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

Polymerization. II. Acid–Salt Interchange and Chain Branching in Sodium Polymerization of Dienes

BY AVERY A. MORTON AND MALCOLM L. BROWN

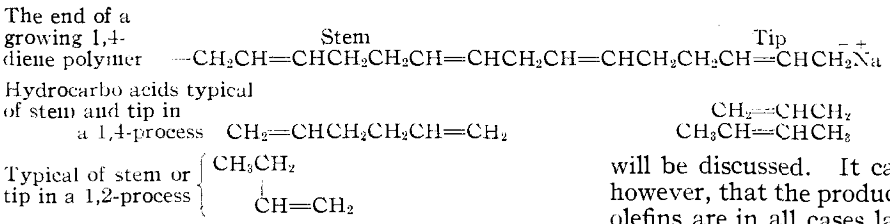
If the polymerization of dienes by organoalkali metal compounds takes place by successive formation of a series of adducts of increasing molecular weight, as indicated below

$$\mathrm{RNa} \xrightarrow{\mathrm{C_4H_6}} \mathrm{R(C_4H_6)_1Na} \cdots \longrightarrow \mathrm{R(C_4H_6)_{\mathit{n}}Na}$$

each intermediate sodium compound, that is, each sodium salt of a hydrocarbo acid, should undergo the reactions characteristic for that class of salts. One of the more common reactions[1] of such salts is metalation or acid–salt interchange. If this process should occur intramolecularly the sodium ion would transfer to a position along the stem of the growing polymer and chain-branching would result when more butadiene is added; if it occurs intermolecularly chain termination will occur on one chain and a new locus of reaction will form on another.

We have studied the likelihood of such changes by a comparison of the relative hydrocarbo acidities of olefins which are representative of the tip, the side, and a vinyl branch of a polymer that is growing by addition of butadiene to an alkylsodium compound. If the representative olefins are of equal acidity the sodium ions in the growing polymer should be distributed among the various hydrocarbo acids in accordance with the relative number of such acids or points of activity. If the acids are of unequal activity the sodium ion should correspondently become attached at the more active position. Our results indicate that the hydrogen atoms on the stem of a polymer that might happen to be growing by a 1,4-process are as active if not more so than those at the tip; and our conclusion from this evidence (presented below) is that the chance of such a polymer ending as a 1,4 product is extremely slight, unless some other factor, at present unknown, intervenes.

Propene and 2-butene represent approximately the end of the chain, diallyl typifies the middle of the chain, and 1-butene represents a vinyl branch formed by 1,2-addition. The comparisons are illustrated below.



The end of a growing 1,4-diene polymer

Stem Tip

$$\text{—}\mathrm{CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2CH{=}CHCH_2CH_2CH{=}CHCH_2\overset{-\,+}{Na}}$$

Hydrocarbo acids typical of stem and tip in a 1,4-process

$$\mathrm{CH_2{=}CHCH_2CH_2CH{=}CH_2} \qquad \begin{matrix}\mathrm{CH_2{=}CHCH_3}\\ \mathrm{CH_3CH{=}CHCH_3}\end{matrix}$$

Typical of stem or tip in a 1,2-process

$$\left\{\begin{matrix}\mathrm{CH_3CH_2}\\ \quad|\\ \quad\mathrm{CH{=}CH_2}\end{matrix}\right.$$

These olefins are readily attacked by a typical organoalkali metal reagent such as amylsodium or benzylsodium; butene-1 least so, butene-2 a little more, and propylene and diallyl to a relatively high degree (see Table I).

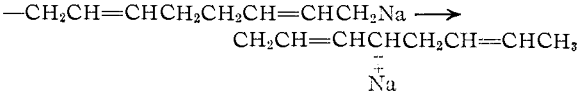
TABLE I

YIELDS OF ACIDS FROM CARBONATION OF THE PRODUCTS OF REACTION OF ORGANOALKALI REAGENTS WITH CERTAIN OLEFINS

	Products from amylsodium acids, %			Products from benzylsodium acids, %		
	Mono	Di	Caproic	Mono	Di	Phenyl-acetic
Butene-1	5	5	68			
Butene-2	10	22	53			
Propylene	27	11	24			
Diallyl	30	62	0	28	..	58[a]
Isobutene	37	26	0	24	5	57[b]

[a] The phenylacetic acid contains whatever disubstitution was produced in the reaction. [b] An additional 14% of the acids recovered were isohomophthalic acid, which is derived as a secondary product from the preparation of benzylsodium.

This result means that the middle of the growing chain is a stronger hydrocarbo[1] acid than is the end of the chain. Hence the sodium ion should shift from the tip to a position along the stem. One illustration of this possibility is given below.



$$\text{—}\mathrm{CH_2CH{=}CHCH_2CH_2CH{=}CHCH_2Na} \longrightarrow \mathrm{CH_2CH{=}CH\underset{\underset{Na}{+}}{\overset{}{\underset{-}{C}}}HCH_2CH{=}CHCH_3}$$

This situation, if impossible of correction, would render impossible the formation of a polymer which is exclusively a 1,4-product, even if 1,4-addition should happen to be the sole method of chain growth.

Data for isobutene are included in this table because this olefin can be regarded as typical of a unit in polyisoprene. Isobutene is metalated with great ease. Hence the introduction of a single methyl group should enhance the prospects of acid-salt interchange and therefore of branching.

The character of the products of metalation of these olefins will be reported in a later paper in which the problem of resonance in these hydrocarbo acids and in the growing polymer will be discussed. It can be stated at this time, however, that the products of metalation of simple olefins are in all cases largely those in which the metal is attached to a carbon atom adjacent to a vinyl group, and that attachment to the carbon atom which is part of the vinyl group is a minor

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

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.

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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).

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

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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.