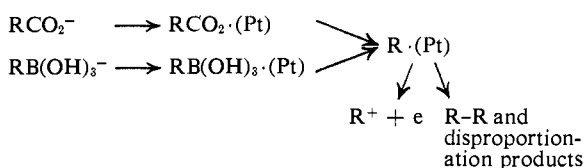


marked differences in the behavior of the carbonium ions.⁴⁸

(3) Anodic oxidations of alkaneboronates and the corresponding carboxylates result in strikingly similar products (both free-radical and carbonium ion products) and product distributions,^{49,50} suggesting similar intermediates and similar product-forming paths.¹¹



(4) Adsorbed carboxylate radicals are implicated by the observation that 60-cycle alternating current results in less than 1% of the reaction which would be obtained by application of direct current in the same set-up.^{51,52} Each electrode is anodic 0.008 sec and then

(48) P. S. Skell and R. A. Plepys, manuscript in preparation.

(49) J. T. Keating, Ph.D. Thesis, The Pennsylvania State University, 1968.

(50) A. A. Humfray and L. F. G. Williams, *Chem. Commun.*, 616 (1965).

cathodic for the same interval. Free $\text{RCO}_2\cdot$ generated during an anodic phase should be completely decomposed to $\text{R}\cdot$ and CO_2 in this time interval,¹³ and Kolbe product R-R should be observed. The small yields of R-R eliminate free $\text{RCO}_2\cdot$ as significant intermediates.

(5) Evidence is presented elsewhere⁴⁹ that dimer formation from alkyl radicals does not occur exclusively in the fluid medium, but to a considerable extent must occur on the platinum electrode, *i.e.*, adsorbed $\text{R}\cdot$.

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(51) R. A. Plepys, Department of Chemistry, The Pennsylvania State University, unpublished results.

(52) Related to this is the fact that hydrocarbon formation does not occur immediately upon closing of the electrolysis circuit (DC); however, opening the circuit for a short time and then closing it causes immediate hydrocarbon evolution.¹⁷ Dickinson and Wynne-Jones¹⁷ ascribe this to the presence of adsorbed carboxylate radicals.

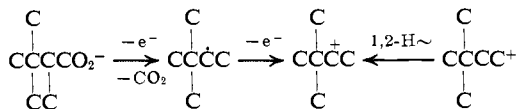
The 3,3-Dimethyl-2-butyl Cation. Pinacolyl Cation

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Contribution from the Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. Received December 22, 1967

Abstract: The 3,3-dimethyl-2-butyl (pinacolyl) cation is generated by anodic oxidation of potassium 2,3,3-trimethylbutanoate at a bright platinum electrode. At pH below 14, the cation reacts mainly by rearrangement to the tertiary cation; higher hydroxide ion concentrations are more effective in trapping the unrearranged cation.

The free 3,3-dimethyl-2-butyl (pinacolyl) cation was produced by the rearrangement of 3,3-dimethyl-1-butyl cation.² The direct generation of this cation by anodic oxidation of the pinacolyl radical is an alternate route to this elusive neopentyl-like cation.



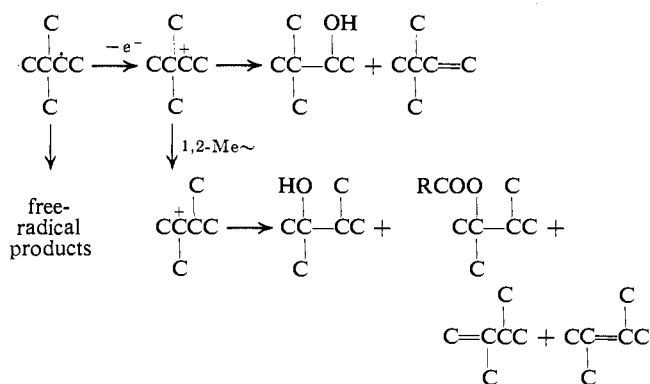
Results and Discussion

Potassium 2,3,3-trimethylbutanoate was electrolyzed at bright platinum electrodes; both carbonium ion and free-radical products were obtained (Table IV). The saturated hydrocarbon products, bipinacolyl and 2,2-dimethylbutane, are typical Kolbe electrolysis products derived from radicals with unrearranged skeletons. The bulk of the products, olefins, alcohols, and esters, are more oxidized than the radical by one electron and for the main have rearranged carbon skeletons. If the 2,2-dimethylbutane is half of a

(1) From the Ph.D. Thesis of P. H. R., The Pennsylvania State University, 1967.

(2) P. S. Skell and P. H. Reichenbacher, *J. Am. Chem. Soc.*, **90**, 2309 (1968).

radical disproportionation couple, an equivalent amount of 3,3-dimethyl-1-butene would be produced. Subtraction of this quantity of olefin and the saturated hydrocarbons leaves the carbonium ion products (Table I). The carbonium ion derived products are those suggested by the first modern theory in this field.³



Two important aspects of this chemistry of the free pinacolyl cation are: (1) although it generally is con-

(3) F. C. Whitmore, *ibid.*, **54**, 3274 (1932).

Table I. Carbonium Ion Products from Electrolyses of Potassium 2,3,3-Trimethylbutanoate

Products	pH ^a		
	13.0	13.8	14.4
	Mole percentages ^b		
3,3-Dimethyl-1-butene	4.9	4.4	31.4
3,3-Dimethyl-2-butanol	3.0	1.3	0.9
2,3-Dimethyl-1-butene	69.0	62.4	56.7
2,3-Dimethyl-2-butene	3.7	2.4	1.9
2,3-Dimethyl-2-butanol	16.2	28.4	9.1
2,3-Dimethyl-2-butyl ester ^c	3.1	1.0	0.06
	99.9	99.9	100.1

^a Determined by weighing the KOH and RCO₂H used and then calculating the pH from the excess KOH. ^b Percentages obtained from the data of Table IV by subtracting the amounts of 2,2,3,4,5,5-hexamethylhexane and 2,2-dimethylbutane and a quantity of 3,3-dimethyl-1-butene equal to the amount of 2,2-dimethylbutane; fragmentation products also were excluded. ^c A 2,3,3-trimethylbutanoate.

sidered to be one of the most rearrangement-prone carbonium ions, it was trapped in 3 M KOH solution 30–60% unrearranged (Tables II and III), and (2) the extent of rearrangement is greater below pH 14 than above.

Table II. 3,3-Dimethyl-2-butyl Cation from Electrolysis of Potassium 2,3,3-Trimethylbutanoate

Products	pH		
	13.0	13.8	14.4
	Mole percentages		
3,3-Me ₂ -2-butyl	8	6	32
2,3-Me ₂ -2-butyl	92	94	68
	100	100	100

Table III. 3,3-Dimethyl-2-butyl Cation from Rearrangement of Electrolytically Generated 3,3-Dimethyl-1-butyl Cation^a

Products	pH						
	6.6	8.2	9.4	10.0	13.6	14.0	14.5
	Mole percentages						
3,3-Me ₂ -2-butyl	6	3	8	11	8	12	61
2,3-Me ₂ -2-butyl	94	97	92	89	92	88	39
	100	100	100	100	100	100	100

^a Data from Table IV of ref 2.

Elementary considerations are sufficient to rationalize these results. It has been shown elsewhere that anodic oxidations of carboxylates can produce free cations,^{4–11} just as do two other exothermic cation-generating reactions, decompositions of alkylidiazonium ions^{12,13} and deoxidations of alkoxides,^{14–16}

(4) 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.

(5) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 581.

(6) E. J. Corey, R. R. Sauers, and S. S. Swan, *J. Am. Chem. Soc.*, **79**, 5826 (1957); E. J. Corey and R. R. Sauers, *ibid.*, **81**, 1743 (1959); E. J. Corey, N. L. Bauld, R. T. LaLonde, J. Casanova, and E. T. Kaiser, *ibid.*, **82**, 2645 (1960).

(7) L. Ebersson, *Acta Chem. Scand.*, **17**, 1196, 2004 (1963).

(8) F. F. Rawlings, G. W. Thiesen, T. G. Lee, M. J. Murray, Jr., and J. L. Seago, *Electrochem. Technol.*, **2**, 217 (1964).

(9) J. A. Waters, *J. Org. Chem.*, **29**, 428 (1964).

(10) W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **86**, 4686 (1964).

(11) J. G. Traynham and J. S. Dehn, *ibid.*, **89**, 2139 (1967).

the products from these seemingly different reactions are similar.^{1,2,4,10,17,18} The free pinacolyl cation can rearrange to the more stable tertiary cation or be encumbered and trapped as unrearranged alcohol and olefin.

Below pH 14 the behavior of this free cation is insensitive to pH, suggesting that water is the important encumbering reagent under these conditions. Encumbrance by water has been estimated to require *ca.* 10⁻¹⁰ sec, collapse to olefin and alcohol following shortly.⁴ The methyl rearrangement which dominates in the domain below pH 14 must be assigned a rate constant equal to or slightly greater than 10¹⁰ sec⁻¹. Above pH 14 encumbrance is faster (less rearrangement), indicating that encumbrance by OH⁻, in excess of 1 M, is faster than encumbrance by water.

The pinacolyl cation produced by rearrangement of the free 3,3-dimethyl-1-butyl cation² is nearly identical with the cation produced by anodic oxidation of the pinacolyl radical. Each method of generation shows similar pH profiles for rearrangement *vs.* trapping. The differences at high hydroxide ion concentration are attributed to the difficulty in maintaining identical conditions throughout a run and the sensitivity of product composition to hydroxide concentration.

None of the early efforts to prepare pinacolyl halides by displacement reactions on the alcohol were successful. Pinacolyl chloride was first prepared by

Table IV. Electrolyses of Potassium 2,3,3-Trimethylbutanoate

	13.0	13.8	14.4
pH	13.0	13.8	14.4
M (RCO ₂ K)	1.0	0.9	1.0
Amperes	2.8	4.1	4.7
Volts	10.0	10.0	7.0
V anode <i>vs.</i> sce	0.8	0.9	0.9
Temp, °C	77.0	75.0	70.0
Time, min	30.0	30.0	30.0
mmoles of RCO ₂ K electrolyzed	...	4.0	...
mmoles of total products	8.0	4.0	0.4
Millifaradays	52.0	76.0	88.0
Current yield, %	30.0	10.0	0.9
Products	Mole percentages		
2,2,3,4,5,5-Hexamethylhexane	0.9	0.7	0.4
2,2-Dimethylbutane	6.7	5.6	3.0
3,3-Dimethyl-1-butene	10.8	9.4	27.6
3,3-Dimethyl-2-butanol	2.5	1.1	0.7
Ethene	0.6	0.04	0.6
2-Methylpropene	0.09	0.3	7.5
2,3-Dimethyl-1-butene	57.2	53.5	44.5
2,3-Dimethyl-2-butene	3.1	2.1	1.5
2,3-Dimethyl-2-butanol	13.4	24.4	7.1
2,3-Dimethyl-2-butyl ester	2.6	0.9	0.05
2-Methyl-1-butene	0.3	0.3	5.6
Unidentified compound(s)	1.8	1.7	2.4
	100.0	100.0	100.0

(12) J. H. Ridd, *Quart. Rev.* (London), **15**, 418 (1961).

(13) H. Zollinger, "Azo and Diazo Chemistry," H. E. Nursten, trans., Interscience Publishers, Inc., New York, N. Y., 1961.

(14) P. S. Skell, Seventh Reaction Mechanisms Conference, Chicago, Ill., Sept 1958.

(15) P. S. Skell and I. Starer, *J. Am. Chem. Soc.*, **81**, 4117 (1959); **82**, 2971 (1960); **84**, 3962 (1962).

(16) P. S. Skell and R. J. Maxwell, *ibid.*, **84**, 3963 (1962).

(17) N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964); *Chem. Eng. News*, **42**, 88 (Oct 5, 1964).

(18) R. J. Maxwell, M.S. Thesis, The Pennsylvania State University, 1963.

photochlorination of neohexane.¹⁹ Further there is no report of a solvolysis of a pinacolyl halide or arenesulfonate leading to unrearranged products. However, the observation²⁰ that active pinacolyl hydrogen sulfate in sulfuric acid racemizes faster than it rearranges is intriguing, implying that rotation within the ion pair and collapse to the starting material are faster than rearrangement. There are no reports of earlier efforts to prepare free pinacolyl cations by deamination, deoxidation, or anodic oxidation.

Experimental Section

2,3,3-Trimethylbutanoic Acid. This acid (prepared by students of F. C. Whitmore) was recrystallized from pentane (-78°) yielding

(19) F. C. Whitmore, H. I. Bernstein, and L. W. Mixon, *J. Am. Chem. Soc.*, **60**, 2539 (1938).

(20) N. C. Deno and M. S. Newman, *ibid.*, **73**, 1920 (1951).

white crystals, mp $53-54^{\circ}$, 98% pure; nmr: singlet (9 H) at 1.00 (δ scale), doublet (3 H) centered at 1.16, quartet (1 H) centered at 2.27, and singlet (1 H) at 12.01 ppm (lit.²¹ mp $48-50^{\circ}$).

Electrolyses of Potassium 2,3,3-Trimethylbutanoate. The electrolysis technique has been reported.² The results are given in Table IV. Because of the small absolute amounts of these products, most of them were identified solely by comparison of vpc retention times to those of known compounds. The major products were also identified by ir.

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(21) W. S. Ropp, Ph.D. Thesis, The Pennsylvania State College, 1949, p 101.

Silylene Chemistry. I. The Thermolysis of Methoxypolysilanes¹

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Received December 26, 1967

Abstract: Kinetic, mass spectral, and chemical evidence is presented for the formation of divalent silicon (silylene) species in the thermolysis of methoxypolysilane derivatives. In the absence of alternative "trapping" agents, the silylenes insert into the silicon-oxygen bond of the parent methoxypolysilane. These silylenes could be intercepted by a variety of acetylenes to give 1,4-disilacyclohexadienes. This reaction appears to involve a rather specific dimerization of silacyclopropene intermediates. The silylenes could also be intercepted by butadienes to give silacyclopent-3-enes. The silylenes could not be intercepted by simple olefins such as tetramethylethylene.

In recent years a number of reports concerning the intermediacy of divalent organosilicon (silylene) species have appeared.² Two general methods have been used for the generation of these silylenes: (1) the reaction of diorganodichlorosilanes with metals,³⁻⁸ and (2) the thermal decomposition of appropriate substrates.^{1, 3, 8, 9}

In 1962, Volpin and coworkers reported³ that the reaction of dimethyldichlorosilane with sodium and the pyrolysis of $(\text{Me}_2\text{Si})_{5.5}$ gave dimethylsilylene. This claim

(1) For a preliminary account of this work, see (a) W. H. Atwell and D. R. Weyenberg, *J. Organometal. Chem.* (Amsterdam), **5**, 594 (1966); (b) *Chem. Eng. News*, **30** (Sept 4, 1967).

(2) (a) The following discussion will be limited to organosilylenes. For an excellent review of inorganic, organometallic, and organic analogs of carbenes, see O. M. Nefedov and M. N. Manakov, *Angew. Chem. Intern. Ed. Engl.*, **5**, 1021 (1966). (b) For a review of silylene chemistry, see W. H. Atwell and D. R. Weyenberg, *ibid.*, in press.

(3) M. E. Volpin, Yu. D. Koshkov, V. G. Dulova, and D. N. Kuranov, *Tetrahedron*, **18**, 107 (1962).

(4) P. S. Skell and E. J. Goldstein, *J. Am. Chem. Soc.*, **86**, 1442 (1964).

(5) O. M. Nefedov and M. N. Manakov, *Angew. Chem.*, **76**, 270 (1964).

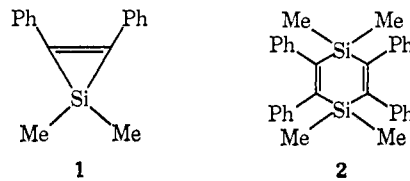
(6) R. A. Braun, *J. Am. Chem. Soc.*, **87**, 5516 (1965).

(7) O. M. Nefedov, M. N. Manakov, and A. D. Petrov, *Dokl. Akad. Nauk SSSR*, **154**, 395 (1964); *Chem. Abstr.*, **60**, 3904 (1964), and references cited therein.

(8) O. M. Nefedov, G. Garzo, T. Szekely, and V. I. Shiryaev, *Proc. Akad. Sci. USSR, Chem. Sect.*, **164**, 945 (1965).

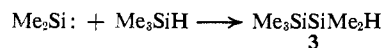
(9) (a) H. Gilman, S. G. Cottis, and W. H. Atwell, *J. Am. Chem. Soc.*, **86**, 1596 (1964); (b) *ibid.*, **86**, 5584 (1964).

was based on the isolation of the novel 1,1-dimethyl-2,3-diphenylsilylene (**1**) when the reactions were carried out in the presence of diphenylacetylene. Since this initial report it has been shown by mass spectral,¹⁰ molecular weight,¹¹ and X-ray¹² studies that the compound believed to have structure **1** is really the dimer **2**. It has been suggested^{9a} that compound **1** might have



been an intermediate in the formation of **2**.

Skell and Goldstein⁴ reported the formation of dimethylsilylene from the reaction of dimethyldichlorosilane with sodium-potassium vapor at $260-280^{\circ}$. Insertion of dimethylsilylene into the Si-H bond of trimethylsilane to give pentamethyldisilane (**3**) was observed,⁴ and the absence of hexamethyldisilane and



(10) F. Johnson, R. S. Gohlke, and W. H. Nasutavicus, *J. Organometal. Chem.* (Amsterdam), **3**, 233 (1965).

(11) R. West and R. E. Bailey, *J. Am. Chem. Soc.*, **85**, 2871 (1963).

(12) N. G. Bokii and Yu. T. Stuchkov, *J. Struct. Chem.*, **6**, 543 (1965).