurs near

(1) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. We are also grateful to the National Science Foundation for assistance during the course of this work.

(2) S. Racine, *Chem. Ber.*, **19**, 778 (1886); *Ann.*, **239**, 78 (1887).

(3) Buu-Hoi and Lin-Chen-Kin, *Compt. Rend.*, **209**, 221 (1939).

(4) J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 877 (1951).

(5) D. D. Wheeler, D. C. Young, and D. S. Erley, *J. Org. Chem.*, **22**, 547 (1957).

(6) E. Bernatek, *Acta Chem. Scand.*, **14**, 785 (1960).

(7) J. Aknin and D. Molho, *Bull. Soc. Chim. France*, 1813 (1967).