was identified as N-benzylethylenediamine (lit.[8] mp of hydrochloride, 253°).

If instead of treating the ether filtrate with anhydrous HCl the ether was evaporated, an oil resulted which was shown to be composed of two compounds by tlc. When the signals of the N-benzylethylenediamine were subtracted from the nmr of the mixture, it was determined that the 3-amino-2-phenylazetidine was obtained and that the mixture was composed of 42% azetidine and 58% ethylenediamine. All efforts to separate these compounds failed.

Attempted Synthesis of *trans*-3-Azido-4-phenyl-2-azetidinone.—Hydrobenzamide (11 g, 0.037 mol) and azidoacetyl chloride (4.4 g, 0.037 mol) were dissolved in 200 ml of methylene chloride and treated dropwise at 0° with triethylamine (3.74 g, 0.037 mol) dissolved in 100 ml of methylene chloride. After the addition was complete the reaction mixture was allowed to warm to room temperature. The reaction mixture was then stirred with 100 ml of 10% HCl. The organic layer was separated from the aqueous phase and evaporated to dryness under reduced pressure to yield a dark oil. A small amount of ether was added to this oil and 1.87 g of solid was collected by filtration. Recrystallization from absolute ethanol yielded a solid, mp 218–219°. The structure of this compound was postulated as 1-azidoacetyl-2,4,5-triphenyl-2-imidazoline (VI).

Anal. Calcd for $C_{23}H_{19}N_5O$: C, 72.42; H, 5.02; N, 18.10. Found: C, 72.69: H, 4.99; N, 18.34.

Registry No.—Ia, 19684-83-4; Ib, 19684-84-5; Ic, 19684-85-6; VI, 19689-63-5.

Acknowledgment.—The authors are indebted to Drs. J. M. Cassady and P. E. Manni for helpful discussions during the course of this work.

(8) J. C. Dickerman and A. J. Besozzi, *J. Org. Chem.*, **19**, 1855 (1954).

Free Carbonium Ions in the Anodic Oxidations of Alkanecarboxylates, Alkaneboronates, and Alkyl Halides[1]

James T. Keating and Philip S. Skell

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received August 26, 1968

A free propyl cation[2] is the postulated intermediate leading to cyclopropane in the deoxideation of *n*-propyl alcohol and in the deamination of *n*-propylamine.[3] Formation of cyclopropane in good amount is a criterion for the free *n*-propyl cation.

Anodic oxidation of *n*-butyrate (the Hofer–Moest or abnormal Kolbe reaction) produces cyclopropane.[4,5] The reaction is best explained with a free *n*-propyl cation (eq 1). The detailed description of the steps leading to the propyl cation is not certain.

$$n\text{-PrCO}_2^- \xrightarrow{-2e^-} CO_2 + n\text{-Pr}^+ \longrightarrow \text{cyclopropane} + H^+ \qquad (1)$$

Alkaneboronic acids are the Lewis acid counterparts of the Brønsted carboxylic acids and would be expected to undergo anodic oxidation also. We have studied the anodic oxidation of propaneboronate. Cyclopropane is among the products, implicating a free propyl cation. Table I gives the results and compares them with our work on butyrate.

TABLE I

ANODIC OXIDATION OF SODIUM BUTYRATE AND POTASSIUM PROPANEBORONATE AT BRIGHT PLATINUM

Products	% Sodium butyrate[a]	% Potassium propaneboronate[b]
Propylene	76	71
Cyclopropane	17	18
Propane	1	1
Hexane	1	2
Ethane	1	2
Ethylene	5	7

[a] The aqueous solution was 1 *M* each in sodium butyrate and sodium hydroxide. [b] The aqueous solution was saturated with potassium propaneboronate (<0.8 *M*) and the pH was adjusted to 11.

The similarity of the products and the product distributions found for propaneboronate and butyrate obtains also in the anodic oxidations of butaneboronate and pentanoate (Table II). This further supports the postulate of a free cation in the alkaneboronate anodic oxidation, linking this reaction with deoxideation, deamination, and the Hofer–Moest reaction.[4,5] Tables I and II also suggest that the formal leaving groups, carbon dioxide and boric acid, have little effect on the behavior of the carbonium ion formed in anodic oxidation at platinum. A possible reason for this is that the radical is the carbonium ion precursor in both cases (eq 2).

TABLE II

ANODIC OXIDATION OF POTASSIUM PENTANOATE AND SODIUM BUTANEBORONATE AT BRIGHT PLATINUM

Products	% Potassium pentanoate[a]	% Sodium butaneboronate[b]
1-Butene	56	60
cis-2-Butene	17	20
trans-2-Butene	27	20
n-Butane	Trace	Trace

[a] The aqueous solution was 1 *M* each in potassium pentanoate and potassium hydroxide. [b] This is from the work of A. A. Humffray and L. F. G. Williams, *Chem. Commun.*, 616 (1965). They say only that excess base was used in making up the solution. The results were interpreted in terms of a radical (Kolbe) mechanism.

$$\begin{tikzcd}[row sep=small]
RCO_2^- \arrow[r, "-e^-"] & RCO_2\cdot \arrow[r] & R\cdot + CO_2 \arrow[d, dash] & \\
 & & {} \arrow[r, "-e^-"] & R^+ \longrightarrow \text{products} \qquad (2) \\
RB(OH)_3^- \arrow[r] & RB(OH)_3\cdot \arrow[r] & R\cdot + B(OH)_3 \arrow[u, dash] &
\end{tikzcd}$$

In contrast to the results found at platinum, at a graphite anode the products and product distributions of the butyrate and propaneboronate anodic oxidations are not identical (Table III). It must be that at graphite the carbonium ion precursor is different in each

---

[1] Taken from the Ph.D. Thesis of J. T. K., The Pennsylvania State University, Sept 1968. For a review of anodic oxidation, see A. K. Vijh and B. E. Conway, *Chem. Rev.*, **67**, 623 (1967); J. T. Keating and P. S. Skell in "Carbonium Ions," G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, New York, N. Y., in press.

[2] A free carbonium ion is one generated in a state not relaxed with respect to neighbor nucleophiles.

[3] P. S. Skell and I. Starer, *J. Amer. Chem. Soc.*, **81**, 4117 (1959); **82**, 2971 (1960). M. S. Silver, *ibid.*, **82**, 2971 (1960).

[4] R. J. Maxwell, M. S. Thesis (Skell), The Pennsylvania State University, 1963.

[5] W. J. Koehl, *J. Amer. Chem. Soc.*, **86**, 4686 (1964).

TABLE III

ANODIC OXIDATION OF POTASSIUM BUTYRATE AND POTASSIUM PROPANEBORONATE AT PYROLYTIC GRAPHITE

	%	
Products	Potassium butyrate[a]	Potassium propaneboronate[b]
Propylene	66	39
Cyclopropane	33	33
Ethylene	0	28

[a] The aqueous solution of 1 M potassium butyrate is at pH 7. Koehl was the first to obtain this result.[5] We confirm this and have shown also that the form of carbon used (porous carbon rods or either plane of pyrolytic graphite) does not affect the product ratios. [b] This was studied as a saturated aqueous solution of the acid and its potassium salt, 10:1. Some ethylene may be a product of β scission of the propyl cation; some may arise from oxidation of propanol, formed from the propaneboronic acid.[c] Since 28% ethylene is found after only 5-min reaction, ethylene is probably a primary product to the extent of at least 10–20%. Its yield increased with reaction time and with pH, while the cyclopropane to propylene ratio remained about constant. [c] A. G. Davies and B. P. Roberts, *J. Chem. Soc., B*, 17 (1967); T. G. Traylor and J. C. Ware, *J. Amer. Chem. Soc.*, **85**, 3026 (1963).

case and makes its influence felt in the reactions of the carbonium ion. In addition, different rates of oxidation and desorption of the precursors on graphite may be responsible for the variation.[6] In any case, both cations exhibit the characteristic of the free cation, substantial production of cyclopropane.

The similarities in the alkaneboronate and alkanecarboxylate oxidations prompted the study of the anodic oxidation of alkyl halides. Propyl bromide was chosen because of the above-mentioned prominent difference between the free and the encumbered propyl cation. The reaction was run in methanol with sodium perchlorate as the electrolyte. The anode and cathode compartments were separated to prevent cathodic reduction of alkyl halide.[7] Table IV shows that the carbonium ion formed in this reaction can indeed be described as free. It is likely that the anodic oxidations of other alkyl halides also yield free carbonium ions.[8] A possible mechanism is shown in eq 3. Rough calculations indicate that the separation in the gas phase of bromine atom from the propyl cation is ~30 kcal mol endothermic. This energy requirement could be ameliorated at the anode surface by adsorption and by charge–charge repulsion of $(PrBr)^+$ and the anode.

$$PrBr \xrightarrow{-e^-} (PrBr)^+ \longrightarrow Pr^+ + Br\cdot \qquad (3)$$

TABLE IV

ANODIC OXIDATION OF PROPYL BROMIDE AT BRIGHT PLATINUM

Products	Propyl bromide,[a] %
Propylene	16
Cyclopropane	78
Propane	6

[a] The methanolic solution was 1 M each in propyl bromide and sodium perchlorate monohydrate. The anode and cathode compartments were separated by an agar bridge saturated with potassium chloride. It was not determined if the propylene would be destroyed by the perchlorate under the electrolysis conditions.

The anodic oxidation of 1-nitropropane was attempted in methanol with sodium perchlorate electrolyte. No products attributable to propyl cation intermediacy were detected. Barnes[9] has anodically oxidized n-propylamine at platinum in acetonitrile and has found propylene among the products. No mention is made of cyclopropane but it may not have been sought. A free propyl cation may be formed. Whatever the details of the Barnes reaction, our work shows that nitropropane is not a carbonium ion producing intermediate in the anodic oxidation of n-propylamine.

Experimental Section

Apparatus.—The cell used in the electrolyses has been described.[10] It was modified for the pyrolytic graphite reactions. In place of the platinum, two strips of graphite, $^1/_2 \times 4 \times {}^1/_8$ in., were fixed in the rubber stopper by means of alligator clips inserted through the stopper. The graphite was purchased from High Temperature Materials, Inc., Boston, Mass. The unit for the anodic oxidation of propyl bromide was two cylinders, closed at the bottom, connected by a tube filled with potassium chloride saturated agar gel. The anode compartment of the unit was fitted with a stopper containing the anode, thermometer, and gas inlet and outlet tubes. A stainless steel cathode was put in the other cylinder.

Technique.—The anodic oxidations were typically run for 5 min at 25–35° at a current density of 0.1 A/cm. The gaseous products were swept into liquid nitrogen cooled traps. The material caught was analyzed by glpc. In addition to being identified by comparative retention times, the peaks were trapped as eluted and their ir and mass spectra were obtained.

Propaneboronic Acid.—This was prepared according to the method of Snyder, Kuck, and Johnson.[11]

Registry No.—Sodium butyrate, 156-54-7; potassium propaneboronate, 19581-69-2; potassium pentanoate, 19455-21-1; sodium butaneboronate, 19581-70-5; potassium butyrate, 589-39-9; propyl bromide, 106-94-5.

Acknowledgment.—We are grateful to the National Science Foundation for a graduate fellowship for J. T. K., and to the Air Force Office of Scientific Research and the Research Office of the U. S. Army for support of this work.

---

(6) A referee suggested this possibility.

(7) J. W. Sease, F. G. Burton, and S. L. Nickol, *J. Amer. Chem. Soc.*, **90**, 2595 (1968).

(8) L. L. Miller and A. K. Hoffman, *ibid.*, **89**, 593 (1967).

(9) K. K. Barnes, *Dissertation Abstr.*, 3805-B, (1967).

(10) P. H. Reichenbacher, M. Y.-C. Liu, and P. S. Skell, *J. Amer. Chem. Soc.*, **90**, 1816 (1968).

(11) H. R. Snyder, J. A. Kuck, and J. R. Johnson, *ibid.*, **60**, 105 (1938).

The Wolff Rearrangement of 1,3-Bisdiazo-2-decalones

RICHARD F. BORCH AND DOUGLAS L. FIELDS

School of Chemistry of the University of Minnesota,
Minneapolis, Minnesota 55455

Received October 30, 1968

Our interest in the stereospecific synthesis of functionalized perhydroindans led us to an examination of the rearrangement of *cis*- and *trans*-1,3-bisdiazo-2-decalone with the aim of discovering (a) whether the ring contraction would be directionally selective, (b) whether the product composition would be dependent upon ring junction stereochemistry, and (c) whether the stereochemistry of the ring junction would be