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Polymerization. I. The Reaction of Organosodium Compounds with Butadiene

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The purpose of this series is to study the reaction of alkali metals and organoalkali metal compounds on dienes in somewhat the same manner as was employed in the study of the Wurtz reaction.[1] That is to say, the attempt will be made to isolate intermediate steps by addition of butadiene to a large excess of the reagent in order to obtain compounds of low molecular weight which can be carbonated. The structure of the carboxylic acids should then give a clue as to the type of reactions which occur. Reactions in which no intermediate products can be isolated can be set off in a separate class and subjected to other tests which will reveal their characteristics. This first paper serves as a general introduction to the series, shows the type of reagents which are suitable for the isolation of intermediate compounds, and describes briefly the character of the compounds formed.

Amyl-, benzyl- and cyclohexyl-sodium react readily with butadiene when the latter is passed into a well-stirred suspension of the organoalkali metal compound in low boiling petroleum. The products are carbonated, the acids are converted to methyl esters by diazomethane, and the esters are then distilled. The yield of low molecular weight compounds is highest from amylsodium, the better the stirring the better the yield. Where one and two butadiene units have added to the reagent, the saponification equivalent and unsaturation value are approximately the values expected. In higher molecular weight products the two figures do not agree. The proportion of carbethoxy group exceeds the required quantity of unsaturation. Some type of side reaction evidently occurs as the chain becomes longer.

Compounds in which the metal is attached to an aromatic ring or a furyl ring as in phenylsodium, *p*-phenylphenylsodium and furylsodium, do not add to butadiene, but give rubber-like products of high molecular weight. The behavior of this type of compound is abnormal from the standpoint of the reactivity observed in acid-salt interchange,[2] because phenylsodium is between amylsodium and benzylsodium in such reactions, and these last two reagents add readily to butadiene. The failure of the phenylsodium is not caused merely by a cyclic structure in the organic component, since cyclohexylsodium reacts satisfactorily. The difficulty must therefore be related to some special factor which may involve phenyl and furyl anions. Further reference to this point will be made in a later paper.

The high-boiling fractions, *i. e.*, those with three and more butadiene units obtained from the reaction of amylsodium and benzylsodium on butadien, have a great tendency to absorb oxygen and to behave like drying oils. They form skins which cover the surfaces of the liquids in containers, dry to hard films when spread on surface, give off water when heated, particularly when samples have stood for a long time in the laboratory, and darken readily when heated in presence of air. Carbon and hydrogen analyses show, as expected, higher percentages of oxygen than can be accounted for on the basis of the saponification equivalents.

The solid rubbery polymers from the addition reaction and the residues from the various distillations share this tendency to absorb oxygen. For example, the insoluble rubbery polymer produced from benzylsodium becomes hard on standing. Its oxygen content is then about 20%, although the ratio of carbon to hydrogen (8.06) suggests that the number of butadiene units is possibly in the neighborhood of one hundred or more and the percentage of carboxylic oxygen therefore about 1.

The residues from the fractionations of some of these esters underwent thermal cross polymerization. The reaction can be followed by noting the decreased hydrogen absorption after samples are heated at about 230° for varying lengths of time, see Fig. 1. After an initial induction period, thermal polymerization occurs at a logarithmic rate. The product is a resilient, rubber-like mass when air is absent; a colored hard resin if air is present. The process so resembles the thickening which occurs when drying oils are heated that suspicion was aroused lest the carbomethoxy group cause the double bonds to rearrange easily. Whether such a change takes place has not yet been determined but a product free from carbomethoxy groups (*viz.*, from the decomposition of the organosodium polymer by alcohol) undergoes the same thermal changes.

This tendency of the product to undergo cross-linking after the sodium compound has been destroyed by carbonation or by addition of alcohol, is probably caused by the presence of peroxides. Nevertheless, it raises the question as to whether such a cross-linking or some related change can occur prior to carbonation, that is, during the addition of butadiene. It will be recalled that in the field of pyrolysis, amylsodium[3] decomposes at a measurable rate even at 50°, and that some tarry products of comparatively high molecular weight simultaneously form. If such a result is

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[1] Morton, Davidson and Newey, THIS JOURNAL, **64**, 2240 (1942); Morton, Davidson and Hakon, *ibid.*, **64**, 2242 (1942).

[2] Morton, *Chem. Rev.*, **35**, 1 (1944).

[3] Morton and Newey, THIS JOURNAL, **64**, 2247 (1942).

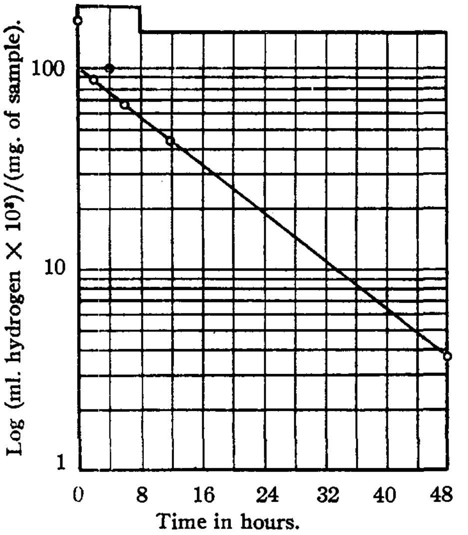

Fig. 1.—Logarithmic decrease in unsaturation with time during thermal polymerization.

indicative of the acceleration or attainment of other reactions when the hydrocarbon component is converted to an anion—and such a view appears reasonable since iodination, oxidation, mercuration, carbonation become possible when the hydrocarbon is in this active form—then the temperature at which cross-linking can occur would be similarly reduced by the presence of a sodium ion, and the final product of polymerization would be one in which a large amount of cross-linking or other change had taken place while the molecular size was increasing by addition of butadiene units. The higher the temperature, the more such a change would occur.

Experimental

Polymerization with Amylsodium (J. D. and G. H. P.).—Experiments were carried out with moderate stirring and with high-speed stirring. The percentage of low molecular weight products increases so greatly when good stirring is used, that the better experiments only will be described in detail. The high speed (10,000 r. p. m.) stirring apparatus already described[4] was employed. The propeller was a six-bladed one[5] which, while excellent, is not as effective as one with a smaller number of blades. The amylsodium was prepared, as usual[1,6] at 0 to −10° from 26.6 g. (0.25 mole) of amyl chloride and 17.3 g. (0.75 g. atoms) of sodium powder suspended in 340 ml. of petroleum ether. The yield of amylsodium prepared under these conditions was approximately 68%. Butadiene (23 g. or 0.44 mole) was bubbled into the petroleum ether at −10° over a period of one and one-half hours. Stirring was continued at this temperature for another half hour during which time the color changed from blue to gray. It was then allowed to warm to 25–30° during a half hour period and was stirred at this temperature for an additional forty-five minutes during which time it became of dark brown color. The mixture underwent most of its reaction at 25 to 30° as judged by the evolution of heat and change in color. The product was subsequently forced by pressure of nitrogen into a large flask which contained lumps of carbon dioxide. After several hours the excess carbon dioxide disappeared. About 100 ml. of water was then added gradually to remove the excess sodium metal. Separation of the aqueous alkaline phase proved extremely difficult, even after addition of more water and salt. The gel-like mass was finally acidified with hydrochloric acid and extracted with petroleum ether. The petroleum ether was then evaporated, the yellow residual liquid mixture of acids was dissolved in ethyl ether and the solution was filtered to remove about 0.4 g. of gummy material. The aqueous layer was saturated with salt and extracted with several portions of ether. The ethereal solutions were combined, concentrated, and methylated with an excess of diazomethane. The resulting ethereal solution was concentrated, freed from any unmethylated acid by extraction with two 50-ml. portions of 5% sodium carbonate, dried over Drierite, and finally distilled at 2–3 mm. in a modified Claisen flask, the side neck of which was a 6-inch Vigreux column. The results showed that out of a total of 36.7 g., about 2.4 g. was methyl caproate, 24.9 g. was a mixture of the methyl esters of carboxylic acid which had less than four butadiene units present and 9.3 g. was residue. The viscosity of each fraction collected increased with increase in boiling point. The final portion (b. p. 190–215°) had the consistency of glycerol; the residue that of molasses. From a somewhat similar experiment in which the stirring was less effective, only 4 g. of the carbonated and esterified product of the addition reaction was obtained by distillation, and the proportion of higher molecular weight products was correspondingly higher.

Since the results in the high-speed stirring apparatus seemed satisfactory, five identical experiments were made and the combined lot of esters fractionated at 8 mm. through a column of about twenty-four theoretical plates. Data are recorded in Table I. Fraction 1 was largely methyl caproate. The second and third fractions contained some unsaponifiable oil, probably decane or other by-products as well as ester. These fractions were therefore saponified, the unsaponifiable matter separated and the neutralization equivalent and absorption of hydrogen determined for the free acid. The analyses of carbon and hydrogen were made on the esters of the purified acids because combustion of the acid was complicated by formation of a resistant copper salt. The weight of product recorded for each of the first three fractions is, in fact, that of the weight of free acid and is therefore less than the true weight of ester obtained. The total weight collected for each of these samples was 12.5, 10.3 and 7.3 g., respectively, of which approximately 80% in each case was the ester. Fractions 4 and 5 were apparently very good products judged by the agreement in the number of butadiene units calculated from the saponification equivalent, carbon and hydrogen content and absorption of hydrogen. Fractions 6, 7, 8 show no agreement in the number of butadiene units, as calculated by the various methods. The difficulty may be caused by ring formation, absorption of oxygen after reaction is completed, or inclusion of hydrocarbon polymers with the long chain acids. This aspect of the problem will be investigated later.

The inadequacy of poorer stirring conditions is shown by the fact that only 4 g. of a mixture of esters which may have had as high as four butadiene units was obtained from the action of 74 g. of butadiene with amylsodium prepared from 32 g. of amyl chloride and 25 g. of sodium.

The failure of metallic sodium to add readily to butadiene under these conditions was demonstrated by an experiment approximately the same as before which employed 9 g. of sodium and 21 g. of butadiene, but no amyl chloride. The amount of acid obtained after carbonating and separating in the usual manner amounted to 0.14 g. It was a dark brown oil which amounted to less than 1% of the butadiene used.

The Horn-like Resin and Pyrolysis During Reaction (G. H. P.).—One of the reactions, carried out as mentioned before but with 40.3 g. (0.75 mole) of butadiene, became very vigorous at 30° and required much more than the usual amount of cooling, though the maximum tem-

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[4] Morton and Davidson, This Journal, **64**, 2240 (1942); Morton, Darling and Davidson, *Ind. Eng. Chem., Anal. Ed.*, **14**, 734 (1942).

[5] Morton and Knott, *ibid.*, **13**, 649 (1941).

[6] Morton and Richardson, This Journal, **62**, 123 (1940).

TABLE I

DATA FOR FRACTONS FROM COMBINED PRODUCTS OF FIVE EXPERIMENTS. CALCULATION OF BUTADIENE UNITS

Frac. no.	B. p., °C.	Wt., g.	Sapon. equiv.	Combustion of ester, %		No. of butadiene units[a] from			C/H
				C	H	H_2	S. E.	Anal.	Ratio
1	28–38	7.6	128.1[b]						
2	64–84	5.5	168.9[b]	71.7	11.0	0.98	0.99	1.00	0.93
3	85–104	4.3	148.3[b]						
4	109–130	18.6	245.2 246.2	75.6	11.0	1.98	2.13	2.00	2.0
5	132–150	10.8	237.7 238.7	75.4	11.1	2.00	2.00	1.99	2.0
6	156–174	18.1	295.9 295.8	75.1	10.5	2.79	3.07	1.99	3.0
7	174–199	12.2	294.4 294.4	75.1	10.4	2.76	3.05	1.99	3.0
8	201–210	15.5	319.1 318.2	75.2	10.6	2.52	3.49	1.99	3.0

[a] The number of butadiene units is calculated from the amount of hydrogen absorbed, the saponification equivalent (or neutralization equivalent), the data on combustion and the ratio of weight of carbon to hydrogen. This last method has some value as a method for approximation of the size of the higher molecular weight products. [b] Neutralization equivalent.

perature observed did not exceed 40° and the mixture was undoubtedly cooled by petroleum ether which distilled from the mixture during the reaction. Fractional distillation of the derived esters gave (a) a portion boiling at 31.5 to 80°, which by saponification equivalents appeared to have about two butadiene units per molecule; and (b) 15.3 g. of unsaponifiable distillate boiling up to 200°. The residue (26 g.) accounted for the greater proportions of the reactants. It was a hard, brown semi-clear thermosetting resin formed by polymerization of the products of high molecular weight. This material was insoluble in ethyl acetate, ethyl alcohol and *n*-heptane but exhibited slight swelling or softening in benzene, acetone and ether, and marked softening in carbon tetrachloride. It was stable to five hours of refluxing with a 2% solution of permanganate in 5% sodium hydroxide. Hot concentrated sulfuric or nitric acids disintegrated the product. Analysis showed that the composition was 80.4% carbon, 9.8% hydrogen and 9.8% oxygen (by difference). The ratio of percentage of carbon to hydrogen is 8.2%. This value is a little larger than that calculated on the basis that the polymer had one hundred or more butadiene units (*ca.* 8.0). If the molecule is this large, the amount of oxygen present would be equivalent only to approximately 0.2 mole of oxygen per double bond.

Thermal Polymerization (G. H. P.).—Small samples (*ca.* 0.2 ml.) of the high boiling polymeric esters were sealed in tubes 7 mm. in diameter and 6 cm. long, and then placed in a vertical position in an oven. At various intervals the tubes were removed, the contents cooled, the physical state noted, and in some cases the unsaturation determined. These preliminary tests showed that the process of thickening or setting to a resilient rubber-like mass was very slow at 160°. At 250°, the samples, particularly the higher fractions and the residue, exhibited a significant increase in viscosity after three hours, but darkened and decomposed after longer periods. At 230°, the thickening process occurred without much discoloration. Polymerization of an ester which had been obtained by distillation at 225–245° (bath temperature) and 4–5 microns and which had a saponification equivalent of 352.4, corresponding to 4.1 butadiene units, was followed by sealing small portions (20–30 mg.), just sufficient for analysis by catalytic hydrogenation, in small hydrogenation vials, and placing them for varying lengths of time in a constant temperature oven at 230°. The measured decrease in the number of double bonds is plotted in Fig. 1 on a logarithm scale. A sample of high molecular weight ester (saponification equivalent, 1562) which had been obtained in the experiment with moderate stirring and had stood in the laboratory for about nine months, was also heated at 230°. The material, which at the start had been colorless, became discolored and cloudy after a day of heating. Water was split from the mixture and condensed as a drop in the capillary at the top of the tube as the sample cooled.

Hydrocarbon Polymers (G. H. P.).—The addition of butadiene (0.45 mole) to 0.17 mole of amylsodium was carried out as described for the reactions with good stirring. The product was decomposed with alcohol instead of carbon dioxide. The products were distilled in an Hickman alembic type apparatus at pressures near 5 microns. Fractions boiling at a bath temperature of 60–100° (5.4 g.), 101–120 (3.3 g.), 120–145 (1.6 g.) and higher—up to 231–255°—were collected. These products, the higher boiling ones particularly, likewise became more viscous when heated at 230°. Cloudiness was then apparent. A droplet of water separated after long heating.

Cyclohexylsodium and Butadiene (G. H. P.)—Chlorocyclohexane[7] (178 g. or 1.5 mole) was added to 104 g. (4.5 g. atoms) of sodium sand in about 300 ml. of petroleum ether at about 25°. To the organosodium compound (9% yield) so prepared, was added 6.5 g. (0.12 mole) of butadiene over a one-half hour period at about −10°. After being stirred for an additional half hour the mixture was allowed to warm to 25–30° within another thirty minutes and was stirred at that temperature for forty-five more minutes. It was then carbonated by pouring on Dry Ice, and the products were treated in the usual manner. The gummy insoluble material amounted to about 1.9 g. The methyl esters (6.6 g.) were distilled at 3 mm. in the Claisen–Vigreux flask. All were distilled below 145° at 3 mm. and showed saponification equivalents which were equivalent to less than four polymeric units of butadiene. The yield of ester per mole of organosodium compound employed was essentially identical with that obtained from amylsodium with butadiene, although the actual number of grams obtained was less because of the low yield of cyclohexylsodium from chlorocyclohexane.

Benzylsodium and Butadiene (E. L.).—Amylsodium was prepared from 10 g. of sodium sand and 15.5 g. of *n*-amyl chloride in *n*-octane by the high speed stirring technique. Sulfur-free toluene (94 g.) was then added rapidly and the mixture allowed to warm to 30–50°. It was stirred at this temperature for three hours, then cooled to −10° and treated with 10 g. of butadiene added gradually at the rate of 6–8 bubbles per minute during one hour. At the end of that time the temperature was allowed to warm to 30° and an hour later the mixture was forced on carbon dioxide by increasing the pressure of nitrogen. The remainder of the treatment was in general the same as before. Fractionation of the methyl esters

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[7] Perlman, Davidson and Bogert, *J. Org. Chem.*, **1**, 294 (1936).

at 3 mm. in a Claisen–Vigreux flask gave the results listed in Table II.

TABLE II

Fraction	Boiling range at 3 mm., °C.	Amt., g.	Sapn. equiv.		Butadiene units calcd.
1	68–75	3.1	214.8	208.1	1.13
2	110–120	1	259.6	263.0	2.05
3	132–140	1.4	246.8	260.0[a]	...
4	160–175	0.8	363.3	357.0	3.92
5	183–190	0.8	566		7.7
Residue above 190°		2	139.0		22.9

[a] Some methyl homoisophthalate obtained in this fraction.

The solid rubbery product isolated from this reaction absorbed oxygen and in time became hard and brittle. Analysis of one of these products which had stood for two months showed average values of 71.0% carbon, 8.9% hydrogen and 20.1% oxygen. The carbon–hydrogen ratio is 0.667 which approaches the value 0.670 for 100 butadiene units (50 units is 0.675). On this basis the absorbed oxygen would have been 0.86 atom per double bond. The true size of the molecule is probably larger than this value.

The residue likewise underwent thermal polymerization to a rubbery solid when heated at 230° for four days.

The Action of Phenylsodium, Furylsodium and *p*-Phenylphenylsodium (G. H. P.).—All attempts to prepare phenylsodium by addition of amyl chloride to a suspension of sodium in benzene or benzene–*n*-octane mixture, while stirred in the high speed stirring apparatus at 25–40°, resulted in the formation of solid gels. This result was unexpected because in previous work[8] with ordinary stirring this method of preparing phenylsodium served excellently. The compound was, however, prepared smoothly from chlorobenzene and sodium. Addition of butadiene to this product failed to produce any short chain acids. As many as five experiments were made. Variation of time and temperature yielded no isolable products of low molecular weight.

2-Furylsodium was prepared by metalation of 51 g. (0.75 mole) of furan with benzylsodium. Addition of 18.5 g. of butadiene in the customary manner led to no short chain acid products.

p-Phenylphenylsodium was prepared from chlorobiphenyl and one and a half equivalents of sodium under conditions which were demonstrated by carbonation to give a 78% yield of *p*-phenylphenylsodium. Addition of butadiene in the customary manner produced no short chain acid products, but yielded small amounts of sticky rubber-like products.

***p*-Dichlorobenzene and Sodium** (G. H. P.).—*p*-Dichlorobenzene (25.4 g.) was treated with 23 g. of sodium powder in 310 ml. of *n*-octane at 62°. (The reaction did not occur appreciably at 25°.) The total time for addition was one hundred minutes. The mixture was stirred for an additional hour and the black-colored product poured on carbon dioxide. A very small amount only of brown resinous acid was obtained. No terephthalic acid could be detected.

Summary

Under the conditions tried butadiene adds with amyl-, benzyl- and cyclohexyl-sodium. The sodium compounds are decomposed by carbon dioxide or by water and alcohol to give acids or hydrocarbons.

The acids and derived esters having saponification equivalents and double bonds which correspond to addition of one or two butadiene units can be isolated readily. Those which have three or more units show unsaturation lower than expected and an oxygen content which is abnormally high. Other properties of the esters suggest that oxygen is absorbed readily.

These compounds, whether as esters or the corresponding hydrocarbons, undergo thickening by a thermal polymerization at 230°. The residues and rubber-like products undergo a similar thermal polymerization.

Phenylsodium, furylsodium and *p*-phenylphenylsodium do not add readily to butadiene. Rubber-like products are formed by these reagents.

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[8] Morton and Fallwell, THIS JOURNAL, **59**, 2387 (1937); **60**, 1429 (1938).

[9] Original manuscript received December 30, 1942.

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Studies in Chemotherapy. XII. Some Sulfanilamidoheterocycles

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Since the original report of the synthesis and high antibacterial[1a] activity of sulfadiazine (2-sulfanilamidopyrimidine), numerous derivatives of the sulfanilamidopyrimidines have been prepared and described.[2] The compounds reported here have been prepared in the continuing search for compounds of higher intrinsic activity and with better pharmacological properties. In addition to the usual bacterial tests, some of these have been subjected to malarial screening using *Plasmodium gallinaceum* in chickens as a test infection.

Most of the required aminopyrimidines were prepared by known methods. 2-Amino-4-*t*-butylpyrimidine was synthesized from guanidine carbonate and the copper derivative of formylpinacolone (4,4-dimethyl-1,3-pentanedione).[3] The procedure was simpler and the yield better than when free formylpinacolone was used.

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[1] Present address: 4717 North Illinois St., Indianapolis 8, Indiana.

[1a] R. O. Roblin, Jr., J. H. Williams, P. S. Winnek and J. P. English, THIS JOURNAL, **62**, 2002 (1940).

[2] *For instance:* (a) W. T. Caldwell, E. C. Kornfeld and C. K. Donnell, *ibid.*, **63**, 2188 (1941); (b) J. M. Sprague, L. W. Kissinger and R. M. Lincoln, *ibid.*, **63**, 3028 (1941; (c) K. Ganapathi, *Proc. Indian Acad. Sci.*, **13A**, 386 (1941); (d) R. O. Roblin, Jr., P. S. Winnek and J. P. English, THIS JOURNAL, **64**, 567 (1942); (e) G. W. Anderson, H. E. Faith, H. W. Marson, P. S. Winnek and R. O. Roblin, Jr., *ibid.*, **64**, 2902 (1942).

[3] Couturier and Vignon, *Compt. rend.*, **140**, 1696 (1905).