ture with 0.39 mole of hydrogen peroxide, as a 40% solution added slowly over a two-hour period. At the end of the addition period a small amount of solid appeared in the flask and the amount of solid increased during a subsequent four-hour period of vigorous stirring. The ether solution was decanted from the solid and the solid extracted with 60 ml. of ether. There was no apparent water layer. The combined ether solutions were dried over anhydrous potassium carbonate and stored over fresh potassium carbonate for eight hours. Ether was removed through a packed column until the solution was concentrated to 50 ml. The column was then washed down with 10 ml. of ether and the combined residue and wash ether were carefully fractionated through a 7 × 600 mm., stainless steel-coil packed, partial reflux, total take-off electrically heated column. *t*-Butyl alcohol (7 g.) was collected at 79 to 82°, and identified by its conversion in 87% yield to its 3,5-dinitrobenzoate ester, m.p. 139–140° (lit.[10] 141°). Isobutyl alcohol, 14.5 g., was collected at 106° and identified by its conversion in 90% yield to its 3,5-dinitrobenzoate ester, m.p. 85–86° (lit.[10] 86°). The total weight of alcohol recovered represents a 90% yield from the oxidation. Isobutyl and *t*-butyl alcohols were obtained in a molar ratio very close to 2:1.

Samples of diisobutyl-*t*-butylborane from each of the other four methods of preparation were subjected to the same oxidation procedure and gave in each case isobutyl alcohol and *t*-butyl alcohol in good yield and in a ratio very close to 2:1.

Acknowledgment.—The work reported in this and previous papers of the series was made possible through the support of the Olin Mathieson Chemical Corporation, Niagara Falls, N. Y.

NOTRE DAME, IND.

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[10] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polymeric Basic Beryllium Carboxylates[1a]

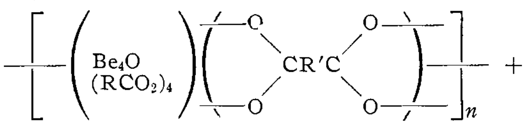
BY C. S. MARVEL AND MICHAEL M. MARTIN[1b]

RECEIVED SEPTEMBER 20, 1957

Low molecular weight polymers of basic beryllium carboxylates and dibasic acids have been prepared and their properties studied. Also polymers have been prepared by the vinyl polymerization of acrylate-containing basic beryllium carboxylates.

The basic beryllium carboxylates, $Be_4O(RCO_2)_6$, comprise a class of covalent compounds which exhibit remarkable thermal stability, being stable to distillation at atmospheric pressure well above 300°. It was the goal of this research to prepare polymeric materials which contain the basic beryllium carboxylate structure, both as a part of the polymer chain and as a substituent on a polymethylene chain, and to study the thermal and mechanical properties of such polymers. The structure of basic beryllium acetate was assigned by Bragg and Morgan[2] in 1923 as a result of X-ray studies. The structure is made up of a tetrahedron with a beryllium atom at each of the vertices bonded to an oxygen atom at the center. The six edges are occupied by acetate groups. To prepare a linear condensation polymer containing the basic carboxylate structure, it is necessary to replace two of the monobasic carboxyl groups by carboxyl groups of dibasic acids, as illustrated in equation 1.

$n\mathrm{Be_4O(RCO_2)_6} + n\mathrm{XOC{-}R'{-}COX} \longrightarrow$



2*n*RCOX (1)

The feasibility of this type of condensation polymerization was indicated by Bragg and Morgan[2] and Tanatar and Kurowski,[3] who reported that if basic beryllium propionate were treated with excess acetyl chloride, carboxyl exchange took place to give basic beryllium triacetate tripropionate, and also that basic beryllium tetrabutyrate diacetate was the exclusive product of a similar reaction involving basic beryllium butyrate and acetyl chloride. These results could not be duplicated since the reaction gave mixtures of the various possible products of carboxyl exchange, but it was verified that carboxyl exchange occurs readily. The original claims that these reactions led to single products seem to rest on insecure evidence, since the structures of such products were assigned solely on the basis of beryllium analysis. The preparation of polymeric basic beryllium carboxylates is not without precedent, since polymeric materials were prepared, though not recognized as such, by Tanatar and Kurowski[3] and Meyer and Mantel,[4] who attempted to prepare basic beryllium succinate, $Be_4O(O_2CCH_2CH_2CO_2)_3$. This material was described as a hard, infusible glass. It seems probable that it was the three dimensional basic succinate polymer rather than the monomeric substance.

With this background in mind, efforts were directed toward developing a method for replacing two carboxylate groups with dibasic acid groups, resulting in the formation of a linear condensation polymer. Polymers so prepared were tested for solubility, viscosity and stability.

Condensation Polymerization.—Polymers were prepared from various combinations of basic beryllium acetate, propionate and benzoate, and the acid chlorides of adipic, sebacic, β-ethyladipic, terephthalic and isophthalic acids. The analytical and viscosity data for these materials appear in Table II in the Experimental part. The general

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[1] (a) The work discussed herein was initiated as part of the synthetic rubber research project sponsored by the National Science Foundation and completed under contract number AF-33(616)-3772 with the Materials Laboratory of Wright Air Development Center, Wright-Patterson Air Force Base, Ohio; Lt. L. E. Coleman, project engineer. (b) National Science Foundation Fellow 1955–1956.

[2] L. W. Bragg and G. Morgan, *Proc. Roy. Soc. (London)*, **104A**, 437 (1923).

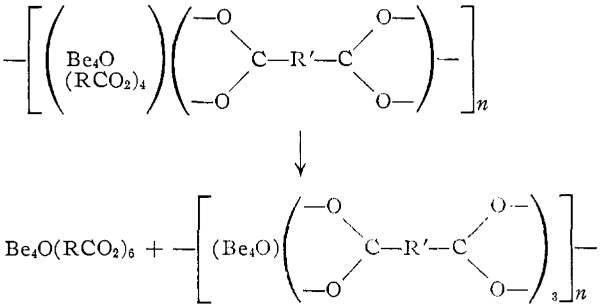
[3] S. Tanatar and E. Kurowski, *J. Rus. Phys. Chem. Soc.*, **39**, 936 (1907); *Chem. Zentr.*, **79I**, 102 (1908).

[4] J. Meyer and E. Mantel, *Z. anorg. u. allgem. Chem.*, **123**, 43 (1922).

technique employed for their preparation was to condense equimolar quantities of the two reactants in a hydrocarbon solvent such as benzene, toluene or xylene, and coagulate the polymers with low boiling petroleum ether.

All of the polymers can be ground into powders when free of solvent. Those polymers containing only aliphatic acids show limited elasticity when plasticized by a little solvent, and can be drawn into short fibers. At a high degree of plasticization they adhere to glass. Viscosity data indicate a very low degree of polymerization, and end groups are doubtless responsible for the discrepancies observed in the analytical values. For instance, the polymer of basic beryllium acetate and terephthalyl chloride (Table II, no. 6) gives a satisfactory analysis for a structure containing four or five repeating units and terephthalate end groups. As is evident in the tables, those samples with highest viscosities also have the best analytical values.

Since the ultimate aim of this research was the preparation of highly thermostable polymers, these materials naturally were tested for their thermal stability. Early experiments were encouraging in that samples were not observed to undergo any visible decomposition at temperatures as high as 400°. Neither could cyclopentanone nor diethyl ketone be isolated as pyrolysis products when the polymer of basic beryllium propionate and adipyl chloride was heated at 350° at 100 to 120 mm. pressure. However, it soon became evident that another sort of decomposition was occurring, specifically a disproportionation of the linear polymer into the monomeric basic beryllium carboxylate and a crosslinked polymer of the type indicated in equation 2.



This reaction occurs even at room temperature. Thus it was found that soluble polymers containing aliphatic monobasic and aliphatic dibasic acid groups became completely insoluble within a few days after their preparation. Those polymers made up of a mixture of aliphatic and aromatic acid units maintain their solubilities for longer periods of time, but after several months they are also considerably less soluble. Heat seems to expedite this type of disproportionation. It was observed that when those polymers which most readily lost their solubilities were heated at 110 to 140° at 0.01 mm. pressure, considerable quantities of the monomeric basic beryllium carboxylate could be sublimed out within a few hours, leaving an insoluble residue. Under these conditions only traces of a basic beryllium carboxylate could be sublimed out of polymers which maintained their solubilities for several months. However, upon raising the temperature to 340°, disproportionation of the more stable linear polymer types was also observed to proceed readily.

Insoluble, and presumably crosslinked, condensation polymers of this type also were prepared by condensation in concentrated solution and at higher temperature. Insoluble polymers were also prepared by a melt technique in which intimate mixtures of basic beryllium propionate and sebacic, adipic and terephthalic acids were fused.

Vinyl Polymerization of Acrylate-containing Basic Beryllium Carboxylates.—Polymers were prepared by the benzoyl peroxide initiated free radical polymerization of two acrylate-containing basic beryllium carboxylates. From basic beryllium acrylate was formed a highly crosslinked, insoluble polymer. A polymer also was formed from basic beryllium pentapropionate monoacrylate, but it was too insoluble to permit a reliable viscosity determination. Since this polymer should be linear and soluble, it is suspected that insolubility is due to crosslinking which could arise from the presence of basic beryllium carboxylates containing more than one acrylate group, or by a reaction similar to the disproportionation described previously. Both of these substances are white powders which undergo extensive decomposition, accompanied by carbonization, at 200°. These results indicate that a polymethylene chain bearing basic beryllium carboxylate side groups is not outstanding in its thermal stability, although it is somewhat more stable than a polyacrylic ester.

Experimental

Due to the extremely toxic properties of beryllium compounds, special precautions must be observed in their handling. All reactions were carried out in a hood, gloves were worn whenever material was being transferred, contaminated glassware was washed immediately, and the desk top was frequently sponged off. The laboratory workers also received chest X-rays every four months to detect any sign of berylliosis.

Preparation of Basic Beryllium Carboxylates.—Beryllium hydroxide was treated with a twofold excess of the organic acid in the presence of a solvent such as benzene. Table I lists the compounds prepared and their melting points.

Table I

Basic Beryllium Carboxylates

RCO_2	Observed m.p., °C.	Literature m.p., °C.
Acetate	290–292	285
Propionate	136.5–137.5	134
n-Butyrate	26–27	26
Pivalate	161.5–162.5	163
Acrylate	Polymerizes	New cmpd.[a]
Phenylacetate	139–140	New cmpd.[b]
Benzoate	318–320	317
Pentapropionate monoacrylate	154–159 (impure)	New cmpd.[c]

[a] Calcd. for $C_{18}H_{18}O_{13}Be_4$: C, 45.19; H, 3.80. Found: C, 45.38; H, 3.92. We are indebted to Mr. J. Nemeth, Mrs. M. Stingl and Miss C. Higham of this University for the microanalytical results. [b] Calcd. for $C_{48}H_{42}O_{13}Be_4$: C, 66.81; H, 4.92. Found: C, 67.03; H, 5.28. [c] Calcd. for $C_{18}H_{20}O_{13}Be_4$: C, 44.25; H, 5.79. Found: C, 44.56; H, 6.08.

Preparation of Dibasic Acid Chlorides.—Sebacyl chloride and β-ethyladipyl chloride were prepared from the acid and thionyl chloride,[5a] while terephthalyl and isophthalyl chloride were prepared from the acid and phosphorus pentachloride.[5b]

Carboxyl Exchange Reactions. Basic Beryllium Propionate and Acetyl Chloride.—Three grams (0.006 mole) of basic beryllium propionate was refluxed with 7.74 g. (0.10 mole) of acetyl chloride for 1.5 hours, then allowed to stand overnight at room temperature. The excess acetyl chloride was removed at reduced pressure, leaving a solid white residue, which was recrystallized from high boiling petroleum ether. The precipitate was recrystallized again, and dried. The yield was 1.3 g., m.p. 170–190°.

Anal. Calcd. for $C_{14}H_{22}O_{13}Be_4$: C, 38.71; H, 5.07. Found: C, 38.67; H, 5.06.

The analysis is satisfactory for a mixed carboxylate of the formula $Be_4O(CH_3CO_2)_4(CH_3CH_2CO_2)_2$. However, the sample obviously is not a pure compound, and must be a mixture of several of the possible replacement products resulting from carboxyl exchange.

The supernate from this product was evaporated to dryness, and the residue sublimed at 130° and 0.05 mm. The yield was 0.25 g., m.p. 126–128°.

Anal. Calcd. for $C_{16}H_{26}O_{13}Be_4$: C, 41.53; H, 5.63. Found: C, 41.46; H, 5.65.

The melting point of this product remained constant after seven months of storage. The analysis corresponds to the mixed carboxylate having the structure $Be_4O(CH_3CH_2CO_2)_4(CH_3CO_2)_2$. This is probably the compound isolated by Tanatar and Kurowski which melted at 127°, and to which they assigned the structure of the triacetate tripropionate.

Basic Beryllium Butyrate and Excess Acetyl Chloride.—The procedure was similar to that described in the previous section. Two fractions were isolated, both of which are mixtures: fraction 1, yield 0.4 g., m.p. 72–112°. *Anal.* Calcd. for $C_{16}H_{26}O_{13}Be_4$, $Be_4O(OAc)_4(OBu)_2$: C, 41.56; H, 5.63. Calcd. for $C_{14}H_{22}O_{13}Be_4$, $Be_4O(OAc)_5(OBu)$: C, 38.72; H, 5.07. Found: C, 40.12; H, 5.23.

Fraction 2, b.p. 151–154° (0.3 mm.). *Anal.* Calcd. for $C_{20}H_{34}O_{13}Be_4$, $Be_4O(OAc)_2(OBu)_4$: C, 46.32; H, 6.44. Calcd. for $C_{18}H_{30}O_{13}Be_4$, $Be_4O(OAc)_3(OBu)_3$: C, 44.08; H, 6.11. Found: C, 45.46; H, 6.20.

Hypothetical mixtures of the various possible exchange products can be constructed which would give analyses which agree with both the carbon and hydrogen found. Thus it seems safe to assume that both of the fractions are mixtures of basic beryllium carboxylates.

Condensation Polymerizations of a Basic Beryllium Carboxylate and Dibasic Acid Derivatives. Solution Polymerization.—Equimolar quantities of the dibasic acid chloride and basic beryllium carboxylate were weighed accurately on a Gram-atic balance. Total monomer weight was about 10 g. The starting materials were placed in a 50-ml. round-bottomed flask, equipped with a Graham coil condenser, and dissolved in 20 ml. of reagent grade toluene. Benzene, xylene, chloroform and tetrahydrofuran were also satisfactory solvents for polymerization, but toluene was most frequently used because of its convenient boiling point and the ease with which the polymer could be coagulated. Some difficulty was encountered in getting complete coagulation from tetrahydrofuran. The solutions were heated, at 65–95° in the case of aliphatic diacid chlorides and 90–110° in the case of aromatic diacid chlorides, for 16 to 20 hours. Water was not circulated through the condenser so that acetyl or propionyl chloride could evaporate from the reaction mixture. After allowing the reaction mixture to cool to room temperature, it was filtered through a coarse, sintered-glass funnel, and the polymers were coagulated by dropping the solution slowly and with efficient stirring into 200 ml. of medium high boiling petroleum ether in a 400-ml. beaker. The supernate was decanted, and the coagulant washed thoroughly with low boiling petroleum ether or *n*-pentane. The samples were then dried in a vacuum desiccator over calcium chloride for 24 hours. A list of the polymers prepared and the experimental conditions appears in Table II. All of the polymers were initially soluble in toluene.

In handling these polymers, substances which are capable of coördinating with beryllium must be avoided. Thus alcohols cannot be used as coagulants or washes, since they react with the basic carboxylate structure.[6,7] When methanol is used as a coagulant, a material is formed which is an infusible, insoluble solid with a carbon analysis below the value calculated for the repeating unit of the condensation polymer, or for either monomer. Similar results are obtained when acetone is used as a wash. Thus the polymers must be handled exclusively in hydrocarbon solvents, coagulants and washes.

Attempted Sublimation of Polymer Sample.—About 0.5 g. of the polymer was placed in a small cold finger sublimator and heated at 120–140° in an oil-bath at a pressure of 0.01 mm. The formation of a sublimate on the cold finger was noted. The results are listed in the last column of Table II. A plus sign in parentheses means that the basic beryllium carboxylate sublimed out, a plus-minus sign denotes that traces were sublimed out, and a minus sign means that nothing sublimed out.

High Temperature Pyrolysis of Polymer Sample.—About 2.0 g. of the polymer was placed in a test-tube equipped with a 24/40 standard taper joint. This led, through glass connections, to a receiver in a Dry Ice–acetone-bath. The sample was heated to 350° in a Wood metal-bath, and a vacuum of about 100 to 120 mm. was applied. Heating was continued for two hours. At the end of this time, no distillate had collected in the receiver, but some basic beryllium carboxylate had sublimed on the walls of the apparatus above the level of the metal-bath. The residue was insoluble.

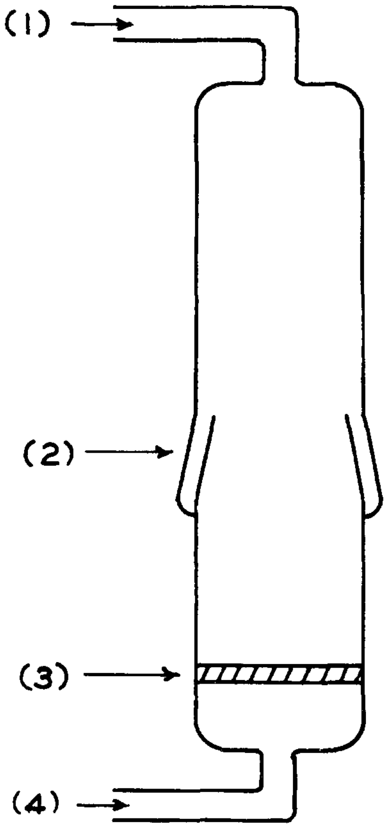


Fig. 1.—Melt polymerization apparatus: 1, to vacuum line; 2, standard taper joint; 3, fine sintered glass plate; 4, nitrogen inlet tube.

Thermal Stability Tests.—Polymers were tested for weight loss by accurately weighing about 30 to 50 mg. of material in a fusion tube, and placing the tube in a furnace. The tube was weighed periodically, and checked for loss of weight.

Melt Polymerization.—Equimolar quantities of the dibasic acid and basic beryllium propionate were weighed accurately on a Gram-atic balance, and mixed intimately by grinding together with a mortar and pestle. They were then

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(5) (a) T. Lieser and K. Macura, *Ann.*, **548**, 226 (1941); (b) P. Ruggli and E. Gassenmeier, *Ber.*, **56**, 1554 (1923).

(6) H. D. Hardt, *Z. anorg. u. allgem. Chem.*, **286**, 254 (1956).

(7) H. D. Hardt, *Angew. Chem.*, **69**, 99 (1957).

TABLE II

POLYMERS OBTAINED FROM BASIC BERYLLIUM CARBOXYLATES

Dibasic acid chloride	Time, hr.	Temp., °C.	$Be_4O(OCOR)_6$		Acid chloride, g.	Acid chloride, mmoles	Yield, %	Carbon, %		Hydrogen, %		Vis-cosity[a]	Concn., g./100 ml.	Days[b,c]
			g.	mmoles				Calcd.	Found	Calcd.	Found			
RCOO = CH_3COO														
Adipic	16	95	6.9510	1.7105	3.1309	1.7105	56	38.89	39.76	4.67	5.13	0.04	0.264	9(+)
Sebacic	16	95	5.4142	1.3323	3.0790	1.3323	25	44.26	44.89	5.79	6.31	..	Insol.	9(+)
Sebacic	20.5	65	5.7157	1.4065	3.2506	1.4065	49	44.26	43.98	5.79	6.05	.06	0.179	5(+)
β-Ethyladipic	16	80	6.0283	1.4834	3.1317	1.4834	56	...	...	..	..	.02	.256	1
Isophthalic	19.75	92	6.0110	1.4792	3.0033	1.4792	63	42.48	43.73	3.56	4.21	.02	.309	7(±)
Terephthalic	17.5	110	6.1265	1.5076	3.0607	1.5075	69	42.48	43.62	3.56	3.99	.01	.269	6(−)
RCOO = CH_3CH_2COO														
Adipic	20.5	65	9.1272	1.8609	3.4062	1.8609	25	44.26	43.91	5.79	5.72	..	Insol.	5(+)
Sebacic	16	95	7.2024	1.4685	3.3939	1.4685	22	48.52	49.19	6.68	7.08	..	Insol.	9(+)
β-Ethyladipic	16	95	7.3165	1.4915	3.1493	1.4918	30	...	...	..	..	..	Insol.	1
Isophthalic	19.75	95	7.4809	1.5253	3.0967	1.5252	63	47.24	47.40	4.78	4.77	0.04	0.269	7(±)
Terephthalic	17.5	108	7.3093	1.4904	3.0260	1.4904	58	47.24	46.80	4.78	4.62	.04	.326	6(−)
RCOO = C_6H_5COO														
Sebacic	17.5	93	3.3798	0.434	1.0023	0.434	47	62.36	61.84	4.93	4.72	0.02	0.280	10(−)[d]
Isophthalic	17.5	100	3.3702	0.304	0.6168	0.304	59	61.71	61.33	3.46	3.95	.02	.259	10(−)[d]

[a] Viscosities in toluene. [b] Days between preparation and viscosity determination. [c] (+) denotes that $Be_4O(RCO_2)_6$ could be sublimed out; (±) means that traces could be sublimed out; (−) means that none could be sublimed out. [d] No $Be_4O(C_6H_5CO_2)_6$ could be sublimed out of the polymers, but the sample had a viscosity of zero and was slightly less soluble after the treatment.

transferred to a melt polymerization apparatus, which is illustrated in Fig. 1. The apparatus was immersed in an oil-bath at 150–160°, and the system was purged with nitrogen. A vacuum (about 120 mm.) was applied in some cases. The mixture soon became a very viscous fluid, and eventually hardened into a glass. Heating was continued until no more bubbles were observed coming through the reaction mixture.

Samples of 4 g. of basic beryllium propionate were heated with molecular equivalent amounts of adipic acid, sebacic acid and terephthalic acid at pressures of 120 mm. and temperatures of 155, 160 and 200°, respectively, for times varying from 3 to 43 hours. All polymeric products thus obtained were insoluble and were not further characterized.

Free Radical Polymerization of Acrylate-containing Basic Beryllium Carboxylates. Basic Beryllium Acrylate.—Six-tenths of a gram (0.0013 mole) of basic beryllium acrylate was dissolved in 73 ml. of *n*-heptane and 5 ml. of toluene. Then 0.0017 g. (0.000007 mole) of benzoyl peroxide (0.5 mole per cent.) was added. After two hours of heating at reflux temperature, the mixture was filtered, and the residue washed with low boiling petroleum ether, then dried at reduced pressure. The yield was 0.5 g. or 80%.

Anal. Calcd. for $C_{18}H_{18}O_{13}Be_4$: C, 45.19; H, 3.80. Found: C, 46.44; H, 4.48.

Basic Beryllium Pentapropionate Monoacrylate.—The procedure was the same as that described in the preceding experiment, using 1.9 g. (0.004 mole) of the basic carboxylate, 0.0126 g. (0.000005 mole) of the initiator (0.13 mole per cent.), and 25 ml. of *n*-heptane. The yield was 1.4 g. or 74%.

Anal. Calcd. for $C_{18}H_{28}O_{13}Be_4$: C, 44.26; H, 5.79. Found: C, 45.12; H, 5.69.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY OF NEW JERSEY]

Studies on the Mechanism of the Wurtz Reaction. The Configurations of 2-Bromoöctane, 3-Methylnonane and 7,8-Dimethyltetradecane

BY EUGENE LEGOFF,[1] STEPHEN E. ULRICH AND DONALD B. DENNEY

RECEIVED AUGUST 9, 1957

The absolute configurations of 3-methylnonane and 7,8-dimethyltetradecane have been determined by relating them to 2-bromoöctane. From this it is concluded that the reaction of 2-chloroöctane with sodium ethyl, although heterogeneous definitely proceeds by an S$_N$2 type of reaction. It also has been shown that the simple Wurtz reaction involving sodium and 2-chloroöctane involves an inversion of configuration of the carbon atom bearing the chlorine. This furnishes further evidence for the hypothesis that the Wurtz reaction proceeds predominantly through an intermediate sodium alkyl, the anion of which then attacks the alkyl halide in an apparent nucleophilic displacement reaction.

In the simple Wurtz reaction,[2] involving metallic sodium and an alkyl halide, presumably a sodium alkyl is formed first[3] and it subsequently reacts with additional alkyl halide to yield the coupled product

$$2Na + RX \longrightarrow RNa + NaX \qquad (1)$$

$$RNa + RX \longrightarrow R{-}R + NaX \qquad (2)$$

The mode of formation of the sodium alkyl,

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[1] Henry Rutgers Scholar, 1955–1956. Abstracted from a thesis submitted by E. LeGoff in partial fulfillment of the B.S. degree, June, 1956.

[2] For a succinct discussion of the mechanism of the Wurtz reaction, and for leading references see J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, pp. 235–237.

[3] A. A. Morton, J. B. Davidson and H. A. Newey, THIS JOURNAL, **64**, 2240 (1942).