aspect of the problem. Considerable disubstitution also occurs in some instances.

The work on the olefins suggests that rubber also should be a hydrocarbo acid and susceptible to metalation by amylsodium or other organoalkali metal reagent. This expectation is realized but the rubber undergoes also considerable cross-linking. The details of this work have an important bearing on the problem of gel formation of rubber during sodium polymerization and will be discussed at length in a paper on that subject.

The activity relationships discussed in this paper are, fundamentally, those in acidity, not merely in reactivity to a specific reagent. Therefore, a similar interchange could be a factor in the case of any reagent that is at the tip of the growing system. In this particular instance the reagent happens to be a metal ion, which can shift from the tip to a position along the stem. If the reagent were an odd electron (a free radical), it too should shift to a lateral position; for one of the accepted reactions of a free radical is the abstraction of reactive or acidic hydrogen,[2] even such hydrogen atoms as are present in olefin-free petroleum ether where the acidity is far less than in the olefins.

The authors are greatly indebted to the Research Corporation for financial support of this study.

Experiments

The general process of preparing amylsodium from amyl chloride and sodium and benzylsodium from toluene and amylsodium was the same as that already described in publication[3] from this Laboratory, one of which is a preliminary account[4] of the metalation of olefins. The reaction with the olefin was effected by addition of the hydrocarbon to the organosodium reagent. The mixture was stirred in the high speed stirrer, and then allowed to stand overnight. The products were carbonated by pouring on solid carbon dioxide. The acids recovered therefrom were distilled at reduced pressure. The monocarboxylic acids derived from the olefins were identified by neutralization equivalents and the presence of unsaturation. The dicarboxylic acids remained as a residue and were similarly characterized. The results are given in Table I.

Summary

Olefins which can be regarded as typical of the tip and stem of a polydiene are shown to be metalated readily by an organoalkali metal reagent such as amylsodium. The result is used as a basis for predicting that the chance of branching in a polymer produced by a stepwise formation of an organosodium compound, will be extremely high even though the mechanism of chain growth might happen to be exclusively 1,4-addition.

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[2] Gomberg, *Chem. Rev.*, **1**, 121 (1924); Hay and Waters, *ibid.*, **21**, 169 (1937).

[3] Morton, Davidson and Newey, THIS JOURNAL, **64**, 2240 (1942); Morton, Little and Strong, *ibid.*, **65**, 1939 (1943).

[4] Morton, Brown, Holden, Letsinger and Magat, *ibid.*, **67**, 2224 (1945).

CAMBRIDGE 39, MASS. RECEIVED APRIL 1, 1946

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polymerization. III. An Examination of Low Molecular Weight Products from the Reaction of Amylsodium with Dienes

BY AVERY A. MORTON, MALCOLM L. BROWN AND EUGENE MAGAT

Previous work[1,2] has shown that low molecular weight products from the polymerization of butadiene by organoalkali metal reagents can be isolated and that there is a great likelihood that the metal ion shifts from the tip to the stem of the growing polymer, thus leading to chain-branching. The present contribution will show: (a) that the mixture of low molecular weight products from the reaction of amylsodium with butadiene contains a small amount of material that is the result of 1,4-addition, but that the larger part is the result of the 1,2-addition or of acid–salt interchanges that simulate 1,2-addition; (b) that methyl groups in the diene at the 2- and 3-positions, as in isoprene and dimethylbutadiene, reduce the rate of polymerization, increase the likelihood of branching and decrease the tendency for 1,2-addition; (c) that the changes caused by methyl groups in the diene correspond with the changes caused by methyl groups in other reactions by organoalkali metal reagents; and (d) that triethylamine accelerates the rate of addition, but cumene as a solvent has little special influence on the reaction.

Low Molecular Weight Addition Products.—The method employed was to add butadiene to amylsodium and, after a period, to force the reaction products on solid carbon dioxide. The mixture of acids thus obtained was separated by combinations of fractionation at reduced pressure, extraction with aqueous alkali in order to remove the acids from the unsaponifiable matter, fractionation by a multiple-fractional extraction process,[3] and by use of the methyl esters and the hydrogenated products; all designed to isolate the products of addition of one amylsodium to one butadiene. From one series of purifications, which ended with the separation of the hydrogen-

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[1] Morton, Patterson, Donovan and Little, THIS JOURNAL, **68**, 93 (1946).

[2] Morton and Brown, *ibid.*, **68**, 160 (1946).

[3] Hunter and Nash, *Ind. Eng. Chem.*, **27**, 836 (1935). See Morton, "Laboratory Technique in Organic Chemistry." McGraw-Hill Book Co., New York, N. Y., p. 200.

TABLE I

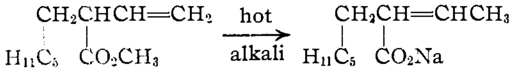
CHANGE IN FORMALDEHYDE ANALYSIS IN ESTERS DERIVED FROM THE MOLECULAR WEIGHT ADDITION PRODUCTS OF AMYLSODIUM WITH DIENES

Diene[a]	Poly. temp., °C.	Esters		Formaldehyde percentages in fractions			Obs. ratio of diene units to carbomethoxy groups in each fraction		
		Total wt., g.	B. r., °C.	First	Middle	Last	First	Middle	Last
B	25	9.5	50–185	47	31	21	1:1	1.9:1	3.1:1.5
B	15	4.3	88–190	27	24	18	1:1	2:1	2.6:1
B	−5	2.1	65–175	38	23	25	1:1	2:1	2.6:1
B[b]	15	10.5	68–180	24	25	..	1:1	1.9:1.1	2.6:1.1
I	25	3.2	60–215	11	12	26	1.3:1.8	2.2:1.6	2.9:1.3
D	25	8	83–155	16	..	8	1:3:1.8	.....	2.0:1.9
B[c]	25	19.1	60–190	40	21	14	1:1	2:1	3.0:1.5
B	25	16.8	95–195	32	27	21	1:1	2.5:1.5	2.5:1.2

[a] B = butadiene; I = isoprene; D = dimethylbutadiene. [b] Excess sodium and diene present. [c] Triethylamine present.

ated acids, crystals of pure capric acid separated. A very small amount of 1,4-addition, therefore, occurs.

Isolation of a crystalline product that stems from 1,2- addition is more difficult and has not yet been effected. Chemical tests show, however, that some, and possibly all, of the 1,2-product has sodium at C_2 because the carbonated product is a β,γ-unsaturated acid with the unsaturation on the end. Before saponification of one fraction of the esters, ozonization and hydrogenation yielded considerable formaldehyde; after saponification it gave acetaldehyde, but no formaldehyde. A β,γ-unsaturated acid, as shown below, would re-



$$\underset{H_{11}C_5\quad CO_2CH_3}{CH_2CHCH{=}CH_2} \xrightarrow[\text{alkali}]{\text{hot}} \underset{H_{11}C_5\quad CO_2Na}{CH_2CH{=}CHCH_3}$$

arrange readily, but the γ,δ-unsaturated acid, $H_2C{=}CHCH(C_5H_{11})CH_2CO_2Na$, the ultimate product of 1,2-addition with sodium at C_1, would not.

The proportion of 1,2-addition in the first adduct is very high, but in higher adducts seems less. For example, ozonization and hydrogenation of the monoadduct (see Table I) yields from 27 to 47% of formaldehyde, isolated as the dimethone derivative. A similar test of various fractions of esters which boil from about 60 to 200° at 3 mm. and which contain from one to three diene units, shows a decrease of formaldehyde with increase in boiling point. Since this method gives lower results than the true value, and in control experiments has often given only half of the theoretical amount of formaldehyde, the assumption might be made that 1,2-addition in the early phases of the reaction was as high as 80%. The 1,2-addition products may of course be derived by rearrangement,[4] shown below

$$RCH_2CH{=}CHCH_2Na \longrightarrow RCH_2CH(Na)CH{=}CH_2$$

of a 1,4-addition compound, or from structures that contribute to resonance

$$[RCH_2CH{=}CHCH_2 \longleftrightarrow RCH_2CHCH{=}CH_2]Na$$

Rearrangements are likely in view of the fact that they occur in the case of the comparatively mild Grignard reagent.[5] The net result, however, would be the same, and branching should increase as a result of the position of sodium at the side of the chain.

One of the important ideas of this study is that the use of an organoalkali metal reagent as the polymerization agent means also that one of the favored reactions of such reagents, namely, acid–salt interchange or metalation, will occur. Two evidences of such an effect can be presented. The first is that some of the non-acidic fraction boils in the range of the C_9 compounds and is unsaturated. An intermolecular acid–salt interchange of the type shown below would account for this material.

$$\begin{aligned}&C_5H_{11}CH_2CH{=}CHCH_2Na\ +\\&\quad C_5H_{11}(CH_2CH{=}CHCH_2)_nCH_2CH{=}CHCH_2Na \longrightarrow\\&\qquad C_5H_{11}CH_2CH{=}CHCH_2H\ +\\&\qquad\quad C_5H_{11}(CH_2CH{=}CHCH_2)_nCH(Na)CH{=}CHCH_2Na\end{aligned}$$

The second evidence is that the higher boiling adducts show too low a saponification equivalent for the boiling points and hydrogenation values. Hence the diallyl or other units along the stem of the polymers suffer metalation by the amylsodium. This metalation shows the acidity of the polymer and the likelihood of the inter- and intramolecular acid–salt interchanges suggested in the second paper[2] of this series.

This study of the carbonated organoalkali metal products has several advantages over the examination by Ziegler[6] of the products obtained by addition of water to the adducts. The variety of methods for separation of products is greater; solid derivatives, whose structures and identities are easily ascertained, can be isolated; the position of the carboxyl group and, therefore, of the sodium ion, can be located.

Effect of Methyl Groups.—Methyl groups at C_2 or C_3 in the diene probably increase the branching, increase the percentage of 1,4-addition and decrease the rate of addition. That they increase the likelihood of branching is shown by the greater ease of metalation of the adducts of isoprene, or of dimethylbutadiene, by amylsodium, during the

(4) Ziegler, Dersch and Wolltham, *Ann.*, **511**, 13 (1934).

(5) Lane, Roberts and Young, THIS JOURNAL, **66**, 543 (1944).

(6) Ziegler, Grimm and Willer, *Ann.*, **542**, 90 (1939).

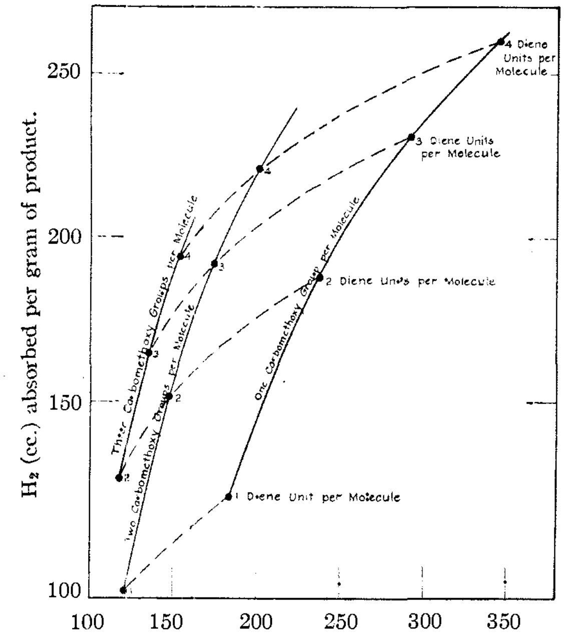


Fig. 1.—Degree of metalation of organoalkali metal diene adduct.

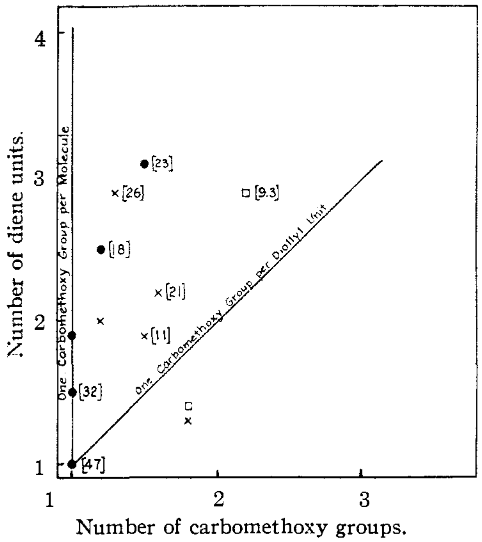


Fig. 2.—Tendency toward branching as indicated by degree of metalation: ●, butadiene; ×, isoprene; □, dimethylbutadiene; values in brackets are percentages of formaldehyde obtained after ozonization.

addition reaction with this reagent, as contrasted for the corresponding adducts with butadiene. Each diene was added dropwise to amylsodium, under conditions as nearly comparable as possible, and the products derived therefrom were carbonated, esterified and then fractionated. The saponification equivalent and unsaturation per gram of each fraction were determined and the values compared with theoretical values on a graph, so that the number of diene units and the degree of metalation (carbomethoxy content) could be approximated. The graph used for butadiene is shown in Fig. 1. Similar graphs were constructed for the isoprene and dimethylbutadiene adducts. All values so obtained were then transferred to a second graph (Fig. 2) which showed the number of carbomethoxy groups per diene unit. One carbomethoxy group should be present for each chain of adducts if no metalation by amylsodium or if no intermolecular acid–salt interchange occurs. All data for fractions, which contain this quantity only of ester groups, lie on the vertical line of the graph. All points to the right of that line represent metalation of the diene adduct; the further to the right, the greater the metalation and therefore the greater the likelihood of acid–salt interchange.

The data show that the isoprene and dimethylbutadiene adducts have more acidity than do the compounds obtained from butadiene. Each fraction of the products of either of the methyl-containing dienes has more carbomethoxy groups than is required for chain growth; in some cases, close to one carbomethoxy group per diallyl unit is present. The products from butadiene, however, seldom contain more than one ester group per chain until over two butadiene units have been added. Since substitution (metalation) occurs along the stem of the growing chain, the acidity of the sides of the chains which contain the methyl groups must be greater than that along the side of the butadiene product. The increase is caused by two factors; one that a vinyl group is appropriately located to activate the methyl group and the other is that the relative proportion of active hydrogen atoms in the stem increased (see Table II). The ratio is higher for the isoprene and dimethylbutadiene adducts in every instance save one, and this exception, for reasons to be discussed later, is the less likely of the two possibilities of addition to isoprene.

TABLE II

COMPARATIVE NUMBER OF ACTIVE HYDROGEN ATOMS AVAILABLE FOR INTERCHANGE IN POLYMER GROWING BY 1,4-ADDITION

Diene used in addition process	Active hydrogen atoms in stem of final diallyl unit[a]	Active hydrogen atoms in tip	Ratio. diallyl/tip
Butadiene	4	3	1.3
Isoprene			
One alternative	10	3	3.3
Second alternative	7	6	1.1
Dimethylbutadiene	13	6	2.2

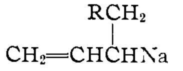
[a] The hydrogen atoms attached to the vinyl group are not included in this calculation.

That methyl groups in isoprene and dimethylbutadiene enhance the amount of 1,4-addition, is evidenced by the fact that ozonolysis leads in general to less formaldehyde from the methyl dienes adducts than from the butadiene adducts, see Table I. Only one exception was found and this result was with a fraction of higher boiling adducts.

The methyl groups suppress the yield of addition product. For instance, the proportion of products boiling below 180° at 3 mm. are as 9.5 to 4.3 to 1.1 as butadiene, isoprene and dimethylbutadiene are employed; and the quantities of unused amylsodium, measured as caproic ester, are as 4 to 11.5 to 16.5, respectively. This fact also has some bearing on 1,4-addition for it agrees with the general theory[7] that alkyl groups reduce acidity, indicates antagonism of a methyl or alkyl group for the attachment of a sodium ion to these dienes by an addition process at C_2, the favorite position of attachment of sodium to butadiene, and suggests that a shift toward a 1,4-addition process could occur.

Comparison with the General Influence of Methyl Groups.—By and large the effect of the methyl groups in these dienes is that expected from the effects noted in the studies of the metalation of simple hydrocarbons. For example, the comparative ease of metalation of benzene toluene and *o*-xylene[8] shows that the first methyl group attached to the aromatic nucleus becomes the center of anion activity, but that the second methyl group markedly depresses this activity. Similarlyin the series ethylene,[9] propylene and 2-butene there is first an increase and then a marked decrease in activity. The activity at a methyl group unquestionably comes from the presence of an adjacent phenyl or vinyl group. In the case of propylene the system can be represented by the formula, $\overset{\curvearrowleft}{CH_2}{=}CHCH_2Na$, in which polarization of the vinyl group occurs. Obviously a methyl or alkyl group on the end away from the anion center would oppose this polarization and thus diminish the acidity. Hence butene-2 is a much weaker hydrocarbo acid than is propene. On the other hand a methyl or alkyl group on the same side of the double bond, as in isobutene, should enhance the polarization of the double bond, though at the same time it will diminish the acidity of the anion center by an inductive effect. In the special case of isobutene, however, the total number of active hydrogens is twice as great as in propene. The net result of these influences is that isobutene has a comparatively high degree of acidity, possibly greater than propene.

These considerations can now be applied to the dienes. The addition of an alkylsodium compound to butadiene, irrespective of whether it is 1,2 or 1,4, or whether it is entirely 1,4- with an allyllic rearrangement or a structure that contributes to resonance, will end with a system that will act as if sodium is at C_2 or C_4. If the metal ion is at C_2 the product will have alkyl groups on one side only of the double bond; if it is at C_4 it will have an alkyl group on the side away from the sodium ion. The former would be the salt of a stronger acid and should be present in larger quantity. According to our measurements it does.



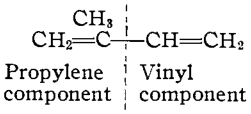
$$CH_2{=}CH\overset{\displaystyle RCH_2}{\overset{|}{C}}HNa$$

1,2-product

$$RCH_2CH{=}CHCH_2Na$$

1,4-product

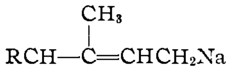
The influence of the methyl group at C_2 as in isoprene or dimethylbutadiene could be twofold; one as a point at which metalation might occur and the other as a group that influences the position where the sodium ion becomes attached. As to the former, the methyl group in isoprene is not properly located[10] to become activated for metalation because the polarization in the propylene component is opposed by the effect of the vinyl component.



$$CH_2{=}\overset{\displaystyle CH_3}{C}{-}CH{=}CH_2$$

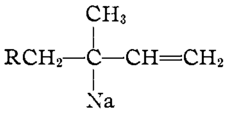
Propylene component | Vinyl component

As to the latter, the methyl group would retard addition of amylsodium because the anion thereby formed would be from a weaker hydrocarbo acid than the corresponding one in the addition to butadiene. The observed results accord with this view. The methyl group would also alter the proportion of the "so-called" 1,2- and 1,4-addition because the general influence of the methyl group would be to repel electrons from the center of the diene chain to the end. The rate of addition is, therefore, greatly retarded, and the trend is for the metal ion to become attached at a point as far removed from the methyl group as possible. This position would be as shown below, and the corresponding hydrocarbo acid would have three active hydrogen atoms. The product of allylic rearrangement of this compound, that is, a 1,2-product, would be a salt of a tertiary hydrocarbo acid, which has only the one active hydrogen atom. The influence of the vinyl group, even though unsubstituted on the far side, is not sufficient to raise the acidity to a high enough level to overcome these adverse factors. Hence the proportion of product that seems to come from a 1,2-addition diminishes. In general, similar considerations apply to the effect of the two methyl groups in dimethylbutadiene.



$$RCH{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CHCH_2Na$$

1,4-Addition



$$RCH_2{-}\underset{\displaystyle Na}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}{-}CH{=}CH_2$$

1,2-Addition or allylic form of 1,4-product

One major purpose of this section has been to emphasize that the methyl group in the

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[7] Morton, *Chem. Rev.*, **35**, 1 (1942).

[8] Morton, Little and Strong, THIS JOURNAL, **65**, 1939 (1943).

[9] Morton, Brown, Holden, Letsinger and Magat, THIS JOURNAL, **67**, 2224 (1945).

[10] The methyl group in piperylene on the other hand is correctly located. Metalation occurs readily. This work will be reported in a later paper.

dienes exerts a normal influence. There is justification, therefore, for expecting normal effects[7] from other groups. Ethyl, *i*-propyl, or better, tertiary alkyl substituents, instead of a methyl group in the middle of the diene, should reduce the acidity markedly, and hence lower the likelihood of branching and raise the tendency toward 1,4-addition. These changes should lead to a better rubber but the rate of polymerization would be very slow.

Effect of Triethylamine and Cumene.—Triethylamine accelerates the addition of amylsodium to the dienes but does not change the manner of addition appreciably because the percentage of formaldehyde obtained after ozonization of the product is essentially unchanged. The amine probably forms a complex with the reagent because tertiary amines form complexes with another organometallic compound, the Grignard reagent. Coördination of the amine with the cation should satisfy some of the attractive force of the cation for electrons and thus make the bond between the organic anion and the sodium cation more labile.

Quite apart from its effect on the addition reaction, the triethylamine has a very interesting influence on the proportion of butylmalonic acid obtained by jet carbonation of the amylsodium. About 50% yield resulted in the presence of the amine, whereas usually the amount is trifling.

Cumene was tried in place of pentane as a solvent since this aromatic compound should be attacked by the amylsodium at a very slow rate and the metalated aromatic compound should not add to the diene, judged by the behavior of phenylsodium. No significant difference from the results in pentane, other than an accelerated reaction, were observed. Hence the addition reaction does not appear to be influenced by hydrocarbon solvents that are not attacked by the amylsodium reagent and this result is as would be predicted.

The authors are greatly indebted to the Research Corporation for financial support of this work.

Experiments

Amylsodium.—This reagent was prepared as usual[8,9] by dropwise addition of an equivalent quantity of amyl chloride to sodium at −5 to −10° in the high speed stirring apparatus. The yield is 75% as a rule and the amount thus prepared is 0.19 mole.

Dienes.—Phillips' research grade butadiene was employed. It was freshly distilled before use although this precaution was probably unnecessary. The isoprene was made by pyrolysis of dipentene. It was carefully fractionated through a twenty-five plate column. The dimethylbutadiene was synthesized by the conventional process[11] from acetone. It was similarly fractionated and the fraction from 68.2 to 68.3 collected.

Butadiene Low Molecular Weight Products (by M. B.).—Butadiene (0.19 mole) was added dropwise at 20° to 0.19 mole of amylsodium suspended in pentane with high speed stirring at 10,000 r. p. m. in an atmosphere of nitrogen. The addition was completed within one to one and a half hours. Stirring was continued until a total time of four hours had elapsed. The color changed from the light blue of amylsodium to olive green to dark brown. Finally the mixture was forced onto solid carbon dioxide.

The aqueous solution of the carbonated products was acidified, and then filtered to remove about 0.4 g. of gummy material. The clear aqueous layer was extracted with 50 ml. of petroleum ether and, after saturation with sodium chloride, extracted with two 75-ml. portions of ethyl ether. The petroleum extract yielded about 27 g. of yellow oily products; the ether extract contained a very small amount of material.

The petroleum extracts from ten separate experiments were combined to give 270 g. and freed from non-acid material by solution in 27 liters of water which contained 80 g. of sodium hydroxide and 2000 g. of sodium chloride, by agitation with 6.1 liters of petroleum ether, and by separation of the layers overnight. These operations were carried out in five gallon bottles. The large amount of water was required because the salts of the high molecular weight acids caused serious foaming. Three layers separated. The lower aqueous layer was removed with a siphon. The upper petroleum layer was separated by decantation. The middle layer was discarded because it was gelatinous and obviously consisted of very high molecular weight products. The petroleum ether layer was washed with 500 ml. of aqueous 0.1 *N* sodium hydroxide in order to remove any trace of acid, dried over anhydrous magnesium sulfate and distilled at 4 mm. Twenty grams of neutral products, which boiled from 35 to 180°, was collected. These products had refractive indices of $n^{20}\mathrm{D}$ 1.4180 to 1.4798 and were unsaturated to bromine. The dark rubbery residue amounted to 13 g. This non-acidic polymer probably arises from intermolecular acid–salt interchange.

The aqueous solution was treated with carbon dioxide and extracted with ether in order to remove some of the weak acids. The remainder was acidified with hydrochloric acid and extracted with ether in order to collect the stronger acids. The weak acid portion weighed 28 g. after evaporation of the ether. The strong acid portion contained 118 g.

The caproic acid (50 g.) was distilled at reduced pressure from the strong acid portion and the residue was methylated with diazomethane. The methyl esters were fractionated at 1 mm. through a thirty plate column. At 30–52°, 1.2 g. was collected which had a refractive index of $n^{20}\mathrm{D}$ 1.4241; at 54–57°, 7.8 g. was obtained which had an index of 1.4342. The remaining fractions boiled over the range from 78 to 175° and weighed 24.4 g. The residue was a brittle resin. The weak acid portion was treated similarly except that distillation was carried out in a 125-ml. Claisen flask because the quantity was much smaller. The fraction which boiled from 55–60° at 2 mm. pressure amounted to 3.5 g. and had an index of refraction of $n^{20}\mathrm{D}$ 1.4334. At 60–70°, 2.4 g. was collected. The remainder boiled from 70 to 195°. The residue amounted to 3.5 g. and was a viscous liquid.

The second fraction of the stronger acids and the first fraction of the weaker acids boiled over the same range approximately and had similar refractive indices. A comparison of these fractions is given in the table below.

Table III

	Stronger acids	Weaker acids	Calcd. for a single 1,4 adduct.
Boiling point, °C.	54–57	55–60	
Low boiling fraction, g.	7.8	3.5	
Saponif. equivalent	184	191	184
Hydrogenation; double bonds per carbethoxy group	0.91	1.02	1
Ozonization; formaldehyde per cent., per total double bonds	23.3	40.5	0

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[11] Allen, "Organic Syntheses," **22**, 39 (1942).

A 1,4-addition of organosodium compound would give, after carbonation, a primary acid which would be comparatively strong. A 1,2-addition would give a secondary acid which would be less strong. In accordance with this view the weaker acid concentrate shows the higher proportion of 1,2-addition, and the stronger acid concentrate shows the lower proportion. No acetaldehyde was found in the products from these ozonizations.

The esters in the 54–60° fraction from the strong and weak acids were saponified by treatment with 10% aqueous sodium by hydroxide for forty-five minutes. This strength of alkali causes rearrangement of the double bond so that the β,γ-acids become α,β-acids. The acids recovered from this treatment were separated by a multiple-fractional extraction process.[2] The results from each fraction accord with those expected from the supposition that each was a mixture in varying proportions of α,β- and β,γ-unsaturated acids and that the α,β-acids are both weaker and have higher refractive indices than the β,γ-acids. The separation is good when the acids are divided into four to six equal portions and are treated successively with eight successive equivalent portions of alkali. A fraction (0.37 g.) from the portion which should have the α,β-acids (which are theoretically the result of 1,2- and 1,4-addition of amylsodium to butadiene) was ozonized. The amount of acetaldehyde dimethone[11] obtained, subsequent to hydrogenation of the ozonide, was 0.3 g., m. p. 135.2–137.5° (recorded[12] vlaue 137°).

The unsaturated acids which should contain the product of 1,4-addition were combined and hydrogenated over platinic oxide as a catalyst. No solid product could be isolated even when the liquid hydrogenated product was cooled as low as −32°. When this mixture (4.0 g.) was divided into eight equal parts and fractionated by the multiple-fractional-extraction process with four equivalent quantities of alkali, the two fractions in the stronger acid end of the series partially crystallized when cooled in the refrigerator. For instance, in the last portion, which amounted to 0.56 g. the quantity of crystals was 0.15 g. These crystals melted at 30°. The recorded value for capric acid is 31°. The *p*-bromophenacyl ester melted at 64.5°. The recorded[12] value is 67°. The carbon and hydrogen analysis accorded with that calculated. Capric acid would result if some 1,4-addition had taken place. Similar attempts to isolate crystals of an acid from the weaker acid portion were unsuccessful, although a very small quantity of crystals of a *p*-bromophenacyl ester derivative was obtained. These crude crystals melted from 80–90° but resisted further purification.

Comparative Addition to Butadiene, Isoprene and Dimethylbutadiene (by E. M.).—The diene was added dropwise to 0.19 mole of amylsodium which was being stirred in the high speed stirring apparatus. The temperature was 25° and the time was usually two hours. The stirring continued for three hours longer. The mixture was then forced on solid carbon dioxide. Water was added after the carbon dioxide had evaporated. The aqueous solution was filtered and acidified. The organic portion was redissolved in potassium hydroxide, the solution saturated with potassium chloride, the layer extracted with petroleum ether in order to remove all non-acidic material, and the aqueous layer then acidified, and extracted with petroleum ether, which removed practically all of the acid. The acids from the petroleum ether extract were then distilled in order to remove the caproic acid. The residue was esterified by diazomethane, and the esters were dried and distilled at 4 mm. in a Claisen flask-Vigreux column combination.

The saponification equivalent and the unsaturation calculated as ml. of hydrogen per gram were determined for each fraction (see Figs. 1 and 2). In a large number of fractions the percentage formaldhyde per double bond was found by ozonization, hydrogenation of the ozonide and precipitation of the dimethone.[12]

Pertinent data on conditions, yields and change of ozonization values, and proportion of diene to carbomethoxy groups are shown in Table III. The data recorded in this table are only a part of those obtained, but are adequate to show the direction of changes.

Effect of Triethylamine (by E. M.).—Triethylamine was fractionated before use. Various quantities as shown in the table below were added to the reaction mixture of 0.19 mole of amylsodium and 0.25 mole of butadiene. The reaction time was five hours, a period sufficiently long to cause the reaction to go largely to completion even without the amine. Nevertheless the yield of adducts was increased a little and the quantity of unused amylsodium, measured as methyl caproate, was correspondingly decreased.

TABLE IV

EFFECT OF TRIETHYLAMINE ON THE ADDITION OF AMYLSODIUM TO BUTADIENE

Products	Grams of ester obtained from the products of reaction in the presence of triethylamine. Equivalents of amine per amylsodium None g.	0.1 g.	0.25 g.	1 g.	3 g.
Mixture that boils below 160–175° (4 mm.)	13.2	14.4	15.1	16.4	15.5
Above 175° (3 mm.)	..	..	..	2.7	1.5
Residue	6.1	5.8	6.9	2.2	4.0
Methyl caproate	4.0	1.5	1.8	0.9	0.5

The effect in the reaction with the slower acting isoprene is observed more easily. The total ester distilled up to 320° (3 mm.) was 4.3 g. when no amine was present, and was 9.2 g. when one equivalent of amine was used. The residues were respectively 10.3 and 7.9 g. and the corresponding quantities of methyl caproate were 11.3 and 3.0 g. For other data on the effect of the amine, see Table I.

Part of this effect, notably the consumption of amylsodium, might be ascribed to the action of the triethylamine on the organosodium reagent. For instance, over a five-hour period, three equivalents of triethylamine caused about 33% decomposition, and, what is more remarkable, caused a shift in the products of jet carbonation from a negligible amount of butylmalonic acid to 50% of that acid. When the amylsodium was prepared in the usual way and the solvent was replaced by triethylamine, the action was more marked in that some of the acid recovered after carbonation contained nitrogen. The other changes are unknown. The amine caused no change in the proportions of carbonated products from phenylsodium and benzylsodium.

Effect of Cumene.—Cumene was used as a solvent because it is attacked only slowly by amylsodium and because the product of metalation, *p*-$(CH_3)_2CHC_6H_4Na$, should not add to a diene. About 25% of the product, however, was the result of the action of amylsodium on the cumene. The reaction mixture was more fluid than observed in the paraffin solvents, possibly because the reagent and products are more soluble. Significant data are recorded in Table I.

Summary

Low molecular weight addition products of amylsodium with butadiene have been found to be a mixture of 1,2- and 1,4-addition, largely the former.

Tests with isoprene and dimethylbutadiene show that the methyl groups increase the likelihood of polymer branching by either increasing the relative strength or the number of hydrocarbo acids in the stem as compared with the tip.

Methyl groups in the center of the diene increase the tendency toward 1,4-addition, and decrease the rate of addition.

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(12) Huntress and Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, New York, N. Y.

The observed effects accord with the general behavior of methyl groups in metalation reactions.

Triethylamine appears to accelerate addition of amylsodium to a diene but not to alter the proportion of 1,2-addition.

Cumene as a solvent has no significant effect on the reaction.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polymerization. IV. The Reaction of Organosodium Reagents with Styrene and 1,1-Diphenylethylene

BY AVERY A. MORTON AND H. C. WOHLERS

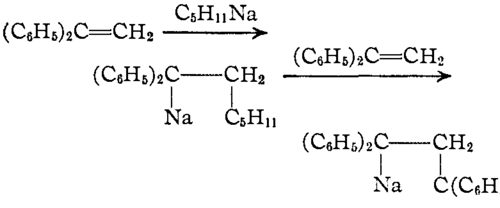
The reaction of organosodium reagents with styrene and *as*-diphenylethylene has been studied to see if any parallelism exists with the action on dienes, especially with respect to any 1,2-process. The results reported in this paper show (a) that organosodium reagents, such as amylsodium and phenylsodium, cause a very rapid polymerization of styrene, (b) that organosodium reagents, such as amylsodium, which add readily to butadiene,[1] also add readily to *as*-diphenylethylene to give a mono-adduct and a di-adduct, and that phenylsodium which does not add to butadiene, also does not add, save for a trace, to this ethylene compound, (c) that the addition of amylsodium to *as*-diphenylethylene has an induction period, the formation of the first adduct is a reaction of the first order, and the formation of the second adduct is a reaction of the second order, and (d) that triethylamine, which accelerates the addition of amylsodium to butadiene,[1] also accelerates the addition to diphenylethylene. Hence these organoalkali metal reagents may not act on butadiene as they do on styrene under the conditions employed, but many similarities exist between their addition to butadiene and to *as*-diphenylethylene. In the latter case the formation of a two stage adduct, hitherto not known, occurs.

Styrene.—The dropwise addition of styrene to either amylsodium or phenylsodium causes polymerization. No intermediate products comparable to those from butadiene and amylsodium are obtained even though the conditions are unusually favorable for the isolation of low molecular weight intermediate products as carboxylic acids subsequent to carbonation.

The final product has superficially the appearance of the usual styrene polymer but contains carboxyl groups undoubtedly as a result of a secondary reaction, an acid-salt interchange between the styrene polymer and the organoalkali metal reagent, in which the metal probably enters the *p*-position of the benzene ring, if metalation of isopropylbenzene,[2] is a criterion. Carbonation converts these products to carboxylates. One carboxyl group is thus introduced for every 5.7 styrene unit by phenylsodium; one for every 1.0 styrene unit by amylsodium. The polymer from phenylsodium is very slightly soluble in 5% methyl alcoholic potassium hydroxide; that from amylsodium is appreciably soluble.

The failure of Staudinger[3] to isolate intermediate products from the polymerization of styrene by peroxides was advanced as a major argument for free radical mechanism. The similar failure in the present work suggests that amyl- and phenylsodium cause styrene to polymerize by a catalytic process, although this mechanism is not of necessity a free radical one because the reagent is an ion-pair or a single ion of that pair and might reasonably be expected to produce another ion. This ion is not from any addition process because: (a) phenylhexylmethylsodium, the expected product of the addition with amylsodium, would be stable, since it is similar to phenylisopropylpotassium,[2] a stable compound, and (b) phenylsodium would probably not add to styrene since it will not add even to 1,1-diphenylethylene. The polymerization induced on styrene may be related to the metalating power of amylsodium or phenylsodium but this problem will be discussed in later phases of this program of research.

1,1-Diphenylethylene.—Amylsodium adds to *as*-diphenylethylene when the latter is added dropwise to a suspension of the reagent. Carbonation then yields two carboxylic acids, the result of a two stage addition, according to the following equation.



$$(C_6H_5)_2C{=}CH_2 \xrightarrow{C_5H_{11}Na} \underset{Na}{(C_6H_5)_2C}-\underset{C_5H_{11}}{CH_2} \xrightarrow{(C_6H_5)_2C=CH_2} \underset{Na}{(C_6H_5)_2C}-\underset{C(C_6H_5)_2C_6H_{13}}{CH_2}$$

A mono-adduct from the reaction of diphenylethylene with organoalkali metal reagents has been observed by other workers[4]; the di-adduct is new. Long periods of stirring and a great excess of the diphenylethylene fail to build higher

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[1] Morton, Brown and Magat, THIS JOURNAL, **68**, 16 (1946).

[2] Morton, Massengale and Brown, *ibid.*, **67**, 1620 (1945).

[3] Staudinger and Frost, *Ber.*, **68**, 2351 (1935); Staudinger, *Trans. Faraday Soc.*, **32**, 323 (1936).

[4] Ziegler and Bahr, *Ber.*, **61**, 253 (1928); Ziegler and Kleiner, *Ann.*, 473 (1929); Gilman, Meals, O'Donnell and Woods, THIS JOURNAL, **65**, 268 (1942).