TABLE I

X-RAY POWDER PATTERN DATA[a] FOR PHENYLSILANETRIOL (PRINCIPAL LINES)

d, kX.	I/I_1	d, kX.	I/I_1
4.79	0.11	3.47	0.14
4.67	.21	3.06	.49
4.53	.40	2.55	.28
4.43	.12	2.18	.05
4.23	.06	2.12	.05
4.13	.06	2.03	.07
3.83	1.00	1.91	.07
3.72	0.14		

[a] CuKα radiation filtered by Ni was used to obtain the powder diffraction data; d = interplanar spacing; I/I_1 = relative intensity.

analytical data for the hard brittle gel finally produced supported the formula of methylpolysiloxane. Calcd. for $(CH_3SiO_{1.5})_n$: C, 17.89; H, 4.51; Si, 41.85. Found: C, 17.6; H, 4.3; Si (Parr bomb method[19]), 40.8.

All runs made at low temperature using low concentration of the reactants (3–5%) have failed to yield monomeric methylsilanetriol owing presumably to the condensation during preparation of the initial monomeric or lower polymeric products.

The X-ray powder pattern for the gel showed a broad halo at 4.09 Å.[20] in entire agreement with that of the gel prepared by dropping pure methyltrichlorosilane in water.

Acknowledgment.—The author gratefully acknowledges the generous gift of the chlorosilanes used in this work by the Shin-etsu Chemical Industrial Co. and the helpful discussions and assistance given by Drs. F. Hirata, S. Otani and Mr. Y. Nakaido of this University, and Mr. K. Kashiwase of the Nippon Chemical Industrial Co. in carrying out various phases of this work.

(19) L. Holzapfel and G. Gottschalk, *Z. anal. Chem.*, **142**, 115 (1954).

(20) T. Takiguchi, *J. Org. Chem.*, **23**, 1216 (1958).

KIRYU, JAPAN

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

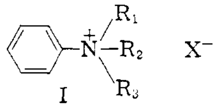
The Electrochemical Degradation of Quaternary Ammonium Salts[1]

BY MANUEL FINKELSTEIN, RAYMOND C. PETERSEN AND SIDNEY D. ROSS

RECEIVED NOVEMBER 22, 1958

The electrolysis of aqueous solutions of a number of quaternary ammonium salts containing allyl, benzyl, fluorenyl, acenaphthenyl, benzhydryl and cinnamyl groups was found to yield, respectively, propylene, toluene, fluorene, acenaphthene, diphenylmethane and a mixture of allylbenzene and propenylbenzene. Evidence is presented which indicates that the mechanism of electrolysis involves a one-electron transfer to form an intermediate radical.

The electrochemical decomposition of quaternary ammonium salts has received little attention since the work of Emmert[2,3] on the electrolysis of various substituted anilinium salts (I). In aqueous solution at a lead cathode he found that if R_1, R_2 and R_3 were simple alkyl or hydroxyalkyl groups, benzene and the corresponding tertiary amine were obtained. When R_3 was allyl and $R_1 = R_2 = CH_3$ no benzene was formed, but dimethylaniline and propylene were identified as the products.



I

Several quaternary salts containing pyridinium[4,5] and quinolinium[4] groups also have been electrolyzed. The products formed resulted from coupling reactions in the 4-position.

On electrolysis of simple tetraalkylammonium halides in liquid ammonia at −78° Schlubach[6] obtained some evidence for the transitory existence of tetrasubstituted ammonium radicals analogous to sodium and potassium atoms. He found also that the electrolysis of triethylanilinium iodide in liquid ammonia resulted in the formation of diethylaniline at the cathode.

The cleavage of quaternary ammonium salts by sodium amalgam or 30% lead–sodium has been investigated extensively by Emde,[7] Fichter[8] and Robinson.[9] These studies have shown that the electrochemical reactions of Emmert often can be duplicated by chemical means.

Of particular interest to us was the observation of Emmert[3] that propylene was formed in the electrolysis of allyldimethylanilinium iodide. It seemed that quaternary ammonium salts containing other groups possessing structural features that could enhance radical or ion stability might lead to the formation of other hydrocarbon fragments on electrolysis. It thus appeared pertinent to investigate some of the factors influencing the electrochemical cleavage of quaternary ammonium salts to form hydrocarbons and tertiary amines.

The present work is of a descriptive and qualitative nature. The main interest was in determining the nature of the radicals which can be cleaved from a quaternary ammonium ion to form a hydrocarbon. No attempt has been made to find experimental conditions for maximizing the yield.

The work of Emmert on the electrolysis of allyldimethylanilinium iodide was extended to include the use of aluminum and platinum cathodes. Propylene was produced in good yield with either

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(1) This research was performed in part under Contract No. DA-36-039-SC-71186 between the Signal Corps Engineering Laboratories, Department of the Army, and the Sprague Electric Co.

(2) B. Emmert, *Ber.*, **42**, 1507 (1909).

(3) B. Emmert, *ibid.*, **45**, 430 (1912).

(4) B. Emmert, *ibid.*, **42**, 1997 (1909).

(5) E. Ochiai and H. Kataoka, *J. Pharm. Soc. Japan*, **62**, 241 (1942); E. Ochiai and N. Kawagoye, *ibid.*, **63**, 313 (1943).

(6) H. H. Schlubach, *Ber.*, **53B**, 1689 (1920).

(7) For example, H. Emde, *ibid.*, **42**, 2590 (1909); *Ann.*, **391**, 88 (1912).

(8) F. Fichter and H. Stenzl, *Helv. Chim. Acta*, **16**, 571 (1933).

(9) P. Groenewoud and R. Robinson, *J. Chem. Soc.*, 1692 (1934)

electrode material. It was further found that a series of quaternary ammonium salts containing the allyl group could be decomposed electrolytically to yield varying quantities of propylene. Among the cations were: *p*-bromophenyldimethylallylammonium, *p*-methoxyphenyldimethylallylammonium, cyclohexyldimethylallylammonium and *m*-tolyldimethylallylammonium.

Since the C–H bonds in the methyl groups of both toluene and propylene have comparable dissociation energies,[10] the electrolysis of some benzyl salts was attempted. The allyl and benzyl radicals have similar resonance energies[11] and the formation of toluene would be expected. However, no toluene could be detected on electrolysis of benzyltrimethylammonium salts or benzyltriethylammonium salts. In fact, the electrolysis of benzylallyldimethylammonium iodide yielded propylene with no isolable quantities of toluene.

Toluene was obtained, however, from the electrolysis of benzyldimethylanilinium trifluoroacetate in water. It was characterized by its infrared spectrum and by vapor phase chromatography. When the same electrolysis was performed in a high dielectric constant, non-reacting solvent, N,N-dimethylacetamide, the product was found to be bibenzyl and not toluene.

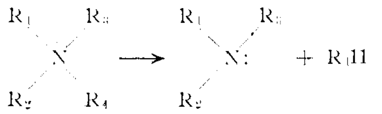
Further phenyl substitution would increase the resonance stabilization of a benzyl or an allyl radical and thus cinnamyltriethylammonium "polyborate"[12] and benzhydryltriethylammonium acetate were studied next.

The electrolysis of cinnamyltriethylammonium "polyborate" led to the formation of a mixture of 80% propenylbenzene and 20% allylbenzene. Vapor phase chromatography showed the presence of allylbenzene while the propenylbenzene was identified through its bromination product. The quantitative data are based on vapor phase chromatography and indices of refraction. Other examples of the formation of these two species from a cinnamyl compound have been reported in the literature.[13]

Similarly, benzhydryltriethylammonium acetate was smoothly electrolyzed to yield diphenylmethane which was identified by its infrared spectrum and index of refraction.

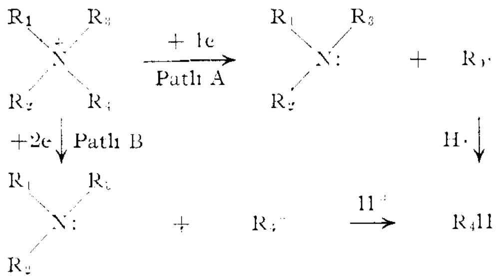
Two more substances, characterized by the stability of the possible degradation fragments, were investigated. The electrolysis of trimethyl-9-fluorenylammonium bromide proceeded readily at an aluminum cathode to produce fluorene, identified by a mixture melting point with an authentic sample. The same electrolysis failed at a platinum cathode. The electrolysis of trimethyl-1-acenaphthenylammonium bromide proceeded similarly to give acenaphthene, identified through its melting point and picrate.

The over-all change involved in the electrochemical decomposition of a quaternary ammonium cation is



the hydrogen attached to R_4H presumably coming from the solvent.

The present experiments do not allow the formulation of a definitive mechanistic scheme. Depending on the number of electrons transferred in the electrode process either path A or path B is possible



The groups corresponding to R_4: benzyl, benzhydryl, fluorenyl, acenaphthenyl, cinnamyl and allyl, by virtue of their resonance possibilities, can exist as more stable radicals and ions than simple alkyl or phenyl groups. This, however, does not help to differentiate between paths A and B. Likewise, the fact that the ease of cleavage of a group appears to be dependent on the amine segment does not help in distinguishing between the two mechanistic possibilities.

In an attempt to distinguish between the mechanisms we may refer to the experiments with benzyldimethylanilinium trifluoroacetate in water and dimethylacetamide. In water the product is toluene, but in dimethylacetamide, which has no active hydrogens, a radical intermediate, if formed, has a greater probability of dimerizing. However, if a carbanion were formed it could either react with the solvent,[14] present in large excess, or engage in a concentration dependent S_N2 displacement on another molecule of the quaternary salt. The latter displacement would seem highly improbable for two reasons: (1) The greater opportunity which the intermediate species has to come in contact with dimethylacetamide molecules (2.17 moles) than with benzyldimethylanilinium ions (0.051 mole); (2) the relatively high dielectric constant of N,N-dimethylacetamide (37.8)[15] which would certainly discourage a nucleophilic displacement of the type required.[16]

In actual fact bibenzyl was produced. While the possibility of the aforementioned displacement reaction is not entirely excluded it seems improbable under our reaction conditions (*i.e.*, it is more likely that the dimer which was isolated arises from the coupling of two benzyl radicals rather than the attack of a benzyl carbanion on the quaternary ammonium ion). The isolation of

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[10] G. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, p. 401.

[11] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p. 50.

[12] The structure of this and similar compounds will be the subject of a future communication from this Laboratory.

[13] T. W. Campbell and W. G. Young, THIS JOURNAL, **69**, 688 (1947); W. G. Young, C. Ballou and K. Nozaki, *ibid.*, **61**, 12 (1939).

[14] For the reaction of Grignard reagents (most likely carbanions) with amides see: M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall, Inc., New York, N. Y., 1954, pp. 870–908.

[15] G. R. Leader and J. F. Gormley, THIS JOURNAL, **73**, 5731 (1951).

[16] E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 244 (1935).

TABLE I

Halide	Amine	Solvent	M.p.,[a] °C.	Halide, % Calcd.	Halide, % Found	Yield, %	Ref.
Allyl iodide	N,N-Dimethylaniline	Acetone	87–88	43.89	44.16	70	17
Allyl bromide	*p*-Bromophenyldimethylamine	Acetone	151–152	24.89	25.38	68	18
Allyl bromide	*p*-Methoxyphenyldimethylamine	Acetone	141–142	29.36	29.87	89	
Allyl iodide	Dimethylcyclohexylamine	Acetone	179–180	43.00	43.00	86	
Allyl bromide	*m*-Tolyldimethylamine	Acetone	139–140	31.19	31.19	80	19
Allyl iodide	Dimethylbenzylamine	Acetone	100–102	41.86	41.48	90	20
Cinnamyl bromide	Triethylamine	Acetonitrile	[b]			93	
9-Bromofluorene	Trimethylamine	Methanol	185–190	26.27	25.68	94	21
1-Bromoacenaphthene	Trimethylamine	Methanol	206–207			74	22
Benzyl bromide	N,N-Dimethylaniline	Acetone	143–145[c]	27.35	27.14	85	19, 23
Benzyl chloride	Triethylamine	Acetone	188	15.57	15.63	75	24
Benzhydryl bromide	Triethylamine	Acetonitrile	137–140	22.94	23.09	80	

[a] All of the salts melted with decomposition. [b] This salt was quite hygroscopic and was converted directly to the polyborate. [c] Ref. 19 lists the m.p. 96–98°; ref. 23 lists the m.p. 200–203°.

bibenzyl, therefore, constitutes evidence that the electrolysis occurs by way of a one-electron transfer to form a radical (path A.)

Acknowledgment.—We are indebted to Professor E. Robert Coburn of Bennington College for the preparation of some of the salts and intermediates.

Experimental

All melting points and boiling points are uncorrected. All halide analyses were performed by the Volhard technique. A Perkin–Elmer 154B vapor fractometer with an "A" column and helium as the carrier gas was used for analysis.

Electrolysis Procedures. Procedure A.—The electrolysis cell consisted of a tall form beaker containing a solution of the organic salt. The cathode was a cylindrical piece of aluminum foil, 12.7 cm. high and 7.6 cm. in circumference, immersed in the solution. A gold wire anode dipped into the solution inside the cylinder. The voltage source was a 45 volt or 22.5 volt dry cell. An ammeter was connected in series.

Procedure B.—The cathode was an aluminum wire, 0.25 cm. in diameter, insulated with Tygon and bent up into an inverted, rubber-capped, 100-ml. buret immersed in a beaker containing the salt solution. The exposed portion was 1.5 cm. in length. The anode was a gold or platinum wire. In the case of the halide salts the anode was immersed in a separate beaker containing potassium chloride solution and connected to the catholyte through a filter paper salt bridge. With other anions the anode merely dipped into the same beaker as the cathode. Before current was passed, part of the solution was drawn up into the buret by a syringe. The progress of the reaction could be followed by the displacement of the solution by gaseous or liquid products. Current was supplied from either a dry cell or a constant voltage power supply operating from the 110 volt a.c. line.

Preparation of Quaternary Ammonium Halides.—The salts were prepared by refluxing the amine and halide in the appropriate solvent. Ether usually was added to complete crystallization. Each salt was recrystallized at least once from ethanol–ether. The pertinent details are summarized in Table I.

Preparation of Quaternary Ammonium Hydroxides.—In each case the quaternary halide was dissolved in water and a slight excess of silver oxide was added. The suspension was stirred, most conveniently by magnet, and more silver oxide was added until a negative halide test was obtained. The precipitated silver halide was filtered through fritted glass with suction.

An alternative procedure consisted of the passage of the aqueous quaternary halide solution through a column of Dowex 2.[25] The silver oxide method was in general more advantageous. In either case the basicity of the solution was determined by titration with standard hydrochloric acid.

The quaternary ammonium acetates or trifluoroacetates were prepared by neutralization of the solutions of quaternary ammonium hydroxides with the appropriate acid (phenolphthalein end-point.) The salts were used directly in solution for most of the electrolyses.

Preparation of Triethylcinnamylammonium Polyborate.[12]—To 500 ml. of a 0.17 *M* aqueous solution of triethylcinnamylammonium hydroxide was added 26 g. (0.42 mole) of boric acid. The solution was heated, filtered and concentrated by distillation *in vacuo*. The residue was directly crystallized from water–isopropyl alcohol and washed with acetone. Three further crystallizations from water gave the analytical sample.

Anal. Calcd. for $C_{15}H_{31}NB_6O_{13}$: C, 36.15; H, 6.27; N, 2.81; B, 13.03. Found: C, 35.97; H, 5.95; N, 2.82; B, 13.21. Neut. equiv. (titration by acid) calcd. 498.3, found 493.9; neut. equiv. (titration by base, addition of mannitol) calcd. 99.7, found 101.5.

Electrolyses. 1-Acenaphthenyltrimethylammonium Bromide.—A solution of 4 g. of the salt in 150 ml. of water was electrolyzed 6 hr. at 40 milliamp. by procedure B. The white solid was filtered and dried, 520 mg. obtained. Sublimation gave 485 mg. of crystals which on crystallization from ethanol had m.p. 93–94°. The picrate prepared in the usual way[26] had m.p. 158–159° dec. (reported[27] for acenaphthene m.p. 95°; picrate, m.p. 161°).

9-Fluorenyltrimethylammonium Bromide.—A solution of 10 g. of the salt in 180 ml. of water was electrolyzed by procedure B for 5 hr. at 40 milliamp. The white solid was filtered and dried, 500 mg. was obtained. Sublimation gave 475 mg. of crystals, m.p. 114–115°; mixture m.p. with authentic fluorene 114–115°.

Benzhydryltriethylammonium Acetate.—A solution of the acetate prepared from 14 g. of benzhydryltriethylammonium bromide in 200 ml. of water was electrolyzed 23 hr. at an average current of 30 milliamp. (initial current of 40 milliamp. dropped to 20 milliamp. during the electrolysis) according to procedure B. The clear, water-white oil floating on the surface was drawn off and the solution was extracted twice with ether. The ether extract was combined with the oil, dried and distilled. Distillation of the residue through a short path still, bath temperature 150–160°, pressure 12 mm., gave 2.5 g. of liquid, $n^{27}D$ 1.5738 (diphenylmethane $n^{20}D$ 1.5770.[28]) The infrared spectrum of this product was identical to the spectrum of diphenylmethane.

Triethylcinnamylammonium Polyborate.—Two separate experiments were performed: (1) A solution of 15 g. of the salt in 150 ml. of water was electrolyzed 21 hr. at an average

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(17) R. W. D. Preston and H. O. Jones, *J. Chem. Soc.*, **101**, 1930 (1912).

(18) H. von Halban, *Z. physik. Chem.*, **67**, 129 (1909).

(19) M. S. Kharasch, G. H. Williams and W. Nudenberg, *J. Org. Chem.*, **20**, 937 (1955).

(20) H. Emde and H. Kull, *Arch. Pharm.*, **274**, 173 (1936).

(21) C. K. Ingold and J. A. Jessop, *J. Chem. Soc.*, 2357 (1929).

(22) G. Wittig and H. Ludwig, *Ann.*, **589**, 55 (1954).

(23) K. Nador and L. Gyermek, *Acta Chim. Acad. Sci. Hung.*, **2**, 95 (1952).

(24) S. D. Ross and M. Finkelstein, THIS JOURNAL, **79**, 6547 (1957).

(25) E. Sándi, *Magyar Kem Folyoirat*, **61**, 29 (1955).

(26) R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 229.

(27) *Ibid.*, p. 313.

(28) I. Heilbron, "Dictionary of Organic Compounds," Vol. 2, Oxford University Press, New York, N. Y., 1953, p. 420.

current of 30 milliamp. (initial current of 40 milliamp. dropped to 20 milliamp. during the electrolysis) using procedure B. The oily liquid was drawn from the top of the aqueous solution and the solution was extracted several times with ether. The ether extracts and the oil were combined and dried and the ether concentrated through a Vigreux column. Bromine was added directly to this ether concentrate. Evaporation left an orange solid which on crystallization from ethanol gave 740 mg., m.p. 63–65°. Recrystallization from ethanol gave white needles, m.p. 64–65° (literature value[29] for propenylbenzene dibromide, m.p. 65.5–66.5°). (2) A solution of 15 g. of the salt in 200 ml. of water was electrolyzed 20 hr. at 30 milliamp. using procedure B. The workup was as above except that the product was vacuum distilled through a short path still rather than brominated. The water-white product had $n^{24.6}_{D}$ 1.5397. (A calculation from literature data[29] indicated a mixture of 80% of propenylbenzene and 20% of allylbenzene.) Vapor phase chromatography of a pure sample of allylbenzene[30] and of the above product confirmed the proportions to be 80 and 20%.

Allyldimethylanilinium Iodide.—Procedure B was followed except that the cathode was sometimes a platinum wire. A solution of 5 g. of the salt in 180 ml. of water was electrolyzed for 6.5 hr. with a current of 40 milliamp. A total of 120 ml. of gas was collected which consisted of 32% propylene as shown by vapor phase chromatography. (The same experiment using 15 g. of the salt gave a gas consisting of 47% propylene.) The electrolysis solution was extracted with ether and the ether extracts dried. Addition of an ethanolic solution of picric acid gave 240 mg. of dimethylaniline picrate, m.p. 158–159° dec., mixture m.p. with authentic material prepared from dimethylaniline and picric acid 159–160° dec.

Benzylallyldimethylammonium Iodide.—Using procedure B a solution of 12 g. of the salt in 180 ml. of water was electrolyzed at a current of 40 milliamp. The gas formed consisted of 46% propylene as analyzed by the vapor fractometer. No toluene could be isolated from this electrolysis.

Benzyldimethylanilinium Trifluoroacetate in Water.—A solution of the salt prepared from 15 g. of benzyldimethylanilinium bromide in 200 ml. of water was electrolyzed 4 hr. at an average current of 400 milliamp. (initial current of 700 milliamp. dropped to 100 milliamp. during the electrolysis) according to procedure A. The dark, blue-violet cell contents were extracted three times with ether, the ether extracts washed with water and extracted twice with 50-ml. portions of 1:1 hydrochloric acid. The ether was dried over magnesium sulfate, distilled through a Vigreux column and the residue was distilled through a short path still. A water-white liquid was obtained, n^{20}_{D} 1.4879 (literature value[31] for toluene n^{20}_{D} 1.4961.) No appreciable solid residue was obtained. The infrared spectrum of the liquid was identical to that of toluene. Confirmation was obtained by vapor phase chromatography.

Benzyldimethylanilinium Trifluoroacetate in Dimethylacetamide.—The salt was prepared as above and the water removed *in vacuo*. The white solid was dissolved in 200 ml. of dimethylacetamide and the electrolysis was performed according to procedure A for 7.5 hr. with an average current of 300 milliamp. (initial current of 400 milliamp. dropped to 200 milliamp. during the electrolysis).

The electrolysis mixture was poured into 700 ml. of water and extracted three times with ether. The ether extract was washed once with water and extracted twice with 50-ml. portions of 1:1 hydrochloric acid. After another washing with water the ether was dried over magnesium sulfate and distilled through a Vigreux column. The dark tan residue solidified on scratching. It was taken up in hot ethanol and cooled; white needles were obtained, m.p. 52–53°, 1.1 g. Recrystallization from ethanol gave m.p. 52–53°, mixed m.p. with bibenzyl, prepared according to Miukhailenko[32] was 52–54°. The hydrochloric acid extract was neutralized with sodium hydroxide and extracted with ether. To the concentrated ethereal solution was added an ethanolic solution of picric acid. On standing, yellow crystals were formed. Crystallization of these from alcohol gave 543 mg., m.p. 156–157° dec. On recrystallization the melting point was 157–159° dec., mixture m.p. with authentic dimethylaniline picrate was 157–159° dec.

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[30] C. Weygand, "Organic Preparations," Interscience Publishers, Inc., New York, N. Y., 1945, p. 356.

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Peroxides. VI.[2] Preparation of *t*-Butyl Peresters and Diacyl Peroxides of Aliphatic Monobasic Acids[3]

BY LEONARD S. SILBERT AND DANIEL SWERN

RECEIVED OCTOBER 18, 1958

Long chain *t*-butyl peresters and diacyl peroxides were prepared in nearly quantitative yields and in high purity by acylation of pure *t*-butyl hydroperoxide and 50–65% hydrogen peroxide, respectively, in ether-pyridine solutions. These peroxides were accurately analyzed by an improved iodometric procedure employing 0.0005 and 0.002% ferric chloride hexahydrate, respectively, in glacial acetic acid. The diacyl peroxides and *t*-butyl peresters show an alternation in melting points.

Organic peroxides have achieved an important position in organic chemistry. Major emphasis in the past has been on the preparation and properties of aromatic and short-chain aliphatic derivatives. A detailed study of the preparation and properties of high purity long-chain peroxides, comparable to the studies on peracids,[2,4] was needed for clarification of peroxide structure, systematization of their chemical and physical properties, and investigation of the kinetics of their decomposition.

Alkyl Peresters.—Milas and Surgenor[5] described the first synthesis and some of the properties of eight *t*-butyl peresters. *t*-Butyl perstearate was the only long-chain saturated derivative mentioned in their paper. These workers employed the Schotten–Baumann technique which has been the major preparative method in use to date.[6] A

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[1] Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] Paper V, THIS JOURNAL, **80**, 323 (1958).

[3] Presented at the Fall Meeting of the American Chemical Society, September 7–12, 1958, Chicago, Ill.

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