feel, however, on the basis of our results, that the large difference in the coupling constants for the phenylglyoxal semidione radical in DMF solution as compared with DMSO solution is not simply due to a normal solvent effect but to the presence of a large excess of the *trans* form in the first solvent and of the *cis* form in DMSO containing alkali metal ions.

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The Electrochemical Oxidation of Aromatic Hydrocarbons in Methylene Chloride[1]

Sir:

The electrochemical reduction and oxidation of aromatic hydrocarbons in nonaqueous solutions have been reviewed recently.[2] While the electroreductions are characterized by the formation of stable anion radicals, much of the past work[3-6] suggests that the electrochemical oxidations occur by the abstraction of two or more electrons. The successful use of methylene chloride as a solvent in electron spin resonance (esr) studies of hydrocarbon oxidation[7] suggested that electrochemistry in this solvent might provide evidence of the initial formation of cation radicals on electrooxidation. We report here some preliminary cyclic voltammetric and coulometric studies. Recent work by Peover[2,8] and Adams and co-workers[9] has also provided evidence of an initial one-electron abstraction during electrochemical oxidations in acetonitrile and nitrobenzene.

The results of cyclic voltammetric oxidation of 9,10-diphenylanthracene (DPA), rubrene, 1,3,6,8-tetraphenylpyrene (TPP), and tetracene are given in Table I. The general behavior of DPA, rubrene, and TPP was similar and was characterized by independence of anodic peak potential, E_{pa}, with scan rate, v, essentially equal anodic (i_{pa}) and reversal cathodic (i_{pc}) peak currents, an independence of $i_{pa}/v^{1/2}$ with v, and a separation of E_{pa} and E_{pc} of 60–80 mv. These results suggest a reversible one-electron abstraction from the parent hydrocarbon to form a cation radical which is stable during the time necessary for sweep reversal. For tetracene, however, E_{pa} and $i_{pa}/v^{1/2}$ change with scan rate, and cathodic waves on reversal are either absent or very small. Results similar to these are obtained with anthracene. The evidence here indicates a fast chemical reaction following the electron transfer.

Table I. Cyclic Voltammetric Data for the Oxidation of Several Hydrocarbons in Methylene Chloride[a]

Sweep rate, mv/sec	i_{pa}, μa	i_{pc}, μa	$i_{pa}/v^{1/2}$, μa sec$^{1/2}$/v$^{1/2}$	*E*, *vs.* sce E_{pa}	E_{pc}
9,10-Diphenylanthracene, 1.2 m*M*					
67	6.2	4.1	24	1.22	1.16
153	8.8	7.8	23	1.22	1.16
222	11.2	11.3	24	1.22	1.16
312	13.7	13.7	24	1.22	1.16
476	16.9	16.8	24	1.22	1.16
714	20.0	21.6	24	1.22	1.16
Rubrene, 0.8 m*M*					
67	2.6	2.7	9.8	0.81	0.74
153	3.6	3.6	9.1	0.82	0.74
222	4.2	4.5	8.8	0.82	0.74
312	4.9	5.1	8.7	0.82	0.74
476	6.0	6.2	8.7	0.82	0.73
1,3,6,8-Tetraphenylpyrene, 0.5 m*M*					
67	1.8	1.9	6.8	1.17	1.09
153	2.2	2.5	5.5	1.17	1.09
222	2.6	2.8	5.5	1.17	1.09
312	3.0	3.4	5.4	1.17	1.09
Tetracene, 0.9 m*M*					
67	10.5	...[b]	40	0.98	..
153	14.7	...[b]	38	1.00	..
222	17.3	...[b]	37	1.01	..
312	19.5	...[b]	35	1.02	..
476	22.9	...[b]	33	1.02	..
714	27.1	...[b]	32	1.02	..

[a] The solution was 0.2 *M* tetra-*n*-butylammonium perchlorate. The electrode was a platinum disk, 0.031 cm^2 (except for TPP, where the area was 0.021 cm^2). [b] Small cathodic current on reversal.

Unequivocal evidence for a one-electron oxidation was obtained by coulometric oxidations with esr observation of the resulting solutions. For the oxidation of DPA and rubrene 1 faraday per mole of hydrocarbon was consumed when oxidation was carried out at controlled potentials about 0.15 v more positive than E_{pa}. Examination of the oxidized solution by cyclic voltammetry showed a cathodic peak at the same potentials as the cathodic peak obtained on reversal in the unoxidized solution.

The esr spectra of the oxidized solutions, transferred to 3-mm Pyrex tubing without exposure to air, were essentially identical with those obtained by chemical oxidation of the hydrocarbons. The electrogenerated radicals appeared to be stable for days in the sealed tubes at liquid-nitrogen temperature. Tetracene and anthracene when subjected to controlled potential coulometric oxidation showed a current which decayed to steady-state values appreciably higher than the background current; this is further evidence of instability of these cation radicals.

The results suggest that the behavior of the aromatic hydrocarbons depends upon whether or not they are substituted in the positions of high electron density. Cation radicals of substituted hydrocarbons (DPA, rubrene, TPP) are stable, whereas unsubstituted ones (anthracene, tetracene) react rapidly. Adams and co-workers[9] have reached a similar conclusion based on results obtained in nitrobenzene. The cation radicals

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(1) This research was supported by the Robert A. Welch Foundation and the National Science Foundation (GP-1921).

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(7) I. C. Lewis and L. S. Singer, *J. Chem. Phys.*, 43, 2712 (1965).

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(9) R. N. Adams, L. S. Marcoux, and J. M. Fritsch, private communication.

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.

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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.

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.

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]

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]

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[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).

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[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.

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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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