are much less stable in acetonitrile. Although cathodic waves can be obtained for DPA on reversal in cyclic voltammetry,[8] coulometric oxidation in acetonitrile shows a decay of the current to a high steady value and rapid disappearance of the radical as it is stirred away from the electrode surface. This lack of stability of the cation radical may be the reason for the past differences in results of different workers[3-6] and the poorer correlation of voltammetric potential data with energy levels calculated by molecular orbital theory.

John Phelps, K. S. V. Santhanam, Allen J. Bard
Department of Chemistry, The University of Texas
Austin, Texas
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A Radical-Induced γ Elimination[1]

Sir:

We wish to report the observation of a radical-induced γ elimination from a carbon skeleton. The reaction involves treatment of 1,3-diiodopropane with a peroxide and results in formation of cyclopropane in high yield.[2] The highest conversions to cyclopropane obtained with benzoyl peroxide and *t*-butyl peroxide were "100" and 90%, respectively. Results are summarized in Tables I and II.

Table I. Reaction of 1,3-Diiodopropane with Benzoyl Peroxide

	Reaction conditions[a]			
	79°, 20 hr	98°, 14 hr	116°, 3.2 hr	116°, 1.5 hr
Reactants, mmole[b]				
$ICH_2CH_2CH_2I$	0.432	0.435	0.361	0.310
$(PhCO_2)_2$[c]	0.438	0.435	0.368	0.448
Products, mmole[d,e]				
Cyclopropane	0.32	0.36	0.29	0.31
$CH_3CH_2CH_2I$	0.003	0.003	Trace	Trace
$PhCH_2CH_2CH_2I$	0.02	0.02	0.02	Trace
$ICH_2CH_2CH_2I$	0.12	0.08	0.07	...
PhI	0.68	0.74	0.62	0.62

[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] In benzene as solvent. [c] No reaction occurred in the absence of peroxide. [d] Yields were estimated by use of nmr spectroscopy and gas chromatographic analysis. [e] In addition, we observed a very small amount of a material which had the same retention time as 3-iodopropyl benzoate.

Although the mechanism of the reaction has not been established, the possibilities which one may envision are all such that our observation is likely to provide the opportunity to study one or more previously unreported free-radical processes such as carbon radical displacement on carbon,[6] formation and reactions of 1,3-bridged halo radicals, concerted radical-induced γ elimination, and neighboring group assistance by a carbon radical site in a radical displacement on halogen. Information is available for only one of these processes, formation of cyclopropane and iodine from the γ-iodopropyl radical. Benson has estimated the reaction to be exothermic by a few tenths of a kilocalorie per mole.[8]

Table II. Reaction of 1,3-Diiodopropane with *t*-Butyl Peroxide

	Reaction conditions[a]			
	133°, 14 hr	148°, 12 hr	169°, 80 min	169°, 50 min
Reactants, mmole[b]				
$ICH_2CH_2CH_2I$	0.412	0.419	0.423	0.420
$(t\text{-BuO})_2$[c]	0.431	0.437	0.437	0.655
Products, mmole[d]				
Cyclopropane	0.24	0.26	0.31	0.38
$CH_3CH{=}CH_2$	0.02	0.02	0.01	0.01
$CH_3CH_2CH_2I$	0.02	0.03	0.02	0.02
$PhCH_2CH_2CH_2I$	0.002	0.002	0.003	Trace
$ICH_2CH_2CH_2I$	0.11	0.09	0.08	...
CH_3I	0.63	0.62	0.69	0.83
CH_3COCH_3	0.64	0.69	0.71	1.07
$(CH_3)_3COH$[e]	0.21	...	0.09	0.17
$(CH_3)_2C{=}CH_2$[e]	0.043	0.14	0.025	0.004
PhI	0.007	0.007	0.007	0.006
$PhCH_3$	0.018	0.012	0.017	0.068

[a-d] See the corresponding footnotes to Table I. [e] The effect of reaction time on the isobutylene:*t*-butyl alcohol ratio was not studied.

Irrespective of mechanistic questions, the synthetic potential of such a cyclization reaction is clear.[9]

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[1] This work was supported by a Frederick Gardner Cottrell grant from the Research Corporation.

[2] In possibly related reactions, cyclopropane has been produced by gas-phase pyrolysis of 1,3-diiodopropane (20% yield),[3] sodium flame reaction of 1,3-dibromopropane (57–87% gaseous products),[4] and reaction of phenylmagnesium bromide–ferric chloride with 1,3-dibromopropane (81% yield), 1-bromo-3-chloropropane (76% yield), or 1-bromo-3-phenoxypropane (26% yield).[5]

[3] R. A. Ogg, Jr., and W. J. Priest, *J. Chem. Phys.*, 7, 736 (1939).

[4] C. E. H. Bawn and R. F. Hunter, *Trans. Faraday Soc.*, 34, 608 (1938).

[5] M. S. Kharasch, M. Weiner, W. Nudenberg, A. Bhattacharya, T.-I. Wang, and N. C. Yang, *J. Am. Chem. Soc.*, 83, 3232 (1961).

[6] In connection with the question of whether the formation of the β-(iodomethyl)cyclohexyl radical and its decomposition to iodine and norcarane is involved in the photolytic reaction of methylene iodide and cyclohexene, Simmons has reported some unsuccessful attempts to observe such a displacement.[7]

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

[8] S. W. Benson, *J. Chem. Phys.*, 34, 521 (1961). It was assumed that $D(ICH_2CH_2CH_2\text{–}H) = D(CH_3CH_2CH_2\text{–}H)$, *i.e.*, that the γ-iodopropyl radical is not appreciably stabilized by iodine bridging.

[9] We have also found that cyclopentane can be produced by reaction of 1,5-diiodopentane with a peroxide and that 1,1-diphenylcyclopropane is produced when methylene iodide, 1,1-diphenylethylene, and a peroxide are allowed to react. Details will be reported later.

Leonard Kaplan
Department of Chemistry, University of Chicago
Chicago, Illinois 60637
Received January 11, 1967

Stereospecific Conversion of *cis–trans* Isomeric Aziridines to Open-Chain Azomethine Ylides

Sir:

Woodward and Hoffmann[1] predicted for the thermal isomerization of cyclopropyl anion to allyl anion a *conrotatory* ring opening, while the photochemical ring cleavage should take a *disrotatory* course. Our results with the isoelectronic aziridine system offer the first verification of this prediction.

We reported recently[2] that dimethyl 1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate (I) is in equilibrium above 100° with a small concentration of the azomethine

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[1] R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, 87, 395 (1965).

[2] R. Huisgen, W. Scheer, G. Szeimies, and H. Huber, *Tetrahedron Letters*, 397 (1966).